SURFACTANTS AND INTERFACIAL PHENOMENA

SURFACTANTS AND INTERFACIAL PHENOMENA

THIRD EDITION

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WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data is available.

Rosen, Milton J.
Surfactants and interfacial phenomena / Milton J. Rosen. – 3rd ed.
p. cm.
Includes bibliographical references and index.
ISBN 0-471-47818-0
1. Surface active agents. 2. Surface chemistry. I. Title.
TP994.R67 2004
668′.1–dc22 2004048079

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Preface

The more than a decade since publication of the second edition has seen considerable progress in a number of important areas of surfactant chemistry, necessitating the publication of a third edition. This edition, consequently, contains a number of areas not included in the previous edition.

These include an entire chapter on ‘‘gemini’’ surfactants (surfactants with two hydrophilic and two or three hydrophobic groups in the molecule), which have evoked intense interest, both academic and industrial, because of their unique properties. Also included are guidelines for the selection of surfactant pairs for the optimization of surfactant properties and sections on ‘‘green’’ surfactants from renewable resources, estimation of marine organism toxicity and bioconcentration of surfactants from their physico-chemical properties, dynamic surface tension reduction, synergy in wetting and ‘‘superwetting’’ by mixtures of surfactants, foaming of aqueous dispersions of finely divided solids, and demulsification by surfactants.

Areas covered in the previous edition have been expanded and upgraded to reflect new developments. Tables of physico-chemical constants of surfactants, including critical micelle concentrations, areas/surfactant molecule at interfaces, and surfactant–surfactant interaction parameters have been greatly increased. Additional problems have been provided at the ends of the chapters.

I should like to acknowledge and thank a number of colleagues and former students for their assistance with this edition. I am grateful to Randy Bernhardt and Gregory Dado of Stepan, Manilal Dahanayake of Rhodia, Paul Berger of Oil Chem Technologies, Kazayuki Tsubone (now retired) of Kanebo, Richard Thomas of OMNOVA Solutions, and Michael Cox and Dewey Smith of Sasol for their help in updating the section on commercially available surfactants. I am indebted to Arno Cahn for his assistance with the section on detergent ‘‘builders.’’ My former doctoral student, Qiong Zhou, provided some of the figures.

Great Neck, New York MILTON J. ROSEN

1 Characteristic Features of Surfactants

Surfactants are among the most versatile products of the chemical industry, appearing in such diverse products as the motor oils we use in our automobiles, the pharmaceuticals we take when we are ill, the detergents we use in cleaning our laundry and our homes, the drilling muds used in prospecting for petroleum, and the flotation agents used in benefication of ores. The last decades have seen the extension of surfactant applications to such high-technology areas as electronic printing, magnetic recording, biotechnology, micro-electronics, and viral research.

A surfactant (a contraction of the term *surface-active agent*) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term *interface* indicates a boundary between any two immiscible phases; the term *surface* denotes an interface where one phase is a gas, usually air.

The interfacial free energy is the minimum amount of work required to create that interface. The interfacial free energy per unit area is what we measure when we determine the interfacial tension between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it by unit area. The interfacial (or surface) tension is also a measure of the difference in nature of the two phases meeting at the interface (or surface). The greater the dissimilarity in their natures, the greater the interfacial (or surface) tension between them.

When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it. When we expand an interface, therefore, the minimum work required to create the additional amount of that interface is the product of the interfacial tension γ_I and the increase in area of the interface; $W_{\min} = \gamma_I \times \Delta$ interfacial area. A surfactant is therefore a substance that at low concentrations adsorbs at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it.

The questions that immediately arise are the following: Under what conditions can surfactants play a significant role in a process? How does one know when to

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Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

expect surfactants to be a significant factor in some system under investigation? How and why do they work as they do?

A. Conditions Under Which Interfacial Phenomena and Surfactants Become Significant

The physical, chemical, and electrical properties of matter confined to phase boundaries are often profoundly different from those of the same matter in bulk. For many systems, even those containing a number of phases, the fraction of the total mass that is localized at phase boundaries (interfaces, surfaces) is so small that the contribution of these ‘‘abnormal’’ properties to the general properties and behavior of the system is negligible. There are, however, many important circumstances under which these ‘‘different’’ properties play a significant, if not a major, role.

One such circumstance is when the phase boundary area is so large relative to the volume of the system that a substantial fraction of the total mass of the system is present at boundaries (e.g., in emulsions, foams, and dispersions of solids). In this circumstance, surfactants can always be expected to play a major role in the system.

Another such circumstance is when the phenomena occurring at phase boundaries are so unusual relative to the expected bulk phase interactions that the entire behavior of the system is determined by interfacial processes (e.g., heterogeneous catalysis, corrosion, detergency, or flotation). In this circumstance also surfactants can play an important role in the process. It is obviously necessary to understand the causes of this abnormal behavior of matter at the interfaces and the variables that affect this behavior in order to predict and control the properties of these systems.

B. General Structural Features and Behavior of Surfactants

The molecules at a surface have higher potential energies than those in the interior. This is because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. Work is therefore required to bring a molecule from the interior to the surface.

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a *lyophobic group*, together with a group that has strong attraction for the solvent, called the *lyophilic group*. This is known as an *amphipathic* structure. When a molecule with an amphipathic structure is dissolved in a solvent, the lyophobic group may distort the structure of the solvent, increasing the free energy of the system. When that occurs, the system responds in some fashion in order to minimize contact between the lyophobic group and the solvent. In the case of a surfactant dissolved in aqueous medium, the lyophobic (hydrophobic) group distorts the structure of the water (by breaking hydrogen bonds between the water molecules and by structuring the water in the vicinity of the hydrophobic group). As a result of this distortion, some of the surfactant molecules are expelled to the interfaces of the system, with their hydrophobic groups oriented so as to minimize contact with the water molecules. The surface of the water becomes covered with a single layer of surfactant molecules with their hydrophobic groups oriented predominantly toward the air. Since air molecules are essentially nonpolar in nature, as are the hydrophobic groups, this decrease in the dissimilarity of the two phases contacting each other at the surface results in a decrease in the surface tension of the water. On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in a less polar solvent only some of these may be suitable (e.g., fluorocarbon or siloxane chains in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at a suitable level. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic *in that solvent under the conditions of use*.

The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as:

1. *Anionic*. The surface-active portion of the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).
2. *Cationic*. The surface-active portion bears a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).
3. *Zwitterionic*. Both positive and negative charges may be present in the surface-active portion, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).
4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol), $R(OC_2H_4)_xOH$(polyoxyethylenated alcohol).

1. General Use of Charge Types Most natural surfaces are negatively charged. Therefore, if the surface is to be made hydrophobic (water-repellent) by use of a surfactant, then the best type of surfactant to use is a cationic. This type of surfactant will adsorb onto the surface with its positively charged hydrophilic head group oriented toward the negatively charged surface (because of electrostatic attraction) and its hydrophobic group oriented away from the surface, making the surface water-repellent. On the other hand, if the surface is to be made hydrophilic (water-wettable), then cationic surfactants should be avoided. If the surface should happen to be positively charged, however, then anionics will make it hydrophobic and should be avoided if the surface is to be made hydrophilic.

Nonionics adsorb onto surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of the surface. If polar groups capable of H bonding with the hydrophilic group of the surfactant are present on the surface, then the surfactant will probably be adsorbed with its hydrophilic group oriented toward the surface, making the surface more hydrophobic; if such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more hydrophilic.

Zwitterionics, since they carry both positive and negative charges, can adsorb onto both negatively charged and positively charged surfaces without changing the charge of the surface significantly. On the other hand, the adsorption of a cationic onto a negatively charged surface reduces the charge on the surface and may even reverse it to a positive charge (if sufficient cationic is adsorbed). In similar fashion, the adsorption of an anionic surfactant onto a positively charged surface reduces its charge and may reverse it to a negative charge. The adsorption of a nonionic onto a surface generally does not affect its charge significantly, although the effective charge density may be reduced if the adsorbed layer is thick.

Differences in the nature of the hydrophobic groups are usually less pronounced than those in the nature of the hydrophilic group. Generally, they are long-chain hydrocarbon residues. However, they include such different structures as:

1. Straight-chain, long alkyl groups (C_8–C_{20})
2. Branched-chain, long alkyl groups (C_8–C_{20})
3. Long-chain (C_8–C_{15}) alkylbenzene residues
4. Alkylnaphthalene residues (C_3 and greater-length alkyl groups)
5. Rosin derivatives
6. High-molecular-weight propylene oxide polymers (polyoxypropylene glycol derivatives)
7. Long-chain perfluoroalkyl groups
8. Polysiloxane groups
9. Lignin derivatives

2. General Effects of the Nature of the Hydrophobic Group

Length of the Hydrophobic Group Increase in the length of the hydrophobic group (1) decreases the solubility of the surfactant in water and increases its solubility in organic solvents, (2) causes closer packing of the surfactant molecules at the interface (provided that the area occupied by the hydrophilic group at the interface permits it), (3) increases the tendency of the surfactant to adsorb at an interface or to form aggregates, called *micelles*, (4) increases the melting point of the surfactant and of the adsorbed film and the tendency to form liquid crystal phases in the solution, and (5) increases the sensitivity of the surfactant, if it is ionic, to precipitation from water by counterions.

Branching, Unsaturation The introduction of branching or unsaturation into the hydrophobic group (1) increases the solubility of the surfactant in water or in organic solvents (compared to the straight-chain, saturated isomer), (2) decreases the melting point of the surfactant and of the adsorbed film, (3) causes looser packing of the surfactant molecules at the interface (the cis isomer is particularly loosely packed; the trans isomer is packed almost as closely as the saturated isomer) and inhibits liquid crystal phase formation in solution, (4) may cause oxidation and color formation in unsaturated compounds, (5) may decrease biodegradability in branched-chain compounds, and (6) may increase thermal instability.

Aromatic Nucleus The presence of an aromatic nucleus in the hydrophobic group may (1) increase the adsorption of the surfactant onto polar surfaces, (2) decrease its biodegradability, and (3) cause looser packing of the surfactant molecules at the interface. Cycloaliphatic nuclei, such as those in rosin derivatives, are even more loosely packed.

Polyoxypropylene or Polyoxyethylene Units Polyoxypropylene units increase the hydrophobic nature of the surfactant, its adsorption onto polar surfaces, and its solubility in organic solvents. Polyoxyethylene units decrease the hydrophobic character of the surfactant.

Perfluoroalkyl or Polysiloxane Group The presence of either of these groups as the hydrophobic group in the surfactant permits reduction of the surface tension of water to lower values that those attainable with a hydrocarbon-based hydrophobic group. Perfluoroalkyl surfaces are both water- and hydrocarbon-repellent.

With such a variety of available structures, how does one choose the proper surfactant for a particular purpose? Alternatively, why are only certain surfactants used for a particular purpose and not other surfactants? Economic factors are often of major importance—unless the cost of using the surfactant is trivial compared to other costs, one usually chooses the most inexpensive surfactant that will do the job. In addition, such considerations as environmental effects (biodegradability, toxicity to and bioconcentration in aquatic organisms) and, for personal care products, skin irritation are important considerations. The selection of the best surfactants or combination of surfactants for a particular purpose in a rational manner, without resorting to time-consuming and expensive trial-and-error experimentation, requires a knowledge of (1) the characteristic features of currently available surfactants (general physical and chemical properties and uses), (2) the interfacial phenomena involved in the job to be done and the role of the surfactant in these phenomena, (3) the surface chemical properties of various structural types of surfactants and the relation of the structure of a surfactant to its behavior in various interfacial phenomena. The following chapters attempt to cover these areas.

I. CHARACTERISTIC FEATURES AND USES OF COMMERCIALLY AVAILABLE SURFACTANTS

Surfactants are major industrial products with millions of metric tons produced annually throughout the world. Table 1-1 lists surfactant consumption in the United States and Canada for the year 2000. Table 1-1A shows consumption of the various surfactant charge types by percentage; Table 1-1B, consumption of the five major types of surfactant by tonnage.

TABLE 1-1 Surfactant Consumption—United States and Canada, (excluding soap), 2000

A. Surfactant, by Charge Type

TYPE	%
Anionics	59
Cationics	10
Nonionics	24
Zwitterionics and others	7
	100

B. Major Surfactants, by Tonnage

SURFACTANT	THOUSAND METRIC TONS
Linear alkylbenzene sulfonates	420
Alcohol ethoxysulfates	380
Alcohol sulfates	140
Alcohol ethoxylates	275
Alkylphenol ethoxylates	225
Other	1625
TOTAL	3065

Source: Colin A. Houston and Associates, Inc.

I.A. Anionics

1. Carboxylic Acid Salts

Sodium and Potassium Salts of Straight-Chain Fatty Acids, $RCOO^-M^+$ (Soaps)

PROPERTIES. Below 10 carbons, too soluble for surface activity; above 20 carbons (straight chain), too insoluble for use in aqueous medium but usable for nonaqueous systems (e.g., detergents in lubricating oils or dry-cleaning solvents).

ADVANTAGES. Easily prepared by neutralization of free fatty acids or saponification of triglycerides in simple equipment. Can be made in situ (e.g., for use as an emulsifying agent) (1) by adding fatty acid to oil phase and alkaline material to aqueous phase or (2) by partial saponification of triglyceride oil. Excellent physical properties for use in toilet soap bars.

DISADVANTAGES. (1) Form water-insoluble soaps with divalent and trivalent metallic ions, (2) insolubilized readily by electrolytes, such as NaCl, (3) unstable at pH below 7, yielding water-insoluble free fatty acid.

MAJOR TYPES AND THEIR USES. Sodium salts of tallow (animal fat) acids. (Tallow acids are oleic, 40–45%; palmitic, 25–30%; stearic, 15–20%.) Used in toilet soap bars and for degumming of silk, where alkaline solution is required. For industrial use in hard water, lime soap-dispersing agents (sulfonates and sulfates) are added to prevent precipitation of insoluble lime soaps.

Sodium and Potassium Salts of Coconut Oil Fatty Acids (Coconut fatty acids are C_{12}, 45–50%; C_{14}, 16–20%; C_{16}, 8–10%; oleic, 5–6%; $<C_{12}$, 10–15%). Used as electrolyte-resistant soaps (seawater washing) and in liquid soaps, especially as the potassium soaps.

Sodium and Potassium Salts of Tall Oil Acids (Tall oil, a by-product of paper manufacture, is a mixture of fatty acids and rosin acids from wood; 50–70% fatty acid, mainly oleic and linoleic, 30–50% rosin acids related to abietic acid, the main constituent of rosin.) Mainly “captive” use or in situ preparation for various industrial cleaning operations. Used as foaming agents for concrete.

ADVANTAGES. Inexpensive. More water-soluble and hard-water resistant than tallow soaps. Lower-viscosity solutions than tallow soaps at high concentrations, better wetting.

Soaps of synthetic long-chain fatty acids are produced in Europe, but not in the United States at present.

Amine Salts Triethanolamine salts are used in nonaqueous solvents and in situ preparation as an emulsifying agent (free fatty acid in oil phase, triethanolamine in aqueous phase). Ammonia, morpholine, and other volatile amine salts are used in polishes, where evaporation of the amine following hydrolysis of the salt leaves only water-resistant material in film.

Other Types

ACYLATED AMINOACIDS. *(See Section IE below)*

Acylated Polypeptides (From partially hydrolyzed protein from scrap leather and other waste protein.) Used in hair preparations and shampoos, alkaline cleaning preparations, wax strippers. Good detergency and resistance to hard water.

ADVANTAGES. Soluble in concentrated aqueous solutions of alkaline salts. Nonirritating to skin; reduces skin irritation produced by other surfactants (e.g., sodium lauryl sulfate). Substantive to hair. Imparts soft "hand" to textiles.

DISADVANTAGES. Precipitated by high concentrations of Ca^{2+} or Mg^{2+}, acids (below pH 5). Lower foaming than lauryl sulfates. Requires foam booster (e.g., alkanolamides) when foaming is important.

Polyoxyethylenated (POE) Fatty Alcohol Carboxylates (Alkyl Ether Carboxylates), $RO(CH_2CH_2O)_xCH_2COOM$ ($x = 4$, usually) Products of the reaction of the terminal OH group of an alcohol ethoxylate (AE) with sodium monochloroacetate. Less basic than soaps of comparable chain length, ascribed to the ether oxygen atom adjacent to the carboxylate group in the molecule.

USES. Hair care and skin care detergents, for the product based on C_{12-14} alcohol with low EO content. Emulsifying agent, solubilizing agent, dispersion agent. Textile and metal detergent. Industrial detergent for products having a short alkyl chain (C_{4-8}) because of low foaming power.

ADVANTAGES. Low skin irritancy. Good resistance to hard water. Good stability in alkaline medium.

2. Sulfonic Acid Salts

Linear Alkylbenzenesulfonates (LAS), $RC_6H_4SO_3^-M^+$ Three processes for the production of alkylbenzenes (*alkylate*) are used commercially. All are based on linear alkenes. They include alkylation with HF, AlC13, and solid acid alkylation catalysts. The product from all alkylation technologies is a mixture of linear alkyl benzene with the phenyl group at all positions in the alkyl chain with the exception of the 1-phenyl position. Alkylation by AlC13 and the current commercial solid acid alkylation catalysts favors the same higher 2- and 3-positions, and these are called *high 2-phenyl alkylates*. The HF alkylation process gives a more uniform or statistical distribution of phenyl groups along the hydrocarbon chain and is considered a low 2-phenyl alkylate. There are some differences as well as many similarities between the two types of alkylate. Alkylate produced from the older HF alkylation technology (low 2-phenyl) is still a large percentage of the production; however, all new plants as well as improved AlCl3 alkylation plants are all high 2-phenyl alkylate. The high 2-phenyl alkylate has advantages for the growing production of liquid detergents, while the low 2-phenyl alkylate is used mainly in powder detergent applications. The sulfonation product is sold mainly as the sodium salt, but calcium salt (which may be oil-soluble or dispersible) and amine salts, which are also organic solvent soluble or dispersible, are also sold. The chain length of the alkyl portions is about 12 carbons in most cases. Linear alkylbenzene sulfonate is relatively cheap, but requires acid-resistant equipment for manufacturing and sophisticated SO_3 sulfonation equipment for large-scale production. This applies also to alcohol sulfates and ether sulfates (see 3 below), which may be manufactured in the same or similar sulfonation equipment. Major amounts are sold as free sulfonic acid for neutralization (by processors) with amines. The sodium salt is the most widely used surfactant in industrial and high-foaming household detergents. The triethanolamine salt is in liquid detergents and cosmetics; the isopropylamine salt in dry cleaning, since it is hydrocarbon-soluble; and the dimethylamine salt in agricultural emulsions and dry-cleaning solvents (to solubilize the water used to remove water-soluble stains).

ADVANTAGES. Completely ionized, water-soluble, free sulfonic acid; therefore solubility is not affected by low pH. Calcium and magnesium salts are water-soluble, and therefore not affected by hard water. Sodium salt is sufficiently soluble in the presence of electrolyte (NaCl, Na_2SO_4) for most uses. Resistant to hydrolysis in hot acid or alkali.

DISADVANTAGES. Sodium alkylbenzenesulfonate (LAS) is not soluble in organic solvents except alcohols. LAS is readily, rapidly, and completely biodegradable under aerobic conditions, which is the critical property for removal in the environment. However, LAS undergoes only primary biodegradation under anaerobic conditions. No evidence of complete biodegradation of LAS under anaerobic conditions has been reported. May cause skin irritation.

The introduction of a methyl group at an internal position in the linear alkyl chain of the hydrophobic group increases the water solubility and the performance properties of LAS.

Higher Alkylbenzenesulfonates C_{13}–C_{15} homologs are more oil-soluble, and are useful as lubricating oil additives.

Benzene-, Toluene-, Xylene-, and Cumenesulfonates Are used as hydrotropes, e.g., for increasing the solubility of LAS and other ingredients in aqueous formulations, for thinning soap gels and detergent slurries.

Ligninsulfonates These are a by-product of paper manufacture, prepared mainly as sodium and calcium salts, also as ammonium salts. They are used as dispersing agents for solids and as O/W emulsion stabilizers. They are sulfonated polymers of molecular weight 1000–20,000 of complex structure containing free phenolic, primary and secondary alcoholic, and carboxylate groupings. The sulfonate groups are at the α- and β-positions of C_3 alkyl groups joining the phenolic structures. They reduce the viscosity of and stabilize aqueous slurries of dyestuffs, pesticides, and cement.

ADVANTAGES. They are among the most inexpensive surfactants and are available in very large quantities. They produce very little foam during use.

DISADVANTAGES. Very dark color, soluble in water but insoluble in organic solvents, including alcohol. They produce no significant surface tension lowering.

Petroleum Sulfonates Products of the refining of selected petroleum fractions with concentrated sulfuric acid or oleum, in the production of white oils. Metal or ammonium salts of sulfonated complex cycloaliphatic and aromatic hydrocarbons.

USES. Tertiary oil recovery. Sodium salts of lower molecular weight (~435–450) are used as O/W emulsifying agents in soluble metal cutting oils, frothing agents in ore flotation, components of dry-cleaning soaps; sodium salts of higher molecular weight (465–500) are used as rust preventatives and pigment dispersants in organic solvents. Ammonium salts are used as ashless rust inhibitors and soluble dispersants in fuel oils and gasoline. Magnesium, calcium, and barium salts are used as sludge dispersants for fuel oils and as corrosion inhibitors for diesel lubricating oils.

ADVANTAGES. Inexpensive.

DISADVANTAGES. Dark in color. Contain unsulfonated hydrocarbon.

N-Acyl-n-Alkyltaurates, $RCON(R')CH_2CH_2SO_3^-M^+$ The solubility, foaming, detergency, and dispersing powers of the *N*-methyl derivatives are similar to those of the corresponding fatty acid soaps in soft water, but these materials are effective both in hard and soft water, are not sensitive to low pH, and are better wetting agents. They show good stability to hydrolysis by acids and alkali, good skin compatibility, and good lime soap-dispersing power.

USES. In bubble baths (together with soap) and in toilet bars together with soap, since they show no decrease in foaming or lathering in combination with the latter (in contrast with other anionics). In alkaline bottle washing compounds and for seawater laundering, since their salts are soluble, even in water containing high electrolyte concentrations. Impart soft feel (“hand”) to fibers and fabrics (similar to soaps and fatty alcohol sulfates, in contrast with nonionics and alkylarylsulfonates). Used as wetting and dispersing agents in wettable pesticide powders.

Paraffin Sulfonates, Secondary n-Alkanesulfonates (SAS) Produced in Europe by sulfoxidation of C_{14}–C_{17} *n*-paraffins with SO_2 and O_2. The *n*-paraffin hydrocarbons are separated from kerosene by molecular sieves.

USES. Performance similar to that of LAS. Used in liquid household detergents, primarily light duty liquids (LDLs). Used as an emulsifier for the polymerization of vinyl polymers. Also used in various polymers (polyvinyl chloride [PVC] and polystyrene) as an anti-static agent. Unpurified paraffin sulfonates containing about 50% paraffin are used in fat liquoring of leather.

ADVANTAGES. Solubility in water is reported to be somewhat better, viscosity of aqueous solutions somewhat lower, skin compatibility somewhat better, and biodegradability at low temperature somewhat better than those of LAS.

α-Olefin Sulfonates (AOS) Produced by reaction of SO_3 with linear α-olefins. Product is a mixture of alkenesulfonates and hydroxyalkanesulfonates (mainly 3- and 4-hydroxy).

ADVANTAGES. Reported to be somewhat more biodegradable than LAS; less irritating to the skin. Show excellent foaming and detergency in hard water. High solubility in water allows products with high concentrations of actives.

Arylalkanesulfonates, $R(CH_2)_mCH(\phi R^1)(CH_2)_nSO_3^-$ Prepared by sulfonating an olefin (alkene) and then treating it with an aromatic compound. Used in agriculture, asphalt, detergents, enhanced oil recovery from petroleum reservoirs, lubricants.

ADVANTAGES. Relatively inexpensive. A large variety of structures are possible by varying the nature of the olefin and the aromatic compound, including gemini (Chapter 12) disulfonates.

Sulfosuccinate Esters, $ROOCCH_2CH(SO_3^-M^+)COOR$ Used as wetting agents for paints, printing inks, textiles, agricultural emulsions. The dioctyl (2-ethylhexyl) ester is soluble in both water and organic solvents, including hydrocarbons, and is therefore used in dry-cleaning solvents. Monoesters used in cosmetics; in combination with other anionic surfactants, they reduce the eye and skin irritation of the latter.

ADVANTAGES. Can be produced electrolyte-free, and is thus completely soluble in organic solvents and usable where electrolyte must be avoided. Amide monoesters are among least eye-irritating of anionic surfactants.

DISADVANTAGES. Hydrolyzed by hot alkaline and acidic solutions. Dialkyl esters are irritating to skin (monoesters are not).

Alkyldiphenylether(di)sulfonates (DPES), $RC_6H_3(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$ Prepared by alkylating diphenyl ether and then sulfonating the reaction product. The C_{16} homolog is used as a detergent in cleaning products, the C_{16} and C_{12} homologs as emulsion stabilizers in emulsion polymerization, the C_{10} homolog in formulations containing high electrolyte content, the C_6 homolog as hydrotrope.

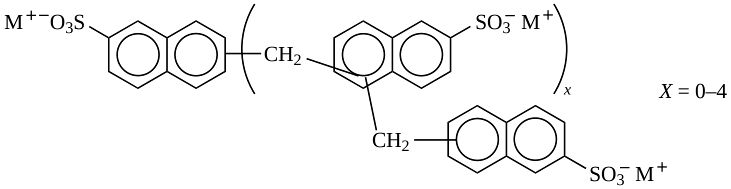
ADVANTAGES. NaOCl shows good stability in solutions of DPES.

DISADVANTAGE. The commercial product is a mixture of mono- and disulfonated mono-, di-, and trialkyldiphenylethers, each showing different performance properties.

Alkylnaphthalenesulfonates Mainly butyl- and isopropylnaphthalenesulfonates, for use as wetting agents for powders (agricultural wettables, powdered pesticides). Also used as wetting agents in paint formulations.

ADVANTAGES. Available in nonhygroscopic powder form for mixing into formulated powders.

Naphthalenesulfonic Acid–Formaldehyde Condensates



USES. Similar to those for ligninsulfonates (dispersing agents for solids in aqueous media, grinding aids for solids). Advantages over the usual ligninsulfonates are lighter color, even less foam.

Isethionates, $RCOOCH_2CH_2SO_3^-M^+$ Used in cosmetic preparations, synthetic toilet soap bars, shampoos, bubble baths.

ADVANTAGES. Excellent detergency and wetting power, good lime soap dispersing power, good forming power. Less irritating to skin than AS (below).

DISADVANTAGE. Hydrolyzed by hot alkali.

3. Sulfuric Acid Ester Salts

Sulfated Primary Alcohols (AS), $ROSO_3^-M^+$ Primary alcohol sulfates are one of the "workhorse" surfactants and are formed by the direct sulfation of an alcohol.

The alcohol may be derived either from oleochemical or from petrochemical sources. Oleochemical alcohol sulfates contain a highly linear hydrophobe, whereas the hydrophobe in petrochemical alcohol sulfates may range from highly linear to highly branched, depending on the method of manufacture. For performance reasons, a mixture of alcohol chain lengths ranging from dodecyl to hexadecyl is preferred for alcohol sulfates.

The most common commercial method of sulfation is "thin film" sulfation in which SO_3 vapor reacts with a thin film of alcohol. An alternative route, using chlorosulfonic acid, is convenient for laboratory sulfation and is sometimes practiced commercially. Both methods are capable of producing alcohol sulfates with excellent color.

ADVANTAGES. Alcohol sulfates have excellent foaming properties, especially if some unsulfated alcohol is retained in the product. Alcohol sulfates are also good detergents in the absence of high water hardness. Food-grade-quality alcohol sulfates are also used in food and pharmaceutical applications.

DISADVANTAGES. Alcohol sulfates readily hydrolyze in hot acid medium. They may cause skin and eye irritation. In the absence of builders, alcohol sulfates readily form calcium and magnesium salts in the presence of high water hardness, reducing their effectiveness as cleaners.

TYPES AVAILABLE AND THEIR USE. Sodium salts are most common. Sodium alcohol sulfate can be used in laundry powders, as a dyeing "retarder" when amino groups are present on the fiber, as a toothpaste foaming agent, as an emulsifier in food and cosmetic products, and as a dyestuff dispersion agent in aqueous solution. Magnesium "lauryl" sulfate is used where a less hydroscopic powder is needed and has greater solubility in hard water and higher alkali tolerance than the corresponding sodium salt.

Diethanol, triethanol, and ammonium salts are used in hand dishwashing liquids and in hair shampoos and cosmetics, where their higher water solubility and slightly acidic pH make them desirable.

Sulfated alcohols that are produced from alcohols that have a methyl branch in the hydrophobic group are more water-soluble than AS made from primary linear alcohols with the same number of carbon atoms in the hydrophobic group and are considerably more tolerant than the latter to calcium ion in the water. Their biodegradability is comparable to that of AS. They have been introduced into some laundry detergents.

Sulfated Polyoxyethylenated (POE) Straight-Chain Alcohols (AES), $R(OC_2H_4)_x SO_4^- M^+$ R usually contains 12 carbon atoms; x usually has an average of 3, but with a broad range of distribution in polyoxyethylenated (POE) chain length; and the product usually contains about 14% of unreacted alcohol. Commercial materials having a narrow range of POE chain length have been developed by the use of new catalysts. These new materials contain less nonoxyethylenated hydrophobe (about

4%). The surface and bulk properties of these new materials are almost the same as those of conventional AES. The hardness tolerance of these new materials is better than that of conventional AES and less irritating to skin because of the less unreacted hydrophobe.

ADVANTAGES OVER AS. More water-soluble, more electrolyte resistant, much better lime soap dispersing agents, foam more resistant to water hardness and protein soil. NH_4 salt is less irritating to skin and eyes, produces higher-viscosity solutions (advantages in shampoos).

USES. In light-duty liquid detergents to improve foaming characteristics; together with nonionic in heavy-duty liquids free of phosphates; in shampoos.

Sulfated Triglyceride Oils (Sulf[on]ated Oils) Produced by sulfation of the hydroxy group and/or a double bond in the fatty acid portion of the triglyceride. (Iodine values of triglycerides used range from 40 to 140.) Mainly castor oil used (fatty acid present is mainly 12-hydroxyoleic acid), but also fish oils, tallow, sperm oil (25% oleyl, 50% C_{16} saturated fatty acid, remainder saturated C_{18} and C_{16} unsaturated). First synthetic surfactant (1850). Mainly used as textile wetting, cleaning, and finishing agent. Also used as emulsifying agent in textile finishing, in metal cutting oils, and in liquoring compositions for leather.

ADVANTAGES. Cheap, easy to produce near room temperature by mixing oil and concentrated H_2SO_4. Product is a complex mixture since hydrolysis to sulfated di- and monoglycerides, and even free fatty acid, occurs during manufacture, and sulfonation occurs to a slight extent (in the α-position of fatty acid), yielding a wide range of properties. Adsorbs onto fibers to yield a soft "hand." Produces very little foam and decreases foaming of other surfactants.

DISADVANTAGES. Readily hydrolyzed in hot acidic or hot alkaline solutions.

Fatty Acid Monoethanolamide Sulfates, ***$RCONHCH_2CH_2OSO_3Na$*** RCO is usually derived from coconut oil. Produced by amidation of fatty acid with monoethanolamine, followed by sulfation.

USES. Shampoos, dishwashing detergents, light-duty liquid detergents, industrial detergents, wetting agents, emulsifying agents.

ADVANTAGES OVER AS. Less irritating to skin, more electrolyte resistant, much better lime soap dispersing agent, foam more resistance to water hardness. Better cleansing power for oily soil.

DISADVANTAGES. Hydrolyzed readily in hot acidic medium.

Polyoxyethylenated (POE) Fatty Acid Monoethanolamide Sulfates, $RCONHCH_2$-$CH_2O(CH_2CH_2O)_3SO_3Na$ RCO is usually derived from coconut oil. Produced by amidation of fatty acid or fatty acid methyl ester with monoethanolamine, followed by polyoxyethyenation and sulfation.

USES. Shampoos, body shampoos, dishwashing detergent.

ADVANTAGES. Better-stabilized foam, less irritating to skin than AES. Produces higher viscosity water solutions. Skin irritation with this type of material is lower than with that of the corresponding fatty acid monoethanolamido sulfates.

DISADVANTAGES. Hydrolyzed readily in hot acidic medium.

4. Phosphoric and Polyphosphoric Acid Esters, $R(OC_2H_4)_xOP(O)(O^-M^+)_2$ and $[R(OC_2H_4)_xO]_2P(O)O^-M^+$ Mainly phosphated POE alcohols and phenols, some sodium alkyl phosphates (not oxyethylenated). The POE materials are available in free acid form or as sodium or amine salts. Products are mixtures of monobasic and dibasic phosphates.

ADVANTAGES. The free acids have good solubility in both water and organic solvents, including some hydrocarbon solvents, and can be used in free acid form since acidity is comparable to that of phosphoric acid. Low foaming. Not hydrolyzed by hot alkali; color unaffected. POE materials show good resistance to hard water and concentrated electrolyte.

DISADVANTAGES. Only moderate surface activity as wetting, foaming, or washing agents. Somewhat more expensive than sulfonates. Sodium salts usually not soluble in hydrocarbon solvents.

USES. The polyoxyethylenated materials are used as emulsifying agents in agricultural emulsions (pesticides, herbicides), especially those blended with concentrated liquid fertilizer solutions, where emulsion stability in the presence of high electrolyte concentration is required; dry-cleaning detergents; metal cleaning and processing; hydrotropes (short-chain products).

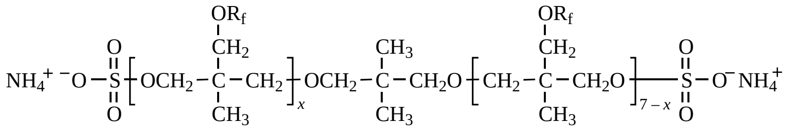
The nonoxyethylenated monoalkyl phosphates cause little skin irritation and are used in personal care products. The sodium salt of monododecyl phosphate, unlike soap, works in a weakly acidic medium and can therefore be used as a detergent in face cleaners and cleansers and in body shampoos. The potassium or alkanolammonium salt of monohexadecyl phosphate is used as an emulsifying agent in skin care products. The dialkyl phosphate must be avoided in the synthesis of these products, since it reduces foaming and water solubility.

5. Fluorinated Anionics Perfluorocarboxylic acids are much more completely ionized than fatty acids, hence are unaffected in aqueous solution by acids or polyvalent cations. They show good resistance to strong acids and bases, reducing and oxidizing agents, and heat (in excess of 600°F in some cases). They are much more surface active than the corresponding carboxylic acids and can reduce the surface tension of water to much lower values than are obtainable with surfactants containing hydrocarbon groups. They are also surface active in organic solvents. Perfluoroalkyl sulfonates, too, have outstanding chemical and thermal stability.

USES. Emulsifiers for aqueous lattices of fluorinated monomers. Suppression of chromic acid mist and spray from chromium plating baths. "Light water" control of oil and gasoline fires. Formation of surfaces that are both hydrophobic and oleophobic on textiles, paper, and leather. Inhibition of evaporation of volatile organic solvents.

DISADVANTAGES. Much more expensive than other types of surfactants; resistant to biodegradation even when straight-chain.

Fluorinated Polyoxetanes



$$NH_4^{+}\,{}^{-}O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\left[OCH_2-\overset{\overset{OR_f}{|}}{\overset{CH_2}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}}-CH_2\right]_x OCH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2O\left[CH_2-\overset{\overset{OR_f}{|}}{\overset{CH_2}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}}-CH_2O\right]_{7-x}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O^{-}NH_4^{+}$$

$R_f = CH_2CF_3, CH_2CF_2CF_3, CH_2CH_2(CF_2)_4F$

Ring-opening cationic polymerization of a perfluoroalkyl-substituted oxetane monomer using a Lewis acid catalyst and a diol initiator leads to an amphiphilic α, ω-diol. Sulfation of the terminal hydroxyl groups leads to an anionic bolaamphiphile.

USES. Are effective and efficient wetting, flow, and leveling aids in aqueous and some solvent-borne coatings. Produce little foam when agitated.

ADVANTAGES. Designed to have less environmental impact than traditional, smaller fluorosurfactants with longer ($\sim C_8F_{17}$) perfluoroalkyl chains.

I.B. Cationics

ADVANTAGES. Compatible with nonionics and zwitterionics. Surface-active moiety has a positive charge, thus adsorbs strongly onto most solid surfaces (which are usually negatively charged), and can impart special characteristics to the substrate. Some examples are given in Table 1-2. This adsorption also makes possible the formation of emulsions that "break" in contact with negatively charged substrates, allowing deposition of active phase on substrate.

DISADVANTAGES. Most types are not compatible with anionics (amine oxides are an exception). Generally, more expensive than anionics or nonionics. Show poor detergency, poor suspending power for carbon.

TABLE 1-2 Some Uses of Cationics Resulting from Their Adsorption onto Solid Substrates

Substrate	Use
Natural and synthetic fibers	Fabric softeners, antistatics, textiles auxiliaries
Fertilizers	Anticaking agents
Weeds	Herbicides
Aggregates	Adhesion promoters in asphalt
Metals	Corrosion inhibitors
Pigments	Dispersants
Plastics	Antistatics
Skin, keratin	Toiletries, hair conditioners
Ores	Flotation agents
Microorganisms	Germicides

Source: M. K. Schwitzer, *Chemistry and Industry*, 822 (1972).

1. Long-Chain Amines and Their Salts, $RNH_3^+X^-$ Primary amines derived from animal and vegetable fatty acids and tall oil; synthetic C_{12}–C_{18} primary, secondary, or tertiary amines. Adsorb strongly onto most surfaces, which are usually negatively charged. Very soluble and stable in strongly acidic solutions. Sensitive to pH changes—become uncharged and insoluble in water at pH above 7.

USES. Cationic emulsifying agents at pH below 7. Corrosion inhibitors for metal surfaces, to protect them from water, salts, acids. Saturated, very long-chain amines best for this purpose, since these give close-packed hydrophobic surface films. Used in fuel and lubricating oils to prevent corrosion of metal containers. Anticaking agents for fertilizers, adhesion promotors for painting damp surfaces. Ore flotation collectors, forming nonwetting films on specific minerals, allowing them to be separated from other ores.

DISADVANTAGES. Poor leveling is characteristic of cationic wax or wax–resin emulsions.

2. Acylated Diamines and Polyamines and Their Salts Uses and properties similar to those above. Products of the type $(RCONHCH_2\text{-}CH_2)_2NH$ are used as adhesion promotors for asphalt coating of wet or damp road surfaces.

OTHER USES. Ore flotation, to produce hydrophobic surface on ore or impurities; pigment coating, to make hydrophilic pigment lipophilic (adsorbed diamine salt yields positively charged surface, which then adsorbs fatty acid anion to give strongly chemisorbed lipophilic monolayer).

3. Quaternary Ammonium Salts

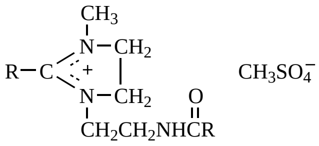
ADVANTAGES. Electrical charge on the molecule is unaffected by pH changes—positive charge remains in acidic, neutral, and alkaline media.

DISADVANTAGES. Since water solubility is retained at all pHs, they are more easily removed from surfaces onto which they may be adsorbed (insolubility of non-quaternary amines in water at pH above 7 is often an advantage). The long-chain dialkyl dimethylammonium chlorides are resistant to biodegradation. Alkyl pyridinium salts in alkaline aqueous solution are unstable and darken; alkyl trimethylammonium halides are stable even in hot aqueous alkaline solution.

USES. *N*-Alkyltrimethylammonium chlorides, $RN^+(CH_3)_3Cl^-$, are used as dye transfer inhibitors in rinse cycle fabric softeners. They are also used as emulsifying agents for acidic emulsions or where adsorption of emulsifying agent onto substrate is desirable (e.g., in insecticidal emulsions, adsorption of emulsifying agent onto substrate breaks emulsion and releases active ingredient as water-insoluble material). Highly effective germicides for industrial use. (Bis [long-chain alkyl] derivatives are less effective than monoalkyls; oxyethylenation drastically reduces germicidal effect; chlorinated aromatic ring increases it.)

N-Benzyl-*N*-alkyldimethylammonium halides $RN^+(CH_2C_6H_5)(CH_3)_2Cl^-$, are used as germicides, disinfectants, sanitizers. They are compatible with alkaline inorganic salts and nonionics and are used together with them in detergent-sanitizers for public dishwashing (restaurants, bars). They are also used as hair conditioners (after shampoo rinses), since they adsorb onto hair, imparting softness and antistatic properties. The cetyl derivative is used in oral antiseptics. Cetylpyridinium bromide is used in mouth washes. Behenyl (C_{22}) trimethylammonium chloride is used in hair rinses and hair conditioners, since it adsorbs more strongly onto hair than shorter-chain cationics, showing softening and antistatic properties.

Dialkyldimethylammonium salts of the type $R_2N^+(CH_3)_2Cl^-$ and imidazolinium salts of structure



(R from tallow or hydrogenated tallow) are used as textile softeners industrially and for home use in the rinse cycle of washing machines. They impart fluffy, soft "hand" to fabrics by adsorbing onto them with hydrophobic groups oriented away from fiber.

At present, triethanolamine ester quats (TEAEQ), with a formal structure of $(RCO_2CH_2CH_2)_2N^+(CH_3)CH_2CH_2OH \cdot CH_3SO_4^-$ are the fabric softeners of choice in Europe and elsewhere, replacing the imidazolinium and dialkyldimethyl ammonium types.

ADVANTAGES OF TEAEQ. Ease of biodegradation and environmentally friendly profile.

DISADVANTAGES OF TEAEQ. Although the diester quat is the desired ingredient, with the best performance characteristics, the commercial TEAEQ is a mixture containing major amounts of monoester quat, the triester quat, and the triester amine. It therefore gives medium performance compared to the other-mentioned types of fabric softeners.

4. Polyoxyethylenated (POE) Long-Chain Amines, $RN[(CH_2CH_2O)_xH]_2$ Combine increased water solubility imparted by POE chains with cationic characteristics of the amino group. As the oxyethylene content increases, cationic properties decrease and materials become more like nonionics in nature (e.g., solubility in water does not change much with pH change; incompatibility with anionics diminishes). If oxyethylene content is high enough, materials do not require acidic solution for water solubility.

USES. In production of xanthate rayon to improve tensile strength of regenerated cellulose filaments and to keep spinnerets free of incrustations. Emulsifying agents for herbicides, insecticides, polishes, and wax emulsions, which "break" on contact with the substrate and deposit the oil phase on it.

ADVANTAGES. Salts with inorganic or low-molecular-weight organic acids are water-soluble, those with high-molecular-weight organic acids are oil-soluble, even when the free POE amines are oil-insoluble. Show inverse solubility in water on heating, like other polyoxyethylene derivatives.

5. Quaternized POE Long-Chain Amines $RN(CH_3)[(C_2H_4O)_xH]_2^+Cl^-$ is used as textile antistatic agent (ionic charge dissipates static charge; polyethylene group adsorbs water, which also dissipates charge). Also used as dyeing leveler (retarder) by competing transiently for dye sites on fabrics during the dyeing process, thereby decreasing the rate of dyeing at its most active sites—where it is most rapidly adsorbed—to that of the less active sites. This causes more uniform dyeing. Used as corrosion inhibitors for metallic surfaces. $(RCONHCH_2CH_2)_2N^+$ $(CH_3)(CH_2CH_2O)_xH \cdot CH_3SO_4^-$ (RCO from tallow) is used as fabric softener in rinse cycle of laundry washing. Promotes adhesion in asphalt (by adsorption to form hydrophobic, oleophilic surface film on substrate). Dispersing agent for clay in greases, emulsifying agent for polar compounds (e.g., fatty acids and amines) in O/W emulsions. Trifluoroacetate salts are used to produce foam that reduces chromic acid spray and mist in chromium plating. $[RCONH(CH_2)_3N(CH_3)_2CH_2CH_2OH]^+$ NO_3^- is used as a surface or internal antistatic for plastics.

6. Amine Oxides, $RN^+(CH_3)_2O^-$ Usually, *N*-alkyldimethylamine oxides. These are usually classified as cationics, although they are actually zwitterionics, and will be so classified in the following chapters (including the tables). They are compatible with anionics, cationics, and nonionics, and other zwitterionics. Show excellent wetting in concentrated electrolyte solutions. The molecule adds a proton under the proper conditions, e.g., at low pH or in the presence of anionic surfactants, to form the cationic conjugate acid. The conjugate acid forms 1 : 1 salts with anionics that are much more surface-active than either the anionic or the amine oxide. Used as foam stabilizer for anionics in detergents, liquid dishwashing compounds, and shampoos. Also increase the viscosity of the shampoo and manageability of hair. Cetyl dimethylamine oxide is used in electroplating baths. The stearyl derivative imparts a smooth "hand" to fabrics and hair.

ADVANTAGE OVER ALKANOLAMIDE FROM STABILIZERS. Effective at lower concentrations.

I.C. Nonionics

ADVANTAGES. Compatible with all other types of surfactants. Generally available as 100% active material free of electrolyte. Can be made resistant to hard water, polyvalent metallic cations, electrolyte at high concentration; soluble in water and organic solvents, including hydrocarbons. POE nonionics are generally excellent dispersing agents for carbon.

DISADVANTAGES. Products are liquids or pastes, rarely nontacky solids. Poor foamers (may be an advantage sometimes); no electrical effects (e.g., no strong adsorption onto charged surfaces). Ethylene oxide derivatives show inverse temperature effect on solubility in water, may become insoluble in water on heating. Commercial material is a mixture of products with a wide distribution of POE chain lengths. POE chains with terminal hydroxyl show yellowing (due to oxidation) in strong alkali that can prevented by etherifying (*capping*) the hydroxyl.

1. POE Alkylphenols, Alkylphenol "Ethoxylates" (APE), $RC_6H_4(OC_2H_4)_xOH$

Mainly POE *p*-nonylphenol, *p*-octylphenol, or *p*-dodecylphenol (sometimes, dinonylphenol), derived from disobutylene, propylene trimer, or propylene tetramer.

ADVANTAGES. Length of alkyl group on phenol or POE chain can be varied to give range of products varying in solubility from water-insoluble, aliphatic hydrocarbon-soluble products (1–5 mol of ethylene oxide) to water-miscible, aliphatic hydrocarbon-insoluble ones. POE linkages are stable to hot dilute acid, alkali (except for some yellowing in the latter), and oxidizing agents results from hydratable multiple ether linkages. Advantage over POE alcohols in that there is never any free alkylphenol in APE, since phenolic OH is more reactive than alcohol OH. Thus no toxicity or dermatology problems associated with free phenol or other problems associated with presence of free hydrophobe.

DISADVANTAGES. Even though APEs will completely biodegrade under aerobic conditions, the rates are slower than with other nonionic surfactants such as linear alcohol ethoxylates. The aerobic biodegradation intermediates are more toxic to fish and other aquatic organisms than the parent APE. Also, there are reports that APEs may show endocrine disruptive activity in model systems in laboratory tests, although no demonstration of APE endocrine disruptive activity in actual environmental systems has been found.

USES. Mainly industrial because of low degradability. Water-insoluble types used for W/O emulsifying agents, foam control agents, cosolvents; water-soluble types for O/W emulsifying agents for paints, agricultural emulsions, miscellaneous industrial and cosmetic emulsions. Materials with high ethylene oxide (EO) content ($>$15 mol EO) are used as detergents and emulsifiers in strong electrolyte systems and as foam entrainment agents in concrete. Also used in liquid detergents and as dyeing retarders for cellulose (surfactant forms complex with dye molecules). Excellent dispersing agents for carbon.

2. POE Straight-Chain Alcohols, Alcohol "Ethoxylates" (AE), $R(OC_2H_4)_xOH$ Alcohol ethoxylates, like alcohol sulfates and alcohol ethoxysulfates, can be made from either oleochemical or petrochemical alcohols. Consequently, the linearity of the hydrophobe can vary from highly linear when the alcohol is derived from oleochemical sources and some petrochemical sources to highly branched from other petrochemical sources. Often a blend of several carbon chain length alcohols is used to produce commercial products. To make these surfactants, EO is added to a blend of alcohols in the presence of a catalyst, often NaOH or KOH, until the average degree of ethoxylation is achieved. The result is a mixture that varies in both the carbon chain length and the distribution of ethoxymers. "Peaking" catalysts can be used to narrow the distribution of ethoxymers. Oleyl derivatives are more fluid than saturated alcohol derivatives; lubricating properties are more pronounced in the saturated alcohol derivatives than in the unsaturated ones. Used for industrial purposes similar to those of APE. In low- and controlled-foam laundry detergents.

ADVANTAGES. The AE structure can be optimized for performance since the average hydrophobe, hydrophile, and distribution of the ethoxymers can be varied. AES biodegrade more readily than alkylphenol ethoxylates. AES are more tolerant of high ionic strength and hard water than anionic surfactants and exhibit better stability in hot alkaline solutions than ethoxylated fatty acids. They also have excellent compatibility with enzymes in laundry formulations. Are more water-soluble and have better wetting powers than corresponding fatty acid ethoxylates. Somewhat better than the corresponding APE for emulsification. More water-soluble than LAS, for use in high active, heavy-duty liquid detergents free of phosphates. More effective detergency than LAS under cool washing conditions and on synthetic fabrics.

DISADVANTAGES. High concentrations of AES in laundry powders often "bleed" from the powder, giving poor powder properties. Because AEs are composed of a distribution of ethoxymers, some unethoxylated alcohol remains in commercial products. If present in sufficient quantity, this can impart an objectionable odor to the ethoxylate. This can be ameliorated to some extent by using a "peaking" ethoxylation catalyst.

Aqueous solutions of these "peaked" materials show lower toxicities, lower viscosities, lower gel temperatures, and remain fluid over a wider concentration range. In spray-drying operations, there is less evolution of volatile material, since they contain less unreacted hydrophobe than conventional materials. They wet cotton more efficiently, show higher initial foam heights (but lower foam stability), reduce interfacial tension against mineral oil more efficiently and effectively than the corresponding conventional types. When sulfated to produce AES, the product has less non-POE alkyl sulfate and, consequently, less skin irritation and a greater tendency to thicken upon salt addition.

USES. AEs are excellent detergents for removal of oily soil and are often used in laundry products, especially liquids. They are also excellent emulsifiers and suspending agents in numerous industrial applications, where they compete with alkylphenol ethoxylates.

3. POE Polyoxypropylene Glycols Block copolymers of EO and propylene oxide. Materials with low EO content have very little foam; materials of high molecular weight with low EO content are wetting agents. Materials with high EO content are dispersing agents. Products range in molecular weight from 1000 to 30,000. Can form aqueous gels when hydrophobe (polypropylene oxide) molecular weight is greater than 1750.

USES. High-molecular-weight materials with high EO content are used as dispersants for pigments in latex paints or for scale removal in boilers; low-molecular-weight materials with low EO content are used as foam control agents in laundry detergents and in rinsing aids for dishwashing. Petroleum demulsifiers.

ADVANTAGES. Both hydrophobic group $\leftarrow\!\!(CH_2CH(CH_3)O)\!\!\rightarrow_x$ and hydrophilic group $(CH_2CH_2O)_y$ can be varied at will to "tailor-make" products with specific properties. Products with high-molecular-weight hydrophobes and high EO contents are nontacky solids (in contrast to other POE nonionics). Better wetting agents than ester-type nonionics.

DISADVANTAGES. Polyoxypropylene group is less biodegradable than POE group.

4. POE Mercaptans, $RS(C_2H_4O)_xH$ Unstable to oxidizing agents, such as chlorine, hypochlorites, per-oxides, and strong acids. (This may be an advantage when inactivation of surfactant after use is desired.) Stable in hot, strong alkali. Good lime soap dispersants.

USES. Textile detergents (cleaning and scouring of wool), metal cleaning, shampoos.

ADVANTAGES. Some evidence that quaternary amonium compounds are more effective as detergent sanitizers when formulated with POE mercaptans rather than with other POE nonionics.

DISADVANTAGES. Have slight, unpleasant odor that is difficult to mask.

5. Long-Chain Carboxylic Acid Esters

ADVANTAGES. In some cases, very easily made in simple equipment. Outstanding emulsifying properties compared to other nonionic types.

DISADVANTAGES. Readily hydrolyzed by hot acids or hot alkalis. Lower foam than other nonionic types (may be advantage for some uses).

Glyceryl and Polyglyceryl Esters of Natural Fatty Acids

ADVANTAGES. Glyceryl esters are easily made by glycerolysis of triglycerides or, somewhat more expensively, by esterification of fatty acids with glycerol in simple equipment. Edible, hence usable in food and pharmaceutical products. May be liquid, soft plastic, or hard wax, depending on fatty acid composition. Can be modified by reaction with acetic, lactic, or tartaric acids. Polyglycerol esters of fatty acids are made by esterification of polymerized glycerol.

DISADVANTAGES. Mixture of mono- and diglycerides (glycerides of ∼90% monoester content must be made by distillation of usual reaction product). Monoglyceride is a better emulsifier than diglyceride.

USES. Cosmetic emulsifiers, food emulsifiers for bread, ice cream, margarine, synthetic cream, and other dairy products.

Propylene Glycol, Sorbitol, and POE Sorbitol Esters Propylene glycol esters are more lipophilic than the corresponding glycerol esters; sorbitol esters are more hydrophilic (unless dehydrated in course of manufacture). Polyoxyethylenation of sorbitol (and anhydrosorbitol produced during manufacture) gives wide range of solubilities and hydrophilic–lipophilic balances to products.

ADVANTAGES. Edible, thus useful for food and drug use (e.g., soluble vitamins).

USES. Food and pharmaceutical emulsifiers.

Polyoxyethylene Glycol Esters and Polyoxyethylenated (POE) Fatty Acids (Including Tall Oil) Prepared either by esterification of polyoxyethylene glycol with fatty acid or by addition of ethylene oxide to fatty acid. Tall oil derivatives have lower foaming properties than corresponding fatty acid derivatives. Advantage over glyceryl esters is that length of hydrophilic group, and hence solubility and hydrophilic–lipophilic balance of product, can be varied as desired. Generally better emulsifying agents than AE or APE.

DISADVANTAGES. Generally poor wetting properties; hydrolyzed by hot alkaline solutions.

USES. Emulsification of all sorts, especially in cosmetics and for textile use, except where hot alkaline solutions are encountered. Textile antistats.

6. Alkanolamine ''Condensates,'' Alkanolamides Mainly of diethanolamine or monoisopropanolamine. Good stability to hydrolysis by hot alkali, poor–fair stability to hot acids.

1 : 1 Alkanolamine–Fatty Acid "Condensates" Made by reaction of methyl or triglyceride ester of fatty acid with equimolar amount of alkanolamine (about 90% alkanolamide content in product from methyl ester, 80% from triglyceride). Mainly based on coconut or purified coconut (lauric) esters.

Diethanolamides are insoluble but dispersible in water, soluble in organic solvents except some aliphatic hydrocarbons. Compatible with both anionics and cationics over wide pH range. Poor wetting and detergent properties, but synergistic to surfactants showing these properties. Show corrosion-inhibiting properties for steel. Easily prepared.

USES. Foam stabilizers for LAS in laundry and dishwashing detergents (alternative to amine oxides). Thickeners for liquid detergents and shampoos (containing sodium lauryl sulfate).

2 : 1 Alkanolamine–Fatty Acid "Condensates" Made by reaction of 2 mol alkanolamine with 1 mol free fatty acid. Contains about 60–70% alkanolamide, 25–30% alkanolamine, 3–5% fatty acid (as soap of alkanolamine). Mainly based on coconut fatty acid.

ADVANTAGES OVER 1 : 1 CONDENSATE. Diethanolamine–coconut fatty acid ''condensate'' is soluble in both water and organic solvents except aliphatic hydrocarbons. Excellent detergent, emulsifier, and viscosity thickener in aqueous medium at low concentrations.

DISADVANTAGES. Complex mixture; foam stabilization depends only on amide content (60–70%). Fatty acid content makes it incompatible with cationics.

USES. Textile detergent, shampoo ingredient, emulsifying agent, rust inhibitor, dry-cleaning soap, fuel oil additive.

7. Tertiary Acetylenic Glycols, $R_1R_2C(OH)C{\equiv}CC(OH)R_1R_2$, and Their ''Ethoxylates,'' $R_1R_2C[(OC_2H_4)_xOH]C{\equiv}CC[(OC_2H_4)_xOH]R_1R_2$

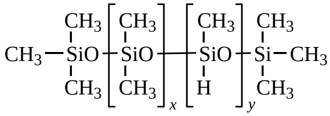
ADVANTAGES OF THE GLYCOLS. Excellent wetting agents at low concentrations and nonfoaming; nonwaxy solids (rare among nonionics); volatile with steam, thus readily removed from system after use.

DISADVANTAGES OF THE GLYCOLS. Very low solubility in water; decompose in acidic medium; relatively expensive.

Polyoxyethylenation of the hydroxyl groups with a few oxyethylene units increases solubility in water without significant change in surface properties, but resulting products are liquid and nonvolatile with steam.

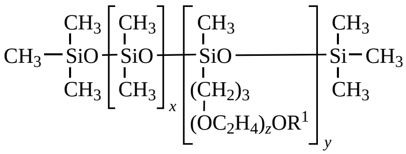
USES. Wetting agents for use in powdered solids (dyestuffs, wettable pesticide powders); synergistic with anionics and nonionics to decrease foam, reduce viscosity, and increase wetting in aqueous solution; rinse aids in dishwashing; wetting agents in emulsion paits.

8. POE Silicones These are the reaction products of a reactive silicone intermediate, such as



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}O\left[\underset{CH_3}{\overset{CH_3}{Si}}O\right]_x\left[\underset{H}{\overset{CH_3}{Si}}O\right]_y\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

with a capped allyl polyalkylene oxide, such as $CH_2{=}CH-CH_2-(OC_2H_4)_z-OR^1$, to yield

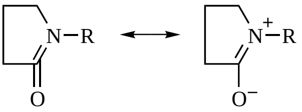


$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}O\left[\underset{CH_3}{\overset{CH_3}{Si}}O\right]_x\left[\underset{\underset{(OC_2H_4)_zOR^1}{|}}{\underset{(CH_2)_3}{\overset{CH_3}{Si}}}O\right]_y\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

The capped allyl polyalkylene oxide can also be based upon propylene oxide or a mixed ethylene oxide–propylene oxide copolymer. The resulting structure is a "comb" polymer, with pendant capped hydrophilic groups. In aqueous solution, the hydrophilic groups may form a sheath around the hydrophobic silicone backbone to minimize its contact with the water.

Minimum surface tensions for products of this type in aqueous solution fall in the 20- to 25-dyn/cm range at 25°C. They are excellent wetting agents at concentrations of a few hundredths of a percent for cotton and show good lubricating properties of textile fibers. They are also excellent wetting agents for polyester and polyethylene. They are low to moderate foamers in aqueous solution. They can also be used to lower the surface tension of nonaqueous solvents such as polyalkylene glycols.

9. N-Alkylpyrrolidones,



These are nonionic surfactants that, because of their dipolar resonance form, also show some of the properties of zwitterionics. They have limited solubility in water

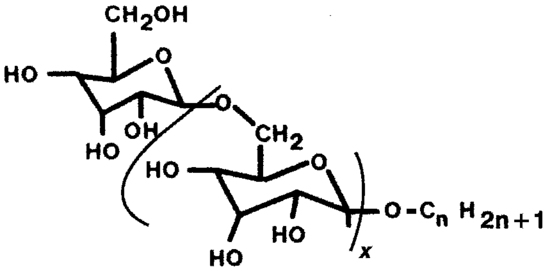


FIGURE 1-1 Alkylpolyglycoside.

and do not form micelles by themselves in it at room temperature, but do form mixed micelles with other surfactants (e.g., LAS).

Their surface activity is high, the *n*-dodecyl compound depressing it to about 26 dyn/cm at a concentration of 0.002%. The *n*-octyl compound is an excellent low-foaming wetting agent. It also interacts synergistically with anionic surfactants, e.g., LAS, to increase their foaming and wetting properties. *N*-alkylpyrrolidones, like polyvinyl pyrrolidone, act as complexing agents, particularly for phenols and other organic compounds that are capable of forming hydrogen bonds with the pyrrolidone ring.

10. Alkylpolyglycosides These are long-chain acetals of polysaccharides. A representative type in shown in Figure 1-1. Commercial products currently available have relatively short alkyl chains (averaging 10 and 12.5 carbon atoms). They show wetting, foaming, detergency, and biodegradation properties similar to those of corresponding alcohol ethoxylates, but have higher solubility in water and in solutions of electrolytes. They are also soluble and stable in sodium hydroxide solutions, in contrast to AE. Although effective fatty soil removers, they show very low skin irritation and are recommended for hand liquid dishwashing and hard surface cleaners.

I.D. Zwitterionics

ADVANTAGES. Compatible with all other types of surfactants. Less irritating to skin and eyes than other types. May be adsorbed onto negatively or positively charged surfaces without forming hydrophobic film.

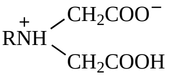
DISADVANTAGES. Often insoluble in most organic solvents, including ethanol.

1. pH-Sensitive Zwitterionics These are ampholytic materials, which may show the properties of anionics at high pHs and those of cationics at low pHs. In the vicinity of their isoelectric points they exist mainly as zwitterionics and show minimum solubility in water, and minimum foaming, wetting, and detergency.

β-N-Alkylaminopropionic Acids, $RN^+H_2CH_2CH_2COO^-$ Isoelectric point at pH ∼ 4. Very soluble in aqueous solutions of strong acids and alkalies, even in the presence of electrolytes like NaCl. Solubility is low in most organic solvents, including ethanol and isopropyl alcohol. Adsorb from aqueous solution onto skin, textiles, fibers, and metals. On hair and textile fibers they confer lubricity, softness, and antistatic properties; on metals they act as corrosion inhibitors. They solubilize many organic and inorganic compounds (e.g., quaternary ammonium salts, phenols, polyphosphates) in aqueous solutions. Effective emulsifying agents for long-chain alcohols and slightly polar compounds, not good for paraffinic oils. Emulsions can be converted from anionic to cationic by pH adjustment. Emulsions more easily prepared at alkaline than at acidic pHs. *N*-Dodecyl derivative is an excellent wetting agent and foam producer at alkaline pHs, less of a foamer at acid pHs.

USES. Bactericides, corrosion inhibitors, pigment dispersion aids, cosmetics, alkaline cleaners with high alkali and electrolyte content.

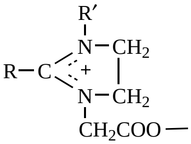
N-Alkyl-β-iminodipropionic Acids,



Isoelectric point, pH 1.7–3.5. More soluble in water than corresponding monopropionic acid derivatives. Show very little skin and eye irritation. May be removed from substrates onto which they have adsorbed at pHs below their isoelectric points by raising the pH.

USES. Fabric softeners (removed by increase in the pH to the alkaline side).

Imidazoline Carboxylates,



R from RCOOH of commercially available fatty acids. When R′ is H, they are ampholytic and show cationic properties at low pHs, anionic properties at high pHs. When R′ = CH_2Z, pH sensitivity is more closely related to that of *N*-alkylbetaines (below). Compatible with anionics, cationics, and nonionics, soluble in water in the presence of high concentrations of electrolytes, acids, and alkalies. When R′ contains a second carboxylic acid group, products show very little skin and eye irritation.

USES. Cosmetic and toilet preparations, fabric softener (which can be removed from substrate by increase in pH to the alkaline side).

N-Alkylbetaines, $RN^+(CH_3)_2CH_2COO^-$ These materials are zwitterionic at pHs at and above their isoelectric points (neutral and alkaline pHs) and cationic below their isoelectric points (acid pHs). They show no anionic properties. Compatible with all classes of surfactants at all pHs, except that at low pHs they yield precipitates with anionics. Acid and neutral aqueous solutions are compatible with alkaline earth and other metallic ions (Al^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}). They show minimum skin irritation at pH 7. Show constant adsorption onto negatively charged surfaces (as cationics), irrespective of pH. Slightly better wetting and foaming properties at acidic than at alkaline pHs. Hard water has no effect on foaming properties in aqueous solution. Emulsification properties are similar to those of β-*N*-alkylaminopropionic acids (not good for paraffinic oils).

USES. Similar to those of β-*N*-alkylaminopropionic acids.

Amidoamines and Amidobetaines These are products, related to the above, of typical structures:$RCONHCH_2CH_2N^+H(CH_2CH_2OH)CH_2COO^-$, $RCONHCH_2CH_2$-$N^+H(CH_2CH_2OH)$–$CH_2CH_2COO^-$, and $RCONHCH_2CH_2CH_2N^+(CH_3)_2COO^-$, that are used in cosmetics and personal care products (shampoos, liquid soaps, facial cleaners) because of their mildness on the skin and compatibility with anionic, cationic, and nonionic surfactants. The RCO group is usually $\sim C_{12}$.

Amine Oxides, $RN^+(CH_3)_2O$ See Cationics, Section I.B, above.

2. pH-Insensitive Zwitterionics These materials are zwitterionics at all pHs (at no pH do they act merely like anionics or cationics).

Sulfobetaines, Sultaines, $RN^+ (CH_3)_2(CH_2)_xSO_3^-$ Adsorb onto charged surfaces at all pHs without forming hydrophobic films. Good lime soap dispersants. Show little skin irritation.

USES. Similar to other zwitterionics. Lime soap dispersants in soap-detergent formulations. Dispersants for textile finishing agents.

I.E. Newer Surfactants Based Upon Renewable Raw Materials

There has been intense interest in recent years in using renewable, readily biodegradable resources for both the hydrophilic and hydrophobic groups of commercial surfactants in order to provide them with a favorable environmental ("green") image. The search has centered upon natural fats as the source for hydrophobic groups and upon naturally occurring carbohydrates and amino acids (from proteins) for hydrophilic groups.

Soaps, of course, are based upon renewable fats and lignin sulfonates upon wood, while sulfated alcohols and sulfated triglycerides among the anionics, and glyceryl, polyglyceryl, sucrose, and sorbitol fatty acid esters and alkyl polyglycosides among the nonionics can be based upon renewable resources and thus considered "green."

1. α-Sulfofatty Acid Methyl Esters (SME), $RCH (SO_3^-Na^+)COOCH_3$ Produced by the reaction of SO_3 with fatty acid methyl esters (derived from triglycerides by transesterification with methanol). Generally from C_{12}–C_{18} fatty acid methyl esters.

ADVANTAGES. Derived from relatively low-cost, renewable raw materials. Good biodegradability. The tallow methyl ester sulfonate has somewhat better detergency than LAS in both hard and soft water, while the palm kernel derivative is somewhat poorer than LAS in soft water but better than it in hard water. Excellent lime soap dispersion properties, which enables effective formulation with soaps. Larger solubilizing capacity for unsaturated oily soil than LAS. Can be produced electrolyte-free.

DISADVANTAGES. Production of low-color SME generally requires complex manufacturing process. Process must be tuned to minimize sulfonated free fatty acid, which has reduced detergency and solubility in water relative to SME. Methyl ester group is prone to hydrolysis at low and high pH; consequently, SME is difficult to incorporate in spray-dried detergents.

USES. Primary or auxiliary anionic surfactant in heavy-duty laundry detergents or light-duty liquid detergents.

2. Acylated Aminoacids These materials have good foaming properties, are less sensitive to hard water than soap, are nonirritating to the skin, and have antibacterial activity and good biodegradability. They are relative expensive but are used in cosmetic, skin cleaning, and food formulations. The *N*-lauroyl (or cocoyl) derivatives generally show optimal properties.

3. N-Acyl L-Glutamates (AG), $RCONHCH(COO^-M^+)CH_2CH_2COO^-M^+$, $M{=}H^+$ ***or Cation*** Produced by *N*-acylation of L-glutamic acid with fatty acid chloride in a mixed solvent of water and water-miscible organic solvent. RCO is usually from coconut and tallow acids. AG is a dibasic acid, so both mono- and di-neutralized materials are possible. The carboxyl group at the α-position is neutralized prior to that at the γ-position. The water solubility of monosodium AG is low, so organic amines, i.e., triethanolamine or diethanolamine, or K^+ are used as counter-ions.

ADVANTAGES. The mono-neutralized AG works in aqueous solutions of weak acids, which is a favorable characteristic for cosmetic products. Mild to the skin. Decreases the skin irritancy of AS or AES.

USES. Mono-neutralized products based upon C_{12} fatty acid are used as detergents in face cleaners (to remove soil) and face cleansers (to remove makeup); those based on C_{18} fatty acids, as emulsifying agents in skin care products.

4. N-Acyl Glycinates, $RCONHCH_2COO^-M^+$ Produced by reaction similar to that of AG above. RCO is usually derived from coconut oil for detergent use.

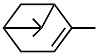
ADVANTAGES. *N*-acylglycinates have better foaming power, especially in the vicinity of pH 9, than sulfated linear primary alcohols (AS), sulfated POE straight-chain alcohols (AES), or alkyl ether carboxylates.

USES. Potassium N-cocoyl glycinate is often used in face cleaners (to remove soil) and face cleansers (to remove make-up). Mild to skin. For baby care products. Creamy foam.

5. N-Acyl DL-Alaninates, $RCONHCH(CH_3)COO^-M^+$ RCO is usually derived from coconut oil.

USES AND ADVANTAGES. Better foaming power for triethanolammonium *N*-dodecanoyl alaninate than AS, AES, and alkyl ether carboxylates in the pH region between weakly acidic and neutral. Good foaming power even in the presence of silicone oil. Used as a detergent in face cleaners and face cleansers. Mild to skin. For baby care products. Fine, creamy foam.

6. Other Acylated Aminoacids *N*-lauroyl sarcosinate, $C_{11}H_{23}CON(CH_3)$-$CH_2COO^-Na^+$, used in toothpaste, is strongly foaming, enzyme-inhibiting, with good detergency (like soap). *N*-oleylsarcosinate is a polyester fiber lubricant. *N*-lauryl-arginylphenylalanine shows strong antimicrobial activity against gram-positive and some gram-negative bacteria.

7. Nopol Alkoxylates,  $CH_2CH_2[OCH(CH_3)CH_2]_x(OC_2H_4)_yOH$

These are surfactants based upon nopol, an alcohol made by the reaction of β-pinene with formaldehyde. The nopol is reacted first with propylene oxide and then with ethylene oxide.

ADVANTAGES. Based upon renewable pine oil. Show good dynamic surface tension reduction, good wetting, extremely low foam, and good rinsing properties. Very low ecotoxicity profile compared to linear C_{12}, branched C_{13}, or nonylphenolethoxylates.

USES. Spray cleaning and other wetting applications.

For additional information on the utilization of surfactants for specific applications, see:

1. *Industrial Utilization of Surfactants: Principles and Practice*, M. J. Rosen and M. Dahanayake, AOCS, 2000.
2. *Surfactants in Agrochemicals*, T. F. Tadros, Marcel Dekker, 1994.
3. *Surfactants in Chemical/Process Engineering*, D. T. Wasan, M. E. Ginn, and D. O. Shah, editors, Marcel Dekker, 1988.
4. *Surfactants in Cosmetics*, M. M. Rieger and L. D. Rhein, 2nd edition, Marcel Dekker, 2002.
5. *Surfactants in Emerging Technologies*, M. J. Rosen, editor, Marcel Dekker, 1987.

II. ENVIRONMENTAL EFFECTS OF SURFACTANTS

II.A. Surfactant Biodegradability

Surfactants are "performance" chemicals; that is, they are used to perform a particular function in some process or product, in contrast to other organic chemicals that may be used to produce another chemical or product. Since they are used in products or processes that impact on the environment, there are concerns regarding their effect, particularly their biodegradability in the environment and their toxicity to marine organisms.

An excellent review of surfactant biodegradability (Swisher, 1987) points out that biodegradability increases with increased linearity of the hydrophobic group and is reduced, for isomeric materials, by branching in that group, particularly by terminal quaternary carbon branching. A single methyl branch in the hydrophobic group does not change the biodegradation rate, but additional ones do.

In isomeric alkylbenzene and alkylphenol derivatives, degradation decreases as the phenyl group is moved from a position near the terminal end of a linear alkyl group to a more central position.

In POE nonionics, biodegradation is retarded by an increase in the number of oxyethylene groups. The inclusion of oxypropylene or oxybutylene groups in the molecule tends to retard biodegradation. Secondary ethoxylates degrade more slowly than primary ethoxylates even when both have linear hydrophobic groups.

In cationic quaternary ammonium surfactants, compounds with one linear alkyl chain attached to the nitrogen degrade faster than those with two, and these degrade faster than those with three. The replacement of a methyl group attached to the nitrogen by a benzyl group retards the rate of degradation slightly. Pyridinium compounds biodegrade significantly more slowly than the corresponding trimethylammonium compounds, while imidazolinium compounds biodegrade rapidly.

II.B. Surfactant Toxicity To and Bioconcentration in Marine Organisms

The toxicity of surfactants to marine organisms and their concentration in them depends upon their tendency to adsorb onto them and their ability to penetrate their cell membranes (Rosen, 1999). The parameter $\Delta G^\circ_{ad}/a^s_m$, where ΔG°_{ad} is the standard free energy of adsorption of the surfactant at the aqueous solution–air interface (Chapter 2, Section IIIF) and a^s_m is the minimum cross-sectional area of the surfactant at that interface (Chapter 2, Section IIIB), was found to correlate well for several anionic and nonionic surfactants with rotifer toxicity. The same parameter was found to correlate well for a series of cationic surfactants with rotifer and green algae toxicity and, for a series of linear alkylbenzenesulfonates, with bioconcentration in fish (Rosen, 2001).

Thus, toxicity increases with an increase in the length of the hydrophobic group and, for isomeric materials, decreases with branching or movement of the phenyl group to a more central position in the linear alkyl chain; in linear POE alcohols, toxicity increases with decrease in the number of oxyethylene units in the molecule, all due to the expected changes in the values of both ΔG°_{ad} and of a^s_m.

Consequently, from the data in this section and in Section IIA above, it appears that some chemical structures in the surfactant molecule that promote biodegradability (such as increased length and linearity of the hydrophobic group or decreased oxyethylene content) increase its toxicity to or bioconcentration in marine organisms.

III. SOME USEFUL GENERALIZATIONS

Anionics are generally not compatible with cationics; that is, they precipitate each other from aqueous solution unless they have water-solubilizing groups in addition to their charges in their hydrophilic heads.

Carboxylic acid salts are more sensitive to low pH, polyvalent cations, and inert electrolyte in the aqueous phase than salts of organic phosphoric acids, and these in turn are more sensitive than organic sulfates or sulfonates.

Branched-chain unsaturated, or ring-containing surfactants are generally more soluble in both water and hydrocarbons and show lower viscosity in aqueous media than straight-chain materials with the same number of carbon atoms; the latter are much more biodegradable but more toxic to marine organisms than the former. Fluorocarbon chains, even when straight, are resistant to biodegradation.

Organic sulfates are readily hydrolyzed by hot acids; esters are readily hydrolyzed by hot alkali (or hot acids). Amides are more resistant to hydrolysis by hot acids or alkali than organic sulfates or esters, respectively.

Nonquaternary cationics are generally sensitive to high pH, polyvalent anions, and inert electrolyte in the aqueous phase; quaternary ammonium salts, on the other hand, are generally insensitive to these additives.

Oxyethylenation of any type of surfactant usually results in an increase in its solubility in water and a decrease in its sensitivity to pH change or electrolyte. Oxypropylenation increases its solubility in organic solvents but decreases its solubility in water.

Oxyethylenation of hydrophobes that are acidic (carboxylic acids, phenols) or basic (amines) leaves essentially no nonoxyethylenated hydrophobe, whereas oxyethylenation of alcohols generally leaves an appreciable amount of unreacted hydrophobe.

Edible ester-type surfactants can be based on glycerol, sorbitol, or propylene glycol. The foam stabilization and viscosity-thickening properties of diethanolamine–fatty acid condensates are related directly to their diethanolamide content; on the other hand, solubility in water is shown only by the 2 : 1 condensate.

Mercaptan-based nonionics are prone to develop a somewhat unpleasant odor and are unstable to oxidizing agents.

N-alkylaminoacids are sensitive to pH change, developing the characteristics of cationics at low pHs and those of anionics at high pHs. Zwitterionics containing a quaternized *N* and one carboxylate group (alkyl betaines) show the characteristics of cationics at low pHs, but show no anionic characteristics at high pHs. Sulfobetaines are insensitive to pH change.

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Rosen, M. J., F. Li, S. W. Morrall, and D. J. Versteeg, *Environ. Sci. Technol.* **35**, 54 (2001).

Swisher, R. D., *Surfactant Biodegradation*, 2nd edition, Marcel Dekker, New York, 1987.

PROBLEMS

Write the structural formula for a surfactant type in current use that fits the general description in each case:

1 Suitable for use in warm alkaline aqueous solution, but decomposes in warm acidic solution

2 An edible nonionic surfactant

3 Suitable, at neutral pH, for making most solid surfaces hydrophobic

4 An anionic surfactant unsuitable for use in a detergent bar for washing hands

5 A surfactant based entirely upon synthetic polymers

6 A zwitterionic surfactant whose structure does not change with change in pH

7 A surfactant that has the same chemical elements in both its hydrophilic and hydrophobic groups

8 An anionic surfactant unsuitable for use in hot alkaline solution.

9 An anionic surfactant based upon renewable resources that is nonirritating to the skin.

10 A surfactant used as a germicide.

2 Adsorption of Surface-Active Agents at Interfaces: The Electrical Double Layer

A fundamental characteristic of surfactants is their tendency to adsorb at interfaces in an oriented fashion. This adsorption has been studied to determine (1) the concentration of surfactant at the interface, since this is a measure of how much of the interface has been covered (and thus changed) by the surfactant; the performance of the surfactant in many interfacial processes (e.g., foaming, detergency, emulsification) depends on its concentration at the interface; (2) the orientation and packing of the surfactant at the interface, since this determines how the interface will be affected by the adsorption, that is, whether it will become more hydrophilic or more hydrophobic; (3) the rate at which this adsorption occurs, since this determines the performance in phenomena such as high-speed wetting or spreading; and (4) the energy changes, ΔG, ΔH, and ΔS, in the system, resulting from the adsorption, since these quantities provide information on the type and mechanism of any interactions involving the surfactant at the interface and the efficiency and effectiveness of its operation as a surface-active material.

In comparing the performance of different surfactants in interfacial phenomena, as in most phenomena, it is usually necessary to distinguish between the *amount* of surfactant required to produce a given amount of change in the phenomenon under investigation and the *maximum change* in the phenomenon that the surfactant can produce, regardless of the amount used. The former parameter is the *efficiency* of the surfactant, the latter its *effectiveness*. These two parameters do not necessarily run parallel to each other—in fact, in many cases they run counter to each other.

Throughout this text, *efficiency* is used as a measure of the equilibrium concentration of surfactant in the liquid phase necessary to produce a given amount of effect, and *effectiveness* is used as a measure of the maximum effect the surfactant can produce in that interfacial process irrespective of concentration.

In dilute solutions of surface-active agents, the amount of change in any interfacial phenomenon produced by the adsorption of surfactant at the interface is a function of the concentration of surfactant absorbed at the interface. Thus *efficiency* is determined by the ratio of surfactant concentration at the interface to that in the bulk (liquid) phase, $C_{\text{interface}}/C_{\text{bulk}}$. This ratio is determined by the free

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

energy change ΔG involved in the transfer of a surfactant molecule from the interior of the bulk phase to the interface by the equation $C_{\text{interface}}/C_{\text{bulk}} = \exp(-\Delta G/RT)$, where $R = 1.99$ cal (or 8.31 J)deg^{-1} mol^{-1} and $T =$ absolute temperature; therefore, efficiency is related to the free energy change associated with that transfer.

The advantage of measuring the effect of a surfactant on some interfacial phenomenon by some parameter that is related to the free energy change associated with the action of the surfactant in that phenomenon is that the total free energy change can be broken into the individual free energy changes associated with the action of the various structural groupings in the molecule; that is, $\Delta G_{\text{total}} = \sum_i \Delta G_i$, where ΔG_i is the free energy change associated with the action of any structural group in the molecule. This enables correlations to be made between the various structural groupings in the surfactant and its interfacial properties. In this fashion, the efficiency with which a surfactant is adsorbed at an interface can be related to the various structural groups in the molecule.

Since the effect of a surfactant on an interfacial phenomenon is a function of the concentration of surfactant at the interface, we can define the *effectiveness* of a surfactant in adsorbing at an interface as the maximum concentration that the surfactant can attain at that interface, i.e., the surface concentration of surfactant at surface saturation. The effectiveness of adsorption is related to the interfacial area occupied by the surfactant molecule; the smaller the effective cross-sectional area of the surfactant at the interface, the greater its effectiveness of adsorption. Effectiveness of adsorption, therefore, depends on the structural groupings in the surfactant molecule and its orientation at the interface. Another parameter characterizing the performance of surfactants, important in high-speed interfacial phenomena such as wetting and spreading, is the *rate* of adsorption of the surfactant at the relevant interface(s). This will be discussed in Section IV of Chapter 5.

Before going further into the adsorption of surfactants at interfaces, it is advisable to discuss the so-called electrical double layer at interfaces, since this is necessary for an understanding of the electrical aspects of adsorption.

I. THE ELECTRICAL DOUBLE LAYER

At any interface there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface and the so-called *electrical double layer.* Of course, since overall electrical neutrality must be maintained, the net charge on one side of the interface must be balanced by an exactly equal net charge of opposite sign on the other side of the interface.

A major problem for investigation has been the determination of the exact distribution of the neutralizing charges (*counterions* or *gegenions*) in the solution surrounding a charged surface, since this distribution determines the rate at which the electrical potential will change with distance from the charged surface. An early

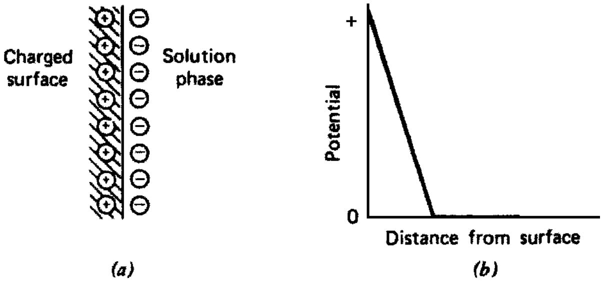

FIGURE 2-1 Helmholtz model of the electrical double layer. (*a*) Distribution of counterions in the vicinity of the charged surface. (*b*) Variation of electrical potential with distance from the charged surface.

theory concerning the distribution of these neutralizing charges in the solution surrounding a plane charged surface was that of Helmholtz (von Helmholtz, 1879), who envisioned all the counterions as being lined up parallel to the charged surface at a distance of about one molecular diameter (Figure 2-1*a*). According to this model, the electrical potential should fall rapidly to zero within a very short distance from the charged surface (Figure 2-1*b*).

This model allowed Helmholtz to treat the electrical double layer mathematically as a parallel plate condenser. However, this model was untenable, since thermal agitation tends to diffuse some of the counterions throughout the solution. Accordingly, it was superseded by a model proposed by Gouy (1910, 1917) and Chapman (1913), who envisioned a diffuse distribution of the counterions, with the concentration of the counterions (and the potential) falling off rapidly at first with distance from the charged surface, because of a screening effect (Figure 2-2*a*), and then more and more gradually with distance (Figure 2-2*b*). This model, useful for planar charged surfaces with low charge densities, or for distances not too close to the surface, was inadequate for surfaces with high charge densities, especially at

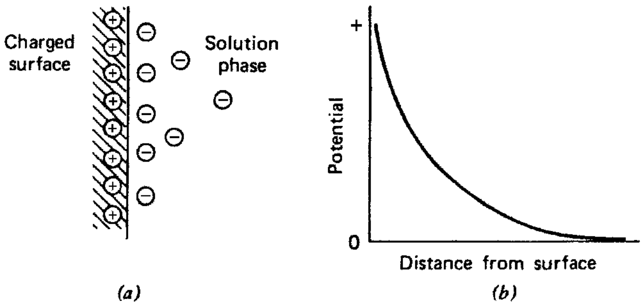

FIGURE 2-2 Gouy–Chapman model of the electrical double layer. (*a*) Distribution of counterions in the vicinity of the charged surface. (*b*) Variation of electrical potential with distance from the charged surface.

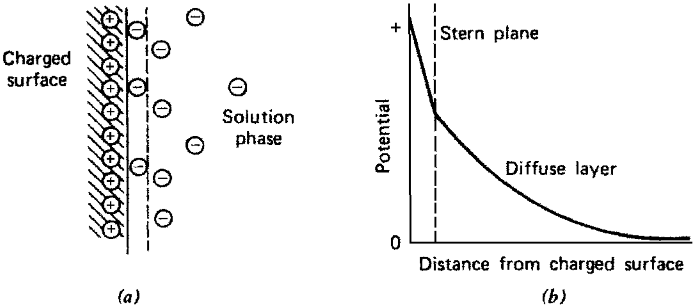

FIGURE 2-3 Stern model of the electrical double layer. (*a*) Distributioin of counterions in the vicinity of the charged surface. (*b*) Variation of electrical potential with distance from the charged surface.

small distances from the charged surface, since it neglected the ionic diameters of the charges in solution and treated them as point charges. It was therefore modified by Stern (1924), who divided the solution side of the double layer into two parts: (1) a layer of strongly held counterions, adsorbed close to the charged surface on fixed sites (to correct the basic defect of the Gouy–Chapman model), and (2) a diffuse layer of counterions similar to that of their model (Figures 2-3 and 2-4). According to this model, the electrical potential drops rapidly in the fixed portion (Stern layer) of the double layer and more gradually in the diffuse portion. The fixed counterions in the Stern layer may even change the sign of the potential resulting from the charged surface (Figure 2-4).

Mathematical treatment of the diffuse portion of the electrical double layer (Adamson, 1976) yields the very useful concept of an effective thickness 1/κ of that layer. This is the distance from the charged surface into the solution within which the major portion of electrical interactions with the surface can be considered to occur. The effective thickness, often called the *Debye length*, is given by

$$\frac{1}{\kappa}=\left(\frac{\varepsilon_r\varepsilon_0 RT}{4\pi F^2\sum_i C_i Z_i^2}\right)^{1/2} \tag{2.1}$$

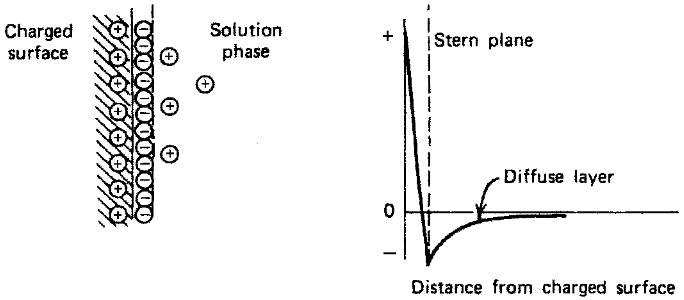

FIGURE 2-4 Stern model of the electrical double layer, showing reversal of the sign of the charged surface caused by adsorption of counterions in the Stern layer.

where $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$ = the relative static permittivity or dielectric constant of the solution (ε = the static permittivity of the solution and ε_0 = the permittivity of a vaccum),

R = the gas constant,

T = the absolute temperature,

F = the Faraday constant,

C_i = the molar concentration of any ion in the solution phase.

From the preceding relation, it is apparent that $1/\kappa$ is inversely proportional to the valence Z of the ions in the solution phase and to the square root of their concentrations. It is also directly proportional to the square roots of the absolute temperature and the relative static permittivity (or dielectric constant) of the medium. It is therefore to be expected that in a solvent of high dielectric constant, such as water, electrical effects extend much further into the solution phase than in a solvent of low dielectric constant, such as a hydrocarbon. Also, in the presence of an electrolyte, electrical effects have shorter ranges than in its absence—that is, the electrical double layer is *compressed.*

For 1 : 1 electrolytes at room temperature in aqueous solution, $1/\kappa \approx 3$Å for $1M$, 10Å for $0.1M$, 30Å for $0.01M$, 100Å for $1 \times 10^{-3}M$, and 300Å for $1 \times 10^{-4}M$ solutions.

A term often associated with the electrical double layer, and one that is often misused, is the *zeta potential*, or electrokinetic potential. This is the potential of a charged particle as calculated from electrokinetic phenomena (electroosmosis, electrophoresis, streaming potential, or sedimentation potential). It is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other. Zeta potentials are conveniently measured (Adamson, 1976), and it is very tempting to place this plane of shear at the solution side of the Stern layer, since this is the boundary of the fixed ion layer and would give us an experimentally calculable value for the potential at that boundary. Unfortunately, although some authors do identify the zeta potential with the potential at the solution edge of the Stern layer, the plane of shear is *not* necessarily at the solution edge of the Stern layer and is at some undetermined point somewhere farther out in the diffuse layer due to bound water moving with the charged particle or being held to it when the solution moves. The zeta potential is consequently smaller in magnitude than the Stern potential, but, unfortunately, exactly how much smaller is not known definitely.

II. ADSORPTION AT THE SOLID–LIQUID INTERFACE

The adsorption of surfactants at the solid–liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface—whether the surface contains highly charged sites or essentially nonpolar groupings,

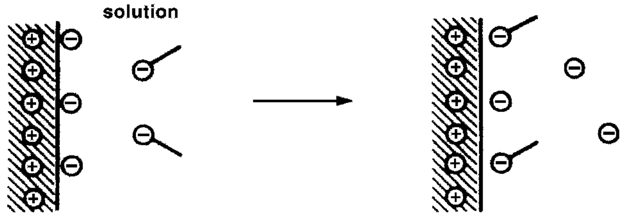

FIGURE 2-5 Ion exchange. Reprinted with permission from M. J. Rosen, *J. Am. Oil Chem. Soc.* **52**, 431 (1975).

and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being adsorbed (the adsorbate)—whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase—its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, urea, etc.), and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption. For a detailed review of cationic adsorption at the solid–liquid interface, see Atkins (2003).

II.A. Mechanisms of Adsorption and Aggregation

There are a number of mechanisms by which surface-active solutes may adsorb onto solid substrates from aqueous solution. In general, adsorption of surfactants involves single ions (Kolbel, 1959; Griffith, 1967) rather than micelles (Chapter 3).

1. *Ion Exchange* (Figure 2-5).* Involves replacement of counterions adsorbed onto the substrate from the solution by similarly charged surfactant ions (Wakamatsu, 1968; Rupprecht, 1972; Law, 1966).

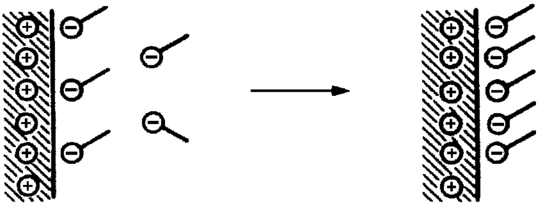

FIGURE 2-6 Ion pairing. Reprinted with permission from M. J. rosen, *J. Am. Oil Chem. Soc.* **52**, 431 (1975).

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*It should be clearly understood that the rigid arrangement of the hydrophobic groups depicted in Figures 2-5–2-10 is only for convenience in illustrating the mechanisms of adsorption. In reality, the hydrophobic groups may assume all conformations, including the interweaving of hydrophobic chains of adjacent molecules, consistent with their surface areas per molecule and the relative orientation of their hydrophobic and hydrophilic groups with respect to the interface.

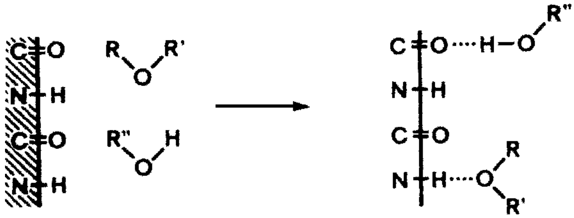

FIGURE 2-7 Hydrogen bonding. Reprinted with permission from M. J. Rosen, *J. Am. Oil Chem. Soc.* **52**, 431 (1975).

2. *Ion Pairing* (Figure 2-6). Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counterions (Rupprecht, 1972; Law, 1966).
3. *Acid–Base Interaction* (Fowkes, 1987). Via either hydrogen bond formation (Figure 2-7) between substrate and adsorbate (Law 1966; Snyder, 1968; Rupprecht, 1972) or Lewis acid–Lewis base reaction (Figure 2-8).
4. *Adsorption by Polarization of* π *Electrons.* Occurs when the adsorbate contains electron-rich aromatic nuclei and the solid adsorbent has strongly positive sites. Attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate results in adsorption (Snyder, 1968).
5. *Adsorption by Dispersion Forces.* Occurs via London–van der Waals dispersion forces acting between adsorbent and adsorbate molecules (Figure 2-9). Adsorption by this mechanism generally increases with an increase in the molecular weight of the adsorbate and is important not only as an independent mechanism, but also as a supplementary mechanism in all other types. For example, it accounts in part for the pronounced ability of surfactant ions

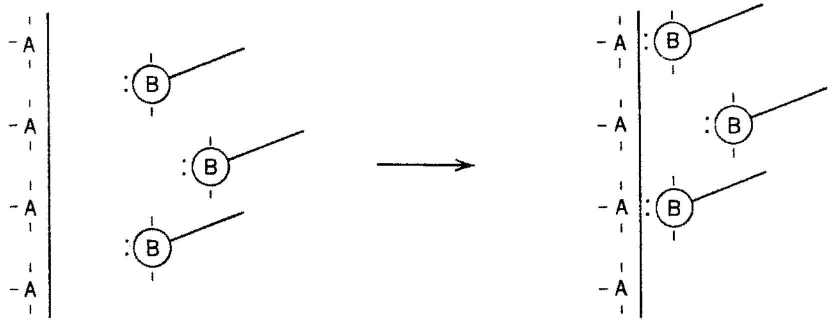

FIGURE 2-8 Adsorption via Lewis acid–Lewis base interaction.

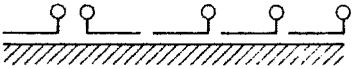

FIGURE 2-9 Adsorption via disperison forces on nonpolar surface.

to displace equally charged simple inorganic ions from solid substrates by an ion exchange mechanism (Kolbel, 1959; Law, 1966).

6. *Hydrophobic Bonding*. Occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains (Wakamatsu, 1968; Dick, 1971; Giles, 1974, Gao, 1987).

These surfactant aggregates, termed *admicelles* or *hemimicelles* by various investigators, were assumed to be more or less flat. Recent investigations (Manne and Gaub, 1995; Grosse and Estel, 2000; Wolgemuth, 2000) indicate that these aggregates, when in the form of monolayers (Figure 2-10*a*), may also be hemispherical and, when in the form of bilayers (Figure 2-10*b*), may also be in the form of cylinders (Figure 2-10*b*). They will be designated *surface aggregates* to distinguish them from micelles (Chapter 3) in the solution phase. Flat sheets of a large number of surfactants have been found (Grant, 1998) on amorphous silica made hydrophobic by reaction with diethyloctychlorosilane, hemispherical structures have been observed (Manne, 1994; Wanless, 1996; Grant, 1997; Jaschke, 1997) on hydrophobic graphite and gold, and spherical or cylindrical structures have been seen on hydrophilic silica (Subramanian, 2000). In aqueous systems, the structures formed depend upon the interaction of the surfactant molecules with the solid surface in such fashion as to minimize exposure of the hydrophobic groups to the aqueous phase.

Orientation of the adsorbed surfactant molecules with their hydrophobic groups predominantly away from the solid substrate will make the surface more hydrophobic than before surfactant adsorption; orientation with their hydrophilic groups

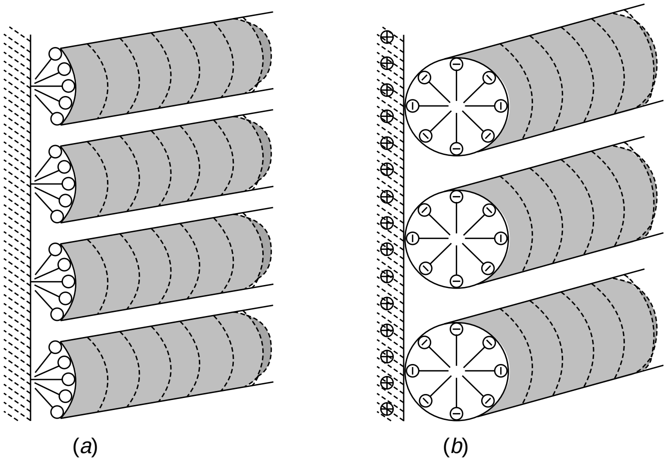

FIGURE 2-10 Adsorption from aqueous solution via hydrophobic bonding on (*a*) an uncharged surface and via electrostatic interaction on (*b*) an oppositely charged surface.

predominantly away from the surface will make it more hydrophilic than before adsorption of the surfactant. There are a number of simple ways of determining the predominant orientation of the surfactant molecules adsorbed on the solid: (1) If the solid can be obtained in the form of a smooth, nonporous planar film or plate, then measurement of the contact angle (Chapter 6, Section 1A2) of a drop of water placed on the solid surface before and after surfactant adsorption can be used. The greater the contact angle, the greater the hydrophobicity of the surface. If the solid can be obtained in the form of finely divided particles, then if surfactant adsorption has made it more hydrophilic, it will disperse better in water after surfactant adsorption than before; if it has made it more hydrophobic, then the particles will either float to the surface when shaken with water or settle out of the water more rapidly than before surfactant adsorption. Alternatively, the particles may be shaken with a mixture of equal volumes of water and a nonpolar solvent (e.g., hexane). If the particles have become more hydrophobic by surfactant adsorption, they will disperse better in the nonpolar phase than before surfactant adsorption; if they have become more hydrophilic, they will disperse better in the aqueous phase than before surfactant adsorption.

II.B. Adsorption Isotherms

At the solid–liquid interface, we are interested in determining (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, that is, the surface concentration of the surfactant (*adsorbate*) at a given temperature, since this is a measure of how much of the surface of the adsorbent has been covered, and hence changed, by the adsorption; (2) the equilibrium concentration of surfactant in the liquid phase required to produce a given surface concentration of surfactant at a given temperature, since this measures the *efficiency* with which the surfactant is adsorbed; (3) the concentration of surfactant on the adsorbent at surface saturation at a given temperature, since this determines the *effectiveness* with which the surfactant is adsorbed; (4) the orientation of the adsorbed surfactant and any other parameters that may shed light on the mechanism by which the surfactant is adsorbed, since a knowledge of the mechanism allows us to predict how a surfactant with a given molecular structure will adsorb at the interface; and (5) the effect of adsorption on other properties of the adsorbent. An adsorption isotherm is a mathematical expression that relates the concentration of adsorbate at the interface to its equilibrium concentration in the liquid phase. Since most of the information that we desire can be obtained from the adsorption isotherm, the isotherm is the usual method of describing adsorption at the liquid–solid interface.

The fundamental equation for calculating the amount of one component (component 1) of a binary solution adsorbed onto a solid adsorbent is (Aveyard, 1973a)

$$\frac{n_0 \Delta \chi_1}{m} = n_1^s \chi_2 - n_2^s \chi_1 \tag{2.2}$$

where n_0 = the total number of moles of solution before adsorption,

$\Delta\chi_1 = \chi_{1,0} - \chi_1$,

$\chi_{1,0}$ = the mole fraction of component 1 before adsorption,

χ_1, χ_2 = the mole fractions of components 1 and 2 at adsorption equilibrium,

m = the mass of the adsorbent, in grams,

n_1^s, n_2^s = the number of moles of components 1 and 2 adsorbed per gram of adsorbent at adsorption equilibrium.

When the liquid phase is a dilute solution of a surfactant (component 1) that is much more strongly adsorbed onto the solid adsorbent than the solvent (component 2), then $n_0\Delta\chi_1 \approx \Delta n_1$ where Δn_1 = the change in the number of moles of component 1 in solution, $n_2^s \approx 0$,and $\chi_2 \approx 1$. Thus

$$n_1^s = \frac{\Delta n_1}{m} = \frac{\Delta C_1 V}{m} \tag{2.3}$$

where $\Delta C_1 = C_{1,0} - C_1$,

$C_{1,0}$ = the molar concentration (in moles/liter) of component 1 before adsorption, in the liquid phase,

C_1 = the molar concentration of component 1 (the surfactant) at adsorption equilibrium, in the liquid phase,

V = the volume of the liquid phase, in liters.

For n_1^s to be determined with suitable accuracy, the value of ΔC_1, the change in the molar concentration of the surfactant solution upon adsorption, must be appreciable when compared to $C_{1,0}$, its initial concentration. For this to be so, the solid adsorbent must have a large surface area/gram (i.e., be finely divided).

For dilute solutions of surfactants then, the number of moles of surface-active solute adsorbed per unit mass of the solid substrate can be calculated from the concentrations of the solute in the liquid phase before and after the solution is mixed with the finely divided solid adsorbent and the mixture is shaken until equilibrium has been reached. Then n_1^s is plotted against C_1 to yield the adsorption isotherm. A variety of analytical techniques are available for determining the change in concentration of the surfactant (Rosen, 1972).

The surface concentration Γ_1, in mol/cm^2, of the surfactant may be calculated when a_s, the surface area per unit mass of the solid adsorbent, in cm^2/g (the specific surface area), is known.

$$\Gamma_1 = \frac{\Delta C_1 V}{a_s \times m} \tag{2.4}$$

For solid substrates that cannot be obtained in finely divided form, but can be obtained as a planar, smooth, nonporous surface on film, surface concentrations can sometimes be calculated from contact angles (Chapter 6, Section IA1).

The adsorption isotherm can then be plotted in terms of Γ_1 as a function of C_1. The surface area per adsorbate molecule on the adsorbent a_1^s in square angstroms* is

$$a_1^s = \frac{10^{16}}{N\Gamma_1} \tag{2.5}$$

where N is Avogadro's number.

1. The Langmuir Adsorption Isotherm A type of adsorption isotherm commonly observed in adsorption from solutions of surfactants is the Langmuir-type isotherm (Langmuir, 1918), expressed by

$$\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \tag{2.6}$$

where Γ_m = the surface concentration of the surfactant, in mol/cm^2, at monolayer adsorption,

C_1 = the concentration of the surfactant in the liquid phase at adsorption equilibrium, in mol/L,

a = a constant $[= 55.3 \exp(\Delta G^\circ / RT)]$, in mol/L, at absolute temperature T, in the vicinity of room temperature and where ΔG° is free energy of adsorption at infinite dilution.

This type of adsorption is valid in theory only under the following conditions (Betts, 1960):

1. The adsorbent is homogeneous.
2. Both solute and solvent have equal molar surface areas.
3. Both surface and bulk phases exhibit ideal behavior (e.g., no solute–solute or solute–solvent interactions in either phase).
4. The adsorption film is monomolecular.

Many surfactant solutions show Langmuir-type behavior even when these restrictions are not met.

When adsorption follows the Langmuir equation, determination of the values of Γ_m and a permits calculation of the area per adsorbed molecule at surface saturation and the free energy of adsorption at infinite dilution. To determine whether adsorption is following the Langmuir equation and to permit calculation of the values of Γ_m and a, the equation is usually transformed into linear form by inverting it. Thus,

$$\frac{C_1}{\Gamma_1} = \frac{C_1}{\Gamma_m} + \frac{a}{\Gamma_m} \tag{2.7}$$

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*For the value in nm^2, divide by 10^2.

or

$$\frac{1}{\Gamma_1} = \frac{a}{\Gamma_m C_1} + \frac{1}{\Gamma_m} \tag{2.8}$$

A plot of C_1/Γ_1 versus C_1 (equation 2.7) should be a straight line whose slope is $1/\Gamma_m$ and whose intercept with the ordinate is a/Γ_m. Alternatively, a plot of $1/\Gamma_1$ versus $1/C_1$ should be a straight line with slope $= a/\Gamma_m$ and intercept $= 1/\Gamma_m$ (equation 2.8).

When the specific surface area of the solid adsorbent a_s is not known, n_1^s may be plotted against C_1 and the Langmuir equation takes the form

$$n_1^s = \frac{n_m^s C_1}{C_1 + a} \tag{2.9}$$

The linear forms are

$$\frac{C_1}{n_1^s} = \frac{C_1}{n_m^s} + \frac{a}{n_m^s} \tag{2.10}$$

and

$$\frac{1}{n_1^s} = \frac{a}{n_m^s C_1} + \frac{1}{n_m^s} \tag{2.11}$$

From equation 2.6, $a = C_1$ when $\Gamma_1 = \Gamma_m/2$; from equation 2.9, when $n_1^s = n_m^s/2$. Therefore, a may also be determined from a plot of C_1^s versus C_1 (or n_1^s versus C_1) at the point where $\Gamma_1 = \Gamma_m/2$ (or where $n_1^m = n_m^s/2$), i.e., it equals the equilibrium surfactant concentration in the liquid phase required for one-half monolayer coverge of the adsorbent surface. In mol/L, $a = 55.3 \exp(\Delta G^\circ/RT)$ in the vicinity of room temperature, and

$$-\log a = -\Delta G^\circ/2.3RT - 1.74 \tag{2.12}$$

Since $-\log a$ is therefore a function of the free energy change involved in the transfer of the surfactant molecule from the liquid phase to the solid substrate, it is a suitable measure of the efficiency of adsorption of the surfactant when adsorption follows the Langmuir equation.

The fact that experimental adsorption data fit the Langmuir equation does *not* mean that the assumptions on which the Langmuir model is based are fulfilled. In the case of surfactants, these assumptions, particularly the absence of lateral interactions, are almost never valid. In spite of this, many surfactants show Langmuir-type adsorption from solution because of the mutual compensation of several factors that affect the shape of the Langmuir isotherm. Some of these factors and the manner in which they modify the shape of the isotherm are as follows (Kitchener, 1965):

1. *Micellization of the Surfactant*. This causes a flattening of the curve, possibly below the level for close packing, because of the almost insignificant increase in activity of the surfactant with increase in its concentration in the liquid phase, once micellation occurs (see Chapter 3).
2. *Surface Potential*. If of the same sign as the surfactant ion, this reduces adsorption and thus reduces the slope of the isotherm; if of opposite sign, it increases adsorption and the slope of the isotherm.
3. *Heterogeneity of the Solid Adsorbent*. Adsorption onto high-energy sites on the substrate yields isotherms with higher slopes than adsorption onto low-energy sites. The summation of adsorptions onto sites of varying energy may yield an isotherm resembling a BET (multilayer) isotherm or a Freundlich isotherm ($n_1^s = kC_1^{1/n}$, where k and n are constants, with n generally greater than unity).
4. *Lateral Interaction*. Where lateral interactions are attractive, a common situation with surfactants, the slope of the isotherm becomes steeper and may become S-shaped or stepped (Kitchener, 1965; Giles, 1974).

A two-step adsorption mechanism has been proposed (Gu and Zhu, 1990; Gu, 1992) for the various types of S-shaped adsorption isotherms (non-Langmuir) that are sometimes obtained. In the first step, the surfactant molecules are adsorbed as individual molecules or ions. In the second step, the adsorption increases dramatically as surface aggregates form through interaction of the hydrophobic chains of the surfactant molecules with each other.

The authors have suggested the equation

$$\Gamma_1 = \Gamma_\infty K C_1^n / (1 + K C_1^n) \tag{2.12a}$$

where $\Gamma\infty$ is the limiting surfactant adsorption at high C_1 concentration, K is the equilibrium constant of the surface aggregation process, and n is the average aggregation number of the surface aggregate as a general adsorption isotherm.

Equation (2.12a) can be transformed to the logarithmic form:

$$\log\,[\Gamma_1/(\Gamma_\infty - \Gamma_1)] = \log K + n \log C \tag{2.12b}$$

A plot of log $[\Gamma_1/(\Gamma_\infty - \Gamma_1)]$ versus log C permits evaluation of K and n when the data give a straight line. When $n = 1$, equation 2.12a becomes the Langmuir adsorption isotherm in the form $\Gamma_1 = \Gamma_\infty K C_1^n/(1 + KC_1)$, where $K = 1/a$. If surface aggregation occurs, then n should be greater than 1.

Adsorption isotherms of poorly purified solutes on heterogeneous or impure adsorbents often pass through a maximum in adsorption. Although such phenomena are possible in adsorption from concentrated solutions or from the gas phase, it is difficult to justify on theoretical grounds the existence of these phenomena in adsorption from dilute solutions of surfactants. They often disappear upon purification of the adsorbent and the solute and are believed to be due to the presence of impurities (Kitchener, 1965).

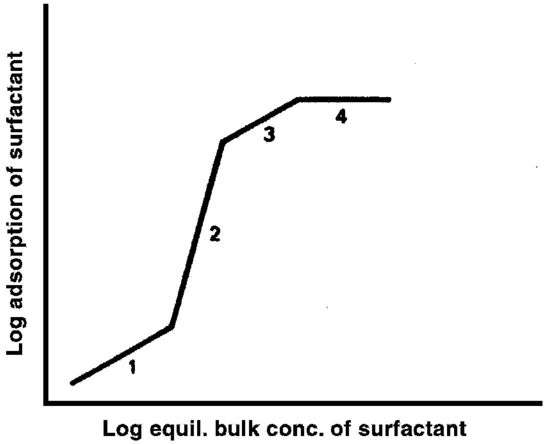

FIGURE 2-11 S-shaped adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

II.C. Adsorption from Aqueous Solution onto Adsorbents with Strongly Charged Sites

Adsorbents with strongly charged sites include such substrates as wool and other polyamides at pH above and below their isoelectric points, oxides such as alumina above and below their points of zero charge, and cellulosic and silicate surfaces at high pH. Adsorption onto these surfaces is a complex process during which adsorption of the solute may occur successively by ion exchange, ion pairing, and hydrophobic bonding mechanisms.

1. Ionic Surfactants The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate, for example, sodium alkanesulfonates (Somasundaran and Fuerstenau, 1966) and alkylbenzenesulfonates (Dick, 1971; Scamehorn, 1982) on positively charged Al_2O_3, is typically S-shaped. The shape of the isotherm (Figure 2-11) is believed to reflect three distinct modes of adsorption. In region 1 the surfactant adsorbs mainly by ion exchange, possibly with the hydrophobic group more or less prone on the substrate (Scamehorn, 1982). The charge density, or potential at the Stern layer of the solid, remains almost constant. In region 2 there is a marked increase in adsorption resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant. This aggregation of the hydrophobic groups, which may occur at concentrations well below the critical micelle concentration (Chapter 3, Section I) of the surfactant, has been called *hemimicelle formation* (Wakamatsu, 1968) or *cooperative adsorption* (Giles, 1974). In this adsorption region the original charge of the solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reversed, so that at the end of region 2, the solid has acquired a charge of the same sign as the surfactant ion. The processes in regions 1 and 2 are

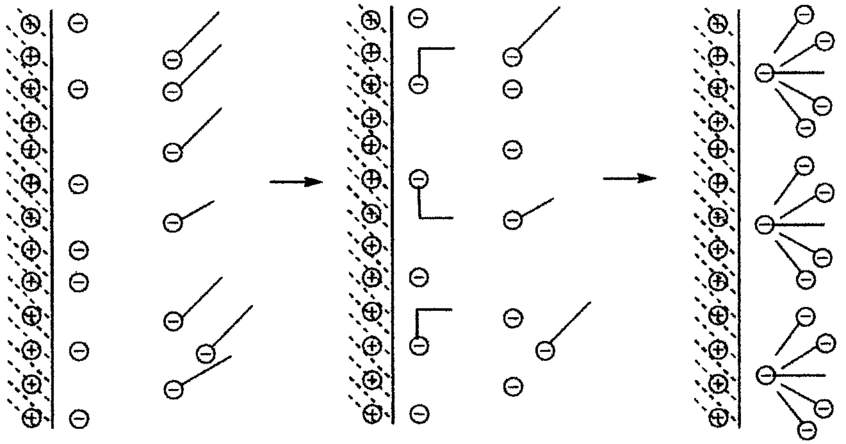

FIGURE 2-12 Adsorption of anionic surfactant onto an oppositely charged substrate by ion exchange (region 1) and by aggregation of oncoming hydrophobic groups with those of previously adsorbed surfactants (region 2).

diagrammed in Figure 2-12. In region 3 the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid. Adsorption in this fashion is usually complete (region 4) in the neighborhood of the critical micelle concentration (Griffith, 1967; Greenwood, 1968; Groot, 1968; Somasundaran, 1983), since adsorption appears to involve single ions rather than micelles.

When the mutual attraction of the hydrophobic groups is insufficient to overcome the mutual repulsion of the ionic hydrophilic groups (e.g., when the hydrophobic groups are short or when there are two or more similarly charged ionized groups in the surfactant molecule and the ionic strength of the aqueous solution is low), then aggregation of the hydrophobic chains may not occur and region 2 may be absent. In these cases the isotherm may be inverted L-shaped when the ionic strength of the solution phase is low, with adsorption in region 1 continuing by ion exchange and ion pairing until the original charge of the substrate has been neutralized and the substrate acquires a charge of the same sign as the surfactant ion. At this point the slope of the isotherm will be reduced and adsorption will continue in the same manner as for region 3 of the S-shaped isotherm. When the ionic strength of the aqueous solution is high, electrical interactions in both region 1 and region 3 are weak and the slopes of the isotherm in these regions will tend to become equal. In this case, if aggregation of the hydrophobic groups does not occur to a significant extent, the shape of the isotherm may be pseudolinear in regions 1–3 (Rosen, 1977).

The *efficiency* of adsorption due to nonelectrical interaction of an ionic surfactant onto an oppositely charged solid adsorbent can be measured by the log of the reciprocal, or negative log, of the equilibrium concentration of the surfactant in the liquid phase (log $1/C_0$ or $-\log C_0$) when the potential at the Stern layer becomes zero (point of zero charge, p.z.c.) This follows from the Stern–Grahame equation for adsorption in the Stern layer (Grahame, 1947) at low surface coverage with the free energy change for the adsorption broken into electrical and nonelectrical parts:

$$\Gamma_\delta = 2 \times 10^{-3} r C_1 \exp \frac{-ZF\psi_\delta - \phi}{RT} \tag{2.13}$$

where Γ_δ = the concentration of surfactant ions adsorbed in the Stern layer of a positively charged surface, in mol/cm$_2$,

r = the effective radius of the adsorbed surfactant ion, in cm,

Z = the valence of the surfactant ion, including the sign,

F = the Faraday constant,

ψ_δ = the potential in the Stern plane,

ϕ = the nonelectrical free energy change upon adsorption.

When ψ_δ is zero,

$$C_{1(0)} = \frac{(\Gamma_\delta)_0}{2 \times 10^{-3} r} \exp \frac{\phi}{RT} \tag{2.14}$$

where $C_{1(0)}$ and $(\Gamma_\delta)_0$ represent the concentrations at zero potential in the Stern layer and

$$-\log C_{1(0)} = -\log \frac{(\Gamma_\delta)_0}{2r} - \frac{\phi}{2.3RT} - 3 \tag{2.15}$$

It has been shown (Wakamatsu, 1968) that the variation in $\log[(\Gamma_\delta)_0/2r]$ is very small compared to the variation in ϕ with changes in the structure of the hydrophobic group, and therefore $-\log C_{1(0)}$ is essentially a function of ϕ and a suitable measure for the efficiency of adsorption due to nonelectrical interactions.

Since region 3 commences at the p.z.c. (when the potential in the Stern layer reaches zero), in those adsorption isotherms where the distinction between region 2 and region 3 is clearly indicated by a change in slope, $C_{1(0)}$ can be taken as the concentration at which the slope decreases and region 3 commences.

An increase in the length of the hydrophobic group increases the efficiency of adsorption, because the free energy decrease associated both with the removal of the hydrophobic chain from contact with the water and with the tendency to aggregate or adsorb via dispersion forces increases with the increase in the length of the chain. Efficiencies calculated from data in the literature are listed in Table 2-1. For this purpose the phenyl ring may be considered to have an effective length of about three and one-half carbon atoms in a straight carbon chain. Carbon atoms on short branches of an alkyl hydrophobic group, on the shorter portion of a hydrophobic group when the hydrophilic group is not terminally located, or between two hydrophilic groups appear to have about one-half the effective length of a carbon atom on a straight alkyl chain with terminal hydrophilic groups. An

TABLE 2-1 Efficiency of Adsorption, $-\log C_{1(0)}$, of Surfactants on Solid Substrates

Surfactant	Solid Substrate	pH	Temperature (°C)	$-\log C_{1(0)}$	Reference
Decylammonium acetate	Quartz	6.5–6.9	22–25	1.7_5	Somasundaran, 1964
Dodecylammonium acetate	Quartz	6.5–6.9	22–25	2.6_0	Somasundaran, 1964
Tetradecylammonium acetate	Quartz	6.5–6.9	22–25	3.4_5	Somasundaran, 1964
Hexadecylammonium acetate	Quartz	6.5–6.9	22–25	4.3_0	Somasundaran, 1964
Octadecylammonium acetate	Quartz	6.5–6.9	22–25	5.1_5	Somasundaran, 1964
Sodium decanesulfonate	α-Alumina	7.2 (I.S.[a] $= 2 \times 10^{-3}$ *M*)	25	2.7_5	Wakamatsu, 1968
Sodium dodecanesulfonate	α-Alumina	4.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	4.4_0	Wakamatsu, 1973
Sodium dodecanesulfonate	α-Alumina	5.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	4.0_0	Wakamatsu, 1973
Sodium dodecanesulfonate	α-Alumina	6.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.8_5	Wakamatsu, 1973
Sodium dodecanesulfonate	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.5_5	Wakamatsu, 1968, 1973
Sodium dodecanesulfonate	α-Alumina	8.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.3_5	Wakamatsu, 1968, 1973
Sodium dodecanesulfonate	α-Alumina	8.6 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.2_0	Wakamatsu, 1968, 1973
Sodium dodecanesulfonate	α-Alumina	6.9 (I.S. $= 2 \times 10^{-3}$ *M*)	45	3.6_2	Somasundaran, 1966
Sodium tetradecanesulfonate	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	4.2_5	Wakamatsu, 1968
Sodium hexadecanesulfonate	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	5.0_0	Wakamatsu, 1968
$NaO_3SC_6H_4(CH_2)_6C_6H_4SO_3Na$	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	2.7_8	Rosen, 1977
$NaO_3SC_6H_4(CH_2)_8C_6H_4SO_3Na$	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.3_2	Rosen, 1977
$NaO_3SC_6H_4(CH_2)_{10}C_6H_4SO_3Na$	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	3.7_0	Rosen, 1977
$NaO_3SC_6H_4(CH_2)_{12}C_6H_4SO_3Na$	α-Alumina	7.2 (I.S. $= 2 \times 10^{-3}$ *M*)	25	4.2_4	Rosen, 1977
Dodecylammonium chloride	Silver iodide			4.0	Ottewill, 1960
Octylpyridinium bromide	Silver iodide			3.8	Ottewill, 1960
Dodecylpyridinium bromide	Silver iodide			5.5_4	Ottewill, 1960
Cetylpyridinium bromide	Silver iodide			6.2_5	Ottewill, 1960
Dodecyltrimethylammonium bromide	Silver iodide			5.0	Ottewill, 1960
Dodecylquinolinium bromide	Silver iodide			6.1_3	Ottewill, 1960

Sodium decyl sulfate	Silver iodide sol	pAg = 3 (I.S. = 1.5×10^{-3} *M*)	20 ± 1	3.4_0	Watanabe, 1960
Sodium dodecyl sulfate	Silver iodide sol	pAg = 3 (I.S. = 1.5×10^{-3} *M*)	20 ± 1	4.3_8	Watanabe, 1960
Sodium dodecanesulfonate	Silver iodide sol	pAg = 3 (I.S. = 1.5×10^{-3} *M*)	20 ± 1	3.9_2	Watanabe, 1960
Sodium tetradecyl sulfate	Silver iodide sol	pAg = 3 (I.S. = 1.5×10^{-3} *M*)	20 ± 1	4.7_8	Watanabe, 1960
Sodium dodecylbenzenesulfonate	Silver iodide sol	pAg = 3 (I.S. = 1.5×10^{-3} *M*)	20 ± 1	4.8_4	Watanabe, 1960
Sodium pentanesulfonate	Silver iodide	3 (I.S. = 1×10^{-3} *M*)	20 ± 2	2.4_6	Osseo-Asare, 1975
		4 (I.S. = 1×10^{-3} *M*)	20 ± 2	2.6_6	Osseo-Asare, 1975
		5 (I.S. = 1×10^{-3} *M*)	20 ± 2	3.1_0	Osseo-Asare, 1975
Sodium octanesulfonate	Silver iodide	3 (I.S. = 1×10^{-3} *M*)	20 ± 2	2.6_0	Osseo-Asare, 1975
		4 (I.S. = 1×10^{-3} *M*)	20 ± 2	2.8_2	Osseo-Asare, 1975
		5 (I.S. = 1×10^{-3} *M*)	20 ± 2	3.8_2	Osseo-Asare, 1975
Sodium decanesulfonate	Silver iodide	3 (I.S. = 1×10^{-3} *M*)	20 ± 2	3.8_9	Osseo-Asare, 1975
		4 (I.S. = 1×10^{-3} *M*)	20 ± 2	4.1_2	Osseo-Asare, 1975
		5 (I.S. = 1×10^{-3} *M*)	20 ± 2	4.6_4	Osseo-Asare, 1975
Sodium dodecanesulfonate	Silver iodide	3 (I.S. = 1×10^{-3} *M*)	20 ± 2	4.5_0	Osseo-Asare, 1975
		4 (I.S. = 1×10^{-3} *M*)	20 ± 2	4.7_0	Osseo-Asare, 1975
		5 (I.S. = 1×10^{-3} *M*)	20 ± 2	4.9_6	Osseo-Asare, 1975
Sodium tetradecanesulfonate	Silver iodide	3 (I.S. = 1×10^{-3} *M*)	20 ± 2	5.1_5	Osseo-Asare, 1975
		4 (I.S. = 1×10^{-3} *M*)	20 ± 2	5.2_5	Osseo-Asare, 1975
		5 (I.S. = 1×10^{-3} *M*)	20 ± 2	5.4_7	Osseo-Asare, 1975

[a] I.S., total ionic strength.

increase in the size of the hydrophilic group also appears to increase the efficiency of adsorption by ion exchange or ion pairing.

The *effectiveness* of adsorption (i.e., the amount adsorbed at surface saturation), however, may increase, decrease, or show no change with increase in the length of the hydrophobic group, depending on the orientation of the adsorbate at the adsorbent–solution interface. If adsorption is perpendicular to the substrate surface in a close-packed arrangement, an increase in the length of a straight-chain hydrophobic group appears to cause no significant change in the number of moles of surfactant adsorbed per unit area of surface at surface saturation (Tamamushi, 1957), presumably because the cross-sectional area occupied by the chain oriented perpendicular to the interface does not change with increase in the number of units in the chain. In perpendicular orientation, moreover, the effectiveness of adsorption may be determined by the size of the hydrophilic group when the cross-sectional area of that group is greater than that of the hydrophobic chain; the larger the hydrophilic group, the smaller the amount adsorbed at surface saturation. If the arrangement is predominantly perpendicular but not close-packed, or if it is somewhat tilted away from the perpendicular, there may be some increase in effectiveness of adsorption with increase in the length of the hydrophobic group, resulting from greater van der Waals attraction and consequent closer packing of longer chains (Connor, 1971). The positioning of a benzenesulfonate group in a more central position in a linear alkylbenzenesulfonate resulted in a decrease in the effectiveness of adsorption (Somasundaran, 1983).

However, if the orientation of the adsorbate is parallel to the interface, as may occur when the surfactant has two ionic groups of charge opposite to that of the substrate at opposite ends of the surfactant molecule, or when the hydrophobic chain interacts strongly with the surface (e.g., electron-rich aromatic nuclei in the adsorbate and positively charged sites on the adsorbent (Snyder, 1968)), then effectiveness of adsorption may decrease with increase in chain length, because this may increase the cross-sectional area of the molecule on the surface, and thus saturation of the surface will be accomplished by a smaller number of molecules (Kölbel, 1959).

2. Nonionic Surfactants POE surfactants may adsorb onto silica surfaces via hydrogen bonding between SiOH groups on the surface and the oxygens of the oxyethylene groups (Rupprecht, 1972; Aston, 1982). On negatively charged silica surfaces, the oxygens of the POE chain may interact electrostatically with negative sites on the surface by picking up protons from the water and acquiring positive charges. Evidence for this is the increase in the pH of the solution with adsorption (Rosen, 1986). Adsorption isotherms are of the Langmuir type, with both efficiency and effectiveness decreasing with increase in the length of the POE group. The latter effect is due to the larger area occupied by the surfactant molecule at the interface as the length of the POE group is increased. At low coverage, the surfactant molecule may lie prone on the surface; at higher coverages, the hydrophobic group may be displaced from the surface by the hydrophilic group and lateral interactions between adjacent hydrophobic groups (hemimicelle formation) may occur (Partyka, 1984). Maximum adsorption, which occurs near the critical micelle concentration of the surfactant (Chapter 3), has been ascribed to both monolayer (Aston, 1982) and bilayer formation (Partyka, 1984).

A POE nonionic, by itself, showed very weak adsorption onto positively charged alumina (Somasundaran, 1983), while dodecyl-β-D-maltoside adsorbed strongly (Zhang, 1997), presumably because of the negative charge on the latter.

3. pH Change This usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrates. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because of adsorption onto charged sites of protons from the solution, with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationics (Van Senden, 1968; Connor, 1971). The reverse is true when the pH of the aqueous phase is raised. These effects are shown markedly by mineral oxides, such as silica and alumina, and by wool and other polyamides.

Change in the pH also may affect surfactant molecules, notably those containing carboxylate groups (soaps) or nonquaternary ammonium groups. In these cases, change in the pH may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent to a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. Changes in pH also may affect nonionic surfactants, notably those having polyoxyethylene chains, because the ether linkages in these chains can be protonated at low pHs, yielding positively charged groupings that may adsorb onto negatively charged substrates.

4. Ionic Strength Addition of neutral electrolyte, such as NaCl or KBr, causes a decrease in the adsorption of ionic surfactants onto an oppositely charged adsorbent and an increase in their adsorption onto a similarly charged adsorbent.

These effects are presumably due to the decreased attraction between oppositely charged species and the decreased repulsion between similarly charged species at higher ionic strength. Both the efficiency and effectiveness of adsorption of ionic surfactants onto similarly charged substrates are increased by an increase in the ionic strength of the aqueous phase (Sexsmith, 1959; Groot, 1968; Connor, 1971).

The presence of polyvalent cations, especially Ca^{2+}, in the solution causes an increase in the adsorption of anionics. This may be due to the adsorption of Ca^{2+} onto the adsorbent, yielding $\oplus$-charged sites onto which negatively charged surfactant can adsorb (Van Senden, 1968).

5. Temperature Temperature increase generally causes a decrease in the efficiency and effectiveness of adsorption of ionic surfactants, the change being relatively small compared to that caused by pH change. However, a rise in temperature usually results in an increase in the adsorption of nonionic surfactants containing a POE chain as the hydrophilic group. This has been attributed to the decreased solute–solvent interaction (i.e., dehydration of the polyoxyethylene group) as the temperature is raised (Corkill, 1966; Partyka, 1984).

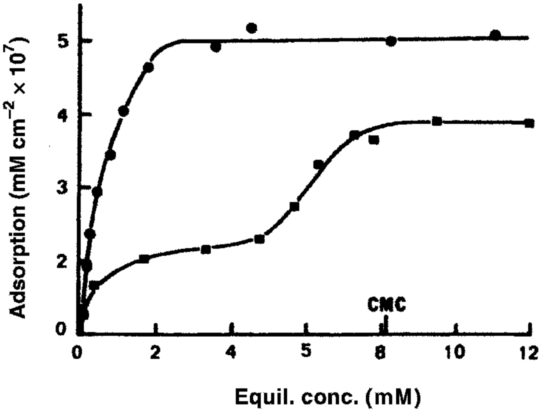

FIGURE 2-13 Adsorption of sodium dodecyl sulfate onto Graphon at 25°C: ■, from pure water; ●, from aqueous 0.1 *M* NaCl. Reprinted with permission from F. G. Greenwood, G. D. Parfitt, N. H. Picton, and D. G. *Wharton, Adsorption from Aqueous Solution. Advances in Chemistry Series 79*, W. J. Weber, Jr., and E. Matijevic (Eds.), American Chemical Society, Washington, DC, 1968, pp. 135–144.

II.D. Adsorption from Aqueous Solution onto Nonpolar, Hydrophobic Adsorbents

Common substrates in this class are carbon and polyethylene or polypropylene. Adsorption isotherms for well-purified monofunctional anionic and cationic surfactants are similar on these adsorbents and are of the Langmuir type (Figures 2-13 and 2-14). They appear to show surface saturation in the vicinity of the critical micelle concentration of the adsorbate, with an orientation of the adsorbate perpendicular to the substrate. Adsorption onto these substrates is mainly by dispersion forces. The orientation of the adsorbate initially may be parallel to the surface of the solid or slightly tilted or L-shaped, with the hydrophobic group close to the surface and the hydrophilic group oriented toward the aqueous phase. As adsorption continues, the adsorbed molecules may become oriented more and more perpendicular to the surface with hydrophilic heads oriented toward the water (Corkill, 1967). In some cases, the adsorption isotherm shows an inflection point (Figure 2-13) that has been ascribed to a change in orientation of the surfactant from parallel to perpendicular. An increase in the length of the hydrophobic group increases efficiency and slightly increases effectiveness of adsorption. The increase in efficiency is due to the increase in the magnitude of the $-\Delta G$ of adsorption with increase in the number of units in the hydrophobic chain; the increase in effectiveness may be due to tighter packing of the hydrophobic chains (Weber, 1964; Zettlemoyer, 1968). Here, as in the case of adsorption onto surfaces having strongly charged sites, the phenyl ring in a *p*-benzenesulfonate may be considered to have an effective length of about three and one-half carbon atoms in a straight alkyl chain. POE nonionics appear to adsorb more efficiently onto hydrophobic

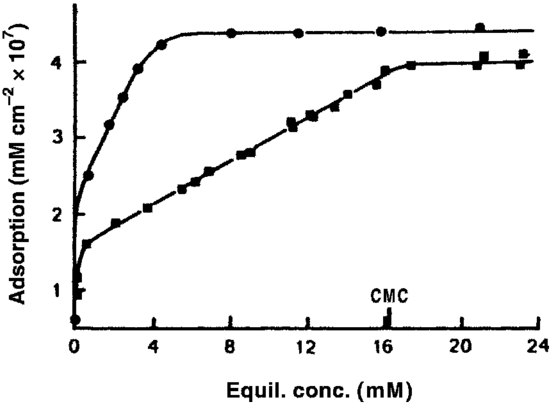

FIGURE 2-14 Adsorption of dodecyltrimethylammonium bromide onto Graphon at 25°C: ■, from pure water; ●, from aqueous 0.1 *M* KBr. Reprinted with permission from F. G. Greenwood, G. D. Parfitt, N. H. Picton, and D. G. Wharton, *Adsorption from Aqueous Solution. Advances in Chemistry Series 79*, W. J. Weber, Jr., and E. Matijevic (Eds.), American Chemical Society, Washington, DC, 1968, pp. 135–144.

surfaces than onto hydrophilic ones (Aston, 1982). An increase in the length of the POE chain appears to decrease both efficiency of adsorption, presumably because the $-\Delta G$ of adsorption is decreased in magnitude as the number of oxyethylene units is increased, and effectiveness, because the cross-sectional area of the molecule at the interface increases with increase in the number of OE units (Abe, 1962; Kronberg, 1984). Increase in the length of the hydrophobic group, however, appears to increase the efficiency of adsorption (Corkill, 1966).

The rate of adsorption has been shown to be a function of the position of the hydrophilic group in the molecule, with surfactants containing the hydrophilic group in a central location in the molecule adsorbing faster than those in which the hydrophilic group is terminally located (Zettlemoyer, 1968). The effect here may be due to either the more compact structure in aqueous solution, and hence the greater diffusion coefficient of surfactants with a hydrophilic group in a central position, or their greater CMC (see p. 104) and the consequent higher activity of their monomeric form in solution (Mukerjee, 1968). The rate of adsorption on carbon also has been shown to be dependent on the presence in the aqueous phase of additives that affect the structure of water. Additives that are structure breakers, such as urea and *N*-methylacetamide, appear to increase the rate of adsorption, whereas those that promote structure, such as xylose and fructose, decrease the rate of adsorption (Schwuger, 1971a).

Neutral electrolyte addition increases both the efficiency of adsorption of ionic surfactants, by decreasing the electrical repulsion between the similarly charged adsorbed ions and oncoming ions, and the effectiveness of adsorption, probably by decreasing the electrical repulsion between the similarly charged adsorbed ions, permitting closer packing (Figures 2-13 and 2-14). The addition of small amounts of cationics to aqueous solutions of anionics (Schwuger, 1971b), or small amounts of metal carboxylates to cationic solutions (Suzuki, 1967), has also been shown to increase the adsorption of the predominant ionic surfactant.

For solid, nonpolar, hydrophobic substrates that are not available in finely divided form, but can be made in the form of nonporous planar sheets or films, surfactant concentrations at the solid–liquid interface can be determined from contact angles (Chapter 6, Section IA1).

II.E. Adsorption from Aqueous Solution onto Polar Adsorbents without Strongly Charged Sites

Adsorption of surfactants onto substrates such as cotton, polyesters, and polyamides in neutral solution is mainly by a combination of hydrogen bonding and adsorption via dispersion forces. For example, free fatty acids from the hydrolysis of soaps are adsorbed, probably by H bonding, onto polyester and nylon 66 (Gavet, 1973). Adsorption isotherms for POE nonionics (AE and APE types) from aqueous solution onto polyester fiber are of the Langmuir type, with areas occupied by the surfactant molecules approximating those occupied at the water–air interface (Gum, 1982). Where the substrate has groups such as —OH or —NH, surfactants containing a POE chain will probably be adsorbed via H bonding. Thus, under laundering conditions, adsorption on nylon and cotton has been reported (Gordon, 1968) to be much greater for nonionics than anionics by a factor of 2:1. POE *n*-dodecanol adsorbs onto cotton from aqueous solutions at 25°C to form a close-packed monolayer with the molecules lying flat on the substrate (Schott, 1967). An increase in the number of units in the POE chains causes a decrease in the efficiency, effectiveness, and rate (Gordon, 1968) of the adsorption. Increase in the length of the hydrophobic chain, on the other hand, increases the efficiency of the adsorption.

A study of the adsorption of POE 1° linear alcohols on desized cotton at 60°C from a heavy-duty built formulation and its desorption by rinsing at 90°C under laundering conditions (Waag, 1968) indicates that at constant ethylene oxide percentage, compounds with short hydrophobic groups are adsorbed more than those with longer hydrophobic groups and that a higher percentage of these shorter-chain compounds than of the longer-chain compounds is retained on the fabric after four rinses. Furthermore, for the *n*-dodecanol–ethylene oxide adducts, only after the percentage of ethylene oxide in the molecule is above 60% does the percentage of the original surfactant remaining on the fabric after rinsing decrease. The fact that shorter-chain compounds are more strongly adsorbed (almost irreversibly) than longer-chain compounds appears to indicate adsorption with the hydrophilic group oriented toward the surface and with the hydrophobic groups toward the aqueous phase.

When the substrate is not capable of donating a hydrogen for bonding of the adsorbate (polyesters, polyacrylonitrile), adsorption is often mainly by dispersion forces; the character of the adsorption will then be similar to that on nonpolar, hydrophobic surfaces.

II.F. Effects of Adsorption from Aqueous Solution on the Surface Properties of the Solid Adsorbent

1. Substrates with Strongly Charged Sites As mentioned earlier, the adsorption of surface-active counterions by an ion-exchange mechanism causes no change in the electrical potential of the adsorbent. However, if adsorption of surface-active counterions continues by an ion-pairing mechanism, then the potential at the Stern layer of the adsorbent decreases and eventually is completely neutralized. During this process the tendency of the surface to repel other, similarly charged surfaces diminishes and ceases when the charge on the adsorbent has been neutralized. Thus, solid adsorbents in the form of finely divided particles, dispersed in the aqueous phase in part because of their mutual electrical repulsion, usually flocculate at some point as their charge is neutralized by the adsorption of oppositely charged surfactant ions.

Furthermore, since adsorption by an ion-exchange or ion-pairing mechanism results in the orientation of the adsorbed surfactant with its hydrophobic group toward the aqueous phase (Figure 2-5), such adsorption causes the surface to become increasingly hydrophobic (Law, 1966; Robb, 1967). This is shown by an increase in the contact angle at the solid-water–air interface as adsorption increases up to the point where the zeta potential is reduced to zero. Negatively charged mineral surfaces such as quartz, when treated with cationic surfactants (e.g., cetyltrimethylammonium bromide), show this effect, becoming more difficult to wet by water and more easily wet by nonpolar compounds (McCaffery, 1970). Adsorption in this manner may account for the reduced swelling of wool fibers in aqueous solution after adsorption of anionic surfactant onto the positively charged sites (Machinson, 1967) and the elimination of shrinkage resistance from oxidized wool by cationic softeners (Stigter, 1971). In both cases, adsorption of oppositely charged surfactant ions makes the wool surface more hydrophobic. If adsorption of surfactant ions onto the adsorbent is continued beyond the p.z.c., however, then the charge at the Stern layer is reversed and the substrate acquires a charge whose sign is that of the adsorbate ion. Orientation of the adsorbed surfactant ion during this process is with the hydrophilic head toward the aqueous phase, imparting increasing hydrophilic character to the substrate as adsorption continues. The contact angle decreases again and the tendency to disperse in water increases (Parfitt, 1972).

Adsorption in this manner may also account for the increased reactivity of wool cystine disulfide bonds to attack by alkali in the presence of cationic surfactants and their decreased reactivity in the presence of anionics (Meichelbeck, 1971). The adsorption of cationic surfactants onto the wool surface, which is negatively charged in an alkaline medium, can impart a positive charge to the surface, thus increasing its attraction for hydroxide and sulfite ions, with consequent increase in its rate of reaction with these ions. In analogous fashion the acid hydrolysis of peptide bonds in the wool is increased by the presence of anionic surfactants (which adsorb onto the wool surface, positively charged in an acid medium, and impart to it a negative charge). The presence of cationic surfactants, on the other hand, decreases the acid hydrolysis of these bonds, whereas nonionic surfactants have no effect.

The adsorption of surfactant ions onto solid surfaces is one of the major factors governing detergency. The greater retention of carbon black in the presence of anionic surfactants by polyester than by wool, for example, has been explained by the greater attraction of the wool (with charged sites) for the surfactant than for the nonpolar carbon, and the reverse in the case of the hydrophobic polyester (Von Hornuff, 1972). The action of surfactants in retarding and leveling the dyeing of fabrics also involves competitive adsorption onto charged sites, with surfactant ions of charge similar to that of the dyes adsorbing competitively onto oppositely charged sites on the fiber, thus reducing the effective rate of adsorption of the dyestuff. In all cases, the more strongly adsorbed the surfactant, the greater its retarding action.

2. Nonpolar Adsorbents Adsorption of surfactants at any concentration onto a well-purified substrate of this type (i.e., free of impurities with polar groups on the surface) occurs with the adsorbate oriented with its hydrophilic group toward the aqueous phase. Thus, adsorption increases the hydrophilicity of the adsorbent and, in the case of ionic surfactants, increases its surface charge density, making it more wettable by the aqueous phase (Elton, 1957; Ginn, 1970b) and more dispersible (if in finely dividing form). These factors account, for example, for the greater dispersibility of carbon black in aqueous medium in the presence of nonionic or ionic surfactants (Corkill, 1967; Greenwood, 1968). In the case of POE nonionics, adsorption may produce a steric barrier to the close approach of another similarly covered particle, since such approach would result in the restriction of the movement of the randomly coiled POE chains, with consequent decrease in the entropy of the system. Adsorption of a nonionic surfactant can thereby also produce an energy barrier to flocculation of a solid if the latter is in finely divided form. These effects, in part, account for the greater desorption of carbon and other hydrophobic pigments from cotton in the presence of surfactants.

II.G. Adsorption from Nonaqueous Solution

The adsorption of surfactants in fuel oil onto pulverized coal has been studied in connection with the development of coal–oil mixtures (COM), i.e., stable dispersions of finely pulverized coal in fuel oil. The stabilization of such dispersions by a cationic surfactant has been shown (Kosman, 1982) to involve adsorption of the cationic via its postively charged head group onto nucleophilic sites on the coal, with its hydrocarbon group oriented toward the oil phase. The adsorption of alkylaromatics on carbon black from *n*-heptane indicates adsorption in an orientation parallel to the interface, with the alkyl chains remaining mobile on the surface (van der Waarden, 1951). Increased length of the alkyl chains increases the degree of dispersion of the carbon.

Adsorption of sodium bis(2-ethylhexyl)sulfosuccinate from benzene solution onto carbon blacks follows the Langmuir equation and depends on the amount of oxygen on the surface. No adsorption onto heat-treated hydrophobic carbon (Graphon) could be detected (Abram, 1962).

II.H. Determination of the Specific Surface Areas of Solids

The most commonly used and most reliable method for determining the specific surface area of finely divided solids is by adsorption of nitrogen or argon at liquid-air temperature. However, for use in measuring the adsorption and orientation of surfactants at the solid–liquid interface, this determination is sometimes better done by adsorption from solution rather than adsorption from the gas phase. The use of an adsorbate of size comparable to that of the surfactant molecule gives a value that may be more indicative of the surface area available for adsorption of surfactant than the use of much smaller (gaseous) adsorbates, which can enter pores and crevices in the surface not accessible to (larger) surfactant molecules. Moreover, adsorption from solution is experimentally much easier than adsorption from the gas phase, which requires vacuum apparatus. However, the orientation of the adsorbate molecule on the adsorbent being studied and the point of monolayer formation must be known with assurance for the method to have validity. Some of the caveats for using adsorption from solution for the determination of specific areas of solids are discussed by Kipling (1965) and Gregg (1967). Using adsorbates of known cross-sectional area at the particular solid–liquid interface under investigation, the saturation adsorption for monolayer formation is determined (e.g., by use of the Langmuir equation in linear form when adsorption fits the equation) and from the results the specific area, a_s, in cm^2/g, is obtained:

$$a_s = \frac{n_m^s \times a_m^s \times N}{10^{16}} \tag{2.16}$$

where n_m^s = the number of moles of solute adsorbed per gram of solid at monolayer saturation

a_m^s = the surface area occupied per molecule of adsorbate at monolayer adsorption, in square angstroms.

Solutes used for this determination by solution adsorption include stearic acid from benzene solution (Daniel, 1951; Kipling, 1962) and *p*-nitrophenol from aqueous or xylene solution (Giles, 1962). Giles (op. cit.) has discussed the requirements for a suitable adsorbate for the purpose.

III. ADSORPTION AT THE LIQUID–GAS AND LIQUID–LIQUID INTERFACES

The direct determination of the amount of surfactant adsorbed per unit area of liquid–gas (*L*/*G*) or liquid–liquid (*L*/*L*) interface, although possible, is not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase(s) for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or interfacial tension measurements. As a result, a plot of surface (or interfacial) tension as a function of (equilibrium) concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption at these interfaces. From such a plot the amount of surfactant adsorbed per unit area of interface can readily be calculated by use of the Gibbs adsorption equation.

III.A. The Gibbs Adsorption Equation

The Gibbs adsorption equation, in its most general form (Gibbs, 1928),

$$\mathrm{d}\gamma = -\sum_i \Gamma_i \mathrm{d}\mu_i \tag{2.17}$$

where $d\gamma$ = the change in surface or interfacial tension of the solvent,
Γ_i = the surface excess concentration* of any component of the system,
$d\mu_i$ = the change in chemical potential of any component of the system,

is fundamental to all adsorption processes where monolayers are formed. At equilibrium between the interfacial and bulk phase concentrations, $d\mu_i = RT\,d\ln a_i$, where a_i = the activity of any component in the bulk (liquid) phase, R = the gas constant, and T = the absolute temperature. Thus

$$\begin{aligned} d\gamma &= -RT\sum_i \Gamma_i d\ln a_i \\ &= -RT\sum_i \Gamma_i d\ln x_i f_i \\ &= -RT\sum_i \Gamma_i d(\ln x_i + \ln f_i) \end{aligned} \tag{2.18}$$

where x_i is the mole fraction of any component in the bulk phase and f_i its activity coefficient.

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*The surface excess concentration is defined here as the excess, per unit area of interface, of the amount of any component actually present in the system over that present in a reference system of the same volume in which the bulk concentrations in the two phases remain uniform up to a hypothetical (Gibbs) dividing surface.

For solutions consisting of the solvent and only one solute, $d\gamma = -RT(\Gamma_0 d\ln a_0 + \Gamma_1 d\ln a_1)$, where subscripts 0 and 1 refer to the solvent and the solute, respectively. For dilute solutions (10^{-2} *M* or less) containing only one nondissociating surface-active solute, the activity of the solvent and the activity coefficient of the solute can both be considered to be constant and the mole fraction of the solute x_1 may be replaced by its molar concentration C_1. Thus

$$\begin{aligned} d\gamma &= -RT\,\Gamma_1 d\ln C_1 \\ &= -2.303\,RT\,\Gamma_1 d\log C_1 \end{aligned} \tag{2.19}$$

which is the form in which the Gibbs equation is commonly used for solutions of nonionic surfactants containing no other materials. When γ is in dyn/cm (= ergs/cm^2) and $R = 8.31 \times 10^7$ ergs mol^{-1} K^{-1}, then Γ_1 is in mol/cm^2; when γ is in mN/m (=*m*J/m^2) and $R = 8.31$ J mol^{-1} K^{-1}, then Γ_1, is in mol/1000 m^2.

For ionic surfactants,

$$d\gamma = -nRT\,\Gamma_1 d\ln C_1, = -2.303\,nRT\,\Gamma_1 d\log C \tag{2.19a}$$

where n is the number of solute species whose concentration at the interface changes with change in the value of C_1. Thus, for solutions of a completely dissociated surfactant of the 1:1 electrolyte type, A^+B^-, as the only solute,

$$d\gamma = RT(\Gamma_{A^+} d\ln a_{A^+} + \Gamma_{B^-} d\ln a_{B^-})$$

Since $\Gamma_{A^+} = \Gamma_{B^-} = \Gamma_1$ to maintain electroneutrality and $a_{A^+} = a_{B^-} = C_1 \times f_\pm$ without significant error,

$$d\gamma = -2\,RT\,\Gamma_1 d(\ln C_1 + \ln f_\pm) \tag{2.20}$$

where $f_\pm$ is the mean activity coefficient of the surfactant.

For dilute solutions (10^{-2} *M* or less),

$$\begin{aligned} d\gamma &= -2\,RT\,\Gamma d\ln C_1 \\ &= -4.606\,RT\,\Gamma\, d\log C_1 \end{aligned} \tag{2.21}$$

without significant error.

For mixtures of two different surfactants, the value of n for the mixture, $n_{\text{mix}} = n_1X_1 + n_2X_2$, where n_1, and n_2 are the n values for individual surfactants 1 and 2 of the mixture and X_1 and X_2 their respective mole fractions at the interface (equation 2.46).

For mixtures of ionic and nonionic surfactants in aqueous solution in the absence of added electrolyte, the coefficient decreases from 4.606 to 2.303 with a decrease in the concentration of the ionic surfactant at the interface (Hua, 1982).

For dilute solutions of a completely dissociated surface-active 1:1 electrolyte in the presence of a swamping, constant amount of electrolyte containing a common nonsurfactant counterion,

$$\begin{aligned} d\gamma &= -RT\Gamma_1 d\ln C_1 \\ &= -2.303RT\Gamma_1 d\log C_1 \end{aligned} \tag{2.22}$$

since under these conditions the change in the concentration of the nonsurfactant common ion at the interface with adsorption is essentially zero. This is the same form as for a nonionic surfactant in dilute solution (equation 2.19). For less than swamping concentrations of a 1:1 non-surface-active electrolyte, for example, NaCl (Matijevic, 1958),

$$\begin{aligned} d\gamma &= -yRT\Gamma\, d\ln C_1 \\ &= -2.303\, yRT\Gamma\, d\log C_1 \end{aligned} \tag{2.23}$$

where $y = 1 + C_1/(C_1 + C_{\mathrm{NaCl}})$.

Where activity coefficients are expected to deviate significantly from unity, for example, when divalent or multivalent ions are present in the solution or concentrations of the surfactant exceed 10^{-2} *M*, $d \log C_1$ in the appropriate equation may be replaced by $d(\log C_1 + \log f_{\pm})$, and $\log f_{\pm}$ calculated in water at 25°C, from the Debye–Hückel equation,

$$\log f_{+(-)} = \frac{-0.509|Z_+ Z_-|\sqrt{I}}{1 + 0.33\alpha\sqrt{I}} \tag{2.24}$$

where the total ionic strength of the solution

$$I = \frac{1}{2}\sum_i C_i Z_i^2$$

and α is the mean distance of approach of the ions, in Å (Boucher, 1968). $\mathrm{Log}\, f_{\pm}$ can be assumed to equal $(\log f_+ + \log f_-)/2$, and α is taken as 0.3 for small counterions ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Br^-}$, $\mathrm{Cl^-}$) and 0.6 for the surfactant ion.

III.B. Calculation of Surface Concentrations and Area Per Molecule at the Interface by Use of the Gibbs Equation

For surface-active solutes the surface excess concentration , Γ_1 can be considered to be equal to the actual surface concentration without significant error. The concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension data by use of the appropriate Gibbs equation. Thus, for dilute solutions of a nonionic surfactant, or for a 1 : 1 ionic surfactant in the presence of a swamping amount of electrolyte containing a common nonsurfactant ion, from equation 2.19,

$$\Gamma_1 = -\frac{1}{2.303\,RT}\left(\frac{\partial \gamma}{\partial \log C_1}\right)_T \tag{2.25}$$

and the surface concentration can be obtained from the slope of a plot of γ versus $\log C_1$ at constant temperature (when γ is in dyn/cm or ergs/cm^2 and $R = 8.31 \times 10^7$ ergs mol^{-1} K^{-}, then Γ_1 is in mol/cm^2; when γ is in m Nm^{-1} or m Jm^{-2} and $R = 8.31$ J mol^{-1} K^{-1}, Γ_1, is in mol/1000 m^2).

For solutions of 1:1 ionic surfactant in the absence of any other solutes, in similar fashion,

$$\Gamma_1 = -\frac{1}{4.606\,RT}\left(\frac{\partial \gamma}{\partial \log C_1}\right)_T \tag{2.26}$$

When activity coefficients are used, γ is plotted versus $(\log C_1 + \log f_\pm)$ to obtain Γ_1.

The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by use of molecular models. From the surface excess concentration, the area per molecule at the interface a_1^s, in square angstroms is calculated from the relation

$$a_1^s = \frac{10^{16}}{N\Gamma_1} \tag{2.27}$$

where N = Avogardo's number and Γ_1 is in mol/cm^2.*

A typical γ–log C_1, plot for a dilute solution of an individual surfactant (surfactants are often used at concentrations of less than $1 \times 10^{-2}\,M$) is shown in Figure 2-15. The break in the curve occurs at the critical micelle concentration

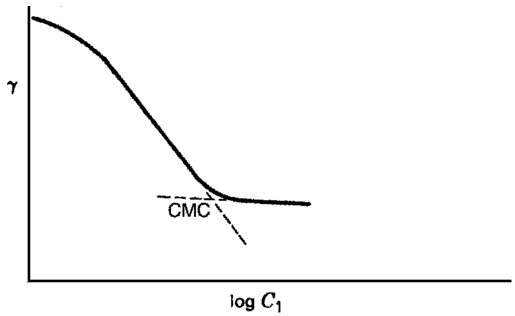

FIGURE 2-15 Plot of surface tension versus log of the bulk phase concentraion for an aqueous solution of a surfactant.

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*For the value in nm^2, divide by 100. When Γ is in mol/1000 m^2, a_1^s, in square angstroms, equals $10^{23}/N\Gamma$.

(CMC), the concentration at which the monomeric form, in which the surfactant exists in very dilute solution, aggregates to form a surfactant cluster known as a *micelle* (Chapter 3). Above this concentration the surface tension of the solution remains essentially constant since only the monomeric form contributes to the reduction of the surface or interfacial tension. For concentrations below but near the CMC the slope of the curve is essentially constant, indicating that the surface concentration has reached a constant maximum value. In this range the interface is considered to be saturated with surfactant (van Voorst Vader, 1960a) and the continued reduction in the surface tension is due mainly to the increased activity of the surfactant in the bulk phase rather than at the interface (equation 2.17). For ionic surfactants in the presence of a constant concentration of counterion, this region of saturated adsorption may extend down to one-third of the CMC.

III.C. Effectiveness of Adsorption at the *L/G* and *L/L* Interfaces

The surface excess concentration (≈surface concentration) at surface saturation Γ_m is a useful measure of the *effectiveness* of adsorption of the surfactant at the *L/G* or *L/L* interface, since it is the maximum value that adsorption can attain. The effectiveness of adsorption is an important factor in determining such properties of the surfactant as foaming, wetting, and emulsification, since tightly packed, coherent interfacial films have very different interfacial properties than loosely packed, noncoherent films. Table 2-2 lists values for the effectiveness of adsorption Γ_m, in mol/cm^2, and the area per molecule at the interface at surface saturation a_m^s, in square angstroms (which is inversely proportional to the effectiveness of adsorption) for a wide variety of anionic, cationic, nonionic, and zwitterionic surfactants at various interfaces.

Since the cross-sectional area of an aliphatic chain oriented perpendicular to the interface is about 20 Å^2 and that of a benzene ring oriented in the same fashion is about 25 Å^2, it is apparent that the hydrophobic chains of surfactants adsorbed at the aqueous solution–air or aqueous solution hydrocarbon interfaces are generally not in the close-packed arrangement normal to the interface at saturation adsorption. On the other hand, since the cross-sectional area of a —CH_2— group lying flat in the interface is about 7 Å^2, the chains in the usual ionic surfactant with a hydrophilic group at one end of the molecule are not lying flat in the interface either, but are somewhat tilted with respect to the interface.

For surfactants with a single hydrophilic group, either ionic and nonionic, the area occupied by a surfactant molecule at the surface appears to be determined by the area occupied by the hydrated hydrophilic group rather than by the hydrophobic group. On the other hand, if a second hydratable, hydrophilic group is introduced into the molecule, that portion of the molecule between the two hydrophilic groups tends to lie flat in the interface, and the area occupied by the molecule in the interface is increased.

The small areas/molecule obtained for polymeric surfactants such as POE polyoxypropylene block copolymers suggest that there is considerable folding of the surfactant molecule at the air–aqueous solution interface with the hydrophobic

TABLE 2-2 Effectiveness of Adsorption Γ_m, Area/Molecule at Surface Saturation a_m^s, and Efficiency of Adsorption pC_{20} of Surfactants from Aqueous Solution at Various Interfaces

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
	Anionics					
$C_{11}H_{23}COO^-Na^+$	0.11 *M* NaCl(aq.)–air	20	3.5	47	—	van Voorst Vader, 1960a
$C_{11}H_{23}COO^-Na^+$	0.11 *M* NaCl(aq.)–heptane	20	3.7	45	—	van Voorst Vader, 1960a
$C_{11}H_{23}COO^-K^+$	0.11 *M* NaCl(aq.)–air	20	3.8_5	43	—	van Voorst Vader, 1960a
$C_{11}H_{23}COO^-K^+$	0.11 *M* NaCl(aq.)–heptane	20	3.8_5	44	—	van Voorst Vader, 1960a
$C_{15}H_{31}COO^-Na^+$	0.1 *M* NaCl(aq.)–air	25	—	—	4.7	Zhu, 1987
$C_{15}H_{31}COO^-Na^+$	0.1 *M* NaCl(aq.)–air	60	5.4	31	4.7	Rosen, 1989
$C_{10}H_{21}OCH_2COO^-Na^+$, pH 10.5	0.1 *M* NaCl(aq.)	30	5.4	31	3.2	Tsubone, 2001
$C_{11}H_{23}CONHCH_2COO^-Na^+$	0.1 *M* NaOH(aq.)	45	3.4_5	48	—	Miyagishi, 1989
$C_{11}H_{23}CONHCH(CH_3)COO^-Na^+$	0.1 *M* NaOH(aq.)	45	2.9	57	—	Miyagishi, 1989
$C_{11}H_{23}CONHCH(C_2H_5)COO^-Na^+$	0.1 *M* NaOH(aq.)	45	2.8	60	—	Miyagishi, 1989
$C_{11}H_{23}CONHCH[CH(CH_3)_2]COO^-Na^+$	0.1 *M* NaOH(aq.)	45	2.7	62	—	Miyagishi, 1989
$C_{11}H_{23}CONHCH[CH_2CH(CH_3)_2]$–$COO^-Na^+$	0.1 *M* NaOH(aq.)	45	2.7	61	—	Miyagishi, 1989
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$, pH 10.5	H_2O	30	2.1	81	2.5	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$, pH 10.5	0.1 *M* NaOH(aq.)–air	30	2.9	58	3.3	Tsubone, 2001
$C_{11}H_{23}CON(C_2H_5)CH_2COO^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	2.7_7	$59._9$	3.8_4	Zhu, 1998a
$C_{11}H_{23}CON(C_4H_9)CH_2COO^-Na^+$	H_2O–air	25	1.5	107	3.6_2	Zhu, 1998a
$C_{11}H_{23}CON(C_4H_9)CH_2COO^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	2.9	$57._3$	4.7_6	Zhu, 1998a

(*Continued next page*)

TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$ pH 10.5	H_2O	30	1.6	104	2.7	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$ pH 10.5	0.1 *M* NaCL(aq.)	30	2.5	66	3.4	Tsubone, 2001
$C_{13}H_{27}CON(C_3H_7)CH_2COO^-Na^+$	H_2O	25	1.5_8	105	4.3_0	Zhu, 1998a
$C_{13}H_{27}CON(C_3H_7)CH_2$-$COO^-Na^+$	"Hard river" water (I.S. = $6.6 \times 10^{-3}M)^a$	25	3.5_0	$47._4$	5.2_8	Zhu, 1998a
$C_{17}H_{33}CON[(CH_2)_3OMe]CH_2$-$COO^-Na^+$	H_2O	25	1.0_5	158	5.3_8	Zhu, 1998a
$C_{17}H_{33}CON[(CH_2)_3OMe]CH_2$-$COO^-Na^+$	"Hard river" water (I.S. = $6.6 \times 10^{-3}M)^a$	25	3.3_3	$49._9$	5.8_6	Zhu, 1998a
$C_{10}H_{21}SO_3^-Na^+$	H_2O–air	10	3.3_7	49	1.7_0	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	H_2O–air	25	3.2_2	52	1.6_9	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	H_2O–air	40	3.0_5	54	1.6_6	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	10	4.0_6	41	2.2_9	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.8_5	43	2.2_9	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	40	3.6_7	45	2.2_7	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	10	4.4_6	37	2.8_9	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	25	4.2_4	41	2.8_7	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	40	4.0_4	41	2.8_4	Dahanayake, 1986
$C_{11}H_{23}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	20	3.2	52	—	van Voorst Vader, 1960a
$C_{12}H_{25}SO_3^-Na^+$	H_2O–air	10	3.0_2	55	2.3_8	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	H_2O–air	25	2.9_3	57	2.3_6	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	H_2O–air	40	2.7_3	60	2.3_3	Bujake, 1965; Dahanayake, 1986

$C_{12}H_{25}SO_3^-Na^+$	H_2O–air	60	2.5	65	2.1_4	Rosen, 1976a
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	10	3.9_2	42	3.4_1	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.7_6	44	3.3_8	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	40	3.5_5	47	3.3_0	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	10	3.9_8	42	4.1_1	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	25	3.8_5	42	4.0_6	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.5 *M* NaCl(aq.)–air	40	3.6_0	44	3.9_3	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl(aq.)–PTFE^b	25	3.0	56	—	Gu, 1989
$C_{12}H_{25}SO_3^-K^+$	H_2O–air	25	3.4	49	2.4_3	Rosen, 1974
$C_{16}H_{33}SO_3^-K^+$	H_2O–air	60	2.8	58	3.3_5	Rosen, 1968, 1974
$C_8H_{17}SO_4^-Na^+$	H_2O–heptane	50	2.3	72	1.6_1	Kling, 1957
$C_9H_{19}SO_4^-Na^+$	H_2O–heptane	20	3.0	56 ± 2	—	van Voorst Vader, 1960a
$C_{10}H_{21}SO_4^-Na^+$	H_2O–air	27	2.9	57	1.8_9	Dreger, 1944; Kling, 1957
$C_{10}H_{21}SO_4^-Na^+$	0.1 *M* NaCl(aq.)	22	3.7	45	—	Betts, 1957
$C_{10}H_{21}SO_4^-Na^+$	H_2O–heptane	50	3.0_5	54	2.1_1	Kling, 1957; van Voorst Vader, 1960a
$C_{10}H_{21}SO_4^-Na^+$	0.032 *M* NaCl(aq.)–heptane	50	3.2	52	—	Lange, 1957
$C_{12}H_{25}SO_4^-Na^+$	H_2O–air	25	3.1_6	53	2.5_1	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	H_2O–air	60	2.6_5	63	2.2_4	Rosen, 1969
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl(aq.)	25	4.0_3	41	3.6_7	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	H_2O–heptane	20	3.1	53	—	van Voorst Vader, 1960a
$C_{12}H_{25}SO_4^-Na^+$	H_2O–heptane	50	2.9_5	56	2.7_2	Kling, 1957; van Voorst Vader, 1960a
$C_{12}H_{25}SO_4^-Na^+$	0.008 *M* NaCl(aq.)–heptane	50	3.2	52	—	Lange, 1957
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl(aq.)–heptane	20	3.3_2	50	—	Vijayendran, 1979
$C_{12}H_{25}SO_4^-Na^+$	H_2O–octane	25	3.3_2	50	2.7_6	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–decane	25	3.5	48	2.7_5	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–heptadecane	25	3.3_2	50	2.7_5	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–cyclohexane	25	3.1_0	54	2.8_2	Rehfeld, 1967

(*Continued next page*)

TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{12}H_{25}SO_4^-Na^+$	H_2O–benzene	25	2.3_3	71	2.5_7	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–1-hexene	25	2.5_1	66	2.4_1	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl(aq.)–ethylbenzene	20	3.0_0	55	—	Vijayendran, 1979
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl(aq.)–ethylpropionate	20	1.2_7	131	—	Vijayendran, 1979
Branched $C_{12}H_{25}SO_4^-Na^{+c}$	H_2O–air	25	1.7	$95._1$	2.9	Varadaraj, 1992
Branched $C_{12}H_{25}SO_4^-Na^{+c}$	0.1 *M* NaCl(aq.)–air	25	3.3	$49._9$	3.6	Varadaraj, 1992
$(C_{11}H_{23})(CH_3)CHSO_4^-Na^+$	H_2O–air	25	2.9_5	56	—	Dreger, 1944; van Voorst Vader, 1960a
$C_{14}H_{29}SO_4^-Na^+$	H_2O–air	25	3.0	56	3.1_1	Huber, 1991; Rosen, 1996
$C_{14}H_{29}SO_4^-Na^+$	H_2O–heptane	50	3.2	52	3.3_1	Kling, 1957; van Voorst Vader, 1960a
$C_{14}H_{29}SO_4^-Na^+$	0.002 *M* NaCl(aq.)–heptane	50	3.2_5	51	—	Lange, 1957
$(C_7H_{15})_2CHSO_4^-Na^+$	H_2O–air	25	3.2_5	51	—	Dreger, 1944; van Voorst Vader, 1960a
$C_{16}H_{33}SO_4^-Na^+$	H_2O–air	25	—	—	3.7_0	Livingston, 1965
$C_{16}H_{33}SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	25	—	—	5.2_4	Caskey, 1971
$C_{16}H_{33}SO_4^-Na^+$	H_2O–heptane	50	3.0_5	54	3.8_9	Kling, 1957; van Voorst Vader, 1960a
$C_4H_9OC_{12}H_{25}SO_4^-Na^+$	H_2O–air	25	1.1_3	147	2.7_7	Livingston, 1965
$C_{12}H_{25}OC_4H_9SO_4^-Na^+$	0.01 *M* NaCl(aq.)–air	20	3.1_5	$52._5$	—	van Voorst Vader, 1960b
$C_{14}H_{29}OC_2H_4SO_4^-Na^+$	H_2O–air	25	2.1	66	3.9_2	Livingston, 1965
$(C_{10}H_{21})(C_7H_{15})CHSO_4^-Na^+$	H_2O–air	20	3.3	50	—	van Voorst Vader, 1960a; Livingston, 1965.

$(C_{10}H_{21})(C_7H_{15})CHSO_4^-Na^+$	H_2O–heptane	20	2.8_5	58	—	van Voorst Vader, 1960a; Livingston, 1965.
$C_{18}H_{37}SO_4^-Na^+$	H_2O–heptane	50	2.3	72	4.4_2	Kling, 1957
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	H_2O–air	25	3.2_2	52	2.1_0	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.8_5	43	2.9_3	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_3^-Na^+$	H_2O–air	25	2.9_2	57	2.7_5	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.7_3	44	4.0_7	Dahanayake, 1986
$C_{10}H_{21}(OC_2H_4)_2SO_4^-Na^+$	0.01 *M* NaCl(aq.)–air	20	2.2	74	—	van Voorst Vader, 1960b
$C_{10}H_{21}(OC_2H_4)_2SO_4^-Na^+$	0.01 *M* NaCl(aq.)–heptane	20	2.3	73	—	van Voorst Vader, 1960b
$C_{10}H_{21}(OC_2H_4)_2SO_4^-Na^+$	0.03 *M* NaCl(aq.)–air	20	2.8	59	—	van Voorst Vader, 1960b
$C_{12}H_{25}(OC_2H_4)_4SO_4^-Na^+$	H_2O–air	25	—	—	3.0_2	Rosen, 1996
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	10	4.0_3	41	4.2_9	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.8_1	44	4.2_3	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	40	3.6_0	46	4.0_9	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O–air	10	2.7_6	60	2.9_6	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O–air	25	2.6_2	63	2.9_2	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O–air	40	2.5_0	66	2.8_6	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	10	3.6_5	46	4.4_0	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	25	3.4_6	48	4.3_6	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl(aq.)–air	40	3.3_0	50	4.2_3	Dahanayake, 1986
o-$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O–air	25	2.5	66	—	Gray, 1955
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O–air	25	3.0	55	—	Gray, 1955
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O–air	70	3.4	49	1.9_6	Lange, 1964
$(C_5H_{11})(C_3H_7)CHCH_2C_6H_4SO_3^-Na^+$	H_2O–air	75	2.7_5	60	—	Greiss, 1955; van Voorst Vader, 1960a
p-$C_{10}H_{21}C_6H_4SO_3^-Na^+$	H_2O–air	70	3.9	43	2.5_3	Lange, 1964
p-$C_{10}H_{21}C_6H_4SO_3^-Na^+$	H_2O–air	75	2.1	78	2.5_2	Greiss, 1955
$C_{10}H_{21}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	30	3.4_5	$48._1$	4.1	Zhu, 1998b
$C_{11}H_{23}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	30	3.6_9	$45._0$	4.6	Zhu, 1998b

(*Continued next page*)

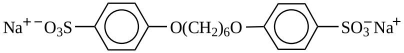
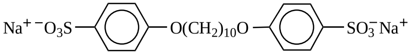
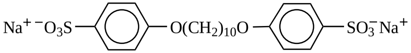
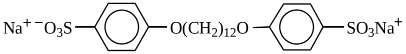
TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{11}H_{23}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	3.2_4	$51._2$	4.5	Zhu, 1998b
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	H_2O–air	70	3.7	45	3.1_0	Lange, 1964
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	H_2O–air	75	3.2	52	3.1_4	Greiss, 1955; van Voorst Vader, 1960a
$C_{12}H_{25}C_6H_4SO_3^-Na^{+d}$	0.1 *M* NaCl(aq.)–air	25	3.6	46	4.9	Zhu, 1987
$C_{12}H_{25}C_6H_4SO_3^-Na^{+d}$	0.1 *M* NaCl(aq.)–air	60	2.8	59	4.9	Rosen, 1989
$C_{12}H_{25}C_6H_4SO_3^-Na^{+d}$	0.1 *M* NaCl(aq.)–Parafilm	25	4.5_6	$36._4$	4.7	Murphy, 1990
$C_{12}H_{25}C_6H_4SO_3^-Na^{+d}$	0.1 *M* NaCl(aq.)–Teflon	25	4.2_3	$38._4$	4.5	Murphy, 1990
$C_{12}H_{25}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	4.1_6	$39._9$	4.9	Zhu, 1998b
$C_{12}H_{25}$-3-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	3.9_8	$41._7$	4.7	Zhu, 1998b
$C_{12}H_{25}$-4-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	3.4_4	$48._3$	4.9	Zhu, 1998b
$C_{12}H_{25}$-5-$C_6H_4SO_3^-Na^+$	H_2O–air	75	2.3	71	2.8_9	Greiss, 1955
$C_{12}H_{25}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	3.3_8	$49._1$	4.7	Zhu, 1998b
$C_{12}H_{25}$-6-$C_6H_4SO_3^-Na^+$	H_2O–air	75	2.2	74	2.5_2	Greiss, 1955
$C_{12}H_{25}$-6-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	3.1_5	$52._7$	4.9	Zhu, 1998b
$C_{13}H_{27}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	30	4.0_5	$41._0$	5.5	Zhu, 1998b
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	H_2O–air	30	2.1_5	$77._2$	4.0	Zhu, 1998b

$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. = 6.6×10^{-3} *M*)[a]	30	3.5_8	$46._4$	5.3	Zhu, 1998b
p-$C_{14}H_{29}C_6H_4SO_3^-Na^+$	H_2O–air	70	2.7	61	3.6_4	Lange, 1964
$C_{14}H_{29}$-6-$C_6H_4SO_3^-Na^+$	H_2O–air	75	3.0_0	57	—	Greiss, 1955; van Voorst Vader, 1960a
p-$C_{16}H_{33}C_6H_4SO_3^-Na^+$	H_2O–air	70	1.9	87	4.2_1	Lange, 1964
$C_{16}H_{33}$-8-$C_6H_4SO_3^-Na^+$	H_2O–air	45	1.6_1	103	5.4_5	Lascaux, 1983
$C_{16}H_{33}$-8-$C_6H_4SO_3^-Na^+$	0.05 *M* NaCl(aq.)–air	45	3.2_7	51	6.6_4	Lascaux, 1983
$C_{10}H_{21}C_6H_3(SO_3^-Na^+)OC_6H_5$	0.1 *M* NaCl(aq.)–air	25	3.4_5	48	5.5	Rosen, 1992
$C_{10}H_{21}C_6H_3(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$	1 *N* NaCl(aq.)–air	25	2.2	75	3.6	Rosen, 1992
$(C_{10}H_{21})_2C_6H_2(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$	0.1 *M* NaCl(aq.)–air	25	1.6	101	—	Rosen, 1992
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$, pH 10.5	H_2O	30	2.2	77	2.3	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$, pH 10.5	0.1 *M* Nacl(aq.)	30	3.0	56	3.6	Tsubone, 2001
$C_4H_9OOCCH_2CH(SO_3^-Na^+)COOC_4H_9$	H_2O–air	25	2.1_3	78	1.4_4	Williams, 1957
$C_6H_{13}OOCCH_2CH(SO_3^-Na^+)COOC_6H_{13}$	H_2O–air	25	1.8_0	92	2.9_4	Williams, 1957
$C_6H_{13}OOCCH_2CH(SO_3^-Na^+)COOC_6H_{13}$	H_2O–benzene	23	1.8_5	89	—	Lange, 1957
$C_6H_{13}OOCCH_2CH(SO_3^-Na^+)COOC_6H_{13}$	0.01 *M* NaCl(aq.)–benzene	23	2.0	84	—	Lange, 1957
$C_4H_9CH(C_2H_5)CH_2OOCCH_2CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	H_2O–air	25	1.5_6	106	4.0_5	Williams, 1957
$C_4H_9CH(C_2H_5)CH_2OOCCH_2CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	0.003 *M* NaCl(aq.)–air	20	1.4_5	115	—	van Voorst Vader, 1960b
$C_8H_{17}COO(CH_2)_2SO_3^-Na^+$	H_2O–air	30	3.2	52	—	Hikota, 1970
$C_{12}H_{25}COO(CH_2)_2SO_3^-Na^+$	H_2O–air	30	2.8_5	58	—	Hikota, 1970
$C_8H_{17}OOC(CH_2)_2SO_3^-Na^+$	H_2O–air	30	2.9	57	—	Hikota, 1970
$C_{10}H_{21}OOC(CH_2)_2SO_3^-Na^+$	H_2O–air	30	2.8	59	—	Hikota, 1970
$C_{12}H_{25}OOC(CH_2)_2SO_3^-Na^+$	H_2O–air	30	2.6	65	—	Hikota, 1970
$C_6H_{13}OOCCH(C_7H_{15})SO_3^-Na^+$	0.01 *M* NaCl(aq.)–air	25	2.8	59	—	Boucher, 1968
$C_6H_{13}OOCCH(C_7H_{15})SO_3^-Na^+$	0.04 *M* NaCl(aq.)–air	25	2.9	57	—	Boucher, 1968
$C_7H_{15}OOCCH(C_7H_{15})SO_3^-Na^+$	0.01 *M* NaCl(aq.)–air	25	2.9	57	—	Boucher, 1968

(*Continued next page*)

TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_7H_{15}OOCCH(C_7H_{15})SO_3^-Na^+$	0.04 *M* NaCl(aq.)–air	25	3.0	56	—	Boucher, 1968
$C_4H_9OOCCH(C_{10}H_{21})SO_3^-Na^+$	0.01 *M* NaCl(aq.)–air	20	2.4	70	—	van Voorst Vader, 1960b
$CH_3OOCCH(C_{12}H_{25})SO_3^-Na^+$	0.01 *M* NaCl(aq.)–air	25	3.0	55	—	Boucher, 1968
$CH_3OOCCH(C_{12}H_{25})SO_3^-Na^+$	0.04 *M* NaCl(aq.)–air	25	3.3	51	—	Boucher, 1968
$CH_3OOCCH(C_{14}H_{29})SO_3^-Na^+$	0.01 *M* NaCl(aq.)–air	25	3.8	44	—	Boucher, 1968
$CH_3OOCCH(C_{14}H_{29})SO_3^-Na^+$	0.04 *M* NaCl(aq.)–air	25	3.5	47	—	Boucher, 1968
$C_9H_{19}C_6H_4(OC_2H_4)_{9.5}OP(O)(OH)_2$	H_2O–air (pH 2.5)	25	1.9	86	—	Groves, 1972
$C_9H_{19}C_6H_4(OC_2H_4)_{8.5}OP(O)(OH)_2$	H_2O–air (0.05 *M* phosphate buffer, pH 6.86)	25	2.8_5	58	—	Groves, 1972
$C_9H_{19}C_6H_4(OC_2H_4)_{8.5}OP(O)(OH)_2$	H_2O–hexane (pH 2.5)	20	2.1_5	77	—	Groves, 1972
$C_9H_{19}C_6H_4(OC_2H_4)_{8.5}OP(O)(OH)_2$	H_2O–hexane (0.05 *M* phosphate buffer, pH 6.88)	20	3.0	56	—	Groves, 1972
	H_2O–air	25	0.3_6	460	—	Rosen, 1976b
	H_2O–air	40	0.6_4	260	—	Rosen, 1976b
	H_2O–air	60	0.2_2	750	—	Rosen, 1976b
	H_2O–air	70	0.2_2	760	—	Rosen, 1976b

$Na^{+-}O_4S(CH_2)_{16}SO_4^-Na^+$	0.001 *M* NaCl(aq.)–air	25	1.7_5	95	—	Elworthy, 1959
$Na^{+-}O_4S(CH_2)_{16}SO_4^-Na^+$	0.2 *M* NaCl(aq.)–air	25	1.9	88	—	Elworthy, 1959
$Na^{+-}O_4S(CH_2)_{16}SO_4^-Na^+$	1 *M* NaCl(aq.)–air	25	1.9	86	—	Elworthy, 1959
$C_7F_{15}SO_3^-Na^+$	H_2O–air	25	3.1	53	2.7_6	Shinoda, 1972
$C_8F_{17}SO_3^-Li^+$	H_2O–air	25	3.0	55	3.2_0	Shinoda, 1972
$C_8F_{17}SO_3^-Na^+$	H_2O–air	25	3.1	53	3.2_3	Shinoda, 1972
$C_8F_{17}SO_3^-K^+$	H_2O–air	25	3.7	45	3.5_6	Shinoda, 1972
$C_8F_{17}SO_3^-NH_4$	H_2O–air	25	4.1	41	3.4_0	Shinoda, 1972
$C_8F_{17}SO_3^-NH_3C_2H_4OH^+$	H_2O–air	25	3.9	43	3.4_4	Shinoda, 1972
$C_7F_{15}COO^-Na^+$	H_2O–air	25	4.0	42	2.5_0	Shinoda, 1972
$C_7F_{15}COO^-K^+$	H_2O–air	25	3.9	43	2.5_7	Shinoda, 1972
$(CF_3)_2CF(CF_2)_4COO^-Na^+$	H_2O–air	25	3.8	44	2.5_7	Shinoda, 1972
		Cationics				
$C_{10}H_{21}N(CH_3)_3^+Br^-$	0.1 *M* NaCl(aq.)–air	25	3.3_9	49	1.8_0	Li, 2001
$C_{12}H_{25}N(CH_3)_3^+Cl^-$	0.1 *M* NaCl(aq.)–air	25	4.3_9	38	2.7_1	Li, 2001
$C_{14}H_{29}N(CH_3)_3^+Br^-$	H_2O–air	30	2.7	61	—	Venable, 1964
$C_{14}H_{29}N(CH_3)_3^+Br^-$	0.1 *M* NaCl(aq.)–air	25	2.3	59	3.8	Rosen, 2001a
$C_{14}H_{29}N(C_3H_7)_3^+Br^-$	H_2O–air	30	1.9	89	—	Venable, 1964
$C_{14}H_{29}N(C_3H_7)_3^+Br^-$	0.05 *M* KBr(aq.)–air	30	2.6	64	—	Venable, 1964
$C_{16}H_{33}N(CH_3)_3^+Cl^-$	0.1 *M* NaCl (aq.)–air	25	3.6	46	5.0_0	Caskey, 1971
$C_{16}H_{33}N(C_3H_7)_3^+Br^-$	H_2O–air	30	1.8	91	—	Venable, 1964
$C_{18}H_{37}N(CH_3)_3^+Br^-$	H_2O–air	25	2.6	64	—	Brashier, 1968
$C_8H_{17}Pyr^+Br^{-e}$	H_2O–air	20	2.3	73	1.2_8	Bury, 1953
$C_{10}H_{21}Pyr^+Br^{-e}$	H_2O–air	25	—	—	1.82	Venable, 1964
$C_{12}H_{25}Pyr^+Br^{-e}$	H_2O–air	25	3.3	50	2.3_3	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-e}$	0.1 *M* NaCl(aq.)–air	10	3.7	45	3.4_8	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-e}$	0.1 *M* NaCl(aq.)–air	25	3.5	48	3.4_0	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-e}$	0.1 *M* NaCl(aq.)–air	40	3.3	51	3.3_0	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-e}$	H_2O–air	10	2.7	61	2.1_2	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-e}$	H_2O–air	25	2.7	62	2.1_0	Rosen, 1982b

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TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{12}H_{25}Pyr^+Cl^{-e}$	H_2O–air	40	2.6	63	2.0_7	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-e}$	0.1 *M* NaCl(aq.)–air	25	3.0	55	2.9_8	Rosen, 1982b
$C_{14}H_{29}Pyr^+Br^{-e}$	H_2O–air	30	2.7_5	60	2.9_4	Venable, 1964
$C_{14}H_{29}Pyr^+Br^{-e}$	0.05 *M* KBr(aq.)–air	30	3.4_5	48	—	Venable, 1964
$C_{14}Pyr^+Cl^{-e}$	0.1 *M* KCl(aq.)	25	3.4_6	46	—	Semmler, 1999
$C_{16}Pyr^+Cl^{-e}$	H_2O–air	25	3.3_7	49	—	Semmler, 1999
$C_{16}Pyr^+Cl^{-e}$	0.1 *M* KCl(aq.)	25	5.0_4	33	—	Semmler, 1999
$C_{12}N^+H_2CH_2CH_2OHCl^-$	H_2O–air	25	1.9_3	86	2.1_9	Omar, 1997
$C_{12}N^+H(CH_2CH_2OH)_2Cl^-$	H_2O–air	25	2.4_9	67	2.3_1	Omar, 1997
$C_{12}N^+(CH_2CH_2OH)_3Cl^-$	H_2O–air	25	2.9_1	57	2.3_4	Omar, 1997
		Nonionics				
NONIONICS (HOMOGENEOUS HEAD GROUP)						
$C_8H_{17}OCH_2CH_2OH$	H_2O–air	25	5.2	32	3.1_7	Shinoda, 1959
$C_8H_{17}CHOHCH_2OH$	H_2O–air	25	5.1	33	3.6_3	Kwan, 1980
$C_8H_{17}CHOHCH_2CH_2OH$	H_2O–air	25	5.3	32	3.5_9	Kwan, 1980
$C_{12}H_{25}CHOHCH_2CH_2OH$	H_2O–air	25	5.1	33	5.7_7	Kwan, 1980
Octyl-β-D-glucoside	H_2O–air	25	4.0	41	—	Shinoda, 1959
Decyl-α-glucoside	H_2O–air	25	3.7_7	44	—	Aveyard, 1998
Decyl-β-glucoside	H_2O–air	25	4.0_5	41	—	Aveyard, 1998
Decyl-β-glucoside	0.1 *M* NaCl(aq.)–air	25	4.1_8	40	3.7_6	Li, 2001
Dodecyl-β-glucoside	H_2O–air	25	4.6_1	36	—	Aveyard, 1998
Decyl-β-maltoside	H_2O–air	25	2.9_6	56	—	Aveyard, 1998
Decyl-β-maltoside	0.01 *M* NaCl(aq.)–air	22	—	—	3.5_8	Liljekvist, 2000
Decyl-β-maltoside	0.1 *M* NaCl(aq.)–air	25	3.3_7	49	3.5_2	Li, 2001

Dodecyl-β-maltoside	H_2O–air	25	3.3_2	50	—	Aveyard, 1998
Dodecyl-β-maltoside	0.1 *M* NaCl(aq.)–air	25	3.6_7	45	4.6_4	Li, 2001
N-(2-ethyl hexyl)2-pyrrolid(in)one	H_2O–air	25	3.5_7	$46._5$	3.0_0	Rosen, 1988
N-(2-ethyl hexyl)2-pyrrolid(in)one	H_2O, pH 7.0–polyethylene	25	3.2_6	$50._9$	—	Rosen, 2001b
N-octyl-2-pyrrolid(in)one	H_2O–air	25	4.3_8	$37._9$	3.1_4	Rosen, 1988
N-octyl-2-pyrrolid(in)one	H_2O, pH 7.0-polyethylene	25	4.2_5	$39._0$	—	Rosen, 2001b
N-octyl-2-pyrrolid(in)one	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	4.0_1	$41._4$	3.3_4	Rosen, 1996
N-octyl-2-pyrrolid(in)one	H_2O-0.1 *M* NaCl(aq.)	25	4.2_7	$38._9$	3.2_1	Rosen, 1988
N-octyl-2-pyrrolid(in)one	0.1 *M* NaCl(aq.)–Parafilm	25	4.1_4	$40._3$	3.2_8	Rosen, 1988
N-octyl-2-pyrrolid(in)one	0.1 *M* NaCl(aq.)–Teflon	25	3.7_9	$43._8$	3.0_4	Rosen, 1988
N-decyl-2-pyrrolid(in)one	H_2O–air	25	4.6_1	$36._0$	4.1_9	Rosen, 1988
N-decyl-2-pyrrolid(in)one	H_2O–Parafilm	25	4.5_4	$36._6$	4.2_4	Rosen, 1988
N-decyl-2-pyrrolid(in)one	H_2O–Teflon	25	4.2_4	$39._2$	4.0_4	Rosen, 1988
N-decyl-2-pyrrolid(in)one	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$*M*)[a]	25	4.1_7	$39._8$	4.3_8	Rosen, 1996
N-dodecyl-2-pyrrolid(in)one	H_2O–air	25	5.0_8	$32._7$	5.3_0	Rosen, 1988
N-dodecyl-2-pyrrolid(in)one	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$*M*)[a]	25	5.1_1	$32._5$	5.3_7	Rosen, 1996
N-dodecyl-2-pyrrolid(in)one	0.1 *M* NaCl(aq.)–air	25	5.1_5	$32._2$	5.3_4	Rosen, 1988
$C_{11}H_{23}CON(C_2H_4OH)_2$	H_2O–air	25	3.7_5	44	4.3_8	Rosen, 1984
$C_{11}H_{23}CON(C_2H_4O)_4OH$	H_2O–air	23	3.4	49	—	Kjellin, 2002
$C_{10}H_{21}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl(aq.)–air	25	3.8_0	44	3.8_0	Zhu. 1999
$C_{11}H_{23}CON(CH_3)CH_2CHOHCH_2OH$	0.1 *M* NaCl(aq.)–air	25	4.3_4	38	4.6_4	Zhu. 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_3CH_2OH$	0.1 *M* NaCl(aq.)–air	25	4.2_9	39	4.4_7	Zhu. 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl(aq.)–air	25	4.1_0	$40._5$	4.4_0	Zhu. 1999
$C_{12}H_{25}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl(aq.)–air	25	4.6_0	36	5.0_2	Zhu. 1999
$C_{13}H_{27}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl(aq.)–air	25	4.6_8	$35._5$	5.4_3	Zhu. 1999
$C_{10}H_{21}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O–air	20	3.9_6	42	3.6_0	Burczyk, 2001
$C_{12}H_{25}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O–air	20	3.9_9	42	4.7_8	Burczyk, 2001
$C_{14}H_{29}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O–air	20	3.9_7	42	5.5_5	Burczyk, 2001

(*Continued next page*)

TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{16}H_{33}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O–air	20	3.6_5	45	6.1_1	Burczyk, 2001
$C_{18}H_{37}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O–air	20	3.9_7	42	6.4_6	Burczyk, 2001
$(C_2H_5)_2CHCH_2(OC_2H_4)_6OH$	H_2O–air	20	2.1_5	77	—	Elworthy, 1964
$C_6H_{13}(OC_2H_4)_6OH$	H_2O–air	25	2.7	62	2.4_8	Elworthy, 1964
$C_8H_{17}(OC_2H_4)_6OH$	H_2O–air	25	1.5_0	111	3.1_4	Varadaraj, 1991
$C_8H_{17}(OC_2H_4)_5OH$	0.1 *M* NaCl(aq.)–air	25	3.4_6	48	3.1_6	Varadaraj, 1991
$(C_4H_9)_2CHCH_2(OC_2H_4)_6OH$	H_2O–air	20	2.8	61	—	Elworthy, 1964
$C_{10}H_{21}(OC_2H_4)_4OH$	H_2O–air	25	4.0_7	41	—	Eastoe, 1997
$C_{10}H_{21}(OC_2H_4)_5OH$	H_2O–air	25	3.1_1	53	—	Eastoe, 1997
$C_{10}H_{21}(OC_2H_4)_6OH$	H_2O–air	23.5	3.0	55	4.2_7	Carless, 1964
$C_{10}H_{21}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	2.8_3	$58._7$	4.2_7	Rosen, 1996
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O–air	25	2.3_8	70	4.2_0	Meguro, 1981
$C_{10}H_{21}(OC_2H_4)_8OH$	0.01 *M* NaCl(aq.)–air	22	—	—	4.2_4	Liljekvist, 2000
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O–air	25	3.9_8	42	5.3_4	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O–air	25	3.6_3	46	5.3_4	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O–hexadecane	25	3.1_6	$52._6$	—	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_5OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	3.8_8	$42._8$	5.3_8	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O–air	25	3.3_1	50	5.3_7	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	0.1 *M* NaCl(aq.)–air	25	3.3_1	50	5.4_6	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_6OH$	H_2O–air	25	3.2_1	52	—	Eastoe, 1997
$C_{12}H_{25}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)[a]	25	3.1_9	$52._0$	5.2_7	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O–air	10	2.8_5	58	5.1_5	Rosen, 1982a

$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O–air	25	2.9_0	57	5.2_6	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O–air	40	2.7_7	60	5.2_8	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	0.1 *M* NaCl(aq.)–air	25	3.6_5	$45._5$	5.2	Rosen, 2001a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–air	10	2.5_6	65	5.0_5	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–air	25	2.5_2	66	5.2_0	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–air	40	2.4_6	67	5.2_2	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–heptane	25	2.6_2	$63._6$	5.2_7^f	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–hexadecane	25	2.6_4	63	5.2_4^f	Rosen, 1991
6-branched $C_{13}H_{27}(OC_2H_4)_5OH$	0.1 *M* NaCl(aq.)–air	25	2.8_7	58	5.1_6	Varadaraj, 1991
$C_{13}H_{27}(OC_2H_4)_5OH$	H_2O–air	25	1.9_6	85	5.3_4	Varadaraj, 1991
$C_{13}H_{27}(OC_2H_4)_5OH$	0.1 *M* NaCl(aq.)–air	25	3.8_9	43	5.6_2	Varadaraj, 1991
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O–air	25	2.7_8	60	5.6_2	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O–air	25	3.4_3	48	6.0_2	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	25	2.6_7	$62._2$	6.1_4	Rosen, 1996
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O–air	25	3.5_9	46	6.3_1	Meguro, 1981
$C_{16}H_{33}(OC_2H_4)_6OH$	H_2O–air	25	4.4	38	6.8_0	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^a	25	3.2_3	$51._4$	6.7_8	Rosen, 1996
$C_{16}H_{33}(OC_2H_4)_7OH$	H_2O–air	25	3.8	44	—	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_9OH$	H_2O–air	25	3.1	53	—	Elworthy, 1962
n-$C_{16}H_{33}(OC_2H_4)_{12}OH$	H_2O–air	25	2.3	72	—	Elworthy, 1962
n-$C_{16}H_{33}(OC_2H_4)_{15}OH$	H_2O–air	25	2.0_5	81	—	Elworthy, 1962
n-$C_{16}H_{33}(OC_2H_4)_{21}OH$	H_2O–air	25	1.4	120	—	Elworthy, 1962
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_3OH$	H_2O–air	25	3.7	45	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_3OH$	H_2O–air	85	3.2	52	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_4OH$	H_2O–air	25	3.3_5	50	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$	H_2O–air	25	3.1	53	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_6OH$	H_2O–air	25	3.0	56	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_6OH$	H_2O–air	55	2.9	58	—	Crook, 1964

(*Continued next page*)

TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_6OH$	H_2O–air	85	2.7	61	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_7OH$	H_2O–air	25	2.9	58	4.9_3	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_8OH$	H_2O–air	25	2.6	64	4.8_9	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_9OH$	H_2O–air	25	2.5	66	4.8_0	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	H_2O–air	25	2.2	$74._5$	4.7_2	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	H_2O–air	55	2.1	79	—	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	H_2O–air	85	2.1	80	—	Crook, 1964
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_5H]$-$OSi(CH_3)_3$	H_2O–air	23±2	5.0	$33._5$	—	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_9H]$-$OSi(CH_3)_3$	H_2O–air	23±2	5.1	$32._6$	—	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_{13}H]$-$OSi(CH_3)_3$	H_2O–air	23±2	4.2	$39._2$	—	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_{8.5}CH_3]$-$OSi(CH_3)_3$	H_2O ph 7.0	25	2.5_2	66	5.9_5	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_{8.5}CH_3]$-$OSi(CH_3)_3$	H_2O, ph 7.0–polyethylene	25	2.7_2	61	—	Rosen, 2001b
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_2OH$	H_2O–air	25	4.7_4	35	—	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_3OH$	H_2O–air	25	4.4_6	37	—	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_5OH$	H_2O–air	25	3.5_6	$46._5$	—	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_7OH$	H_2O–air	25	3.1_9	52	—	Matos, 1989
		Zwitterionics				
$C_{12}H_{25}N(CH_3)_2O$	H_2O–air	25	3.5	47	3.6_2	Rosen, 1974
$C_8H_{17}CH(COO^-)N^+(CH_3)_3$	H_2O–air	27	2.8	60	—	Tori, 1963a
$C_{10}H_{21}CH(COO^-)N^+(CH_3)_3$	H_2O–air	10	3.0	55	—	Tori, 1963b

$C_{10}H_{21}CH(COO^-)N^+(CH_3)_3$	H_2O–air	27	2.8	60	—	Tori, 1963a
$C_{10}H_{21}CH(COO^-)N^+(CH_3)_3$	H_2O–air	60	2.5	66	—	Tori, 1963b
$C_{12}H_{25}CH(COO^-)N^+(CH_3)_3$	H_2O–air	27	3.1	54	—	Tori, 1963a
$C_{10}H_{21}N^+(CH_3)_2CH_2COO^-$	H_2O–air	23	4.1_5	40	2.5_9	Beckett, 1963
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	H_2O–air	25	3.2	52	—	Chevalier, 1991
$C_{14}H_{29}N^+(CH_3)_2CH_2COO^-$	H_2O–air	23	3.5_3	47	4.6_2	Beckett, 1963
$C_{16}H_{33}N^+(CH_3)_2CH_2COO^-$	H_2O–air	23	4.1_3	40	5.5_4	Beckett, 1963
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3COO^-$	H_2O–air	25	2.5	67	—	Chevalier, 1991
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_5COO^-$	H_2O–air	25	2.4	68	—	Chevalier, 1991
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_7COO^-$	H_2O–air	25	2.1_5	77	—	Chevalier, 1991
$C_{10}H_{21}CH(Pyr^+)COO^-$	H_2O–air	25	3.5_9	46	2.8_7	Zhao, 1984
$C_{12}H_{25}CH(Pyr^+)COO^-$	H_2O–air	25	3.5_7	46	3.9_8	Zhao, 1984
$C_{14}H_{29}CH(Pyr^+)COO^-$	H_2O–air	40	3.4_0	49	4.9_2	Zhao, 1984
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–air	25	2.9_1	57	3.3_6	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–air	10	2.9_6	56	4.4_2	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–air	25	2.8_6	58	4.4_2	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–air	40	2.7_6	60	4.3_2	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	0.1 *M* NaCl(aq.), pH 5.7	25	3.1_3	$53._0$	4.6	Rosen, 2001a
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–heptane	25	2.7_6	60	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–isooctane	25	2.7_7	60	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–heptamethylnonane	25	2.7_8	60	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–dodecane	25	2.8_3	59	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–hexadecane	25	2.9_0	57	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–cyclohexane	25	2.6_4	63	—	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	H_2O–toluene	25	2.5_1	66	—	Murphy, 1988
$C_8H_{17}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	H_2O–air	25	2.7_2	61	2.2_3	Dahanayake, 1984
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	H_2O–air	25	2.7_2	61	3.3_4	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	H_2O–air	10	2.8_1	59	4.5_2	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	H_2O–air	25	2.7_2	61	4.4_4	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	H_2O–air	40	2.5_9	64	4.3_2	Dahanayake, 1984

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TABLE 2-2 (*Continued*)

Compound	Interface	Temp. (°C)	Γ_m, (mol/cm^2 $\times 10^{10}$)	a_m^s, Å^2	pC_{20}	Reference
$C_{12}H_{25}CHOHCH_2N^+(CH_3)_2CH_2CH_2OP$-(O)(OH)$O^-$	H_2O–air	25	3.8	$43._8$	—	Tsubone, 1990
Anionic–Cationic Salts						
$C_2H_5N^+(CH_3)_3 \cdot CH_{12}H_{25}SO_4^-$	H_2O–air	25	2.6_3	63	3.0_4	Lange, 1971
$C_4H_9N^+(CH_3)_3 \cdot C_{10}H_{21}SO_4^-$	H_2O–air	25	2.8_5	58	2.5_7	Lange, 1971
$C_6H_{13}N^+(CH_3)_3 \cdot C_8H_{17}SO_4^-$	H_2O–air	25	2.5_0	67	2.5_7	Lange, 1971
$C_8H_{17}N^+(CH_3)_3 \cdot C_6H_{13}SO_4^-$	H_2O–air	25	2.5_3	66	2.5_7	Lange, 1971
$C_{10}H_{21}N^+(CH_3)_3 \cdot C_4H_9SO_4^-$	H_2O–air	25	2.5_0	67	2.5_7	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot CH_3SO_4^-$	H_2O–air	25	2.7_0	61	2.3_2	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot C_2H_5SO_4^-$	H_2O–air	25	2.8_5	58	2.5_7	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot C_4H_9SO_4^-$	H_2O–air	25	2.6_7	62	3.0_2	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot C_6H_{13}SO_4^-$	H_2O–air	25	2.5_8	64	3.7_0	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot C_8H_{17}SO_4^-$	H_2O–air	25	2.7_2	61	4.2_7	Lange, 1971
$C_{12}H_{25}N^+(CH_3)_3 \cdot C_{12}H_{25}SO_4^-$	H_2O–air	25	2.7_4	61	5.3_2	Lange, 1971
$C_{10}H_{21}N^+(CH_3)_3 \cdot C_{10}H_{21}SO_4^-$	H_2O–air	25	3.3_5	58	—	Corkhill, 1963
$C_{12}H_{25}N^+(CH_3)_2OH \cdot C_{12}H_{25}SO_3^-$	H_2O–air	25	2.1_4	78	5.6_6	Rosen, 1964
$C_{16}H_{33}N^+(CH_3)_3 \cdot C_{12}H_{25}SO_4^-$	H_2O–air	30	2.8_0	59	—	Tomasic, 1999

[a] I.S. = ionic strength of solution.

[b] PTFE = polytetra fluoroethylene.

[c] From branched dodecyl alcohol with 4.4 methyl branches in the molecule.

[d] Commercial material.

[e] Pyr^+ = pyridinium.

[f] pC^{30}.

polyoxypropylene group looping away from the aqueous phase into the air and the POE groups extending into the aqueous phase (Alexandridis, 1994).

The data in Table 2-2 indicate the following relations between the structure of the surfactant and its effectiveness of adsorption at the aqueous solution–air and aqueous solution–hydrocarbon interfaces.

Change in the length of the hydrophobic group of straight-chain ionic surfactants beyond 10 carbon atoms appears to have almost no effect on the effectiveness of adsorption at the aqueous solution–heptane interface and very little effect on the effectiveness at the aqueous solution–air interface.

A phenyl group that is part of a hydrophobic group has the effect of about three and one-half $—CH_2—$ groups in a straight hydrophobic chain. When the number of carbon atoms in a straight-chain hydrophobic group exceeds 16 at either the aqueous solution–air or aqueous solution–hydrocarbon interface, there is a significant decrease in the effectiveness of adsorption, which has been attributed (Mukerjee, 1967) to coiling of the long chain, with a consequent increase in the cross–sectional area of the molecule at the interface.

The positioning of the hydrophilic group in a central, rather than in a terminal, position in a straight alkyl chain or branching of the alkyl chain results in an increase in the area per molecule at the liquid/air interface.

Replacement of the usual hydrocarbon-based hydrophobic group by a fluorocarbon-based hydrophobic group appears to cause only a small increase in the effectiveness of adsorption at the aqueous solution–air interface, in contrast to its large effect on most other interfacial properties.

In ionic surfactants, those with more tightly bound counterions (ions with small hydrated radii, e.g., Cs^+,K^+,NH_4^+) appear to be more effectively adsorbed than those with less tightly bound ones (Na^+, Li^+, F^-), although the effect, except for tetraalkylammonium salts (Tamaki, 1967) is rather small. In quaternary ammonium salts of structure $R(CH_2)_m\ N(R')_3^+X^-$ (e.g., $C_{14}H_{29}N(CH_3)_3^+Br^-$ and $C_{14}H_{29}N(C_3H_7)_3^+Br^-$), an increase in the size of R' results in an increase in a_m^s and a consequent decrease in Γ_m. Salt formation between an ionic surfactant and an oppositely charged surfactant of approximately equal hydrophobic chain length (e.g., $C_{10}H_{21}N(CH_3)_3^+ \cdot C_{10}H_{21}\ SO_4^-$ or $C_{12}H_{25}N\ (CH_3)_3OH^+ \cdot C_{12}H_{25}SO_3^-$) produces a large increase in the effectiveness of adsorption, with the area per molecule at the interface approaching that of a close-packed film with the hydrophobic chains oriented perpendicular to the interface. This is probably the result of the combined effects of mutual attraction of ionic groups and mutual attraction of hydrophobic chains.

In POE materials in which the POE group constitutes either the entire hydrophilic group, as in POE nonionics, or a portion of the hydrophilic group, as in $C_{16}H_{33}(OC_2H_4)_xSO_4^-Na^+$ or $C_9H_{19}C_6H_4(OC_2H_4)_xOPO(OH)_2$, the POE chain, immersed in the aqueous phase in the form of a coil whose cross-sectional area increases with the number of OE units (Schick, 1962), determines a_m^s and therefore Γ_m. As the number of EO units increases, a_m^s increases and Γ_m decreases. In nonionic POE materials containing the same mole ratio of OE, effectiveness increases with increase in the length of the hydrophobic group, due to the larger lateral interaction.

Other factors that produce significant changes in Γ_m are:

1. The addition of neutral electrolyte (NaCl, KBr) to an aqueous solution of an ionic surfactant containing no electrolyte. This results in increased adsorption at the aqueous solution–air interface because of the decrease in repulsion between the oriented ionic heads at the interface when the ionic strength of the solution is increased (see Section I of this chapter). For nonionics there appears to be only a small increase in the saturation adsorption upon addition of neutral electrolyte (Shinoda, 1961; Schick, 1962) and little change on the addition of either water structure-breaking (urea, *N*-methylacetamide) or -promoting (fructose, xylose) additives (Schwuger, 1969, 1971b).
2. The nature of the nonaqueous phase in adsorption at the liquid–liquid interface. It has been found that saturation adsorption increases with increase in the interfacial tension between the two phases (van Voorst Vader, 1960a).

   When the nonaqueous phase is a straight-chain saturated hydrocarbon, the value of Γ_m is close to that at the aqueous solution–air interface, with possibly a slight increase in the effectiveness of adsorption as the length of the alkane is increased. When the nonaqueous phase is a short-chain unsaturated or aromatic hydrocarbon, however, there is a significant decrease in the effectiveness of adsorption at the aqueous solution–hydrocarbon interface (Rehfeld, 1967; Murphy, 1988).
3. Temperature. An increase in temperature results in an increase in the area per molecule, presumably due to increased thermal motion, with a consequent decrease in the effectiveness of adsorption.

III.D. The Szyszkowski, Langmuir, and Frumkin Equations

In addition to the Gibbs equation, three other equations have been suggested that relate concentration of the surface-active agent at the interface, surface or interfacial tension, and equilibrium concentration of the surfactant in a liquid phase. The Langmuir equation (Langmuir, 1917)

$$\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \tag{2.6}$$

discussed previously, relates surface concentrations with bulk concentration. The Szyszkowski equation (Szyszkowski, 1908)

$$\gamma_0 - \gamma = \pi = 2.303\,RT\,\Gamma_m \log\left(\frac{C_1}{a} + 1\right) \tag{2.28}$$

where γ_0 is the surface tension of the solvent and π is the surface pressure (the reduction in surface tension), relates surface tension and bulk concentration. The Frumkin equation (Frumkin, 1925)

$$\gamma_0 - \gamma = \pi = -2.303\,RT\,\Gamma_m \log\left(1 - \frac{\Gamma_1}{\Gamma_m}\right) \tag{2.29}$$

relates surface tension and surface (excess) concentration. These equations, first formulated as empirical relations, can be obtained from a general surface equation of state (Lucassen-Reynders, 1967) if one assumes ideal surface behavior (i.e., surface activity coefficients close to unity). This assumption has been found to be generally valid for ionic surfactants at the aqueous solution–air and aqueous solution–hydrocarbon interfaces (Lucassen-Reynders, 1966), with the exception of C_{18} or longer compounds at the aqueous solution–air interface.

III.E. Efficiency of Adsorption at the *L/G* and *L/L* Interfaces

As in the case of adsorption at the solid–liquid interface, in comparing the performance of surfactants at the *L/G* or *L/L* interfaces, it is useful to have a parameter that measures the concentration of surfactant in the liquid phase required to produce a given amount of adsorption at the interface, the efficiency of adsorption of the surfactant, especially when it can be related to the free energy change involved in the adsorption. A convenient measure of the efficiency of adsorption is the negative logarithm of the concentration of surfactant in the bulk phase required to produce a 20-mN/m(dyn/cm) reduction in the surface or interfacial tension of the solvent, $-\log C_{(-\Delta\gamma=20)} \equiv pC_{20}$. This is based on the following considerations: The ideal measure of efficiency of adsorption would be some function of the minimum concentration of surfactant in the bulk phase necessary to produce maximum (saturation) adsorption at the interface. However, determining this concentration would require a complete γ–log C_1 plot for each surfactant being investigated. Observation of γ–log C_1 plots in the literature reveals that when the surface (or interfacial) tension of the pure solvent has been decreased about 20 dyn/cm by adsorption of the surfactant, the surface (excess) concentration Γ_1 of the surfactant is close to its saturation value. This is confirmed by use of the Frumkin equation (2.29). From Table 2-2, Γ_m is $1 - 4.4 \times 10^{-10}$ mol/cm^2. Solving for Γ_1 in the Frumkin equation, when $\gamma_0 - \gamma = \pi = 20$ dyn/cm and $\Gamma_m = 1 - 4.4 \times 10^{-10}$ mol/cm^2, $\Gamma_1 = 0.84$ to $0.999\ \Gamma_m$ at 25°C, indicating that when the surface (or interfacial) tension has been reduced by 20 dyn/cm, the surface concentration is 84–99.9% saturated.

Thus, the bulk liquid phase concentration of surfactant required to depress the surface (or interfacial) tension of the solvent by 20 dyn/cm (m N m^{-1}) is a good measure of the efficiency of adsorption of the surfactant; that is, it is close to the minimum concentration needed to produce saturation adsorption at the interface. The negative logarithm of the bulk phase concentration of surfactant in mol dm^{-3}, pC_{20}, rather than the concentration C_{20} itself, is used because the negative logarithm can be related to standard free energy change ΔG° involved in the transfer of the surfactant molecule from the interior of the bulk liquid phase to the interface (see below).

The advantage of measuring the effect of a surfactant in an interfacial phenomenon by some parameter that is related to the standard free energy change associated with the action of the surfactant in that phenomenon is that the total standard free energy change can be broken into the individual standard free energy changes associated with the action of the various structural groupings in the molecule. This enables correlations to be made between the various structural groupings in the surfactant and its interfacial properties. In this fashion, the efficiency with which a surfactant is adsorbed at an interface can be related to the various structural groups in the molecule.

The relation of pC_{20} to the free energy change on adsorption at infinite dilution ΔG° can be seen by use of the Langmuir (2.6) and Szyszkowski equations (2.28). Since at $\pi = 20$ mN/m(dyn/cm), $\Gamma_1 = 0.84$ to $0.999\ \Gamma_m$, from the Langmuir equation $C_1 = 5.2$ to $999 \times a$; thus the quantity $\log[(C_1/a) + 1] \approx \log(C1/a)$ and the Szyszkowski equation becomes $\gamma_0 - \gamma = \pi = 2.303\,RT\Gamma_m \log(C_1/a)$. In this case, then,

$$\log\,(1/C_1)_{\pi=20} = -\left(\log a + \frac{\gamma_0 - \gamma}{2.303\,RT\Gamma_m}\right)$$

Since $a = 55\exp(\Delta G^\circ/RT)$ and $\log a = 1.74 + \Delta G^\circ/2.303\,RT$,

$$\log\left(\frac{1}{C_1}\right)_{\pi=20} \equiv pC_{20} = -\left(\frac{\Delta G^\circ}{2.303\,RT} + 1.74 + \frac{20}{2.303\,RT\Gamma_m}\right) \tag{2.30}$$

For a straight-chain surfactant of structure, $CH_3(CH_2)_nW$, where W is the hydrophilic portion of the molecule, the standard free energy of adsorption ΔG° can be broken into the standard free energy changes associated with the transfer of the terminal methyl group, the $—CH_2—$ groups of the hydrocarbon chain, and the hydrophilic group, from the interior of the liquid phase to the interface at $\pi = 20$, i.e., under conditions where the surface (or interfacial) tension has been reduced by 20 mN/m(dyn/cm).

$$\Delta G^\circ = m \cdot \Delta G^\circ(—CH_2—) + \Delta G^\circ(W) + \text{constant}$$

where $m =$ the total number of carbon atoms $(n + 1)$ in the hydrocarbon chain, and the constant equals $\Delta G^\circ(CH_3—) - \Delta G^\circ(—CH_2—)$.

When, for a homologous series of surfactants (with the same hydrophilic group), the value of Γ_m (or a_m^s) does not change much (Table 2-2) with increase in the number of carbon atoms in the molecule at constant microenvironmental conditions (temperature, ionic strength of the solution), and $\Delta G^\circ(W)$ can be considered to be a constant, the relation between pC_{20} and $\Delta G^\circ(—CH_2—)$, under these conditions, is

$$pC_{20} = \left[\frac{-\Delta G^\circ(—CH_2—)}{2.3RT}\right] m + \text{constant} \tag{2.31}$$

This equation indicates that the efficiency factor pC_{20} is a linear function of the number of carbon atoms in a straight-chain hydrophobic group, increasing as the number of carbon atoms increases. Figure 2-16 shows this linear relation for several homologous series of surfactants of different charge type.

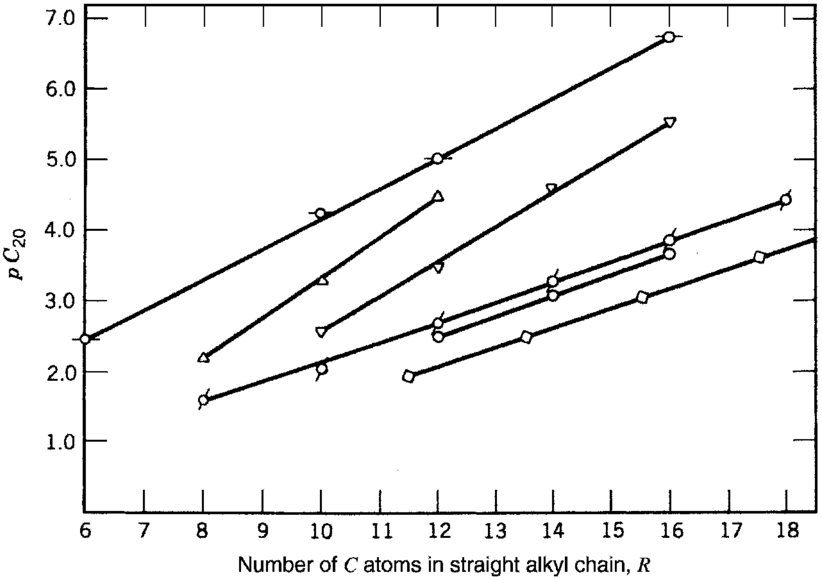

FIGURE 2-16 Effect of length of the hydrophobic group R on the efficiency of adsorption at the aqueous solution–air (*A*/*A*) and aqueous solution–heptane (*A*/*H*) interfaces: —⊙—R$(OC_2H_4)_6OH$ at 25°C (*A*/*A*); △ $RN^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$ at 25°C (*A*/*A*); ▽$RN^+(CH_3)_2CH_2COO^-$ at 23°C (*A*/*A*); ⌽ RSO_4^- Na^+ at 50°C (*A*/*H*); ⊙ RSO_4^- Na^+ at 25°C (*A*/*A*); ◇*p*-$R'C_6H_4SO_3^-Na^+$ (R=R′ + 3.5) at 70°C (*A*/*A*). Data from Table 2-2.

The larger the value of pC_{20}, the more efficiently the surfactant is adsorbed at the interface and the more efficiently it reduces surface or interfacial tension, i.e., the smaller the bulk liquid phase concentrations required either to attain saturation adsorption or to reduce the surface or interfacial tension by 20 mN/m(dyn/cm). Since this is a logarithmic relation, a value of pC_{20} one unit greater means 10 times the efficiency, that is, 1/10 the bulk phase concentration required to produce surface saturation.

Table 2-2 lists the efficiency of adsorption pC_{20} for a number of surfactants of different structural type at the aqueous solution–air and aqueous solution–hydrocarbon interfaces. The data indicate the following relations between the structure of the surfactant and its efficiency of adsorption at aqueous solution–air and aqueous solution–hydrocarbon interfaces.

The efficiency of adsorption at these interfaces increases linearly with an increase in the number of carbon atoms in a straight-chain hydrophobic group (Figure 2-16), reflecting the negative free energy of adsorption of a methylene group at these interfaces. If the hydrophobic group of an ionic surfactant is increased by two $—CH_2—$ groups, pC_{20} appears to be increased by 0.56 – 0.6 for adsorption at the aqueous solution–air or aqueous solution–hydrocarbon interfaces, meaning that a surface concentration close to the saturation value can be obtained with only 25–30% of the bulk phase surfactant concentration previously required.

For POE nonionic surfactants at the aqueous solution–air interface, pC_{20} appears to be increased by about 0.9 when the chain length is increased by two methylene groups, meaning that a bulk phase surfactant concentration of only one-seventh is required. The larger slope of the POE nonionic curve is due to the fact that, in this case, Γ_m increases with increase in the number of C atoms in the alkyl chain (Table 2-2).

In contrast to the situation with effectiveness of adsorption, where an increase in the length of the hydrophobic group beyond 16 carbon atoms appears to cause a decrease in effectiveness, efficiency of adsorption appears to increase steadily with increase in the length of the hydrophobic group up to at least 20 carbon atoms.

As in effectiveness of adsorption, a phenyl group in the hydrophobic portion appears to be equivalent to about three and one-half carbon atoms in a straight carbon chain. Methylene groups between two hydrophilic groups appear to be equivalent to about one-half —CH_2— a group in a straight carbon chain with a single, terminal hydrophilic group.

When the hydrophobic group has side chains, the carbon atoms on the side chains seem to have about two-thirds the effect of carbon atoms in a straight alkyl chain with a single terminal hydrophilic group. When the hydrophilic group is at a nonterminal position in the hydrophobic group, the latter appears to act as if it were branched at the position of the hydrophilic group with the carbon atoms on the shorter portion of the hydrophobic group having about two-thirds the effect of the carbon atoms in the longer portion.

In POE compounds of structure $R(OC_2H_4)_xSO_4^-Na^+$, where $x = 1, 2,$ or 3, and in $RCONH(C_2H_4OH)_2$, the first oxyethylene group appears to be equivalent to about 2.5 —CH_2— groups in a straight alkyl chain, with the additional oxyethylene groups having little or no effect.

Short alkyl groups (totaling four carbon atoms or less), including the pyridine nucleus, surrounding the N in quaternary ammonium salts or amine oxides, appear to have little effect. In these cases efficiency of adsorption seems to be determined almost exclusively by the length of the long carbon chain attached to the N.

In POE nonionics, an increase in the number of oxyethylene units in the hydrophilic group above six units, in contrast to its large effect in decreasing the effectiveness of adsorption, seems to cause only a small decrease in the efficiency of adsorption. This appears to indicate a very small change in the free energy of transfer of the molecule from bulk phase interior to the interface with change in the number of oxyethylene units above six in the hydrophilic head.

In nonionic surfactants generally, the efficiency of adsorption is much greater than in ionic surfactants with the same number of carbon atoms in the hydrophobic group. This is because in the adsorption of ionic surfactants, electrical repulsion between the ionic heads of surfactant ions already at the interface and the similarly charged oncoming surfactant ions increases the positive free energy of transfer of the hydrophilic head from the interior of the bulk phase to the interface.

A change in the sign of the charge of a univalent ionic hydrophilic group produces little if any effect on the efficiency of adsorption. However, the replacement of the counterion by one that is more tightly bound increases the efficiency.

This increased efficiency is probably the result of the greater neutralization of the charge on the surfactant ion by the more tightly bound counterion. This would result in a smaller electrical repulsion between already adsorbed surfactant ions and oncoming surfactant ions at the interface.

The addition of inert electrolyte containing a common, nonsurfactant ion to a solution of ionic surfactant in an aqueous medium causes a large increase in the efficiency of its adsorption at the liquids–air interface (Boucher, 1968). In sharp contrast to their lack of significant effect on the effectiveness of adsorption, the addition of water structure breakers, such as urea and *N*-methylacetamide, to aqueous solutions of nonionic surfactants results in a decrease in efficiency of adsorption at the interface (Schwuger, 1969), whereas the addition of structure formers, such as fructose and xylose, increases the efficiency of adsorption (Schwuger, 1971b).

In summary, the efficiency of adsorption of a surfactant at the aqueous solution–air interface, as measured by the pC_{20} value, is increased by the following factors:

1. Increase in the number of carbon atoms in the hydrophobic chain.
2. A straight alkyl chain as the hydrophobic group, rather than a branched alkyl chain containing the same number of carbon atoms.
3. A single hydrophilic group situated at the end of the hydrophobic group, rather than one (or more) at a central position.
4. A nonionic or zwitterionic hydrophilic group, rather than an ionic one.
5. For ionic surfactants, decrease in the effective charge of the hydrophilic group by
   (a) use of a more tightly bound (less hydrated) counterion,
   (b) increase in the ionic strength of the aqueous phase.

Temperature increase in the 10–40°C range causes an increase in the efficiency of adsorption for POE nonionics but a decrease for ionics and zwitterionics.

III.F. Calculation of Thermodynamic Parameters of Adsorption at the *L*/*G* and *L*/*L* Interfaces

Standard thermodynamic parameters, ΔG°, ΔH°, and ΔS°, tell us what is happening in a process. The standard free energy change upon adsorption $\Delta G^\circ_{\mathrm{ad}}$ tells us whether adsorption (in the standard states) is spontaneous ($\Delta G^\circ{}_{\mathrm{ad}}$ negative) or not and the magnitude of the driving force. The standard enthalpy change upon adsorption $\Delta H^\circ_{\mathrm{ad}}$ indicates whether bond making ($\Delta H^\circ_{\mathrm{ad}}$ negative) or bond breaking ($\Delta H^\circ_{\mathrm{ad}}$ positive) predominates in the adsorption process. The standard entropy change $\Delta S^\circ_{\mathrm{ad}}$ indicates whether the system becomes more structured ($\Delta S^\circ_{\mathrm{ad}}$ negative) or more random ($\Delta S^\circ_{\mathrm{ad}}$ positive).

To calculate standard parameters of adsorption, ΔG°, ΔH°, and ΔS°, it is necessary to define standard states of the surface and bulk phases. If one uses the usual convention of unit concentrations in the bulk and interface as the standard states (Adam, 1940), then it is necessary to choose an appropriate thickness for the interface, which is not readily accomplished. Another convention has consequently been proposed (Betts, 1957, 1960) in which the standard states for the surface and bulk phases are unit surface pressure (unit fugacity) and unit activity, respectively, and $-\Delta G^\circ = RT \ln \pi^*/a$, where π^* is the surface fugacity and a the bulk phase activity of the solute. For very dilute solutions of surfactants ($\pi = 0$–3 dyn/cm), the reduction in surface tension (or surface pressure π) varies linearly with the molar bulk phase concentration C_1 of the surfactant:

$$\left(\frac{\partial \pi}{\partial C_1}\right)_{C_1 \to 0} = \alpha \quad \text{(Traube's constant)}$$

Fugacity and activity coefficients are assumed to approach unity under the above conditions, and a standard free energy of adsorption $\Delta G^\circ_{\mathrm{Tr}}$ can be obtained

$$\Delta G^\circ_{\mathrm{Tr}} = -2.303\, RT \log \left(\frac{\partial \pi}{\partial C_1}\right)_{C_1 \to 0}$$

and a standard molar free energy of adsorption can be calculated from the linear, low concentration region of the γ (or π)-C_1 curve (Tamaki, 1967; Gillap, 1968; Naifu, 1979; Spitzer, 1983).

Unfortunately, good surface tension data in this region are difficult to obtain, since traces of impurities adsorbed from the air or present in the solvent or in the surfactant can markedly affect the results. Second, there are only a few studies in the literature on this region of the surface tension–concentration curves, since investigators of the effect of surfactants on the surface tension of solvents generally are interested in the region where surfactants show the maximum effect, rather than the region where they show little effect.

Standard free energies at the aqueous solution–air interface can be calculated from surface tension data in the vicinity of the CMC, where such data are commonly and conveniently taken, by use of equation 2.32 (Rosen, 1981),

$$\Delta G^\circ_{\mathrm{ad}} = RT \ln a_\pi - \pi A^s_m \tag{2.32}$$

where a_π = activity of the surfactant in the aqueous phase at a surface pressure of $\pi (= \gamma_0 - \gamma)$ in the region of surface saturation (i.e., where $\Gamma = \Gamma_m$ and the molar area of the surfactant $A^s = A^s_m$).

The standard state for the surface phase is a hypothetical monolayer of the surfactant at its closest packing (minimum surface area/molecule) but at a surface pressure of zero. For nonionic surfactants at dilute concentrations ($<1 \times 10^{-2}\, M$) in the solution phase, we can substitute mole fractions for activities and the relation becomes

$$\Delta G^\circ_{\mathrm{ad}} = RT \ln C_\pi/\omega - \pi A^s_m \tag{2.33}$$

where C_π = molar concentration of surfactant in the aqueous phase at a surface pressure of π and ω is the number of moles of water per liter of water. When C_π is in mol/L, π in dyn/cm (mJm^{-2}), a_m^s in Å^2 per molecule, and $R = 8.314$ J mol^{-1}, this becomes

$$\Delta G^\circ_{\text{ad}}(\text{in } J/\text{mol}) = 2.3\,RT\log C_\pi/\omega - 6.023\pi \cdot a_m^s \tag{2.33a}$$

For an ionic surfactant of the type AB,

$$\begin{aligned}\Delta G^\circ_{\text{ad}}(\text{in J/mol}) = {} & 2.3\,RT[\log C_{\text{A}}/\omega + \log f_{\text{A}} + \log C_{\text{B}}/\omega + \log f_{\text{B}}] \\ & - 6.023\pi \cdot a_m^s\end{aligned} \tag{2.33b}$$

The activity coefficients f_{A} and f_{B} can be evaluated by equation 2.24. The standard free energies of adsorption calculated by use of equation 2.33b are independent of the ionic strength of the solution.

When the surface tension of the solvent has been reduced by 20 mN/m(dyn/cm), i.e., $\pi = 20$ mN/m(dyn/cm), then the relation (equation 2.33a) for a nonionic surfactant becomes

$$\Delta G^\circ_{\text{ad}} = -(2.303\,RT)pC_{20} - 6.023 \times 20a_m^s - 2.303\,RT\log\omega \tag{2.34}$$

and

$$pC_{20} = -\left(\frac{\Delta G^\circ_{\text{ad}}}{2.303\,RT} + \frac{6.023 \times 20a_m^s}{2.303\,RT}\right) - \log\omega \tag{2.35}$$

Since $a_m^s = 10^{16}/\Gamma_m N$, this relation is similar to the one (2.30) obtained previously from the Langmuir and Szyszkowski equations. For surfactants whose a_m^s values do not vary much,

$$p\,C_{20} = \frac{-\Delta G^\circ_{\text{ad}}}{2.303\,RT} - K \tag{2.36}$$

and the pC_{20} value is a measure of the standard free energy of adsorption.

Since

$$\Delta G^\circ_{\text{ad}} = \Delta H^\circ_{\text{ad}} - T\,\Delta S^\circ_{\text{ad}} \tag{2.37}$$

standard entropies and enthalpies of adsorption, $\Delta S^\circ_{\text{ad}}$ and $\Delta H^\circ_{\text{ad}}$, respectively, can be calculated from the relation

$$d\,\Delta G^\circ_{\text{ad}}/dT = -\Delta\,S^\circ_{\text{ad}} \tag{2.38}$$

if $\Delta H^\circ_{\text{ad}}$ is constant over the temperature range investigated. Alternatively,

$$T^2 d(\Delta G^\circ_{\text{ad}}/T)\text{d}T = -\Delta H^\circ_{\text{ad}} \tag{2.38a}$$

can be used, if $\Delta S^\circ_{\text{ad}}$ is constant over that temperature range.

Standard thermodynamic parameters of adsorption calculated by use of equations 2.33, 2.34, 2.37, and 2.38 or 2.38a are listed in Table 2-3. All the $\Delta G^\circ{}_{\text{ad}}$

TABLE 2-3 Standard Thermodynamic Parameters of Adsorption for Surfactants at the Aqueous Solution–Air Interface or Aqueous Solution–Hydrocarbon Interface[a]

Compound	Tem. (°C)	$\Delta G^\circ_{\mathrm{ad}}$ (kJ mol^{-1})[b]	$\Delta H^\circ_{\mathrm{ad}}$ (kJ mol^{-1})	$T\,\Delta S^\circ_{\mathrm{ad}}$ (kJ mol^{-1})	Reference[c]
$C_{10}H_{21}SO_3^-Na^+$	10	$-43._{3}$			Dahanayake, 1986
			$+2$	$+4_{7}$	
$C_{10}H_{21}SO_3^-Na^+$	25	$-45._{7}$			Dahanayake, 1986
			-4	$+4_{3}$	
$C_{10}H_{21}SO_3^-Na^+$	40	$-47._{9}$			Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	10	$-50._{7}$			Dahanayake, 1986
			-7	$+4_{5}$	
$C_{12}H_{25}SO_3^-Na^+$	25	$-53._{0}$			Dahanayake, 1986
			-1_{0}	$+4_{4}$	
$C_{12}H_{25}SO_3^-Na^+$	40	$-55._{3}$			Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	25	$-54._{4}$	—	—	Rehfeld, 1967; Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$ (aq. soln.–octane interface)	25	$-56._{9}$	—	—	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (aq. soln.–heptadecane interface)	25	$-56._{5}$	—	—	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (aq. soln.–cyclohexane interface)	25	$-58._{0}$	—	—	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (aq. soln.–benzene interface)	25	$-57._{9}$	—	—	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (aq. soln.–butyl benzene interface)	25	$-55._{8}$	—	—	Rehfeld, 1967
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	10	$-47._{2}$			Dahanayake, 1986
			$+3$	$+5_{1}$	
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	25	$-49._{7}$			Dahanayake, 1986
			-6	$+4_{5}$	
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	40	$-51._{9}$			Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_3^-Na^+$	10	$-54._{5}$			Dahanayake, 1986
			-6	$+4_{9}$	

$C_{12}H_{25}OC_2H_4SO_3^-Na^+$	25	$-57._0$			Dahanayake, 1986
			-1_1	$+4_7$	
$C_{12}H_{25}OC_2H_4SO_3^-Na^+$	40	$-59._3$			Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	10	$-54._7$			Dahanayake, 1986
			-3	$+5_3$	
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	25	$-57._5$			Dahanayake, 1986
			-1_7	$+4_1$	
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	40	$-59._5$			Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	10	$-56._4$			Dahanayake, 1986
			-5	$+5_3$	
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	25	$-59._1$			Dahanayake, 1986
			-8	$+5_2$	
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	40	$-61._7$			Dahanayake, 1986
$C_{12}H_{25}Pyr^+Br^{-d}$	10	$-50._0$			Rosen, 1982b
			-7	$+4_4$	
$C_{12}H_{25}Pyr^+Br^-$	25	$-52._3$			Rosen, 1982b
			-9	$+4_4$	
$C_{12}H_{25}Pyr^+Br^-$	40	$-54._5$			Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^-$	10	$-49._0$			Rosen, 1982b
			-1_1	$+3_9$	
$C_{12}H_{25}Pyr^+Cl^-$	25	$-51._1$			Rosen, 1982b
			-1_1	$+4_1$	
$C_{12}H_{25}Pyr^+Cl^-$	40	$-53._1$			Rosen, 1982b
$C_8H_{17}OCH_2CH_2OH$	25	$-31._8$	—	—	Shinoda, 1959
$C_8H_{17}CHOHCH_2OH$	25	$-34._7$	—	—	Kwan, 1980
$C_8H_{17}CHOHCH_2CH_2OH$	25	$-34._3$	—	—	Kwan, 1980
$C_{10}H_{21}CHOHCH_2CH_2OH$	25	$-40._4$	—	—	Kwan, 1980
$C_{12}H_{25}CHOHCH_2CH_2OH$	25	$-46._9$	—	—	Kwan, 1980
N-hexyl-2 pyrrolid(in)one, pH 7.0	25	$-28._8$			Rosen, 2001b
N-(2-ethylhexy)-2-pyrrolid(in)one, pH 7.0	25	$-33._0$			Rosen, 2001b

(*Continued next page*)

TABLE 2-3 (*Continued*)

Compound	Tem (°C)	$\Delta G^\circ_{\mathrm{ad}}$ (kJ mol^{-1})^b	$\Delta H^\circ_{\mathrm{ad}}$ (kJ mol^{-1})	$T\,\Delta S^\circ_{\mathrm{ad}}$ (kJ mol^{-1})	Reference^c
N-octyl-2-pyrrolid(in)one, pH 7.0	25	$-33._1$			Rosen, 2001b
N-decyl-pyrrolid(in)one, pH 7.0	25	$-38._7$			Rosen, 2001b
$C_{12}H_{25}(OC_2H_4)_3OH$	10	$-43._0$			Rosen, 1982a
			+4	$+4_8$	
$C_{12}H_{25}(OC_2H_4)_3OH$	25	$-45._5$			Rosen, 1982a
			-1_2	$+3_5$	
$C_{12}H_{25}(OC_2H_4)_3OH$	40	$-47._2$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	10	$-43._7$			Rosen, 1982a
			+3	$+4_8$	
$C_{12}H_{25}(OC_2H_4)_5OH$	25	$-46._2$			Rosen, 1982a
			−5	$+4_3$	
$C_{12}H_{25}(OC_2H_4)_5OH$	40	$-48._3$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	10	$-44._2$			Rosen, 1982a
			+7	$+5_2$	
$C_{12}H_{25}(OC_2H_4)_7OH$	25	$-46._9$			Rosen, 1982a
			−3	$+4_5$	
$C_{12}H_{25}(OC_2H_4)_7OH$	40	$-49._1$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	10	$-44._7$			Rosen, 1982a
			+6	$+5_2$	
$C_{12}H_{25}(OC_2H_4)_8OH$	25	$-47._7$			Rosen, 1982a
			−2	$+4_7$	
$C_{12}H_{25}(OC_2H_4)_8OH$	40	$-49._7$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$ (aq. soln.–cyclohexane)	25	$-52._8$			Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$ (aq. soln.–heptane)	25	$-51._5$			Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$ (aq. soln.–hexadecane)	25	$-51._5$			Rosen, 1991
t-$C_8H_{17}(OC_2H_4)_3OH$	25	$-44._8$	—	—	Crook, 1964

t-$C_8H_{17}(OC_2H_4)_5OH$	25	$-45._6$	—	—	Crook, 1964
t-$C_8H_{17}(OC_2H_4)_7OH$	25	$-45._1$	—	—	Crook, 1964
t-$C_8H_{17}(OC_2H_4)_9OH$	25	$-45._4$	—	—	Crook, 1964
$(CH_3)_3SiOSi(CH_3)[CH_2(CH_2CH_2O)_{8.5}$–$CH_3]$ $OSi(CH_3)_3$, pH 7.0	25	$-51._9$			Rosen, 2001b
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	10	$-34._2$			Dahanayake, 1984
			$-0._2$	$+3_5$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	25	$-36._0$			Dahanayake, 1984
			-4	$+3_3$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	40	$-37._6$			Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	10	$-40._3$			Dahanayake, 1984
			-6	$+3_5$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	25	$-42._1$			Dahanayake, 1984
			-1_2	$+3_1$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$	40	$-43._6$			Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$ (aq. soln.–heptane interface)	25	$-46._7$	-2_1(35°)	$+2_6$(35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$ (aq. soln.–isooctane interface)	25 25	$-46._6$	-1_9(35°)	$+2_9$(35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$ (aq. soln.–hexadecane interface)	25	$-45._5$	-1(35°)	$+4_6$(35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$ (aq. soln.–cyclohexane interface)	25	$-48._0$	-1_4(35°)	$+3_4$(35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)$-$CH_2COO^-$ (aq. soln.–toluene interface)	25	$-46._9$	-2_4(35°)	$+2_4$(35°)	Murphy, 1988
$C_8H_{17}N^+(CH_3)(CH_2C_6H_5)$-$CH_2CH_2SO_3^-$	10	$-28._2$			Dahanayake, 1984
			$+6$	$+3_5$	
$C_8H_{17}N^+(CH_3)(CH_2C_6H_5)$-$CH_2CH_2SO_3^-$	25	$-30._0$			Dahanayake, 1984
			-8	$+2_2$	
$C_8H_{17}N^+(CH_3)(CH_2C_6H_5)$-$CH_2CH_2SO_3^-$	40	$-31._1$			Dahanayake, 1984

(*Continued next page*)

TABLE 2-3 (*Continued*)

Compound	Tem (°C)	ΔG°_{ad} (kJ mol^{-1})^b	ΔH°_{ad} (kJ mol^{-1})	$T\,\Delta S^\circ_{ad}$ (kJ mol^{-1})	Reference^c
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	10	$-34._6$			Dahanayake, 1984
			-1	$+3_5$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	25	$-36._4$			Dahanayake, 1984
			-1_5	$+2_2$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	40	$-37._5$			Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	10	$-41._0$			Dahanayake, 1984
			-9	$+3_3$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	25	$-42._7$			Dahanayake, 1984
			-1_5	$+2_8$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)\text{-}CH_2CH_2SO_3^-$	40	$-44._0$			Dahanayake, 1984
$C_{10}H_{21}CH(Pyr^+)COO^-$	25	$-31._9$	—	—	Zhao, 1984
$C_{12}H_{25}CH(Pyr^+)COO^-$	25	$-38._2$	—	—	Zhao, 1984
$C_{14}H_{29}CH(Pyr^+)COO^-$	40	$-45._8$	—	—	Zhao, 1984

[a] Values are for the aqueous solution–air interface unless otherwise indicated.

[b] Values are independent of total ionic strength and are averages of values at different electrolyte contents.

[c] Parameters calculated from data in listed reference.

[d] Pyr^+, pyridinium

values are negative, indicating that adsorption of these compounds at the aqueous solution–air and aqueous solution–air hydrocarbon interfaces is spontaneous.

It is evident that the positive entropy change upon adsorption is by far the major contributor to the negative values of the free energy change and thus the main driving force for adsorption at the interface in these compounds. The $-\Delta G^{\circ}_{\text{ad}}$ per —CH_2— group at 25°C is 3.0–3.5 kJ; increase in the length of the alkyl chain therefore increases the tendency of the compound to adsorb.

It is noteworthy that, for all the compounds listed, $\Delta G^{\circ}_{\text{ad}}$ and $\Delta H^{\circ}_{\text{ad}}$ become more negative with increase in temperature, which appears to indicate that some dehydration of the hydrophilic group is required for adsorption. At higher temperatures, the surfactant is less hydrated, requires less dehydration to adsorb, and adsorbs more readily.

In the POE nonionics listed, the $\Delta G^{\circ}_{\text{ad}}$ becomes slightly more negative with increase in the EO content of the molecule, reflecting the increasing value of $\Delta S^{\circ}_{\text{ad}}$ with this change. This increase and the concomitant increase in $\Delta H^{\circ}_{\text{ad}}$ seem to indicate that adsorption at the aqueous solution–air interface is accompanied by partial dehydration of the POE chain, with the amount of dehydration per molecule increasing with increase in the number of EO units.

This increase in $-\Delta G^{\circ}_{\text{ad}}$ with increase in the EO content of the molecule is seen also in the EO alkyl sulfates, where the addition of the first EO group to the alkyl sulfate molecule increases the $-\Delta G^{\circ}_{\text{ad}}$ value by about 3 kJ/mol and the addition of the second by about half that value.

The presence of a second liquid (hydrocarbon) phase increases the $-\Delta G^{\circ}_{\text{ad}}$ value by a few kJ/mol, with the increase being largest for cyclohexane (of the hydrocarbons investigated) and becoming smaller with increase in the chain length of the hydrocarbon.

Relationships have been found between the adsorption properties described above of surfactants and their environmental effects (toxicity, bioconcentration) on aquatic organisms (algae, fish, rotifers). The log of the EC 50 (the surfactant molar concentration in the water at which the organism population is reduced by 50% relative to a no-dose control) and the log of the BCF (the ratio of surfactant concentration in the fish relative to that in the water) have both been shown (Rosen, 1999, 2001c) to be linearly related to the parameter $\Delta G^{\circ}_{\text{ad}}/a^s_m$ for a series of anionic, cationic, and nonionic surfactants. The values of a^s_m and $\Delta G^{\circ}_{\text{ad}}$ were obtained by the methods described above in Sections IIIB and IIIF, respectively.

III.G. Adsorption from Mixtures of Two Surfactants

Mixtures of two or more different types of surfactants often show a “synergistic” interaction, i.e., the interfacial properties of the mixture are more pronounced than those of the individual components by themselves. As a result, in many industrial products and processes, mixtures of different types of surfactants, rather than individual materials, are used. A study of the adsorption of the individual surface-active components in the mixture and of the interaction between them affords an understanding of the role of each and makes possible the selection in a rational, systematic manner of components for optimal properties.

The Gibbs adsorption equation (2.17) for two surface-active solutes in dilute solution can be written as

$$d\gamma = RT(\Gamma_1 d \ln a_1 + \Gamma_2 d \ln a_2) \tag{2.39}$$

where Γ_1, Γ_2 are the surface (excess) concentrations of the two solutes at the interface and a_1, a_2 their respective activities in the solution phase. From this expression, since molar concentrations can be substituted for activities in dilute solution,

$$\Gamma_1 = \frac{1}{RT}\left(\frac{-\partial\gamma}{\partial \ln C_1}\right)_{C_2} = \frac{1}{2.303\,RT}\left(\frac{-\partial\gamma}{\partial \log C_1}\right)_{C_2} \tag{2.40}$$

and

$$\Gamma_2 = \frac{1}{RT}\left(\frac{-\partial\gamma}{\partial \ln C_2}\right)_{C_1} = \frac{1}{2.303\,RT}\left(\frac{-\partial\gamma}{\partial \log C_2}\right)_{C_1} \tag{2.41}$$

Therefore, the concentration of each surfactant at the interface can be calculated from the slope of a γ–ln C (or log C) plot of each surfactant, holding the solution concentration of the other surfactant constant.

When the absolute concentrations of the surfactants at the interface are not required, but only their relative concentrations, i.e., their relative effectiveness of adsorption, then these can be obtained in convenient fashion by use of non-ideal solution theory.

From the thermodynamics of the system, it has been shown (Rosen and Hua, 1982) that the molar concentrations of the two surfactants in the solution phase are given by the expressions

$$C_1 = C_1^0 f_1 X_1 \tag{2.42}$$

and

$$C_2 = C_2^0 f_2 X_2 \tag{2.43}$$

where f_1 and f_2 are the activity coefficients of the surfactants (1 and 2, respectively) in the interface; X_1 is the mole fraction of surfactant 1 in the total surfactant at the interface (i.e., $X_1 = 1 - X_2$), C_1^0 is the molar concentration required to attain a given surface tension in a solution of pure surfactant 1, and C_2^0 is the molar concentration required to attain the same surface tension in a solution of pure surfactant 2.

From nonideal solution theory, the activity coefficients at the interface can be approximated by the expressions

$$\ln f_1 = \beta^\sigma (1 - X_1)^2 \tag{2.44}$$

$$\ln f_2 = \beta^\sigma (X_1)^2 \tag{2.45}$$

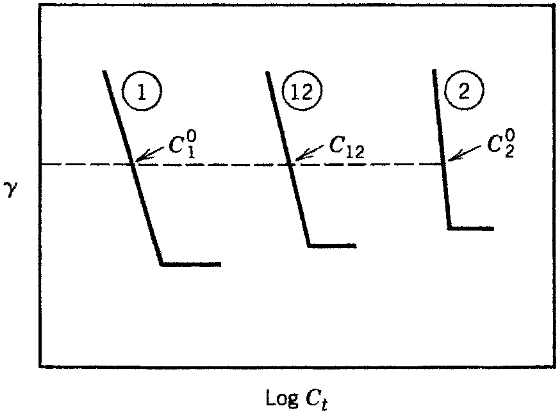

FIGURE 2-17 Evaluation of X_1 and X_2. (1) Pure surfactant 1. (2) Pure surfactant 2. (12) Mixture of 1 and 2 at a fixed value of α.

where β^σ is a parameter related to the interaction between the two surfactants at the interface. From equations 2.42–2.45,

$$\frac{(X_1)^2 \ln(C_1/C_1^0 X_1)}{(1 - X_1)^2 \ln[C_2/C_2^0(1 - X_1)]} = 1 \tag{2.46}$$

Surface tension–total surfactant concentration (C_t) curves for the two pure surfactants and a mixture of them at a fixed value of α, the mole fraction of surfactant 1 in the total surfactant in the solution phase, are used (Figure 2-17) to determine $C_1(= \alpha_1 C_{12})$, C_1^0, $C_2[= (1 - \alpha_1)C_{12}]$, and C_2^0, the molar concentrations at the same surface tension. Substitution of these values into equation 2.46 permits it to be solved iteratively for X_1 and $X_2(= 1 - X_1)$. The ratio of surfactant 1 : surfactant 2 at the interface at that particular value of α is then X_1/X_2.

The conditions for synergistic interaction between the two surfactants are discussed in Chapter 11.

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PROBLEMS

1 A nonionic surface-active solute in aqueous solution at 30°C gives the following γ-log C data (C in moles dm^{-3}):

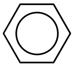
γ(mJm^{-2}):	71.4	60.0	52.0	40.6	29.2	29.2	29.2
log C:	−6.217	−5.992	−5.688	−5.255	−4.822	−4.691	−4.552

The slope of the γ–log C plot is linear at $\gamma < 60$ mJm^{-2} down to the c.m.c.

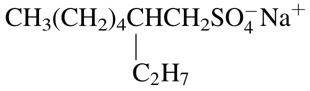
- **(a)** Calculate the surface excess concentration, Γ, in moles cm^{-2} at $\gamma <$ 60 mJm^{-2}.
- **(b)** Calculate the minimum surface area/molecule, in Å^2.
- **(c)** Calculate ΔG^0_{ad}, in kJ mol^{-1}.

2 Without looking at the tables, place the following compounds in order of increasing efficiency of adsorption (increasing pC_{20} value at the aqueous solution–air interface):

(a) $CH_3(CH_2)_{10}CH_2SO_4^-Na^+$

(b) $CH_3(CH_2)_9$  $SO_3^-Na^+$

(c) $CH_3(CH_2)_8CH_2N^+(CH_3)_3Cl^-$

(d) 

$CH_3(CH_2)_4\underset{\displaystyle C_2H_7}{\underset{|}{C}}HCH_2SO_4^-Na^+$

(e) $CH_3(CH_2)_{10}CH_2(OC_2H_4)_6OH$

3 Without looking at the tables, place the following compounds in order of increasing effectiveness of adsorption (increasing Γ_m) at the aqueous solution–air interface. Use $\simeq$ if two or more compounds have approximately equal Γ_m values:

(a) $C_{10}H_{21}SO_4^-Na^+$ (in H_2O)

(b) $C_{12}H_{25}SO_4^-Na^+$ (in H_2O)

(c) $C_{16}H_{33}SO_4^-Na^+$ (in H_2O)

(d) $C_{16}H_{33}SO_4^-Na^+$ (in 0.1 M NaCl)

(e) $C_{18}H_{37}SO_4^-Na^+$ (in H_2O)

4 If $1/k \simeq 10$ Å for 0.1 M NaCl in aqueous solution at room temperature, calculate $1/k$ for 0.1 M $CaCl_2$ under the same conditions.

5 2.0 g of a solid, whose specific surface area is 50 m^2/g, is shaken with 100 mL of a $1 \times 10^{-2} M$ solution of a surfactant. After equilibrium is reached, the concentration of the surfactant solution is 7.22×10^{-3} M. Calculate the average area occupied per surfactant molecule on the solid surface in Å^2.

6 The molar concentrations of two individual surfactants required to yield a surface tension value of 36 dynes/cm in aqueous solution are 2.6×10^{-3} and 1.15×10^{-3}, respectively. The total molar surfactant concentration required to yield a surface tension of 36 dynes/cm is 6.2×10^{-4} for a mixture of the two surfactants in which the mole fraction of the first surfactant (on a surfactant-only basis) is 0.41. Calculate the value of X_1, the mole fraction of surfactant 1 in the total surfactant at the aqueous solution–air interface for this mixture.

7 **(a)** 50 mL of a cationic surfactant solution is placed in a glass beaker for determination of its surface tension. Since the glass carries a negative charge, the cationic surfactant adsorbs onto it. Assuming that it forms at least an adsorbed monolayer on the glass, with an area/molecule at that interface of 50 Å^2, and at the surface of 60 Å^2, calculate the surfactant concentration at which adsorption at the glass interface and at the surface will result in about a 10% reduction in the surfactant bulk phase concentration.

(b) What procedures could be taken to avoid this error when surfactant solutions must be used at that concentration?

3 Micelle Formation by Surfactants

We now turn our attention to a property of surfactants that may be as fundamental, and certainly is as important, as their property of being adsorbed at interfaces. This property is micelle formation—the property that surface-active solutes have of forming colloidal-sized clusters in solution.* Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but also because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles. Micelles have become a subject of great interest to the organic chemist and the biochemist—to the former because of their unusual catalysis of organic reactions (Fendler, 1975) and to the latter because of their similarity to biological membranes and globular proteins.

I. THE CRITICAL MICELLE CONCENTRATION (CMC)

Almost from the very beginning of the study of the properties of surfactant solutions (actually, soap solutions), it was recognized that their bulk properties were unusual and indicated the presence of colloidal particles in the solution.

When the equivalent conductivity (specific conductance per gram-equivalent of solute) of an anionic surfactant of the type $Na^+ R^-$ in water is plotted against the square root of the normality of the solution, the curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it at low concentrations (Figure 3-1). This break in the curve, with its sharp reduction in the conductivity of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence of the formation at that point of micelles from the unassociated molecules of surfactant, with part of the charge of the micelle neutralized by associated counterions.

*Only those polar solvents that have two or more potential hydrogen-bonding centers and thus are capable of forming three-dimensional hydrogen-bonded networks appear capable of showing micelle formation (Ray, 1971a). In nonpolar solvents, clusters of surfactants may form, but they are generally not of colloidal size and their behavior is not analogous to that of micelles in aqueous media.

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

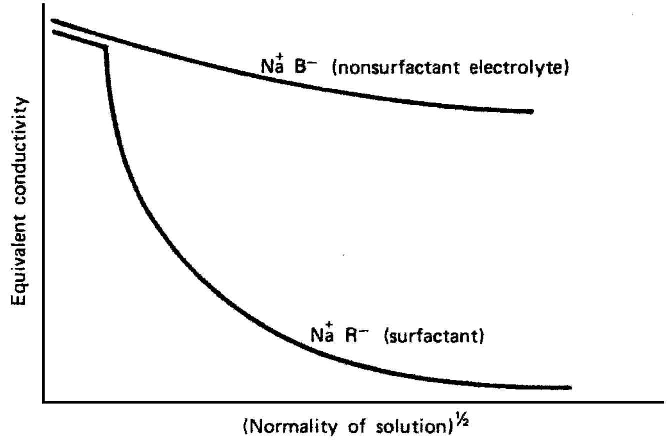


FIGURE 3-1 Plot of equivalent conductivity versus $\sqrt{\text{normality of solution}}$ for an aqueous solution of surfactant of type Na^+R^-.

The concentration at which this phenomenon occurs is called the *critical micelle concentration* (CMC). Similar breaks in almost every measurable physical property that depends on size or number of particles in solution, including micellar solubilization of solvent-insoluble material (Chapter 4) and reduction of surface or interfacial tension (Chapter 5), are shown by all types of surfactants—nonionic, anionic, cationic, and zwitterionic in aquecus media.

In some cases, particularly where the hydrophobic group is long (e.g., $>C_{16}$), a second break in the conductivity–surfactant concentration curve has been observed. It has been suggested (Treiner, 1992) that this indicates change in the micellar structure (Section II, below).

The determination of the value of the CMC can be made by use of any of these physical properties, but most commonly the breaks in the electrical conductivity,* surface tension, light scattering, or fluorescence spectroscopy–concentration curves have been used for this purpose. Critical micelle concentrations have also very frequently been determined from the change in the spectral characteristics of some dyestuff added to the surfactant solution when the CMC of the latter is reached. However, this method is open to the serious objection that the presence of the dyestuff may affect the value of the CMC. An excellent critical evaluation of the methods for determining CMCs is included in the comprehensive compilation of CMCs in aqueous solution by Mukerjee and Mysels (1971).

Based on a vast amount of data concerning the phenomenon, a picture of the process of micellization and the structure of the micelles formed has slowly emerged. It has previously been mentioned (Chapter 1) that when they are dissolved

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*When electrolyte (other than the ionic surfactant) is present in the aqueous solution, it is preferable to use a plot of $\Delta\kappa/\Delta c$ vs. $(c)^{1/2}$, where $\Delta\kappa$ is the change in the specific conductivity of the surfactant-containing solution, Δc the change in the surfactant concentration, and c the average value of c over the Δc range (Fujiwara, 1997).

in water, materials that contain a hydrophobic group distort the structure of the water and therefore increase the free energy of the system. They therefore concentrate at the surface, where, by orienting so that their hydrophobic groups are directed away from the solvent, the free energy of the solution is minimized. However, there is another means of minimizing the free energy in these systems. The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by the aggregation of the surface-active molecules into clusters (micelles) with their hydrophobic groups directed toward the interior of the cluster and their hydrophilic groups directed toward the solvent. Micellization is therefore an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with the water, thereby reducing the free energy of the system. When there is little distortion of the structure of the solvent by the lyophobic group (e.g., in water, when the hydrophobic group of the surfactant is short), then there is little tendency for micellization to occur. This is often the case in nonaqueous solvents, and therefore micelles of size comparable to those formed in aqueous media are seldom found in other solvents.

Although removal of the lyophobic group from contact with the solvent may result in a decrease in the free energy of the system, the surfactant molecule, in transferring from solution in the solvent to the micelle, may experience some loss of freedom in being confined to the micelle and, in the case of ionic surfactants, from electrostatic repulsion from other similarly charged surfactant molecules in the micelle. These forces increase the free energy of the system and thus oppose micellization. Whether micellization occurs in a particular case and, if so, at what concentration of monomeric surfactant, therefore depends on the balance between the factors promoting micellization and those opposing it.

As will be seen in the following chapters, micelles have a vast number of uses. An interesting use of micelles of anionic surfactants that involves both their adsorption and solubilization (Chapter 4) properties is for the removal of pollutants such as metallic ions and organic material from water. Metallic ions bind to the negatively charged surface of micelles of anionic surfactants, and organic material is solubilized in the interior of the micelles. The micellar solution is forced through an ultrafiltration membrane with pores small enough to block the passage of the micelles with their associated metallic ions and organic material (Fillipi, 1999).

II. MICELLAR STRUCTURE AND SHAPE

II.A. The Packing Parameter

The shape of the micelle produced in aqueous media is of importance in determining various properties of the surfactant solution, such as its viscosity, its capacity to solubilize water-insoluble material (Chapter 4), and its cloud point (Chapter 4, Section IIIB).

At the present time, the major types of micelles appear to be (1) relatively small, spherical structures (aggregation number <100), (2) elongated cylindrical, rodlike micelles with hemispherical ends (prolate ellipsoids), (3) large, flat lamellar micelles (disklike extended oblate spheroids), and (4) vesicles—more or less spherical structures consisting of bilayer lamellar micelles arranged in one or more concentric spheres.

In aqueous media, the surfactant molecules are oriented, in all these structures, with their polar heads predominantly toward the aqueous phase and their hydrophobic groups away from it. In vesicles, there will also be an aqueous phase in the interior of the structure. In ionic micelles, the aqueous solution–micelle interfacial region contains the ionic head groups, the Stern layer of the electrical double layer with the bound counterions, and water. The remaining counterions are contained in the Gouy–Chapman portion of the double layer that extends further into the aqueous phase. For POE nonionics the structure is essentially the same, except that the outer region contains no counterions, but includes coils of hydrated POE chains.

The interior region of the micelle, containing the hydrophobic groups, has a radius approximately equal to the length of the fully extended hydrophobic chain. The aqueous phase is believed to penetrate into the micelle beyond the hydrophobic head groups, and the first few methylene groups of the hydrophobic chain adjacent to the hydrophobic head are often considered in the hydration sphere. It is therefore useful to divide the interior region into an outer core that may be penetrated by water and an inner core from which water is excluded (Muller, 1972).

In nonpolar media, the structure of the micelle is similar but reversed, with the hydrophilic heads comprising the interior region surrounded by an outer region containing the hydrophobic groups and nonpolar solvent (Hirschhorn, 1960). Dipole–dipole interactions hold the hydrophilic heads together in the core (Singleterry, 1955).

Changes in temperature, concentration of surfactant, additives in the liquid phase, and structural groups in the surfactant may all cause change in the size, shape, and aggregation number of the micelle, with the structure varying from spherical through rod- or disklike to lamellar in shape (Winsor, 1968).

A theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules, has been developed by Israelachvili, Mitchell, and Ninham (1976, 1977) and Mitchell and Ninham (1981). The volume V_H occupied by the hydrophobic groups in the micellar core, the length of the hydrophobic group in the core l_c, and the cross-sectional area a_0 occupied by the hydrophilic group at the micelle–solution interface are used to calculate a "packing parameter," $V_H/l_c a_0$, which determines the shape of the micelle.

Value of $V_H/l_c a_0$	Structure of the Micelle
$0-\frac{1}{3}$	Spheroidal in aqueous media
$\frac{1}{3}-\frac{1}{2}$	Cylindrical in aqueous media
$\frac{1}{2}-1$	Lamellar in aqueous media
>1	Inverse (reversed) micelles in nonpolar media

II.B. Surfactant Structure and Micellar Shape

From Tanford (1980), $V_H = 27.4 + 26.9n$ Å^3, where n is the number of carbon atoms of the chain embedded in the micellar core (the total number of carbon atoms in the chain, or one less); $l_c \leq 1.5 + 1.265n$ Å, depending upon the extension of the chain. For saturated, straight chains, l_c may be 80% of the fully extended chain.

The solubilization of hydrocarbons in the interior of the micelle (Chapter 4, Section I) increases the value of V_H.

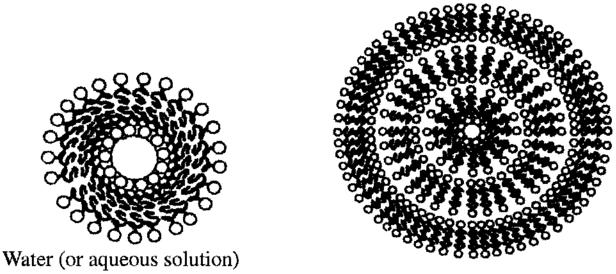
The value of a_0 varies not only with the structure of the hydrophilic head group, but also with changes in the electrolyte content, temperature, pH, and the presence of additives in the solution. Additives, such as medium-chain alcohols that are solubilized in the vicinity of the head groups (Chapter 4, Section IIIA), increase the value of a_0. With ionic surfactants, a_0 decreases with increase in the electrolyte content of the solution, due to compression of the electrical double layer, and also with increase in the concentration of the ionic surfactant, since that increases the concentration of counterions in the solution. This decrease in the value of a_0 promotes change in the shape of the micelle from spherical to cylindrical. For POE nonionic surfactants, an increase in temperature may cause a change in shape if temperature increase results in increased dehydration of the POE chain.

Some ionic surfactants form long, wormlike micelles in aqueous media, especially in the presence of electrolyte or other additives that decrease the repulsion between the ionic head groups (Raghavan, 2001). These giant, wormlike micelles give rise to unusually strong viscoelasticity because of the entanglement of these structures.

When the value of the parameter $V_H/l_c a_0$ reaches a value of approximately 1, the surfactant can form either normal lamellar micelles in aqueous media or reversed micelles in nonpolar media. As the value of the parameter gets larger and larger than 1, the reverse micelles in nonpolar media tend to become less asymmetrical and more spherical in shape.

In aqueous media, surfactants with bulky or loosely packed hydrophilic groups and long, thin hydrophobic groups tend to form spherical micelles, while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form lamellar or cylindrical micelles.

Surfactants having two long alkyl chains may, upon sonification in aqueous media, form vesicles (Figure 3-2). Thus, fatty acid esters of sucrose, especially the diesters, form vesicles upon sonification (Ishigami, 1989). Since vesicles are curved, closed lamellar bilayers, there are critical geometric and flexibility requirements for their formation. The packing parameter, $V_H/l_C a_o$ must be close to 1. However, some structure must be present in the molecule to keep the hydrophobic groups from becoming closely packed; otherwise, the flexibility requirement will not be met. And, since the hydrophobic groups cannot be closely packed, the hydrophilic head groups must also not pack closely to retain the packing parameter value close to 1. Vesicles have been formed from short-chain POE alcohols and perfluoroalcohols with short POE groups (Ravey, 1994) and from cetyl trimethylammonium p-toluenesulfonate plus sodium dodecyl benzene



Unilamellar vesicle
(*a*)

Multilamellar vesicle
(*b*)

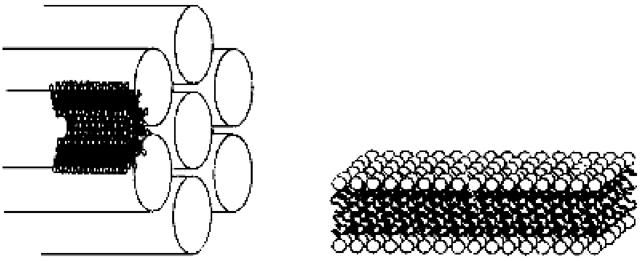
FIGURE 3-2 Vesicles: (*a*) unilamellar; (*b*) multilamellar.

sulfonate, but not plus sodium dodecyl sulfate. The sulfate head group in the latter compound is stated to pack too closely with the trimethylammonium group to form vesicles; the benzenesulfonate group packs more loosely (Salkar, 1998). Mixtures of dodecyl dimethylammonium bromide with dodecyl trimethylammonium chloride spontaneously form vesicles. The spontaneous formation is attributed to differences in the packing parameter of the two surfactants (Viseu, 2000). Interest in vesicles stems from their possible medical use as carriers for toxic drug delivery, although there are other applications.

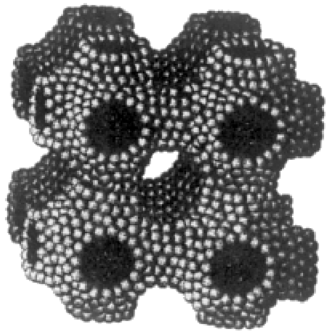
The shape of the micelle may change when material is solubilized by the micelle (Chapter 4, Section IIIA) and by change in molecular environmental factors (Figure 4-4).

II.C. Liquid Crystals

When there is a sufficient number of micelles in the solution phase, they start to pack together in a number of geometric arrangements, depending upon the shape of the individual micelles. These packing arrangements are known as *liquid crystals*. Liquid crystals have the ordered molecular arrangement of solid crystals but the mobility of liquids. Because of this ordered arrangement of the molecules, they increase the viscosity of the solution phase, sometimes very considerably. Spherical micelles pack together into cubic liquid crystals, cylindrical micelles pack to form hexagonal liquid crystals, and lamellar micelles form lamellar liquid crystals (Figure 3-3). It is easier to pack surfactant molecules having a bulky head group into hexagonal phases, while surfactants having two alkyl groups pack better into a lamellar phase. Both normal cylindrical micelles in aqueous media and reverse cylindrical micelles in nonpolar media can form hexagonal liquid crystals. Because some types of micelles change their structure from spherical to cylindrical to lamellar with increase in surfactant concentration, hexagonal phases are usually encountered at lower surfactant concentrations than lamellar phases. With increase in surfactant concentration, some cylindrical micelles become branched and interconnected, leading to a bicontinuous liquid crystalline phase (Figure 3-3c) in



Hexagonal (*a*) Lamellar (*b*)



Bicontinuous (*c*)

FIGURE 3-3 Hexagonal (*a*), Lamellar (*b*), and Bicontinuous (*c*) liquid crystal structures.

which there are no distinct micelles. Hexagonal and lammellar phases are anisotropic and can be detected by their radiance under the polarizing microscope. Hexagonal liquid crystals appear as fan-like structures or with a variety of nongeometrical structures; lamellar liquid crystals appear as Maltese crosses or as oil streaks. Hexagonal phases are more viscous than lamellar phases, which in turn are more viscous than ordinary solutions. Spherical micelles pack together at high surfactant concentrations to form cubic liquid crystals that are very high-viscosity gels. Bicontinuous structures also form cubic phases. Cubic phases may therefore be formed from normal spherical or reverse spherical micelles, or from normal bicontinuous or reverse bicontinuous structures. These are all isotropic structures, as are spherical micelles, and cannot be observed under the polarizing microscope. They can be identified by use of water-soluble and oil-soluble dyes (Kunieda, 2003).

Plots that show the conditions (temperature, composition) at which various phases exist in a system are known as *phase diagrams*. Figure 3-4 is one type of phase diagram showing the effects of temperature and surfactant concentration on the various solution phases of an aqueous surfactant system. The order of the various liquid crystal phases with increase in surfactant concentration—micellar ⇒ hexagonal ⇒ bicontinuous cubic ⇒ lamellar—is found in many surfactant systems.

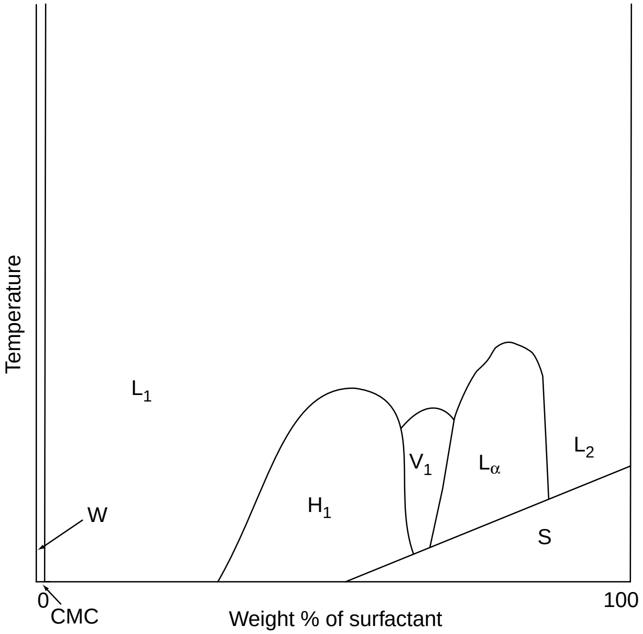


FIGURE 3-4 Phase diagram showing location of hexagonal (H_1), normal bicontinuous cubic (V_1), and lamellar ($L\alpha$) liquid phases, aqueous nonmicellar solution (*W*), micellar solution (L_1), liquid surfactant containing water (L_2), and solid surfactant (*S*).

The effect of temperature increase is typical for surfactants whose solubility increases with temperature increase, converting all liquid crystal phases to micellar solutions when the temperature is high enough. At high surfactant concentration and low temperature, solid surfactant may precipitate.

Liquid crystal structures are important not only in the viscosity modification of surfactant solutions, but also in the stabilization of foams and emulsions, in detergency, in lubrication (Boschkova, 2002), and in other applications.

Another type of phase diagram, when two or more components in addition to water are present, shows the effect of the composition of the system at constant temperature on the number and location of the different phases in the system. These are known as (*isothermal*) *ternary phase diagrams*. Each vertex of the triangle represents the point of 100% of the solvent, the surfactant, and any other component (or combination of components at a constant ratio of the two). Phase diagrams of this type are often used to show the location of microemulsion phases (Chapter 8, Section II), when hydrocarbon and water phases are present, in addition to the surfactant. A highly simplified phase diagram of this type is shown in Figure 3-5. The locations and numbers of phases change with temperature and with the nature of the surfactant and the water-insoluble liquid.

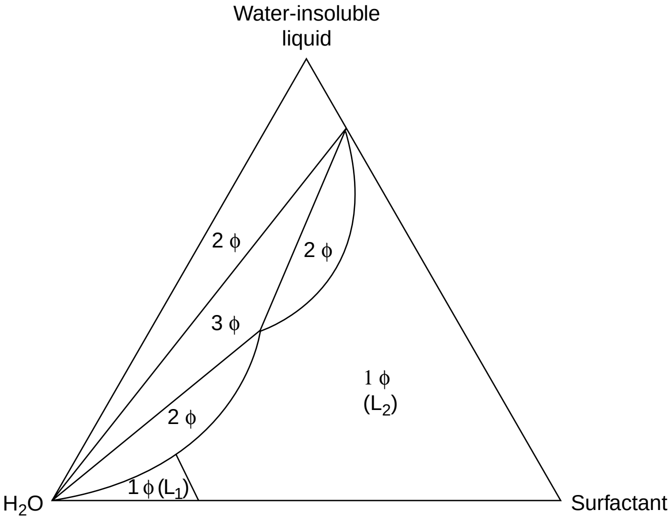


FIGURE 3-5 Simplified isothermal ternary phase diagram (liquid crystalline phases omitted) showing the number of phases (ϕ) in each location. L_1 = aqueous micellar phase, L_2 = reverse micellar phase, with microemulsion phase adjacent to the 3ϕ region.

III. MICELLAR AGGREGATION NUMBERS

NMR self-diffusion coefficients (Lindman, 1983), small-angle neutron scattering (SANS) (Cebula, 1982; Triolo, 1983; Corti, 1984), freezing point and vapor pressure methods (Herrington, 1986) and fluorescent probes (Atik, 1979) have been used to calculate aggregation numbers of several different types of surfactants (Zana, 1980; Lianos, 1980, 1981, 1982, 1983). Some aggregation numbers of surfactants are listed in Table 3-1.

From geometric considerations, the aggregation numbers n of micelles in aqueous media should increase rapidly with increase in the length of the hydrophobic group l_c of the surfactant molecule and decrease with increase in the cross-sectional area of the hydrophilic group a_0 or the volume of the hydrophobic group V_H. For example, in a spherical micelle in aqueous media, the surface area, $n \times a_0 = 4\pi(l_c + \Delta)^2$, or $n = 4\pi(l_c + \Delta)^2/a_0$, where Δ is the added length of the radius of the sphere due to the hydrophilic group (Lianos, 1982). Similarly, the volume of the hydrophobic core $n \times V_H = \frac{4}{3}\pi(l_c)^3$ or $n = \frac{4}{3}\pi(l_c)^3/V_H$.

In agreement with the geometric considerations mentioned above, aggregation numbers in aqueous solution increase with increase in the length of the hydrophobic group (greater l_c), decrease in the number of OE units in POE nonionics (smaller a_0), and increase in the binding of the counterions to the micelle in ionics (smaller a_0). They decrease with increase in the size of the hydrophilic group (larger a_0). Surfactants in which the hydrophobic group is based on a dimethylsiloxane rather

TABLE 3-1 Aggregation Numbers of Some Surfactant Micelles

Compound	Solvent	Temp. (°C)	Aggregation Number	Reference
Anionics				
$C_8H_{17}SO_3^-Na^+$	H_2O	23	25	Tartar, 1955
$(C_8H_{17}SO_3^-)_2Mg^{2+}$	H_2O	23	51	Tartar, 1955
$C_{10}H_{21}SO_3^-Na^+$	H_2O	30	40	Tartar, 1955
$(C_{10}H_{21}SO_3^-)_2Mg^{2+}$	H_2O	60	103	Tartar, 1955
$C_{12}H_{25}SO_3^-Na^+$	H_2O	40	54	Tartar, 1955
$(C_{12}H_{25}SO_3^-)_2Mg^{2+}$	H_2O	60	107	Tartar, 1955
$C_{14}H_{29}SO_3^-Na^+$	H_2O	60	80	Tartar, 1955
$C_{14}H_{29}SO_3^-Na^+$	0.01 *M* NaCl	23	138	Tartar, 1955
$C_{10}H_{21}SO_4^-Na^+$	H_2O	23	50	Tartar, 1955
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	80	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl	25	112	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$	0.2 *M* NaCl	25	118	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$	0.4 *M* NaCl	25	126	Sowada, 1994
$C_6H_{13}OOCCH_2SO_3Na$	H_2O	25	16	Jobe, 1984
$C_8H_{17}OOCCH_2SO_3Na$	H_2O	25	37, 42	Jobe, 1984
$C_{10}H_{21}OOCCH_2SO_3Na$	H_2O	25	69, 71	Jobe, 1984
$C_6H_{13}OOCCH_2CH(SO_3Na)COOC_6H_{13}$	H_2O	25	30, 36	Jobe, 1984
$C_8H_{17}OOCCH_2CH(SO_3Na)COOC_8H_{17}$	H_2O	25	59, 56	Jobe, 1984
$C_{10}H_{21}$-1-$\phi SO_3^-Na^+$	H_2O (0.05 *M* conc.)	25	60	Binana-Limbele, 1991a
$C_{10}H_{21}$-1-$\phi SO_3^-Na^+$	0.1 *M* Nacl (0.05 *M* conc.)	25	78	Binana-Limbele, 1991a
p-C_{10}-5-$\phi SO_3^-Na^+$	H_2O (0.05 *M* conc.)	25	47	Binana-Limbele, 1991a
p-C_{10}-5-$\phi SO_3^-Na^+$	H_2O (0.1 *M* conc.)	25	76	Binana-Limbele, 1991a
p-C_{10}-5-$\phi SO_3^-Na^+$	0.1 *M* Nacl (0.1 *M* conc.)	25	81	Binana-Limbele, 1991a
p-C_{12}-3-$\phi SO_3^-Na^+$	H_2O (0.05 *M* conc.)	25	77	Binana-Limbele, 1991a

		Cationics		
$C_{10}H_{21}N^+(CH_3)_3Br^-$	H_2O	20	39	Lianos, 1981
$C_{10}H_{21}N^+(CH_3)_3Cl^-$	H_2O	25	36	Sowada, 1994
$C_{12}H_{25}N^+(CH_3)_3Br^-$	H_2O (0.04 *M* conc.)	25	42	Rodenas, 1994
$C_{12}H_{25}N^+(CH_3)_3Br^-$	H_2O (0.10 *M* conc.)	25	69	Rodenas, 1994
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.02 *M* KBr (0.04 *M* conc.)	25	49	Rodenas, 1994
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.08 *M* KBr (0.04 *M* conc.)	25	59	Rodenas, 1994
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	H_2O	25	50	Sowada, 1994
$[C_{12}H_{25}N^+(CH_3)_3]_2SO_4{}^{2-}$	H_2O	23	65	Tartar, 1955
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	5	131	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	10	122	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	20	106	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	40	88	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	60	74	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O (1.05×10^{-1} *M* conc.)	80	73	Gorski, 2001
$C_{14}H_{29}N^+(C_2H_5)_3Br^-$	H_2O	20	55	Lianos, 1982
$C_{14}H_{29}N^+(C_4H_9)_3Br^-$	H_2O	20	35	Lianos, 1982
$C_{16}H_{33}N^+(CH_3)_3Br^-$	H_2O (0.005 *M* conc.)	25	44	Rodenas, 1994
$C_{16}H_{33}N^+(CH_3)_3Br^-$	H_2O (0.021 *M* conc.)	25	75	Rodenas, 1994
$C_{16}H_{33}N^+(CH_3)_3Br^-$	0.1 *M* KBr (0.005 *M* conc.)	25	57	Rodenas, 1994
$C_{16}H_{33}N^+(CH_3)_3Br^-$	0.1 *M* KBr (0.021 *M* conc.)	25	71	Rodenas, 1994
		Zwitterionics		
$C_8H_{17}N^+(CH_3)_2CH_2COO^-$	H_2O	21	24	Tori, 1963a
$C_8H_{17}CH(COO^-)N^+(CH_3)_3$	H_2O	21	31	Tori, 1963a
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	H_2O	25	80–85	Chorro, 1996
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3COO^-$	H_2O	25	55–56	Kamenka, 1995a
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_5COO^-$	H_2O	25	39–43	Kamenka, 1995a
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3SO_3{}^-$	H_2O	25	59–67	Kamenka, 1995a

(*Continued next page*)

TABLE 3-1 (*Continued*)

Compound	Solvent	Temp. (°C)	Aggregation Number	Reference
	Anionic–Cationic Salts			
$C_8H_{17}NH_3{}^+C_2H_5COO^-$	C_6H_6	30	5±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+C_2H_5COO^-$	CCl_4	30	3±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+C_2H_5COO^-$	C_6H_6	30	3±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_3H_7COO^-$	CCl_4	30	4±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_5H_{11}COO^-$	C_6H_6	30	3±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_5H_{11}COO^-$	CCl_4	30	5±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_8H_{17}COO^-$	C_6H_6	30	3±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_8H_{17}COO^-$	CCl_4	30	5±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_{11}H_{23}COO^-$	C_6H_6	30	7±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_{13}H_{27}COO^-$	C_6H_6	30	3±1	Fendler, 1973a
$C_8H_{17}NH_3{}^+\cdot C_{13}H_{27}COO^-$	CCl_4	30	3±1	Fendler, 1973a
$C_4H_9NH_3{}^+\cdot C_2H_5COO^-$	C_6H_6	—	4	Fendler, 1973b
$C_4H_9NH_3{}^+\cdot C_2H_5COO^-$	CCL_4	—	3	Fendler, 1973b
$C_6H_{13}NH_3{}^+\cdot C_2H_5COO^-$	C_6H_6	—	7	Fendler, 1973b
$C_6H_{13}NH_3{}^+\cdot C_2H_5COO^-$	CCl_4	—	7	Fendler, 1973b
$C_8H_{17}NH_3{}^+\cdot C_2H_5COO^-$	C_6H_6	—	5	Fendler, 1973b
$C_8H_{17}NH_3{}^+\cdot C_2H_5COO^-$	CCl_4	—	5	Fendler, 1973b
$C_{10}H_{21}NH_3{}^+\cdot C_2H_5COO^-$	C_6H_6	—	5	Fendler, 1973b
$C_{10}H_{21}NH_3{}^+\cdot C_2H_5COO^-$	CCl_4	—	4	Fendler, 1973b
	Nonionics			
$C_8H_{17}O(C_2H_4O)_6H$	H_2O	18	30	Balmbra, 1964
$C_8H_{17}O(C_2H_4O)_6H$	H_2O	30	41	Balmbra, 1964

$C_8H_{17}O(C_2H_4O)_6H$	H_2O	40	51	Balmbra, 1964
$C_8H_{17}O(C_2H_4O)_6H$	H_2O	60	210	Balmbra, 1964
$C_{10}H_{21}O(C_2H_4O)_6H$	H_2O	35	260	Balmbra, 1964
$C_{12}H_{25}O(C_2H_4O)_2H$	C_6H_6	—	34	Becher, 1960
$C_{12}H_{25}O(C_2H_4O)_6H$	H_2O	15	140	Balmbra, 1962
$C_{12}H_{25}(OC_2H_4)_6OH$	H_2O	20	254–345	Lianos, 1981
$C_{12}H_{25}O(C_2H_4O)_6H$	H_2O	25	400	Balmbra, 1962
$C_{12}H_{25}O(C_2H_4O)_6H$	H_2O	35	1,400	Balmbra, 1962
$C_{12}H_{25}O(C_2H_4O)_6H$	H_2O	45	4,000	Balmbra, 1962
$C_{12}H_{25}O(C_2H_4O)_8H^a$	H_2O	25	123	Becher, 1961
$C_{12}H_{25}O(C_2H_4O)_{12}H^a$	H_2O	25	81	Becher, 1961
$C_{12}H_{25}O(C_2H_4O)_{18}H^a$	H_2O	25	51	Becher, 1961
$C_{12}H_{25}O(C_2H_4O)_{23}H^a$	H_2O	25	40	Becher, 1961
$C_{13}H_{27}O(C_2H_4O)_6H$	C_6H_6	—	99	Becher, 1960
$C_{14}H_{29}O(C_2H_4O)_6H$	H_2O	35	7,500	Balmbra, 1964
$C_{16}H_{33}O(C_2H_4O)_6H$	H_2O	34	16,600	Balmbra, 1964
$C_{16}H_{33}O(C_2H_4O)_6H$	H_2O	25	2,430	Elworthy, 1963
$C_{16}H_{33}O(C_2H_4O)_7H$	H_2O	25	594	Elworthy, 1963, 1964b
$C_{16}H_{33}O(C_2H_4O)_9H$	H_2O	25	219	Elworthy, 1963
$C_{16}H_{33}O(C_2H_4O)_{12}H$	H_2O	25	152	Elworthy, 1963
$C_{16}H_{33}O(C_2H_4O)_{21}H$	H_2O	25	70	Elworthy, 1963
$C_9H_{19}C_6H_4O(C_2H_4O)_{10}H^b$	H_2O	25	276	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{15}H^b$	H_2O	25	80	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{15}H^b$	0.5 *M* urea	25	82	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{15}H^b$	0.86 *M* urea	25	83	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{20}H^b$	H_2O	25	62	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{30}H^b$	H_2O	25	44	Schick, 1962b
$C_9H_{19}C_6H_4O(C_2H_4O)_{50}H^b$	H_2O	25	20	Schick, 1962b
$C_{10}H_{21}O(C_2H_4O)_8CH_3$	H_2O	30	83	Nakagawa, 1960
$C_{10}H_{21}O(C_2H_4O)_8CH_3$	$H_2O + 2.3\%$ *n*-decane	30	90	Nakagawa, 1960

(*Continued next page*)

TABLE 3-1 (*Continued*)

Compound	Solvent	Temp. (°C)	Aggregation Number	Reference
$C_{10}H_{21}O(C_2H_4O)_8CH_3$	$H_2O + 4.9\%$ *n*-decane	30	105	Nakagawa, 1960
$C_{10}H_{21}O(C_2H_4O)_8CH_3$	$H_2O + 3.4\%$ *n*-decanol	30	89	Nakagawa, 1960
$C_{10}H_{21}O(C_2H_4O)_8CH_3$	$H_2O + 8.5\%$ *n*-decanol	30	109	Nakagawa, 1960
$C_{10}H_{21}O(C_2H_4O)_{11}CH_3$	H_2O	30	65	Nakagawa, 1960
α-Monocaprin	C_6H_6	—	42	Debye, 1958
α-Monolaurin	C_6H_6	—	73	Debye, 1958
α-Monomyristin	C_6H_6	—	86	Debye, 1958
α-Monopalmitin	C_6H_6	—	15	Debye, 1958
α-Monostearin	C_6H_6	—	11	Debye, 1958
Sucrose monolaurate	H_2O	0–60	52	Herrington, 1986
Sucrose monooleate	H_2O	0–60	99	Herrington, 1986

[a] Commercial material.

[b] Molecularly distilled commercial material.

than on a hydrocarbon chain appear to have aggregation numbers less than 5 in aqueous solution (Schwarz, 1963), possibly because of the bulky dimethylsiloxane chain (large V_H).

Ionic surfactants containing a single long alkyl chain and zwitterionics (containing a single long alkyl chain) in which the electrical charges are not on adjacent atoms show aggregation numbers of less than 100 in aqueous solutions containing low or moderate concentrations of NaCl (≤ 0.1 *M*), and these vary only slightly with the surfactant concentration up to about 0.1–0.3 *M* (Lianos, 1981). This is indicative of spherical micelle formation. At high salt content, however, *n* increases sharply with surfactant concentration (Mazer, 1976), with formation of rodlike cylindrical or disklike lamellar micelles. The formation of rodlike micelles and the sharp increase in aggregation number result in an increase in the viscosity of the aqueous solution (Kumar, 2002).

Ionic surfactants with two long (six or more carbons) alkyl chains have high V_H values relative to l_c, and probably do not form spherical micelles. They have values of *n* that increase with surfactant concentration, the increase becoming more pronounced with increase in the length of the chains. Some of these micellar solutions are in equilibrium with lamellar liquid crystal structures (Lianos, 1983).

The addition of neutral electrolyte to solutions of ionic surfactants in aqueous solution causes an increase in the aggregation number, presumably because of compression of the electrical double layer surrounding the ionic heads. The resulting reduction of their mutual repulsion in the micelle permits closer packing of the head groups (a_0 is reduced), with a consequent increase in *n*.

The addition of certain large anions, such as sodium salicylate (2-hydroxybenzoate), sodium *p*-toluenesulfonate, or sodium 3-hydroxynaphthalene-2-carboxylate, to aqueous solutions of quatemary cationic surfactants such as $C_{16}H_{33}N^+(CH_3)_3Br^-$ produces long, threadlike micelles (Shikata, 1987; Imae, 1990; Hassan and Yakhmi, 2000). Above a certain critical surfactant concentration, these threadlike micelles entangle to form highly viscous solutions. These long, threadlike micelles can act as drag reducers for aqueous solutions; that is, they reduce the turbulence of the solution flowing in tubes or pipes (Harwigsson, 1996; Zakin, 1998).

For zwitterionics of the betaine and sulfobetaine types, $C_{12}H_{25}N^+(CH_3)_2(CH_2)_m COO^-$ and $C_{12}H_{25}N^+(CH_3)_2(CH_2)_3SO_3{}^-$, respectively, the micellar aggregation number varies very little with change in surfactant concentration or electrolyte content (Kamenka, 1995a).

For POE nonionics, *n* increases considerably with surfactant concentration in the range below 0.1 *M*, even in pure water, with aggregation numbers of several hundred or more, indicating that the micelles are not spherical in shape.

The effect of neutral electrolyte on the aggregation number of micelles of POE nonionics in aqueous solution is somewhat unclear, with both increases and decreases being observed on the addition of electrolyte. In either case, however, the effect appears to be small.

An increase in the temperature appears to cause a small decrease in the aggregation number in aqueous medium of ionics, presumably because a_0 is increased due to thermal agitation. For POE nonionics there is a slow increase in n until the emperature reaches 40°C below the '*cloud point*' (Chapter 4, Section IIIA), the temperature at which the solution, on being heated, begins to show turbidity because of dehydration of the POE chains, and then starts rapidly to increase (Binana-Limbele, 1991a). Dehydration of the POE chains causes a decrease in a_0. It also appears to produce a sharp increase in the asymmetry of the nonionic micelle. Nonionic surfactants with cloud points above 100°C show no change in aggregation number at temperatures below 60°C.

If small amounts of hydrocarbons or long-chain polar compounds are added to an aqueous solution of a surfactant above its CMC, these normally water-insoluble materials may be solubilized in the micelles (Chapter 4). This solubilization generally causes an increase in the aggregation number of the micelle, and as the amount of material solubilized by the micelle increases, the aggregation continues to increase until the solubilization limit is reached.

There is much less information on aggregation numbers of micelles in nonaqueous solvents, and some of it is controversial. From the data available, the average aggregation number in nonpolar media increases with increase in dipole–dipole attraction or intermolecular bonding between the polar head groups and decreases with increase in the number of alkyl chains per surfactant molecule, the length of the chains, the steric requirements of the chain close to the polar head group, and the temperature (Ruckenstein, 1980). The addition of water that is solubilized in the interior of a micelle in hydrocarbon medium has been shown to cause an increase in the aggregation number (Mathews, 1953), similar to the effect of hydrocarbon addition to micelles in aqueous medium. Temperature change from 25°C to 90°C had almost no effect on the aggregation numbers of some dialkylnaphthalenesulfonates in *n*-decane (Heilweil, 1964).

In polar solvents, such as chloroform or ethanol, either micellization does not occur or, if it does, the aggregation number is very small, presumably because the polar surfactant molecules can dissolve in the solvent without distorting its liquid structure significantly. As might be expected, in these solvents, surfactants have also almost no tendency to adsorb at the interfaces.

In addition to its effect on the value of l_c mentioned above, the number of carbon atoms in the hydrophobic group may also affect the aggregation number in other ways (Nagarajan, 2002). For example, increase in the number of carbon atoms in the hydrophobic group decreases the value of the CMC (see Section IV below). For ionic surfactants, this means a decrease in the ionic strength of the solution and a resulting increase in the value of a_0, producing a smaller aggregation number than expected from the increase in the value of l_c.

IV. FACTORS AFFECTING THE VALUE OF THE CMC IN AQUEOUS MEDIA

Since the properties of solutions of surface-active agents change markedly when micelle formation commences, many investigations have been concerned with determining values of the CMC in various systems, and a great deal of work has been done on elucidating the various factors that determine the CMC at which micelle formation becomes significant, especially in aqueous media. An extensive compilation of the CMCs of surfactants in aqueous media has been published (Mukerjee, 1971). Some typical CMC values are listed in Table 3-2.

Among the factors known to affect the CMC in aqueous solution are (1) the structure of the surfactant, (2) the presence of added electrolyte in the solution, (3) the presence in the solution of various organic compounds, (4) the presence of a second liquid phase, and (5) temperature of the solution. Some examples of the effects of these factors are apparent from the data in Table 3-2.

IV.A. Structure of the Surfactant

In general, the CMC in aqueous media decreases as the hydrophobic character of the surfactant increases.

1. The Hydrophobic Group In aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic group increases to about 16, and a general rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight-chain hydrophobic group attached to a single terminal hydrophilic group. For nonionics and zwitterionics the decrease with increase in the hydrophobic group is somewhat larger, an increase by two methylene units reducing the CMC to about one-tenth its previous value (compared to one-quarter in ionics). A phenyl group that is part of a hydrophobic group with a terminal hydrophilic group is equivalent to about three and one-half methylene groups. When the number of carbon atoms in a straights-chain hydrophobic group exceeds 16, however, the CMC no longer decreases so rapidly with increase in the length of the chain, and when the chain exceeds 18 carbons it may remain substantially unchanged with further increase in the chain length (Greiss, 1955). This may be due to the coiling of these long chains in water (Mukerjee, 1967).

When the hydrophobic group is branched, the carbon atoms on the branches appear to have about one-half the effect of carbon atoms on a straight chain (Götte, 1969). When carbon–carbon double bonds are present in the hydrophobic chain, the CMC is generally higher than that of the corresponding saturated compound, with the cis isomer generally having a higher CMC than the trans isomer. This may be the result of a steric factor in micelle formation. Surfactants with either bulky hydrophobic or bulky hydrophilic groups have larger CMC values than those with similar, but less bulky, groups. The increase in the CMC upon introduction of a bulky hydrophobic group in the molecule is presumably due to the difficulty of incorporating the bulky hydrophobic group in the interior of a spherical or cylindrical micelle.

The introduction of a polar group such as —O— or —OH into the hydrophobic chain generally causes a significant increase in the CMC in aqueous medium at

TABLE 3-2 Critical Micelle Concentrations of Some Surfactants in Aqueous Media

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
		Anionics		
$C_{10}H_{21}OCH_2COO^-Na^+$	0.1 *M* NaCl, pH 10.5	30	2.8×10^{-3}	Tsubone, 2001
$C_{12}H_{25}COO^-K^+$	H_2O, pH 10.5	30	1.2×10^{-2}	Tsubone, 2001
$C_9H_{19}CONHCH_2COO^-Na^+$	H_2O	40	3.8×10^{-2}	Desai, 1992
$C_{11}H_{23}CONHCH_2COO^-Na^+$	H_2O	40	1.0×10^{-2}	Desai, 1992
$C_{11}H_{23}CONHCH_2COO^-Na^+$	0.1 *M* NaOH (aq.)	45	3.7×10^{-3}	Miyagishi, 1989
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$	H_2O, pH 10.5	30	1.0×10^{-2}	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$	0.1 *M* NaCl, pH 10.5	30	3.5×10^{-3}	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$	H_2O, pH 10.5	30	7.6×10^{-3}	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$	0.1 *M* NaCl, pH 10.5	30	2.7×10^{-3}	Tsubone, 2001
$C_{11}H_{23}CONHCH(CH_3)COO^-Na^+$	0.1 *M* NaOH (aq.)	45	3.3×10^{-3}	Miyagishi, 1989
$C_{11}H_{23}CONHCH(C_2H_5)COO^-Na^+$	0.1 *M* NaOH (aq.)	45	2.1×10^{-3}	Miyagishi, 1989
$C_{11}H_{23}CONHCH[CH\ (CH_3)_2]COO^-Na^+$	0.1 *M* NaOH (aq.)	45	1.4×10^{-3}	Miyagishi, 1989
$C_{11}H_{23}CONHCH[CH_2CH(CH_3)_2]COO^-Na^+$	0.1 *M* NaOH (aq.)	45	5.8×10^{-4}	Miyagishi, 1989
$C_{13}H_{27}CONHCH_2COO^-Na^+$	H_2O	40	4.2×10^{-3}	Desai, 1992
$C_{15}H_{31}CONHCH[CH(CH_3)_2]COO^-Na^+$	H_2O	25	1.9×10^{-3}	Ohta, 2003
$C_{15}H_{31}CONHCH[CH_2CH(CH_3)_2]COO^-Na^+$	H_2O	25	1.5×10^{-3}	Ohta, 2003
$C_8H_{17}SO_3{}^-Na^+$	H_2O	40	1.6×10^{-1}	Klevens, 1948
$C_{10}H_{21}SO_3{}^-Na^+$	H_2O	10	4.8×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	H_2O	25	4.3×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	H_2O	40	4.0×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.1 *M* NaCl	10	2.6×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.1 *M* NaCl	25	2.1×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.1 *M* NaCl	40	1.8×10^{-2}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.5 *M* NaCl	10	7.9×10^{-3}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.5 *M* NaCl	25	7.3×10^{-3}	Dahanayake, 1986
$C_{10}H_{21}SO_3{}^-Na^+$	0.5 *M* NaCl	40	6.5×10^{-3}	Dahanayake, 1986

$C_{12}H_{25}SO_3^-Na^+$	H_2O	25	$1.2_4 \times 10^{-2}$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	H_2O	40	$1.1_4 \times 10^{-2}$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl	25	2.5×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl	40	2.4×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.5 *M* NaCl	40	7.9×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Li^+$	H_2O	25	1.1×10^{-2}	Mohle, 1993
$C_{12}H_{25}SO_3^-NH_4^+$	H_2O	25	8.9×10^{-3}	Mohle, 1993
$C_{12}H_{25}SO_3^-K^+$	H_2O	25	9.3×10^{-3}	Mohle, 1993
$C_{14}H_{29}SO_3^-Na^+$	H_2O	40	2.5×10^{-3}	Klevens, 1948
$C_{16}H_{33}SO_3^-Na^+$	H_2O	50	7.0×10^{-4}	Klevens, 1948
$C_8H_{17}SO_4^-Na^+$	H_2O	40	1.4×10^{-1}	Evans, 1956
$C_{10}H_{21}SO_4^-Na^+$	H_2O	40	3.3×10^{-2}	Evans, 1956
$C_{11}H_{23}SO_4^-Na^+$	H_2O	21	1.6×10^{-2}	Huisman, 1964
Branched $C_{12}H_{25}SO_4^-Na^+$	H_2O	25	1.42×10^{-2}	Varadaraj, 1992
Branched $C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl	25	3.8×10^{-3}	Varadaraj, 1992
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	8.2×10^{-3}	Elworthy, 1966
$C_{12}H_{25}SO_4^-Na^+$	H_2O	40	8.6×10^{-3}	Flockhart, 1961
$C_{12}H_{25}SO_4^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3} M)^{c,e}$	25	$>1.58 \times 10^{-3}$	Rosen, 1966
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl	21	5.6×10^{-3}	Huisman, 1964
$C_{12}H_{25}SO_4^-Na^+$	0.3 *M* NaCl	21	3.2×10^{-3}	Huisman, 1964
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl	25	1.62×10^{-3}	Huisman, 1964
$C_{12}H_{25}SO_4^-Na^+$	0.2 *M* NaCl (aq.)	25	8.3×10^{-4}	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$	0.4 *M* NaCl (aq.)	25	5.2×10^{-4}	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$	0.3 *M* urea	25	9.0×10^{-3}	Schick, 1964
$C_{12}H_{25}SO_4^-Na^+$	H_2O–cyclohexane	25	7.4×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–octane	25	8.1×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–decane	25	8.5×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–heptadecane	25	8.5×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–cyclohexane	25	7.9×10^{-3}	Rehfeld, 1967

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
$C_{12}H_{25}SO_4^-Na^+$	H_2O–carbon tetrachloride	25	6.8×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O–benzene	25	6.0×10^{-3}	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl (aq.)–heptane	20	1.4×10^{-3}	Vijayendran, 1979
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl (aq.)–ethylenzene	20	1.1×10^{-3}	Vijayendran, 1979
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl (aq.)–ethylacetate	20	1.8×10^{-3}	Vijayendran, 1979
$C_{12}H_{25}SO_4^-Li^+$	H_2O	25	8.9×10^{-3}	Mysels, 1959
$C_{12}H_{25}SO_4^-K^+$	H_2O	40	7.8×10^{-3}	Meguro, 1956
$(C_{12}H_{25}SO_4^-)_2Ca^{2+}$	H_2O	70	3.4×10^{-3}	Corkill, 1962
$C_{12}H_{25}SO_4^-N(CH_3)_4^+$	H_2O	25	5.5×10^{-3}	Mysels, 1959
$C_{12}H_{25}SO_4^-N(C_2H_5)_4^+$	H_2O	30	4.5×10^{-3}	Meguro, 1959
$C_{12}H_{25}SO_4^-N(C_3H_7)_4^+$	H_2O	25	2.2×10^{-3}	Mukerjee, 1967
$C_{12}H_{25}SO_4^-N(C_4H_9)_4^+$	H_2O	30	1.3×10^{-3}	Meguro, 1959
$C_{13}H_{27}SO_4^-Na^+$	H_2O	40	4.3×10^{-3}	Götte, 1969
$C_{14}H_{29}SO_4^-Na^+$	H_2O	25	2.1×10^{-3}	Lange, 1968
$C_{14}H_{29}SO_4^-Na^+$	H_2O	40	2.2×10^{-3}	Flockhart, 1961
$C_{15}H_{31}SO_4^-Na^+$	H_2O	40	1.2×10^{-3}	Götte, 1969
$C_{16}H_{33}SO_4^-Na^+$	H_2O	40	5.8×10^{-4}	Evans, 1956
$C_{13}H_{27}CH(CH_3)CH_2SO_4^-Na^+$	H_2O	40	8.0×10^{-4}	Götte, 1969
$C_{12}H_{25}CH(C_2H_5)CH_2SO_4^-Na^+$	H_2O	40	9.0×10^{-4}	Götte, 1969
$C_{11}H_{23}CH(C_3H_7)CH_2SO_4^-Na^+$	H_2O	40	1.1×10^{-3}	Götte, 1969
$C_{10}H_{21}CH(C_4H_9)CH_2SO_4^-Na^+$	H_2O	40	1.5×10^{-3}	Götte, 1969
$C_9H_{19}CH(C_5H_{11})CH_2SO_4^-Na^+$	H_2O	40	2×10^{-3}	Götte, 1969
$C_8H_{17}CH(C_6H_{13})CH_2SO_4^-Na^+$	H_2O	40	2.3×10^{-3}	Götte, 1969
$C_7H_{15}CH(C_7H_{15})CH_2SO_4^-Na^+$	H_2O	40	3×10^{-3}	Götte, 1969
$C_{12}H_{25}CH(SO_4^-Na^+)C_3H_7$	H_2O	40	1.7×10^{-3}	Evans, 1956
$C_{10}H_{21}CH(SO_4^-Na^+)C_5H_{11}$	H_2O	40	2.4×10^{-3}	Evans, 1956
$C_8H_{17}CH(SO_4^-Na^+)C_7H_{15}$	H_2O	40	4.3×10^{-3}	Evans, 1956

$C_{18}H_{37}SO_4^-Na^+$	H_2O	50	2.3×10^{-4}	Gotte, 1960
$C_{10}H_{21}OC_2SO_3^-Na^+$	H_2O	25	$1.5_9 \times 10^{-2}$	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	0.1 *M* NaCl	25	5.5×10^{-3}	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	0.5 *M* NaCl	25	2.0×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	H_2O	25	3.9×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^{c,e}	25	8.1×10^{-4}	Rosen, 1996
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.1 *M* NaCl	25	4.3×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.5 *M* NaCl	25	1.3×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	10	3.1×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	25	2.9×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	40	2.8×10^{-3}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^{c,e}	25	5.5×10^{-4}	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl	10	3.2×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl	25	2.9×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl	40	2.8×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.5 *M* NaCl	10	1.1×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.5 *M* NaCl	25	1.0×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.5 *M* NaCl	40	1.0×10^{-4}	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_3SO_4^-Na^+$	H_2O	50	2.0×10^{-3}	Götte, 1960
$C_{12}H_{25}(OC_2H_4)_4SO_4^-Na^+$	H_2O	50	1.3×10^{-3}	Götte, 1960
$C_{16}H_{33}(OC_2H_4)_5SO_4^-Na^+$	H_2O	25	2.5×10^{-5}	Varadaraj, 1991a
$C_8H_{17}CH(C_6H_{13})CH_2(OC_2H_4)_5SO_4^-Na^+$	H_2O	25	8.6×10^{-5}	Varadaraj, 1991a
$C_6H_{13}OOCCH_2SO_3^-Na^+$	H_2O	25	1.7×10^{-1}	Jobe, 1984
$C_8H_{17}OOCCH_2SO_3^-Na^+$	H_2O	25	6.6×10^{-2}	Jobe, 1984
$C_{10}H_{21}OOCCH_2SO_3^-Na^+$	H_2O	25	2.2×10^{-2}	Jobe, 1984
$C_8H_{17}OOC(CH_2)_2SO_3^-Na^+$	H_2O	30	4.6×10^{-2}	Hikota, 1970
$C_{10}H_{21}OOC(CH_2)_2SO_3^-Na^+$	H_2O	30	1.1×10^{-2}	Hikota, 1970
$C_{12}H_{25}OOC(CH_2)_2SO_3^-Na^+$	H_2O	30	2.2×10^{-3}	Hikota, 1970
$C_{14}H_{29}OOC(CH_2)_2SO_3^-Na^+$	H_2O	40	9×10^{-4}	Hikota, 1970

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
$C_4H_9OOCCH_2CH(SO_3^-Na^+)COOC_4H_9$	H_2O	25	2.0×10^{-1}	Williams, 1957
$C_5H_{11}OOCH_2(SO_3^-Na^+)COOC_5H_{11}$	H_2O	25	5.3×10^{-2}	Williams, 1957
$C_6H_{13}OOCH_2CH(SO_3^-Na^+)COOC_6H_{13}$	H_2O	25	1.4×10^{-2}	Jobe, 1984
$C_4H_9CH(C_2H_5)CH_2OOCCH_2CH(SO_3^-Na^+)$ $COOCH_2CH(C_2H_5)C_4H_9$	H_2O	25	2.5×10^{-3}	William, 1957
$C_8H_{17}OOCCH_2CH(SO_3^-Na^+)COOC_8H_{17}$	H_2O	25	9.1×10^{-4}	Nave, 2000
$C_{12}H_{25}CH(SO_3^-Na^+)COOCH_3$	H_2O	13	2.8×10^{-3}	Ohbu, 1998
$C_{12}H_{25}CH(SO_3^-Na^+)COOC_2H_5$	H_2O	25	2.25×10^{-3}	Ohbu, 1998
$C_{12}H_{25}CH(SO_3^-Na^+)COOC_4H_9$	H_2O	25	1.35×10^{-3}	Ohbu, 1998
$C_{14}H_{29}CH(SO_3^-Na^+)COOCH_3$	H_2O	23	7.3×10^{-4}	Ohbu, 1998
$C_{16}H_{33}CH(SO_3^-Na^+)COOCH_3$	H_2O	33	1.8×10^{-4}	Ohbu, 1998
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_4^-Na^+$	H_2O pH 10.5	30	8.9×10^{-3}	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_4^-Na^+$	0.1 *M* NaCl, pH 10.5	30	1.6×10^{-3}	Tsubone, 2001
$C_{12}H_{25}NHCOCH_2SO_4^-Na^+$	H_2O	35	5.2×10^{-3}	Mizushima, 1999
$C_{12}H_{25}NHCO(CH_2)_3SO_4^-Na^+$	H_2O	35	4.4×10^{-3}	Mizushima, 1999
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O	35	1.5×10^{-2}	Greshman, 1957
p-$C_{10}H_{21}C_6H_4SO_3^-Na^+$	H_2O	50	3.1×10^{-3}	Greshman, 1957
$C_{10}H_{21}$-2-$C_6H_4SO_3^-Na^+$	H_2O	30	4.6×10^{-3}	Van Os, 1991
$C_{10}H_{21}$-3-$C_6H_4SO_3^-Na^+$	H_2O	30	6.1×10^{-3}	Van Os, 1991
$C_{10}H_{21}$-5-$C_6H_4SO_3^-Na^+$	H_2O	30	8.2×10^{-3}	Van Os, 1991
$C_{11}H_{23}$-2-$C_6H_4SO_3^-Na^+$	H_2O	35	2.5×10^{-3}	Zhu, 1998
$C_{11}H_{23}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. = 6.6×10^{-3} *M*)^e	30	2.5×10^{-4}	Zhu, 1998
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	H_2O	60	1.2×10^{-3}	Greshman, 1957
$C_{12}H_{25}C_6H_4SO_3^-Na^{+d}$	0.1 *M* NaCl	25	1.6×10^{-4}	Murphy, 1990
$C_{12}H_{25}$-2-$C_6H_4SO_3^-Na^+$	H_2O	30	1.2×10^{-3}	Zhu, 1998
$C_{12}H_{25}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. = 6.6×10^{-3} *M*)^e	30	6.3×10^{-5}	Zhu, 1998
$C_{12}H_{25}$-3-$C_6H_4SO_3^-Na^+$	H_2O	30	2.4×10^{-3}	Van Os, 1991

$C_{12}H_{25}$-5-$C_6H_4SO_3^-Na^+$	H_2O	30	3.2×10^{-3}	Zhu, 1998
$C_{12}H_{25}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^e	30	4.6×10^{-4}	Zhu, 1998
$C_{13}H_{27}$-2-$C_6H_4SO_3^-Na^+$	H_2O	35	7.2×10^{-4}	Zhu, 1998
$C_{13}H_{27}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^e	30	1.1×10^{-5}	Zhu, 1998
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	H_2O	30	7.6×10^{-4}	Zhu, 1998
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^e	30	8.3×10^{-5}	Zhu, 1998
$C_{16}H_{33}$-7-$C_6H_4SO_3^-Na^+$	H_2O	45	5.1×10^{-5}	Lascaux, 1983
$C_{16}H_{33}$-7-$C_6H_4SO_3^-Na^+$	0.051 *M* NaCl	45	3.2×10^{-6}	Lascaux, 1983
	Fluorinated Anionics			
$C_7F_{15}COO^-K^+$	H_2O	25	2.9×10^{-2}	Shinoda, 1964
$C_7F_{15}COO^-Na^+$	H_2O	25	3.0×10^{-2}	Shinoda, 1977
$C_7F_{15}COO^-Li^+$	H_2O	25	3.3×10^{-2}	Muzzalupo, 1995
$(CF_3)_2CF(CF_2)_4COO^-Na^+$	H_2O	25	3.0×10^{-2}	Shinoda, 1977
$C_8F_{17}COO^-Na^+$	H_2O	35	1.1×10^{-2}	Nakano, 2002
$C_8F_{17}COO^-Li^+$	H_2O	25	4.9×10^{-3}	Muzzalupo, 1995
$C_8F_{17}SO_3^-Li^+$	H_2O	25	6.3×10^{-3}	Shinoda, 1977
$C_4F_9CH_2OOCCH(SO_3^-Na^+)$ $CH_2COOCH_2C_4F_9$	H_2O	30	1.6×10^{-3}	Downer, 1999
	Cationics			
$C_8H_{17}N^+(CH_3)_3Br^-$	H_2O	25	1.4×10^{-1}	Klevens, 1948
$C_{10}H_{21}N^+(CH_3)_3Br^-$	H_2O	25	6.8×10^{-2}	Klevens, 1948
$C_{10}H_{21}N^+(CH_3)_3Br^-$	0.1 *M* NaCl	25	$4.2_7 \times 10^{-2}$	Li, 2001
$C_{10}H_{21}N^+(CH_3)_3Cl^-$	H_2O	25	6.8×10^{-2}	Sowada, 1994
$C_{12}H_{25}N^+(CH_3)_3Br^-$	H_2O	25	1.6×10^{-2}	Klevens, 1948
$C_{12}H_{25}N^+(CH_3)_3Br^-$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^e	25	$1.2_6 \times 10^{-2}$	Rosen, 1996

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (M)	Reference
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.01 M NaBr	25	1.2×10^{-2}	Tanaka, 1991
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.1 M NaBr	25	4.2×10^{-3}	Tanaka, 1991
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.5 M NaBr	31.5	1.9×10^{-3}	Anacker, 1963
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	H_2O	25	2.0×10^{-2}	Osugi, 1995
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	0.1 M NaCl	25	$5.7_6 \times 10^{-3}$	Li, 2001
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	0.5 M NaCl	31.5	3.8×10^{-3}	Anacker, 1963
$C_{12}H_{25}N^+(CH_3)_3F^-$	0.5 M NaF	31.5	8.4×10^{-3}	Anacker, 1963
$C_{12}H_{25}N^+(CH_3)_3NO_3{}^-$	0.5 M $NaNO_3$	31.5	8×10^{-4}	Anacker, 1963
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O	25	3.6×10^{-3}	Lianos, 1982
$C_{14}H_{29}N^+(CH_3)_3Br^-$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ M)[e]	25	$2.4_5 \times 10^{-3}$	Rosen, 1996
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O	40	4.2×10^{-3}	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O	60	5.5×10^{-3}	Gorski, 2001
$C_{14}H_{29}N^+(CH_3)_3Cl^-$	H_2O	25	4.5×10^{-3}	Hover, 1961
$C_{16}H_{33}N^+(CH_3)_3Br^-$	H_2O	25	9.8×10^{-4}	Okuda, 1987
$C_{16}H_{33}N^+(CH_3)_3Br^-$	0.001 M KCl	30	5×10^{-4}	Varjara, 1996
$C_{16}H_{33}N^+(CH_3)_3Cl^-$	H_2O	30	1.3×10^{-3}	Raston, 1947
$C_{18}H_{37}N^+(CH_3)_3Br^-$	H_2O	40	3.4×10^{-4}	Swanson, Vethamutha, 1998
$C_{10}H_{21}Pyr^+Br^{-b}$	H_2O	25	4.4×10^{-2}	Skerjanc, 1999
$C_{10}H_{21}Pyr^+Br^{-b}$	H_2O	25	6.3×10^{-2}	Mehrian, 1993
$C_{11}H_{23}Pyr^+Br^{-b}$	H_2O	25	2.1×10^{-2}	Skerjanc, 1999
$C_{12}H_{25}Pyr^+Br^{-b}$	H_2O	10	$1.1_7 \times 10^{-2}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	H_2O	25	$1.1_4 \times 10^{-2}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	H_2O	40	$1.1_2 \times 10^{-2}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	0.1 M NaBr	10	$2.7_5 \times 10^{-3}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	0.1 M NaBr	25	$2.7_5 \times 10^{-3}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	0.1 M NaBr	40	$2.8_5 \times 10^{-3}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	0.5 M NaBr	10	$1.0_7 \times 10^{-3}$	Rosen, 1982b

$C_{12}H_{25}Pyr^+Br^{-b}$	0.5 *M* NaBr	25	$1.0_8 \times 10^{-3}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-b}$	0.5 *M* NaBr	40	$1.1_6 \times 10^{-3}$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	H_2O	10	$1.7_5 \times 10^{-2}$	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	H_2O	25	1.7×10^{-2}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	H_2O	40	1.7×10^{-2}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.1 *M* NaCl	10	5.5×10^{-3}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.1 *M* NaCl	25	4.8×10^{-3}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.1 *M* NaCl	40	4.5×10^{-3}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.5 *M* NaCl	10	1.9×10^{-3}	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.5 *M* NaCl	25	$1.7_8 \times 10^{-3}$	Rosen 1982b
$C_{12}H_{25}Pyr^+Cl^{-b}$	0.5 *M* NaCl	40	$1.7_8 \times 10^{-3}$	Rosen 1982b
$C_{12}H_{25}Pyr^+I^{-b}$	H_2O	25	5.3×10^{-3}	Mandru, 1972
$C_{13}H_{27}Pyr^+Br^{-b}$	H_2O	25	5.3×10^{-3}	Skerjanc, 1999
$C_{14}H_{29}Pyr^+Br^{-b}$	H_2O	25	2.7×10^{-3}	Skerjanc, 1999
$C_{14}H_{29}Pyr^+Cl^{-b}$	H_2O	25	3.5×10^{-3}	Mehrian, 1993
$C_{14}H_{29}Pyr^+Cl^{-b}$	0.1 *M* NaCl	25	4×10^{-4}	Mehrian, 1993
$C_{15}H_{31}Pyr^+Br^{-b}$	H_2O	25	1.3×10^{-3}	Skerjanc, 1999
$C_{16}H_{33}Pyr^+Br^{-b}$	H_2O	25	6.4×10^{-4}	Skerjanc, 1999
$C_{16}H_{33}Pyr^+Cl^-$	H_2O	25	9.0×10^{-4}	Hartley, 1938
$C_{18}H_{37}Pyr^+Cl^-$	H_2O	25	2.4×10^{-4}	Evers, 1948
$C_{12}H_{25}N^+(C_2H_5)(CH_3)_2Br^-$	H_2O	25	1.4×10^{-2}	Lianos, 1983
$C_{12}H_{25}N^+(C_4H_9)(CH_3)_2Br^-$	H_2O	25	7.5×10^{-3}	Lianos, 1983
$C_{12}H_{25}N^+(C_6H_{13})(CH_3)_2Br^-$	H_2O	25	3.1×10^{-3}	Lianos, 1983
$C_{12}H_{25}N^+(C_8H_{17})(CH_3)_3Br^-$	H_2O	25	1.1×10^{-3}	Lianos, 1983
$C_{14}H_{29}N^+(C_2H_5)_3Br^-$	H_2O	25	3.1×10^{-3}	Lianos, 1982
$C_{14}H_{29}N^+(C_3H_7)_3Br^-$	H_2O	25	2.1×10^{-3}	Venable, 1964; Lianos, 1982
$C_{14}H_{29}N^+(C_4H_9)_3Br^-$	H_2O	25	1.2×10^{-3}	Lianos, 1982
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)_2Cl^-$	H_2O	25	3.9×10^{-2}	de Castillo, 2000
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)_2Cl^-$	H_2O	25	8.8×10^{-3}	Rodriguez, 1995
$C_{14}H_{29}N^+(CH_2C_6H_5)(CH_3)_2Cl^-$	H_2O	25	2.0×10^{-3}	Rodriguez, 1995
$C_{12}H_{25}NH_2{}^+CH_2CH_2OH^-Cl^-$	H_2O	25	4.5×10^{-2}	Omar, 1997

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
$C_{12}H_{25}N^{+}H(CH_2CH_2OH)_2Cl^{-}$	H_2O	25	3.6×10^{-2}	Omar, 1997
$C_{12}H_{25}N^{+}H(CH_2CH_2OH)_3Cl^{-}$	H_2O	25	2.5×10^{-2}	Omar, 1997
$(C_{10}H_{21})_2N^{+}(CH_3)_2Br^{-}$	H_2O	25	$1.8_5 \times 10^{-3}$	Lianos, 1983
$(C_{12}H_{25})_2N^{+}(CH_3)_2Br^{-}$	H_2O	25	$1.7_6 \times 10^{-4}$	Lianos, 1983
		Anionic–Cationic Salts		
$C_6H_{13}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_6H_{13}$	H_2O	25	1.1×10^{-1}	Corkill, 1966
$C_6H_{13}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_8H_{17}$	H_2O	25	2.9×10^{-2}	Lange, 1971
$C_8H_{17}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_6H_{13}$	H_2O	25	1.9×10^{-2}	Lange, 1971
$C_4H_9SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{10}H_{21}$	H_2O	25	1.9×10^{-2}	Lange, 1971
$CH_3SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	1.3×10^{-2}	Lange, 1971
$C_2H_5SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	9.3×10^{-3}	Lange, 1971
$C_{10}H_{21}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_4H_9$	H_2O	25	9.3×10^{-3}	Lange, 1971
$C_8H_{17}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_8H_{17}$	H_2O	25	7.5×10^{-3}	Corkill, 1965
$C_4H_9SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	5.0×10^{-3}	Lange, 1971
$C_6H_{13}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	2.0×10^{-3}	Lange, 1971
$C_{10}H_{21}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{21}$	H_2O	25	4.6×10^{-4}	Corkill, 1963a
$C_8H_{17}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	5.2×10^{-4}	Lange, 1971
$C_{12}H_{25}SO_4^{-} \cdot {}^{+}N(CH_3)_3C_{12}H_{25}$	H_2O	25	4.6×10^{-5}	Lange, 1971
		Zwitterionics		
$C_8H_{17}N^{+}(CH_3)_2CH_2COO^{-}$	H_2O	27	2.5×10^{-1}	Tori, 1963a
$C_{10}H_{21}N^{+}(CH_3)_2CH_2COO^{-}$	H_2O	23	1.8×10^{-2}	Beckett, 1963
$C_{12}H_{25}N^{+}(CH_3)_2CH_2COO^{-}$	H_2O	25	2.0×10^{-3}	Chevalier, 1991
$C_{12}H_{25}N^{+}(CH_3)_2CH_2COO^{-}$	0.1 *M* NaCl	25	1.6×10^{-3}	Zajac, 1997
$C_{14}H_{29}N^{+}(CH_3)_2CH_2COO^{-}$	H_2O	25	2.2×10^{-4}	Zajac, 1997
$C_{16}H_{33}N^{+}(CH_3)_2CH_2COO^{-}$	H_2O	23	2.0×10^{-5}	Beckett, 1963
$C_{12}H_{25}N^{+}(CH_3)_2(CH_2)_3COO^{-}$	H_2O	25	4.6×10^{-3}	Zajac, 1997

$C_{12}H_{25}N^+(CH_3)_2(CH_2)_5COO^-$	H_2O	25	2.6×10^{-3}	Chevalier, 1991
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_7COO^-$	H_2O	25	1.5×10^{-3}	Chevalier, 1991
$C_8H_{17}CH(COO^-)N^+(CH_3)_3$	H_2O	27	9.7×10^{-2}	Tori, 1963a
$C_8H_{17}CH(COO^-)N^+(CH_3)_3$	H_2O	60	8.6×10^{-2}	Tori, 1963b
$C_{10}H_{21}CH(COO^-)N^+(CH_3)_3$	H_2O	27	1.3×10^{-2}	Tori, 1963b
$C_{12}H_{25}CH(COO^-)N^+(CH_3)_3$	H_2O	27	1.3×10^{-3}	Tori, 1963b
p-$C_{12}H_{25}Pyr^+COO^{-b}$	H_2O	50	1.9×10^{-3}	Amrhar, 1994
m-$C_{12}H_{25}Pyr^+COO^{-b}$	H_2O	50	1.5×10^{-3}	Amrhar, 1994
$C_{10}H_{21}CH(Pyr^+)COO^{-b}$	H_2O	25	5.2×10^{-3}	Zhao, 1984
$C_{12}H_{25}CH(Pyr^+)COO^{-b}$	H_2O	25	6.0×10^{-4}	Zhao, 1984
$C_{14}H_{29}CH(Pyr^+)COO^{-b}$	H_2O	40	7.4×10^{-5}	Zhao, 1984
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 5.5–5.9	25	5.3×10^{-3}	Dahanayake, 1984
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 5.5–5.9	40	4.4×10^{-3}	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 5.5–5.9	25	5.5×10^{-4}	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.1 *M* NaCl, pH 5.7	25	4.2×10^{-4}	Rosen, 2001
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–cyclohexane	25	3.7×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–isooctane	25	4.2×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–heptane	25	4.4×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–dodecane	25	4.9×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–heptamethylnonane	25	5.0×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–hexadecane	25	5.3×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O–toluene	25	1.9×10^{-4}	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.1 *M* NaBr, ph 5.9	25	3.8×10^{-4}	Zhu, 1985
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2CH_2SO_3^-$	H_2O, pH 5.5–5.9	40	4.6×10^{-3}	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3SO_3^-$	H_2O	25	3.0×10^{-3}	Zajac, 1997
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3SO_3^-$	0.1 *M* NaCl	25	2.6×10^{-3}	Zajac, 1997
$C_{14}H_{29}N^+(CH_3)_2(CH_2)_3SO_3^-$	H_2O	25	3.2×10^{-4}	Zajac, 1997
$C_{12}H_{25}N(CH_3)_2O$	H_2O	27	2.1×10^{-3}	Hermann, 1962

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
		Nonionics		
$C_8H_{17}CHOHCH_2OH$	H_2O	25	2.3×10^{-3}	Kwan, 1980
$C_8H_{17}CHOHCH_2CH_2OH$	H_2O	25	2.3×10^{-3}	Kwan, 1980
$C_{10}H_{21}CHOHCH_2OH$	H_2O	25	1.8×10^{-4} [c]	Kwan, 1980
$C_{12}H_{25}CHOHCH_2CH_2OH$	H_2O	25	1.3×10^{-5}	Kwan, 1980
n-Octyl-β-D-glucoside	H_2O	25	2.5×10^{-2}	Shinoda, 1961
n-Decyl-α-D-glucoside	H_2O	25	8.5×10^{-4}	Aveyard, 1998
n-Decyl-β-D-glucoside	H_2O	25	2.2×10^{-3}	Shinoda, 1961
n-Decyl-β-D-glucoside	0.1 *M* NaCl (aq.), pH = 9	25	1.9×10^{-3}	Li, 2001
n-Dodecyl-α-D-glucoside	H_2O	60	7.2×10^{-5}	Bocker, 1989
Dodecyl-β-D-glucoside	H_2O	25	1.9×10^{-4}	Shinoda, 1961
Decyl-β-D-maltoside	H_2O	25	2.0×10^{-3}	Aveyard, 1988
Decyl-β-D-maltoside	0.1 *M* NaCl(aq.), pH = 9	25	$1.9_5 \times 10^{-3}$	Li, 2001
Dodecyl-α-D-maltoside	H_2O	20	1.5×10^{-4}	Bocker, 1989
Dodecyl-β-D-maltoside	H_2O	25	1.5×10^{-4}	Aveyard, 1998
Dodecyl-β-D-maltoside	0.1 *M* NaCl (aq.), pH = 9	25	1.6×10^{-4}	Li, 2001
$C_{12.5}H_{26}$alkylpolyglucoside (degree of polym., 1.3)[d]	H_2O	25	1.9×10^{-4}	Balzer, 1993
Tetradecyl-α-D-maltoside	H_2O	20	2.2×10^{-5}	Bocker, 1989
Tetradecyl-β-D-maltoside	H_2O	20	1.5×10^{-5}	Bocker, 1989
n-$C_4H_9(OC_2H_4)_6OH$	H_2O	20	8.0×10^{-1}	Elworthy, 1964a
n-$C_4H_9(OC_2H_4)_6OH$	H_2O	40	7.1×10^{-1}	Elworthy, 1964a
$(CH_3)_2CHCH_2(OC_2H_4)_6OH$	H_2O	20	9.1×10^{-1}	Elworthy, 1964a
$(CH_3)_2CHCH_2(OC_2H_4)_6OH$	H_2O	40	8.5×10^{-1}	Elworthy, 1964a
n-$C_6H_{13}(OC_2H_4)_6OH$	H_2O	20	7.4×10^{-2}	Elworthy, 1964a
n-$C_6H_{13}(OC_2H_4)_6OH$	H_2O	40	5.2×10^{-2}	Elworthy, 1964a
$(C_2H_5)_2CHCH_2(OC_2H_4)_6OH$	H_2O	20	1.0×10^{-1}	Elworthy, 1964a
$(C_2H_5)_2CHCH_2(OC_2H_4)_6OH$	H_2O	40	8.7×10^{-2}	Elworthy, 1964a

$C_8H_{17}OC_2H_4OH$	H_2O	25	4.9×10^{-3}	Shinoda, 1959
$C_8H_{17}(OC_2H_4)_3OH$	H_2O	25	7.5×10^{-3}	Corkill, 1964
$C_8H_{17}(OC_2H_4)_5OH$	H_2O	25	9.2×10^{-3}	Varadaraj, 1991b
$C_8H_{17}(OC_2H_4)_5OH$	0.1 *M* NaCl	25	5.8×10^{-3}	Varadaraj, 1991b
$C_8H_{17}(OC_2H_4)_6OH$	H_2O	25	9.9×10^{-3}	Corkill, 1964
$(C_3H_7)_2CHCH_2(OC_2H_4)_6OH$	H_2O	20	2.3×10^{-2}	Elworthy, 1964a
$C_{10}H_{21}(OC_2H_4)_4OH$	H_2O	25	6.8×10^{-4}	Hudson, 1964
$C_{10}H_{21}(OC_2H_4)_5OH$	H_2O	25	7.6×10^{-4}	Eastoe, 1997
$C_{10}H_{21}(OC_2H_4)_6OH$	H_2O	25	9.0×10^{-4}	Corkill, 1964
$C_{10}H_{21}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^{e}	25	8.7×10^{-4}	Rosen, 1996
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O	15	1.4×10^{-3}	Meguro, 1981
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O	25	1.0×10^{-3}	Meguro, 1981
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O	40	7.6×10^{-4}	Meguro, 1981
$(C_4H_9)_2CHCH_2(OC_2H_4)_6OH$	H_2O	20	3.1×10^{-3}	Elworthy, 1964a
$(C_4H_9)_2CHCH_2(OC_2H_4)_9OH$	H_2O	20	3.2×10^{-3}	Elworthy, 1964a
$C_{11}H_{23}(OC_2H_4)_8OH$	H_2O	15	4.0×10^{-4}	Meguro, 1981
$C_{11}H_{23}(OC_2H_4)_8OH$	H_2O	25	3.0×10^{-4}	Meguro, 1981
$C_{11}H_{23}(OC_2H_4)_8OH$	H_2O	40	2.3×10^{-4}	Meguro, 1981
$C_{12}H_{25}(OC_2H_4)_2OH$	H_2O	10	3.8×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_2OH$	H_2O	25	3.3×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_2OH$	H_2O	40	3.2×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O	10	6.3×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O	25	5.2×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O	40	5.6×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	10	8.2×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	25	6.4×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	40	5.9×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ *M*)^{e}	25	4.8×10^{-5}	Rosen, 1996

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TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (M)	Reference
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	10	9.0×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	25	6.4×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	40	5.9×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	0.1 M NaCl	25	6.4×10^{-5}	Varadaraj, 1991b
$C_{12}H_{25}(OC_2H_4)_5OH$	0.1 M NaCl	40	5.9×10^{-5}	Varadaraj, 1991b
$C_{12}H_{25}(OC_2H_4)_6OH$	H_2O	20	8.7×10^{-5}	Corkill, 1961
$C_{12}H_{25}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ M)^e	25	6.9×10^{-5}	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	10	12.1×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	25	8.2×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	40	7.3×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	0.1 M NaCl (aq.)	25	7.9×10^{-5}	Rosen, 2001
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	10	$1.5_6 \times 10^{-4}$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	25	$1.0_9 \times 10^{-4}$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	40	9.3×10^{-5}	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–cyclohexane	25	$1.0_1 \times 10^{-4}$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–heptane	25	$0.9_9 \times 10^{-4}$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–hexadecane	25	$1.0_2 \times 10^{-4}$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_9OH$	H_2O	23	10.0×10^{-5}	Lange, 1965
$C_{12}H_{25}(OC_2H_4)_{12}OH$	H_2O	23	14.0×10^{-5}	Lange, 1965
6-branched $C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	25	2.8×10^{-4}	Varadaraj, 1991b
6-branched $C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	40	2.1×10^{-4}	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	25	4.9×10^{-5}	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_5OH$	0.1 M NaCl	25	2.1×10^{-5}	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O	15	3.2×10^{-5}	Meguro, 1981
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O	25	2.7×10^{-5}	Meguro, 1981
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O	40	2.0×10^{-5}	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_6OH$	H_2O	25	1.0×10^{-5}	Corkill, 1964

$C_{14}H_{29}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ M)[e]	25	6.9×10^{-5}	Rosen, 1996
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O	15	1.1×10^{-5}	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O	25	9.0×10^{-6}	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O	40	7.2×10^{-6}	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ M)[e]	25	1.0×10^{-5}	Rosen, 1996
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O	15	4.1×10^{-6}	Meguro, 1981
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O	25	3.5×10^{-6}	Meguro, 1981
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O	40	3.0×10^{-6}	Meguro, 1981
$C_{16}H_{33}(OC_2H_4)_6OH$	H_2O	25	$1.6_6 \times 10^{-6}$	Rosen, 1996
$C_{16}H_{33}(OC_2H_4)_6OH$	"Hard river" water (I.S. $= 6.6 \times 10^{-3}$ M)[e]	25	2.1×10^{-6}	Rosen, 1996
$C_{16}H_{33}(OC_2H_4)_7OH$	H_2O	25	1.7×10^{-6}	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_9OH$	H_2O	25	2.1×10^{-6}	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_{12}OH$	H_2O	25	2.3×10^{-6}	Elworthy, 1962
$C_{16}H_{33}O(C_2H_4O)_{15}H$	H_2O	25	3.1×10^{-6}	Elworthy, 1962
$C_{16}H_{33}O(C_2H_4O)_{21}H$	H_2O	25	3.9×10^{-6}	Elworthy, 1962
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_2H$	H_2O	25	1.3×10^{-4}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_3H$	H_2O	25	9.7×10^{-5}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_4H$	H_2O	25	1.3×10^{-4}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_5H$	H_2O	25	1.5×10^{-4}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_6H$	H_2O	25	2.1×10^{-4}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_7H$	H_2O	25	2.5×10^{-4}	Crook, 1963
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_8H$	H_2O	25	2.8×10^{-4}	Crook, 1964
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_9H$	H_2O	25	3.0×10^{-4}	Crook, 1964
p-t-$C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$	H_2O	25	3.3×10^{-4}	Crook, 1964
p-$C_9H_{19}C_6H_4(OC_2H_4)_8OH$	H_2O	—	1.3×10^{-4}	Voicu, 1994
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	H_2O	25	7.5×10^{-5}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	3 M Urea	25	10×10^{-5}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	6 M Urea	25	24×10^{-5}	Schick, 1965

(*Continued next page*)

TABLE 3-2 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC (*M*)	Reference
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	3 *M* guanidinium Cl	25	14×10^{-5}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	1.5 *M* dioxane	25	10×10^{-5}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$[g]	3 *M* dioxane	25	18×10^{-5}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{31}OH$[g]	H_2O	25	$1.8\ \ 10^{-4}$	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{31}OH$[g]	3 *M* urea	25	3.5×10^{-4}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{31}OH$[g]	3 *M* urea	25	7.4×10^{-4}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{31}OH$[g]	3 *M* guanidinium Cl	25	4.3×10^{-4}	Schick, 1965
$C_9H_{19}C_6H_4(OC_2H_4)_{31}OH$[g]	3 *M* dioxane	25	5.7×10^{-4}	Schick, 1965
$C_6H_{13}[OCH_2CH(CH_3)]_2(OC_2H_4)_{9.9}OH$	H_2O	20	4.7×10^{-2}	Kucharski, 1974
$C_6H_{13}[OCH_2CH(CH_3)]_3(OC_2H_4)_{9.7}OH$	H_2O	20	3.2×10^{-2}	Kucharski, 1974
$C_6H_{13}[OCH_2CH(CH_3)]_4(OC_2H_4)_{9.9}OH$	H_2O	20	1.9×10^{-2}	Kucharski, 1974
$C_7H_{15}[OCH_2CH(CH_3)]_3(OC_2H_4)_{9.7}OH$	H_2O	20	1.1×10^{-2}	Kucharski, 1974
Sucrose monolaurate	H_2O	25	3.4×10^{-4}	Herrington, 1986
Sucrose monooleate	H_2O	25	5.1×10^{-6}	Herrington, 1986
$C_{11}H_{23}CON(C_2H_4OH)_2$	H_2O	25	$2.6_4 \times 10^{-4}$	Rosen, 1964
$C_{15}H_{31}CON(C_2H_4OH)_2$	H_2O	35	11.5×10^{-6}	Hayes, 1980
$C_{11}H_{23}CONH(C_2H_4O)_4H$	H_2O	23	5.0×10^{-4}	Kjellin, 2002
$C_{10}H_{21}CON(CH_3)(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$1.5_8 \times 10^{-3}$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2CHOHCH_2OH$	0.1 *M* NaCl	25	$2.3_4 \times 10^{-4}$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_3CH_2OH$	0.1 *M* NaCl	25	$3.3_1 \times 10^{-4}$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$3.4_7 \times 10^{-4}$	Zhu, 1999
$C_{12}H_{25}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$7.7_6 \times 10^{-5}$	Zhu, 1999
$C_{13}H_{27}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$1.4_8 \times 10^{-5}$	Zhu, 1999
$C_{10}H_{21}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$1.2_9 \times 10^{-3}$	Burczyk, 2001
$C_{12}H_{25}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$1.4_6 \times 10^{-4}$	Burczyk, 2001
$C_{14}H_{29}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$2.3_6 \times 10^{-5}$	Burczyk, 2001
$C_{16}H_{33}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$7.7_4 \times 10^{-6}$	Burczyk, 2001
$C_{18}H_{37}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$2.8_5 \times 10^{-6}$	Burczyk, 2001

		Fluorinated Nonionics		
$C_6F_{13}CH_2CH_2(OC_2H_4)_{11.5}OH$	H_2O	20	4.5×10^{-4}	Mathis, 1980
$C_6F_{13}CH_2CH_2(OC_2H_4)_{14}OH$	H_2O	20	6.1×10^{-4}	Mathis, 1980
				(*Continued next page*)
$C_8F_{17}CH_2CH_2N(C_2H_4OH)_2$	H_2O	20	1.6×10^{-4}	Mathis, 1980
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_2OH$	H_2O	25	2.5×10^{-3}	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_3OH$	H_2O	25	2.8×10^{-3}	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_5OH$	H_2O	25	3.7×10^{-3}	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_7OH$	H_2O	25	4.8×10^{-3}	Matos, 1989
		Siloxane-Based Nonionics		
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_5H]OSi(CH_3)_3$	H_2O	23±2	7.9×10^{-5}	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_9H]OSi(CH_3)_3$	H_2O	23±2	1.0×10^{-4}	Gentle, 1995
$(CH_3)_3SiOSi(CH_3)[CH_2(C_2H_4O)_{13}H]OSi(CH_3)_3$	H_2O	23±2	6.3×10^{-4}	Gentle, 1995

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[a] From branched dodecyl alcohol with 4.4 branches in the molecule.

[b] Pyr^+ = pyridinium.

[c] Below Krafft point (p. 214) supersaturated solution.

[d] Commercial product.

[e] I.S. = ionic strength.

[f] Solubility too low to reach CMC.

[g] Hydrophilic group not homogeneous, but distribution of POE chains reduced by molecular distillation. Hydrophobic group equivalent to 10.5 C atoms in the straight chain.

room temperature, the carbon atoms between the polar group and the hydrophilic head appearing to have about one-half the effect on the CMC that they would have were the polar group absent. When the polar group and the hydrophilic group are both attached to the same carbon atom, that carbon atom seems to have no effect on the value of the CMC.

In POE polyoxypropylene block copolymers with the same number of OE units in the molecule, the CMC decreases significantly with increase in the number of oxypropylene units (Alexandridis, 1994).

The replacement of a hydrocarbon-based hydrophobic group by a fluorocarbon-based one with the same number of carbon atoms appears to cause a decrease in the CMC (Shinoda, 1977). By contrast, the replacement of the terminal methyl group of a hydrocarbon-based hydrophobic group by a trifluoromethyl group has been shown to cause the CMC to increase. For 12, 12, 12-trifluorododecyltrimethylammonium bromide and 10, 10, 10-trifluorodecyltrimethylammonium bromide, the CMCs are twice those of the corresponding nonfluorinated compounds (Muller, 1972).

2. The Hydrophilic Group In aqueous medium, ionic surfactants have much higher CMCs than nonionic surfactants containing equivalent hydrophobic groups; 12-carbon straight-chain ionics have CMCs of approximately $1 \times 10^{-2}\ M$, whereas nonionics with the same hydrophobic group have CMCs of approximately $1 \times 10^{-4}\ M$. Zwitterionics appear to have slightly smaller CMCs than ionics with the same number of carbon atoms in the hydrophobic group.

As the hydrophilic group is moved from a terminal position to a more central position, the CMC increases. The hydrophobic group seems to act as if it had become branched at the position of the hydrophilic group, with the carbon atoms on the shorter section of the chain having about half their usual effect on the CMC (Evans, 1956). This may be another example of the steric effect in micelle formation noted above.

It has been found (Stigter, 1974) that the CMC is higher when the charge on an ionic hydrophilic group is closer to the α-carbon atom of the (alkyl) hydrophobic group. This is explained as being due to an increase in electrostatic self-potential of the surfactant ion when the ionic head group moves from the bulk water to the vicinity of the nonpolar micellar core during the process of micellization; work is required to move an electric charge closer to a medium of lower dielectric constant. The order of decreasing CMC in some *n*-alkyl ionics was aminium salts > carboxylates (with one more carbon atom in the molecule) > sulfonates > sulfates. This same order had been noted earlier (Klevens, 1953).

As expected, surfactants containing more than one hydrophilic group in the molecule show larger CMCs than those with one hydrophilic group and the equivalent hydrophobic group.

In quaternary cationics, pyridinium compounds have smaller CMCs than the corresponding trimethylammonium compounds. This may be due to the greater ease of packing the planar pyridinium, compared to the tetrahedral trimethylammonium, group into the micelle. In the series $C_{12}H_{25}N^{+}(R)_3Br^{-}$, the CMC decreases with increase in the length of R, presumably due to the increased hydrophobic character of the molecule.

For the usual type of POE nonionic (in which the hydrophobic group is a hydrocarbon residue), the CMC in aqueous medium increases with increase in the number of oxyethylene units in the polyoxyethylene chain. However, the change per oxyethylene unit is much smaller than that per methylene unit in the hydrophobic chain. The greatest increase per oxyethylene unit seems to be obtained when the POE chain is short and the hydrophobic group is long. Since commercial POE nonionics are mixtures containing POE chains with different numbers of oxyethylene units clustered about some mean value, their CMCs are slightly lower than those of single species materials containing the same hydrophobic group and with oxyethylene content corresponding to that mean value, probably because the components with low oxyethylen content in the commercial material reduce the CMC more than it is raised by those with high oxyethylene content (Crook, 1963). POE fatty amides have lower CMC values than their corresponding polyoxyethylenated fatty alcohols, presumably due to hydrogen bonding between the head groups, in spite of their increased hydrophilicity (Folmer, 2001).

When the hydrophobic group of the POE nonionic is oleyl, or 9,10-dibromo-, 9,10-dichloro-, or 9,10-dihydroxystearyl, the CMC decreases with increase in the number of EO units in the molecule (Garti, 1985). The effect here may be due to the bulky nature of the hydrophobic group in these molecules, which produces an almost parallel arrangement of the surfactant molecules in the micelle, similar to that at the planar liquid–air interface. At that interface, the introduction of an EO group causes a slight increase in the *hydrophobic* nature of the molecule, as evidenced by an increase in the value of $-\Delta G^{\circ}_{\text{ad}}$ (p. 87). Such an increase in the hydrophobic character of the molecule when the surfactant molecules are arranged in the micelle in a similar, more or less parallel fashion should produce a decrease in the CMC. For silicone-based nonionics of the type $(CH_3)_3SiO[Si\text{-}(CH_3)_2O]_x\text{-}Si(CH_3)_2CH_2(C_2H_4O)_yCH_3$, too, the CMC appears to decrease with increase in the OE content of the molecule (Kanner, 1967). Here, too, the hydrophobic group is bulky. However, only a few compounds have been studied.

In POE polyoxypropylene block copolymers with a constant number of oxypropylene units in the molecule, the CMC increases with increase in the number of OE units. At a constant POE/polyoxypropylene ratio, increase in the molecular weight of the surfactant decreases the CMC (Alexandridis, 1994).

3. The Counterion in Ionic Surfactants; Degree of Binding to the Micelle A plot of the specific conductivity, κ, of an ionic surfactant versus its concentration, C, in the aqueous phase is linear, with a break at the CMC, above which the (decreased) slope of the plot again becomes linear (Figure 3-6). The break in the plot is due to the binding of some of the counterions of the ionic surfactant to the micelle. The degree of ionization, α, of the micelle near its CMC can be obtained from the ratio, s_2/s_1, of the slopes above and below the break indicative of the CMC (Yiv and Zana, 1980). The degree of binding of the counterion to the micelle, for a surfactant with a single ionic head group in the molecule, is $(1 - \alpha)$.

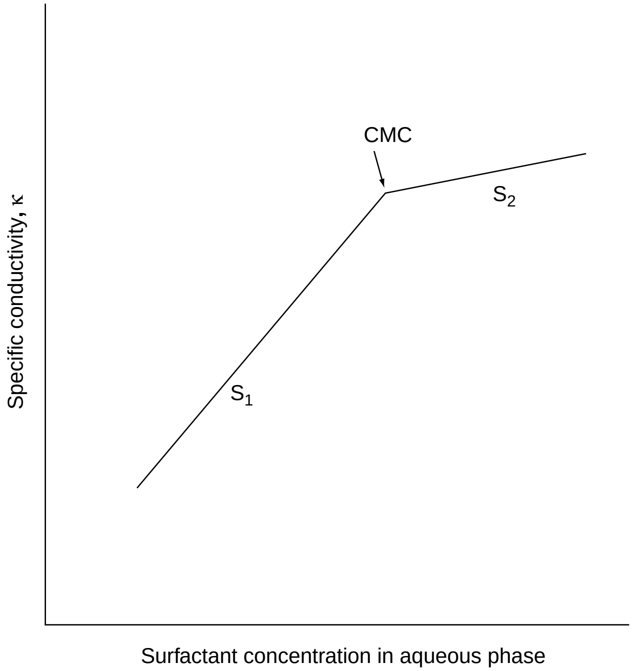

FIGURE 3-6 Plot of specific conductivity, κ, versus surfactant concentration in the aqueous phase, showing change in slopes before (S_1) and after (S_2) the CMC.

The larger the hydrated radius of the counterion, the weaker the degree of binding; thus $NH_4^+ > K^+ > Na^+ > Li^+$ and $I^- > Br^- > Cl^-$.*

In a number of series of cationic surfactants, Zana (1980) has shown (Table 3-3) that the degree of binding (or ionization) is related to the surface area per head group, a_m^s, in the ionic micelle, with the degree of binding increasing as the surface area per head group decreases (i.e., as the surface charge density increases). This is also apparent from the data of Granet (1988) and of Binana-Limbele (1988) in Table 3-3, where, with increase in the length of the 2-alkyl side chain in the decanesulfonates or of the POE group in the carboxylates, respectively, and the presumable resulting increase in the surface area per head group, the degree of binding decreases.

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*For anionic surfactants of structure $RC(O)N(R^1)CH_2CH_2COO^-Na^+$, it has been found (Tsubone, 2001, 2003a, 2003b) that this break in the conductance-surfactant concentration may be smaller than expected or absent, yielding binding $(1-\alpha)$ values much smaller than those of comparable surfactants without the amide group (Table 3-3). This may be due to protonatlon of the carboxylate group and hydrogen bonded ring formation with the amido group, with simultaneous release of the Na^+, upon micellization. This absence of a break in the conductance-surfactant concentration plot at the CMC is even more prone to occur in gemini surfactants (Chapter 12) with the above structure in the molecule.

TABLE 3-3 Degree of Binding $(1-\alpha)$, Surface Area at Surface Saturation (a_m^s) per Head Group, and CMC of Some Ionic Micelles in H_2O

Compound	Temp. (°C)	Degree of Binding	a_m^s (Å^2)	CMC (*M*)	Reference
		Anionics			
$C_{11}H_{23}COO^-Na^+$	25	0.54	—	2.8×10^{-3}	De Lisi, 1997
$C_{12}H_{25}(OC_2H_4)_5OCH_2COO^-Na^+$ (pH 8.2)	25	0.19	—	3.5×10^{-3}	Binana-Limbele, 1988
$C_{12}H_{25}(OC_2H_4)_9OCH_2COO^-Na^+$ (pH 8.2)	25	0.14	—	5.9×10^{-3}	Binana-Limbele, 1988
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	0.41	58	3.5×10^{-3}	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	0.36	66	2.7×10^{-3}	Tsubone, 2001
$C_7F_{15}COO^-Na^+$	25	0.44	—	3.0×10^{-2}	De Lisi, 1997
$C_8F_{17}COO^-Na^+$	40	0.47	—	1.0×10^{-2}	Nakano, 2002
$C_9H_{19}CH_2SO_3^-Na^+$	45	0.88	—	4.0×10^{-2}	Granet, 1988
$C_9H_{19}CH(C_2H_5)SO_3^-Na^+$	45	0.86	—	1.8×10^{-2}	Granet, 1988
$C_9H_{19}CH(C_4H_9)SO_3^-Na^+$	45	0.83	—	6.8×10^{-3}	Granet, 1988
$C_9H_{19}CH(C_6H_{13})SO_3^-Na^+$	45	0.77	—	1.7×10^{-3}	Granet, 1988
$C_9H_{19}CH(C_8H_{17})SO_3^-Na^+$	45	0.67	—	2.4×10^{-4}	Granet, 1988
$C_9H_{19}CH(C_9H_{19})SO_3^-Na^+$	45	0.59	—	8.9×10^{-5}	Granet, 1988
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	0.42	56	1.6×10^{-3}	Tsubone, 2001
$C_{12}H_{25}SO_4^-Na^+$	25	0.82	—	8.1×10^{-3}	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$ (0.1 *M* NaCl)	25	0.88	—	1.6×10^{-3}	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$ (0.2 *M* NaCl)	25	0.86	—	8.3×10^{-4}	Sowada, 1994
$C_{12}H_{25}SO_4^-Na^+$ (0.4 *M* NaCl)	25	0.87	—	5.2×10^{-4}	Sowada, 1994
$C_{14}H_{29}SO_4^-Na^+$	40	0.85	—	2.23×10^{-3}	Nakano, 2002
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	25	0.84	—	—	Zoeller, 1998
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	25	0.87	—	—	Zoeller, 1998

(*Continued next page*)

TABLE 3-3 (*Continued*)

Compound	Temp. (°C)	Degree of Binding	a_m^s (Å^2)	CMC (*M*)	Reference
$C_{12}H_{25}(OC_2H_4)_4SO_4^-Na^+$	25	0.84	—	—	Zoeller, 1998
$C_{12}H_{25}(OC_2H_4)_6SO_4^-Na^+$	25	0.81	—	—	Zoeller, 1998
		Cationics			
$C_8H_{17}N^+(CH_3)_3Br^-$	25	0.64	83.3	2.9×10^{-1}	Zana, 1980, 1981
$C_{10}H_{21}N^+(CH_3)_3Br^-$	25	0.73	79.7	6.4×10^{-2}	Zana, 1980, 1981
$C_{10}H_{21}N^+(CH_3)_3Cl^-$	25	0.75	—	6.8×10^{-2}	Sowada, 1994
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)_2Cl^-$	25	0.46	—	3.9×10^{-2}	de Castillo, 2000
$C_{12}H_{25}N^+(CH_3)_3Br^-$	25	0.78	77.2	1.5×10^{-2}	Zana, 1980, 1981
$C_{12}H_{25}N^+(CH_3)_2(C_2H_5)Br^-$	25	0.72	89	1.4×10^{-2}	Zana, 1980, 1981
$C_{12}H_{25}N^+(CH_3)_2(C_2H_5)Br^-$	25	0.68	96	1.1×10^{-2}	Zana, 1980, 1981
$C_{12}H_{25}N^+(CH_3)_3Cl^-$	25	0.66	—	2.2×10^{-2}	Zana, 1995
$C_{14}H_{29}N^+(CH_3)_3Br^-$	25	0.81	75.3	3.2×10^{-3}	Zana, 1980, 1981
$C_{14}H_{29}N^+(CH_3)_3Br^-$	40	0.75	—	4.2×10^{-3}	Gorski, 2001
$C_{16}H_{33}N^+(CH_3)_3Br^-$	25	0.84	74	8.5×10^{-3}	Zana, 1980, 1981
$C_{16}H_{33}N^+(CH_3)_3Cl^-$	25	0.63	—	1.4×10^{-3}	Sepulveda, 1985
$C_{10}H_{21}Pyr^+Br^-$	25	0.62	—	4.4×10^{-2}	Skerjanc, 1999
$C_{11}H_{23}Pyr^+Br^-$	25	0.64	—	2.1×10^{-2}	Skerjanc, 1999
$C_{12}H_{25}Pyr^+Br^-$	25	0.66	—	1.0×10^{-2}	Skerjanc, 1999
$C_{13}H_{27}Pyr^+Br^-$	25	0.66	—	5.3×10^{-3}	Skerjanc, 1999
$C_{14}H_{29}Pyr^+Br^-$	25	0.69	—	2.7×10^{-3}	Skerjanc, 1999
$C_{15}H_{31}Pyr^+Br^-$	25	0.69	—	1.3×10^{-3}	Skerjanc, 1999
$C_{16}H_{33}Pyr^+Br^-$	25	0.69	—	6.4×10^{-4}	Skerjanc, 1999

The degree of counterion binding also decreases with solubilization of short (C_2–C_6) alcohols in the palisade layer of the micelle, whereas the solubilization of octane, which occurs in the interior of the micelle (Chapter 4, Section I1A), does not affect the degree of counterion binding (Bostrom, 1989). This is presumably because solubilization in the palisade layer increases the surface area per ionic head group, whereas solubilization in the interior of the micelle does not. It is also decreased by the addition of urea, replacing water from the interface (Souza, 1995). Counterion binding also increases with increase in the electrolyte content of the solution (Asakawa, 2001) and may also increase when surfactant concentration increase produces micellar growth (Quirion, 1986; Iijima, 2000), presumably because both of these are accompanied by a decrease in head group area. Ionic micelles that have more tightly bound counterions are more nonionic in character than those with a greater degree of ionization, have lower water solubility, and are more likely to have nonspherical micelles and to show viscoelasticity in aqueous solution.

The binding of the counterions Na^+ and Cl^- to zwitterionics of the betaine and sulfobetaine types starts well above the CMC and hence does not affect its value. The degree of binding of the Cl^- is always larger than that of the Na^+ (Kamenka, 1995b).

The CMC in aqueous solution for a particular surfactant reflects the degree of binding of the counterion to the micelle. Increased binding of the counterion, in aqueous systems, causes a decrease in the CMC of the surfactant. The extent of binding of the counterion increases also with increase in the polarizability and charge of the counterion and decreases with increase in its hydrated radius. Thus, in aqueous medium, for the anionic lauryl sulfates, the CMC decreases in the order $Li^+ > Na^+ > K^+ > Cs^+ > N(CH_3)_4^+ > N(C_2H_5)_4^+ > Ca^{2+}$, Mg^{2+}, which is the same order as the increase in the degree of binding of the cation (Robb, 1974). The depression of the CMC from Li^+ to K^+ is small, but for the other counterions it is quite substantial. When the counterion is a cation of a primary amine, RNH_3^+, the CMC decreases with increase in the chain length of the amine (Packter, 1963). For the cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order of decreasing CMC in aqueous medium is $F^- > Cl^- > Br^- > I^-$ (Mukerjee, 1967), which is the same order as the increase in degree of binding of the anion (Ottewill, 1962).

On the other hand, when comparing surfactants of different structural types, the value of the CMC does not always increase with decrease in the degree of binding of the counterion. Thus, although in the series $RN^+(CH_3)_3Br^-$ the degree of binding increases and the CMC decreases with increase in the length of R, the decrease in the CMC is due mainly to the increased hydrophobicity of the surfactant as a result of the increase in the alkyl chain length, and only to a minor extent due to the smaller area per head group, a_m^s. This is seen also in the series, $C_{12}H_{25}N^+(CH_3)_2(R^1)Br^-$ and $C_9H_{19}CH(R^1)SO_3^-Na^+$ (Table 3-3), where, although the degree of binding decreases with increase in the length of the alkyl chain, R^1, the CMC decreases due to the increase in the hydrophobicity of the surfactant with increase in R.

TABLE 3-4 Constants for the Relation log CMC $= A - BN$

Surfactant Series	Temp. (°C)	A	B	Reference
Na carboxylates (soaps)	20	1.8_5	0.30	Markina, 1964
K carboxylates (soaps)	25	1.9_2	0.29	Klevens, 1953
Na (K) alkyl 1-sulfates or -sulfonates	25	1.5_1	0.30	Rosen, 1976
Na alkane-1-sulfonates	40	1.5_9	0.29	Klevens, 1953
Na alkane-1-sulfonates	55	1.1_5	0.26	Schick, 1957
Na alkyl-1-sulfates	45	1.4_2	0.30	Klevens, 1953
Na alkyl-1-sulfates	60	1.3_5	0.28	Rosen, 1976
Na alkyl-2-sulfates	55	1.2_8	0.27	Schick, 1957
Na *p*-alkylbenzenesulfonates	55	1.6_8	0.29	Schick, 1957
Na *p*-alkylbenzenesulfonates	70	1.3_3	0.27	Lange, 1964
Alkyltrimethylammonium bromides	25	2.0_1	0.32	Zana, 1980
Alkyltrimethylammonium chlorides (0.1 *M* NaCl)	25	1.2_3	0.33	Caskey, 1971
Alkyltrimethylammonium bromides	60	1.7_7	0.29	Klevens, 1953
Alkylpyridinium bromides	30	1.7_2	0.31	Venable, 1964
$C_nH_{2n+1}(OC_2H_4)_6OH$	25	1.8_2	0.49	Rosen, 1976
$C_nH_{2n+1}(OC_2H_4)_8OH$	15	2.1_8	0.51	Meguro, 1981
$C_nH_{2n+1}(OC_2H_4)_8OH$	25	1.8_9	0.50	Meguro, 1981
$C_nH_{2n+1}(OC_2H_4)_8OH$	40	1.6_6	0.48	Meguro, 1981
$C_nH_{2n+1}N^+(CH_3)_2CH_2COO^-$	23	3.1_7	0.49	Beckett, 1963

4. Empirical Equations Many investigators have developed empirical equations relating the CMC to the various structural units in surface-active agents. Thus, for homologous straight-chain ionic surfactants (soaps, alkanesulfonates, alkyl sulfates, alkylammonium chlorides, alkyltrimethylammonium bromides) in aqueous medium, a relation between the CMC and the number of carbon atoms N in the hydrophobic chain was found (Klevens, 1953) in the form

$$\log \mathrm{CMC} = A - BN, \tag{3.1}$$

where A is a constant for a particular ionic head at a given temperature and B is a constant ≈ 0.3 ($= \log 2$) at 35°C for the ionic types cited previously. The basis for the rule mentioned earlier about the CMC being halved for each increase in the hydrophobic chain by one carbon atom is apparent from this relation. Nonionics and zwitterionics also show this relation, but the value of B is ≈ 0.5, which is the basis for the rule that the CMC decreases by a factor of about 10 for each two methylene groups added to the hydrophobic chain. Table 3-4 lists some values of A and B determined from experimental data.

IV.B. Electrolyte

In aqueous solution the presence of electrolyte causes a change in the CMC, the effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionics than for nonionics. Experimental data indicate that for the first two classes of surfactants, the effect of the concentration of electrolyte is given by (Corrin, 1947)

$$\log \mathrm{CMC} = -a \log C_i + \mathrm{b} \tag{3.2}$$

where *a* and *b* are constants for a given ionic head at a particular temperature and C_i is the total counterion concentration in equivalents per liter. The depression of the CMC in these cases is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the micelle. For sodium laurate and sodium naphthenate, the order of decreasing effectiveness of the anion in depressing the CMC is $PO_4^{3-} > B_4O_7^{2-} > OH^- > CO_3^{2-} > HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$ (Demchenko, 1962).

For nonionics and zwitterionics the preceding relation does not hold. Instead, the effect is given better by (Shinoda, 1961; Tori, 1963b, Ray, 1971b)

$$\log \mathrm{CMC} = -KC_s + \mathrm{constant} \quad (C_s < 1) \tag{3.3}$$

where *K* is a constant for a particular surfactant, electrolyte, and temperature and C_s is the concentration of electrolyte in moles per liter. For alkylbetaines, the value of *K* increases with increase in the length of the hydrophobic group and the charge on the anion of the electrolyte (Tori, 1963b).

The change in the CMC of nonionics and zwitterionics on the addition of electrolyte has been attributed (Mukerjee, 1967; Ray, 1971a) mainly to the "salting out" or "salting in" of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant. Salting in or salting out by an ion depends upon whether the ion is a water structure breaker or a water structure maker. Ions with a large ionic charge/radius ratio, such as F^-, are highly hydrated and are water structure makers. They salt out the hydrophobic groups of the monomeric form of the surfactant and decrease the CMC. Ions with a small ionic charge/radius ratio, such as CNS^-, are water structure breakers; they salt in the hydrophobic groups of the monomeric form of the surfactant and increase the CMC. The total effect of an electrolyte appears to approximate the sum of its effects on the various parts of the solute molecule in contact with the aqueous phase. Since the hydrophilic groups of the surfactant molecules are in contact with the aqueous phase in both the monomeric and micellar forms of the surfactant, while the hydrophobic groups are in contact with the aqueous phase only in the monomeric form, the effect of the electrolyte on the hydrophilic groups in the monomeric and micellar forms may cancel each other, leaving the hydrophobic groups in the monomers as the moiety most likely to be affected by the addition of electrolyte to the aqueous phase.

The effects of the anion and the cation in the electrolyte are additive. For anions, the effect on the CMC of POE nonionics appears to depend on the charge/radius (water structure) effect. Thus, the order of effectiveness in decreasing the CMC is

$\frac{1}{2}SO_4^{2-} > F^- > BrO_3^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$. For cations, the order is $NH_4^+ > K^+ > Na^+ > Li^+ > \frac{1}{2}Ca^{2+}$ (Schick, 1962a; Ray, 1971b). Here, the reason for the order is not clear. Similar anion and cation effects have been observed on the CMC value of *n*-dodecyl-β-maltoside solutions (Zhang, 1996).

Investigation of the effect of electrolyte on the CMC of a high-molecular-weight nonionic of the POE polyoxypropylene type (Pandit, 2000) found that the CMC decreased in the order $Na_3PO_4 > Na_2SO_4 >$ NaCl. The addition of NaSCN increased the CMC, consistent with its action as a water structure breaker.

Tetraalkytammonium cations increase the CMC values of POE nonionics, the order of their effectiveness in increasing them being $(C_3H_7)_4N^+ > (C_2H_5)_4N^+ > (CH_3)_4N^+$. This is the order of their effectiveness in water structure breaking.

IV.C. Organic Additives

Small amounts of organic materials may produce marked changes in the CMC in aqueous media. Since some of these materials may be present as impurities or by-products of the manufacture of surfactants, their presence may cause significant differences in supposedly similar commercial surfactants. A knowledge of the effects of organic materials on the CMC of surfactants is therefore of great importance for both theoretical and practical purposes.

To understand the effects produced, it is necessary to distinguish between two classes of organic materials that markedly affect the CMCs of aqueous solutions surfactants: class I, materials that affect the CMC by being incorporated into the micelle; and class II, materials that change the CMC by modifying solvent–micelle or solvent–surfactant interactions.

1. Class I Materials Materials in the first class are generally polar organic compounds, such as alcohols and amides. They affect the CMC at much lower liquid phase concentrations than those in the second class. Water-soluble compounds in this class may operate as members of the first class at low bulk phase concentrations (Miyagishi, 1976) and, at high bulk phase concentrations, as members of the second class.

Members of class I reduce the CMC. Shorter-chain members of the class are probably adsorbed mainly in the outer portion of the micelle close to the water–micelle "interface." The longer-chain members are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules. Adsorption of the additives in these fashions decreases the work required for micellization, in the case of ionic surfactants probably by decreasing the mutual repulsion of the ionic heads in the micelle.

Depression of the CMC appears to be greater for straight-chain compounds than for branched ones and increases with chain length to a maximum when the length of the hydrophobic group of the additive approximates that of the surfactant. An explanation for these observations (Schick, 1957) is that those molecules that are most effective at reducing the CMC are solubilized in the outer portion of the micelle core and are there under lateral pressure tending to force them into the inner portion of the core. This pressure increases with the cross-sectional area of the molecule. Thus, straight-chain molecules, with smaller cross-sectional areas than branched-chain ones, have a greater tendency to remain in this outer portion and consequently reduce the CMC more than do the latter, which are forced into the interior. Another factor may be the greater degree of interaction between the hydrophobic group of the surfactant and the hydrophobic chain of the additive when the latter is straight rather than branched. This also would tend to keep straight-chain molecules, compared to branched-chain ones, in the outer portions of the micelle. It also explains the greater effect on the CMC of additives containing hydrophobic groups of approximately the same length as those of the surfactant molecules comprising the micelle, since in this condition maximum interaction between hydrophobic groups in additive and surfactant is obtained.

Additives that have more than one group capable of forming hydrogen bonds with water in a terminal polar grouping appear to produce greater depressions of the CMC than those with only one group capable of hydrogen bonding to water. Here the explanation offered (Schick, 1957) is that hydrogen bonding between the polar groups of the additive and water molecules helps counterbalance the lateral pressure tending to push the additive into the interior of the micelle. Therefore, a higher proportion of those additives with more than one group capable of forming hydrogen bonds with water will remain in the outer core between the surfactant molecules than will be the case with those with only one group of this type; consequently, the CMC will be reduced more by the former type of additive.

Just as polar compounds that are believed to penetrate into the inner portion of the core produce only small depressions of the CMC, so, too, hydrocarbons, which are solubilized in the inner portion of the core, decrease the CMC only slightly. Very short-chain polar compounds, (e.g., dioxane and ethanol) at low bulk phase concentrations also depress the CMC, but the effect here, too, is small (Shirahama, 1965). In these compounds, adsorption probably occurs on the surface of the micelle, close to the hydrophilic head.

2. Class II Materials Members of class II change the CMC, but at bulk phase concentrations usually considerably higher than those at which class I members are effective. The members of this class change the CMC by modifying the interaction of water with the surfactant molecule or with the micelle, doing this by modifying the structure of the water, its dielectric constant, or its solubility parameter (cohesive energy density). Members of this class include urea, formamide, *N*-methylacetamide, guanidinium salts, short-chain alcohols, water-soluble esters, dioxane, ethylene glycol, and other polyhydric alcohols such as fructose and xylose.

Urea, formamide, and guanidinium salts are believed to increase the CMC of surfactants in aqueous solution, especially polyoxyethy-lenated nonionics because of their disruption of the water structure (Schick, 1965). This may increase the degree of hydration of the hydrophilic group, and since hydration of the hydrophilic group opposes micellization, may cause an increase in the CMC. These water structure breakers may also increase the CMC by decreasing the entropy effect accompanying micellization (Section VIII). The hydrophobic hydrocarbon chain of the surfactant is believed to create structure in the liquid water phase when it is dissolved in it, and its removal from it via micellization consequently produces an increase in the entropy of the system that favors micellization. The presence of structure breakers in the aqueous phase may disrupt the organization of the water produced by the dissolved hydrophobic group, thereby decreasing the entropy increase on micellization. Since the entropy increase favoring micellization is decreased, a higher bulk concentration of surfactant is needed for micelle formation; that is, the CMC is increased.

Materials that promote water structure, such as xylose or fructose (Schwuger, 1971), for similar reasons decrease the CMC of the surfactant.

The effect of urea on the CMC of ionic surfactants is smaller and complex. Although urea addition was found to increase the CMCs of $C_{12}H_{25}SO_4^-Li^+$ and $C_{14}H_{29}SO_4^-NH_2(C_2H_5)_2^+$, it decreased slightly the CMCs or $C_8F_{17}SO_4^-Li^+$ and $C_8F_{17}COO^-Li^+$. It is suggested that the effect here may be due to direct action of the urea, replacing the water surrounding the hydrophilic head group (Asakawa, 1995).

Dioxane, ethylene glycol, water-soluble esters, and short-chain alcohols at high bulk phase concentrations may increase the CMC because they decrease the cohesive energy density, or solubility parameter, of the water, thus increasing the solubility of the monomeric form of the surfactant and hence the CMC (Schick, 1965). An alternative explanation for the action of these compounds in the case of ionic surfactants is based on the reduction of the dielectric constant of the aqueous phase that they produce (Herzfeld, 1950). This would cause increased mutual repulsion of the ionic heads in the micelle, thus opposing micellization and increasing the CMC.

IV.D. The Presence of a Second Liquid Phase

The CMC of the surfactant in the aqueous phase is changed very little by the presence of a second liquid phase in which the surfactant does not dissolve appreciably and which, in turn, either does not dissolve appreciably in the aqueous phase or is solubilized only in the inner core of the micelles (e.g., saturated aliphatic hydrocarbons). When the hydrocarbon is a short-chain unsaturated, or aromatic hydrocarbon, however, the value of the CMC is significantly less than that in air, with the more polar hydrocarbon causing a larger decrease (Rehfeld, 1967; Vijayendran, 1979; Murphy, 1988). This is presumably because some of this second liquid phase adsorbs in the outer portion of the surfactant micelle and acts as a class I material (Section C). On the other hand, the more polar ethyl acetate increases the CMC of sodium dodecyl sulfate slightly, presumably either because it has appreciable solubility in water and thus increases its solubility parameter, with consequent increase in the CMC of the surfactant, or because the surfactant has appreciable solubility in the ethyl acetate phase, thus decreasing its concentration in the aqueous phase with consequent increase in the CMC.

IV.E. Temperature

The effect of temperature on the CMC of surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. From the data available, the minimum in the CMC–temperature curve appears to be around 25°C for ionics (Flockhart, 1961) and around 50°C for nonionics (Crook, 1963; Chen, 1998). For bivalent metal alkyl sulfates, the CMC appears to be practically independent of the temperature (Mujamoto, 1960). Data on the effect of temperature on zwitterionics are limited. They appear to indicate a steady decrease in the CMC of alkylbetaines with increase in the temperature in the range 6–60°C (Tori, 1963b; Dahayanake, 1984). Whether further increase in temperature will cause an increase in the CMC is not evident from the data.

V. MICELLIZATION IN AQUEOUS SOLUTION AND ADSORPTION AT THE AQUEOUS SOLUTION–AIR OR AQUEOUS SOLUTION–HYDROCARBON INTERFACE

Although similar factors, such as the structure of the surfactant molecule and the microenvironmental conditions surrounding it, affect both micellization and adsorption, the effect of these factors on these two phenomena are generally not equal.

Steric factors in the surfactant molecule, such as the presence of a bulky hydrophilic or hydrophobic group, inhibit micellization more than they do adsorption at the aqueous solution–air interface. On the other hand, electrical factors such as the presence of an ionic, rather than a nonionic, hydrophilic group in the surfactant molecule, appear to inhibit adsorption at the aqueous solution–air interface more than they do micellization.

V.A. The CMC/C_{20} Ratio

A convenient way of measuring the relative effects of some structural or microenvironmental factor on micellization and on adsorption is to determine its effect on the CMC/C_{20} ratio, where C_{20} (Chapter 2, Section IIIE) is the concentration of surfactant in the bulk phase that produces a reduction of 20 dyn/cm in the surface tension of the solvent. An increase in the CMC/C_{20} ratio as a result of the introduction of some factor indicates that micellization is inhibited more than adsorption or adsorption facilitated more than micellization; a decrease in the CMC/C_{20} ratio indicates that adsorption is inhibited more than micellization or micellization facilitated more than adsorption. The CMC/C_{20} ratio, therefore, affords insights into the adsorption and micellization processes. The CMC/C_{20} ratio is also an important factor in determining the value to which the surface tension of the solvent can be reduced by the presence in its solution of the surfactant (Chapter 5, Section IIB).

Some CMC/C_{20} ratios are listed in Table 3-5. The data show that for single-chain compounds of all types listed the CMC/C_{20} ratio:

1. Is not increased substantially by increase in the length of the alkyl chain of the hydrophobic group (from C_{10} to C_{16}) in ionic surfactants.
2. Is increased by the introduction of branching in the hydrophobic group or positioning of the hydrophilic group in a central position in the molecule.
3. Is increased by the introduction of a larger hydrophilic group.
4. Is increased greatly for ionic surfactants by increase in the ionic strength of the solution or by the use of a more tightly bound counterion, especially one containing an alkyl chain of six or more carbon atoms. For a nonionic surfactant, the effect of the addition of electrolyte is more complex, depending upon the nature of the electrolyte added, its salting-in or salting-out effect, and its possible complex formation with the nonionic. In some cases the CMC/C_{20} ratio is increased, in other cases it is decreased by the addition of electrolyte, and in still others there is little effect.
5. Is decreased by an increase in temperature in the range 10–40°C.
6. Is increased considerably by the replacement of a hydrocarbon chain by a fluorocarbon- or silicone-based chain.
7. Is increased considerably by the replacement of air as the second phase at the interface by a saturated aliphatic hydrocarbon and decreased slightly when the second liquid phase is a short-chain aromatic or unsaturated hydrocarbon.

The greater steric effect on micellization than on adsorption at the aqueous solution–air interface is illustrated by (2), (3), (5), and (6); the greater effect of the electrical factor on adsorption than on micellization is illustrated by (4). The greater difficulty of accommodating a bulky hydrophobic group in the interior of a spherical or cylindrical micelle rather than at a planar interface (e.g., air–water) is presumably the reason for observations (2) and (6) above. The increase in the CMC/C_{20} ratio with replacement of air by a saturated aliphatic hydrocarbon is due to an increased tendency to adsorb at the latter interface (as evidenced by larger pC_{20} values, Table 2-2), while the micellization tendency is not changed significantly. The small decrease in the ratio when the second phase is an aromatic or unsaturated hydrocarbon is due to the increased tendency to form micelles, which is almost equaled by the increased tendency to adsorb.

For POE nonionics, (1) the ratio increases with increase in the number of OE units in the POE chain at constant hydrophobic chain length, the effect becoming less pronounced as the number of EO units increases, and (2) the ratio decreases with increase in the length of the alkyl chain, at constant number of EO units in the POE chain. The first effect is due to the increase in the size of the hydrophilic head

TABLE 3-5 CMC/C_{20} Ratios

Compound	Solvent	Temp. (°C)	CMC/C_{20} Ratio	Reference
	Anionics			
$C_{10}H_{21}OCH_2COO^-Na^+$	0.1 *M* NaCl (aq.), pH 10.5	30	$4._9$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$	H_2O, pH 10.5	30	$3._5$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$	0.1 *M* NaCl (aq.), pH 10.5	30	$6._5$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$	H_2O, pH 10.5	30	$3._7$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$	0.1 *M* NaCl (aq.), pH 10.5	30	$6._9$	Tsubone, 2001
$(CF_3)_2CF(CF_2)_4COO^-Na^+$	H_2O	25	$11._1$	Shinoda, 1977
$C_7F_{15}COO^-Na^+$	H_2O	25	$9._5$	Shinoda, 1977
$C_7F_{15}COO^-K^+$	H_2O	25	$10._8$	Shinoda, 1977
$C_{10}H_{21}SO_3^-Na^+$	H_2O	10	$2._4$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	H_2O	25	$2._1$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	H_2O	40	$1._8$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaCl (aq.)	25	$4._1$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	0.5 *M* NaCl (aq.)	25	$5._4$	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	H_2O	25	$2._0$	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	0.1 *M* NaCl (aq.)	25	$4._5$	Dahanayake, 1986
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	0.5 *M* NaCl (aq.)	25	$7._1$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	H_2O	25	$2._8$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl (aq.)	25	$5._9$	Dahanayake, 1986
$C_{16}H_{33}SO_3^-K^+$	H_2O	60	$1._9$	Rosen, 1968
Branched $C_{12}H_{25}SO_4Na^b$	H_2O	25	$11._3$	Varadaraj, 1992
Branched $C_{12}H_{25}SO_4Na^b$	0.1 *M* NaCl	25	$15._2$	Varadaraj, 1992
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	$2._6$	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	0.1 *M* NaCl (aq.)	25	$6._0$	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	H_2O (1-hexene satd.)	25	$1._5$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O (benezene satd.)	25	$2._2$	Rehfeld, 1967

(*Continued next page*)

TABLE 3-5 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC/C_{20} Ratio	Reference
$C_{12}H_{25}SO_4^-Na^+$	H_2O (cyclohexane satd.)	25	$4._9$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O (octane satd.)	25	$4._7$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	H_2O (heptadecane satd.)	25	$4._8$	Rehfeld, 1967
$C_{14}H_{29}SO_4^-Na^+$	H_2O	25	$2._6$	Lange, 1968
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	H_2O	25	$2._6$	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.1 *M* NaCl	25	$7._3$	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	0.5 *M* NaCl	25	$8._3$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	10	$2._8$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	25	$2._5$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	40	$2._0$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.1 *M* NaCl (aq.)	25	$6._7$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	0.5 *M* NaCl (aq.)	25	$10._0$	Dahanayake, 1986
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O	70	$1._4$	Lange, 1964
p-$C_{10}H_{21}C_6H_4SO_3^-Na^+$	H_2O	70	$1._4$	Lange, 1964
$C_{11}H_{23}$-2-$C_6H_4SO_3^-Na^+$	“Hard river” water (I.S. = 6.6×10^{-3} *M*)[d]	30	$9._7$	Zhu, 1998
p-(1,3,5,7-tetra Me)$C_8H_{17}C_6H_4SO_3^-Na^+$	H_2O	75	$2._8$	Greiss, 1955
$C_{12}H_{25}$-2-$C_6H_4SO_3^-Na^+$	“Hard river” water (I.S. = 6.6×10^{-3} *M*)[d]	30	$5._0$	Zhu, 1998
$C_{12}H_{25}$-4-$C_6H_4SO_3^-Na^+$	“Hard river” water (I.S. = 6.6×10^{-3} *M*)[d]	30	$17._4$	Zhu, 1998
$C_{12}H_{25}$-6-$C_6H_4SO_3^-Na^+$	“Hard river” water (I.S. = 6.6×10^{-3} *M*)[d]	30	$21._5$	Zhu, 1998
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	H_2O	70	$1._3$	Lange, 1964
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	H_2O	75	$1._5$	Greiss, 1955
$C_{12}H_{25}C_6H_4SO_3^-Na^+$[c]	0.1 *M* NaCl	25	$11._6$	Murphy, 1990

$C_{13}H_{27}$-2-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. = 6.6×10^{-3} *M*)[d]	30	$3._1$	Zhu, 1998
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	H_2O	30	$7._6$	Zhu, 1998
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	"Hard river" water (I.S. = 6.6×10^{-3} *M*)[d]	30	$15._8$	Zhu, 1998
p-$C_{14}H_{29}C_6H_4SO_3^-Na^+$	H_2O	70	$1._5$	Lange, 1964
p-$C_{16}H_{33}C_6H_4SO_3^-Na^+$	H_2O	70	$1._9$	Lange, 1964
$C_{16}H_{33}$-7-$C_6H_4SO_3Na$	H_2O	45	$14._4$	Lascaux, 1983
$C_4H_9OOCCH_2CH(SO_3^-Na^+)COOC_4H_9$	H_2O	25	$5._6$	Williams, 1957
$C_6H_{13}OOCCH_2CH(SO_3^-Na^+)COOC_6H_{13}$	H_2O	25	$11._0$	Williams, 1957
$C_4H_9CH(C_2H_5)CH_2COOCH_2CH(SO_3^-Na^+)$-$COOCH_2CH(C_2H_5)C_4H_9$	H_2O	25	28.	Williams, 1957
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$	H_2O, pH 10.5	30	$2._0$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$	0.1 *M* NaCl (aq.), pH 10.5	30	$5._5$	Tsubone, 2001
	Cationics			
$C_{10}H_{21}N(CH_3)_3^+Br^-$	0.1 *M* NaCl (aq.)	25	$2._7$	Li, 2001
$C_{12}H_{25}N^+(CH_3)_3Br^-$	H_2O	25	$2._4$	Zhu, 1985
$C_{12}H_{25}N^+(CH_3)_3Br^-$	0.1 *M* NaBr (aq.)	25	$6._9$	Zhu, 1985
$C_{12}H_{25}N(CH_3)_3^+Cl^-$	0.1 *M* NaCl (aq.)	25	$3._0$	Li, 2001
$C_{14}H_{29}N^+(CH_3)_3Br^-$	H_2O	30	$2._4$	Venable, 1964
$C_{12}H_{25}Pyr^+Br^-$[a]	H_2O	10	$2._7$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^-$[a]	H_2O	25	$2._5$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^-$[a]	H_2O	40	$2._1$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^-$[a]	0.1 *M* NaBr (aq.)	25	$6._9$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^-$[a]	0.5 *M* NaBr (aq.)	25	$8._9$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^-$	H_2O	10	$2._3$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^-$	H_2O	25	$2._0$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^-$	H_2O	40	$1._8$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^-$	0.1 *M* NaCl (aq.)	25	$4._6$	Rosen, 1982b

(*Continued next page*)

TABLE 3-5 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC/C_{20} Ratio	Reference
$C_{12}H_{25}Pyr^+Cl^-$	0.5 *M* NaCl (aq.)	25	$5._5$	Rosen, 1982b
$C_{12}H_{25}NPyr^+I^{-a}$	H_2O	25	$2._4$	Mandru, 1972
	Anionic-Cationic Salts			
$C_{10}H_{21}N(CH_3)_3{}^+ \cdot C_{10}H_{21}SO_4{}^-$	H_2O	25	$9._1$	Corkill, 1983a, b
$C_{12}H_{25}SO_3{}^- \cdot {}^+HON(CH_3)_2C_{12}H_{25}$	H_2O	25	$13._6$	Rosen, 1964
	Zwitterionics			
$C_{10}H_{21}N^+(CH_3)_2CH_2COO^-$	H_2O	23	$7._0$	Beckett, 1963
$C_{10}H_{21}CH(Pyr^+)COO^-$	H_2O	25	$3._9$	Zhao, 1984
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	10	$13._8$	Dahanayake, 1984
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	25	$12._0$	Dahanayake, 1984
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	40	$8._7$	Dahanayake, 1984
$C_{10}H_{21}CH(COO^-)N(CH_3)_3{}^+$	H_2O	27	$5._7$	Tori, 1963b
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2CH_2SO_3{}^-$	H_2O	40	$7._6$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	H_2O	23	$6._5$	Beckett, 1963
$C_{12}H_{25}CH(Pyr^+)COO^-$	H_2O	25	$5._7$	Zhao, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	10	$15._8$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	25	$14._4$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	40	$11._0$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.1 *M* NaCl (aq.), pH 5.7	25	$15._1$	Rosen, 2001
$C_{12}H_{25}CH(COO^-)N(CH_3)_3{}^+$	H_2O	27	$7._8$	Tori, 1963b
$C_{14}H_{29}N(CH_3)_2CH_2COO^-$	H_2O	25	$7._5$	Beckett, 1963
$C_{14}H_{29}CH(Pyr^+)COO^-$	H_2O	40	$6._2$	Zhao, 1984
$C_{16}H_{33}N(CH_3)_2CH_2COO^-$	H_2O	23	$6._9$	Beckett, 1963

	Nonionics			
$C_8H_{17}OCH_2CH_2OH$	H_2O	25	$7._2$	Shinoda, 1959
$C_8H_{17}CHOHCH_2OH$	H_2O	25	$9._6$	Kwan, 1980
$C_8H_{17}CHOHCH_2CH_2OH$	H_2O	25	$8._9$	Kwan, 1980
$C_{12}H_{25}CHOHCH_2CH_2OH$	H_2O	25	$7._7$	Kwan, 1980
β-decyl glucoside	0.1 *M* NaCl, pH = 9	25	$11._1$	Li, 2001
β-Decyl maltoside	0.1 *M* NaCl, pH = 9	25	$6._5$	Li, 2001
β-Dodecyl maltoside	0.1 *M* NaCl, pH = 9	25	$7._1$	Li, 2001
$C_{11}H_{23}CON(CH_2CH_2OH)_2$	H_2O	25	$6._3$	Rosen, 1964
$C_{11}H_{23}CON(CH_3)CH_2CHOHCH_2OH$	0.1 *M* NaCl	25	$10._9$	Zhu, 1999
$C_{10}H_{21}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$10._5$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$8._7$	Zhu, 1999
$C_{12}H_{25}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$7._8$	Zhu, 1999
$C_{13}H_{27}CON(CH_3)CH_2(CHOH)_4CH_2OH$	0.1 *M* NaCl	25	$4._0$	Zhu, 1999
$C_{10}H_{21}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$5._2$	Burczyk, 2001
$C_{12}H_{25}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$8._8$	Burczyk, 2001
$C_{14}H_{29}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$8._5$	Burczyk, 2001
$C_{16}H_{33}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$10._1$	Burczyk, 2001
$C_{18}H_{37}N(CH_3)CO(CHOH)_4CH_2OH$	H_2O	20	$8._1$	Burczyk, 2001
$C_8H_{17}(OC_2H_4)_5OH$	H_2O	25	$12._7$	Varadaraj, 1991b
$C_8H_{17}(OC_2H_4)_5OH$	H_2O	40	$15._1$	Varadaraj, 1991b
$C_8H_{17}(OC_2H_4)_5OH$	0.1 *M* NaCl	25	$8._4$	Varadaraj, 1991b
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O	25	$16._7$	Meguro, 1981
4-branched $C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	25	$23._0$	Varadaraj, 1991b
4-branched $C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	40	$37._6$	Varadaraj, 1991b
4-branched $C_{12}H_{25}(OC_2H_4)_5OH$	0.1 *M* NaCl	40	$19._2$	Varadaraj, 1991b
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O	25	$11._4$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	10	$17._9$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	25	$13._7$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	40	$11._8$	Rosen, 1982a

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TABLE 3-5 (*Continued*)

Compound	Solvent	Temp. (°C)	CMC/C_{20} Ratio	Reference
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	25	$15._0$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$	0.1 *M* NaCl	25	$18._5$	Varadaraj, 1991
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	10	$17._1$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	25	$14._9$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	40	$13._9$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	10	$17._5$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	25	$17._3$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	40	$15._4$	Rosen, 1982a
6-branched $C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	25	$43._0$	Varadaraj, 1991b
6-branched $C_{13}H_{27}(OC_2H_4)_5OH$	0.1 *M* NaCl	25	$35._7$	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	25	$10._7$	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_5OH$	H_2O	40	$19._0$	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_5OH$	0.1 *M* NaCl	25	$8._8$	Varadaraj, 1991b
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O	25	$11._3$	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O	25	$8._4$	Meguro, 1981
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O	25	$7._1$	Meguro, 1981
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_3OH$	H_2O	25	$11._1$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_3OH$	H_2O	55	$8._9$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_4OH$	H_2O	25	$17._3$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_4OH$	H_2O	55	$10._7$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_6OH$	H_2O	25	$18._2$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_6OH$	H_2O	55	$10._9$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_8OH$	H_2O	25	$21._5$	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	H_2O	25	$17._4$	Crook, 1964

[a] Pyr^+, pyridinium.

[b] From dodecyl alcohol with 4.4 methyl branches in the molecule.

[c] Commercial material.

[d] I.S. = ionic strength.

with this change; the second effect may reflect the larger diameter of the micelle as the alkyl chain is increased, with a resulting larger surface area to accommodate the hydrophilic head groups.

The decrease in the CMC/C_{20} ratio with increase in temperature (10–40°C) presumably occurs either because the size of the hydrophilic group decreases as a result of dehydration with this change or because the surface area of the micelle increases with this change.

In general, then, ionic surfactants (both anionic and cationic) with a single straight-chain hydrophobic group, in distilled water against air at room temperature, show low CMC/C_{20} ratios of 3 or less, while POE nonionics under the same conditions show ratios of about 7 or more. Increase in the electrolyte content of the solution causes the CMC/C_{20} ratios of ionics to approach those of nonionics. Zwitterionics have CMC/C_{20} ratios intermediate between those of ionics and POE nonionics.

VI. CMCs IN NONAQUEOUS MEDIA

When the structure of the solvent is not distorted significantly by the presence in it of a surfactant, a CMC of the type observed in aqueous media is not present (Ruckenstein, 1980). There is no sharp change in aggregation number over a narrow concentration range and consequently no marked change in the surface or bulk properties of the solution in that region. In nonpolar solvents, the surfactant molecules may aggregate due to dipole–dipole interactions between the hydrophilic head groups, producing structures that have been called *reverse micelles*, with the head groups oriented toward each other in the interior of the structure and the hydrophobic groups oriented toward the nonpolar solvent. However, in the absence of additives such as water, the aggregation numbers are generally so small (seldom exceeding 10) that analogies with micelles in aqueous media are misleading. When the polarity of the solvent is large, solvent–surfactant interaction is not very different from that between surfactant molecules themselves and the latter consequently remain essentially individually dissolved. In ethylene glycol, glycerol, and similar solvents having multiple hydrogen-bonding capacity, surfactant aggregates are assumed to have the normal structure.

Some investigators have assigned a CMC value to the range where a discontinuity appears in the plot of some property of the surfactant solution in nonaqueous media, even when the change is not sharp. Some values are listed in Table 3-6.

VII. EQUATIONS FOR THE CMC BASED ON THEORETICAL CONSIDERATIONS

Equations relating the CMC to the various factors that determine it have been derived from theoretical considerations by Hobbs (1951), Shinoda (1953), and Molyneux (1965). These equations are based on the fact that for nonionics the CMC

TABLE 3-6 CMCs of Surfactants in Nonaqueous Media

Surfactant	Temp. (°C)	Solvent	CMC (*M*)	Reference
$C_4H_9NH_3{}^+ \cdot C_2H_5COO^-$	30	Benzene	$(4.5-5.5) \times 10^{-2}$	Fendler, 1973b
$C_4H_9NH_3{}^+ \cdot C_2H_5COO^-$	30	CCl_4	$(2.3-2.6) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH^{+3} \cdot C_2H_5COO^-$	30	Benzene	$(1.5-1.7) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH_3{}^+ \cdot C_2H_5COO^-$	30	CCl_4	$(2.6-3.1) \times 10^{-2}$	Fendler, 1973b
$C_{12}H_{25}NH_3{}^+ \cdot C_2H_5COO^-$	30	Benzene	$(3–7) \times 10^{-3}$	Fendler, 1973b
$C_{12}H_{25}NH_3{}^+ \cdot C_2H_5COO^-$	30	CCl_4	$(2.1-2.5) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH_3{}^+ \cdot C_5H_{11}COO^-$	30	Benzene	$(4.1-4.5) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH_3{}^+ \cdot C_5H_{11}COO^-$	30	CCl_4	$(4.2-4.5) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH_3{}^+ \cdot C_{13}H_{27}COO^-$	30	Benzene	$(1.9-2.2) \times 10^{-2}$	Fendler, 1973b
$C_8H_{17}NH_3{}^+ \cdot C_{13}H_{27}COO^-$	30	CCl_4	$(2.8-4.0) \times 10^{-2}$	Fendler, 1973b
$C_{12}H_{25}NH_3{}^+ \cdot C_3H_7COO^-$	10	Benzene	3×10^{-3}	Kitahara, 1956
$C_{12}H_{25}NH_3{}^+ \cdot C_5H_{11}COO^-$	10	Benzene	18×10^{-3}	Kitahara, 1956
$C_{12}H_{25}NH_3{}^+ \cdot C_7H_{15}COO^-$	10	Benzene	20×10^{-3}	Kitahara, 1956
$C_{18}H_{37}NH_3{}^+ \cdot C_3H_7COO^-$	10	Benzene	5×10^{-3}	Kitahara, 1956
Na bis (2-ethylhexyl)-sulfosuccinate	20	Benzene	3×10^{-3}	Kon-no, 1965
Na bis(2-ethylhexyl)-sulfosuccinate	25	Pentane	4.9×10^{-4}	Eicke, 1976
$C_9H_{19}C_6H_4(OC_2H_4)_9OH$	27.5	Glycerol	8.0×10^{-6}	Ray, 1971a
$C_9H_{19}C_6H_4(OC_2H_4)_9OH$	27.5	Ethylene glycol	7.1×10^{-4}	Ray, 1971a
$C_9H_{19}C_6H_4(OC_2H_4)_9OH$	27.5	Propylene glycol	5.0×10^{-2}	Ray, 1971a
$C_{12}H_{25}(OC_2H_4)_2OH$	—	Benzene	7.6×10^{-3}	Becher, 1960
$C_{13}H_{27}(OC_2H_4)_6OH$	—	Benzene	2.6×10^{-3}	Becher, 1960
$C_{12}H_{25}Pyr^+Br^a$	40	Benzene	5.5×10^{-3}	Miyagishi, 1977
$C_{18}H_{37}Pyr^+Br$	40	Benzene	4.4×10^{-3}	Miyagishi, 1977
$C_6F_{13}(CH_2)_3(OC_2H_4)_2OH$	—	C_6F_6	9.3×10^{-3}	Mathis, 1980
$C_8F_{17}C_2H_4N(C_2H_4OH)_2$	—	C_6F_6	3.65×10^{-4}	Mathis, 1980

[a] Pyr^+, pyridinium.

is related to the free energy change ΔG_{mic} associated with the aggregation of the individual surfactant molecules to form micelles by the expression

$$\Delta G_{\text{mic}} = 2.3RT \log x_{\text{CMC}} \tag{3.4}$$

x_{CMC} is the mole fraction of the surfactant in the liquid phase at the CMC. In aqueous solutions where the CMC is generally $<10^{-1}$ M, $x_{\text{CMC}} = \text{CMC}/\omega$ without significant error, and

$$\Delta G_{\text{mic}} = 2.3RT(\log \text{CMC} - \log \omega) \tag{3.5}$$

from which

$$\log \text{CMC} = \frac{\Delta G_{\text{mic}}}{2.3RT} + \log \omega \tag{3.6}$$

where ω is the molar concentration of water (55.3 at 25°C).

ΔG_{mic} can be broken into contributions from the component parts of the surfactant molecule, $\text{CH}_3(\text{CH}_2)_m W$, where $W =$ the hydrophilic group, in the following fashion:

$$\Delta G_{\text{mic}} = \Delta G_{\text{mic}}(\text{—CH}_3) + m\Delta G_{\text{mic}}(\text{—CH}_2\text{—}) + \Delta G_{\text{mic}}(\text{—}W) \tag{3.7}$$

Studies on the solubility of alkanes in water indicate that $\Delta G_{\text{mic}}(\text{—CH}_3)$ does not change with increase in the length of the alkyl chain and can be represented by $\Delta G_{\text{mic}}(\text{—CH}_3) = \Delta G_{\text{mic}}(\text{—CH}_2\text{—}) + k$, where k is a constant. Thus

$$\log \text{CMC} = \frac{\Delta G_{\text{mic}}(-W) + k}{2.3RT} + \log \omega + \left[\frac{\Delta G_{\text{mic}}(\text{—CH}_2\text{—})}{2.3RT}\right] N \tag{3.8}$$

where $N = m + 1$, the total number of carbon atoms in the hydrophobic group.

If we assume that the contribution of the hydrophilic head group $\Delta G(-W)$ and the fraction of counterions bound to the micelle, α, do not change with increase in the length of the hydrophobic group, then for any homologous series of surfactants, the relations between the CMC and the number of carbon atoms in the hydrophobic group can be put into the form

$$\log \text{CMC} = A - BN \tag{3.1}$$

where

$$A = \frac{-\Delta G_{\text{mic}}(-W) + k}{2.3RT} + \log \omega \tag{3.9}$$

and

$$B = \frac{-\Delta G_{\mathrm{mic}}(\text{—CH}_2\text{—})}{2.3RT} \tag{3.10}$$

Thus A and B are constants reflecting the free energy changes involved in transferring the hydrophilic group and a methylene unit of the hydrophobic group, respectively, from an aqueous environment to the micelle. This accounts for both the form of the empirical relation between the CMC and the number of carbon atoms in the hydrophobic group that has been discussed previously, and the relatively small variation of B in different homologous series of ionic surfactants.

We can also see from equations 3.1 and 3.10 and the experimental values of B given in Table 3-4 that the free energy change $\Delta G(\text{—CH}_2\text{—})$ involved in the transfer of a methylene unit of the hydrophobic group from an aqueous environment to the interior of the micelle is negative, thus favoring micellization, which accounts for the fact that the CMC decreases with increase in the length of the hydrophobic group. From equation 3.9 and the values of A in Table 3-4 we can see that the free energy change involved in the transfer of the hydrophilic group from an aqueous environment to the exterior of the micelle is positive, and therefore oppose micellization.

If the value of the CMC is replaced by the *activity* of the surfactant at the CMC (CMA), and log CMA is plotted against N (Nakagaki, 1984), then the value of the slope B for ionics is close to that for nonionics and zwitterionics, indicating similar values for $-\Delta G_{\mathrm{mic}}$ $(\text{—CH}_2\text{—})$, the free energy change involved in the transfer of a methylene group from the aqueous solution to the micelle, for all types of surfactants. The value of CMA is obtained for univalent surfactants such as sodium alkyl sulfates or alkyltrimethylammonium halides from

$$\mathrm{CMA} = f_{\pm}^{2}\mathrm{CMC}(\mathrm{CMC} + C_i) \tag{3.11}$$

and in the case of divalent surfactants, such as disodium alkyl phosphates, from

$$\mathrm{CMC} = f_{\pm}^{3}\mathrm{CMC}(\mathrm{CMC} + C_i)^2 \tag{3.12}$$

where C_i is the concentration of added electrolyte with a common counterion and $f_{\pm}$ is the mean ionic activity coefficient of the surfactant, calculated by

$$\log f_{\pm} = \frac{-A \mid Z^{+} \cdot Z^{-} \mid (I)^{1/2}}{1 + (I)^{1/2}} \tag{3.13}$$

Z^{+}, Z^{-} are the valences of the ions comprising the surfactant, I is the ionic strength of the solution, and $A = 1.825 \times 10^{6}(DT)^{3/2}$, with D being the dielectric constant of the solvent.

The value of $\Delta G_{\text{mic}}(\text{—CH}_2\text{—})$ obtained in this fashion falls in the range −(2.8–3.3) kJ[−(708–777)cal]/mol for all types of surfactants (nonionics, zwitterionics, uni- and divalent ionics), irrespective of the presence or amount of added electrolyte.

For ionic surfactants $\Delta G(-W)$, the electrical energy E_{e1} involved in transferring the ionic hydrophilic group from an aqueous environment to the micelle is given, when the aggregation number is not too small, by (Shinoda, 1977)

$$E_{\text{el}} = (K_g/Z_i)RT\left(\ln\frac{2000\pi\sigma^2}{\varepsilon_r RT} - \ln C_i\right) \tag{3.14}$$

where (K_g/Z_i) is the slope of the plot of CMC versus total concentration C_i, in equivalents per liter, of the counterions of charge Z_i in the solution, σ is the charge density on the micelle surface, ε_r is the dielectric constant of the solvent, and K_g is the effective coefficient of electrical energy of micellization. From this,

$$\begin{aligned}\log \text{CMC} = {} & K_g/Z_i\left(\log\frac{2000\pi\sigma^2}{\varepsilon_r RT} - \log C_i\right) \\ & + \left[\frac{\Delta G(-\text{CH}_2-)}{2.3RT}\right]N + \text{constant}\end{aligned} \tag{3.15}$$

Equation 3.15 predicts the effect of electrolyte on the CMC of ionic surfactants, indicating that the log of the CMC will decrease linearly with log C_i, which is in accordance with experimental findings (equation 3.3). It also indicates that the CMC of ionic surfactants will decrease with increase in the extent of binding of the counterion to the micelle since that decreases the charge density on the micellar surface. Organic additives that decrease the dielectric constant of the solvent will increase the CMC of the surfactant, both of which are consistent with the experimental results discussed previously. The effect of temperature on the CMC of ionic surfactants is difficult to predict from equation 3.15. An increase in the temperature should cause a direct decrease in the CMC, but since an increase in temperature causes a decrease in the dielectric constant ε_r of the solvent and may also affect σ, the overall effect of an increase in temperature is not readily determinable from the equation alone.

VIII. THERMODYNAMIC PARAMETERS OF MICELLIZATION

As is evident from the previous discussion, a clear understanding of the process of micellization is necessary for rational explanation of the effects of structural and environmental factors on the value of the CMC and for predicting the effects on it of new structural and environmental variations. The determination of thermodynamic parameters of micellization ΔG_{mic}, ΔH_{mic}, and ΔS_{mic} has played an important role in developing such an understanding.

A standard free energy of micellization $\Delta G^\circ_{\text{mic}}$ may be calculated by choosing (Molyneux, 1965) for the standard initial state of the nonmicellar surfactant species a hypothetical state at unit mole fraction x, but with the individual ions or molecules behaving as at infinite dilution, and for the standard final state, the micelle itself. For nonionic surfactants, the standard free energy of micellization is given by

$$\Delta G^\circ_{\text{mic}} = RT \ln x_{\text{CMC}} \tag{3.16}$$

When the CMC is $10^{-2}M$ or less, this can be approximated without significant error by

$$\Delta G^\circ_{\text{mic}} = 2.3\,RT \log(\text{CMC}/\omega) \tag{3.16a}$$

where the CMC is expressed in molar units and ω is the number of moles of water per liter of water at that absolute temperature T. For ionic surfactants, a standard free energy change of micellizatiori, $\Delta G^\circ_{\text{mic}}$, can be calculated by taking into account the degree of binding of the counterion to the micelle, $1 - \alpha$. Thus, for ionic surfactants of the 1:1 electrolyte type (Nakagaki, 1984; Zana, 1996),

$$\begin{aligned}\Delta G^\circ_{\text{mic}} &= RT[1 + (1 - \alpha)]\ln x_{\text{CMC}} \\ &= 2.3RT(2 - \alpha)\ln x_{\text{CMC}}\end{aligned} \tag{3.16b}$$

where α is the degree of ionization of the surfactant, measured by the ratio of the slopes of the specific conductivity versus C plotted above and below the CMC (Figure 3-6, Section IVA3, above), and χ_{CMC} is the mole fraction of the surfactant in the liquid phase at the CMC.

For ionic surfactants with divalent counterions (Zana, 1996),

$$\begin{aligned}\Delta G^\circ &= RT\,[1 + (1 - \alpha)/2]\ln \text{CMC}/\omega \\ &= 2.3\,RT\,[1 + (1 - \alpha)/2] \log \text{CMC}/\omega\end{aligned} \tag{3.16c}$$

Since

$$\Delta G^\circ_{\text{mic}} = \Delta H^\circ_{\text{mic}} - T\Delta S^\circ_{\text{mic}} \tag{3.17}$$

$$d(\Delta G^\circ_{\text{mic}})/dT = -\Delta S^\circ_{\text{mic}} \tag{3.18}$$

if $\Delta H^\circ_{\text{mic}}$ is constant over the temperature range investigated. Alternatively,

$$T^2 d(\Delta G^\circ_{\text{mic}}/T)/dT = -\Delta H^\circ_{\text{mic}} \tag{3.19}$$

if $\Delta S^\circ_{\text{mic}}$ is constant over the temperature range investigated. These relations are strictly correct only when the variation in aggregation number of the micelles with temperature is negligible (Birdi, 1974), which is often not true for polyoxyethylenated nonionics. This has usually been disregarded by most investigators.

Some values of $\Delta G^\circ_{\text{mic}}$, $\Delta H^\circ_{\text{mic}}$, and $\Delta S^\circ_{\text{mic}}$ are listed in Table 3-7. Values of $\Delta H^\circ_{\text{mic}}$ can also be determined calorimetrically, thus avoiding some of the problems mentioned here.

The data available (mainly for aqueous systems) indicate that the negative values of $\Delta G^\circ_{\text{mic}}$ are due mainly to the large positive values of $\Delta S^\circ_{\text{mic}}$. $\Delta H^\circ_{\text{mic}}$ is often positive and, even when negative, is much smaller than the value of $T\Delta S^\circ_{\text{mic}}$. Therefore, the micellization process is governed primarily by the entropy gain associated with it, and the driving force for the process is the tendency of the lyophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle.

This large entropy increase on micellization in aqueous medium has been explained in two ways: (1) structuring of the water molecules surrounding the hydrocarbon chains in aqueous medium, resulting in an increase in the entropy of the system when the hydrocarbon chains are removed from the aqueous medium to the interior of the micelle—"hydrophobic bonding" (Nemethy, 1962); (2) increased freedom of the hydrophobic chain in the nonpolar interior of the micelle compared to the aqueous environment (Stainsby, 1950; Aranow, 1960, 1961, 1965). Any structural or environmental factors that may affect solvent–lyophobic group interactions or interactions between the lyophobic groups in the interior of the micelle will therefore affect $\Delta G^\circ_{\text{mic}}$ and consequently the value of the CMC.

In aqueous medium, an increase in the length of the hydrophobic group causes an increase in the value of $\Delta S^\circ_{\text{mic}}$, and a usually smaller decreas in $\Delta H^\circ_{\text{mic}}$, making $\Delta G^\circ_{\text{mic}}$ more negative by about 3 kJ per —CH_2— group. Variations in this value, $\Delta G^\circ_{\text{mic}}$ (—CH_2—), have been ascribed (Clint, 1975) to change in the degree of nonpolarity of the interior of the micelle with change in the polarity of the hydrophilic head, since penetration of water into the micelle, at least in the vicinity of the first five or six carbon atoms adjacent to the hydrophilic head, has been pointed out by several investigators (Clifford, 1964; Benjamin, 1966; Walker, 1971).

In POE nonionics, both $\Delta H^\circ_{\text{mic}}$ and $\Delta S^\circ_{\text{mic}}$ appear to increase with increase in the number of oxyethylene units in the hydrophilic head, with the net result that $\Delta G^\circ_{\text{mic}}$ becomes slightly less negative. The increase in $\Delta H^\circ_{\text{mic}}$ is probably due to reduction in the degree of hydration of the oxyethylene groups on micellization. The change in $\Delta G^\circ_{\text{mic}}$ per oxyethylene unit above three units, $\Delta G^\circ_{\text{mic}}$ (—EO—), appears to be about one-tenth of the change in $\Delta G^\circ_{\text{mic}}$ per methylene group, $\Delta G^\circ_{\text{mic}}$ (—CH_2—), and is opposite in sign (Corkill, 1964), since EO groups oppose micellization, whereas methylene groups favor it. The terminal hydroxyl group appears to be the main structural unit opposing micellization (McDonald, 1970).

An increase in temperature seems to cause both $\Delta H^\circ_{\text{mic}}$ and $\Delta S^\circ_{\text{mic}}$ to become less positive (Hudson, 1964) in POE nonionics, presumably because both the amount of water structured by the hydrophobic chain and the amount of water bound by the hydrophilic POE group in the nonmicellar species decrease with increase in temperature, resulting in a decrease in $\Delta S^\circ_{\text{mic}}$ and $\Delta H^\circ_{\text{mic}}$, respectively. Since these two parameters have opposite effects on $\Delta G^\circ_{\text{mic}}$, it may become more negative or less negative with temperature change, depending on the relative

TABLE 3-7 Thermodynamic Parameters of Micellization

Compound	Solvent	Temp. (°C)	$\Delta G^\circ{}_{\mathrm{mic}}$ (kJ/mol)[a]	$\Delta H^\circ{}_{\mathrm{mic}}$ (kJ/mol)[a]	$T\Delta S^\circ{}_{\mathrm{mic}}$ (kJ/mol)[a]	Reference[b]
$C_{10}H_{21}SO_3^-Na^+$	H_2O	10	$-33._3$			Dahanayake, 1986
				-3	$+3_1$	
$C_{10}H_{21}SO_3^-Na^+$	H_2O	25	$-34._9$			Dahanayake, 1986
				$+8$	$+4_4$	
$C_{10}H_{21}SO_3^-Na^+$	H_2O	40	$-37._0$			Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	H_2O	10	$39._7$			Dahanayake, 1986
				$+5$	$+4_6$	
$C_{12}H_{25}SO_3^-Na^+$	H_2O	40	$-42._0$			Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	H_2O	21	$-42._4$			Mukerjee, 1967
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	H_2O	10	$-34._7$			Dahanayake, 1986
				-2_0	$+1_5$	
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	H_2O	25	$-35._5$			Dahanayake, 1986
				-7	$+3_0$	
$C_{10}H_{21}OC_2H_4SO_3^-Na^+$	H_2O	40	$-37._0$			Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	H_2O	10	$-42._2$			Dahanayake, 1986
				-5	$+3_8$	
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	H_2O	25	$-44._1$			Dahanayake, 1986
				-1_0	$+3_5$	
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	H_2O	40	$-45._8$			Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	10	$-41._7$			Dahanayake, 1986
				$+2$	$+4_5$	
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	25	$-44._0$			Dahanayake, 1986
				-2	$+4_4$	
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	H_2O	40	$-46._2$			Dahanayake, 1986
$C_{12}H_{25}Pyr^+Br^{-c}$	H_2O	10	$-36._4$			Rosen, 1982b
				-2	$+3_5$	
$C_{12}H_{25}Pyr^+Br^-$	H_2O	25	$-38._2$			Rosen, 1982b
				-1_4	$+2_5$	
$C_{12}H_{25}Pyr^+Br^-$	H_2O	40	$-39._4$			Rosen, 1982b

$C_{12}H_{25}Pyr^+Cl^-$	H_2O	10	$-35._2$			Rosen, 1982b
				+2	$+3_8$	
$C_{12}H_{25}Pyr^+Cl^-$	H_2O	25	$-37._1$			Rosen, 1982b
				−4	$+3_4$	
$C_{12}H_{25}Pyr^+Cl^-$	H_2O	40	$-38._8$			Rosen, 1982b
$C_{10}H_{25}N^+(CH_3)_2CH_2COO^-$	H_2O	23	$-19._8$			Beckett, 1963
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	H_2O	23	$-25._4$			Beckett, 1963
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	10	$-21._4$			Dahanayake, 1984
				+8	$+3_1$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	25	$-23._0$			Dahanayake, 1984
				−9	$+3_3$	
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	40	$-24._6$			Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	10	$-26._9$			Dahanayake, 1984
				+4	$+3_2$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	25	$-28._6$			Dahanayake, 1984
				−2	$+3_1$	
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O	40	$-30._1$			Dahanayake, 1984
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O (dodecane satd.)	25	$-28._9$	−3 (35°)	$+2_7$ (35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O (isooctane satd.)	25	$-29._2$	−3 (35°)	$+2_7$ (35°)	Murphy, 1988
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O (toluene satd.)	25	$-30._8$	−2 (35°)	$+3_4$ (35°)	Murphy, 1988
$C_{12}H_{25}N(CH_3)_2O$	H_2O	30	$-25._9$	+7	$+3_3$	Hermann, 1962
$C_{10}H_{21}(OC_2H_4)_8OH$	H_2O	25	$-27._0$	$+1_8$	$+4_5$	Meguro, 1981
$C_{11}H_{23}(OC_2H_4)_8OH$	H_2O	25	$-30._0$	$+1_7$	$+4_7$	Meguro, 1981
$C_{12}H_{25}(OC_2H_4)_2OH$	H_2O	25	$-35._5$	+3	$+3_9$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_3OH$	H_2O	25	$-34._3$	+5	$+3_9$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	H_2O	25	$-33._8$	+8	$+4_2$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$	55% w/w $HCONH_2$—H_2O	21	$-26._1$	—	—	McDonald, 1970

(*Continued next page*)

TABLE 3-7 (*Continued*)

Compound	Solvent	Temp. (°C)	ΔG°_{mic} (kJ/mol)[a]	ΔH°_{mic} (kJ/mol)[a]	$T\Delta S^\circ_{mic}$ (kJ/mol)[a]	Reference[b]
$C_{12}H_{25}(OC_2H_4)_2OH$	$HCONH_2$	25	$-17._0$	-2	$+1_5$	McDonald, 1970
$C_{10}H_{25}(OC_2H_4)_5OH$	H_2O	10	$-31._4$			Rosen, 1982a
				$+1_6$	$+4_8$	
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	25	$-33._9$			Rosen, 1982a
				$+4$	$+3_9$	
$C_{12}H_{25}(OC_2H_4)_5OH$	H_2O	40	$-35._7$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_6OH$	H_2O	25	$-33._0$	$+1_6$	$+4_9$	Corkill, 1964
$C_{12}H_{25}(OC_2H_4)_6OH$	55% w/w $HCONH_2$–H_2O	25	$-25._2$	$+2$	$+2_7$	McDonald, 1970
$C_{12}H_{25}(OC_2H_4)_6OH$	$HCONH_2$	25	$-16._6$	-4	$+1_3$	McDonald, 1970
$C_{12}H_{25}(OC_2H_4)_7OH$	H_2O	25	$-33._2$	$+1_2$	$+4_5$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	10	$-30._1$			Rosen, 1982a
				$+1_7$	$+4_8$	
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	25	$-32._6$			Rosen, 1982a
				$+9$	$+4_3$	
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O	40	$-34._6$			Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	55% w/w $HCONH_2$–H_2O	25	$-24._3$	$+2$	$+2_7$	McDonald, 1970
$C_{12}H_{25}(OC_2H_4)_8OH$	$HCONH_2$	25	$-16._2$	-3	$+1_3$	McDonald, 1970
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–cyclohexane	25	$-32._8$			Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–heptane	25	$-33._0$			Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$	H_2O–hexadecane	25	$-32._7$			Rosen, 1991
$C_{13}H_{27}(OC_2H_4)_8OH$	H_2O	25	$-35._9$	$+1_4$	$+5_0$	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$	H_2O	25	$-38._7$	$+1_3$	$+5_1$	Meguro, 1981
$C_{15}H_{31}(OC_2H_4)_8OH$	H_2O	25	$-41._0$	$+1_1$	$+5_2$	Meguro, 1981

[a] To convert to kcal/mol, divide by 4.18 Values for ionic surfactants are independent of total ionic strength and are averages of values at different electrolyte contents.

[b] Parameters calculated from data in listed reference.

[c] Pyr^+, pyridinium.

magnitude of the changes in $\Delta S^\circ_{\text{mic}}$ and $\Delta H^\circ_{\text{mic}}$. From the available data, $\Delta G^\circ_{\text{mic}}$ appears to become more negative with increase in temperature up to about 50°C in most cases and then to become more positive with further increase in temperature (Crook, 1963).

In highly polar nonaqueous solvents, such as formamide, *N*-methylformamide, and *N,N*-dimethylformamide, from the limited data available, it appears that the driving force for micellization is again mainly entropic, i.e., the tendency of the lyophobic group to transfer from the solvent environment to the interior of the micelle (McDonald, 1970).

IX. MIXED MICELLE FORMATION IN MIXTURES OF TWO SURFACTANTS

In many products or processes, two surfactants are used together to improve the properties of the system. In some cases, the two surfactants interact in such fashion that the CMC of the mixture (C^M_{12}) is always intermediate in value between those of the two components (C^M_1, C^M_2). In other cases they interact in such fashion that C^M_{12} at some ratio of the two surfactants is less than either C^M_1 or C^M_2. When the latter case occurs, the system is said to exhibit *synergism* in mixed micelle formation. In still other cases, C^M_{12} at some ratio of the two surfactants may be larger than either C^M_1 or C^M_2. Here the system is said to exhibit antagonism (*negative* synergism) in mixed micelle formation.

The CMC of the mixture is given by

$$\frac{1}{C^M_{12}} = \frac{\alpha}{f_1 C^M_1} + \frac{1-\alpha}{f_2 C^M_2} \tag{3.20}$$

where α is the mole fraction of surfactant 1 in the solution phase on a surfactant-only basis (i.e., the mole fraction of surfactant 2 in the mixture is $1-\alpha$) and f_1, f_2 are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. Using regular solution equations (2.44 and 2.45) for the activity coefficients f_1 and f_2, Rubingh (1979) developed a convenient method (equations 11.3 and 11.4) for predicting the CMC of any mixture of two surfactants from the CMC values (C^M_1, C^M_2) of the individual surfactants and one or more mixtures of them. When the values of the individual CMCs (Table 3-2) and of the interaction parameter for mixed micelle formation β^M are known (Table 11-1), the value of C^M_{12} can be calculated directly from these without any other experimental data. However, on commercial materials, the presence of surface-active impurities may cause serious deviations from values obtained without the use of some experimental data.

When there is no interaction between the two surfactants, i.e., the mixed is ideal, then $f_1 = f_2 = 1$ and equation 3.20 becomes

$$\frac{1}{C^M_{12}} = \frac{\alpha}{C^M_1} + \frac{1-\alpha}{C^M_2} \tag{3.21}$$

or

$$C_{12}^M = \frac{C_1^M C_2^M}{C_1^M(1-\alpha) + C_2^M \alpha} \tag{3.22}$$

The CMC value of any mixture can then be calculated at any value of α directly from the CMC values of the individual surfactants.

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PROBLEMS

1 If we assume that the length of the alkyl chain of a surfactant in a micelle is 80% of its fully extended length, what would be the shape of the micelle of a surfactant whose hydrophobic group is a straight 12-carbon chain and whose hydrophilic group has cross-sectional area at the micellar surface of 60 Å^2?

2 Indicate in the table below the effect of each change on the aggregation number of a micelle. Use symbols: + = increase; − = decrease; 0 = little or no effect; ? = effect not clearly known.

For compounds $R(OC_2H_4)_xOH$ in water (R = straight chain):	Effect
(a) Increase in temperature	
(b) Increase in the number of carbon atoms in R	
(c) Increase in the value of x	

For compounds $RSO_4^-Na^+$ in water:	Effect
(a) Addition of electrolyte to the solution	
(b) Replacement of Na^+ by Li^+	
(c) Replacement of water as a solvent by methyl alcohol	

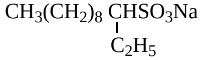
3 Place in order of increasing CMC in aqueous solution (list answers by letters):

(**a**) $CH_3(CH_2)_{11}SO_3Na$

(**b**) $CH_3(CH_2)_{11}(OC_2H_4)_8OH$

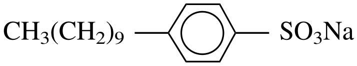
(**c**) $CH_3(CH_2)_9SO_3Na$

(**d**)



$CH_3(CH_2)_8\underset{C_2H_5}{\underset{|}{C}}HSO_3Na$

(**e**)



(**f**) $CH_3(CH_2)_{11}(OC_2H_4)_4OH$

4 Calculate the $\Delta G^\circ_{\text{mic}}$, in kJ mol^{-1}, for a nonionic surfactant whose CMC is 4×10^{-4} mol/liter at 27°C.

5 Indicate in the table below the effect of each change on the CMC/C_{20} ratio of the surfactant in aqueous solution. Use symbols: $+ =$ increase; $- =$ decrease; $0 =$ little or no effect; ? = effect not clearly known.

Change	Effect
(a) Increase in the length of the hydrophobic group	
(b) Branched-, instead of straight-chain, isomeric hydrophobic group	
(c) Addition of urea to aqueous solution	
(d) Addition of NaCl to aqueous solution of ionic surfactant	
(e) Decrease in the length of the POE chain (nonionic surfactant).	

6 Derive the following relationships for mixed micelle formation in a mixture of the two surfactants in aqueous solution. Define all symbols.

(**a**) $f_1^M X_1^M = \dfrac{C_1^M}{C_1^{M,0}}$

(**b**) $C_{12}^M = \dfrac{C_1^{M,0} \cdot C_2^{M,0}}{C_1^{M,0}(1 - \alpha_1) + C_2^{M,0}\alpha_1}$ for ideal mixed micelle formation.

7 Without using the tables, place the following compounds in order of decreasing CMC/C_{20} ratios. Use $\simeq$ if values are approximately equal.

(**a**) $C_{12}H_{25}SO_4{}^-Na^+$, in H_2O, 25°C
(**b**) $C_{12}H_{25}SO_4{}^-Na^+$, in H_2O, 40°C
(**c**) $C_{12}H_{25}SO_4{}^-Na^+$, in 0.1 *M* NaCl (aq.), 25°C

(**d**) $C_{12}H_{25}N(CH_3)_3{}^+Br^-$, in H_2O, 25°C

(**e**) $C_{12}H_{25}(OC_2H_4)_6OH$, in H_2O, 25°C

8 Why are ionic micelles that have more tightly bonded counterions more likely to have nonspherical micelles?

9 Explain why the data on micellar aggregation numbers in Table 3-1 for ionic surfactants often include the surfactant concentration at which the value was determined (the value in parentheses in the table), while the data for nonionics and zwitterionics do not include the concentration.

4 Solubilization by Solutions of Surfactants: Micellar Catalysis

One of the important properties of surfactants that is directly related to micelle formation is *solubilization*. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Although both solvent-soluble and solvent-insoluble materials may be dissolved by the solubilization mechanism, the importance of the phenomenon from the practical point of view is that it makes possible the dissolving of substances in solvents in which they are normally insoluble. For example, although ethylbenzene is normally insoluble in water, almost 5 g of it may be dissolved in 100 mL of a 0.3 M aqueous solution of potassium hexadecanoate to yield a clear solution.

Solubilization into aqueous media is of major practical importance in such areas as the formulation of products containing water-insoluble ingredients, where it can replace the use of organic solvents or cosolvents; in detergency, where solubilization is believed to be one of the major mechanisms involved in the removal of oily soil; in micellar catalysis of organic reactions; in emulsion polymerization, where it appears to be an important factor in the initiation step; in the separation of materials for manufacturing or analytical purposes; and in enhanced oil recovery, where solubilization produces the ultralow interfacial tension required for mobilization of the oil. Solubilization into nonaqueous media is of major importance in dry cleaning. The solubilization of materials in biological systems (Florence, 1984) sheds light on the mechanisms of the interaction of drugs and other pharmaceutical materials with lipid bilayers and membranes.

Solubilization is distinguished from *emulsification* (the dispersion of one liquid phase in another) by the fact that in solubilization, the solubilized material (the '*solubilizate*') is in the same phase as the solubilizing solution and the system is consequently thermodynamically stable.

If the solubility of a normally solvent-insoluble material is plotted against the concentration of the surfactant solution that is solubilizing it, we find that the solubility is very slight until a critical concentration is reached at which the solubility increases approximately linearly with the concentration of the surfactant. That critical concentration is the CMC of the surfactant in the presence of the

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

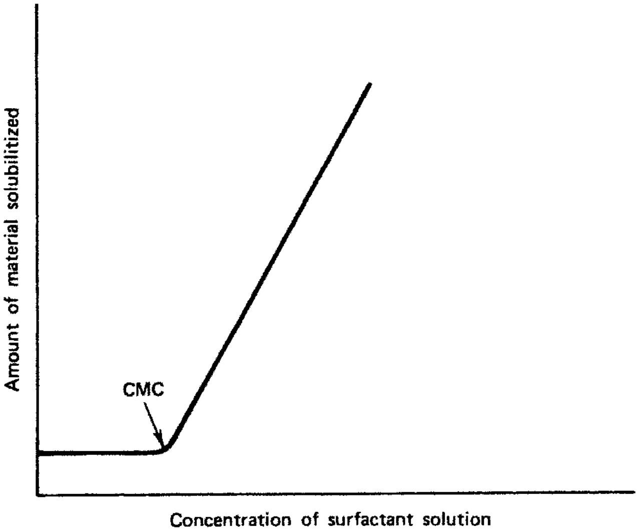


FIGURE 4-1 Plot of amount of material solubilized as a function of concentration of the surfactant in the bulk phase.

solubilizate* (Figure 4-1). This indicates that solubilization is a micellar phenomenon, since it occurs only to a negligible extent at concentrations where micelles, if they exist at all, are found only in insignificant numbers.

I. SOLUBILIZATION IN AQUEOUS MEDIA

I.A. Locus of Solubilization

The exact location in the micelle at which solubilization occurs (i.e., the locus of solubilization) varies with the nature of the material solubilized and is of importance in that it reflects the type of interaction occurring between surfactant and solubilizate. Data on sites of solubilization are obtained from studies on the solubilizate before and after solubilization, using X-ray diffraction (Hartley, 1949; Philipoff, 1950), ultraviolet spectroscopy (Reigelman, 1958), NMR spectrometry (Eriksson, 1963, 1966), and fluorescence spectroscopy (Saito, 1993; Paterson, 1999). Diffraction studies measure changes in micellar dimensions on solubilization, whereas UV, NMR and fluorescence spectra indicate changes in the environment of the solubilizate on solubilization. Based on these studies, solubilization is believed to occur at a number of different sites in the micelle (Figure 4-2): (1) on

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*Since activity of the surfactant in the micelle is changed by the introduction of the solubilizate, the concentration of monomeric surfactant in the aqueous phase in equilibrium with it must change. Therefore, the presence of the solubilizate changes the CMC, in most cases reducing it. Methods for determining the CMC that use *probes* (solubilized materials) consequently give values that are generally less than the CMC of the surfactant in the absence of the probe.

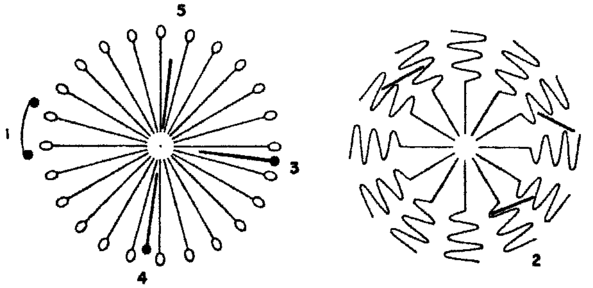


FIGURE 4-2 Loci of solubilization of material in a surfactant micelle. Reprinted with permission from P. H. Elworthy, A. T. Florence, and C. B. MacFarlane, *Solubilization by Surface-Active Agents*, Chapman & Hall, London, 1968, p. 68.

the surface of the micelle, at the micelle–solvent interface; (2) between the hydrophilic head groups (e.g., in POE materials); (3) in the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micellar interior; (4) more deeply in the palisade layer; and (5) in the inner core of the micelle.

Based upon UV spectral studies and the interfacial activity of benzene in heptane–water systems, Mukerjee (1979) postulated a two-state model for polar and polarizable solubilizates, involving a distribution between *adsorbed state* at the micellar–water interface and a *dissolved state* in the hydrocarbon core. Although a distribution favoring the adsorbed state is expected of solubilizates with high polarity, increased concentration of the solubilizate appears to produce a redistribution favoring the dissolved state. Heats of solution support the two-state model for the solubilization of molecules containing aromatic nuclei (Bury, 1985). The distribution of benzene between the two loci depends also upon the hydrophilic group of the surfactant (Nagarajan, 1984).

Saturated aliphatic and alicyclic hydrocarbons and other types of molecules that are not polarized or not easily polarizable are solubilized in aqueous medium in the inner core of the micelle between the ends of the hydrophobic groups of the surfactant molecules. Their UV and NMR spectra indicate a completely nonpolar environment on solubilization.

Polarizable hydrocarbons, such as short-chain arenes (benzene, isopropylbenzene), have been shown to be solubilized in quaternary ammonium solutions initially by absorption at the micelle–water interface, replacing water molecules that may have penetrated into the outer core of the micelle close to the polar heads, but solubilization of additional material is either deep in the palisade layer or located in the inner core of the micelle (Eriksson, 1965). The polarizability of the π-electron cloud of the aromatic nucleus and its consequent ability to interact with the positively charged quaternary ammonium groups at the micelle–water interface may account for the initial adsorption of these hydrocarbons in that location. In POE nonionics, benzene may be solubilized between the polyoxyethylene chains of the hydrophilic groups (Nakagawa, 1967).

Large polar molecules, such as long-chain alcohols or polar dyestuffs, are believed to be solubilized, in aqueous medium, mainly between the individual molecules of surfactant in the palisade layer with the polar groups of the solubilizate oriented toward the polar groups of the surfactants and the nonpolar portions oriented toward the interior of the micelle. Interaction here is presumably by H bonding or dipole–dipole attraction between the polar groups of solubilizate and surfactant. The spectrum of the solubilizate in these cases indicates that at least part of the molecule is in a polar environment when solubilized. Depth of penetration in the palisade layer depends on the ratio of polar to nonpolar structures in the solubilizate molecule, longer-chain and less polar compounds penetrating more deeply than shorter-chain and more polar materials. In POE materials the locus of solubilization for polar dyestuffs may change with change in the length of the POE chain, more of the solubilizate being solubilized in the vicinity of the oxyethylene groups as the length of the POE chain increases (Tokiwa, 1968; Schwuger, 1970).

Small polar molecules in aqueous medium are generally solubilized close to the surface in the palisade layer or by adsorption at the micelle–water interface. The spectra of these materials after solubilization indicate that they are in a completely, or almost completely, polar environment. Short-chain phenols, when solubilized in POE nonionics, appear to be located between the POE chains (Nakagawa, 1967).

In concentrated aqueous surfactant solutions, although the shape of the micelles may be very different from that in dilute solution, the locus of solubilization for a particular type of solubilizate appears to be analogous to that in dilute solution; that is, polar molecules are solubilized mainly in the outer regions of the micellar structures, whereas nonpolar solubilizates are contained in the inner portions.

I.B. Factors Determining the Extent of Solubilization

Because of the importance of solubilization in the removal of oily soil by detergents and in the preparation of pharmaceutical, cosmetic, insecticide, and other types of formulations, a good deal of work has been done on elucidating the factors that determine the amount of solubilizate that can be solubilized by various types of surfactants. The situation is complicated by the existence of the different sites for the solubilization of different types of materials.

The solubilization capacity or solubilizing power of the micelle is defined (Stearns, 1947; Paterson, 1999) as the number of moles of solubilizate per mole of micellized surfactant, given by the ratio $(S_W - S_{CMC})/(C_{surf} - CMC)$, where S_W is the molar solubility of the solubilizate in the aqueous system, S_{CMC} its molar solubility at the CMC, and C_{surf} the molar concentration of the surfactant (Edwards, 1991). It often remains constant for a particular surfactant over a wide concentration range above the CMC, although some surfactants show increasing solubilizing power at higher concentrations. In general, solubilization capacity is greater for polar solubilizates than for nonpolar ones, especially for spherical micelles (because of the larger volume available at the surface of the micelle than in the interior), and decreases with increase in the molar volume of the solubilizate. Also, factors that promote micellization (e.g., electrolyte addition to ionic surfactants) increase solubilization capacity.

The extent to which a substance can be solubilized into a particular micelle depends upon the portion of the micelle that is the locus of the solubilization. The volume of that portion depends upon the shape of the micelle. As we have seen (Chapter 3, Section IIA), the shape of the micelle is determined by the value of the parameter $V_H/l_c a_0$. As that value increases, the micelle in aqueous medium becomes increasingly asymmetrical, with the result that the volume of the inner core increases relative to that of the outer portion. We can therefore expect that the solubilization of material in the core will increase relative to that in the outer region of the micelle with increase in asymmetry (increase in the value of $V_H/l_c a_0$). The amount solubilized in any location will also increase with increase in the volume of the micelle, e.g., with increase in the diameter of a spherical micelle.

The effect of the curvation of the micelle on solubilization capacity has been pointed out by Mukerjee (1979, 1980). The convex surface produces a considerable Laplace pressure (equation 7.1) inside the micelle. This may explain the lower solubilizing power of aqueous micellar solutions of hydrocarbon-chain surfactants for hydrocarbons, compared to that of bulk phase hydrocarbons, and the decrease in solubilization capacity with increase in molar volume of the solubilizate. On the other hand, reduction of the tension or the curvature at the micellar–aqueous solution interface should increase solubilization capacity through reduction in Laplace pressure. This may in part account for the increased solubilization of hydrocarbons by aqueous solutions of ionic surfactants upon the addition of polar solubilizates or upon the addition of electrolyte. The increase in the solubilization of hydrocarbons with decrease in interfacial tension has been pointed out by Bourrel (1983).

1. Structure of the Surfactant For hydrocarbons and long-chain polar compounds that are solubilized in the interior of the micelle or deep in the palisade layer, the amount of material solubilized generally increases with increase in the size of the micelles. Therefore, any factor that causes an increase in either the diameter of the micelle or its aggregation number (Chapter 3, Section III) can be expected to produce an increase in the solubilization capacity for this type of material. Since aggregation numbers increase with increase in the degree of "dissimilarity" between solvent and surfactant, an increase in the chain length of the hydrophobic portion of the surfactant generally results in increased solubilization capacity for hydrocarbons in the interior of the micelle in aqueous media. Fluorocarbon chain surfactants appear to solubilize fluorocarbons better than do hydrocarbon chain surfactants (Asakawa, 1998).

Bivalent metal alkyl sulfates appear to show greater solubilizing power than the corresponding sodium salts for hydrocarbons, probably reflecting the greater micellar aggregation numbers, asymmetry, and volumes of the former compared to the latter (Satake, 1963).

In aqueous solutions of POE nonionics, the extent of solubilization of aliphatic hydrocarbons at a given temperature appears to increase as the length of the hydrophobic group increases and as the length of the POE chain decreases (Saito, 1967), reflecting the increase in the aggregation number of the micelles produced by these changes. Fluorescence studies of the solubilization of *n*-octane and *n*-octanol in aqueous solutions of POE nonionics indicate that it is the volumes of the hydrophilic and hydrophobic regions, rather than the size or aggregation number of the micelle, that determines the solubilization of polar and nonpolar solubilizates, respectively (Saito, 1993). In POE polyoxypropylene glycols, the solubilization of naphthalene increases with increase in the size of the polyoxypropylene group relative to that of the POE group (Paterson, 1999).

Nonionic surfactants, because of their lower critical micelle concentrations, are better solubilizing agents than ionics in very dilute solutions. In general, the order of solubilizing power for hydrocarbons and polar compounds that are solubilized in the inner core appears to be as follows: nonionics > cationics > anionics for surfactants with the same hydrophobic chain length (McBain, 1946; Saito, 1967; Tokiwa, 1968). The greater solubilizing power of cationics, compared to anionics of equivalent hydrophobic chain length, may be due to looser packing of the surfactant molecules in the micelles of the former (Klevens, 1950; Schott, 1967).

Polymeric quaternary ammonium surfactants, made from *n*-dodecyl bromide and poly(2-vinylpyridine), are better solubilizers for aliphatic and aromatic hydrocarbons than *N*-laurylpyridinium chloride, with the extent of solubilization increasing as the alkyl content of the polymeric quaternary is increased (Strauss, 1951; Inoue, 1964).

For polar compounds, very few generalizations relating the degree of solubilization to the structure of the surfactant can be made from the available data, since solubilization can occur in both the inner and outer regions of the micelle. Thus, methyl isobutyl ketone and *n*-octyl alcohol show greater solubilization in 0.1 *N* sodium oleate than in potassium laurate of the same concentration at 25°C, whereas octylamine shows about equal solubilization in each (McBain, 1946). The solubilization of chloroform in soap micelles increases with increase in the number of carbon atoms in the soap (Demchenko, 1959) and the solubilization of 1-heptanol increases with increase in the number of carbon atoms in sodium alkanesulfonates (Demchenko, 1973). Yellow OB (l-*o*-tolyl-azo-2-naphthylamine), which is solubilized in both the interior and the POE portion of the micelle in sodium dodecyl polyoxyethy-lenesulfates, $C_{12}H_{25}(OC_2H_4)_xSO_4Na$, where $x = 1\text{–}10$, shows increased solubilization with increase in the length of the POE chain in these compounds. On the other hand, this same solubilizate shows almost no change in extent of solubilization with increases in the length of the POE chain in the corresponding nonionic, unsulfated dodecyl POE glycols, $C_{12}H_{25}(OC_2H_4)_xOH$, where $x = 6\text{–}20$ (Tokiwa, 1968). This latter effect may be the result of two compensating factors: increased oxyethylene content and decreased aggregation number. Other oil-soluble azo dyes similarly show little change in the amount solubilized as the length of the POE chain in nonionics is increased Schwuger, 1970). In both nonionic and anionic POE surfactants the extent of solubilization of Yellow OB is much greater than in sodium alkyl sulfates (C_8–C_{14}) without polyoxyethylene chains (Tokiwa, 1968).

Polymeric quaternary ammonium surfactants made from *n*-dodecyl bromide and poly(2-vinylpyridine) are better solubilizers for oil-soluble azo dyes and for *n*-decanol than monomeric quaternary cationics with similar (monomeric) structures (Tokiwa, 1963; Inoue, 1964). Solubilization of *n*-decanol in the polycationics increased as the alkyl chain content increased to a maximum at 24% alkyl content and resulted, at high decanol content, in intermolecular aggregation of the polycationic molecules (Inoue, 1964).

The introduction into the surfactant molecule of a second ionic head group affords some further insights into the solubilization of polar and nonpolar materials. A comparison of the two series of surfactants, the monosodium salts of the monoesters of maleic acid, $ROOCCH{=}CHCOO^{-}Na^{+}$, and the disodium salts of the corresponding monoesters of sulfosuccinic acid, $ROOCCH_2CH(SO_3{}^{-}Na^{+})$-$COO^{-}Na^{+}$, where $R = C_{12}$–C_{20}, shows that the introduction of the sulfonate group into the molecule decreases its solubilizing power for the nonpolar compound *n*-octane and increases its solubilizing power for the polar substance *n*-octyl alcohol (Reznikov, 1966). This may be explained as follows: The introduction of the sulfonate groups increases the cross-sectional area a_0 of the hydrophilic portion of the surfactant molecule and consequently decreases the aggregation number of the micelles (Chapter 3, Section III). It also causes increased repulsion between the head groups in the micelles, with consequent increase in the space available for solubilization between the surfactant molecules in the palisade layer. The decreased aggregation number in the micelles causes reduced solubilization of nonpolar substances, whereas the increased repulsion between the head groups results in increased solubilization of polar molecules.

Consistent with the above, in aqueous solutions of two different surfactants that interact strongly with each other (Chapter 11, Table 11-1), mixed micelle formation is unfavorable for the solubilization of polar solubilizates that are solubilized in the palisade layer and favorable for the solubilization of nonpolar ones that are solubilized in the micellar inner core. This is due to the reduction of a_0 and the sphere-to-cylindrical micelle transition and the increase in aggregation number resulting from the interaction (Treiner, 1990).

2. Structure of the Solubilizate Crystalline solids generally show less solubility in micelles than do liquids of similar structure, the latent heat of fusion presumably opposing the change. For aliphatic and alkylaryl hydrocarbons, the extent of solubilization appears to decrease with increase in the chain length and to increase with unsaturation or cyclization if only one ring is formed (McBain, 1946). For condensed aromatic hydrocarbons the extent of solubilization appears to decrease with increase in the molecular size (Schwuger, 1972). Branched-chain compounds appear to have approximately the same solubility as their normal chain isomers. Short-chain alkylaryl hydrocarbons may be solubilized both at the micelle–water interface and in the core, with the proportion in the core increasing with increase in the concentration of the solubilizate.

For polar solubilizates, the situation is complicated by the possibility of variation in the depth of penetration into the micelle as the structure of the solubilizate is changed. If the micelle is more or less spherical in shape, we can expect that space will become less available as the micelle is penetrated more deeply. Thus, polar compounds that are solubilized close to the micelle–water interface should be solubilized to a greater extent than nonpolar solubilizates that are located in the inner core. This is generally the case, if the surfactant concentration is not high (McBain, 1946; Nakagawa, 1960). We should also expect that polar compounds that are solubilized more deeply in the palisade layer would be less soluble than those whose locus of solubilization is closer to the micelle–water interface. Usually, the less polar the solubilizate (or the weaker its interaction with either the polar head of the surfactant molecules in the micelle or the water molecules at the micelle–water interface) and the longer its chain length, the smaller its degree of solubilization; this may reflect its deeper penetration into the palisade layer.

3. Effect of Electrolyte The addition of small amounts of neutral electrolyte to solutions of ionic surfactants appears to increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of the palisade layer (Klevens, 1950). The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC (Chapter 3, Section IVB) and increasing the aggregation number (Chapter 3, Section III) and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. The decrease in mutual repulsion of the ionic head groups causes closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available there for solubilization of polar compounds. This may account for the observed reduction in the extent of solubilization of some polar compounds. As the chain length of the polar compound increases, this reduction of solubility by electrolytes appears to decrease and the solubility of *n*-dodecanol is increased slightly by the addition of neutral electrolyte. This is believed to be due to its location deep in the palisade layer close to the locus of solubilization of nonpolar materials (Klevens, 1950).

The addition of neutral electrolyte to solutions of nonionic POE surfactants increases the extent of solubilization of hydrocarbons at a given temperature in those cases where electrolyte addition causes an increase in the aggregation number of the micelles. The order of increase in solubilization appears to be the same as that for depression of the cloud point (Section IIIB, below) (Saito, 1967): $K^+ > Na^+ > Li^+$; $Ca^{2+} > Al^{3+}$; $SO_4^= > Cl^-$. The effect of electrolyte addition on the solubilization of polar materials is not clear.

4. Effect of Monomeric Organic Additives The presence of solubilized hydrocarbon in the surfactant micelles generally increases the solubility of polar compounds in these micelles. The solubilized hydrocarbon causes the micelle to swell, and this may make it possible for the micelle to incorporate more polar material in the palisade layer. On the other hand, the solubilization of such polar material as long-chain alcohols, amines, mercaptans, and fatty acids into the micelles of a surfactant appears to increase their solubilization of hydrocarbons. The longer the chain length of the polar compound and the less capable it is of hydrogen bonding, the greater appears to be its power to increase the solubilization of hydrocarbons, that is, $RSH > RNH_2 > ROH$ (Klevens, 1949); Shinoda, 1958; Demchenko, 1970). One explanation for this is that the increased chain length and lower polarity result in a lower degree of order in the micelle, with a consequent increase in solubilizing power for hydrocarbons. Another is that the additives with longer chain length and lesser hydrogen bonding power are solubilized more deeply in the interior of the micelle, and hence expand this region, producing the same effect as a lengthening of the hydrocarbon chain of the micelle-producing molecule.

However, the addition of long-chain alcohols to aqueous solutions of sodium dodecyl sulfate decreased its solubilization of oleic acid. The extent of solubilization of the latter decreased as both the concentration and the chain length of the added alcohol increased. These effects are believed to be due to competition between oleic acid and added alcohol for sites in the palisade layer of the micelle (Matsuura, 1961).

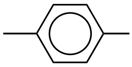
5. Effect of Polymeric Organic Additives Macromolecular compounds, including synthetic polymers, proteins, starches, and cellulose derivatives, interact with surfactants to form complexes in which the surfactant molecules are absorbed onto the macromolecules, mainly by electrical and hydrophobic interactions. When the surfactant concentration in the complex is sufficiently high, the polymer–surfactant complex may show solubilization power, in some cases greater than that of the surfactant alone, and at concentrations below the CMC of the surfactant (Saito, 1957, 1959; Blei, 1959, 1960; Breuer, 1960). The addition of macromolecules of the proper structure to surfactant solutions can therefore increase the solubilizing power of the latter. Thus, sodium alkyl sulfates containing 10 to 16 carbon atoms, at concentrations below their CMCs, form complexes with serum albumin that solubilize oil-soluble azo dyes and isooctane. The moles of dye solubilized per mole of surfactant appear to increase with increase in the chain length of the surfactant, the number of surfactant molecules adsorbed per mole of protein, and the concentration of the protein (Blei, 1959, 1960; Breuer, 1960). The amount of Yellow OB solubilized by sodium dodecyl sulfate–polymer complexes appears to increase with increase in the hydrophobic nature of the polymers (Arai, 1969) and on the addition of small amounts of NaCl (Horin, 1970).

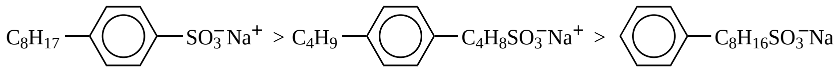
The addition of POE glycols to aqueous solutions of sodium dodecyl sulfate and sodium *p*-octylbenzenesulfonate increased their solubilization power for the azo dye Yellow OB. As the degree of polymerization of the glycol increased, the extent of solubilization for the dye increased. The effect is believed to be due to the formation of two types of complexes between the surfactant micelles and the glycol. Low-molecular-weight POE glycols (degree of polymerization <10–15) are believed to form micelle–glycol complexes in which the glycol is adsorbed on the surface of the micelle in a manner similar to that of small polar compounds and the solubilized dye is located mainly in the inner core of the micelle.

Higher-molecular-weight glycols are believed to form true polymer–surfactant complexes in which the glycol is in the form of a random coil bound to the surfactant with its hydrophilic groups oriented toward the aqueous phase. Here the dye is solubilized in the POE-rich region (Tokiwa, 1973b).

Generally, the more hydrophobic the polymer, the greater the adsorption of surfactant onto it from water, since hydrophilic groups on the macromolecule can interact with water and weaken surfactant–polymer interaction. The adsorption of anionic surfactants onto nonionic macromolecules appears to follow the approximate order polyvinylpyrrolidone $\sim$ polypropylene glycol $>$ polyvinylacetate $>$ methylcellulose $>$ polyethylene glycol $>$ polyvinyl alcohol. Long-chain alkyl ammonium chlorides appear to follow the same general order of interaction, except for much weaker interaction with polyvinylpyrrolidone (less than with polyethylene glycol). The very strong interaction of anionic surfactants, especially sulfated anionics, and very weak interaction of cationics with polyvinylpyrrolidone may be due to protonation of the latter in aqueous solution (Breuer, 1972; Roscigno, 2001). Nonionic surfactants interact only weakly with nonionic macromolecules (Saito, 1960).

The relation between the extent of solubilization and the structures of solubilizate and surfactant–polymer complex is not completely clear. Aromatic hydrocarbons appear to be more highly solubilized than aliphatic hydrocarbons by complexes of anionic surfactants and hydrophilic polymers with no proton-donating groups, such as polyvinylpyrrolidone, but the nature of the forces involved is not clear. Some cationic surfactant–polymer complexes are broken by the solubilization of aromatic hydrocarbons. It has been suggested that structural compatibility between solubilizate and polymer may be a factor and that the function of the surfactant is to increase the hydrophilic character of the polymer and to promote contact between polymer and solubilizate (Saito, 1967).

6. Mixed Anionic–Nonionic Micelles An investigation of the solubilization of Yellow OB by mixed micelles of anionics and a POE nonionic, $C_{12}H_{25}(OC_2H_4)_9$-OH, indicated that increased solubilization of the dye occurs when there is interaction between the POE chain and the benzenesulfonate groups, SO_3^-, rather than the phenyl or sulfonate groups alone (Tokiwa, 1973a). The degree of interaction of the aromatic nucleus with the POE chain decreased with separation of the ring from the sulfonate groups, giving the following order of interaction:



Only the first compound increased the extent of solubilization of Yellow OB by the nonionic. The addition of $C_{10}H_{21}SO_3^-Na^+$ to the nonionic decreased its solubilization of Yellow OB.

7. ***Effect of Temperature*** For ionic surfactants an increase in temperature generally results in an increase in the extent of solubilization for both polar and nonpolar solubilizates, possibly because increased thermal agitation increases the space available for solubilization in the micelle. Thus, the solubilization of cyclohexane in an aqueous solution of sodium di(2-ethylhexyl) sulfosuccinate above 50°C increases with increase in the temperature (Kunieda and Shinoda, 1979).

For nonionic POE surfactants, on the other hand, the effect of temperature increase appears to depend on the nature of the solubilizate. Nonpolar materials, such as aliphatic hydrocarbons and alkyl halides, which are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised, the increase becoming very rapid as the cloud point (Section IIIB below) of the surfactant is approached (Saito, 1967).

Figure 4-3 illustrates this, and also the effect of increase in the length of the hydrophobic group. The upper curves in I and II, respectively, are for the cloud point in the presence of excess heptane; the lower curves, for the amount of heptane solubilized. This rapid increase just below the cloud point probably reflects the large increase in aggregation number of the micelles in this region (Chapter 3, Section III) and the transition from spherical to more asymmetric micelles. The solubility of the oil-soluble azo dye Sudan Red G also increases with increase in temperature (Schwuger, 1970). However, the solubility behavior of polar materials, whose locus of solubilization is the palisade layer of the micelle, appears to be very different, the amount of material solubilized generally going through a maximum as

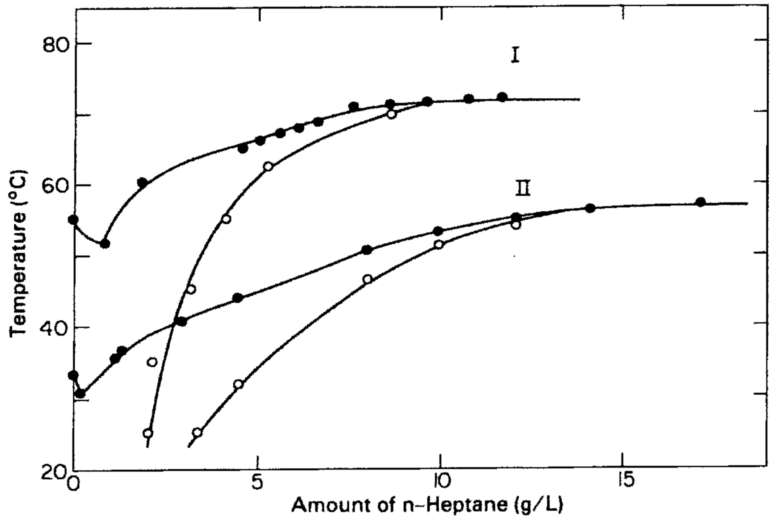


FIGURE 4-3 The effect of temperature on the solubilization of *n*-heptane in 1% aqueous solution of I, POE (9.2) nonylphenyl ether and II, POE (9.0) dodecylphenyl ether. ●, Cloud point; ○, solubilization limit. Reprinted with permission from K. Shinoda and S. Friberg. *J. Colloid Interface Sci.* **24**, 4 [1967].

the temperature is increased to the cloud point (Nakagawa, 1960). When the temperature is raised above 10°C, there is at first a small or moderate increase in the extent of solubilization, presumably reflecting the increase in thermal agitation of the surfactant molecules in the micelles. This is followed by a decrease in the amount of material solubilized as further increase in temperature causes increased dehydration and tighter coiling of the POE chains, decreasing the space available in the palisade layer. As the cloud point is approached, this decrease in the amount solubilized may become marked, particularly for short-chain polar compounds that are solubilized close to the surface of the micelle.

8. Hydrotropy When there are strong chain–chain and head–head interactions between surfactant molecules (due to long, straight chains and close-packed heads), either insoluble crystal formation (low Krafft point, p. 214) or liquid-crystal formation (Chapter 3, Section IIC) may occur. Since there is much less space available for solubilization in rigid liquid-crystal structures than in the more flexible types of micelles, the onset of crystal formation usually limits the solubilization capacity of the solution. The tendency to form crystalline structures can be reduced by the addition of certain nonsurfactant organic additives called *hydrotropes*.

Hydrotropes have been known for decades as organic substances that increase the solubility and reduce the viscosity in water of other organic susbstances. They have a structure somewhat similar to those of surfactants in that they have a hydrophilic and a hydrophobic group in the molecule, but are different from surfactants in that the hydrophobic group is generally short, cyclic, and/or branched. Typical hydrotropes include sodium benzene-, toluene-, xylene-, cumene-, and *p*-cymenesulfonates, 1-hydroxy-2-naphthoate, 2-hydroxy-1-naphthalenesulfonate, and sodium 2-ethylhexyl sulfate.

The mechanism by means of which hydrotropes operate in surfactant solutions was elucidated by Friberg and coworkers (1970, 1971; Cox, 1981), who showed that it is due to the inhibition of the formation of surfactant liquid-crystalline phases by the hydrotrope. Since they have structures similar to those of surfactants, hydrotropes can form mixed micellar structures with surfactants. However, since their hydrophilic heads are large and their hydrophobic groups are small (their $V_H/l_c a_0$ ratio [Chapter 3, Section II] is $\ll 1$), they tend to form spheroidal rather than lamellar or liquid-crystalline structures and thus inhibit the formation of the latter. This destruction or inhibition of the liquid-crystalline phase increases the solubility of the surfactant in the aqueous phase and the capacity of its micellar solution to solubilize material. Hydrotropic action occurs at concentrations at which the hydrotrope self-associates to form these mixed structures with the surfactant (Gonzalez, 2000).

Short-chain alkyl polyglycosides (C_4–C_{10}), because they have the large hydrophilic head group and short hydrophobic group needed to disrupt liquid-crystalline phases, are also effective hydrotropes. The C_8 and C_{10} homologs are very effective in raising the cloud points (Section IIIB below) of some alcohol ethoxylates (Matero, 1998).

I.C. Rate of Solubilization

For the solubilization of highly insoluble hydrocarbons by POE nonionics into water, the rate of solubilization has been found (Carroll, 1981, 1982) to be directly proportional to the surfactant concentration above the CMC, and to increase with the polarity and decrease with the molecular weight of the oil. The rate is also strongly temperature dependent in the region of the cloud point (Section IIIB below), increasing rapidly as that temperature is approached. The mechanism suggested involves diffusion of the micelles to the hydrocarbon–water interface, where they dissociate and adsorb as monomers. This adsorption produces concerted desorption from the interface of an equivalent amount of monomeric surfactant, but in the form of micelles containing a quantity of solubilizate.

A study of the rate of solubilization of *n*-hexadecane by mixtures of different sodium linear alkylarenesulfonates with a nonionic (C_{12}–C_{15} alcohol oxyethylenated with 9 mol of EO) in the presence of 3–10 m*M* Ca^{2+} showed that the rate of solubilization increases dramatically: (1) as the position of the phenylsulfonate group on the linear chain becomes more central and (2) as the position of the sulfonate group approaches that of the long alkyl group on the ring. Thus, the order of decreasing rate of solubilization was 2-alkyl-4, 5-dimethylbenzene-sulfonate $\gg$ 3-alkyl-6-methylbenzenesulfonate $>$ 4-alkyl-2,5-dimethyl-benzene-sulfonate $\approx$ 4-alkylbenzenesulfonate. For *n*-hexadecane solubilization, the rate increases with increase in the length of the alkyl chain of the alkylarensulfonate to a maximum at 11–12 carbon atoms (Bolsman, 1988).

II. SOLUBILIZATION IN NONAQUEOUS SOLVENTS

Surfactants can also solubilize materials into solvents other than water. Even when surfactant aggregation does not occur or the aggregation number is small in a particular solvent in the absence of other material, the addition of solvent-insoluble material, such as water, may give rise to aggregation with consequent solubilization of the additive (Kitahara, 1980). The solubilization of water and aqueous solutions into organic solvents has been especially studied in connection with dry cleaning, and the solubilization of organic acids has been studied in connection with corrosion prevention in fuels and lubricants. Investigations have been confined almost exclusively to solubilizates that are small polar molecules, especially water, and to solvents that are hydrocarbons or chlorinated hydrocarbons. Since the surfactant molecules in these solvents have their polar or ionic heads buried in the inner core of the micelles and their hydrophobic groups oriented toward the solvent, solubilization of these small polar materials in these solvents occurs in the interior of the micelle. The surfactants used in these systems must necessarily be soluble in the solvent, and since many ionic surfactants are not soluble in hydrocarbons, only a few ionic surfactants have been used for this purpose. Anionics that have been most commonly used are the amine soaps of fatty acids and various metal dialkylsulfosuccinates (Mathews, 1953) and dinonylnaphthalenesulfonates (Honig, 1954); cationics used include dodecylammonium carboxylates

(Palit, 1954), didodecyldimethylammonium halides, and di(2-ethylhexyl)ammonium halides. Since many POE nonionics are soluble in aliphatic and aromatic hydrocarbons, structural limitations on the use of these materials for this purpose are not as restrictive as in the case of ionics. Polyanionic soaps made by copolymerization of maleic anhydride and dodecyl (or octadecyl) vinyl ether followed by treatment with morpholine have been used to solubilize water into nonaqueous solvents (Ito, 1964).

In micellar solutions of ionic surfactants the mechanism for solubilization of the small polar molecules appears to involve, initially at least, ion–dipole interaction between the solubilizate and the counterion of the surfactant present in the interior of the micelle, possibly followed by weaker interaction (e.g., via hydrogen bonding) between the solubilizate and the surfactant ion (Kaufman, 1964; Kitahara, 1969, Kon-no, 1971a). In solutions of nonionic POE surfactants, solubilization of polar molecules appears to be by interaction with the ether oxygens of the POE chain.

A classification of solubilization isotherms for small polar molecules into nonaqueous solvents by surfactants, based on the strength of interaction between solubilizate and surfactant, has been proposed by Kon-no and Kitahara (Kon-no, 1972a). When the moles of material solubilized per mole of surfactant are plotted against the relative vapor pressure, p/p°, of the system at constant temperature (where p is the vapor pressure of the water in the system and p° is the vapor pressure of pure water), isotherms are obtained whose shapes reflect the strength of the solubilizate–surfactant interaction. Systems having strong surfactant–solubilizate interaction are concave to the p/p° axis, whereas those showing weak interaction are convex to that axis. Systems with very weak solubilizate–surfactant interaction show almost linear isotherms.

The maximum amount of water solubilized into hydrocarbon solvents by ionic surfactants appears to increase with increase in the concentration of the surfactant, the valence of the counterion, and the length of the alkyl chain (Kon-no, 1971b) and with the introduction of double bonds into the hydrophobic group (Demchenko, 1971). Straight-chain compounds appear to solubilize less water than branched-chain ones, possibly because the former form micelles that are more compact and rigid than the latter (Frank, 1969; Kon-no, 1971c).

The addition of neutral electrolyte appears to decrease markedly the solubilization power of ionic surfactants for water, ions of charge opposite to that of the surfactant ion having a much greater effect than similarly charged ions (Kitahara, 1966). This is explained in the case of anionics (Kon-no, 1972) as caused by the decreased repulsion between the ionic heads of the surfactant molecules in the interior of the micelle resulting from the compression of the electrical double layer in the presence of the electrolyte. This decrease in repulsion permits the ionic heads to approach each other more closely, thereby decreasing the space available for solubilization of water. Temperature increase appears to cause an increase in the solubilization of water by ionic surfactants by increasing the distance between the ionic heads (Kon-no, 1972b).

Change in the nature and molecular weight of the solvent affects the extent of solubilization of water. The amount solubilized by sodium di(2-ethylhexyl)sulfosuccinate goes through a maximum with increase in the molecular weight of the solvent in the *n*-alkane series, with *n*-dodecane showing the greatest solubilizing power. Cyclohexane and toluene showed much lower solubilizing power (Frank, 1969). In general, solubilizing power for water appears to decrease as the polarity of the solvent increases, presumably because of increased competition by the solvent for the surfactant molecules and the smaller aggregation number of the micelles in the more polar solvents.

The amount of water solubilized into hydrocarbon solvents by POE nonionics appears to increase with increase in the concentration of the surfactant and the length of the POE chain (Nakagaki, 1964; Saito, 1972). The amount of H_2O solubilized into aliphatic, aromatic, and chlorinated solvents showed little change with increase in the temperature from 15°C to 35°C for a series of POE nonionics and only a small increase for some ionic surfactants (Kitahara, 1980). The extent of solubilization of water into hydrocarbon solvents by POE nonionics is not affected as much as for ionic surfactants by the addition of electrolytes. Here the anion of the added electrolyte appears to have a much greater effect than the cation in decreasing the solubilizing power for water, the order being as follows: $Na_2SO_4 \gg NaCl > MgCl_2 > AlCl_3$. This order corresponds to that of increasing lyotropic numbers for anions and cations and is the same as that for their effect on the CMC of POE nonionics (Chapter 3, Section IVB). This indicates that their action must involve a salting out of the hydrogen bonds between the ether oxygen of the POE chains and the solubilized water molecules (Kitahara, 1966).

From the data available for surfactants with similar hydrophobic groups, the solubilizing power for water into hydrocarbon solvents appears to decrease in the following order: anionics > nonionics > cationics (Kon-no, 1971c).

In the presence of 15% pentanol, large amounts of water can be solubilized into heptane or toluene solutions of C_{12}–C_{16} alkylpyridinium or alkyltrimethylammonium bromides (Venable, 1985). In heptane/pentanol, the longer-chain surfactants appear to be more effective than the shorter ones, while in toluene/pentanol the shorter ones appear to be more effective. In both solvent mixtures, the pyridinium salts are more effective solubilizers than the corresponding trimethylammonium salts. All the quaternaries investigated were more effective than sodium dodecyl sulfate.

These effects on the solubilization of water are in agreement with the prediction of Mitchell and Ninham that bringing the >1 value of the ratio $V_H/l_C a_0$ (Chapter 3, Section II) closer to 1 should increase the solubilization of water in inverted micelles. This is also consistent with increases in the solubilization of water observed upon the addition of benzene or nitrobenzene to solutions of sodium di(2-ethylhexyl)sulfosuccinate in isooctane (Maitra, 1983). The effects were explained as caused by desolvation of the surfactant by the additives, with consequent decrease in the value of V_H.

II.A. Secondary Solubilization

The secondary solubilization of such water-soluble materials as salts, sugars, and water-soluble dyes into nonaqueous solutions of surfactants containing solubilized water is of great importance in dry cleaning, since it is a major mechanism by means of which water-soluble stains can be removed. The data available indicate that the tightly bound, initially solubilized water is not available for this purpose and that only the subsequently solubilized, more loosely bound water is responsible for such secondary solubilization (Aebi, 1959; Wentz, 1969; Kon-no, 1971a). The strength of the binding of water molecules to the ionic head group in sulfosuccinates appears to be a function of the size of the groups around the hydrophilic head, the heats of solubilization of water decreasing in the following order: Na di(*n*-octyl)sulfosuccinate $>$ Na di(l-methylheptyl)sulfosuccinate $>$ Na di(2-ethylhexyl)-sulfosuccinate. Water appears to be less strongly bound in the potassium di(2-ethylhexyl)sulfosuccinate than in the corresponding sodium salt, presumably because of the greater bulk of the K^+ compared to the Na^+ (Kon-no, 1971a).

III. SOME EFFECTS OF SOLUBILIZATION

III.A. Effect of Solubilization on Micellar Structure

The incorporation of solubilizate into a micelle may change the nature and shape of the micelle considerably. With the incorporation of increasing amounts of nonpolar material into its inner core, the value of V_H in the structure parameter $V_H/l_C a_0$ (Chapter 3, Section IIA) increases and a normal micelle in aqueous medium may become more and more asymmetric, eventually becoming lamellar in shape. Continued addition of nonpolar material may result in the conversion of the normal lamellar micelle to an inverted lamellar micelle and eventually to a spherical inverted micelle in the nonpolar medium. The reverse process, the conversion of an inverted micelle in the nonpolar medium to a normal micelle in aqueous medium upon the addition of increasing amounts of water, is also possible. These conversions are diagrammed in Figure 4-4. Liquid-crystalline phases (Section IB8 above) may also appear, along with these micellar structures, depending upon the structure of the surfactant and the nonpolar solubilizate, at various ratios of surfactant to water and/or nonpolar material.

The addition of medium-chain alcohols that are solubilized close to the surface of the micelle in the palisade layer increases the value of a_0, resulting in a greater tendency to form spherical micelles. Increase in the ionic strength of the aqueous solution or increase in the concentration of an ionic surfactant in the aqueous phase, on the other hand, decreases the value of a_0 and promotes the tendency to form cylindrical or lamellar micelles.

III.B. Change in the Cloud Points of Aqueous Solutions of Nonionic Surfactants

Aqueous solutions of POE nonionics, if the oxyethylene content is below about 80%, become turbid on being heated to a temperature known as the *cloud point*, following which there is separation of the solution into two phases. This phase separation occurs within a narrow temperature range that is fairly constant for

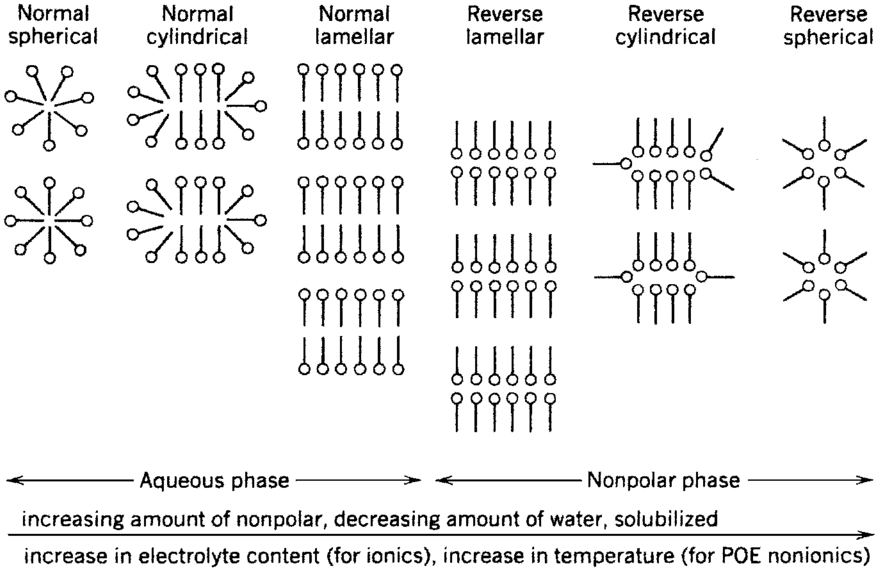


FIGURE 4-4 Effect of solubilization content and other molecular environmental factors on micellar structure. Note that interconversion of normal and reverse lamellar micelles involves only small changes in distances between hydrophilic and hydrophobic groups.

surfactant concentrations below a few percent (Nakagawa, 1963). The phases appear to consist of an almost micelle-free dilute solution of the nonionic surfactant at a concentration equal to its CMC at that temperature and a surfactant-rich micellar phase, which appears only when the solution is above its cloud point. The phase separation is reversible, and on cooling of the mixture to a temperature below the cloud point, the two phases merge to form once again a clear solution.

The separation is believed to be due to the sharp increase in the aggregation number of the micelles and the decrease in intermicellar repulsions (Staples, 1978; Tiddy, 1980) resulting from the decreased hydration of the oxyethylene oxygens in the POE hydrophilic group with increase in temperature (Chapter 3, Section III). As the temperature increases, micellar growth and increased intermicellar attraction cause the formation of particles, e.g., rodlike micelles, that are so large that the solution becomes visibly turbid (Glatter, 2000). Phase separation occurs because of the difference in density of the micelle-rich and micelle-poor phases (Nakagawa, 1963). Some cloud points are listed in Table 4-1.

The temperature at which clouding occurs depends on the structure of the POE nonionic surfactant. For a particular hydrophobic group, the larger the percentage of oxyethylene in the surfactant molecule, the higher the cloud point, although the relation between oxyethylene percentage and cloud point is not linear. A study of the effect of structural changes in the surfactant molecule on the cloud point (Schott, 1969) indicates that, at constant oxyethylene percentage, the cloud point is lowered by the following: decreased molecular weight of the surfactant, broader

TABLE 4-1 Cloud Points of POE Nonionics

Substance	Solvent	Cloud Point (°C)	Reference
n-$C_6H_{13}(OC_2H_4)_3OH$[a]	H_2O	37	Mulley, 1967
n-$C_6H_{13}(OC_2H_4)_5OH$[a]	H_2O	75	Mulley, 1967
n-$C_6H_{13}(OC_2H_4)_6OH$[a]	H_2O	83	Mulley, 1967
$(C_2H_5)_2CHCH_2(OC_2H_4)_6OH$[a]	H_2O	78	Elworthy, 1964
n-$C_8H_{17}(OC_2H_4)_4OH$[a]	H_2O	35.5	Mulley, 1967
n-$C_8H_{17}(OC_2H_4)_6OH$[a]	H_2O	68	Shinoda, 1967b
$C_{10}H_{21}(OC_2H_4)_4OH$[a]	H_2O	21	Mitchell, 1983
$C_{10}H_{21}(OC_2H_4)_5OH$[a]	H_2O	44	Mitchell, 1983
n-$C_{10}H_{21}(OC_2H_4)_6OH$[a]	H_2O	60	Mulley, 1967
$(n$-$C_4H_9)_2CHCH_2(OC_2H_4)_6OH$[a]	H_2O	27	Elworthy, 1964
$C_{11}H_{23}CONH(CH_2CH_2O)_4H$[a]	H_2O	52	Kjellin, 2002
n-$C_{12}H_{25}(OC_2H_4)_3OH$[a]	H_2O	25	Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_4OH$[a]	H_2O	4	Mitchell, 1983
$C_{12}H_{25}(OC_2H_4)_5OH$[a]	H_2O	27	Mitchell, 1983
n-$C_{12}H_{25}(OC_2H_4)_6OH$[a]	H_2O	52	Cohen, 1981
n-$C_{12}H_{25}(OC_2H_4)_7OH$[a]	H_2O	62	Cohen, 1981
n-$C_{12}H_{25}(OC_2H_4)_7OH$[b]	H_2O	58.5	Schott, 1969
n-$C_{12}H_{25}(OC_2H_4)_8OH$[a]	H_2O	79	Mulley, 1967
n-$C_{12}H_{25}(OC_2H_4)_8OH$[b]	H_2O	73	Fineman, 1952
n-$C_{12}H_{25}(OC_2H_4)_{9.4}OH$	H_2O	84	Kuwamura, 1984
$C_{12}H_{23}(OC_2H_4)_{9.2}OH$	H_2O	75	Kuwamura, 1984
n-$C_{12}H_{25}(OC_2H_4)_{10}OH$[a]	H_2O	95	Mulley, 1967
n-$C_{12}H_{25}(OC_2H_4)_{10}OH$[b]	H_2O	88	Wrigley, 1957
n-$C_{13}H_{27}(OC_2H_4)_{8.9}OH$[b]	H_2O	79	Kuwamura, 1984
$(n$-$C_6H_{13})_2CH(OC_2H_4)_{9.2}OH$[b]	H_2O	35	Kuwamura, 1984
$(n$-$C_4H_9)_3CH(OC_2H_4)_{9.2}OH$[b]	H_2O	34	Kuwamura, 1984
n-$C_{14}H_{29}(OC_2H_4)_6OH$[a]	H_2O	45	Mulley, 1967
n-$C_{16}H_{33}(OC_2H_4)_6OH$[a]	H_2O	32	Mulley, 1967
n-$C_{16}H_{33}(OC_2H_4)_{12.2}OH$	H_2O	97	Kuwamura, 1984
$(n$-$C_5H_{11})_3C(OC_2H_4)_{12.0}OH$	H_2O	48	Kuwamura, 1984
$C_{16}H_{31}(OC_2H_4)_{11.9}OH$	H_2O	80	Kuwamura, 1984
$C_8H_{17}C_6H_4(OC_2H_4)_7OH$[b]	H_2O	15	Mansfield, 1964
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	H_2O	64.3	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* NH_4Cl	60.0	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* NH_4Br	62.5	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* NH_4NO_3	63.2	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* $(CH_3)_4NCl$	59.6	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* $(CH_3)_4Nl$	67.0	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* $(C_2H_5)_4NCl$	61.0	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$[b]	0.2 *M* $(C_3H_7)_4Nl$	78.5	Schott, 1977
$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$[b]	H_2O	75	Mansfield, 1964
$C_8H_{17}C_6H_4(OC_2H_4)_{13}OH$[b]	H_2O	89	Fineman, 1952
$C_9H_{19}C_6H_4(OC_2H_4)_8OH$[b]	H_2O	34	Fineman, 1952
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH$[b]	H_2O	56	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH$[b]	n-$C_{16}H_{34}$-saturated H_2O	80	Shinoda, 1967b

(*Continued next page*)

TABLE 4-1 (*Continued*)

Substance	Solvent	Cloud Point (°C)	Reference
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH^b$	n-$C_{10}H_{22}$-saturated H_2O	79	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH^b$	n-C_7H_{16}-saturated H_2O	71.5	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH^b$	Cyclohexane-saturated H_2O	54	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH^b$	$C_2H_5C_6H_5$-saturated H_2O	30.5	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{9.2}OH^b$	Benzene-saturated H_2O	<0	Shinoda, 1967b
$C_9H_{19}C_6H_4(OC_2H_4)_{12.4}OH^b$	H_2O	87	Fineman, 1952
$C_{12}H_{25}C_6H_4(OC_2H_4)_9OH^b$	H_2O	33	Shinoda, 1967a
$C_{12}H_{25}C_6H_4(OC_2H_4)_{11.1}OH^b$	H_2O	50	Fineman, 1952
$C_{12}H_{25}C_6H_4(OC_2H_4)_{15}OH^b$	H_2O	90	Fineman, 1952

[a] Single compound.
[b] Distribution of POE chains.

distribution of POE chain length in commercial materials, branching of the hydrophobic group, more central position of the POE hydrophilic group in the surfactant molecule, replacement of the terminal hydroxyl group of the hydrophilic group by a methoxyl, and replacement of the ether linkage between the hydrophilic and the hydrophobic grojp by an ester linkage. On the other hand, the replacement of the ether linkage by an amide linkage raised the cloud point (Kjellin, 2002).

Schott (2003) has found the following linear equation between the cloud point (CP) of water-soluble POE nonionics and the average number, P, of POE units in the molecule.

$$(p - p^{\circ})/\mathrm{CP} = a + b(p - p^{\circ}) \tag{4.1}$$

where p° is the number of POE units where CP $= 0°$C and a and b are constants. This equation covers the entire range for the POE nonionics, including when $P \geq 100$.

The appearance of turbidity in the aqueous solution and its separation into two phases introduce certain disadvantages, esthetic as well as practical, in its utilization, and has resulted in investigations to determine the effect of solubilization on the temperature at which clouding appears. In general, long-chain nonpolar solubilizates, such as saturated aliphatic hydrocarbons, which are solubilized in the inner core of the micelle, appear to cause an increase in the cloud point of the solution, whereas polar and polarizable compounds, such as fatty acids and alcohols of moderate chain length, phenol, or benzene, which are solubilized in the outer regions of the micelle, depress it (Maclay, 1956; Nakagawa, 1960). Figure 4-3 shows the effect of solubilization of n-heptane on the cloud points of two POE nonionics. The upper curves in I and II, respectively, are for the cloud point in the presence of excess heptane.

The increase in the cloud point on solubilization of long-chain nonpolar material interior of the micelle may be due to the resulting increase in the radius, and hence the surface of the micelle, leaving more room at the micelle–water interface for increased hydration of the POE chains. On the other hand, the decrease when polar compounds are solubilized in the outer regions may be due to decreased hydration of the POE chains as a result of competition for the hydratable sites by the polar solubilizate.

Ions that are water structure formers, lower the cloud point of POE nonionics, $OH^- > F^- > Cl^- > Br$, by decreasing the availability of nonassociated water molecules to hydrate the ether oxygens of the POE chain. Ions that are water structure breakers (large, polarizable anions; soft bases: SCN^-, I^-) increase the cloud point by making more water molecules available to interact with the POE chain (Schott, 1984). Thus, chloride ions, which are water structure makers, lower the cloud point; iodide ions, which are structure breakers, raise it; bromide ions have no pronounced effect.

Ammonium ions and alkali metal cations, except lithium, tend to lower the cloud point of POE nonionics ($Na^+ > K^+ > Cs^+ > NH_4{}^+$) by salting them out, whereas polyvalent cations, H^+, and lithium ion form complexes with the ether oxygens of the POE chain, thereby increasing intermicellar repulsions and increasing the cloud point (Schott, 1973, 1975, 1996). Hydrogen ions and polyvalent cations are particularly effective, with the result that the addition of hydrogen chloride raises the cloud point of $C_{12}H_{25}(OC_2H_4)_6OH$, LiCl has almost no effect, and NaCl lowers it (Nakanishi, 1984). All divalent cations and Ag^+ increase the cloud point (Schott, 1996) by complexing with the ether oxygens of the POE chain.

On the other hand, whereas tetraalkylammonium ions are water structure formers and this effect increases with increase in the length of the alkyl group from one to four carbon atoms, tetramethylammonium and tetraethylammonium chlorides decrease the cloud point (the former more than the latter), while tetrapropyl and tetrabutylammonium chlorides increase it (the latter more than the former). All these quaternary cations, as do the iodides, increase the cloud point of POE nonionics, with the tetrabutyl ammonium ion producing the largest increase. The cloud point raising in the case of the tetrapropyl and tetrabutylammonium cations is ascribed to mixed micelle formation, with the nonionic predominating over water structure formation (Schott, 1977). The mixed micelles, with their cationic components, should presumably have greater intermicellar repulsions and stronger interaction with water, and consequently higher cloud points than the original POE nonionic micelles.

The cloud points of nonionics can also be increased by the addition of polyelectrolytes or ionic surfactants that interact with them and cause them to acquire a charge (Goddard, 1986; Saito, 1986).

Alkylpolyglycosides also show cloud points, with the effect of electrolytes on their cloud points being greater than for POE alcohols. Salts generally reduce their cloud points, with cations having a greater effect than anions. On the other hand, NaOH sharply increases their cloud points. Both effects are presumably due to the negative charge on the glucoside molecule in the pH range of 3–9 (Balzer, 1993).

III.C. Reduction of the CMC

See Chapter 3, Section IVC1.

III.D. Miscellaneous Effects of Solubilization

Other useful effects of solubilization are the binding of organic acids soluble in lubricating oils to the cations of metal sulfonate detergents in these oils, thereby decreasing the corrosion of metals by these acids (Bascom, 1958) and the solubilization of foamicidal oils by foam-producing surfactants, leading to increased foam life.

In some cases, solubilization of physiologically active materials enhances their potency; in other cases, it diminishes their potency. Moreover, the use of surfactants in preparations that are ingested by organisms may increase their solubilization of other physiologically active undesirable materials, such as bacterial toxins or carcinogens. Solubilization may also inactivate preservatives in pharmaceutical preparations by incorporating the former into the micelles of surfactants used in the formulation.

Cell membranes may also be affected by solubilizing surfactants, which may disrupt lysosomes, mitochondria, and erythrocytes. Triton X-100 is particularly effective in this respect. Details of these and other effects may be found in the monograph on solubilization by Elworthy, Florence, and MacFarlane (Elworthy, 1968a,b).

IV. MICELLAR CATALYSIS

The reactions of organic compounds can be catalyzed markedly in micellar solution. Catalysis by both normal micelles in aqueous medium and by reversed micelles in nonpolar solvents is possible (Fendler and Fendler, 1975; Kitahara, 1980). In normal micelles in aqueous medium, enhanced reaction of the solubilized substrate generally, but not always, occurs at the micelle–aqueous solution interface; in reversed micelles in nonaqueous medium, this reaction occurs deep in the inner core of the micelle.

The effect of micelles on organic reactions can be attributed to both electrostatic and hydrophobic interactions. Electrostatic interaction may affect the rate of a reaction either by its effect on the transition state of the reaction or by its effect on the concentration of reactant in the vicinity of the reaction site. Thus, a cationic micelle with its multiplicity of positively charged hydrophilic heads may catalyze the reaction between a nucleophilic anion and a neutral substrate by delocalizing the negative charge developing in the transition state of this reaction, thereby decreasing the energy of activation of the reaction. It may also catalyze the reaction by increasing the concentration of nucleophilic anion at the micelle–water interface close to the reactive site of the substrate. For catalysis to occur, it is necessary (1) that the substrate be solubilized by the micelle and (2) that the locus of solubilization be such that the reactive site of the substrate is accessible to the attacking reagent. It is here that hydrophobic interactions become important, because they determine the extent and the locus of solubilization in the micelle (Section IA above).

In the simplest case, where we assume that the surfactant does not complex with (i.e., solubilize) the substrate S, except when the former is in the form of micelles M and that complexing between the substrate and the micelle is in a 1:1 stoichiometric ratio, we can symbolize the formation of a reaction product P as (Fendler and Fendler, 1975)

$$\begin{array}{ccc} M+S & \overset{K}{\rightleftarrows} & MS \\ \downarrow k_0 & & \downarrow k_m \\ P & & P \end{array}$$

where k_0 is the rate constant for the reaction of the substrate in the bulk phase and k_m is the rate constant for the reaction of the substrate in the micelle. The overall rate constant for the reaction k_p is then given by the expression

$$k_p = k_0[F_0] + k_m[F_m] \tag{4.1}$$

where F_0 is the fraction of the uncomplexed substrate and F_m is the fraction of the complexed substrate. The equilibrium constant K for the interaction between substrate and micelle, usually called the *binding constant*, is then given by the relation

$$K = \frac{[F_m]}{[M]\,[F_0]} \tag{4.2}$$

from which

$$k_p = k_0[F_0] + k_m K[M]\,[F_0] = (k_0 + k_m[M]K)F_0 \tag{4.3}$$

Since $F_0 + F_m = 1$,

$$K = \frac{[F_m]}{[M]\,[F_0]} = \frac{[1 - F_0]}{[M]\,[F_0]}$$

and

$$F_0 = \frac{1}{1 + K[M]}$$

from which

$$k_p = \frac{k_0 + k_m[M]K}{1 + K[M]} \tag{4.4}$$

If we assume that $[M]$ is correctly given by the expression

$$[M] = \frac{(C - \mathrm{CMC})}{N} \tag{4.5}$$

where C is the total concentration of surfactant, CMC its critical micelle concentration, and N the aggregation number in its micelles, then the expression for the overall rate constant can be put in the form

$$\frac{1}{k_0 - k_p} = \frac{1}{k_0 - k_m} + \left(\frac{1}{k_0 - k_m}\right)\left[\frac{N}{K(C - \mathrm{CMC})}\right] \tag{4.6}$$

Since the overall rate constant for the reaction k_p and the rate constant for the reaction in the absence of micelles k_0 are readily obtained from kinetic data, a plot of $1/(k_0 - k_p)$ versus $[1/(C - \mathrm{CMC})]$, which should be a straight line with slope $= N/K(k_0 - k_m)$ and intercept $= 1/(k_0 - k_m)$, allows the calculation of k_m, the rate constant for the substrate complexed with the micelle, and K, the binding constant of the substrate to the micelle. This treatment is also applicable to bimolecular micelle-inhibited reactions in which one reagent is excluded from the micelle, for example, by electrostatic repulsion between an ionic reagent and a similarly charged micelle (Menger, 1967). Quantitative treatment of more complex reactions and some of the problems involved has been discussed by Bunton (1979).

Since surfactant concentrations are usually below $10^{-1}\,M$ and often one or two orders of magnitude below that, there will generally be little enhancement of the rate of reaction in the presence of micelles unless the product k_mK is 10^2 or more. Since the binding constant K depends on the extent of hydrophobic bonding between surfactant and substrate, it can be expected that K will increase with increase in the chain length of both the surfactant and the substrate. However, if the hydrophobic group of the substrate is too long, it may be solubilized so deeply in the micelle that access to its reactive site by a reagent in an aqueous solution phase is hindered. In that case, solubilization will inhibit, rather than catalyze, the reaction.

In accordance with these principles, the alkaline hydrolysis in aqueous medium of *p*-nitrophenyl esters is catalyzed by cationic *n*-alkyltrimethylammonium bromide micelles and retarded by anionic sodium laurate micelles (Menger, 1967). Nonionic surfactants either decrease the rate or have no significant effect on the rates of hydrolysis of carboxylic acid esters. The ester is probabily solubiized at the micelle–water interface. The transition state for alkaline hydrolysis of the ester linkage carries a negative charge due to the oncoming OH^-, and this charge can be stabilized by the adjacent positive charges of the hydrophilic heads of cationic micelles and destabilized by the adjacent negative charges in anionic micelles. In addition, the concentration of OH^- at the micelle–water interface is increased by the multiple positive charges on the cationic micelles and decreased by the multiple negative charges on the anionic micelles. Both of these effects may account for the enhancement and diminution of reaction rates in the respective cases. These effects also explain the observation that the rate of reaction with neutral nucleophiles, such as morpholine, is not accelerated by cationic micelles (Behme, 1965). They also explain the inhibiting action of small concentrations of inorganic anions (F^-, Cl^-, Br^-, NO_3^-, $SO_4^=$) on micellar catalysis by cationic surfactants, since these anions compress the electrical double layer surrounding the positively charged hydrophilic head groups, thus weakening their interaction with negative charges. The extent of both rate enhancement by cationics and diminution by anionics increased as the change length of the acyl group of the ester was increased, the order being *p*-nitrophenyl dodecanote $>$ *p*-nitrophenylhexanoate $\gg$ *p*-nitrophenylacetate.

In the case of certain other esters, however (e.g., ethyl benzoate and acetyl salicylate [Nogami, 1962; Mitchell, 1964]), both anionic and cationic micelles retard the rate of hydrolysis. These effects are attributed either to small binding constants between substrate and micelle or to solubilization into micelles in such fashion as to remove the reaction site from the attacking reagent.

The increase in the rate of acid-catalyzed hydrolysis of esters in aqueous media by anionic micelles can be explained in similar fashion as being due to stabilization of the positively charged transition state or to concentration of H^+ at the micelle–water interface by the negatively charged adjacent hydrophilic head groups.

Plots of rate constant versus surfactant concentration often show a maximum at some surfactant concentration above the CMC. There are a number of explanations for this. First, the number of micelles increases with increase in the surfactant concentration. When the number of micelles exceeds that required to solubilize all of the substrate, there is a dilution of the concentration of substrate per micelle as the surfactant concentration is increased further. This causes a reduction in the rate constant. Second, the charged surface of an ionic micelle in aqueous media may cause not only the concentration at the micelle–solution interface of an oppositely charged reactant in the solution phase, but the adsorption of that reactant on it, or even the solubilization of the reactant into the micelle. Such adsorption or solubilization of the reactant will result in a decrease in its activity in the solution phase. An increase in the concentration of surfactant over that required to effect substantially complete solubilization of the substrate may therefore result in a decrease in the rate constant, even in those cases where rate enhancement by micelles occurs.

Aliphatic and aromatic nucleophilic substitution reactions are also subject to micellar effects, with results consistent with those in other reactions. In the reaction of alkyl halides with CN^- and $S_2O_3^{2-}$ in aqueous media, sodium dodecyl sulfate micelles decreased the second-order rate constants and dodecyltrimethylammonium bromide increased them (Winters, 1965; Bunton, 1968). The reactivity of methyl bromide in the cationic micellar phase was 30 to 50 times that in the bulk phase and was negligible in the anionic micellar phase; a nonionic surfactant did not significantly affect the rate constant for *n*-pentyl bromide with $S_2O_3^{2-}$. Micellar effects on nucleophilic aromatic substitution reactions follow similar patterns. The reaction of 2, 4-dinitrochlorobenzene or 2, 4-dinitrofluorobenzene with hydroxide ion in aqueous media is catalyzed by cationic surfactants and retarded by sodium dodecyl sulfate (Bunton, 1968, 1969). Cetyltrimethylammonium bromide micelles increased the reactivity of dinitrofluorobenzene 59 times, whereas sodium dodecyl sulfate decreased it by a factor of 2.5; for dinitrochlorobenzene, the figures are 82 and 13 times, respectively. A POE nonionic surfactant had no effect.

Diquatemary ammonium halides of the gemini type (Chapter 12) are particularly effective micellar catalysts for nucleophilic substitution and decarboxylation reactions (Bunton, 1971, 1972, 1973).

The hydrolysis of long-chain alkyl sulfates in aqueous solution is an example of a reaction where micellar effects can be observed without the complicating presence of a solubilizate. Here the rate of acid-catalyzed hydrolysis is increased about 50 times by micellization because of the high concentration of H^+ on the negatively charged micellar surface (Nakagaki, 1986). As the chain length of the alkyl group is increased, the rate constant increases, reflecting the lower CMC of the surfactant. On the other hand, alkaline hydrolysis of these compounds is retarded considerably by micelle formation. Micelle formation has a negligible effect on the neutral hydrolysis of these materials (Kurz, 1962; Nogami, 1963).

A study of two-tailed (sodium dialkylsulfosuccinate) and two-headed (disodium monoalkylsulfosuccinate) surfactants revealed that these types have no advantage over similar single-headed, single-tailed (sodium alkylsulfoacetate) materials (Jobe, 1984). The second tail does not increase substantially the binding of the substrate (pyridine-*z*-azo-*p*-dimethylaniline) to the micelles, and the second head decreased, rather than increased, the binding of the reagent (Ni^{2+}) to the micelle. The latter effect may be due to the competition of the addition Na^+ present.

The presence of micelles can also result in the formation of different reaction products. A diazonium salt, in an aqueous micellar solution of sodium dodecyl sulfate, yielded the corresponding phenol from reaction with OH^- in the bulk phase but the corresponding hydrocarbon from material solubilized in the micelles (Abe, 1983).

Micellar effects are also apparent in reactions involving free radicals. Surfactants have been used extensively for the enhancement or inhibition of industrially and biologically important free radical processes, such as emulsion polymerization and the oxidation of hydrocarbons and unsaturated oils. An investigation of the free radical oxidation of benzaldehyde and *p*-methylbenzaldehyde by oxygen in aqueous nonionic surfactant solutions indicated that the rate of oxidation is increased when the aldehyde is solubilized in the interior region of the micelles. As the alkyl chain length of the surfactant was increased, the oxidation rate of *p*-methylbenzaldehyde increased because of the increased solubilization of the aldehyde in the interior region of the micelle. However, the oxidation rate for benzaldehyde was not increased by this change in the structure of the surfactant. Spectroscopic observations indicated that *p*-methylbenzaldehyde is solubilized in both the outer and inner regions of the micelles and increase in the length of the alkyl chain of the surfactant increases the proportion of aldehyde in the inner region, whereas benzaldehyde is solubilized only in the polyoxyethylene region of the micelle (Mitchell, 1965).

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PROBLEMS

1 Predict the locations of the following solubilizates in a micelle of $C_{12}H_{25}SO_4Na$ in aqueous medium:

(**a**) Toluene
(**b**) Cyclohexane
(**c**) *n*-Hexyl alcohol
(**d**) *n*-Dodecyl alcohol

2 Predict the effect of the following changes on the solubilization capacity of a micelle of $R(OC_2H_4)_xOH$ in aqueous medium for the two solubilizates given below. Use the symbols: + = increase; − = decrease; 0 ≅ little or no effect; ? = effect not clearly predictable.

Change	Effect for	
	n-Octane	n-Octylamine
(**a**) Increase in the value of x		
(**b**) Increase in the temperature to the cloud point		
(**c**) Addition of electrolyte		
(**d**) Addition of HCl		
(**e**) Increase in the chain length, R		

3 Predict the effect on the solubilization of water by micelles of $R(OC_2H_4)_xOH$ in heptane of:

(**a**) Increase in the value of x
(**b**) Increase in the temperature
(**c**) Addition of electrolyte
(**d**) Addition of HCl
(**e**) Increase in the chain length, R.

4 Explain why it is advisable to use a solution of $C_{11}H_{23}CO_2CH_2CH_2SO_3^-$ at a concentration above its CMC in distilled water soon after it is prepared, if one wishes to obtain an accurate measurement of its surface tension. (The pH of distilled water is about 5.8.)

5 Predict and explain the effect of each of the following on the cloud point of a nonionic surfactant, $R(OC_2H_4)_xOH$:

(**a**) Decrease in the pH of the solution below 7
(**b**) Saturation of the aqueous solution with n-hexane
(**c**) Addition of NaF to the solution
(**d**) Use of a commercial, rather than a pure grade, of $R(OC_2H_4)_xOH$
(**e**) Addition of $CaCl_2$ to the solution

5 Reduction of Surface and Interfacial Tension by Surfactants

Reduction of surface or interfacial tension is one of the most commonly measured properties of surfactants in solution. Since it depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface (or interfacial) excess concentration of the surfactant, as shown by the Gibbs equation

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{2.17}$$

it is also one of the most fundamental of interfacial phenomena.

The molecules at the surface of a liquid have potential energies greater than those of similar molecules in the interior of the liquid. This is because attractive interactions of molecules at the surface with those in the interior of the liquid are greater than those with the widely separated molecules in the gas phase. Because the potential energies of molecules at the surface are greater than those in the interior of the phase, an amount of work equal to this difference in potential energy must be expended to bring a molecule from the interior to the surface. The surface free energy per unit area, or surface tension, is a measure of this work; it is the minimum amount of work required to bring sufficient molecules to the surface from the interior to expand it by unit area. Although more correctly thought of as a surface free energy per unit area, surface tension is often conceptualized as a force per unit length *at a right angle to the force* required to pull apart the surface molecules in order to permit expansion of the surface by movement into it of molecules from the phase underneath it.

At the interface between two condensed, phases, the dissimilar molecules in the adjacent layers facing each other across the interface (Figure 5-1) also have potential energies different from those in their respective phases. Each molecule at the interface has a potential energy greater than that of a similar molecule in the interior of its bulk phase by an amount equal to its interaction energy with the molecules in the interior of its bulk phase minus its interaction energy with

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

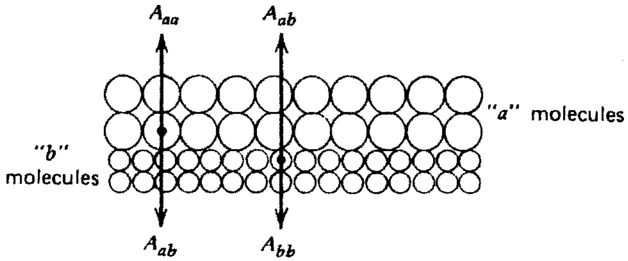

FIGURE 5-1 Simplified diagram of the interface between two condensed phases *a* and *b*.

the molecules in the bulk phase across the interface. For most purposes, however, only interactions with adjacent molecules need be taken into account. If we consider an interface between two pure liquid phases *a* and *b* (Figure 5-1), then the increased potential energy of the *a* molecules at the interface over those in the interior of that phase is $A_{aa} - A_{ab}$, where A_{aa} symbolizes the molecular interaction energy between *a* molecules at the interface and similar molecules in the interior of the bulk phase and A_{ab} symbolizes the molecular interaction energy between *a* molecules at the interface and *b* molecules across the interface. Similarly, the increased potential of *b* molecules at the interface over those in the interior is $A_{bb} - A_{ab}$. The increased potential energy of all the molecules at the interface over those in the interior of the bulk phases, the interfacial free energy, is then $(A_{aa} - A_{ab}) + (A_{bb} - A_{ab})$ or $A_{aa} + A_{bb} - 2A_{ab}$, and this is the minimum work required to create the interface. The interfacial free energy per unit area of interface, the interfacial tension γ_I is then given by the expression

$$\gamma_I = \gamma_a + \gamma_b - 2\gamma_{ab} \tag{5.1}$$

where γ_a and γ_b are the surface free energies per unit area (the surface tensions) of the pure liquids *a* and *b*, respectively, and γ_{ab} is the $a - b$ interaction energy per unit area across the interface.

The value of the interaction energy per unit area across the interface γ_{ab} is large when molecules *a* and *b* are similar in nature to each other (e.g., water and short-chain alcohols). When γ_{ab} is large, we can see from equation 5.1 that the interfacial tension γ_I will be small; when γ_{ab} is small, γ_I is large. The value of the interfacial tension is therefore a measure of the disimilarity of the two types of molecules facing each other across the interface.

In the case where one of the phases is a gas (the interface is a surface), the molecules in that phase are so far apart relative to those in the condensed phase that tensions produced by molecular interaction in that phase can be disregarded. Thus if phase *a* is a gas, γ_a and γ_{ab} can be disregarded and $\gamma_I \approx \gamma_b$, the surface tension of the condensed phase *b*.

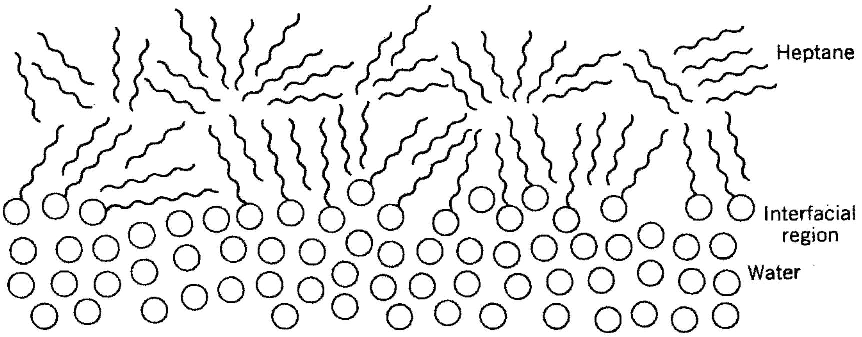

FIGURE 5-2 Diagrammatic representation of heptane–water interface with adsorbed surfactant.

When the two phases are immiscible liquids, γ_a and γ_b, their respective surface tensions, are experimentally determinable, pennitting the evaluation of γ_{ab}, at least in some cases. If one of the phases is solid, on the other hand, experimental evaluation of γ_{ab} is difficult, if not impossible. However here, too, the greater the similarity between *a* and *b* in structure or in the nature of their inkrmolecular forces, the greater the interaction between them (i.e., the greater the value of γ_{ab}) and the smaller the resulting interfacial tension between the two phases. When $2\gamma_{ab}$ becomes equal to $\gamma_a + \gamma_b$, the interfacial region disappears and the two phases spontaneously merge to form a single one.

If we now add to a system of two immiscible phases (e.g., heptane and water), a surface-active agent that is adsorbed at the interface between them, it will orient itself there, mainly with the hydrophilic group toward the water and the hydrophobic group toward the heptane (Figure 5-2). When the surfactant molecules replace water and/or heptane molecules of the original interface, the interaction across the interface is now between the hydrophilic group of the surfactant and water molecules on one side of the interface and between the hydrophobic group of the surfactant and heptane on the other side of the interface. Since these interactions are now much stronger than the original interaction between the highly dissimilar heptane and water molecules, the tension across the interface is significantly reduced by the presence there of the surfactant. Since air consists of molecules that are mainly nonpolar, surface tension reduction by surfactants at the air–aqueous solution interface is similar in many respects to interfacial tension reduction at the heptane–aqueous solution interface.

We can see from this simple model why a necessary but not sufficient condition for surface or interfacial tension reduction is the presence in the surfactant molecule of both lyophobic and lyophilic portions. The lyophobic portion has two functions: (1) to produce spontaneous adsorption of the surfactant molecule at the interface and (2) to increase interaction across the interface between the adsorbed surfactant molecules there and the molecules in the adjacent phase. The function of the lyophilic group is to provide strong interaction between the molecules of surfactant at the interface and the molecules of solvent. If any of these functions is not performed, then the marked reduction of interfacial tension characteristic of surfactants will probably not occur. Thus, we would not expect ionic surfactants containing hydrocarbon chains to reduce the surface tensions of hydrocarbon solvents, in spite of the distortion of the solvent structure by the ionic groups in the surfactant molecules. Adsorption of such molecules at the air–hydrocarbon interface with the ionic groups oriented toward the predominantly nonpolar air molecules would result in *decreased* interaction across the interface, compared to that with their hydrophobic groups oriented toward the air.

For significant surface activity, a proper balance between lyophilic and lyophobic character in the surfactant is essential. Since the lyophilic (or lyophobic) character of a particular structural group in the molecule varies with the chemical nature of the solvent and such conditions of the system as temperature and the concentrations of electrolyte and/or organic additives, the lyophilic–lyophobic balance of a particular surfactant varies with the system and the conditions of use. In general, good surface or interfacial tension reduction is shown only by those surfactants that have an appreciable, but limited, solubility in the system under the conditions of use. Thus surfactants which may show good surface tension reduction in aqueous systems may show no significant surface tension reduction in slightly polar solvents such as ethanol and polypropylene glycol in which they may have high solubility.

Measurement of the surface or interfacial tension of liquid systems is accomplished readily by a number of methods of which the most useful and precise for solutions of surfactants are probably the drop-weight and Wilhelmy plate methods. An excellent discussion of the various methods for determining surface and interfacial tension is included in the monograph on emulsions by Becher (1965).

For the purpose of comparing the performance of surfactants in reducing surface or interfacial tension, as in adsorption, it is necessary to distinguish between the efficiency of the surfactant (i.e., the bulk phase concentration of surfactant required to reduce the surface or interfacial tension by some significant amount) and its effectiveness, the maximum reduction in tension that can be obtained, regardless of bulk phase concentration of surfactant. These two parameters do not necessarily run parallel to each other and sometimes even run counter to each other.

The *efficiency* of a surfactant in reducing surface tension can be measured by the same quantity that is used to measure the efficiency of adsorption at the liquid–gas interface (Chapter 2, Section IIIE), pC_{20}, the negative log of the bulk phase concentration necessary to reduce the surface tension by 20 dyn/cm (mN m^{-1}). The *effectiveness* of a surfactant in reducing surface tension can be measured by the amount of reduction, or surface pressure, Π_{CMC}, $(= \gamma_o - \gamma_{CMC})$ attained at the critical micelle concentration, since reduction of the tension beyond the CMC is relatively insignificant (Figure 5-3).

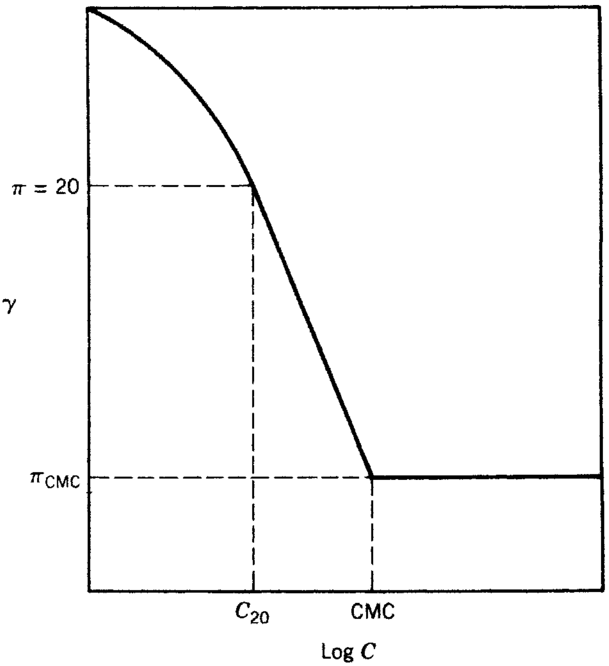

FIGURE 5-3 Surface tension-log C plot illustrating efficiency, $-\log C_{20}(pC_{20})$, and effectiveness of surface tension reduction, Π_{CMC}.

I. EFFICIENCY IN SURFACE TENSION REDUCTION*

Since surface or interfacial tension reduction depends on the replacement of solvent molecules at the interface by surfactant molecules, the efficiency of a surfactant in reducing surface tension should reflect the concentration of the surfactant at the interface relative to that in the bulk liquid phase. A suitable measure for the efficiency with which a surfactant performs this function would therefore be the ratio of the concentration of surfactant at the surface to that in the bulk liquid phase at equilibrium, both concentrations being expressed in the same units, e.g., $[C_1^s]/C_1$, where both concentrations are in moles/liter.

The surface concentration of surfactant $[C_1^s]$, in moles per liter, is related to its surface excess concentration Γ_1, in moles per cm^2, by the relation $[C_1^s] = (1000\Gamma_1/d) + C_1$, where $d =$ the thickness of the inter-facial region, in centimeters. For surfactants, Γ_1 is in the range $1\text{–}5 \times 10^{-10}$ mol/cm^2, while $d = 50 \times 10^{-8}$ cm or less and $C_1 = 0.01\ M$ or less. Thus, $[C_1^s] = 1000\Gamma_1/d$ without significant error, and $[C_1^s]/C_1 = 1000\Gamma_1/Cd$.

When the tension has been reduced by 20 mN/m (dyn/cm), the value of Γ is close to its maximum value, Γ_m, as shown in Chapter 2, and most surfactant

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*Rosen (1974).

molecules are lying slightly tilted to the interface. If we assume that the thickness of the interfacial region d is determined by the height of the surfactant normal to the interface, then d is inversely proportional to the minimum surface area per adsorbed molecule a_m^s; a larger value of a_m^s generally indicates a smaller angle of the surfactant with respect to the interface, a smaller value of a_m^s indicates an orientation of the surfactant more perpendicular to the interface. Since $a_m^s = (K/\Gamma_1) \propto (1/d)$, the quantity Γ_1/d may be considered to be a constant, and $[C_1^s]/C_1 = (K_1/C_1)_{\pi=20}$, where K and K_1 are constants. This indicates that the bulk concentration of surfactant necessary to produce a 20-mN/m (dyn/cm) reduction in tension, C_{20} (Chapter 2, Section IIIE), is not only a measure of the efficiency of adsorption at the liquid–gas interfaces but also a measure of the efficiency of surface tension reduction by the surfactant (Figure 5-3).

Again, as discussed there, it is more useful and convenient to use the quantity C_{20} in the form of its negative logarithm pC_{20}, since the latter quantity is related (equations 2.30, 2.31, 2.35, 2.36) to standard free energies of adsorption. The factors that determine the value of pC_{20} have been discussed in Chapter 2, Section IIIE.

For surfactants in aqueous solution, the efficiency increases with increase in the hydrophobic character of the surfactant. Equation 2.31 indicates that the efficiency factor pC_{20} is often a linear function of the number of carbon atoms in a straight-chain hydrophobic group, increasing as the number of carbon atoms increases. This has been shown (Rosen, 1974) to be valid for several homologous series of anionic, cationic, and nonionic surfactants. Some plots of pC_{20} as a function of the number of carbon atoms in the (straight hydrocarbon chain) hydrophobic group are given in Figure 2-16.

In its effect on the efficiency of surface tension reduction, as in both efficiency and effectiveness of adsorption, a phenyl group in the hydrophobic chain appears to be equivalent to about three and one-half $—CH_2—$ groups in a straight alkyl chain with a single terminal hydrophilic group. This same effect has been noted in measurements of relative adsorptivity at the aqueous solution–air interface (Shinoda, 1960) and of critical micelle concentrations (Chapter 3, Section IVA). Replacement of a single straight-chain hydrophobic group by a branched or an unsaturated one containing the same number of carbon atoms, or by two or more groups with the same total number of carbon atoms, decreases the efficiency. When the hydrophobic group has side chains, the carbon atoms on the side chains appear to have about two-thirds the effect of carbon atoms in a straight alkyl chain with a single, terminal hydrophilic group. Thus, the efficiency of $C_6H_{13}CH(C_4H_9)CH_2C_6H_4SO_3^-Na^+$ at 75°C is between those of the sodium *p*-*n*-decyl- and *p*-*n*-dodecylbenzenesulfonates. When the hydrophilic group is at a nonterminal position in the hydrophobic group, the latter appears to act as if it were branched at the position of the hydrophilic group, with the carbon atoms on the shorter portion of the hydrophobic group having about two-thirds the effect of the carbon atoms in the longer portion. Thus sodium *p*-*n*-dodecyl-6-benzenesulfonate, $C_6H_{13}CH(C_5H_{11})C_6H_4SO_3Na$, has a surface tension concentration curve at 75°C, which is practically identical with that of sodium *p*-*n*-decylbenzenesulfonate (Greiss, 1955).

For the series $RCOO(CH_2)_nSO_3^-Na^+$, where $n = 2$, 3, or 4, the $—CH_2—$ groups between the two hydrophilic groups, $—COO—$ and $—SO_3^-Na^+$, appear to be equivalent to about one-half $—CH_2—$ group in a straight alkyl chain with a single terminal hydrophilic group. In compounds of structure $R(OC_2H_4)_nSO_4^-Na^+$, where $n = 1$, 2, or 3, or in $RCONH(C_2H_4OH)_2$, at 25°C, the first oxyethylene group appears to be equivalent to about two and one-half $—CH_2—$ groups in a straight chain, with the additional oxyethylene groups having little or no effect.

The replacement of the usual hydrocarbon-based hydrophobic group by a fluorocarbon-based hydrophobic group causes a very large increase in the efficiency of surface tension reduction (Shinoda, 1972), the C_7 perfluorosulfonate showing greater efficiency than the corresponding C_{12} hydrocarbon-based sulfonate.

A change in the sign of the charge of a univalent ionic hydrophilic group produces little, if any, effect on the efficiency. However, the replacement of the counterion by one that is more tightly bound increases the efficiency, presumably by decreasing the net electrical charge on the surfactant molecule. For similar reasons, the replacement of an ionic hydrophilic group by a nonionic one or the addition of neutral electrolyte to a solution of an ionic surfactant in pure water results in a large increase in the value of pC_{20}. Temperature increase in the 10–40°C range causes a small decrease in the pC_{20} value for ionics and zwitterionics, a somewhat larger *increase* for POE nonionics.

The addition of water structure promoters (fructose, xylose) or a water structure breaker (*N*-methylacetamide) to an aqueous solution of a POE nonionic has been shown to affect markedly the efficiency of the surfactant in reducing surface tension (Schwuger, 1971). Water structure promoters appear to increase the efficiency of the surfactant, whereas structure breakers decrease it. The reasons for these changes are probably the same as those that account for the effect of these additives on the critical micelle concentrations of nonionics (Chapter 3).

II. EFFECTIVENESS IN SURFACE TENSION REDUCTION*

II.A. The Krafft Point

We have seen in Figure 2-15 that the surface tension of a solution of an individual surfactant decreases steadily as the bulk concentration of surfactant is increased until the concentration reaches a value known as the *critical micelle concentration* (CMC), above which the tension remains virtually unchanged. The surface tension at the CMC is therefore very close to the minimum tension (or maximum surface pressure) that the system can achieve. The surface pressure at this point, Π_{CMC}, is therefore a suitable measure of the "effectiveness" of a surfactant in reducing surface tension (Figure 5-3).

If the CMC exceeds the solubility of the surfactant at a particular temperature, then the minimum surface tension will be achieved at the point of maximum

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*Rosen (1976).

solubility, rather than at the CMC. The temperature at which the solubility of an ionic surfactant becomes equal to the CMC is known as the *Krafft point* (T_k). For surfactants being used below T_k, then, the maximum reduction in surface tension will be determined by the concentration of surfactant at solution saturation and these materials may show lower effectiveness in reducing surface tension than similar materials that are being used above their Krafft points. Krafft points of some surfactants are given in Table 5-1. These are for purified compounds; mixtures of isomeric materials generally have T_k's that are considerably lower than those of individual compounds.

The Krafft point increases with increase in the number of carbon atoms in the hydrophobic group and decreases with branching or unsaturation in that group in an homologous series of ionic surfactants (Gu, 1992). It also depends upon the nature of the counterion, increasing in the order $\mathrm{Li}^+ < \mathrm{NH}_4^+ < \mathrm{Na}^+ < \mathrm{K}^+$ for anionics. Oxyethylenation of alkyl sulfates decreases their Krafft points; oxypropylenation decreases them even further. Alkanesulfonates have higher Krafft points than their corresponding alkyl sulfates. The substitution of triethyl for trimethyl in the head groups of cationic alkyl trimethylammonium bromides leads to significant reduction in their Krafft points (Davey, 1998).

For surfactants that are being used above T_k, maximum reduction, for all practical purposes, is reached at the CMC. Since surfactants are normally used above their Krafft points, we restrict our discussion to that condition and consider maximum surface tension reduction to occur at the CMC.

II.B. Interfacial Parameter and Chemical Structural Effects

We have seen that at some point below but near the CMC the surface becomes essentially saturated with surfactant ($\Gamma \approx \Gamma_m$). The relation between γ and log C_1, the Gibbs equation, $d\gamma = -2.3nRT\Gamma_m \log C_1$ (equation 2.19a), in that region therefore becomes essentially linear. This inear relation continues to the CMC (in fact, it is usually used to determine the CMC).

When the point, C_{20}, is on the linear portion of the curve (Figure 5-3), that is, if the surface is essentially saturated when the surface tension of the solvent has been reduced by 20 dyn/cm (20 mN m^{-1}), which is generally the case for most surfactants, then for the linear portion of the plot, the Gibbs adsorption equation becomes

$$\Delta\gamma = -\Delta\pi \approx -2.3nRT\Gamma_m\Delta \log C$$

and

$$(\Pi_{\mathrm{CMC}} - 20) \approx 2.3nRT\Gamma_m(\log \mathrm{CMC} - \log C_{20})$$

or

$$\Pi_{\mathrm{CMC}} \approx 20 + 2.3nRT\Gamma_m \log(\mathrm{CMC}/C_{20}). \tag{5.1}$$

TABLE 5-1 Krafft Points of Surfactants

Compound	Krafft Point (°C)	Reference
$C_{12}H_{25}SO_3^-Na^+$	38	Weil, 1963
$C_{14}H_{29}SO_3^-Na^+$	48	Weil, 1963
$C_{16}H_{33}SO_3^-Na^+$	57	Weil, 1963
$C_{18}H_{37}SO_3^-Na^+$	70	Weil, 1963
$C_{10}H_{21}SO_4^-Na^+$	8	Raisen, 1957
$C_{12}H_{25}SO_4^-Na^+$	16	Weil, 1963
$2\text{-}MeC_{11}H_{23}SO_4^-Na^+$	<0	Gotte, 1969
$C_{14}H_{29}SO_4^-Na^+$	30	Weil, 1963
$2\text{-}MeC_{13}H_{27}SO_4^-Na^+$	11	Gotte, 1969
$C_{16}H_{33}SO_4^-Na^+$	45	Weil, 1963
$2\text{-}MeC_{15}H_{31}SO_4^-Na^+$	25	Gotte, 1969
$C_{16}H_{33}SO_4^-\ {}^+NH_2(C_2H_4OH)_2$	<0	Weil, 1959
$C_{18}H_{37}SO_4^-Na^+$	56	Weil, 1963
$2\text{-}MeC_{17}H_{35}SO_4^-Na^+$	30	Gotte, 1969
$Na^+\ {}^-O_4S(CH_2)_{12}SO_4^-Na^+$	12	Ueno, 1974
$Na^+\ {}^-O_4S(CH_2)_{14}SO_4^-Na^+$	24.8	Ueno, 1974
$Li^+\ {}^-O_4S(CH_2)_{14}SO_4^-Li^+$	35	Ueno, 1974
$Na^+\ {}^-O_4S(CH_2)_{16}SO_4^-Na^+$	39.1	Ueno, 1974
$K^+\ {}^-O_4S(CH_2)_{16}SO_4^-K^+$	45.0	Ueno, 1974
$Li^+\ {}^-O_4S(CH_2)_{16}SO_4^-Li^+$	39.0	Ueno, 1974
$Na^+\ {}^-O_4S(CH_2)_{18}SO_4^-Na^+$	44.9	Ueno, 1974
$K^+\ {}^-O_4S(CH_2)_{18}SO_4^-K^+$	55.0	Ueno, 1974
$C_8H_{17}COO(CH_2)_2SO_3^-Na^+$	0	Hikota, 1970
$C_{10}H_{21}COO(CH_2)_2SO_3^-Na^+$	8.1	Hikota, 1970
$C_{12}H_{25}COO(CH_2)_2SO_3^-Na^+$	24.2	Hikota, 1970
$C_{14}H_{29}COO(CH_2)_2SO_3^-Na^+$	36.2	Hikota, 1970
$C_8H_{17}OOC(CH_2)_2SO_3^-Na^+$	0	Hikota, 1970
$C_{10}H_{21}OOC(CH_2)_2SO_3^-Na^+$	12.5	Hikota, 1970
$C_{12}H_{25}OOC(CH_2)_2SO_3^-Na^+$	26.5	Hikota, 1970
$C_{14}H_{26}OOC(CH_2)_2SO_3^-Na^+$	39.0	Hikota, 1970
$C_{12}H_{25}CH(SO_3^-Na^+)COOCH_3$	6	Ohbu, 1998
$C_{12}H_{25}CH(SO_3^-Na^+)COOC_2H_5$	1	Ohbu, 1998
$C_{14}H_{29}CH(SO_3^-Na^+)COOCH_3$	17	Ohbu, 1998
$C_{16}H_{33}CH(SO_3^-Na^+)COOCH_3$	30	Ohbu, 1998
$C_{10}H_{21}CH(CH_3)C_6H_4SO_3^-Na^+$	31.5	Smith, 1966
$C_{12}H_{25}CH(CH_3)C_6H_4SO_3^-Na^+$	46.0	Smith, 1966
$C_{14}H_{29}CH(CH_3)C_6H_4SO_3^-Na^+$	54.2	Smith, 1966
$C_{16}H_{33}CH(CH_3)C_6H_4SO_3^-Na^+$	60.8	Smith, 1966
$C_{14}H_{26}OCH_2CH(SO_4^-Na^+)CH_3$	14	Weil, 1966
$C_{14}H_{29}[OCH_2CH(CH_3)]_2SO_4^-Na^+$	<0	Weil, 1966
$C_{16}H_{33}OCH_2CH_2SO_4^-Na^+$	36	Gotte, 1969
$C_{16}H_{33}(OCH_2CH_2)_2SO_4^-Na^+$	24	Gotte, 1969
$C_{16}H_{33}OCH_2CH(SO_4^-Na^+)CH_3$	27	Weil, 1966
$C_{18}H_{37}OCH_2CH(SO_4^-Na^+)CH_3$	43	Weil, 1966

TABLE 5-1 (*Continued*)

Compound	Krafft Point (°C)	Reference
$C_{16}H_{33}OCH_2CH_2SO_4^-Na^+$	36	Weil, 1959
$C_{16}H_{33}(OC_2H_4)_2SO_3^-Na^+$	24	Weil, 1959
$C_{16}H_{33}(OC_2H_4)_3SO_4^-Na^+$	19	Weil, 1959
$C_{16}H_{33}[OCH_2CH(CH_3)]_2SO_4^-Na^+$	19	Gotte, 1969
$C_{18}H_{37}(OC_2H_4)_3SO_4^-Na^+$	32	Weil, 1959
$C_{18}H_{37}(OC_2H_4)_4SO_4^-Na^+$	18	Weil, 1959
$C_{18}H_{37}[OCH_2CH(CH_3)]_2SO_3^-Na^+$	31	Gotte, 1969
n-$C_7F_{15}COO^-Li^+$	<0	Shinoda, 1972
n-$C_7F_{15}COO^-Na^+$	8.0	Shinoda, 1972
n-$C_7F_{15}COO^-K^+$	25.6	Shinoda, 1972
n-$C_7F_{15}COOH$	20	Shinoda, 1972
n-$C_7F_{15}COO^-NH_4{}^+$	2.5	Shinoda, 1972
$(CF_3)_2CF(CF_2)_4COO^-K^+$	<0	Shinoda, 1972
$(CF_3)_2CF(CF_2)_4COO^-Na^+$	<0	Shinoda, 1972
n-$C_7F_{15}SO_3^-Na^+$	56.5	Shinoda, 1972
n-$C_8F_{17}SO_3^-Li^+$	<0	Shinoda, 1972
n-$C_8F_{17}SO_3^-Na^+$	75	Shinoda, 1972
n-$C_8F_{17}SO_3^-K^+$	80	Shinoda, 1972
n-$C_8F_{17}SO_3^-NH_4{}^+$	41	Shinoda, 1972
n-$C_8F_{17}SO_3^-\,{}^+NH_3C_2H_4OH$	<0	Shinoda, 1972
	Cationics	
$C_{16}H_{33}N^+(CH_3)_3Br^-$	25	Davey, 1998
$C_{16}H_{33}N^+(C_2H_5)_3Br^-$	<0	Davey, 1998
$C_{18}H_{37}N^+(CH_3)_3Br^-$	36	Davey, 1998
$C_{18}H_{37}N^+(C_2H_5)_3Br^-$	12	Davey, 1998
$C_{16}H_{33}Pyr^+Br^-$ [a]	25	Davey, 1998
	Zwitterionics	
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_{1\text{-}6}COO^-$	<1	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2CH_2COO^-$	17	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2(CH_2)_3COO^-$	13	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2(CH_2)_5COO^-$	<0	Weers, 1991
$C_{10}H_{21}(Pyr^+)COO^-$ [a]	<0	Zhao, 1984
$C_{12}H_{23}CH(Pyr^+)COO^-$ [a]	23	Zhao, 1984
$C_{14}H_{29}CH(Pyr^+)COO^-$ [a]	38	Zhao, 1984
$C_{12}H_{25}N^+(CH_3)_2CH_2CH_2SO_3^-$	70	Weers, 1991
$C_{12}H_{25}N^+(CH_3)_2(CH_2)_3SO_3^-$	<0	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2SO_3^-$	90	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2(CH_2)_3SO_3^-$	28	Weers, 1991
$C_{16}H_{33}N^+(CH_3)_2(CH_2)_4SO_3^-$	30	Weers, 1991

[a] Pyr^+, pyridinium.

From this, we see that the effectiveness of a surfactant in reducing the surface tension of a solvent depends upon:

1. The number of ions n whose surface concentration changes with change in the liquid-phase concentration of the surfactant;
2. The effectiveness of adsorption of the surfactant Γ_m; and
3. The CMC/C_{20} ratio.

The larger each of these quantities, the greater the reduction in surface tension attained at the CMC.

The factors that affect Γ_m, the effectiveness of adsorption, have been discussed previously (Chapter 2, Section IIIC). We can summarize their effects as follows:

1. Change in the length of the hydrophobic group (from 10 to 16 carbon atoms), or the introduction of some branching into the hydrophobic group, has very little effect on Γ_m in ionic surfactants.
2. As the size of the hydrophilic group, or its distance from a second hydratable group in the molecule, increases, Γ_m decreases.
3. For ionic surfactants, an increase in the ionic strength of the solution causes an increase in Γ_m.
4. For POE nonionics, an increase in the length of the POE chain at constant hydrophobic chain length causes a decrease in Γ_m; an increase in the hydrophobic chain length at constant POE chain length causes an increase in Γ_m.
5. Temperature increase causes a small decrease in Γ_m.

The factors that affect the CMC/C_{20} ratio have also been previously discussed (Chapter 3, Section VA). We have seen that:

1. The ratio is increased only slightly, if at all, by an increase in the length of the hydrophobic group in ionic surfactants.
2. The ratio is increased by the introduction of branching into the hydrophobic group or the positioning of the hydrophilic group in a central position in the molecule.
3. The ratio is increased by the introduction of a larger hydrophilic group.
4. For ionic surfactants, the ratio is increased greatly by an increase in the ionic strength of the solution or by a more tightly bound counterion, especially one containing an alkyl chain of six or more carbon atoms.
5. The ratio is increased for POE nonionics, with increase in the length of the POE chain at constant hydrophobic chain length and decreased with increase in the length of the hydrophobic chain at constant POE chain length.
6. The ratio is decreased by an increase in temperature in the 10–40°C range.

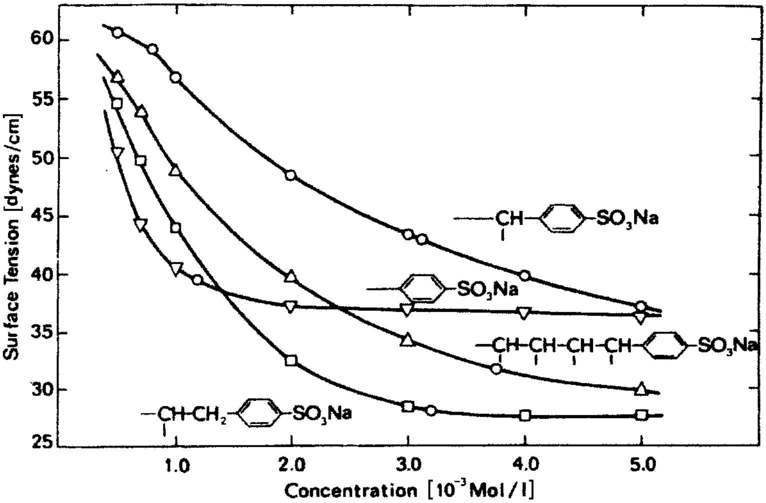

FIGURE 5-4 Surface tension of aqueous solutions of isomeric *p*-dodecylbenzenesulfonates at 75°C as a function of their concentration. Reprinted with permission from W. Greiss, *Fette, Seifen, Anstrichm.* **57**, 24, 168, 236 (1955).

Some of these factors affect Γ_m and the CMC/C_{20} ratio in parallel fashion (i.e., they increase both or decrease both); some in opposing fashion. When the effects are parallel, we can readily predict the resulting change in the effectiveness of surface tension reduction; when they are opposed, it is difficult to do so. Thus, increase in the length of the hydrophobic group in ionic surfactants has little effect on either Γ_m or the CMC/C_{20} ratio, and we can therefore expect that an increase in the length of the hydrophobic group will have little effect on their effectiveness of surface tension reduction.

On the other hand, the introduction of some branching into the hydrophobic group increases the CMC/C_{20} ratio but has little effect on Γ_m. We can therefore expect that the introduction of branching into the hydrophobic group will make the surfactant a more effective surface tension reducer. This is seen in the isomeric *p*-dodecylbenzene-sulfonates (Figure 5-4), where the isomers with branched alkyl chains, although less efficient reducers of the surface tension than the isomer with the straight alkyl chain, reduce the surface tension to lower values than does the latter.

Table 5-2 lists some experimental values of Γ_m, CMC/C_{20} and π_{CMC}. The experimental π_{CMC} values are very close to those calculated from the Γ_m and CMC/C_{20} values and equation 5.1. For surfactants with hydrocarbon-chain hydrophobic groups, the most effective surface tension reducers (largest Π_{CMC} values) are (1) nonionic compounds having small hydrophilic head groups and (2) anionic–cationic salts where both hydrophobic chains contain six carbon atoms or more, especially when both chains are approximately of the same length. Because of the

TABLE 5-2 Values of Γ_m, CMC/C_{20}, and Π_{CMC} in Aqueous Medium

Surfactant	Temp. (°C)	$\Gamma_m \times 10^{10}$ mol/cm^2	CMC/C_{20}	Π_{CMC} (dyn/cm)	References
Anionics					
$C_{10}H_{21}OCH_2COO^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	5.4	4.9	$40._5$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$ (pH 10.5)	30	2.1	3.5	$32._9$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2COO^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	2.9	6.5	$32._5$	Tsubone, 2001
$C_{11}H_{23}CON(C_4H_9)CH_2COO^-Na^+$	25	1.55	9.3	$36._8$	Zhu, 1998a
$C_{11}H_{23}CON(C_4H_9)CH_2COO^-Na^+$ ("hard river" water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	2.90	28.8	$43._9$	Zhu, 1998a
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$ (pH 10.5)	30	1.6	3.7	$30._6$	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2COO^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	2.5	6.9	$31._5$	Tsubone, 2001
$C_{13}H_{27}CON(C_3H_7)CH_2COO^-Na^+$	25	1.58	12.0	$39._2$	Zhu, 1998a
$C_{13}H_{27}CON(C_3H_7)CH_2COO^-Na^+$ ("Hard river" water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	3.50	14.1	$42._9$	Zhu, 1998a
$C_{10}H_{21}SO_3^-Na^+$	10	3.4	2.4	$33._0$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	25	3.3	2.1	$31._0$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$	40	3.05	1.8	$29._2$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$ (in 0.1 *M* NaCl)	25	3.85	4.1	$32._6$	Dahanayake, 1986
$C_{10}H_{21}SO_3^-Na^+$ (in 0.5 *M* NaCl)	25	4.2	5.4	$37._1$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	25	2.9	2.8	$33._0$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$	60	2.5	1.92	29	Rosen, 1969
$C_{12}H_{25}SO_3^-Na^+$ ("hard river" water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	2.34	9.97	$36._2$	Rosen, 1996
$C_{12}H_{25}SO_3^-Na^+$ (in 0.1 *M* NaCl)	25	3.8	5.9	$36._4$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-Na^+$ (in 0.5 *M* NaCl)	40	3.6	6.8	$39._0$	Dahanayake, 1986
$C_{12}H_{25}SO_3^-K^+$	25	3.3	2.38	34	Rosen, 1974
$C_{16}H_{33}SO_3^-K^+$	60	2.9	2.4	33	Rosen, 1969
$C_8H_{17}SO_4^-Na^+$ (heptane–H_2O)	50	2.3	4.0	39	Kling, 1957
$C_{10}H_{21}SO_4^-Na^+$	27	2.9	2.56	32	Dreger, 1944
$C_{10}H_{32}SO_4^-Na^+$ (heptane–H_2O)	50	2.3	4.4	39	Kling, 1957
branched $C_{12}H_{25}SO_4^-Na^+$	25	1.7	11.3	$40._1$	Varadaraj, 1992
branched $C_{12}H_{25}SO_4^-Na^{+\,a}$ (in 0.1 *M* NaCl)	25	3.3	15.2	$42._7$	Varadaraj, 1992

$C_{12}H_{25}SO_4^-Na^+$	25	3.2	2.6	32.$_5$	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$ (in 0.1 *M* NaCl)	25	4.0	6.0	38.$_0$	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$	25	3.2	2.6	32.$_5$	Dahanayake, 1986
$C_{12}H_{25}SO_4^-Na^+$ (H_2O–octane)	25	3.3	4.7	42.$_8$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (H_2O–heptadecane)	25	3.3	4.8	42.$_5$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (H_2O–cyclohexane)	25	3.1	4.9	43.$_2$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (H_2O–benzene)	25	2.3	2.2	29.$_1$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$ (H_2O–1-hexene)	25	2.5	1.5	25.$_8$	Rehfeld, 1967
$C_{12}H_{25}SO_4^-Na^+$	60	2.6	1.74	28	Rosen, 1969
$C_{14}H_{29}SO_4^-Na^+$	25	—	2.6	37.$_2$	Lange, 1968
$C_{14}H_{29}SO_4^-Na^+$ (heptane–H_2O)	50	3.0	4.5	43	Kling, 1957
$C_{16}H_{33}SO_4^-Na^+$	60	3.3	2.5	35	Rosen, 1969
$C_{16}H_{33}SO_4^-Na^+$ (heptane–H_2O)	50	2.6	5.0	43.$_5$	Kling, 1957
$C_{18}H_{37}SO_4^-Na^+$ (heptane–H_2O)	50	2.5	5.0	44	Kling, 1957
$C_{10}H_{21}OCH_2CH_2SO_3^-Na^+$	25	3.2	2.0	30.$_8$	Dahanayake, 1986
$C_{10}H_{21}OCH_2CH_2SO_3^-Na^+$ (in 0.1 *M* NaCl)	25	3.85	4.5	34.$_7$	Dahanayake, 1986
$C_{10}H_{21}OCH_2CH_2SO_3^-Na^+$ (in 0.5 *M* NaCl)	25	4.3	7.1	39.$_0$	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$	25	2.9	2.6	32.$_8$	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	3.59	10.2	40.$_8$	Rosen, 1996
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$ (in 0.1 *M* NaCl)	25	3.8	7.3	38.$_6$	Dahanayake, 1986
$C_{12}H_{25}OC_2H_4SO_4^-Na^+$ (in 0.5 *M* NaCl)	25	4.4	8.3	42.$_4$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	10	2.8	2.8	32.$_6$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	25	2.6	2.5	30.$_6$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$	40	2.5	2.0	28.$_6$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	3.24	11.5	39.$_0$	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$ (in 0.5 *M* NaCl)	25	3.5	6.7	36.$_5$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$ (in 0.5 *M* NaCl)	25	3.8	10.0	40.$_2$	Dahanayake, 1986
$C_{12}H_{25}(OC_2H_4)_2SO_4^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	2.41	10.5	33.$_4$	Rosen, 1996
$C_4H_9OC_{12}H_{24}SO_4^-Na^+$	25	1.1	4.2	28	Livingston, 1955
$C_{14}H_{29}OC_2H_4SO_4^-Na^+$	25	2.1	8.8	40	Livingston, 1955
$C_{14}H_{29}OC_2H_4SO_4^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	3.91	7.9	40.$_0$	Rosen, 1996

(*Continued next page*)

TABLE 5-2 (*Continued*)

Surfactant	Temp. (°C)	$\Gamma_m \times 10^{10}$ mol/cm^2	CMC/C_{20}	Π_{CMC} (dyn/cm)	References
$C_4H_9CH(C_2H_5)CH_2OOCCH(SO_3^-Na^+CH_2COOCH_2CH(C_2H_5)C_4H_9$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$ *M*)^b	25	2.28	151.	47.0	Rosen, 1996
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$ (pH 10.5)	30	2.2	2.0	27.2	Tsubone, 2001
$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3^-Na^+$ (0.1 *M* NaCl, pH 10.5)	30	3.0	5.5	31.7	Tsubone, 2001
$C_8H_{17}C_6H_4SO_3^-Na^+$	70	2.6	1.36	24.7	Lange, 1964
p-$C_9H_{19}C_6H_4SO_3^-Na^-$	75	1.8	1.3	23	Greiss, 1955
$C_{10}H_{21}C_6H_4SO_3^-Na^+$	70	3.2	1.33	25.4	Lange, 1964
p-$C_{10}H_{21}C_6H_4SO_3^-Na^+$	75	2.1	1.4	23.5	Greiss, 1955
$C_{11}H_{23}$-2-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	3.69	9.7	40.0	Zhu, 1998b
p-Sodium 1, 3, 5, 7-tetramethyl-(*n*-octyl)-1-benzenesulfonate	75	2.4	2.5	32	Greiss, 1955
$C_{12}H_{25}$-2-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	4.16	5.0	35.6	Zhu, 1998b
$C_{12}H_{25}$-4-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	3.44	17.4	43.8	Zhu, 1998b
p-$C_6H_{13}CH(C_4H_9)CH_2C_6H_4SO_3^-Na^+$-	75	2.85	3.2	35	Greiss, 1955
p-$C_6H_{13}CH(C_5H_{11})C_6H_4SO_3^-Na^+$-	75	2.1	>1.7	>26	Greiss, 1955
$C_{12}H_{25}$-6-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	3.15	21.5	44.5	Zhu, 1998b
$C_{12}H_{25}C_6H_4SO_3^-Na^+$	70	3.7	1.33	25.8	Lange, 1964
$C_{12}H_{25}C_6H_4SO_3^-Na^+$ (0.1 *M* NaCl)	25	3.6	11.6	41.9	Murphy, 1990
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	75	2.8	1.6	24	Greiss, 1955
$C_{13}H_{27}$-2-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	4.05	3.1	30.7	Zhu, 1998b
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$ (“hard river” water, I.S. $= 6.6 \times 10^{-3}$*M*)^b	30	3.58	15.8	44.1	Zhu, 1998b
$C_{13}H_{27}$-5-$C_6H_4SO_3^-Na^+$	30	2.15	7.6	39.0	Zhu, 1998b
$C_{14}H_{29}C_6H_4SO_3^-Na^+$	70	2.7	1.53	26.5	Lange, 1964
p-$C_{14}H_{29}C_6H_4SO_3^-Na^+$	70	2.2	1.6	24.5	Greiss, 1955
$C_{16}H_{33}C_6H_4SO_3^-Na^+$	70	1.9	1.93	27.8	Lange, 1964
$C_{16}H_{33}$-8-$C_6H_4SO_3^-Na^+$	45	1.61	14.4	42.5	Lascaux, 1983
n-$C_7F_{15}COO^-Na^+$	25	4.0	9.4	47.4	Shinoda, 1972
n-$C_7F_{15}COO^-K^+$	25	3.9	9.3	51.4	Shinoda, 1972
$(CF_3)_2CF(CF_2)_4COO^-Na^+$	25	2.8	11.2	51.8	Shinoda, 1972

n-$C_8F_{17}SO_3^-Li^+$	25	3.0	10.0	$42._2$	Shinoda, 1972
$C_4F_9CH_2OOCCH_2CH(SO_3^-Na^+)OOCCH_2C_4F_9$	30	3.0	—	$53._5$	Downer, 1999
		Cationics			
$C_{10}H_{21}N(CH_3)_3{}^+Br^-$(in 0.1 *M* NaCl)	25	3.39	2.7	$30._4$	Li, 2001
$C_{12}H_{25}N(CH_3)_3{}^+Br^-$ (“hard river” water, I.S. $= 6.6 \times 10^{-3} M)^b$	25	2.72	3.99	$33._9$	Rosen, 1996
$C_{12}H_{25}N(CH_3)_3{}^+Cl^-$ (in 0.1 *M* NaCl)	25	4.39	2.95	$31._5$	Li, 2001
$C_{14}H_{29}N(CH_3)_3{}^+Br^-$	30	2.7	2.1	31	Venable, 1964
$C_{14}H_{29}N(CH_3)_3{}^+Br^-$ (“hard river” water, I.S. $= 6.6 \times 10^{-3} M)^b$	25	3.18	6.45	$34._6$	Rosen, 1996
$C_{14}H_{29}N(C_3H_7)_3{}^+Br^-$	30	1.9	2.4	29	Venable, 1964
$C_{16}H_{33}N(CH_3)_3{}^+Cl^-$ (in 0.1 *M* NaCl)	25	3.4	10.0	38	Caskey, 1971
$C_{10}H_{21}Pyr^+Br^{-\ c}$	25	2.01	3.97	$31._7$	Rosen, 1996
$C_{12}H_{25}Pyr^+Br^{-\ c}$	10	3.5	2.7	$34._6$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-\ c}$	25	3.3	2.5	$32._9$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-\ c}$	40	3.2	2.1	$30._8$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-\ c}$ (in 0.1 *M* NaBr)	25	3.5	6.9	$35._2$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Br^{-\ c}$ (in 0.1 *M* NaBr)	25	3.5	8.9	$37._2$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-\ c}$	10	2.7	2.3	$29._6$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-\ c}$	25	2.7	2.0	$28._3$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-\ c}$	40	2.6	1.8	$26._9$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-\ c}$ (in 0.1 *M* NaCl)	25	3.0	4.6	$30._4$	Rosen, 1982b
$C_{12}H_{25}Pyr^+Cl^{-\ c}$ (in 0.1 *M* NaCl)	25	3.1	5.5	$32._8$	Rosen, 1982b
$C_{14}H_{29}Pyr^+Br^{-\ c}$	30	2.8	2.2	31	Venable, 1964
$C_{12}N^+H_2CH_2CH_2OHCl^-$	25	1.93	7.0	31	Omar, 1997
$C_{12}N^+H(CH_2CH_2OH)_2Cl^-$	25	2.49	7.3	32	Omar, 1997
$C_{12}N^+(CH_2CH_2OH)_3Cl^-$	25	2.91	5.6	34	Omar, 1997
		Anionic–Cationic Salts			
$CH_3SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$	25	2.70^d	2.7	$33._5$	Lange, 1971
$C_2H_5SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$	25	2.85^d	3.4	$37._5$	Lange, 1971
$C_{12}H_{25}SO_4^- \cdot {}^+N(CH_3)_3C_2H_5$	25	2.63^d	2.7	$33._0$	Lange, 1971

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TABLE 5-2 (*Continued*)

Surfactant	Temp. (°C)	$\Gamma_m \times 10^{10}$ mol/cm^2	CMC/C_{20}	Π_{CMC} (dyn/cm)	References
$C_4H_9SO_4^- \cdot {}^+N(CH_3)_3C_{10}H_{21}$	25	2.50^d	7.0	$44._2$	Lange, 1971
$C_{10}H_{21}SO_4^- \cdot {}^+N(CH_3)_3C_4H_9$	25	2.85^d	3.4	$37._5$	Lange, 1971
$C_6H_{13}SO_4^- \cdot {}^+N(CH_3)_3C_8H_{17}$	25	2.53^d	10.4	$49._8$	Lange, 1971
$C_8H_{17}SO_4^- \cdot {}^+N(CH_3)_3C_6H_{13}$	25	2.50^d	7.0	$44._2$	Lange, 1971
$C_4H_9SO_4^- \cdot N(CH_3)_3C_{12}H_{25}$	25	2.67^d	5.3	$42._0$	Lange, 1971
$C_6H_{13}SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$	25	2.58^d	10.0	$49._5$	Lange, 1971
$C_8H_{17}SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$	25	2.72^d	9.6	$50._6$	Lange, 1971
$C_{10}H_{21}SO_4^- \cdot C_{10}H_{21}N(CH_3)_3^+$	25	2.9^d	9.1	50	Corkill, 1963
$C_{12}H_{25}SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$	25	2.74^d	9.6	$50._8$	Lange, 1971
$C_{12}H_{25}SO_3^- \cdot {}^+HON(CH_3)_2C_{12}H_{25}$	25	2.14^d	13.6	$48._5$	Rosen, 1964
Nonionics					
$C_8H_{17}CHOHCH_2OH$	25	5.1	9.6	$48._6$	Kwan, 1980
$C_8H_{17}CHOHCH_2CH_2OH$	25	5.3	8.9	$48._4$	Kwan, 1980
$C_{10}H_{21}CHOHCH_2OH$	25	6.3	6.5	$49._3{}^e$	Kwan, 1980
$C_{10}H_{23}CHOHCH_2CH_2OH$	25	5.8	6.8	$48._3{}^e$	Kwan, 1980
$C_{12}H_{25}CHOHCH_2CH_2OH$	25	5.1	7.7	$45._5$	Kwan, 1980
Decyl-β-D-glucoside (in 0.1 *M* NaCl, pH = 9)	25	4.18	11.1	$44._2$	Li, 2001
Decyl-β-D-maltoside (in 0.1 *M* NaCl, pH = 9)	25	3.37	6.5	$35._7$	Li, 2001
Dodecyl-β-D-maltoside (in 0.1 *M* NaCl, pH = 9)	25	3.67	7.1	$37._3$	Li, 2001
$C_6H_{13}(OC_2H_4)_6OH$	25	2.7	21.5	40	Mulley, 1962; Elworthy, 1964
$C_8H_{17}OCH_2CH_2OH$	25	5.2	7.2	$45._0$	Shinoda, 1959
$C_8H_{17}(OC_2H_4)_5OH$ (in 0.1 *M* NaCl)	25	3.46	8.4	$38._3$	Varadaraj, 1991
$C_{10}H_{21}(OC_2H_4)_6OH$	25	3.0	17.0	42	Carless, 1964; Corkill, 1964
$C_{10}H_{21}(OC_2H_4)_6OH$ (in "hard river" water, I.S. $= 6.6 \times 10^{-3}$M)^b	25	2.83	16.2	$39._4$	Rosen, 1996
$C_{10}H_{21}(OC_2H_4)_8OH$	25	2.38	16.7	$36._4$	Meguro, 1981

$C_{12}H_{25}(OC_2H_4)_3OH$	25	3.98	11.4	$44._1$	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_4OH$	25	3.63	13.7	$43._4$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_4OH$ (H_2O–hexadecane)	25	3.16	16.8^f	$52._1$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_5OH$	25	3.33	15.0	$41._5$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_5OH$ (in 0.1 *M* NaCl)	25	3.31	18.5	$41._5$	Varadaraj, 1991
$C_{12}H_{25}(OC_2H_4)_6OH$	25	3.7	9.6	41	Carless, 1964; Corkill, 1964
$C_{12}H_{25}(OC_2H_4)_6OH$ (in “hard river” water, I.S. $= 6.6 \times 10^{-3} M)^b$	25	3.19	12.8	$40._2$	Rosen, 1996
$C_{12}H_{25}(OC_2H_4)_7OH$	25	2.90	14.9	$38._3$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	10	2.56	17.5	$37._4$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	25	2.52	17.3	$37._2$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$	40	2.46	15.4	$37._3$	Rosen, 1982a
$C_{12}H_{25}(OC_2H_4)_8OH$ (H_2O–hexadecane)	25	2.64	17.5^f	$48._7$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_8OH$ (H_2O–heptane)	25	2.62	18.6^f	$48._5$	Rosen, 1991
$C_{12}H_{25}(OC_2H_4)_9OH$	23	2.3	17.0	36	Lange, 1965
$C_{12}H_{25}(OC_2H_4)_{12}OH$	23	1.9	11.8	32	Lange, 1965
6-branched $C_{13}H_{17}(OC_2H_4)_3OH$ (in 0.1 *M* NaCl)	25	2.87	35.7	$45._5$	Varadaraj, 1991
$C_{13}H_{27}(OC_2H_4)_3OH$ (in 0.1 *M* NaCl)	25	3.89	8.8	$40._9$	Varadaraj, 1991
$C_{13}H_{27}(OC_2H_4)_8OH$	25	2.78	11.3	$36._7$	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_6OH$ (in “hard river” water, I.S. $= 6.6 \times 10^{-3}$ $M)^b$	25	3.34	10.5	$39._6$	Rosen, 1996
$C_{14}H_{29}(OC_2H_4)_8OH$	25	3.43	8.4	$38._0$	Meguro, 1981
$C_{14}H_{29}(OC_2H_4)_8OH$ (in “hard river” water, I.S. $= 6.6 \times 10^{-3}$ $M)^b$	25	2.67	13.8	$37._1$	Rosen, 1996
$C_{15}H_{31}(OC_2H_4)_8OH$	25	3.59	7.1	$37._4$	Meguro, 1981
$C_{16}H_{33}(OC_2H_4)_6OH$	25	4.4	6.3	40	Corkill, 1961; Elworthy, 1964
$C_{16}H_{23}(OC_2H_4)_6OH$ (in “hard river” water, I.S. $= 6.6 \times 10^{-3}$ $M)^b$	25	3.23	12.7	$40._1$	Rosen, 1996
$C_{16}H_{33}(OC_2H_4)_7OH$	25	3.8	8.3	39	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_9OH$	25	3.1	7.8	36	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_{12}OH$	25	2.3	8.5	33	Elworthy, 1962
$C_{16}H_{33}(OC_2H_4)_{15}OH$	25	2.1	8.9	32	Elworthy, 1962

(*Continued next page*)

TABLE 5-2 (*Continued*)

Surfactant	Temp. (°C)	$\Gamma_m \times 10^{10}$ mol/cm^2	CMC/C_{20}	Π_{CMC} (dyn/cm)	References
$C_{16}H_{33}(OC_2H_4)_{21}OH$	25	1.4	8.0	27	Elworthy, 1962
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_7OH$	25	2.9	22.9	42	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_8OH$	25	2.6	21.4	40	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_9OH$	25	2.5	18.6	$38._5$	Crook, 1963, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	25	2.2	17.4	37	Crook, 1963, 1964
$C_9H_{19}C_6H_4(OC_2H_4)_{10}OH^g$	25	2.95	13.5	41	Schick, 1962b
$C_9H_{19}C_6H_4(OC_2H_4)_{15}OH^g$	25	2.4	12.9	$35._5$	Schick, 1962b
$C_9H_{19}C_6H_4(OC_2H_4)_{30}OH^g$	25	1.9	12.3	31	Schick, 1962b
$C_{11}H_{23}CON(CH_2CH_2OH)_2$	25	3.75	6.3	$37._1$	Rosen, 1964
$C_{10}H_{21}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (in 0.1 M NaCl)	25	3.80	10.5	$41._4$	Zhu, 1999
$C_{11}H_{23}CONH(C_2H_4O)_4H$	23	3.4	—	$41._3$	Kjellin, 2002
$C_{11}H_{23}CON(CH_3)CH_2CHOHCH_2OH$ (in 0.1M NaCl)	25	4.34	10.9	$46._2$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_3CH_2OH$ (in 0.1M NaCl)	25	4.29	9.8	$44._7$	Zhu, 1999
$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (in 0.1M NaCl)	25	4.10	8.7	$42._3$	Zhu, 1999
$C_{12}H_{25}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (in 0.1M NaCl)	25	4.60	7.8	$43._9$	Zhu, 1999
$C_{13}H_{27}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (in 0.1M NaCl)	25	4.68	4.0	$36._0$	Zhu, 1999
$C_{10}H_{21}N(CH_3)CO(CHOH)_4CH_2OH$	20	3.96	5.2	$36._1$	Burczyk, 2001
$C_{12}H_{25}N(CH_3)CO(CHOH)_4CH_2OH$	20	3.99	8.8	$37._6$	Burczyk, 2001
$C_{14}H_{29}N(CH_3)CO(CHOH)_4CH_2OH$	20	3.97	8.5	$37._8$	Burczyk, 2001
$C_{16}H_{33}N(CH_3)CO(CHOH)_4CH_2OH$	20	3.65	10.1	$38._5$	Burczyk, 2001
$C_{18}H_{37}N(CH_3)CO(CHOH)_4CH_2OH$	20	3.97	8.1	$39._7$	Burczyk, 2001
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_2OH$	25	4.74	—	54	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_3OH$	25	4.46	—	$53._4$	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_5OH$	25	3.56	—	54	Matos, 1989
$C_6F_{13}C_2H_4SC_2H_4(OC_2H_4)_7OH$	25	3.19	—	51	Matos, 1989
$(CH_3)_3SiO[Si(CH_3)_2O]_3^-Si(CH_3)_2CH_2(C_2H_4O)_{8.2}CH_3$	25	3.4	37	50	Kanner, 1967
$(CH_3)_3SiO[Si(CH_3)_2O]_3Si(CH_3)_2CH_2(C_2H_4O)_{12.8.}CH_3$	25	4.2	19.5	51	Kanner, 1967
$(CH_3)_3SiO[Si(CH_3)_2O]_3Si(CH_3)_2CH_2(C_2H_4O)_{17.3.}CH_3$	25	4.2	17.4	$50._5$	Kanner, 1967

$(CH_3)_3SiO[Si(CH_3)_2O]_9Si(CH_3)_2CH_2(C_2H_4O)_{17.3.}CH_3$	25	3.6	11.8	42	Kanner, 1967
Zwitterionics					
$C_{10}H_{21}N^+(CH_3)_2COO^-$	23	4.15	7.0	39.$_7$	Beckett, 1963
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	23	3.57	6.5	36.$_5$	Beckett, 1963
$C_{14}H_{29}N^+(CH_3)_2CH_2COO^-$	23	3.53	7.5	37.$_5$	Beckett, 1963
$C_{16}H_{33}N^+(CH_3)_2CH_2COO^-$	23	4.13	6.9	39.$_7$	Beckett, 1963
$C_{10}H_{21}CH(Pyr^+)COO^-$	25	3.59	3.90	32.$_1$	Zhao, 1984
$C_{12}H_{33}CH(Pyr^+)COO^-$	25	3.57	5.66	35.$_0$	Zhao, 1984
$C_{14}H_{29}CH(Pyr^+)COO^-$	40	3.40	6.16	36.$_0$	Zhao, 1984
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	25	2.91	12.0	38.$_0$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$	25	2.86	14.4	39.$_0$	Dahanayake, 1984
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ (in 0.1 *M* NaCl, pH 5.7)	25	3.1	15.1	39.$_9$	Rosen, 2001
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ (H_2O–heptane)	25	2.81	—	48.$_4$	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ (H_2O–hexadecane)	25	2.90	—	48.$_6$	Murphy, 1988
$C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ (H_2O–toluene)	25	2.22	—	35.$_8$	Murphy, 1988
$C_{10}H_{21}N^+(CH_2C_6H_5)(CH_3)CH_2CH_2SO_3^-$	40	2.59	11.0	33.$_8$	Dahanayake, 1984

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[a] From dodecyl alcohol with 4.4 methyl branches in the molecule.

[b] I.S. = ionic strength of the solution.

[c] Pyr^+, pyridinium.

[d] Since there are two chains in each molecule, the number of *hydrophobic chains* per centimeter is twice the value of Γ_m.

[e] Below the Krafft point; supersaturated solution.

[f] CMC/C_{30} value.

[g] Hydrophilic head is not homogeneous, but distribution of POE chain lengths is reduced by molecular distillation.

small hydrophilic groups and the absence of ionic repulsive forces at the aqueous solution–air interface, both of these types of surfactants have their hydrophobic groups closely packed at the interface (large Γ_m values) and relatively large CMC/C_{20} ratios, producing large Π_{CMC} values. Examples of the first type are the 1,2- and 1,3-alkanediols; of the latter, the salts $C_{12}H_{25}SO_4^- \cdot {}^+N(CH_3)_3C_{12}H_{25}$ and $C_{12}H_{25}SO_3^- \cdot {}^+HON(CHS_3)_2\text{-}C_{12}H_{25}$.

The replacement of the usual small, inorganic counterion in ionic surfactants by an organic straight-chain one that is itself surface-active (e.g., in $C_{12}H_{25}SO_4^- \cdot C_{12}H_{25}N(CH_3)_3^+$) produces an ion pair that is strongly adsorbed at the aqueous solution–air interface. The mutual neutralization of charge in the ion pair results in (1) close packing at the interface (30.3×10^{-2} nm^2 per hydrophobic chain in this particular case) and (2) a high value for the CMC/C_{20} ratio, similar to that found in nonionic surfactants. Similar types of compounds, such as $C_{12}H_{25}N(CH_3)_2OH^+ \cdot C_{12}H_{25}SO_3^-$, are formed when long-chain amine oxides are added to anionic detergent compositions and are the basis for the foam-stabilization properties of amine oxides in these compositions.

The replacement of the usual hydrocarbon-chain hydrophobic group by a silicone- or fluorocarbon-chain hydrophobic group produces a large increase in the CMC/C_{20} ratio even, in the case of perfluoro compounds, when the surfactant is ionic. The large values of the CMC/C_{20} ratio in these cases may be due to steric barriers associated with the packing of these bulky chains into the micelle. The Γ_m values for these compounds (Table 5-2) are also high, even when ionic. The combination of large CMC/C_{20} ratios and large Γ_m values puts these compounds among the best surface tension reducers in aqueous media.

The addition of neutral electrolyte to an aqueous solution of an ionic surfactant, as mentioned above (Chapter 3, Section V), produces a much greater increase in adsorption at the aqueous solution–air interface than in micellization. Thus, the value of C_{20} is reduced more than the CMC, with the result that the CMC/C_{20} value is increased. In addition, Γ_m is increased by the increase in electrolyte. The increased values for Γ_m and CMC/C_{20} cause an increase in effectiveness.

The effect of an increase in the size of the hydrophilic head, without significant change in its nature, can be observed by comparing $C_{14}H_{29}N(CH_3)_3^+Br^-$ (or tetradecylpyridinium bromide) with $C_{14}H_{29}N(C_3H_7)_3^+Br^-$ (Table 5-2). The increase in the size of the three short alkyl groups surrounding the nitrogen results in a larger cross-sectional area of the molecule at the interface and therefore a smaller value of Γ_m. The log CMC/C_{20} ratio, however, shows only a small change in all three compounds, with the result that Π_{CMC} is reduced with increase in the size of the hydrophilic head.

For POE nonionics with the same (C_{12}) hydrophobic group, increase in the length of the POE chain from 1 to about 8 units causes a decrease in Γ_m but an increase in the CMC/C_{20} ratio. The change in Γ_m is greater than the change in log CMC/C_{20} and, as a result, the effectiveness of surface tension reduction decreases with increase in the length of the POE chain over this range. Above 8 OE units, there is little change in log CMC/C_{20} and a small decrease in Γ_m with increase in the OE content of the molecule, with the result that there is a continued small decrease in surface tension reduction effectiveness as the OE content is increased.

On the other hand, at constant POE content, an increase in the length of the hydrophobic group causes an increase in the value of Γ_m but an almost equal decrease in log CMC/C_{20}. As a result, as in the case of ionic surfactants, there is very little change in the surface tension reduction effectiveness of POE nonionic with increase in the length of the hydrophobic group.

For both ionic and POE nonionics, as the temperature is increased, there is a decrease in both Γ_m and the CMC/C_{20} ratios. As a result, although the surface *tension* of the solution may be reduced to a lower value by increase in the temperature, the surface tension reduction *effectiveness*, Π_{CMC} $(= \gamma_0 - \gamma_{\text{CMC}}$, where γ_0 is the surface tension of the pure solvent at that temperature), is always reduced by increase in temperature.

In contrast to their marked effect on the efficiency with which a POE nonionic reduces the surface tension of water, water structure promoters and breakers seem to show almost no effect on the effectiveness with which it reduces the tension (Schwuger, 1971).

Surfactants with hydrocarbon-chain hydrophobic groups generally do not lower the surface tension of alkanes, since any orientation of adsorbed surfactant of this type at the air–alkane surface would not reduce the surface free energy. However, fluorinated surfactants can adsorb and orient at the hydrocarbon–air surface to reduce the free energy there. Fluorinated surfactants of the type $C_6H_5CF(CF_3)O[CF_2CF(CF_3)O]_mC_3F_7$ have been observed to reduce the surface tension of *m*-xylene (28 mN/in) to 10 mN/in (Abe, 1992).

III. LIQUID–LIQUID INTERFACIAL TENSION REDUCTION

The reduction of the tension at an interface by a surfactant in aqueous solution when a second liquid phase is present may be considerably more complex than when that second phase is absent, i.e., when the interface is a surface. If the second liquid phase is a nonpolar one in which the surfactant has almost no solubility, then adsorption of the surfactant at the aqueous solution–nonpolar liquid interface closely resembles that at the aqueous solution–air interface and those factors that determine the efficiency and effectiveness of surface tension reduction affect interfacial tension reduction in a similar manner (Chapter 2, Section IIIC,E). When the nonpolar liquid phase is a saturated hydrocarbon, both the efficiency and effectiveness of interfacial tension reduction by the surfactant at the aqueous solution–hydrocarbon interface are greater than at the aqueous solution–air interface, as measured by pC_{20} and Π_{CMC}, respectively. The replacement of air as the second phase by a saturated hydrocarbon increases the tendency of the surfactant to adsorb at the interface, while the tendency to form micelles is not affected significantly. This results in an increase in the CMC/C_{20} ratio. Since the value of Γ_m, the effectiveness of adsorption (Chapter 2, Section IIIC), is not affected significantly by the presence of the saturated hydrocarbon, the increase in the value of Π_{CMC} is due mainly to this increase in the CMC/C_{20} ratio. When the hydrocarbon is a short-chain unsaturated or aromatic hydrocarbon, however, the Π_{CMC} value is smaller than when the second phase is air. Here, the effect is due mainly to the decrease in the value of Γ_m in the presence of these types of hydrocarbons. Both the tendency to adsorb and the tendency to form micelles are increased slightly in the presence of these types of hydrocarbons, but in almost equal amounts, resulting in little change in the CMC/C_{20} ratio.*

On the other hand, if the surfactant has appreciable solubility in both liquids, then very different factors may determine the value of the interfacial tension. Although low liquid–liquid interfacial tension is important in promoting emulsification (Chapter 8) and in the removal of oily soil by detergents (Chapter 10), advances in our knowledge of the factors governing the reduction at that interface stem from the intense interest in enhanced oil recovery by use of surfactant solutions.

III.A. Ultralow Interfacial Tension

For displacement of the oil in the pores and capillaries of petroleum reservoir rock, an aqueous solution–oil interfacial tension of $\approx 10^{-3}$ mN/m (dyn/cm) is generally required. To reach so low a value, the value of γ_{ab} (equation 5.1), the interaction energy across the interface (Figure 5-1) must be large. This means that the nature of the material on both sides of the interface must be very similar. Since oil and water have very different natures, a situation where both sides of an oil–water interface can have similar natures can occur only when both sides of the interface have similar concentrations of surfactant, oil, and water. There are a number of ways in which such a situation can be created.

In our discussion of the effect of temperature on solubilization capacity (Chapter 4, Section 1B7), we mentioned that when the temperature of an aqueous micellar solution W_D of a POE nonionic surfactant is increased, its solubilization of nonpolar material O increases due to the increased dehydration of the POE chains, which increases the lipophilic character of the surfactant. If this occurs for POE nonionics of the proper structure in the presence of excess nonpolar material, the volume of the aqueous phase W_D increases and that of the nonpolar phase oil decreases as the temperature increases (Figure 5-5*a,b*). This is accompanied by a decrease in the tension γ_{OW} at the O/W interface. With further increase in temperature, the POE chains become more and more dehydrated, the surfactant becomes more lipophilic, and more and more nonpolar material oil is solubilized into the increasingly asymmetric micelles. When the vicinity of the cloud point of the nonionic is reached the surfactant micelles, together with solubilized material, will start to separate from W_D as a separate phase D. If excess oil is still present, the system now contains three phases (Shinoda, 1968): excess oil; a phase D, the

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*At the hydrocarbon–aqueous solution interface, the CMC/C_{30} ratio, where C_{30} is the molar surfactant concentration in the aqueous phase needed to produce a 30 mN/m (dyne/cm) reduction in the interfacial tension, is a better determinant of Π_{CMC} than CMC/C_{20}, since the interfacial tension–log C curve is often not linear from the CMC to surface pressures as low as 20 mN/m (dyne/cm).

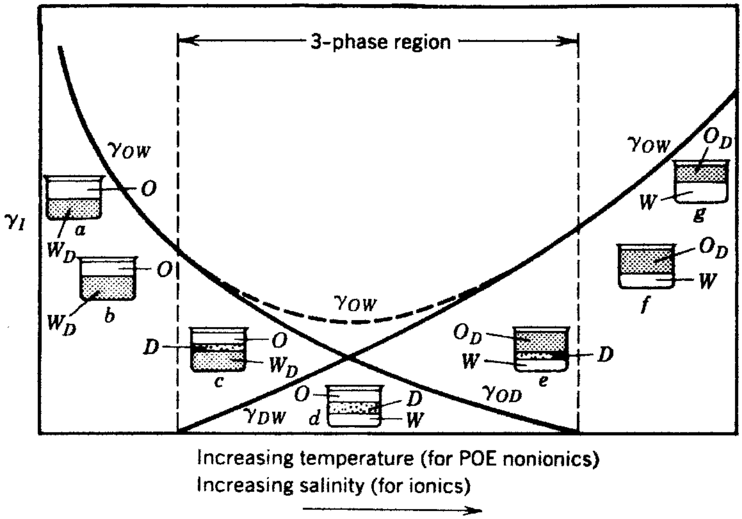

FIGURE 5-5 Effect of molecular environmental conditions on interfacial tension and phase volumes. Shaded phases indicate locations of the surfactant.

so-called middle phase, containing surfactant together with solubilized water and oil, and an aqueous phase W_D (Figure 5-5*c*).

The O/W_D interface is now replaced by a D/W_D interface, whose interfacial tension γ_{DW} is close to zero. At this point, there is also an *O*/*D* interface, whose interfacial tension γ_{OD} is low. As the temperature continues to increase, more and more surfactant micelles separate out of W_D, carrying with them solubilized *O* and *W*. The volume of W_D decreases and that of the middle phase *D* increases; γ_{OD} continues to decrease and γ_{DW} increases. Separation of the surfactant micelles from it has converted the aqueous phase into one (*W*) that contains only a small amount of unmicellized surfactant (Figure 5-5*d*). When *D* is very small in the three-phase region, γ_{OW} is approximately the sum of γ_{DW} and γ_{OD}.

As the surfactant continues to become more and more lipophilic with increase in temperature, a point is reached at which the micelles start to invert (Figure 4-4) and these dissolve in the excess *O*, carrying with them solubilized water and forming a reversed micellar solution O_D This is accompanied by an increase in O_D and a decrease in *D* to a very small volume (Figure 5-5*e*). γ_{OD} is close to zero; γ_{DW} continues to increase. Eventually, all of *D* dissolves in O_D, leaving only *W* (Figure 5-5*f*). At this point, the *DW* interface disappears and Γ_{DW}, still low, is replaced by γ_{OW}. With further increase in temperature, the surfactant becomes even more lipophilic, the solubilization capacity of the inverted micelles decreases, more *W* separates out, and γ_{OW} increases (Figure 5-5*g*).

The maximum volume of the surfactant (middle) phase *D* at the temperature where all three phases exist is dependent upon the percentage of surfactant in the system. If the percentage is very small, the surfactant phase may not be visible to the naked eye and the system may appear to contain only two phases; if the percentage of surfactant is large, the aqueous and nonpolar phases may be completely solubilized in the surfactant phase and the system may contain only one phase. In the latter case, the system is called a *microemulsion* (Chapter 8, Section II).

The structure of the surfactant phase D in equilibrium with both excess W and O phases has been a subject of considerable interest and speculation (Shinoda, 1975, 1983; Huh, 1979). Data indicate that, at the point of minimum interfacial tension against both W and O phases, this phase may not be homogeneous, but may consist of a mixture of normal and reverse micelles, since gradients of concentration, density, and other properties appear upon standing for some time under normal gravity, or upon centrifugation (Hwan, 1979; Rosen, 1984; Zhao, 1984; Good, 1986). It has also been suggested that the structure is bicontinuous (Scriven, 1977). If the surface-active material(s) present have long, straight hydrophobic groups, rodlike cylindrical or lamellar micelles may be present (Fowkes, 1985).

Temperature change in POE nonionic systems is not the only method of producing these phase changes and ultralow interfacial tension. For ionic surfactants of the proper structure, the addition of electrolyte, such as NaCl, with its consequent reduction of the electrical interactions of the ionic head groups, can cause the surfactant to change from hydrophilic to lyophilic. With increasing "salinity," such systems may show changes in phases, solubilization, and interfacial tension similar to those shown by POE nonionics with temperature change. The addition of hydrophilic or lipophilic polar compounds (*cosurfactants*) can also change the hydrophilic or lipophilic character of the system, its solubilization of water or oil, and the interfacial tension.

From the above discussion, it should be apparent that for POE nonionics, there is a particular temperature where the hydrophilic and lipophilic characters of the surfactant "balance" each other and γ_{OW} is at, or close to, its minimum value. It is usually defined operationally, for example, as the temperature where the surfactant phase solubilizes equal volumes of water and nonpolar material or the temperature at which an emulsion (Chapter 8) of the surfactant, water, and nonpolar material inverts. In the latter case, it is known as the *phase-inversion temperature* (PIT) (Chapter 8, Section IVB). Similarly, there is an electrolyte content at which the hydrophilic and lipophilic characters of ionic surfactants balance. The point at which equal volumes of water and nonpolar material are solubilized into the surfactant is known as the *optimal salinity* (Healy, 1974) and has been extensively investigated for enhanced oil recovery (Healy, 1977; Hedges, 1979; Nelson, 1980). The optimal salinity or PIT is at or close to the point where the parameter $V_H/l_c a_0$ (Chapter 3, Section II) equals 1 and lamellar normal and reverse micelles are readily interconvertable.

The larger the volume of water (V_W) (or nonpolar material $V_o)$ solubilized into the surfactant phase relative to its volume V_s, the lower the interfacial tensions γ_{DW}, γ_{OD}, and γ_{OW} (Robbins, 1974; Healy, 1976). This is understandable, since for both normal and reverse micelles, the interfacial tension against the second liquid phase decreases as the amount of second phase solubilized increases. The greater the amount solubilized in the presence of excess solubilizate, the more closely the natures of the two phases approach each other.

The Winsor ratio R (1948, 1968) is convenient for relating changes in the hydrophilic solvent W, the lipophilic solvent oil, and the surfactant C to interfacial tensions and phase volumes and for explaining them in terms of the molecular interactions involved (Bourrel, 1983, 1984). It is based upon the relative tendencies of the system to solubilize water and oil. The ratio,

$$R = \frac{A_{CO} - A_{OO} - A_{ll}}{A_{CW} - A_{WW} - A_{hh}} \tag{5.2}$$

measures the solubilization capacity of the surfactant micelles for W relative to that for O. A_{CO} and A_{CW} are the interaction strengths per unit area of interface of C with oil and water, respectively, promoting solubilization of the *other* liquid phase; A_{OO} and A_{WW} are the respective self-interaction strengths of the solvent molecules in oil and water, respectively, opposing solubilization into them; A_{ll} and A_{hh} are the strengths of the self-interactions between the lipophilic and hydrophilic portions, respectively, of the surfactant molecules, also opposing solubilization. When $R \ll 1$, the micelles solubilize oil much more readily than W, and a Type I system forms (Figure 5-5*a*,*b*); when $R \gg 1$, they solubilize water much more readily than oil, and a Type II forms (Figure 5-5*f*,*g*). When $R \simeq 1$, Type III or IV systems form, depending upon the magnitude of the numerator (or denominator). Type III is a three-phase system (Figure 5-5*d*); Type IV is a one-phase microemulsion (Chapter 8, Section II). When $R \simeq 1$, the larger the value of the numerator (or denominator) of the expression for R, the greater the solubilization capacity for water (or oil) and consequently the greater the tendency to form a Type IV system. R is therefore a semiquantitative method of measuring the balance between the hydrophilic and lipophilic characters of the surfactant *in the particular system in which it finds itself.*[*]

The Winsor R parameter and the Mitchell–Ninham $V_H/l_c a_o$ parameter are related to each other in that both specify that when the value of the parameter exceeds 1, normal micelles in aqueous media in the presence of excess nonpolar solvent will be converted into reverse micelles in nonpolar solvent in the presence of excess aqueous phase. The former concept bases this on molecular interactions, the latter on molecular geometry.

The lowest interfacial tension values are produced when $R \simeq 1$ and the value of the numerator (or denominator) in the expression for R is greatest. This produces the largest V_W/V_s and V_H/V_s ratios. To reduce γ_{OW}, then, R should be made to approach 1; in the case where $R < 1$[†] by increasing the value of the numerator in the case where $R > 1$[†] increasing the denominator, rather then decreasing the numerator.

The value of the numerator in equation 5.2 can be increased by increasing the value of A_{CO}, the interaction of the surfactant with oil, and/or by decreasing the values of A_{OO} and A_{ll}, the self-interaction of the lipophilic solvent molecules and of the lipophilic portions of the surfactant, respectively. A_{CO} can be increased by

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[*] When $R = 1$ and the A_{ll} and A_{hh} interactions are large, liquid crystals or gels may form (Bourrel, 1984).

[†] Determined by observing the type of system produced. when $R < 1$, a Type I system is formed; when $R > 1$, a Type II system.

increasing the length of the lipophilic group of the surfactant, although this simultaneously increases, to a smaller extent, the value of A_{ll}. A_{CO} can also be increased by adding a moderately lipophilic nonionic *cosurfactant* (e.g., an alcohol, amide, or amine of intermediate chain length) or a *lipophilic linker* (Chapter 8, Section II) to an ionic surfactant or by any additive that increases the packing of the surfactant at the interface (since A_{CO} is an interaction strength per unit area of interface). When oil is an alkane, A_{OO} can be decreased by decrease in the alkane chain length.

The value of the denominator can be increased by increasing the value of A_{CW} by the interaction of the surfactant with W, and/or by decreasing the values of A_{WW} and A_{hh}, the self-interaction of the hydrophilic solvent molecules and the hydrophilic portions of the surfactant, respectively. A_{CW} can be increased in the case of POE nonionics by increase in the length of the POE chain, although this simultaneously increases the value of A_{hh} slightly. It can also be increased by addition of a hydrophilic linker. All of these changes have been shown to decrease the value of A_{OW} when they bring the value of R closer to 1 (Healy, 1976; Salter, 1977; Bourrel, 1980; Shinoda, 1986; Verzaro, 1984; Valint, 1987). In addition, from equation 5.2, surfactants with large hydrophobic groups (large A_{CO} values) and large hydrophilic groups (large A_{CW} values) should show lower interfacial tension values than similar-type surfactants of lower molecular weight with the same balance of hydrophilic and lipophilic groups. This has been confirmed experimentally (Kunieda, 1982; Barakat, 1983).

From the above, a surfactant capable of being both an efficient and an effective γ_{OW} reducer should have a balanced structure ($R \simeq 1$) in the system and under the conditions of use, with a considerable amount of both hydrophilic and lipophilic character (large values of A_{CW} and A_{CO}). The value of $R \simeq 1$ and large values of A_{CW} and A_{CO} will cause reduction of γ_{OW} to a very low value, i.e., make it an effective reducer of γ_{OW}. A surfactant of this type will also have limited solubility in a hydrophilic solvent because of the large lipophilic (hydrophobic) portion of the molecule and limited solubility in a lipophilic solvent because of the large hydrophilic (lipophobic) portion of the molecule. This limited solubility in both liquids will cause the surfactant to adsorb strongly at the interface and consequently to be a very efficient reducer of γ_{OW}.

The addition of an alcohol that adsorbs at the interface, such as *n*-pentanol, decreases A_{CW} by increasing the interfacial area per surfactant molecule. The addition of electrolyte, in the case of an ionic surfactant, decreases A_{CW} and increases A_{hh}. All these changes result in an increase in the value of R.

Another approach to obtaining ultralow interfacial tension is via the microemulsion *solubility parameter at optimum formulation* (Chapter 8, Section II).

IV. DYNAMIC SURFACE TENSION REDUCTION

IV.A. Dynamic Regions

In many interfacial processes, such as in high-speed wetting of textile, paper, and other substrates (Chapter 6, Section IIC), or in foaming (Chapter 7), equilibrium

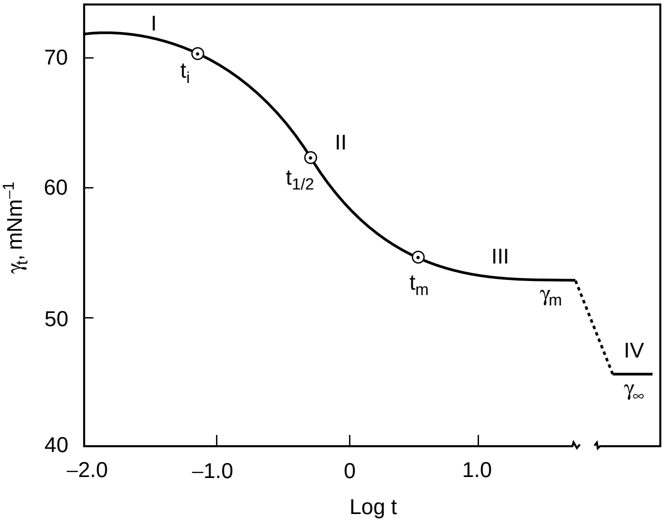

FIGURE 5-6 Generalized dynamic surface tension, γ_t versus log time, t, curve: region I, induction; region II, rapid fall; region III, meso-equilibrium; region IV, equilibrium. Reprinted with permission from X.Y. Hua and M. J. Rosen, *J. Colloid Interface Sci.* **124**, 652 (1988).

conditions are not attained. In such cases, the dynamic surface tension (surface tension as a function of time) of the surfactant is a more important factor in determining the performance of the surfactant in the process than its equilibrium surface tension. With the introduction of simple instruments (such as the maximum bubble pressure apparatus, which measures the pressure and bubble rate of gas fed through a capillary), a considerable body of research data has accumulated on the dynamic surface tension of surfactant solution during the past decade or so.

The typical plot of the change in surface tension with time (Figure 5-6) contains four regions: an induction region (I), a rapid fall region (II), a meso-equilibrium region (III), and equilibrium (IV). Equation 5.3 (Hua and Rosen, 1988) fits the three dynamic regions (I–III) of this plot:

$$\gamma_t = \gamma_m + (\gamma_o - \gamma_m)/[1 + (t/t^*)^n], \tag{5.3}$$

where γ_t is the surface tension of the surfactant solution at time t, γ_m is the meso-equilibrium surface tension (where γ_t shows only a small change with time), and γ_o is the surface tension of the pure solvent. Equation 5.3 can be converted to its logarithmic form

$$\log(\gamma_o - \gamma_t) - \log(\gamma_t - \gamma_m) = n \log t - n \log t^* \tag{5.4}$$

to calculate the values of n and t^*. The value of t^* is the time required for γ_t to reach half of the value between γ_o and γ_m and is related to the surfactant concentration. As the surfactant concentration increases, t^* decreases. From equation 5.3, by differentiation, t^* is also the time at which, at constant surfactant concentration, the

TABLE 5-3 Values of *n* (Equations 5.3 and 5.4) at 25°C

Compound	Medium	*n*	Reference
$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl	0.9_0	Hua, 1991
$C_{12}H_{25}OCH_2CH_2SO_4^-Na^+$	0.1 *M* NaCl	0.9_3	Gao, 1995
$C_{12}H_{25}OCH_2CH_2SO_4^-Na^+$	0.5 *M* NaCl	1.0_5	Gao, 1995
$C_{12}H_{25}(OCH_2CH_2)_2SO_4^-Na^+$	0.1 *M* NaCl	0.8_7	Gao, 1995
$C_{12}H_{25}(OCH_2CH_2)_2SO_4^-Na^+$	0.5 *M* NaCl	0.9_8	Gao, 1995
Branched $C_{16}H_{33}(OC_2H_4)_5SO_4^-Na^+$	0.1 *M* NaCl	0.9_9	Hua, 1991
Linear $C_{16}H_{33}(OC_2H_4)_5SO_4^-Na^+$	0.1 *M* NaCl	1.4_5	Hua, 1991
$C_4H_9CH(C_2H_5)CH_2COOCH(SO_3^-Na^+)$–$CH_2COOCH_2CH(C_2H_5)C_4H_9$	0.1 *M* NaCl	1.6_6	Hua, 1991
$[C_8H_{17}N^+(CH_3)_2CH_2]_2C_6H_4 \cdot 2Br^-$	0.1 *M* NaBr	1.1_5	Rosen, 1996
$[C_{10}H_{21}N^+(CH_3)_2CH_2]_2C_6H_4 \cdot 2Br^-$	0.1 *M* NaBr	1.1	Rosen, 1996
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2C_6H_4 \cdot 2Cl^-$	0.1 *M* NaCl	1.5	Rosen, 1996
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Cl^-$	0.1 *M* NaCl	1.8	Rosen, 1996
N-octyl-2-pyrrolidinone	H_2O	0.7_3	Hua, 1991
N-decyl-2-pyrrolidinone	H_2O	0.9_8	Hua, 1991
N-dodecyl-2-pyrrolidinone	H_2O	1.5_4	Hua, 1991
$C_{12}H_{25}(OC_2H_4)_4HO$	H_2O	1.0_6	Gao, 1995
$C_{12}H_{25}(OC_2H_4)_7HO$	H_2O	0.9_6	Hua, 1991
$C_{12}H_{25}(OC_2H_4)_7HO$	4 *M* urea	0.7_8	Hua, 1991
$C_{12}H_{25}(OC_2H_4)_8HO$	H_2O	0.8_6	Gao, 1995
$C_{12}H_{25}(OC_2H_4)_{10}HO$	H_2O	0.7_1	Gao, 1995
$C_{12}H_{25}(OC_2H_4)_{11}HO$	H_2O	0.6_1	Tamura, 1995
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 9	1.1_5	Hua, 1991
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 9.0	1.4_0	Gao, 1995
$C_{14}H_{29}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	H_2O, pH 9.0	1.5_0	Gao, 1995
$[C_{14}H_{29}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Cl^-$	0.1 *M* NaCl	3.1	Rosen, 1996
$C_{14}H_{29}N(CH_3)_2O$	H_2O, pH 3.0	0.9_5	Gao, 1995
$C_{14}H_{29}N(CH_3)_2O$	H_2O, pH 9.5	1.1_6	Gao, 1995

rate of surface tension change with log *t* (equation 5.5) reaches its maximum value (Hua and Rosen, 1991):

$$[\delta\gamma_\tau/\delta \log t)_{\text{max.c}} = 0.576n(\gamma_o - \gamma_m)] \tag{5.5}$$

N is a constant related to the molecular structure of the surfactant. It has been suggested (Gao and Rosen, 1995) that *n* is related to the difference between the energies of adsorption and desorption of the surfactant. Some values of *n* are listed in Table 5-3. From the data, it is apparent that the value of *n* increases with increase in the hydrophobicity of the surfactant, thus increasing with (1) increase in the NaCl concentration of the solution for anionic surfactants (due to compression of the electrical double layer [Chapter 2, Section I]); (2) increase in the length of the hydrophobic group; (3) increase in the pH of the solution for the amine oxide, $C_{14}H_{29}N(CH_3)_2O$, which decreases its tendency to pick up a proton and become cationic; and (4) decrease in the number of OE units in POE nonionics. It decreases with branching of the hydrophobic group in isomeric surfactants and with the addition of a structure breaker (urea) to the water. From equation 5.5, the maximum rate of surface tension change with log t, at constant surfactant concentration, increases with n, the hydrophobicity of the surfactant molecule.

The time, t_i, for the induction period (region I) to end is an important factor in determining the surface tension as a function of time, since only when that period ends does the surface tension start to fall rapidly. The value of t_i has been shown (Gao, 1995; Rosen, 1996) to be related to the surface coverage of the air–aqueous solution interface and to the apparent diffusion coefficient, D_{ap}, of the surfactant, calculated by use of the short-time approximation of the Ward–Tordai equation (Ward, 1946) for diffusion-controlled adsorption (equation 5.6):

$$\Gamma_t = 2(D_{\mathrm{ap}}/\pi)^{1/2} C t^{1/2} \tag{5.6}$$

From this,

$$\ln t_i = 2 \ln(\Gamma_i/C) + \ln(\pi/4D_{\mathrm{ap}}) \tag{5.7}$$

From equation 5.7, the greater the amount of surfactant, Γ_i, at the surface at the end of the induction period, and the smaller the apparent diffusion coefficient of the surfactant, the longer the time, t_i, needed for the surface tension to start decreasing rapidly. Calculation of surface coverages at time t_i (Gao and Rosen, 1995; Rosen and Song, 1996) for the surfactants in Table 5-3 and others has shown that the rapid fall of surface tension starts when two-thirds of the maximum coverage, Γ_m (Chapter 2, Section IIIC) of the surface has been attained. Consequently, at the same use concentration, surfactants that have smaller Γ_m values, i.e., larger areas per molecule at the air–aqueous solution interface, meaning less molecules needed to attain this degree of coverage, and those that have larger apparent diffusion coefficients (D_{ap}, Section IVB below), meaning faster diffusion of these molecules to their interface, should show shorter induction times (faster reduction of surface tension). This explains why branched-chain surfactant molecules (which have larger a_m^s values [Table 2-2]) and small molecules (which have larger D_{ap} values) reduce surface tension faster than linear, larger surfactant molecules. This is consistent with their use as textile wetting agents (Chapter 6, Section IIC).

IV.B. Apparent Diffusion Coefficients of Surfactants

As mentioned above, the value of t_i has been shown to be related to the coverage of the air–aqueous solution interface by the surfactant and to its apparent diffusion coefficient, D_{ap} (equation 5.7). To calculate the values of D_{ap} at short times, equation 5.8 (Bendure, 1971), based upon the short-time approximation equation of Ward and Tordai (equation 5.6), and using dynamic short-time surface tension data, may be used:

$$(\gamma_o - \gamma_t/C = 2RT(D_{ap}/\pi)^{1/2} t^{1/2} \tag{5.8}$$

At constant surfactant concentration, C, in the solution, a plot of $(\gamma_o - \gamma_t)$ versus $t^{1/2}$ should be linear, if adsorption is diffusion-controlled (generally true, for simple-structured surfactants) and permits evaluation of D_{ap} from the slope of the plot.

Apparent diffusion coefficients may also be calculated from longer-time dynamic surface tension data by use of equation 5.9 (Joos, 1992):

$$\underset{t\to\infty}{\gamma_t} = \gamma_e + n(RT\Gamma^2/C)(7\pi/12D_{ap}t)^{1/2} \tag{5.9}$$

where Γ is calculated from the Gibbs adsorption equation (equation 2.19a), n is the constant in that equation, and γ_e is the surface tension at infinite time (close to the equilibrium surface tension value). For solutions of constant surfactant concentration, C, a plot of γ_t versus $t^{-1/2}$ should be linear if adsorption is diffusion-controlled and permits evaluation of D_{ap}, again from the slope of the plot. The value of γ_e can be evaluated from the Y-axis intercept and should be close to the value of the equilibrium surface tension.

Values of D_{ap} for simple, conventional surfactants (with a single hydrophilic head group and a single hydrophobic group) are of the order of 10^{-6}cm^2/s. The values decrease with increase in the alkyl chain length of the hydrophobic group and with the degree of hydration of the hydrophilic group. The value increases with branching of the alkyl chain compared to that of the isomeric straight-chain compound.

Interaction between two surfactants, producing an increase in the molecular weight of the complex, decreases the value of D_{ap} considerably (Gao, 1994; Rosen, 1995). When interaction between the two surfactants is weak, the surface tension at short times ($t < 1$ s) is close to that of the component with the lower surface tension value; at longer times, it is closer to that of the component that has the lower equilibrium tension. When interaction is strong, the surface tension at short times is greater than that of either component (Gao, 1994).

A fair correlation has been found (Smith, 2000) between diffusion coefficients and wetting times for cotton twill tape (using a modified Draves wetting test (Chapter 6, Section IIC).

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PROBLEMS

1 Indicate, in the table below, the effect of each of the following changes on the surface tension reduction effectiveness Π_{CMC} of the surfactant in aqueous solution. Use symbols: + = increase; − = decrease; 0 = little or no effect; ? = effect not clearly known.

Change	Effect
(a) Increase in the length of the hydrophobic group	
(b) Replacement of straight chain hydrophobic group by isomeric branched chain.	
(c) For ionics, increase in the electrolyte content of the aqueous solution	
(d) Increase in the temperature of the solution	

2 Predict the effect of each of the following changes on the value of the Winsor ratio, R:

(a) Increase in the length of the hydrophobic group of the surfactant
(b) Increase in the length of the POE chain of a nonionic surfactant
(c) Replacement of *n*-hexane by *n*-octane as the hydrocarbon phase
(d) Addition of *n*-pentanol to the system
(e) Addition of NaCl to the system

3 Account for the following observations:

The value of *n* in equations 5.3 and 5.4: (**a**) increases with decrease in the number of oxyethylene units in nonionic surfactants with the same number of carbon atoms in their alkyl chains; (**b**) decreases when 4 *M* urea is added to the water.

4 A nonionic surfactant has a minimum area per molecule, a_m^s, value of 60 Å^2 in water. Its CMC value is 2×10^{-4} and its pC_{20} value is 4.8.

(**a**) Estimate the surface tension of its aqueous solution at the CMC, γ_{CMC}, at 25°C, in mN/m (dyn/cm).
(**b**) If the above values are the same at 40°C, what would the γ_{CMC} value be?

6 Wetting and Its Modification by Surfactants

Wetting in its most general sense is the displacement from a surface of one fluid by another. Wetting, therefore, always involves three phases, at least two of which are fluids: a gas and two immiscible liquids, or a solid and two immiscible liquids, or a gas, a liquid, and a solid, or even three immiscible liquids. Commonly, however, the term *wetting* is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution, and we restrict our discussion for the most part to those situations. The term *wetting agent* is applied to any substance that increases the ability of water or an aqueous solution to displace air from a liquid or solid surface. Wetting is a process involving surfaces and interfaces, and the modification of the wetting power of water is a surface property shown to some degree by all surface-active agents, although the extent to which they exhibit this phenomenon varies greatly. When the surface to be wet is small, as in the wetting of nongranular, nonporous solids (*hard surface wetting*), equilibrium conditions or conditions close to it can be attained during the wetting process and the free energy changes involved in the process determine the degree of wetting attained. On the other hand, when the surface to be wet is large, as in the wetting of porous or textile surfaces or finely powdered solids, equilibrium conditions are often not reached during the time allowed for wetting, and the degree of wetting is determined by the kinetics rather than the thermodynamics of the wetting process.

I. WETTING EQUILIBRIA

Three types of wetting have been distinguished (Osterhuf, 1930): (1) spreading wetting, (2) adhesional wetting, and (3) immersional wetting. The equilibria involved in these phenomena are well known.

I.A. Spreading Wetting

In spreading wetting (Figure 6-1), a liquid in contact with a substrate spreads over the substrate and displaces another fluid, such as air, from the surface. For the spreading to occur spontaneously, the surface free energy of the system must

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

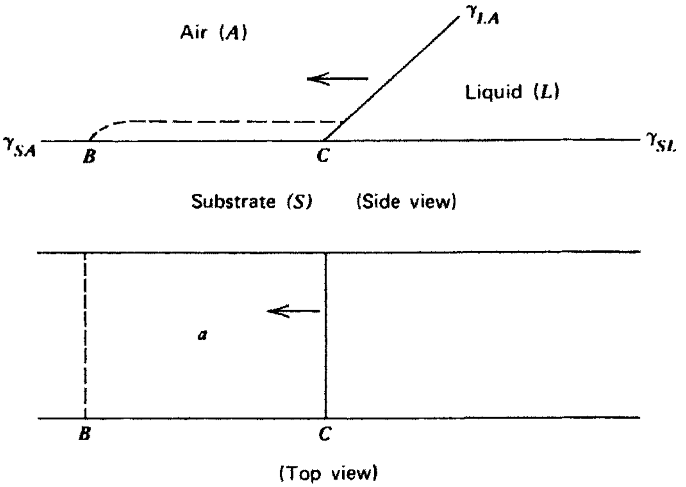

FIGURE 6-1 Spreading wetting.

decrease during the spreading process. When the area of an interface increases, the surface free energy at that interface increases; when the area decreases, the surface free energy decreases. If the liquid L in Figure 6-1 spreads from C to B, covering an area a, then the decrease in surface free energy of the system due to decrease in area of the substrate–air interface is $a \times \gamma_{SA}$, where γ_{SA} is the interfacial free energy per unit area of the substrate in equilibrium with liquid-saturated air above it. At the same time, the free energy of the system has been increased because of the increase in liquid–substrate and liquid–air interfaces. The increase in surface free energy of the system due to the increase in the liquid–substrate interface is $a \times \gamma_{SL}$ (where γ_{SL} is the interfacial free energy per unit area at the liquid–substrate interface), and since the liquid–air interface has also been increased by area a, the increase in surface free energy due to increase in this interface is $a \times \gamma_{LA}$, where γ_{LA} is the surface tension of L. The total decrease in surface free energy per unit area of the system due to the spreading wetting, $-\Delta G_w/a$, is therefore $\gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$. If the quantity $\gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$ is positive, the system decreases in surface free energy during the spreading process, and the process can then occur spontaneously.

The quantity $\gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$ is then a measure of the *driving force* behind the spreading process and is usually called the *spreading coefficient* $S_{L/S}$. If $S_{L/S}$, as defined by

$$S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \tag{6.1}$$

is positive, spreading can occur spontaneously; if $S_{L/S}$ is negative, the liquid will not spread spontaneously over the substrate.

When a thin layer of liquid L_1 is being spread over a second liquid L_2 as substrate, $S_{L_1/L_2} = \gamma_{L_2A} - (\gamma_{L_1L_2} + \gamma_{L_1A})$, and the value of S can be obtained directly by measuring the surface tensions of the two liquids and the interfacial tension between them. However, this gives the initial spreading coefficient. The two phases will quickly become saturated with each other in the vicinity of the interface and the equilibrium spreading coefficient will be that based on the tensions of the mutually saturated phases, which may be very different. As an example, the surface tensions of pure water and pure benzene, each at 20°C, are 72.8 and 28.9 dyn/cm, respectively, and their interfacial tension is 35.0 dyn/cm. Using these figures, the initial spreading coefficient of benzene on water is $72.8 - (28.9 + 35.0) = 8.9$ dyn/cm. This means that benzene will initially spread spontaneously over water. However, the surface tensions of water saturated with benzene and benzene saturated with water at 20°C are 62.2 and 28.8 dyn/cm, respectively. Thus, the spreading coefficient a short time after both phases come in contact with each other becomes $62.2 - (28.8 + 35.0) = -1.4$, and spontaneous spreading ceases to occur. The benzene retracts to a lens after the initial spreading.

Since the spreading coefficient involves only the surface tensions of the two liquids (in the case of one liquid spreading over another) and the interfacial tension between them, if we have a method for determining the interfacial tension between the two liquids from their respective surface tensions, we can calculate the spreading coefficient without additional experimental data and predict whether spreading will occur spontaneously. Good (1960) and Girifalco (1957) have suggested a method of doing this. According to them, $\gamma_{L_1L_2} = \gamma_{L_1A} + \gamma_{L_2A} - 2\phi\ \sqrt{\gamma_{L_1A}\gamma_{L_2A}}$, where ϕ is an empirical factor measuring the degree of interaction between L_1 and L_2. Since $S_{L_1/L_2} = \gamma_{L_2A} - (\gamma_{L_1A} + \gamma_{L_1/L_2})$, by substituting for $\gamma_{L_1L_2}$ we obtain

$$\begin{aligned} S_{L_1/L_2} &= \gamma_{L_2A} - (\gamma_{L_1A} + \gamma_{L_1A} + \gamma_{L_2A} - 2\phi\sqrt{\gamma_{L_1A}\gamma_{L_2A}}) \\ &= 2(\phi\sqrt{\gamma_{L_1A}\gamma_{L_2A}} - \gamma_{L1A}) \\ &= 2\gamma_{L_1A}(\phi\sqrt{\gamma_{L_2A}/\gamma_{L_1A}} - 1) \end{aligned} \tag{6.2a}$$

In systems where there is no strong interaction between L_1 and L_2, ϕ is less than 1. Thus, in those systems γ_{L_1A} must be less than γ_{L_2A} for spreading to occur spontaneously (i.e., for the spreading coefficient to be positive, the spreading liquid must have a lower surface tension than the liquid over which it is spreading). The same is assumed to be true if the substrate over which the liquid is spreading is a solid:

$$S_{L/S} = 2(\phi\sqrt{\gamma_{LA}\gamma_{SA}} - \gamma_{LA}) = 2\gamma_{LA}\left(\phi\sqrt{\gamma_{SA}/\gamma_{LA}} - 1\right) \tag{6.2b}$$

This concept of a *critical surface tension* for spreading on low-energy surfaces is one that was developed by Zisman and coworkers (Fox, 1950; Shafrin, 1960; Zisman, 1964). They demonstrated that, at least for low-energy substrates, in order to wet the substrate the surface tension of the wetting liquid must not exceed a certain critical value that is characteristic of the particular substrate.

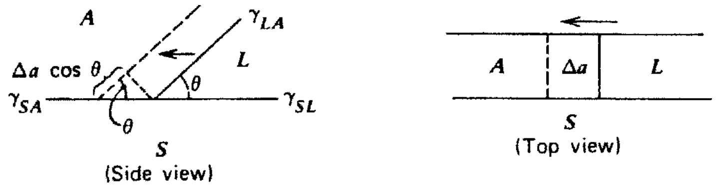

FIGURE 6-2 Contact angle.

High-melting solids such as silica and most metals have high surface free energies ranging from several thousand to several hundred mJ/m^2 (ergs/cm^2). Low-melting solids, such as organic polymers, waxes, and covalent compounds, in general have surface free energies ranging from 100 to 25 mJ/m^2 (ergs/cm^2). Since nearly all liquids other than liquid metals have surface tensions of less than 75 mN/m (dyn/cm) (i.e., surface free energies of <75 (mJ/m^2), they usually spread readily on metallic or siliceous surfaces but may not spread on low-melting solids.

1. The Contact Angle When the substrate is a solid, the spreading coefficient is usually evaluated by indirect means, since surface and interfacial tensions of solids cannot easily be measured directly. The method of doing this involves measuring the contact angle the substrate makes with the liquid in question.

The contact angle θ that the liquid makes when it is at equilibrium with the other phases in contact with it is related to the interfacial free energies per unit area of those phases. When the liquid is at equilibrium with the other two phases, gas and solid substrate, we can diagram the contact angle θ as shown in Figure 6-2. For a small reversible change in the position of the liquid on the surface so as to cause an increase, Δa, in the *L*/*S* interfacial area, there is a corresponding decrease Δa in the area of the *S*/*A* interface and an increase in the *L*/*A* interface of $\Delta a \cos\theta$. Thus $\Delta G_w = -\gamma SA\Delta a + \gamma_{LS}\Delta a + \gamma_{LA}\Delta a \cos\theta$. As $\Delta a \to 0$, $\Delta G \to 0$), $\therefore \gamma_{LA} da \cos\theta + \gamma_{LS} da - \gamma_{SA} da = 0$. Therefore

$$\gamma_{LA}\cos\theta = \gamma_{SA} - \gamma_{SL} \tag{6.3}$$

or

$$\cos\theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \tag{6.4}$$

Equation 6.3 is generally called *Young's equation* and the quantity $\gamma_{LA}\cos\theta$ the *adhesion tension* (Bartell, 1934). Note that γ_{SA}, the interfacial tension in equilibrium with the gas and liquid phases in the system, is *not* γ_S, the free energy per unit area of the solid in a vacuum, but $\gamma_S - \pi$, where π is the reduction in interfacial free energy per unit area of *S* resulting from adsorption of vapor of *L*; that is, $\pi = \gamma_S - \gamma_{SA}$.

If the contact angle is larger than 0°, then the spreading coefficient cannot be positive or zero. Since $S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$, and $\gamma_{SA} - \gamma_{LA} \cos\theta$ when $\theta > 0°$, substituting $\gamma_{LA} \cos\theta$ for $\gamma_{SA} - \gamma_{SL}$ yields

$$\begin{aligned} S_{L/S} &= \gamma_{LA} \cos\theta - \gamma_{LA} \\ &= \gamma_{LA}(\cos\theta - 1) \end{aligned} \tag{6.5}$$

When θ is finite, $(\cos\theta - 1)$ is always negative, and $S_{L/S}$, too, is always negative. If the contact angle is 0°, then $S_{L/S}$ may be zero or positive. In either case here, complete spreading wetting occurs.

When the solid substrate is a nonpolar, low-energy surface, the contact angle can be used to determine the surface (excess) concentration of the surfactant at the solid–liquid interface Γ_{SL}.

From Young's equation,

$$\frac{d(\gamma_{LA}\cos\theta)}{d\ln C} = \frac{d(\gamma_{SA})}{d\ln C} - \frac{d(\gamma_{SL})}{d\ln C} \tag{6.6}$$

If we assume that, for a low-energy surface, γ_{SA} does not change with change in the liquid phase surfactant concentration, i.e., $d(\gamma_{SA})/d\ln C = 0$, then

$$\frac{d(\gamma_{LA}\cos\theta)}{d\ln C} = \frac{-d(\gamma_{SL})}{d\ln C} \tag{6.7}$$

The Gibbs adsorption equation (equations 2.19, 2.19a) at the solid–liquid interface can be written as

$$-d\gamma_{LS} = (1, n)RT\,\Gamma_{LS} d\ln C$$

from which

$$\frac{d(\gamma_{LA}\cos\theta)}{d\ln C} = (1, n)RT\,\Gamma_{LS} \tag{6.8}$$

The value of Γ_{LS} can therefore, under these conditions, be determined from the slope of a $\gamma_{LA}\cos\theta - \ln C(= 2.303 \log C)$ plot at constant temperature.

2. Measurement of the Contact Angle Contact angles are measured on macroscopic, smooth, nonporous, planar substrates by merely placing a droplet of the liquid or solution on the substrate and determining the contact angle by any of a number of techniques (Adamson, 1997, pp. 362ff.). The contact angle can be measured directly by use of a microscope fitted with a goniometer eyepiece or by photographing the droplet. However, obtaining a valid, reproducible contact angle is more complicated and difficult than it appears for a number of reasons:

1. Contamination of the droplet by adsorption of impurities from the gas phase tends to reduce θ if γ_{LA} and/or γ_{SL} is reduced and γ_{SA} remains more or less constant.
2. A solid surface, even when apparently smooth, may have impurities and defects that vary from place to place on the surface and from sample to sample. Roughness reduces θ when the value on a smooth surface is $<90°$ and increases it when the value there is $<90°$.
3. The contact angle may show hysteresis. In this case the advancing contact angle will always be greater than the receding contact angle, sometimes differing by as much as 60°. Contact angle hysteresis is always present when the surface is not clean or when it contains a considerable amount of impurity. However, even when the surface is clean and the substrate pure, it may show hysteresis. For example, stearic acid becomes more wettable (shows a smaller contact angle) after being contacted with water. The explanation has been advanced that there is a change in orientation of the surface molecules in the presence of water, with more of the molecules becoming oriented with their carboxylic acid groups facing the water, thus decreasing the interfacial free energy. Other reasons for low receding angles are penetration of the wetting liquid into the substrate, removal of an adsorbed surface film from the substrate by the wetting liquid, and microscopic surface roughness.

Contact angles on finely divided solids are more difficult to measure, but are often more desired and more important than those on large solid surfaces. One method of obtaining such contact angles is to pack the powder into a glass tube and measure the rate of penetration of the liquid into it (Bruil, 1974). The distance of penetration l in time t of a liquid of surface tension γ_{LA} and viscosity η is given by the modified Washburn equation (Washburn, 1921):

$$l^2 = \frac{(kr)t\gamma_{LA}\cos\theta}{2\eta} \tag{6.9}$$

where r is the mean equivalent radius of the capillary passages through the powder and k is a constant to allow for the tortuous path through them. The (kr) product depends on the packing of the powder. When the powder is packed to the same bulk density, (kr) is assumed to be constant. The (kr) product is evaluated by passing through the powder a pure liquid of known γ_{LA} whose contact angle is known or assumed to be 0°. A limitation of the method is the assumption that (kr) will not change with change in the nature of the wetting liquid. This is justified only when the particle size of the powder is not changed by flocculation or dispersion produced by the passage through it of the surfactant solution.

This method is not reliable for dilute solutions of surfactants in many cases since it depends upon knowing the (constant) value of γ_{LA}. If adsorption of the surfactant onto the solid decreases its solution phase concentration to a value below the CMC, then γ_{LA} will change and it will be impossible to determine θ accurately.

Adsorption of the surfactant onto the solid also makes this an unreliable method for determining the wetting effectiveness of dilute surfactant solution for powdered solids. Because of the small ratio of solution volume to solid–liquid interface, solutions that contain highly surface-active material that adsorbs well at the solid–liquid interface are rapidly depleted of surfactant and may penetrate more slowly than solutions of weakly surface-active material.

Another method of measuring the contact angles of powders involves measuring the height h of a drop of the wetting liquid on a cake of the powder, prepared by compressing it in a mold (Heertjes, 1967). The contact angle is obtained from

$$\cos\theta = 1 - \sqrt{\frac{1}{3(1-\varepsilon)(1/Bh^2 - 1/2)}} \quad \text{for } \theta < 90^\circ \tag{6.10}$$

$$\cos\theta = -1 + \sqrt{\frac{2}{3(1-\varepsilon)}\left(\frac{2}{Bh^2} - 1\right)} \quad \text{for } \theta > 90^\circ \tag{6.11}$$

where $B = \rho_L g/2\gamma_{LA}$ for the wetting liquid of density ρ_L and surface tension γ_{LA}, g = the gravitational constant, and ε = the porosity of the cake. This method assumes that the powder consists of identical spheres.

I.B. Adhesional Wetting

In spreading wetting, a liquid in contact with a substrate and another fluid increases its area of contact with the substrate at the expense of the second fluid. In adhesional wetting, a liquid *not* originally in contact with a substrate makes contact with that substrate and adheres to it. We can diagram this process as shown in Figure 6-3. In this case the change in surface free energy is $-\Delta G_w = a(\gamma_{SA} + \gamma_{LA} - \gamma_{SL})$, where a is the surface area of the substrate in contact with (an equal) surface area of the liquid after adhesion and the "driving force" of this type of wetting phenomenon is $\gamma_{SA} + \gamma_{LA} - \gamma_{SL}$. This quantity is known as the *work of adhesion*, W_a, the reversible work required to separate the unit area of liquid from the substrate:

$$W_a = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \tag{6.12}$$

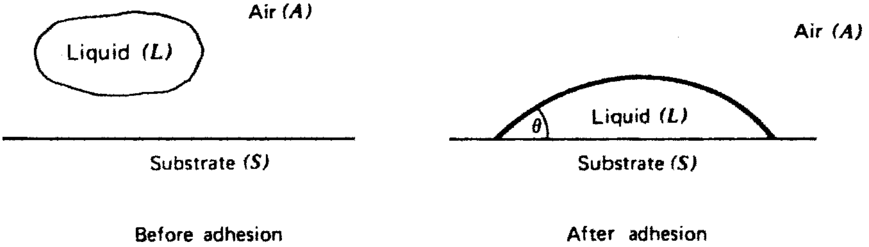

FIGURE 6-3 Adhesional wetting.

The equation is from Dupré (1869). In this process any reduction of the interfacial tension between substrate and the wetting liquid results in an increased tendency for adhesion to occur, but reduction of either the surface tension of the liquid or the surface tension of the substrate *decreases* the tendency of adhesion to occur. This accounts for the poor adhesion of substances to low-energy surfaces, especially when the natures of substance and substrate are very different (i.e., γ_{SL} is large).

If the contact angle θ between liquid, substrate, and air, after adhesion, measured in the liquid, is finite (Figures 6.2 and 6.3), we can write, as before,

$$\gamma_{LA}\cos\theta = \gamma_{SA} - \gamma_{SL} \tag{6.3}$$

Substituting for $\gamma_{SA} - \gamma_{SL}$ in equation 6.12,

$$W_a = \gamma_{LA}\cos\theta + \gamma_{LA} = \gamma_{LA}(\cos\theta + 1) \tag{6.13}$$

from which it is apparent that an increase in the surface tension of the wetting liquid always causes increased adhesional wetting, whereas an increase in the contact angle obtained after wetting may or may not indicate a decreased tendency for adhesion to occur. If the increase in the contact angle (and consequent decrease of $\cos\theta$) reflects an increase in γ_{SL}, there is a diminished tendency to adhere; if it reflects merely an increase in γ_{LA}, there is increased tendency to adhere. The driving force in adhesional wetting can never be negative and is equal to zero only when the contact angle is 180°, which is never achieved in practice. Since equation 6.13 involves directly measurable quantities, γ_{LA} and θ, the driving force behind this type of wetting is readily evaluated.

The work of self-adhesion of a liquid is known as the *work of cohesion*, $W_c = 2\gamma_{LA}$. It is the work required to produce two unit areas of interface from an original unbroken column of the liquid or the $(-\Delta G_w)/a$ when the two columns are joined (Figure 6-4).

The difference between the work of adhesion of the liquid for the substrate and its work of cohesion equals the spreading coefficient $S_{L/S}$:

$$\begin{aligned} W_a - W_c &= \gamma_{SA} - \gamma_{SL} + \gamma_{LA} - 2\gamma_{LA} \\ &= \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \\ &= S_{L/S} \end{aligned} \tag{6.14}$$

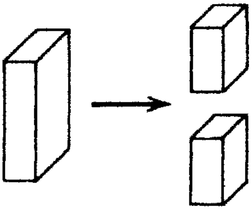

FIGURE 6-4 Work of adhesion.

Therefore, if $W_a > W_c$, the spreading coefficient is positive, $\theta = 0°$, and the liquid spreads spontaneously over the substrate to form a thin film. If $W_a < W_c$, the spreading coefficient is negative, θ is greater than zero, and the liquid does not spread over the substrate but forms droplets or lenses with a finite contact angle.

When the work of adhesion equals the work of cohesion,

$$\gamma_{LA}(\cos\theta + 1) = 2\gamma_{LA}$$

or

$$\gamma_{SA} - \gamma_{SL} + \gamma_{LA} = 2\gamma_{LA}$$

and

$$\cos\theta = 1 \quad \theta = 0° \quad \text{and} \quad S_{L/S} = 0$$

I.C. Immersional Wetting

A third type of wetting is *immersional wetting*, where a substrate not previously in contact with a liquid is immersed completely by the liquid (Figure 6-5). In this case, the surface free energy change per unit area is

$$-\Delta G_w/a = \gamma_{SA} - \gamma_{SL} \tag{6.15}$$

and the driving force of the wetting phenomenon in this case is the quantity $(\gamma_{SA} - \gamma_{LA})$.

If immersion of the solid in the wetting liquid gives a finite equilibrium contact angle θ, i.e., $\theta > 0°$, then $(\gamma_{SA} - \gamma_{SL})$ equals $\gamma_{LA}\cos\theta$. We can determine $(\gamma_{SA} - \gamma_{SL})$, therefore, by observing the contact angle the solid makes with the liquid–air interface (Figure 6-6). If θ is >90°, then $\gamma_{SA} - \gamma_{SL}$ is negative; if $\theta < 90°$, then $\gamma_{SA} - \gamma_{SL}$ is positive.

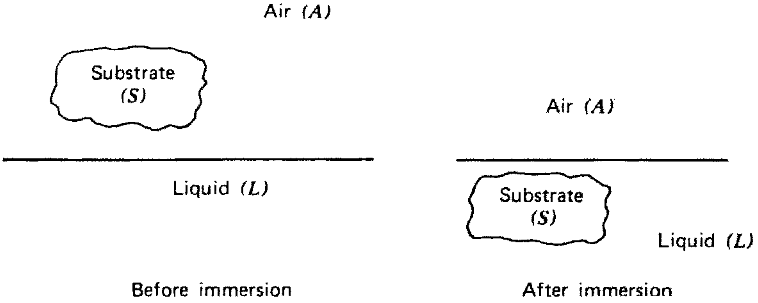

FIGURE 6-5 Immersional wetting.

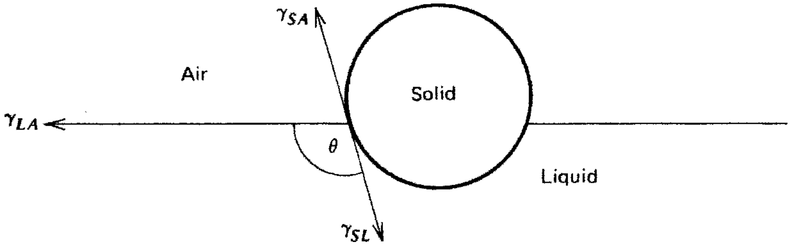

FIGURE 6-6 Contact angle of partially immersed solid

However, since spreading occurs during the immersion process, the value of the spreading coefficient $S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$ (equation 6.1) determines the ease of complete immersion. When the spreading coefficient is ≥ 0(i.e., $\gamma_{SA} - \gamma_{SL} \geq \gamma_{LA}$), then, from equation 6.4, $\theta = 0°$ and complete immersion is spontaneous; when the spreading coefficient is negative ($\gamma_{SA} - \gamma_{SL} < \gamma_{LA}$), then θ is finite and work must be done to immerse the solid completely. In this latter case, to achieve spontaneous immersion of the solid, the values of any or all of the three quantities, γ_{SA}, γ_{SL}, and γ_{LA}, must be changed in such a manner as to make the spreading coefficient greater than zero.

The depth of immersion of the solid in the wetting liquid is determined by the contact angle θ; the smaller the value of θ, the greater the depth of immersion. When $\theta = 0°$, immersion is complete. Here again, the relation of $\gamma_{SA} - \gamma_{SL}$ to γ_{LA}, as given in equation 6.4, determines the value of θ.

When $\theta \leq 0°$, $\gamma_{SA} - \gamma_{SL}$ cannot be determined from the contact angle. Another experimentally determinable quantity, the heat of immersion ΔH^i, which is the heat change measured calorimetrically when the substrate is immersed in the wetting liquid, is then often used as a measure of immersional wetting. The heat of immersion per unit area of substrate is related to the surface free energy change per unit area due to immersional wetting by the relation $\Delta G_w/a = \Delta H^i/a - T\Delta S^i/a$, and is therefore equal to it only when the entropy change per unit area due to immersional wetting $\Delta S^i/a$ is insignificant.

The surface free energy change per unit area or driving force for the three different types of wetting can be expressed as

Spreading:

$$\frac{-\Delta G_w}{a} = \gamma_{SA} - \gamma_{LA} - \gamma_{SL} = S_{L/S}$$

Adhesion:

$$\frac{-\Delta G_w}{a} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} = W_a$$

Immersion:

$$\frac{-\Delta G_w}{a} = \gamma_{SA} - \gamma_{SL} (= \gamma_{SL} \cos\theta \quad \text{when } \theta > 0^\circ)$$

From these expressions we can see that in *all* wetting processes, reduction of the interfacial tension between substrate and the wetting liquid γ_{SL} is beneficial, but that reduction of the surface tension of the liquid γ_{LA} per se is not always of benefit.

I.D. Adsorption and Wetting

A convenient method of analyzing the relation of adsorption to equilibrium wetting has been developed by Lucassen-Reynders (1963). Combination of the Gibbs adsorption equation (2.19) with Young's equation (6.3) yields

$$\frac{d(\gamma_{LA}\cos\theta)}{d\gamma_{LA}} = \frac{\Gamma_{SA} - \Gamma_{SL}}{\Gamma_{LA}} \tag{6.16}$$

The slope of a plot of $\gamma_{LA}\cos\theta$, the *adhesion tension* (Equation 6.3), versus γ_{LA} consequently provides information on the surface (excess) concentrations of the surfactant at the three interfaces (Padday, 1967; Bargeman, 1973; Pyter, 1982).

Some typical $\gamma_{LA}\cos\theta$ versus γ_{LA} plots for surfactant solutions on solid substrates are shown diagrammatically in Figure 6-7. In this type of plot, the solution wets the substrate completely $(\theta = 0^\circ)$ when the curve reaches line *AB* (points *G*, *E*, *L*); it dewets it completely $(\theta = 180^\circ)$ when it reaches line *BC*. Solutions that produce contact angles between 0 and 180° have points that fall in the region between those two lines (e.g., points *D*, *F*, *K*, *M*, *N*). When the slope of the plot is negative, wetting is improved by the presence of the surfactant; when it is positive, wetting is impaired by its presence.

On low-surface-energy (hydrophobic) solids such as paraffin and Teflon, data for several types of surfactants show constant slopes very close to -1 (lines *DE*, *EG*, and *HJ*), both for solid–aqueous–air systems and solid–aqueous–mineral oil systems (Bernett, 1959; Bargeman, 1973; Pyter, 1982). This is usually taken to indicate that Γ_{SA} is close to 0 and $\Gamma_{SL/\Gamma_{LA}} \simeq 1$. This is reasonable since, as shown in Chapter 2, Section IIIC, the effectiveness of adsorption at the nonpolar liquid (heptane)–aqueous solution interface is not very different from that at the air–aqueous solution interface, and we would therefore expect approximately equal adsorption at nonpolar solid–aqueous and air–aqueous interfaces. On these nonpolar solid surfaces, then, $\gamma_{LA}\cos\theta \simeq -\gamma_{LA} + \text{constant}$ (Bargeman, 1973) and complete wetting is therefore achieved $(\theta = 0^\circ)$ when $\gamma_{LA} \simeq \text{constant}/2$. Thus, for paraffin wax in the presence of air (line *DE*), $\gamma_{LA}\cos\theta \simeq -\gamma_{LA} + 49.4$, meaning that γ_{LA} must be decreased to ≃25 dyn/cm for complete wetting to occur. For Teflon in the presence of air (line *FG*), the constant is 40.6, and complete wetting occurs when $\gamma_{LA} \simeq 20$ dyn/cm. When mineral oil replaces air on both of these solids (line

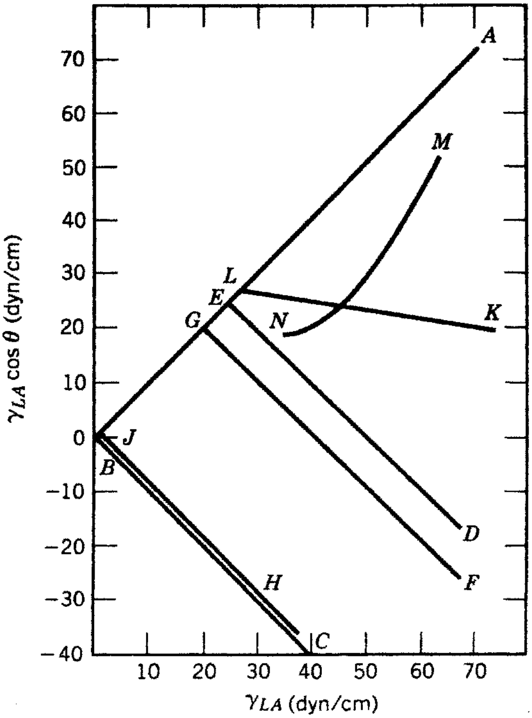

FIGURE 6-7 Plots of adhesion tension ($\gamma_{LA}\cos\theta$) versus surface tension (γ_{LA}) for surfactant solutions on different substrates: *DE*, paraffin in the presence of air; *FG*, Teflon in the presence of air; *HJ*, paraffin or Teflon in the presence of mineral oil (plot of $\gamma_{LO}\cos\theta$ versus γ_{LO}); *KL*, anionic surfactant solution on nylon or polymethyl methacrylate in the presence of air; *MN*, mineral in the presence of air.

HJ), the constant is almost zero, indicating the γ_{ow} must be very low for complete wetting to occur.

On negatively charged polar organic surfaces, such as polymethyl methacrylate or nylon, data by Pyter and coworkers (1982) show negative slopes close to zero for anionic surfactants (line *KL*), indicating either Γ_{SA} approaching Γ_{SL} or, if Γ_{SA} remains close to zero, very low values of Γ_{SL}/Γ_{LA}, with the authors favoring the latter alternative. The solid–liquid interfacial tension γ_{SL} of a negatively charged solid is much lower than that of a nonpolar solid against water. Low adsorption of anionic surfactants at the aqueous interface with a negatively charged polar organic solid is consequently reasonable since adsorption would place either the hydrophobic group of the surfactant or its negatively charged hydrophilic group adjacent to the negatively charged polar surface, neither of which would be expected to reduce the solid–liquid interfacial tension. On the other hand, when the solid phase is nonpolar, the interfacial tension at the solid–aqueous solution interface is high and adsorption of the surfactant with its nonpolar hydrophobic group oriented toward the nonpolar solid and its hydrophilic group oriented toward the water would reduce γ_{SL}.

On high-energy surfaces with both positively and negatively charged sites, $\gamma_{LA}\cos\theta$ versus γ_{LA} plots show large positive slopes (curve *MN*), especially at low surfactant concentrations (high γ_{LA} values), indicating that $\Gamma_{SA} \gg \Gamma_{SL}$ (Finch, 1973; Aronson, 1978; Bargava, 1978). This is presumably because direct adsorption onto oppositely charged sites on the solid substrate of ionic surfactants via their hydrophilic heads is occurring (Chapter 2, Sections IIA,F). Wetting is impaired and the solid becomes more hydrophobic. This is the basis for the flotation process for ore beneficiation. At higher surfactant concentrations, the slope may become negative due to increased adsorption of surfactant at the now hydrophobic solid–aqueous solution interface, making $\Gamma_{SL} > \Gamma_{SA}$.

Perfluoroalkyl chain surfactants are much poorer wetting agents than alkyl chain surfactants for both paraffin and polymethyl methacrylate surfaces (Pyter, 1982). One explanation may be the mutual "phobicity" of alkyl and perfluoroalkyl chains, causing perfluoroalkyl chain surfactants to be adsorbed more poorly than alkyl chain surfactants at these solid–aqueous solution interfaces.

II. MODIFICATION OF WETTING BY SURFACTANTS

II.A. General Considerations

Since water has a rather high surface tension, 72 mN/m(dyn/cm), (reflecting the high intermolecular attractions of water molecules), it does not spontaneously spread over covalent solids that have surface free energies of less than 72 mJ/m^2(erg/cm^2). The addition of a surface-active agent to water, to modify the interfacial tensions of the system, is therefore often necessary to enable water to wet a solid or liquid surface. For water to wet a substrate spontaneously, the spreading coefficient $S_{W/S} = \gamma_{SA} - (\gamma_{SW} + \gamma_{WA})$ must be positive (equation 6.1). The addition of a surface-active agent to the water, by reducing the surface tension of the water γ_{WA} and perhaps also the interfacial tension between the water and the substrate γ_{SW}, may cause the spreading coefficient to have a positive value and make spreading or immersion spontaneous.

However, the addition of a surface-active agent to water does not *always* increase its wetting power. Under certain conditions the addition of a surface-active agent to the water may make spreading more difficult. In cases where the substrate is porous and can be considered to consist of a mass of capillaries, the pressure causing movement of liquid into the capillaries because of the curvature of the liquid surface is given by

$$\Delta P = \frac{2\gamma_{LA}\cos\theta}{r} = \frac{2(\gamma_{SA} - \gamma_{SL})}{r} \qquad (6.17)$$

where r is the equivalent radius of the capillaries and θ the contact angle at the air–liquid–substrate interface. When the contact angle is greater than 0°, ΔP depends only on the quantity $(\gamma_{SA} - \gamma_{SL})$, and any reduction only in γ_{LA} as a result of the addition of a surfactant to the system (i.e., without any change in γ_{SL}) merely causes a corresponding increase in cos θ, with ΔP remaining unchanged. However, if θ is already 0°, then

$$\Delta P = \frac{2\gamma_{LA}}{r} \tag{6.18}$$

and any reduction of γ_{LA} by the surfactant in the system *decreases* the tendency of the liquid to move into the capillaries of the substrate.

Another situation in which the addition of a surface-active agent to water *decreases* its wetting power is when adsorption of the surfactant at the substrate–liquid interface occurs in such fashion that the amphipathic surfactant molecules are oriented with their polar ends toward the substrate and their hydrophobic tails toward the water. Adsorption in this manner can occur with ionic or polar substrates when there is strong interaction between the hydrophilic groups in the surfactant and the ionic or polar sites on the substrate. Such adsorption makes the surface of the substrate more nonpolar. The resulting increase in the interfacial tension between the substrate and the aqueous solution γ_{SL} results in a *decrease* in the spreading coefficient. Furthermore, since the surfactant molecules are strongly adsorbed at the substrate surface in this case, if the wetting liquid retracts from the substrate because of the decrease in spreading coefficient, it will expose a substate with a surface free energy that has been decreased by adsorption of the surfactant. Thus, portions of the substrate that have already been wet by the solution will become even more difficult to wet (more hydrophobic) than they were originally. Cationic surfactants are adsorbed in this manner onto negatively charged solid surfaces, such as quartz, cellulose textile fibers, or glass, and render them more difficult to wet with aqueous solutions than they were originally, and more easily wet by nonpolar materials. This phenomenon is the basis for ore "flotation" processes (Somasundaran, 1972).

II.B. Hard Surface (Equilibrium) Wetting

In hard surface wetting, the substrate to be wet is a nonporous, nongranular solid or a nonporous film, and since the area to be wet is relatively small, conditions close to equilibrium are usually attained and the thermody-namics of the wetting process is a major factor determining the extent of wetting.

The effectiveness of a surfactant in modifying the wetting properties of a liquid for this process can be evaluated by determining the spreading coefficient $S_{L/S}$ of the surfactant solution on the substrate at a given temperature. This can be done by measuring the surface tension γ_{LA} of the surfactant solution and the contact angle the solution makes with the substrate. The less negative the spreading coefficient, the more effective the wetting agent.

When the spreading coefficient is negative, the contact angle is finite and spreading is not complete. Since $S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$ (equation 6.1) and

$\gamma_{SA} - \gamma_{SL} = \gamma_{LA}) \cos \theta$ (equation 6.3) in this case, $S_{L/S} = \gamma_{LA}(\cos \theta - 1$ (equation 6.5). When the spreading coefficient is zero, spreading wetting is complete, since $S_{L/S} = \gamma_{LA}(\cos \theta - 1) = 0$, and thus $\theta + 0°$. In this latter case, since $S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} = 0$, then $\gamma_{LA} = \gamma_{SA} - \gamma_{SL}$, meaning that the surface tension of the spreading liquid must be reduced to a value equal to $\gamma_{SA} - \gamma_{SL}$ for spreading to be complete.

On nonpolar (low-energy) surfaces, Zisman (1964) has shown that complete wetting can occur only when the surface tension of the wetting liquid has been reduced to a critical value γ_c characteristic of the substrate (e.g., about 31 mN/m for polyethylene and about 18 mN/m for Teflon), thus equating γ_c with $\gamma_{SA} - \gamma_{SL}$. γ_c is obtained by measuring the contact angles that liquids of different surface tension produce on a particular substrate. For many liquids a plot of $\cos\theta$ versus γ_{LA} is linear. Extrapolation of this linear plot to $\cos\theta = 1$, i.e., $\theta = 0°$, yields γ_c. A critical surface tension for complete wetting γ_c, which is constant for a particular substrate irrespective of the nature of the wetting agent, requires that $\gamma_{SA} - \gamma_{SL}$ be reduced to the same value in all cases. This is possible only on low-energy surfaces, where the following two necessary conditions may be obtained: (1) γ_{SA}, the free energy per unit area of the surface in equilibrium with the liquid-saturated air above it, may be equated with γ_s, the free energy per unit area of the surface free of adsorbed material (only on low-energy surfaces is it likely that γ_s will not be reduced by the adsorption of surfactant or solvent molecules), and (2) adsorption of the surfactant at the substrate–solution interface occurs with the same orientation and degree of packing, producing the same value of γ_{SL} (and thus a constant value for $\gamma_{SA} - \gamma_{SL}$) as the surface tension of the spreading liquid approaches γ_c.

Thus, for example, in the presence of some highly fluorinated carboxylic acids and their salts, the value γ_c for polyethylene is decreased from its usual value of almost 31 mN/m to about 20 mN/m (Bernett, 1959) by adsorption of the fluorinated surfactants onto the polyethylene surface, with the result that solutions of these surfactants having surface tensions less than the normal γ_c for polyethylene do not spread on it. The requirement that the surface tension of the wetting liquid be reduced by the surfactant to some critical value characteristic of the substrate is thus a necessary, but not sufficient, condition for complete spreading wetting. A surfactant solution whose surface tension is above the critical tension for the substrate does not produce complete wetting, but a solution whose surface tension is below the critical tension for the substrate may or may not produce complete wetting (Schwarz, 1964).

On nonpolar surfaces, any structural or other factor that results in a decrease in γ_{LA} (Chapter 5) decreases the contact angle and improves wetting. Thus, the addition of a water structure-breaking additive (*N*-methylacetamide), which increases the surface tension of an aqueous solution of sodium dodecyl sulfate, causes an increase in its contact angle on polyethylene, whereas the addition of a (Water structure promoter (fructose, xylose), which decreases the surface tension of the surfactant solution, reduces its contact angle (Schwuger, 1971).

On ionic solid surfaces, if an aqueous wetting liquid contains surfactant ions of charge opposite to that of the surface, they will generally be adsorbed on the surface with their ionic hydrophilic heads oriented toward the solid and their hydrophobic groups oriented toward the aqueous phase (Chapter 2, Section IIC). Increase in the concentration of surfactant in the aqueous phase will then result in decreasing γ_{SA} and/or increasing γ_{SL}, thus decreasing wetting of the solid surface (decrease in $\cos\theta$), in spite of decreasing values for γ_{LA}, until the charge on the solid surface has been neutralized by adsorption of oppositely charged surfactant ions. Once the surface charge has been neutralized, further adsorption of surfactant ions will generally occur, with their hydrophobic groups oriented toward the surface and their hydrophilic heads toward the aqueous phase. This will result in γ_{SL} being reduced, and wetting will improve as the bulk concentration of the surfactant increases.

Ionic solid surfaces in contact with aqueous solutions containing surfactant ions of charge similar to that of the surface generally show only small adsorption of surfactant ions onto the similarly charged solid surface. As a result, γ_{SL} can be expected to show little change with change in the bulk concentration of surfactant, and any improvement in wetting with increase in the latter is due mainly to the decrease in the value of γ_{LA}.

A simple experimental method of evaluating the performance of a surfactant as a wetting agent for a liquid on a hard surface consists of measuring the area to which a drop of the surfactant-containing liquid spreads in a given amount of time and then comparing it with the area to which the pure liquid spreads in the same time. For example, a film of the surface to be wetted may be placed on a horizontal planar glass plate (10 cm × 10 cm) which has four small (1 cm^2) pieces of glass at each corner. Using a microsyringe, a 20-μl drop of the surfactant solution is placed on the film. The time is measured and another 10 cm × 10 cm glass square is immediately placed over the four pieces of glass at the corners, so that it is parallel to the film. After a given amount of time (e.g., 3 minutes), an outline of the spread solution is traced on the top glass. This area is then retraced on standard white paper from which it is cut and weighed. With the assumption that the paper has a constant mass per unit area, the exact spreading area is then calculated from the mass of a piece of the same paper of known area (Wu, 2002). The ratio of the area spread by the surfactant solution to the area spread by the same volume of pure liquid under the same conditions is called the *spreading factor* (SF). Some SF values are listed in Table 6-3 (Section IV below).

II.C. Textile (Nonequilibrium) Wetting

Textiles have large surface areas, and consequently equilibrium conditions are seldom attained in the times allowed for wetting in practical processes. As a result, the rate of wetting of the surface is generally a more important factor than wetting equilibria in determining the suitability of a surfactant as a wetting agent for a particular system, and evaluation of the surfactant is generally by some kinetic test. The performance of the surfactant can be evaluated by determining (1) the efficiency of the wetting agent, i.e., the minimum concentration of the surfactant that will produce a given amount of wetting in a certain time at a specific temperature, (2) the effectiveness of the wetting agent, i.e., the minimum wetting time that can be achieved by the surfactant in a given system, regardless of the surfactant concentration used, or (3) the wetting time at a fixed concentration of surfactant in a given system at a specific temperature. The performance rating of surfactants relative to each other may vary with the method of evaluation and with the temperature at which the evaluation is done, and it is therefore necessary to specify these conditions. Most frequently, the third method given above is used to evaluate performance, since it requires only one determination, generally by use of 0.1% solutions of surfactant at 25°C.

The most commonly used practical test for textile wetting ability is probably the Draves test (Draves, 1939), in which a 5-g skein of gray, naturally waxed cotton yarn (54-in. loops containing 120 threads) is attached to a 3-g hook and totally immersed in a tall cylinder of surfactant solution by means of a weight tied to the hook by a thread. The surfactant solution displaces the air in the skein by a spreading wetting process, and when sufficient air has been displaced, the skein suddenly sinks in the cylinder. The better the wetting agent, the shorter the time required for sinking to occur. This test is widely used, since it approximates important use conditions for wetting agents in the textile industry.

The physicochemical basis for this test was investigated by Fowkes (1953), who explained the well-known observation that the log of the wetting time (WOT) is a linear function of the log of the bulk phase concentration C_1 of the surfactant when the latter is used at concentrations below its CMC. Fowkes stated that the penetration of the surfactant into the cotton proceeds at a rate that is a function of the contact angle θ of the advancing liquid front such that

$$\log \mathrm{WOT} = A - B\cos\theta \tag{6.19}$$

where A and B are empirical constants. He also showed that for this system $\cos\theta$ is a linear function of γ, the surface tension at the wetting front, and that for surfactants used at concentrations below their CMCs where their surface excess concentration Γ_1 is a constant, γ is a linear function of $\log C_1$; that is, the Gibbs adsorption equation in the form

$$d\gamma = -2.303\,RT\,\Gamma_1 d\,\log C_1 \tag{2.19}$$

can be integrated. Therefore

$$\log \mathrm{WOT} = A^1 - B^1\,\log C_1 \tag{6.20}$$

where A^1 and B^1 are empirical constants.

When adsorption of the surfactant onto the substrate is strong, however, Fowkes found that the rate of wetting was determined not by the bulk phase concentration of the surfactant, but by the rate of diffusion of the surfactant to the wetting front. In this case the concentration of surfactant present at the advancing liquid front was so depleted by adsorption that the surface tension (or contact angle) there, and consequently the wetting time, were determined solely by the rate at which new surfactant arrived at the front.

For a nonionic surfactant that is used at a concentration considerably above its CMC under diffusion-controlled conditions, the Fowkes (1953) equation for the factors determining WOT can be transformed (Cohen, 1981) to

$$\log \mathrm{WOT} = K - 2\log(C - C^1) - \log D \tag{6.21}$$

where K depends upon the physical characteristics of the skein being wetted and upon the surface area per gram of adsorbed surfactant at the air–aqueous solution interface S^1; C is the initial surfactant concentration, in g/L, in the aqueous phase; C^1 is the surfactant concentration, in g/L, at the skein–solution interface required to produce a given WOT; and D is the apparent diffusion coefficient of the surfactant.

For the wetting of similar skeins by a particular surfactant at $C \gg C^1$, a log–log plot of WOT versus. C should be linear with a slope of -2 if the diffusion coefficient D remains constant with change in C. Diffusion data available (Fowkes, 1953) for solutions of individual nonionics considerably below their cloud points but above their CMC indicate that D increases by a factor of about 2 in the concentration range between 0.25 and 1.0 g/L. This should yield a slope of -1.5 for a log–log plot of WOT versus. C under these conditions. Wetting data for a series of well-purified individual nonionic surfactants of structure $C_{12}H_{25}(OC_2H_4)_x$ OH, where $x = 4, 5, 6, 7$, or 8, yielded linear log–log plots with slopes close to that value in that initial surfactant concentration range, indicating the $C \gg C^1$ in that range and that wetting is diffusion controlled for these compounds under these conditions.

For various nonionic surfactants at concentrations considerably above their CMC, the WOT at a given temperature depends also on their diffusion, coefficients D and on their surface areas per gram of adsorbed surfactant S^1 at the air–aqueous solution interface. Thus, from equation 6.21

$$\frac{\mathrm{WOT}_1}{\mathrm{WOT}_2} = \frac{D_2}{D_1}\frac{C_2 - C_2^1}{C_1 - C_1^1}\left(\frac{MW_1}{a_1^s}\right)^2\left(\frac{a_2^s}{MW_2}\right)^2 \tag{6.22}$$

since $S^1 = Na^s/MW$, where a^s is the molecular area of the surfactant of molecular weight (MW) at the air–aqueous solution interface at that temperature and $N =$ Avogadro's number.

When nonionic surfactants are compared at similar temperatures and similar initial surfactant concentrations in the aqueous phase such that $C \gg C^1$, then

$$\frac{\mathrm{WOT}_1}{\mathrm{WOT}_2} = \frac{D_2}{D_1}\left(\frac{MW_1}{a_1^s}\right)^2\left(\frac{a_2^s}{MW_2}\right)^2 \tag{6.23}$$

Equation 6.23 indicates that, under these conditions, the shortest wetting times will be shown by those surfactants with the largest diffusion coefficients, largest surface areas per molecule at the air–aqueous solution interface, and smallest molecular weights. This is consistent with the finding (Chapter 5, Section IV) that surfactant molecules with larger areas per molecule at the air–aqueous solution interface and larger diffusion coefficients show shorter induction times in dynamic surface tension reduction, i.e., show lower surface tensions at short times.

This may explain why short-chain surfactants with highly branched hydrophobic groups show such good wetting properties (see below). Since values of a^s are readily obtained (Chapter 2, Section IIIB), equation 6.23 can also be used to obtain relative diffusion coeffficients from wetting times (Cohen, 1981).

Since the rate of wetting is a function of the surface tension of the wetting front, the wetting power of a surfactant in wetting tests is a function of the concentration of molecularly dispersed material at the front, and those structural factors in the surfactant molecule that inhibit micelle formation and that increase the rate of diffusion of the monomeric surfactant to the interface should enhance its performance as a wetting agent. Some evidence that diffusion of surfactants is decreased by increase in the length of the (straight) alkyl chain and increased by branching in isomer alkyl chains has been supplied by Schwuger (1982). Data by Longsworth (1953) on the diffusion coefficients of amino acids indicate that the diffusion coefficient in aqueous solution is decreased by increase in the degree of hydration of the molecule and by increase in the chain length of the alkyl group. Branching of the alkyl group gave a more compact structure and a greater diffusion coefficient compared to the isomeric straight-chain compound. This is consistent with data showing that the fastest textile wetting is given by surfactants having relatively short, highly branched hydrophobic groups and that the highly hydrated POE nonionics are not as rapid textile wetting agents as the less hydrated anionics.

A fairly good correlation has been observed between the wetting time on cotton skeins, measured by the Draves test, and the dynamic surface tension (Chapter 5, Section IV) at 1 s. To achieve a 1-s dynamic surface tension value, γ_{1s}, that does not change much with decrease in surfactant concentration, a bulk phase surfactant concentration of at least 5×10^{-4} *M* is required (Rosen, 1990).

Wetting times for some surfactants, using the Draves test at 25°C, with a 3-g hook and a 5-g cotton skein, are listed in Table 6-1.

In water at 25°C containing no more than 300 ppm $CaCO_3$, and at a surfactant concentration of 0.1%, ionic surfactants having a terminal hydrophilic group seem to show optimum wetting when the hydrophobic group has an effective length of about 12–14 carbon atoms. When the hydrophilic group is centrally located, optimum wetting appears to be shown when the hydrophobic group has an effective length of almost 15 carbon atoms. The CMCs of ionic surfactants of these types generally fall in the range $1–8 \times 10^{-3}$ *M*. At very low concentrations, as in the case of surface tension, longer-chain compounds often perform better than shorter ones (Komor, 1966), presumably because of their greater efficiency in reducing surface tension. However, at higher concentrations the shorter-chain compounds appear to become more effective and reach lower minimum wetting times than the long-chain ones. Thus, for aqueous solutions of sodium alkyl sulfates at 0.10% concentration,

TABLE 6-1 Wetting Times of Surfactants in Aqueous Solution (Draves Test, 25°C)

		Wetting Times (s)		
Compound	Concentration (%)	Distilled Water	300 ppm $CaCO_3$	Reference
$C_{10}H_{21}SO_3Na$	0.1	>300		Dahanayake, 1985
$C_{10}H_{21}SO_3Na$	0.1 (in 0.1 *M* NaCl)	65		Dahanayake, 1985
$C_{12}H_{25}SO_3Na$	0.1	28		Dahanayake, 1985
n-$C_{12}H_{25}SO_4^-Na^+$	0.02	>300		Weil, 1960
n-$C_{12}H_{25}SO_4^-Na^+$	0.05	39.9		Weil, 1960
$C_{12}H_{25}SO_4Na$	0.1	7.5		Weil, 1960, Dahanayake, 1985
n-$C_{14}H_{29}SO_4^-Na^+$	0.10	12[a]		Weil, 1954
n-$C_{16}H_{33}SO_4^-Na^+$	0.10	59[a]		Weil, 1954
n-$C_{18}H_{37}SO_4^-Na^+$	0.10	280[a]		Weil, 1954
Na oleyl sulfate	0.10	19[a]		Weil, 1954
Na elaidyl sulfate	0.10	20[a]		Weil, 1954
sec-n-$C_{13}H_{27}SO_4^-Na^+$	0.063	180+		Livingston, 1965
(random-SO_4Na positions)	0.125	11.6		Livingston, 1965
sec-n-$C_{14}H_{29}SO_4^-Na^+$	0.063	19.4		Livingston, 1965
(random-SO_4Na positions)	0.125	7.0		Livingston, 1965
sec-c-$C_{15}H_{31}SO_4^-Na^+$	0.063	14.0		Livingston, 1965
(random-SO_4Na positions)	0.125	7.0		Livingston, 1965
sec-n-$C_{16}H_{33}SO_4^-Na^+$	0.063	22		Livingston, 1965
(random-SO_4Na positions)	0.125	9		Livingston, 1965
sec-n-$C_{17}H_{35}SO_4^-Na^+$	0.063	25		Livingston, 1965
(random-SO_4Na positions)	0.125	9		Livingston, 1965
sec-n-$C_{18}H_{37}SO_4^-Na^+$	0.063	39		Livingston, 1965
(random-SO_4Na positions)	0.125	26		Livingston, 1965

$C_{12}H_{25}OC_2H_4SO_4Na$	0.1	6		Dahanayake, 1985
$C_{12}H_{25}OC_2H_4SO_4Na$	0.088 (in 0.1 *M* NaCl)	6		Dahanayake, 1985
$C_{12}H_{25}(OC_2H_4)_2SO_4Na$	0.1	11		Dahanayake, 1985
$C_{12}H_{25}(OC_2H_4)_2SO_4Na$	0.1 (in 0.1 *M* NaCl)	13		Dahanayake, 1985
$C_{12}H_{25}C_6H_4SO_3^-Na^+$ (from propylene teramer)	0.125	6.9		Livingston, 1965
n-$C_{10}H_{21}CH(CH_3)C_6H_4SO_3^-Na^+$	0.10	10.3	80	Smith, 1966
n-$C_{12}H_{25}CH(CH_3)C_6H_4SO_3^-Na^+$	0.10	30	>300	Smith, 1966
n-$C_{14}H_{29}CH(CH_3)C_6H_4SO_3^-Na^+$	0.10	155	>300	Smith, 1966
$C_{10}DADS^b$	0.1	431		Rosen, 1993
$C_{12}H_{25}(C_2H_4)_3OH + C_{10}DADS$ mixture, 8:2(w/w)	0.1	14.5		Rosen, 1993
N-dodecyl-2-pyrrolid(in)one + $C_{10}DADS$ mixture, 8:2(w/w)	0.1	8.6		Rosen, 1993
$C_{12}H_{25}OCH_2CH(SO_4^-Na^+)CH_3$	0.10	6		Weil, 1966
$C_4H_9CH(C_2H_5)CH_2OOCCH_2\text{-}CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	0.025	20.1		Weil, 1960
$C_4H_9CH(C_2H_5)CH_2OOCCH_2\text{-}CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	0.05	6.3		Weil, 1960
$C_4H_9CH(C_2H_5)CH_2OOCCH_2\text{-}CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	0.10	1.9		Weil, 1960
$C_7H_{15}CH(SO_3^-Na^+)COOC_5H_{11}$	0.10	12.1	5.3	Stirton, 1962b
$C_8H_{17}CH(SO_3^-Na^+)COOC_8H_{17}$	10 m***M***	$<2^c$		Ohbu, 1998
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_{10}H_{21}$	10 m*M*	$<2^c$		Ohbu, 1998
$C_{12}H_{25}CH(SO_3^-Na^+)COOCH_3$	10 m*M*	34^c		Ohbu, 1998
$C_{12}H_{25}CH(SO_3^-Na^+)COOC_3H_7$	0.10	5.0	3.8	Stirton, 1962b
$C_{12}H_{29}CH(SO_3^-Na^+)COOCH_3$	0.10	25	16	Stirton, 1962b
$C_8H_{17}C(C_4H_9)(SO_3^-Na^+)COOCH_3$	0.10	13.3	5.2	Stirton, 1962b
$C_8H_{17}C(C_6H_{13})(SO_3^-Na^+)COOCH_3$	0.10	1.3	3.7	Stirton, 1962b
$C_8H_{17}C(C_8H_{17})(SO_3^-Na^+)COOCH_3$	0.10	2.8	3.8	Stirton, 1962b
$C_7H_{15}CH(SO_3^-Na^+)COOC_6H_{13}$	0.10	2.2	1.4	Stirton, 1962a

(*Continued next page*)

TABLE 6-1 (*Continued*)

		Wetting Times (s)		
Compound	Concentration (%)	Distilled Water	300 ppm $CaCO_3$	Reference
$C_7H_{15}CH(SO_3^-Na^+)COOC_7H_{15}$	0.10	0.0	3.0	Stirton, 1962b
$C_7H_{15}CH(SO_3^-Na^+)COOC_8H_{17}$	0.025	15.4		Weil, 1960
$C_7H_{15}CH(SO_3^-Na^+)COOC_8H_{17}$	0.05	5.0		Weil, 1960
$C_7H_{15}CH(SO_3^-Na^+)COOC_8H_{17}$	0.10	1.5	10.8	Stirton, 1962b
$C_7H_{15}CH(SO_3^-Na^+)COOCH(CH_3)C_6H_{13}$	0.10	1.3	4.5	Stirton, 1962a
$C_7H_{15}CH(SO_3^-Na^+)COOCH_2CH(C_2H_5)C_4H_9$	0.10	0.0	4.5	Stirton, 1962a
$C_7H_{15}CH(SO_3^-Na^+)COOC_9H_{19}$	0.10	3.8	33.1	Stirton, 1962a
$C_2H_5CH(SO_3^-Na^+)COOC_{12}H_{25}$	0.10	5.5	4.4	Stirton, 1962b
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_4H_9$	0.10	1.6	1.5	Stirton, 1962b
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_5H_{11}$	0.10	1.6	4.9	Stirton, 1962b
$C_{12}H_{25}Pyr^+Cl^d$	0.1	250		Dahanayake, 1985
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.1	250		Dahanayake, 1985
N-dodecyl-2-pyrrolid(in)one	0.1	131		Rosen, 1993
$C_8H_{17}CHOHCH_2OH$	0.047	7		Rosen, 1979
$C_8H_{17}CHOHCH_2CH_2OH$	0.041	8		Rosen, 1979
$C_8H_{17}(OC_2H_4)_2OH$	0.1	5		Weil, 1979
$C_8H_{17}(OC_2H_4)_3OH$	0.1	22		Weil, 1979
$C_{10}H_{21}(OC_2H_4)_2OH$	0.1	10		Weil, 1979
$C_{10}H_{21}(OC_2H_4)_3OH$	0.1	4		Weil, 1979
$C_{10}H_{21}(OC_2H_4)_4OH$	0.1	5		Weil, 1979
$C_{12}H_{25}(OC_2H_4)_3OH$	0.1	129		Rosen, 1993
$C_{12}H_{25}(OC_2H_4)_4OH$	0.1	19		Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_5OH$	0.1	$4._8,6._0$(10°C) $13._5$(40°C)		Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_{5.1}OH^c$	0.1	14		Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_6OH$	0.1	$3._9,5._5$(10°C) $4._1$(40°C) $9._5$(60°C)		Cohen, 1981

$C_{12}H_{25}(OC_2H_4)_7OH$	0.1	$5._9, 10._5$(10°C) $4._0$(40°C)$3._8$(60°C)	Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_8OH$	0.1	$8._3$, 18(10°C) $6._3$(40°C) $4._0$(60°C)	Cohen, 1981
$C_{12}H_{25}(OC_2H_4)_{9.6}OH^e$	0.1	11	Weil, 1979
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_4OH$ (normal EO distribution)	0.05	50	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$	0.05	25	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_8OH$	0.05	~25	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_9OH$	0.05	25	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	0.05	30	Crook, 1964
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_{12}OH$	0.05	50	Crook, 1964
Igepal CO-630	0.05	27	Komor, 1966
$(C_9H_{19}C_6H_4(OC_2H_4)_9OH)$	0.10	12	Komor, 1966
Igepal CO-710	0.05	33	Komor, 1966
$(C_9H_{19}C_6H_4(OC_2H_4)_{10\text{-}11}OH)$	0.10	15	Komor, 1966
Igepal CO-730	0.05	>50	Komor, 1966
$(C_9H_{19}C_6H_4(OC_2H_4)_{15}OH)$	0.10	>50	Komor, 1966
$(C_9H_{19}C_6H_4(OC_2H_4)_{15}OH)$	0.05 (70°C)	37	Komor, 1966
$(C_9H_{19}C_6H_4(OC_2H_4)_{15}OH)$	0.10 (70°C)	17	Komor, 1966
$C_7H_{15}CO(OC_2H_4)_2OH$	0.1	>300	Weil, 1979
$C_7H_{15}CO(OC_2H_4)_4OH$	0.1	>300	Weil, 1979
$C_8H_{17}CO(OC_2H_4)_2OH$	0.1	72	Weil, 1979
$C_8H_{17}CO(OC_2H_4)_3OH$	0.1	6	Weil, 1979
$C_8H_{17}CO(OC_2H_4)_4OH$	0.1	48	Weil, 1979
$C_9H_{19}CO(OC_2H_4)_2OH$	0.1	41	Weil, 1979
$C_9H_{19}CO(OC_2H_4)_3OH$	0.1	7	Weil, 1979
$C_9H_{19}CO(OC_2H_4)_4OH$	0.1	11	Weil, 1979
$C_9H_{19}CO(OC_2H_4)_5OH$	0.1	12	Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_4OH$	0.1	23	Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_5OH$	0.1	7	Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_6OH$	0.1	34	Weil, 1979
$C_{13}H_{27}CO(OC_2H_4)_5OH$	0.1	52	Weil, 1979

(*Continued next page*)

TABLE 6-1 (*Continued*)

Compound	Concentration (%)	Wetting Times (s)		Reference
		Distilled Water	300 ppm $CaCO_3$	
$C_{13}H_{27}CO(OC_2H_4)_6OH$	0.1	21		Weil, 1979
$C_{10}H_{19}(\Delta 10\text{-}11)CO(OC_2H_4)_3OH$	0.1	9		Weil, 1979
$C_{10}H_{19}(\Delta 10\text{-}11)CO(OC_2H_4)_4OH$	0.1	6		Weil, 1979
$C_{10}H_{19}(\Delta 10\text{-}11)CO(OC_2H_4)_5OH$	0.1	7		Weil, 1979
$C_7H_{15}CO(OC_2H_4)_4OCH_3$	0.1	>300		Weil, 1979
$C_7H_{15}CO(OC_2H_4)_5OCH_3$	0.1	>300		Weil, 1979
$C_8H_{17}CO(OC_2H_4)_4OCH_3$	0.1	248		Weil, 1979
$C_8H_{17}CO(OC_2H_4)_5OCH_3$	0.1	12		Weil, 1979
$C_8H_{17}CO(OC_2H_4)_6OCH_3$	0.1	23		Weil, 1979
$C_9H_{19}CO(OC_2H_4)_4OCH_3$	0.1	24		Weil, 1979
$C_9H_{19}CO(OC_2H_4)_5OCH_3$	0.1	9		Weil, 1979
$C_9H_{19}CO(OC_2H_4)_7OCH_3$	0.1	9		Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_5OCH_3$	0.1	12		Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_6OCH_3$	0.1	5		Weil, 1979
$C_{11}H_{23}CO(OC_2H_4)_7OCH_3$	0.1	9		Weil, 1979
$C_{13}H_{27}CO(OC_2H_4)_5OCH_3$	0.1	64		Weil, 1979
$C_{13}H_{27}CO(OC_2H_4)_6OCH_3$	0.1	35		Weil, 1979
$C_{13}H_{27}CO(OC_2H_4)_7OCH_3$	0.1	17		Weil, 1979
Dimethylhexadecynediol + 15 mol EO	0.05	11		Leeds, 1965
	0.1	9		Leeds, 1965
Tetramethyldecynediol + 5 mol EO	0.1	24		Leeds, 1965

[a] $1\frac{1}{4}$-in. binding tape, 1-g hook, and 40-g anchor (L. Shapiro, *Am. Dyestuff Reptr.* **39**, 38–45, 62[1950]).

[b] $(C_{10}H_{21})_2C_6H_2(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$.

[c] 10 × 10 × 2 mm wool felt strip.

[d] Pyr^+, pyridinium.

[e] Mixture with average EO number shown.

the order of increasing wetting time is tetradecyl < dodecyl < oleyl ≪ hexadecyl ≪ octadecyl, but at 0.15% concentration the order is dodecyl < tetradecyl < oleyl, and this is the order of minimum wetting times attained at any concentration (Stirton, 1952: Weil, 1954).

As the temperature of the water is raised, the chain length for optimum wetting by ionic surfactants generally increases, probably because of the increased solubility of the surfactant at higher temperatures and its consequent lesser tendency to migrate to the interface. Thus, at 60°C, $C_{16}H_{33}SO_4^-Na^+$ shows better wetting than $C_{12}H_{25}SO_4^-Na^+$ (Weil, 1959) and in *p*-(*n*-alkyl) benzenesulfonates, the *n*-dodecyl compound (equivalent length = 15.5 carbons) gives the most rapid wetting (Greiss, 1955).

For determining the effective length of the hydrophobic groups, a carbon atom on a branch attached to the main chain appears to be equivalent to about two-thirds of a carbon atom on the main chain, one between an ionic hydrophilic group and a polar group in the molecule to about one-half of a carbon atom on the main chain, and a phenyl group to three and one-half carbon atoms in a straight chain. The ester linkage —COO— appears not to contribute to the length of the hydrophobic group.

Surfactants with a centrally located hydrophilic group are especially good textile wetting agents, particularly when they have branched hydrophobic groups, presumably because of their larger area/molecule at the air–aqueous solution interface and their more rapid diffusion to and orientation at the wetting front. For probably similar reasons, *o*-sulfonated alkylbenzenes and *N*-acylanilides are better wetting agents than the corresponding *p*-sulfonates (Shirolkar, 1941; Gray, 1965). In compounds such as $RCH(R')SO_4^-M^+$ (Dreger, 1944; Püschel, 1966; Götte, 1969a), $RCH(R')CH_2SO_4^-Na^+$ (Machemer, 1959), $RCH(R')C_6H_4SO_3^-Na^+$ (Baumgartner, 1954), and $RCH(SO_3^-M^+)COOR'$ (Weil, 1960; Stirton, 1962a, 1962b), wetting appears to improve as R and R′ approach each other in equivalent length. The excellent wetting properties of sulfated castor oil are attributed to the presence in the product of sulfated glyceryl ricinoleates with centrally located sulfate groups. Other structures that produce good wetting agents are $RC(R')(OH)C{\equiv}CC(OH)(R')R$ and $ROOCH_2CH(SO_3^-Na^+)COOR$.

The introduction of a second ionic hydrophilic group into the molecule is generally unfavorable to wetting power (Götte, 1969b). Thus α-sulfocarboxylic acids and monoalkylsulfosuccinic acid esters are better wetting agents at acid pHs than at alkaline pHs; in sulfated ricinoleates at alkaline pHs, those in which the carboxylic acid group is esterified show better wetting properties than those in which it is not. Similary, the introduction of oxyethylene groups between the hydrophilic and hydrophobic groups in the surfactant molecule in compounds of structure $R(OC_2H_4)_xSO_4^-Na^+$, where R is $C_{16}H_{33}$ or $C_{18}H_{37}$ and $x = 1$–4, is unfavorable to wetting power, with the wetting time increasing with the introduction of each additional oxyethylene group (Weil, 1959).

A study of the wetting power of well-purified individual POE nonionics (Cohen, 1981) showed that individual surfactants of this type, $C_{12}H_{25}(OC_2H_4)_xOH$, are better wetting agents than a Poisson distribution mixture with the same average number of oxyethylene units. Temperature increase caused an increase in the wetting power of individual POE nonionics until the cloud point of the compound was approached. When the cloud point of the surfactant was exceeded, the wetting power markedly diminished. Best wetting was obtained when the wetting temperature was 10–30°C below the cloud point of the compound.

For commercial nonionic POE alcohols, alkylphenols, and mercaptans, wetting times go through a minimum with increase in the number of OE units in the POE chain, and optimum wetting power is generally shown by those surfactants whose cloud points are just above the temperature at which the wetting test is conducted (Komor, 1966). In distilled water at 25°C, materials having an effective hydrophobic chain length of 10–11 carbon atoms and a POE chain of 6–8 OE units appear be the best wetting agents (Crook, 1964). POE alcohols and mercaptans appear to be better wetting agents than the corresponding POE fatty acids (Wrigley, 1957).

In POE polyoxypropylene block copolymers, wetting power appears to improve as the molecular weight of the polyoxypropylene portion of the molecule is increased and to be at a maximum when the molecule contains the minimum oxyethylene content consistent with solubility in the aqueous phase at the use temperature.

In a study of POE straight-chain amines (Ikeda, 1984), the best wetting among isomeric materials was shown by compounds with two oxyethylene groups of approximately equal oxyethylene content attached to the nitrogen. Here, again, a more compact branched, structure produced bettter wetting.

The importance of the absence of undesirable reaction products and impurities for good wetting power by aqueous surfactant solutions has been pointed out in a series of articles by Micich (1984, 1985, 1986) on wetting agents for hydrophobic soils. Water-insoluble unreacted starting material and other reaction products markedly increased wetting times for cotton skeins (Draves test) and drop penetration times on hydrophobic soil. In a series of ethenoxylated secondary amides, $RCON(R^1)(EO)_xH$, best results were obtained when both hydrophobic groups (R, R^1) were branched and each contained 7–8 carbon atoms. This structure, with the hydrophilic group in the center of the molecule and an effective hydrophobic chain length of 12–14 carbon atoms, is typical of excellent wetting agents. When the compounds were synthesized in such manner as to minimize unreacted water-insoluble starting material and reaction products, almost instantaneous wetting and rewetting of both skeins and hydrophobic soil was obtained with compounds of this type whose cloud points were in the neighborhood of the wetting temperature.

Work on the wetting of hydrophobic sand by POE nonionics showed that both wetting rate and wetting effectiveness (measured by weight gain of the sand column) were greater for branched hydrophobic chain compounds than for linear ones (Varadaraj, 1994).

Wetting efficiencies of some nonionic surfactants are given in Table 6-2.

II.D. Effect of Additives

The electrolyte content of the aqueous phase has a considerable effect on the wetting time of ionic surfactants, reflecting its effect on the reduction of surface tension by the surfactant, its solubility in water, and its CMC. Electrolytes that

TABLE 6-2 Wetting Efficiencies of Surfactants in Aqueous Solution (Concentrations for 25 s Sinking Time at 25°C in Draves Test)

Surfactant	Concentration (%)	Reference
t-$C_8H_{17}S(C_2H_4O)_2H$	0.098	Olin, 1951
t-$C_8H_{17}S(C_2H_4O)_{2.93}H$	0.084	Olin, 1951
t-$C_8H_{17}S(C_2H_4O)_{3.92}H$	0.102	Olin, 1951
t-$C_8H_{17}S(C_2H_4O)_{6.86}H$	0.175	Olin, 1951
t-$C_{12}H_{25}S(C_2H_4O)_{7.85}H$	0.074	Olin, 1951
t-$C_{12}H_{25}S(C_2H_4O)_{8.97}H$	0.051	Olin, 1951
t-$C_{12}H_{25}S(C_2H_4O)_{10.02}H$	0.046	Olin, 1951
t-$C_{12}H_{25}S(C_2H_4O)_{11.03}H$	0.047	Olin, 1951
t-$C_{12}H_{25}S(C_2H_4O)_{12.25}H$	0.052	Olin, 1951
t-$C_{14}H_{29}S(C_2H_4O)_{7.98}H$	0.132	Olin, 1951
t-$C_{14}H_{29}S(C_2H_4O)_{9.00}H$	0.135	Olin, 1951
t-$C_{14}H_{29}S(C_2H_4O)_{10.98}H$	0.113	Olin, 1951
t-$C_{14}H_{29}S(C_2H_4O)_{12.11}H$	0.108	Olin, 1951
t-$C_{14}H_{29}S(C_2H_4O)_{13.13}H$	0.135	Olin, 1951
n-$C_{11}H_{23}O(C_2H_4O)_8H$	0.035	Komor, 1966
n-$C_{12}H_{25}O(C_2H_4O)_{10}H$	0.046	Komor, 1966
p-n-$C_{10}H_{21}C_6H_4O(C_2H_4O)_{11}H$	0.054	Komor, 1966
iso-$C_8H_{17}O(C_2H_4O)_4H$	0.13	Komor, 1966
oxo-$C_{10}H_{21}O(C_2H_4O)_{10}H$	0.095	Komor, 1966
Igepal CO-610 (nonylphenol + 8–9 mol EO)	0.05–0.06	GAF, 1965
Igepal CO-630 (nonylphenol + 9 mol EO)	0.03–0.05	GAF, 1965
Igepal CO-710 (nonylphenol + 10–11 mol EO)	0.04–0.07	GAF, 1965
Igepal CO-730 (nonylphenol + 15 mol EO)	0.14–0.16	GAF, 1965

decrease the surface tension of the surfactant solution (Chapter 5, Section III), such as Na_2SO_4, NaCl, and KCl, increase its wetting power (Gerault, 1964). When the aqueous phase contains added electrolyte or additional hardness, optimum wetting with anionic surfactants is generally obtained when the hydrophobic group is somewhat shorter than the optimum length for pure water. For solutions containing high concentrations of electrolyte, hydrophobic groups with lengths as short as seven to eight carbon atoms are effective.

The addition of long-chain alcohols to aqueous anionic and nonionic surfactant solutions is reported to increase their wetting power (Gerault, 1964; Bland, 1968) and the addition of metal soaps, especially those of the alkaline earth metals, is stated to increase the wetting power of dodecylpyridinium chloride solutions (Suzuki, 1967).

III. SYNERGY IN WETTING BY MIXTURES OF SURFACTANTS

As will be described in Chapter 11, the interaction of two different types of surfactants with each other, either in mixed monolayers at an interface or in mixed micelles in aqueous solution, can result in synergistic enhancement of their interfacial properties. Such an enhancement can result in improved *performance properties*, such as wetting, foaming, solubilization, and so on.

In some cases, enhancement of (textile) wetting is the result of synergistic interaction producing a decrease in dynamic and equilibrium surface tension values (Section IIA above) (Zhu, 1989). In other cases, enhancement of wetting is due to solubilization by a water-soluble surfactant of a water-insoluble but highly surface-active surfactant (Rosen, 1993). Surfactants with limited solubility in water (less than 0.25 g/L) generally show poor textile wetting power, sometimes in spite of low equilibrium surface tension values. When some of these surfactants are mixed with a water-soluble surfactant that can interact with them to solubilize them into the aqueous phase, the wetting times of the mixture decrease, sometimes dramatically. Thus, short-chain alcohols or alkylphenol ethoxylates with just a few oxyethylene groups in the molecule, or *n*-dodecyl-2-pyrrolidinones, which show low solubility in water and poor textile wetting power, become excellent wetting agents when mixed with various anionic surfactants that can solubilize them into the water phase. The addition of a POE nonionic surfactant has been shown to increase the wetting power of some anionics and to diminish the wetting power of a cationic surfactant (Biswas, 1960). This is attributed to an increase by the nonionic in the mobility of the anionics and a decrease by it in the mobility of the cationic, resulting in more rapid diffusion of the former and slower diffusion by the latter to the wetting front.

IV. SUPERSPREADING (SUPERWETTING)

It is difficult to wet highly hydrophobic hard surfaces (e.g., with contact angles against water $>100°$) even with surfactant solutions. The areas to which the solutions spread (See method in Section II B, above) is often just a small multiple of the area spread by pure water. Some data are shown in Table 6-3.

Some POE trisiloxanes, e.g., $[(CH_3)_3SiO]_2Si(CH_3)[CH_2(CH_2CH_2O)_{8.5}CH_3]$, on the other hand, spread readily to much greater areas on these highly hydrophobic areas. This phenomenon has been called *superspreading* or *superwetting* and has attracted considerable interest (Ananthapadmonabhan, 1990; He, 1993; Lin, 1993; Zhu, 1994; Gentle, 1995; Rosen, 1996; Stoebe, 1996, 1997; Svitova, 1996). This superspreading is usually attributed to the ability of trisiloxane surfactants to decrease the surface tension of their aqueous solutions to 20–21 mN/m, significantly lower than the 25 mN/m minimum attainable with hydrocarbon chain surfactants. However, mixtures of certain short-hydrocarbon chain surfactants with the POE trisiloxane mentioned above show even greater superspreading ability than the latter (Rosen, 1996). This synergistic effect (Table 6-3) has been shown (Rosen, 2001; Wu, 2002) to be due not to a further reduction of the surface tension by the mixture, but to greater adsorption of the mixture at the aqueous solution–hydrophobic solid interface than at the aqueous solution–air interface.

TABLE 6-3 Spreading Factors of Aqueous Solutions of Some Surfactants and Their Mixtures on Polyethylene Film at 25°C (0.1% conc., 3-min time)[a]

System	Medium	SF[b]	Reference
$C_{12}SO_4^-Na^+$	H_2O	5	Rosen, 2002
$(CH_3)_2CHC_6H_4SO_3^-Na^+$	H_2O	5	Rosen, 2002
$C_4H_9OC_6H_4SO_3^-Na^+$	H_2O	5	Zhou, 2003
Na diamylsulfosuccinate	H_2O	5	Rosen, 2002
Na di(2-ethylhexyl)sulfosuccinate	H_2O	8	Rosen, 2002
$C_{10}Pyr^+Br^-$	H_2O	5	Rosen, 2002
$C_{12}N^+Me_3Cl^-$	H_2O	3	Rosen, 2002
$C_{10}N^+(CH_3)_2O^-$	H_2O	3	Rosen, 2002
$C_2H_5C(CH_3)(OH)C{\equiv}CC(CH_3)(OH)\text{-}C_2H_5$[d]	H_2O	5	Rosen, 2002
$(CH_3)_2CHCH_2CH(CH_3)CH_2C\text{—}(OC_2H_4)_8CH_2CH(CH_3)_2$[d]	H_2O	65	Rosen, 2002
tert-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$[d]	H_2O	15	Zhou, 2003
tert-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$[d]	0.1 *M* NaCl	10	Zhou, 2003
N-hexylpyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	5	Wu, 2002
N-(2-ethylhexyl)pyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	5	Wu, 2002
N-octylpyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	5	Wu, 2002
N-octylpyrrolid(in)one	H_2O	15	Zhou, 2003
N-octylpyrrolid(in)one	0.1 *M* NaCl	10	Zhou, 2003
N-dodecylpyrrolid(in)one	H_2O	45	Zhou, 2003
N-dodecylpyrrolid(in)one	0.1 *M* NaCl	30	Zhou, 2003
L 77[c]	Aqueous phosphate buffer, pH = 7.0	150	Wu, 2002
L 77[c]–*N*-hexylpyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	210	Wu, 2002
L 77[c]–*N*-(ethylhexyl)pyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	235	Wu, 2002
L 77[c]–*N*-octylpyrrolid(in)one	Aqueous phosphate buffer, pH = 7.0	210	Wu, 2002
n-$C_4H_9OC_6H_4SO_3^-Na^+$-*N*-dodecylpyrrolid(in)one	H_2O	80	Zhou, 2003
n-$C_4H_9OC_6H_4SO_3^-Na^+$-*N*-dodecylpyrrolid(in)one	0.1 *M* NaCl	85	Zhou, 2003
t-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$[d]-*N*-octylpyrrolid(in)one	H_2O	100	Zhou, 2003
t-$C_8H_{17}C_6H_4(OC_2H_4)_5OH$[d]-*N*-octylpyrrolid(in)one	0.1 *M*	130	Zhou, 2003

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[a] Values are approximate and depend upon the humidity.

[b] For mixtures, the largest value obtained for any ratio of the two surfactants.

[c] L 77 = commercial $(CH_3)_3SiOSi(CH_3)[CH_2(CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$.

[d] Commercial material.

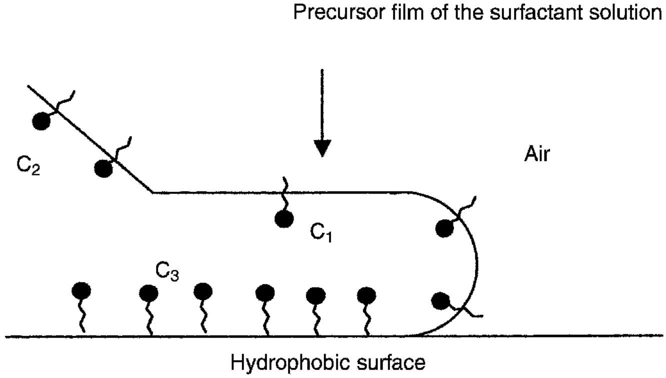

FIGURE 6-8 Precursor film of aqueous surfactant solution on a hydrophobic substrate, with surfactant concentration $C_1 < C_2 < C_3$ at the interfaces, and γ in the precursor film greater than in the bulk surfactant solution, due to the greater adsorption of the surfactant at the solid–liquid than at the air–liquid interface.

For a series of *N*-alkyl-2-pyrrolidinones that produce enhanced superspreading of the POE trisiloxane mentioned above on polyethylene film, it has been shown (Rosen, 2001) that the addition of the alkylpyrrolidinone to the trisiloxane surfactant produces little or no increase in the total surfactant at the hydrophobic solid–air or aqueous solution–air interfaces, but a considerable increase in the total surfactant adsorption at the hydrophobic solid–aqueous solution interface. This enhanced adsorption of surfactant at the aqueous solution–solid interface relative to that at the aqueous solution–air interface produces a decrease in the surfactant concentration at the air–solution interface in the thin precursor film at the wetting front (Figure 6-8). This results in a surface tension gradient in the precursor film promoting movement of the aqueous phase to the wetting front.

The order of increased surfactant adsorption on the solid produced by the different alkyl pyrrolidinones parallels the order of their enhancement of superspreading. In addition, it was shown (Wu, 2002) (1) that the change in the spreading coefficient (equation 6.1) parallels enhancement of superspreading and (2) that the order of increased attractive molecular interaction between the different alkylpyrrolidinones and the trisiloxane surfactant at the hydrophobic solid–aqueous solution interface, as measured by the interaction parameter $\beta_{SL}{}^{\sigma}$ (Chapter 11): *n*-butyl < *n*-cyclohexyl < *n*-octyl < *n*-hexyl < 2-ethylhexyl, is exactly the same order as that of their enhancement of the superspreading.

Recently, it has been found that aqueous solutions of two different hydrocarbon chain surfactants can also show superspreading on highly hydrophobic substrates (Rosen, 2002; Zhou, 2003). In these mixtures, the two different hydrocarbon-chain surfactants also interact to produce synergistic enhancement of the total surfactant adsorption at the hydrophobic solid–aqueous solution interface relative to that at the air–aqueous solution interface, and this is accompanied by an enhanced rate of reduction of the contact angle (Zhou, 2003). SF values for these mixtures are also listed in Table 6-3.

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PROBLEMS

1 **(a)** The Good–Girifalco factor ϕ, which is a measure of the degree of interation between the two phases in contact at an interface, varies from 0.5 when interaction is minimal to about 1.1 when interaction is strong. What can you conclude regarding the strength of the interaction of water ($\gamma_{LA} = 72$ dyn/cm at 25°C) and a liquid, X, whose surface tension is 20 dyn/cm at 25°C if the interfacial tension between them at that temperature is 45 dyn/cm?

(b) What is the value of the spreading coefficient in this system?

2 For low-energy surfaces, γ_c, the critical surface tension for wetting, is often equated with γ_{SA}. What is the implication of this?

3 Water at 25°C ($\gamma_{LA} = 72$ dyn/cm) makes a contact angle of 102° on a solid substrate. The addition of a surfactant to the water decreases the surface tension to 40 dyn/cm and the contact angle to 30°. Calculate the change in the work of adhesion of the water to the substrate as a result of the surfactant addition.

4 Suggest a reason for the observation that POE nonionics often show shorter wetting times than anionics on hydrophobic substrates but show longer wetting times than anionics on cellulosic substrates.

5 Without consulting the tables, place the following surfactants in order of decreasing wetting time for a cellulosic substrate at alkaline pH:

(a) $C_{12}H_{25}CH(SO_3^-Na^+)COOC_4H_9$

(b) $C_{16}H_{33}CH(SO_3^-Na^+)COOCH_3$

(c) $C_{12}H_{25}N^+(CH_3)_3Cl^-$

(d) $C_{10}H_{21}CH(SO_3^-Na^+)\text{-}COOC_{10}H_{21}$

(e) $C_{16}H_{33}CH(SO_3^-Na^+)COOC_4H_9$

6 **(a)** For what types of surfactants and low-energy surfaces can the assumption be made that the $d(\gamma_{SA})/d \ln C$ in equation 6.6 equals zero?

(b) Give examples of systems for which this may not be true.

7 Foaming and Antifoaming by Aqueous Solutions of Surfactants

Foam is produced when air or some other gas in introduced beneath the surface of a liquid that expands to enclose the gas with a film of liquid. Foam has a more or less stable honeycomb structure of gas cells whose walls consist of thin liquid films with approximately plane parallel sides. These two-sided films are called the *lamellae* of the foam. Where three or more gas bubbles meet, the lamellae are curved, concave to the gas cells, forming what is called the *Plateau border* or *Gibbs triangles* (Figure 7-1).

The pressure difference across a curved interface due to the surface or interfacial tension of the solution is given by the Laplace equation

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{7.1}$$

where R_1 and R_2 are the radii of curvature of the interface. Since the curvature in the lamellae is greatest in the Plateau borders, there is a greater pressure across the interface in these regions than elsewhere in the foam. Since the gas pressure inside an individual gas cell is everywhere the same, the liquid pressure inside the lamella at the highly curved Plateau border (B) must be lower than in the adjacent, less curved regions (A) of the Plateau area. This causes drainage of the liquid from the lamellae into the Plateau borders. In a column of foam, liquid also drains as a result of hydrostatic pressure, with the result that lamellae are thinnest in the upper region of the column and thickest in the lower region. Foams are destroyed when the liquid drains out from between the two parallel surfaces of the lamella, causing it to get progressively thinner. When it reaches a critical thickness (50–100 Å), the film collapses.

Absolutely pure liquids do not foam. Foam is also not pronounced in mixtures of similar types of materials (e.g., aqueous solutions of hydrophilic substances). Bubbles of gas introduced beneath the surface of an absolutely pure liquid rupture immediately on contacting each other or escape from the liquid as fast as the liquid can drain away from them. For true foaming to occur, the presence of a solute capable of being adsorbed at the *L/G* interface is required. The presence of this surface-active solute produces lamellae between the gas cells of the foam that have

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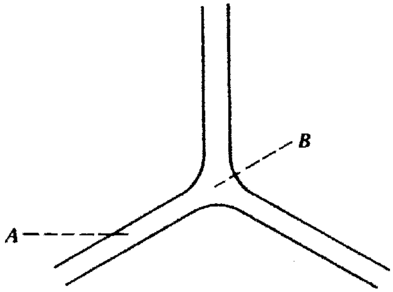

FIGURE 7-1 Plateau border at point of meeting of three bubbles.

adsorbed monomolecular films of surfactant molecules on both sides at the *L/G* interface. These adsorbed films provide the system with the property that distinguishes foaming from nonfoaming systems—the ability of the former to resist excessive *localized* thinning of the lamella surrounding the bubbles—while general thinning of the lamella proceeds. This property, which is generally known as *film elasticity,* is a necessary condition for the production of foam; however, it is not sufficient for the formation of a *persistent* foam; the foam formed may subsequently prove persistent or transient. Persistent foams (often called *metastable foams,* to distinguish them from *transient* or unstable foams, since no foams are thermodynamically stable) are produced when some mechanism exists to prevent rupture of the lamella after most of the liquid has drained out of it. The lifetimes of persistent foams are measured in hours or days, whereas the lifetimes of transient foams are of the order of a few seconds to a few tens of seconds (less than a minute).

I. THEORIES OF FILM ELASTICITY

For a liquid to foam (persistently or transiently), the liquid membrane surrounding the bubbles must possess a special form of elasticity such that any applied stresses that tend toward local thinning or stretching of the membrane are rapidly opposed and counterbalanced by restoring forces generated during the initial displacement of the material of the foam film. That is, the very process of stretching or thinning must produce forces that tend to counteract stretching or thinning. Moreover, these restoring forces must increase with the amount of displacement of the film, like the stretching of a rubber band. This film elasticity is possible only if a surface-active solute is present.

Theories concerning the mechanisms of operation of this film elasticity depend on two observations concerning the surface tension of aqueous solutions of surface-active solutes: (1) its increase in value with decrease in concentration of the surface-active solute, at concentrations of the latter below the CMC, and (2) the time required for it to obtain its equilibrium value (the fact that the initial value of these surface tension at a new surface is always greater than the equilibrium

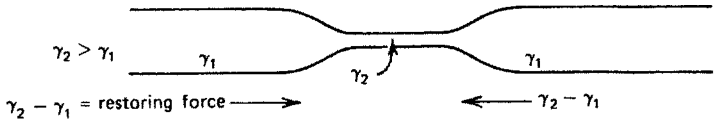

FIGURE 7-2 Stretched portion of foam lamella, illustrating the mechanism of film elasticity.

value). The theory based on the first effect, the change in surface tension with change in concentration of the surface-active solute, is known as the *Gibbs effect* (Gibbs, 1878); that based on the second, the change in surface tension with time, is known as the *Marangoni effect* (Marangoni, 1872). The two theories are complementary and provide mechanisms for the operation of film elasticity under different conditons (Kitchener, 1959).

Both film elasticity theories postulate that elasticity is due to the local increase in surface tension with extension of the film, i.e., $d\gamma/dA = +$. As a local spot in the film thins and stretches and the area of the film in that region (Figure 7-2) increases, its surface tension increases and a gradient of tension is set up that causes liquid to flow toward the thinned spot from the thicker portions around it. The thinning spot thereby automatically draws liquid from its perimeter and prevents further thinning of the film In addition, the movement of surface material carries with it underlying material that helps "heal" and thicken a thinned spot by a surface transport mechanism (Ewers, 1952). The theories differ in that the Marangoni theory explains this increase on the basis of the *instantaneous* value of γ, whereas the Gibbs theory explains it on the basis of the *equilibrium* value of γ.

The Marangoni effect is significant only in dilute solution and within a limited concentration range. The amount of solute adsorbed at a new surface in the absence of stirring or an energy barrier to adsorption is given by (Ward, 1946)

$$n = 2\left(\frac{D}{\pi}\right)^{1/2} ct^{1/2}\frac{N}{1000} \tag{7.2}$$

where n = number of molecules/cm^2,

D = bulk diffusion, coefficient cm^2/s,

c = bulk concentration, in mol/L,

t = time, in seconds,

N = Avogadro's number.

The times involved in foam production are in the range of 0.001–0.1 s; the value of D/π for the usual surface-active solute (with a hydrocarbon chain of 12–18 carbon atoms) is of the order of 1×10^{-6} cm^2/s; equilibrium surface concentrations for this same type of material are about 2×10^{14} molecules/cm^2. Thus, if the time needed to replace the solute at a new surface is to be no shorter than the time required to produce the foam, the concentration of the solution should not exceed, in the absence of an energy barrier to desorption,

$$c = \frac{n \times 1000}{2(D/\pi)^{1/2} t^{1/2} N} = \frac{2 \times 10^{17}}{2(1 \times 10^{-3})(1 \times 10^{-1}) \times 6 \times 10^{23}}$$
$$= (1.7 \times 10^{-3} M)$$

(Here a mean time of 0.01 s for the production of the foam is used.)

On the other hand, if the solution is too dilute, then the surface tension of the solution will approach that of the pure solvent, and then the restoring force, which is the difference between the surface tension of the clean surface (than of the pure solvent) and the equilibrium surface tension of the solution, will be too small to withstand the usual thermal and mechanical shocks. Thus, according to this mechanism, there should be an optimum concentration for maximum foaming in any solution producing transient foams. (In these solutions the foam stabilization effects are much less important than the foam-producing effects, and therefore the latter can be measured more or less independently of the former.) This maximum in the foam valume–concentration curve of solution producing transient foams has been well verified experimentally.

From the discussion of dynamic surface tension (Chapter 5, Section IV), the maximum rate of reduction of surface tension occurs when $t = t^*$, the time required for the surface tension to reach half of the value between that of the solvent, γ_o, and the meso-equilibrium surface tension value, γm. From equation 5.3, it has been shown (Rosen, 1991) that

$$(-\delta\gamma/\delta t)_{t=t^*} = n(\gamma_o - \gamma_m)/4t^* \tag{7.3}$$

where n is the constant (Table 5-3), essentially independent of suffactant concentration, that increases with increasing tendency of the surfactant to adsorb on the surface. This implies that the parameter $n(\gamma_o - \gamma_m)t^*$ should be related to the foaming of the surfactant solution.

This has been shown to be valid for a series of pure and commercial POE dodecyl alcohols, POE nonylphenols, and POE alcohol sulfates (Varadaraj, 1990; Rosen, 1991; Tamura, 1995).

The Gibbs theory of film elasticity postulates that, on thinning and expansion of local areas of the lamellae, the rise in surface tension is due to depletion of the solute from the underlying layer of solution in the interior of the lamella. This theory is based on the assumption that in thin films the length along the surface of the film is so much greater than the distance normal to the surface that equilibrium may be established normal to the surface much more rapidly than along the surface. The lamella may thus be regarded as consisting of individual sections of constant volume and constant solute content within which equilibrium is attained following some change in the surface of the lamella. If that section of the lamella is stretched, the surface area increases and the thickness decreases. However, if the film is thin, the concentration of solute in the solution beneath the surface may be insufficient to maintain the surface concentration of the surfactant as the film expands, and the surface tension of this section will increase. This effect is also significant only within a certain concentration range of the solute. If the concentration is very low, the change in surface tension with concentration will be too small and the consequent tension gradient insufficient to prevent further thinning and eventual rupture of the film. On the other hand, if the concentration is too far above the CMC of the solute, the change in surface tension with increase in the area of the film will also be too small to prevent rupture of the film because the surface tension does not vary much, if at all, with concentration change above the CMC and because the large reserve of surfactant in the solution will prevent significant change in the surface tension unless the film becomes very thin. The Gibbs effect, therefore, also accounts for the fact that in transient foams, foaming power goes through a maximum as the concentration of the solute is varied.

The Gibbs effect can be evaluated quantitatively. Gibbs defined a coefficient of surface elasticity E as the stress divided by the strain per unit area, $E = [2dy/(dA/A)]$. The greater the value of E, the greater the ability of the film to withstand shocks on thinning.

On the basis of the previously described model in which each section of the lamella is considered to act as an independent unit of constant volume containing a fixed amount of surfactant, E is given by the expression (Sheludko, 1966; Rosen, 1967)

$$E = \frac{4\Gamma^2 RT}{h_b C + 2\Gamma\left(1 - \frac{\Gamma}{\Gamma_m}\right)} \tag{7.4}$$

where h_b = thickness of the bulk solution in the lamella,
Γ = surface concentration of the surfactant, in mol/cm^2,
Γ_m = surface concentration of the surfactant, in mol/cm^2, at surface "saturation,"
C = bulk concentration of the surfactant, in mol/cm^3.

This expression implies, as expected, that E increases as the thickness of the bulk solution in the lamella or the bulk concentration of the surfactant in the lamella decreases. It also implies a very great dependence on the surface excess concentration of the surfactant, Γ, and indicates that if Γ is zero, there is no film elasticity.

From equation 7.4 the thickness of the bulk solution in the lamella h_b at which the surface elasticity coefficient E becomes significant can be calculated. For surfactant concentrations greater than about one-third the CMC, Γ/Γ_m is very close to 1; thus the second term in the denominator may be disregarded without significant error, and

$$E = \frac{4\Gamma^2 RT}{h_b C} \tag{7.5}$$

The surface elasticity, therefore, decreases when either the thickness of the lamella or the bulk concentration of surfactant in it increases. Moreover, since Γ is proportional (equation 2.25) to $(\delta\gamma/\delta \log C)_T$, the elasticity is very sensitive to change in the surface tension of the solution with change in the bulk phase concentration of the surfactant. Surface excess concentrations Γ for surfactants usually fall in the range $1-4 \times 10^{-10}$ mol/cm^2. Thus at 27°C (300 K), since $R = 8.3 \times 10^7$ ergs mol^{-1} deg^{-1},

$$E = \frac{4(1-6) \times 10^{-20} \times 8.3 \times 10^7 \times 3.00}{h_b C} = \frac{(1-6) \times 10^{-9}}{h_b C}$$

For E to be 10 dyn or more, h_b must be 10^{-3}–10^{-4} cm when $C = 1 \times 10^{-6}$ mol/cm^3 (1×10^{-3} M); 10^{-4}–10^{-5} cm when $C = 1 \times 10^{-5}$ mol/cm^3 (1×10^{-2} M), and so on.

II. FACTORS DETERMINING FOAM PERSISTENCE

For a foam to be persistent, mechanisms must be present to retard the loss of liquid and gas from the foam and to prevent rupture of the lamellae when they are subjected to mechanical shock or when a certain critical thickness is reached.

II.A. Drainage of Liquid in the Lamellae

The extent and rate of drainage of surplus solution from the interior of the lamellae is one of the important factors determining foam stability, since drainage causes thinning of the film, and when the film reaches a critical thickness (50–100 Å), the film may rupture spontaneously. Drainage of the film occurs under two influences: gravity and pressure difference.

Drainage by gravity is important mainly in very thick lamellae, such as are present when the foam is first formed; drainage under the influence of pressure difference is more important when the lamellae are thin. The bulk viscosity of the foaming solution is a major factor in determining the rate of drainage by gravity in thick lamellae. Electrolyte or organic additives (Chapter 3, Section III) that increase the bulk viscosity of the foaming solution decrease the rate of drainage of the liquid in the lamellae. Polymeric thickeners are often added to increase the bulk viscosity when very stable foams are desired. The formation of a viscous liquid-crystalline phase (Chapter 3, Section IIC) in the bulk solution in the lamellae at certain concentrations above the CMC may increase the stability of the foam by retarding drainage. When the lamellae become thin, because of the drainage of liquid out of the interior of the lamellae, the viscosity of the remaining liquid is greatly affected by the oriented monolayers comprising the external surfaces of the lamellae. The orienting forces caused by these monolayers are transmitted to a significant depth in thin lamellae through successive polarization of the underlying layers of water molecules. In films 1000 Å thick, the viscosity of the water has been shown to be twice that of normal water, and in films 200 Å thick, five times that of normal water.

Drainage by pressure difference is due to the differences in curvature of the surface of the lamella. As mentioned earlier (Figure 7-1), at the intersection of three or more air bubbles, the lamella has a greater curvature than at the boundary between only two air secs. The pressure difference causing drainage of liquid into the Plateau border at point B from point A outside it is given by the expression $\Delta P = \gamma(1/R_B + 1/R_A)$, where R_B and R_A are the radii of curvature of the lamella at points B and A, respectively. The greater the difference between R_A and R_B (i.e., the larger the bubble size in the foam) and the greater the surface tension of the solution in the lamella, the greater the pressure difference causing drainage.

II.B. Diffusion of Gas Through the Lamellae

Another factor determining the stability of foams is the rate of diffusion of gas from one bubble to another through the lamella separating them. The rate of diffusion q of a gas between two bubbles of different radii, R_1 and R_2, is given by the equation

$$q = -\mathrm{J}A\Delta P \tag{7.6}$$

where J = the permeability of the diffusion path,

A = the effective perpendicular area through which diffusion occurs between the bubbles,

ΔP = the difference in gas pressures of the two bubbles,

$$= 2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \tag{7.1}$$

γ = the surface tension of the solution.

Since the negative sign in the equation indicates that diffusion is in the direction of pressure decrease and the gas pressure in small bubbles is higher than in larger bubbles ($\Delta P = 2\gamma/R$), large bubbles tend to grow at the expense of smaller ones. This growth may change the character of the foam completely from an initial one of small, spherical air cells to one containing large polyhedral cells. This change to large polyhedral cells increases the curvature in the Plateau borders and increases the forces causing drainage into these borders. This growth also may necessitate a rearrangement of the bubbles in the foam, with the consequent possibility of rupture of the lamellae at some points because of mechanical shocks occasioned by the rearrangement.

The value of J in the preceding diffusion equation depends on the resistance to gas transfer of the two interfaces and the liquid between them. Data indicate that this transfer of gas takes place through aqueous pores between the surfactant molecules in the surface films of the lamellae (Princen, 1967). Closer packing of the surfactant molecules in the film would therefore be expected to decrease the rate of diffusion of the gas between bubbles. Consistent with this, interfacial resistance to gas diffusion has been shown to increase with increase in the number of carbon atoms in the hydrophobic group of the surfactant and with decrease in the molecular mass of the hydrophilic group (Caskey, 1972). The addition of certain concentrations of lauryl alcohol has been shown to decrease sharply the permeability of surface films of sodium lauryl sulfate, presumably because of condensation of the lauryl sulfate film by the lauryl alcohol.

II.C. Surface Viscosity

Qualitatively, in a number of cases, foam stability has been correlated with viscosity of the surface film, but the relation is not really clear. There are stable foams in which the viscosity of the surface film is not particularly high and viscous monolayers that do not produce particularly stable foams. However, it appears well accepted that if the viscosity of the surface film is either very low (a "gaseous" monomolecular film) or very high (a "solid" monomolecular film), the foam produced will be unstable. In both of these cases film elasticity is low. In addition, too high a surface viscosity can slow down self-healing of thinned spots in the film by the surface transport mechanism.

II.D. The Existence and Thickness of the Electrical Double Layer

Factors that may prevent the thinning of foam films (at least in the case of ionic surfactants) are electrostatic repulsion between the two sides of the film and the high osmotic pressure due to the large concentration of counterions present. These factors have been suggested by the existence of persistent foam in cases where the film is known *not* to have great surface viscosity—and this is true of foaming solutions of purified surface-active agents, where it is known that the surface films are not particularly coherent. In these cases, it has been suggested that when the film becomes very thin (<0.2 μm or 200 nm), stability is obtained chiefly because of the electrical repulsion between the ionic double layers associated with the adsorbed ionic surfactant on the two sides of the liquid film. Since the addition of electrolyte to the foaming solution causes compression of the electrical double layers associated with the surface films, such addition decreases their mutual repulsion. This is believed to account for the decreased thickness of liquid films with increase in their electrolyte content (Davies, 1963) and for the decreased stability of many foams on the addition of electrolyte.

In summary then, the factors promoting foaming in aqueous surfactant solutions are (1) low equilibrium surface tension, (2) moderate rate of attaining equilibrium surface tension, (3) large surface concentration of surfactant, (4) high bulk viscosity, (5) moderate surface viscosity, and (6) electrical repulsion between the two sides of the foam lamella. The first three promote film elasticity; the last three promote foam persistence.

III. THE RELATION OF SURFACTANT CHEMICAL STRUCTURE TO FOAMING IN AQUEOUS SOLUTION

In foaming, as in other surface properties, correlations between surfactant structure and foaming in aqueous solution require a distinction between the efficiency of the surfactant, its bulk phase concentration required to produce a significant amount of foam, and its effectiveness, the maximum foam height obtained with the surfactant solution regardless of its concentration. A distinction must also be made between foam production, measured by the height of the foam initially produced, and foam stability, the height after a given amount of time. Therefore, in comparing the foaming properties of different surfactants, the term *foaming ability* must be clearly defined. In addition, such conditions as the method used to produce the foam, the temperature of the solution, the hardness of the water used, and its electrolyte content must all be specified. Since most of the foaming data on surfactants with clearly defined structures have been obtained by use of the Ross–Miles method (Ross, 1953), the structural correlations discussed here are based mainly on data obtained by that method.

In the Ross–Miles method, 200 mL of a solution of surfactant contained in a pipette of specified dimensions with a 2.9-mm-i.d. orifice is allowed to fall 90 cm onto 50 mL of the same solution contained in a cylindrical vessel maintained at a given temperature (often 60°C) by means of a water jacket. The height of the foam produced in the cylindrical vessel is read immediately after all the solution has run out of the pipette (initial foam height) and then again after a given amount of time (generally, 5 min).

A somewhat related but different method of measuring foam height and foam stability has been suggested by Lunkenheimer and Malysa (2003). The surfactant solution (50 mL) is poured into a 42-mm-i.d. glass cylinder with a fritted glass G-2 disc at the bottom, with a syringe attached to the bottom by means of a stopcock. Gas (50 or 100 mL) is introduced manually via the syringe and stopcock, in a fixed time (e.g., 20 s), into the bottom of the column and the stopcock closed. The initial heights of the foam generated and the solution column are measured. The changes in foam height and solution level are measured as a function of time.

III.A. Efficiency as a Foaming Agent

Foam height generally increases with increase in surfactant concentration below the CMC until the neighborhood of the CMC is reached, where foam height reaches a maximum value or increases slowly to a maximum value somewhat above the CMC. Thus, the CMC of a surfactant is a good measure of its efficiency as a foaming agent; the lower the CMC, the more efficient the surfactant as a foamer. Those structural factors that produce a lower CMC—for example, increased length of the hydrophobic group—would therefore be expected to increase the efficiency of the surfactant as a foaming agent. The addition of neutral electrolyte (which decreases the CMC of the surfactant) increases the efficiency of ionic surfactants. Table 7-1 lists the bulk phase concentrations at which foam height reaches a

TABLE 7-1 Foaming Efficiency of Aqueous Surfactant Solutions (Ross–Miles Method[a])

Surfactant	Temperature (°C)	Concentration (M) to Reach Maximum Foam Height	CMC	Height (mm)	Reference
p-$C_8H_{17}C_6H_4SO_3^- Na^+$	60	13×10^{-3}	16×10^{-3}	165	Gray, 1955
p-$C_{10}H_{21}C_6H_4SO_3^- Na^+$	60	4.5×10^{-3}	3×10^{-3}	185	Gray, 1965
o-$C_{12}H_{25}C_6H_4SO_3^- Na^+$	60	4×10^{-3}	3×10^{-3}	205	Gray, 1955
p-$C_{12}H_{25}C_6H_4SO_3^- Na^+$	60	4×10^{-3}	1.2×10^{-3}	200	Gray, 1955
o-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^- Na^+$	60	8×10^{-3}	—	195	Gray, 1965
p-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^- Na^+$	60	8×10^{-3}	5×10^{-3}	215	Gray, 1955
p-$C_7H_{15}CH(C_4H_9)C_6H_4SO_3^- Na^+$	60	7×10^{-3}	4×10^{-3}	230	Gray, 1955
$C_5H_{11}CH(C_5H_{11})SO_4^- Na^+$	60	10×10^{-3}	83×10^{-3}	130	Dreger, 1944
$C_{12}H_{25}SO_3^- Na^+$	60	11×10^{-3}	13×10^{-3}	210	Rosen, 1969
$C_{12}H_{25}SO_4^- Na^+$	46	5×10^{-3}	9×10^{-3}	205	Dreger, 1944
$C_{11}H_{23}CH(CH_3)SO_4^- Na^+$	46	5×10^{-3}	6.5×10^{-3}	205	Dreger, 1944
$C_6H_{13}CH(C_6H_{13})SO_4^- Na^+$	46	$>15 \times 10^{-3}$	19×10^{-3}	220	Dreger, 1944
$C_{14}H_{29}SO_3^- K^+$	60	3×10^{-3}	3×10^{-3}	217	Rosen, 1969
$C_{14}H_{29}SO_4^- Na^+$	46	3×10^{-3}	2.3×10^{-3}	225	Dreger, 1944
$C_{13}H_{27}CH(CH_3)SO_4^- Na^+$	46	3×10^{-3}	1.7×10^{-3}	220	Dreger, 1944
$C_7H_{15}CH(C_7H_{15})SO_4^- Na^+$	46	5×10^{-3}	6.7×10^{-3}	240	Dreger, 1944
$C_{16}H_{33}SO_3^- K^+$	60	0.8×10^{-3}	0.9×10^{-3}	233	Rosen, 1969
$C_{16}H_{33}SO_4^- Na^+$	60	0.8×10^{-3}	0.7×10^{-3}	220	Rosen, 1969
$C_{15}H_{31}CH(CH_3)SO_4^- Na^+$	46	$<1 \times 10^{-3}$	0.5×10^{-3}	212	Dreger, 1944
$C_8H_{17}CH(C_8H_{17})SO_4^- Na^+$	46	4×10^{-3}	2.3×10^{-3}	245	Dreger, 1944
p-$C_9H_{19}CH(CH_3)C_6H_4SO_3^- Na^+$	60	13×10^{-3}	—	190	Gray, 1965
p-$C_{13}H_{27}CH(CH_3)C_6H_4SO_3^- Na^+$	60	4×10^{-3}	—	175	Gray, 1965
$pC_{15}H_{31}CH(CH_3)C_6H_4SO_3^- Na^+$	60	0.7×10^{-3}	—	126	Gray, 1965

[a] Ross, (1953).

maximum for some aqueous solutions of surfactants, together with their CMCs at the same temperature at which the foaming data were obtained. It is apparent that surfactants with longer hydrophobic groups are more efficient but not necessarily more effective, foaming agents. Since the Ross—Miles foaming test is usually done at a 0.25% surfactant concentration, equivalent to about 8×10^{-3} M for most surfactants, only those materials having CMCs greater than that will not have reached their maximum foam volume at that concentration.

III.B. Effectiveness as a Foaming Agent

The effectiveness of a surfactant as a foaming agent appears to depend both on its effectiveness in reducing the surface tension of the foaming solution and on the magnitude of its intermolecular cohesive forces. The volume of foam produced when a given amount of work is done on an aqueous solution of surfactant to create foam depends on the surface tension of the solution, since the minimum amount of work required to produce the foam is $\gamma \cdot \Delta A$, the product of the surface tension and the change in the area of the liquid–gas interface as a result of the foaming. The lower the surface tension of the aqueous solution, the greater appears to be the volume of foam of the same average bubble size produced by a given amount of work under the same foaming conditions (Rosen, 1969). It has also been suggested (Dreger, 1944) that the rate of attainment of surface tension reduction may also be a factor in determining the effectiveness of a surfactant as a foaming agent. Therefore branched-chain surfactants and those containing centrally located hydrophobic groups, which are believed to diffuse rapidly to the interface, would be expected to produce higher volumes of initial foam. However, not only must the surfactant produce the foam, it must also maintain it—the foam must have appreciable stability. This should require an interfacial film with sufficient cohesion to impart elasticity and mechanical strength to the liquid lamellae enclosing the gas in the foam. Since interchain cohesion increases with increase in the length of the hydrophobic group, this may account for the observation that foam height often goes through a maximum with increase in the length of the chain. Too short a chain probably produces insufficient cohesiveness, whereas too great a length produces too much rigidity for good film elasticity (or too low a solubility in water).

Shah and coworkers (Shah, 1998; Jha, 1999) have pointed out the relationship between micellar stability and foaming effectiveness. Micellar stability is inversely related to foaming ability, since very stable micelles are less capable of providing the flux of surfactants necessary to stabilize the new air–solution interface created during the foaming process. Thus, POE glycols, which decrease the stability of micelles of sodium dodecyl sulfate, increase the foaming of aqueous solutions of the latter (Dhara, 2001). For sodium dodecyl sulfate–alkyl trimethylammonium bromide mixtures, maximum micellar stability is observed for the sodium dodecyl sulfate–dodecyl trimethylammonium bromide mixtures when the alkyl chains of the two surfactants are of equal length, reflecting the maximum interaction obtained (Table 11-1). These mixtures, because of the close packing at both air–water interface and in the micelles, showed minimum surface tension, maximum surface viscosity, maximum foam stability, but minimum foam height (Patist, 1997). This concept is consistent with the explanation (below) offered by Dupré (1960) for the marked decrease in foaming observed when POE nonionics reach their cloud points.

Since branched-chain surfactants and those with centrally located hydrophilic groups can depress the surface tension of water to lower values than isomeric straight-chain compounds or those with terminally located hydrophilic groups (Chapter 5, Section II), the former types of compounds would be expected to show higher initial foam heights than the latter. However, since hydrophobic groups with branches have weaker intermolecular cohesive forces than straight-chain ones, the former would be expected to show less foam stability. The result of these two opposing factors is that when the hydrophilic group of a straight-chain surfactant is moved from a terminal to a more central position in the molecule, foam heights generally increase, provided that the materials are all compared above their CMCs where foaming is at a maximum. This is necessary here because the shift of the hydrophilic group to a more central position in the molecule causes an increase in the CMC of the surfactant with a resulting decrease in its efficiency as a foaming agent. Surfactants with highly branched chains, on the other hand, generally show lower foam heights than isomeric straight-chain materials, except where the length of the hydrophobic group becomes too long for straight-chain compounds to have adequate water solubility for good foaming (e.g., >16 carbon atoms at 40°C). Presumably for a similar reason, 2, 5-di-*n*-alkylbenzenesulfonates show lower foam heights and stabilities than the corresponding *p*-*n*-alkylbenzenesulfonates (Kölbel, 1960b). Since branched-chain hydrophobic groups show greater water solubility than straight-chain ones and intermolecular cohesive forces increase with increase in chain length, good foaming at 40°C can be obtained with branched-chain surfactants containing up to 20 carbon atoms and foam heights in the C_{20} branched compounds appear to exceed those obtained with any shorter straight-chain compounds (Kölbel, 1960a).

In ionic surfactants the effectiveness of foaming appears to depend also on the nature of the counterion, those with smaller counterions showing greater initial foam heights and foam stabilities. Thus, in the dodecyl sulfate series, the effectiveness decreases with increased size of the counterion in the order $NH_4^+ >$ $(CH_3)_4 N^+ > (C_2H_5)_4N^+ > C_4H_9)_4N^+$ (Kondo, 1960).

The poor foaming of aqueous solutions of cationic surfactants in this and similar foaming tests may be due not to some inherent lack of foaming ability, but to the dewetting of the walls of the glass foaming apparatus as a result of adsorption of the cationic surfactant onto it with its hydrophobic group oriented toward the aqueous phase, causing foam rupture.

Table 7-2 lists the foaming effectiveness of some surfactants in aqueous solutions, as well as some data on their (short-term) stability.

In distilled water at room temperature, sodium alkyl sulfates and soaps with saturated straight-chain hydrophobic groups containing 12–14 carbon atoms seem to show the best foaming capacities (Broich, 1966); at higher temperatures, homologous materials with somewhat longer chains give optimum foaming. Thus, at 60°C, saturated straight-chain alkyl sulfates containing 16 carbon atoms,

TABLE 7-2 Foaming Effectiveness of Aqueous Surfactant Solutions (Ross–Miles Method[a])

			Foam Height (mm)			
			Distilled Water			
Surfactant	Concentration (%)	Temp. (°C)	Initial	After Time (min)	300 ppm $CaCO_3$ Initial	Reference
$C_{15}H_{31}COO^-Na^+$	0.25(pH 10.7)	60	236	232 (5)		Rosen, 1988
$C_{10}H_{21}SO_3Na$	0.68	60	160	5 (5)		Dahanayake, 1985
$C_{12}H_{25}SO_3Na$	0.32	60	190	125 (5)		Dahanayake, 1985
$C_{14}H_{29}SO_3^-Na^+$	0.11	60	—	214 (1)	—	Rosen, 1969
$C_{16}H_{33}SO_3^-K^+$	0.033	60	—	233 (1)	—	Rosen, 1969
$C_{12}H_{25}SO_4^-Na^+$	0.25	60	220	200 (5)	240[b]	Weil, 1954, 1966; Dahanayake, 1985
$C_{14}H_{29}SO_4^-Na^+$	0.25	60	231	184 (5)	246[b]	Weil, 1954
$C_{16}H_{33}SO_4^-Na^+$	0.25	60	245	240 (5)	178[b]	Weil, 1954, 1966
$C_{18}H_{37}SO_4^-Na^+$	0.25	60	227	227 (5)	151[b]	Weil, 1954
Sodium oleyl sulfate	0.25	60	246	240 (5)	226[b]	Weil, 1954
Sodium elaidyl sulfate	0.25	60	243	241 (5)	202[b]	Weil, 1954
$C_{12}H_{25}OC_2H_4SO_4Na$	0.14	60	246	241 (5)		Dahanayake, 1985
$C_{12}H_5(OC_2H_4)_2SO_4Na$	0.11	60	180	131 (5)	—	Dahanayake, 1985
$C_{12}H_{25}OCH_2CH(CH_3)SO_4^-Na^+$	0.25	60	200	—	—	Weil, 1966
$C_{14}H_{29}OCH_2CH(CH_3)SO_4^-Na^+$	0.25	60	215	—	—	Weil, 1966
$C_{14}H_{29}[OCH_2CH(CH_3)]_2SO_4^-Na^+$	0.25	60	210	—	—	Weil, 1966
$C_{16}H_{33}OCH_2CH(CH_3)SO_4^-Na^+$	0.25	60	200	—	—	Weil, 1966
$C_{18}H_{37}OCH_2CH(CH_3)SO_4^-Na^+$	0.25	60	160	—	—	Weil, 1966
$C_{18}H_{37}OCH_2CH_2SO_4^-Na^+$	0.25	60	160	—	—	Weil, 1966
o-$C_8H_{17}C_6H_4SO_3^-\ Na^+$	0.15	60	148	—	—	Gray, 1965
p-$C_8H_{27}C_6H_4SO_3^-Na^+$	0.15	60	134	—	—	Gray, 1965
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	0.25	60	150	—	—	Gray, 1955
o-$C_9H_{19}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	165	—	—	Gray, 1965

(*Continued next page*)

TABLE 7-2 (*Continued*)

Surfactant	Concentration (%)	Temp. (°C)	Foam Height (mm)			Reference
			Distilled Water		300 ppm $CaCO_3$	
			Initial	After Time (min)	Initial	
p-$C_9H_{19}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	162	—	—	Gray, 1965
o-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.15	60	206	—	—	Gray, 1965
o-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.25	60	208	—	—	Gray, 1955
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.15	60	201	—	—	Gray, 1965
$C_{10}H_{21}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	245	Smith, 1966
o-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	190	—	—	Gray, 1965
p-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	210	—	—	Gray, 1955
p-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	218	—	—	Gray, 1955
p-$C_7H_{15}CH(C_4H_9)C_6H_4SO_3^-Na^+$	0.15	60	219	—	—	Gray, 1955
p-$C_7H_{15}CH(C_4H_9)C_6H_4SO_3^-Na^+$	0.25	60	230	—	—	Gray, 1955
$C_{12}H_{25}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	80	Smith, 1966
$C_{14}H_{29}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	10	Smith, 1966
o-$C_{15}H_{31}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	105	—	—	Gray, 1965
p-$C_{15}H_{31}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	129	—	—	Gray, 1965
$C_{16}H_{33}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	0	Smith, 1966
$CH_3CH(SO_3^-Na^+)COOC_{14}H_{29}$	0.25	60	220	—	240	Stirton, 1962
$C_2H_5CH(SO_3^-Na^+)COOC_{12}H_{25}$	0.25	60	220	—	225	Stirton, 1962
$C_7H_{15}CH(SO_3^-Na^+)COOC_8H_{17}$	0.25	60	—	—	185	Weil, 1960
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_4H_9$	0.25	60	220	—	230	Stirton, 1962
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_5H_{11}$	0.25	60	220	—	235	Stirton, 1962
$C_{14}H_{29}CH(SO_3^-Na^+)COOCH_3$	0.25	60	210	200 (5)	225	Stirton, 1962
$C_{14}H_{29}CH(SO_3^-Na^+)COO^-Na^+$	0.25	60	175	165 (5)	125	Micich, 1962
$C_{14}H_{29}CH(SO_3^-Na^+)COOC_2H_5$	0.25	60	210	—	215	Stirton, 1962
$C_{13}H_{27}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	180	160 (5)	200	Micich, 1966
$C_{16}H_{33}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	175	165 (5)	35	Micich, 1966

$C_{18}H_{37}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	140	130 (5)	30	Micich, 1966
$C_8H_{17}C(C_8H_{17})(SO_3^-Na^+)COOCH_3$	0.25	60	210	200 (5)	215	Micich, 1966
$C_8H_{17}C(C_8H_{17})(SO_3^-Na^+)COO^-Na^+$	0.25	60	0	0	95	Micich, 1966
$C_8H_{17}C(C_6H_{13})(SO_3^-Na^+)COOCH_3$	0.25	60	204	190 (5)	213	Micich, 1966
$C_8H_{17}C(C_4H_9)(SO_3^-Na^+)COOCH_3$	0.25	60	170	5 (5)	200	Micich, 1966
$C_{12}H_{25}Pyr^+Br^{-e}$	0.37	60	135	3 (5)	—	Dahanayake, 1985
$C_{10}H_{21}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.14	60	35	2 (5)	—	Dahanayake, 1985
$C_{12}H_{25}N^+(CH_3)(CH_2C_6H_5)CH_2COO^-$	0.018	60	50	2 (5)	—	Dahanayake, 1985
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^{-c}$	0.25 (pH 5.8)	60	199	29 (5)	—	Rosen, 1988
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^{-c}$	0.25 (pH 9.3)	60	197	34 (5)	—	Rosen, 1988
$C_{12}H_{25}(OC_2H_4)_{10}OH^{-c}$	0.25	60	168	26 (5)	—	Rosen, 1988
$C_{12}H_{25}O(C_2H_4O)_{15}H^c$	0.25	60	—	—	197	Wrigley, 1957
$C_{12}H_{25}O(C_2H_4O)_{20}H^c$	0.25	60	—	—	195	Wrigley, 1957
$C_{12}H_{25}O(C_2H_4O)_{33}H^c$	0.25	60	—	—	180	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{15}H^c$	0.25	60	—	—	153	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{20}H^c$	0.25	60	—	—	167	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{30}H^c$	0.25	60	—	—	149	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{15}H^c$	0.25	60	—	—	165	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{21}H^c$	0.25	60	—	—	152	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{30}H^c$	0.25	60	—	—	115	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{15}H^{c,d}$	0.25	60	—	—	140	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{20}H^{c,d}$	0.25	60	—	—	160	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{31}H^{c,d}$	0.25	60	—	—	140	Wrigley, 1957
$t\text{-}C_9H_{19}C_6H_4O(C_2H_4O)_8H^c$	0.10	25	55	45 (5)	—	GAF, 1965
$t\text{-}C_9H_{19}C_6H_4O(C_2H_4O)_9H^c$	0.10	25	80	60 (5)	—	GAF, 1965
$t\text{-}C_9H_{19}C_6H_4O(C_2H_4O)_{10-11}H^c$	0.10	25	110	80 (5)	—	GAF, 1965
$t\text{-}C_9H_{19}C_6H_4O(C_2H_3O)_{13}H^c$	0.10	25	130	110 (5)	—	GAF, 1965
$t\text{-}C_9H_{19}C_6H_4O(C_1H_4O)_{20}H^c$	0.10	25	120	110 (5)	—	GAF, 1965

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[a] J. Ross and G. D. Miles, Am. Soc. Testing Materials, Method D1173-53, Philadelphia, PA, 1953; *Oil and Soap* **18**, 99 (1941).

[b] 0.1. in 100 ppm $CaCO_3$.

[c] Commercial-type material.

[d] From oleyl alcohol.

[e] Pvr^+, pyridinium.

palmitate soaps, dodecyl- and tetradecylbenzenesulfonates (hydrophobic groups equivalent to 15.5–17.5 carbon chains), and α-sulfoesters containing 16–17 carbon atoms show maximum foaming power (Weil, 1954, 1966; Gray, 1955; Kölbel, 1959; Stirton, 1962; Micich, 1966). Near the boiling point, C_{18} compounds are best. Since interchain cohesion must overcome thermal agitation of the molecules, which increases with increase in temperature, it is to be expected that optimum chain lengths should increase with increase in temperature. The disodium salts of α-sulfocarboxylic acids produce much less foam than the monosodium salts of α-sulfoesters, presumably because increased electrostatic repulsion between hydrophilic groups counters interchain cohesive forces.

In hard water somewhat shorter anionic compounds seem to give optimum foaming, probably because of the greater cohesiveness of anionic surface films in the presence of Ca^{2+}. Thus, in 300 ppm $CaCO_3$ solution at 60°C, C_{12}–C_{14} saturated straight-chain alkyl sulfates show the highest foaming cpacities (Weil, 1954). A similar progressive shift to shorter chain lengths for optimum foam stability with increase in water hardness was found in a dishwashing study at 46°C in the presence of triglyceride soil (Matheson, 1983).

POE nonionic surfactants generally produce less foam and much less stable foam than ionic surfactants in aqueous media. These effects are probably due to the larger surface area per molecule and the absence of highly charged surface films in these foams. Conversion of these materials to their corresponding sulfates generally increases their foaming ability. In POE nonionics both foam stability and foam volume reach a maximum at a particular oxyethylene chain length and then decrease (Schick, 1963). This is ascribed to a maximum in intermolecular cohesive forces in the adsorbed film as the oxyethylene content increases. Van der Waals forces between surfactant molecules decrease with increasing oxyethylene content, since the area per molecule at the surface increases with this change. However, the POE chain is believed to be coiled in the aqueous phase, and the cohesive forces due to intra- and intermolecular hydrogen bonding are stated to pass through a maximum with increasing oxyethylene content. The summation of the van der Waals and hydrogen bonding cohesive forces consequently passes through a maximum as the oxyethylene content of the molecule is increased. In 300 ppm $CaCO_3$ solution at 60°C, POE alcohols appear to be considerably better foaming agents than POE fatty acids. Immediate foam heights for POE *n*-dodecanol are higher than those for corresponding hexadecanol, octadecanol, or oleyl alcohol derivatives. Optimum oxyethylene content in these cases is at 15–20 mol of ethylene oxide per mole of hydrophobe (Wrigley, 1957). There appears to be no significant difference in foaming properties between POE linear primary alcohols and secondary alcohols. In distilled water at 25°C the optimum oxyethylene content for nonylphenol derivates is about 13 mol of ethylene oxide per mole of hydrophobe (GAF, 1965). Homogeneous (single-species) POE materials show higher initial foam heights but lower foam stabilities than commercial materials of the same nominal structure (Crook, 1964).

The replacement of a straight-alkyl-chain hydrophobic group in POE nonionics by a cycloalkyl or 1-alkylcyclohexyl group with the same number of carbon atoms produces little or no decrease in initial foam volume but a marked decrease in foam stability. Somewhat similar effects are produced when the single-alkyl-chain hydrophobic group is replaced by two or three alkyl chains containing the same total number of carbon atoms (Kuwamura, 1979). The magnitude of the effect appears to decrease with increase in the number of carbon atoms in the hydrophobic portion and in the length of the POE chain.

The foam of POE nonionics decreases markedly at or above their cloud points. This has been attributed to a rate effect, the cloud point being marked by the aggregation of the dehydrated micelles into larger aggregates. Diffusion of surfactant molecules from these aggregated micelles to the newly created interface involved in bubble formation might be much slower than from the smaller, more highly hydrated micelles, thus decreasing the stabilization of the liquid lamellae in the forming foam (Dupré, 1960).

III.C. Low-Foaming Surfactants

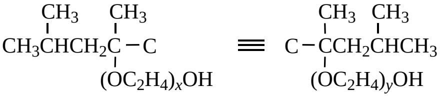
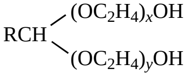
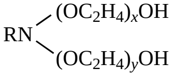
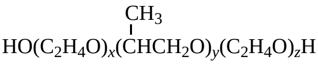
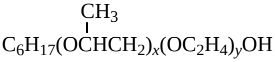
In many industrial processes, it is often useful to add surfactants that can show certain types of surface activity without producing much foam. For example, in paper-making or textile dyeing processes that involve the high-speed movement of belts of material through an aqueous bath, surfactants are added that promote the wetting of the material passing through the bath. However, if the surfactant produces foam when the material is moved rapidly through the bath, then the foam bubbles will adhere to the surface of the material and blemish it. In processes such as these, consequently, low-foaming or nonfoaming surfactants are used.

Low-foaming surfactants can be produced by changing the structure of the surfactant molecule so that it retains its surface activity but produces an unstable foam. We mentioned above that if the surfactant is rapidly diffusing, it can destroy the elasticity of the surface film and thus prevent or minimize foaming.

Therefore, replacing a large, straight-chain hydrophobic group with an isomeric branched-chain one and positioning the hydrophilic group in a central, rather than a terminal, position in the molecule can reduce the foaming properties of the surfactant, while retaining, if not increasing, its surface activity.

Another method of decreasing the foaming of surfactants is to structure the surfactant molecule so that it has a large area/molecule at the liquid–air interface, thus forming a loosely packed noncoherent film that produces unstable foam. This can be accomplished by putting a second hydrophilic group into the molecule some distance from the first one, thus forcing the entire molecule between the two hydrophilic groups to lie flat in the interface. Another way of doing this is to use for the hydrophobic group a relatively short, highly branched or cis-unsaturated alkyl group rather than a long, straight, saturated one or by using a polyoxypropylene chain as part of the hydrophobic group. This type of modification, however, is sometimes not effective if the hydrophilic head already has a sizable cross-sectional area (as in POE nonionics). A third way of increasing the surface area/molecule of surfactant is to put a second hydrophobic group into the molecule, preferably of different size or shape from that of the first hydrophobic group, at some distance

TABLE 7-3 Structures of Some Very Low-Foaming Surfactants

Structure		Reference
 $\overset{CH_3}{CH_3CH}CH_2\underset{(OC_2H_4)_xOH}{\overset{CH_3}{C}}-C\equiv C-\underset{(OC_2H_4)_yOH}{\overset{CH_3}{C}}CH_2\overset{CH_3}{CH}CH_3$	$x+y\leq 4$	Leeds, 1965
	$R < C_{11}, x=y\leq 5$	Kuwamura, 1972
	$R = C_{10}, x=y\leq 3$	Ikeda, 1984
$HO(C_2H_4O)_x(CH_2)_{12}(OC_2H_4)_yOH$	$x+y\leq 12$	Takahasi, 1975
$HO(C_2H_4O)_x(CH_2CH_2CH_2CH_2O)_y(C_2H_4O)_zH$	$y\leq 27, x+z\leq 82$	Kuwamura, 1971
 $HO(C_2H_4O)_x(\overset{CH_3}{CH}CH_2O)_y(C_2H_4O)_zH$	$y=35, x+z=45$	Kuwamura, 1971
 $C_6H_{17}(O\overset{CH_3}{CH}CH_2)_x(OC_2H_4)_yOH$	$x=y\approx 10$	Kucharski, 1974

from the first one. Thus, high-foaming POE nonionics can be coverted to lower-foaming ones by "capping" the —OH of the POE chain with a short alkyl group or by replacing the terminal —OH group by —Cl. Capping the —OH group or replacing it by —Cl also decreases the cloud point of the POE nonionic and, above the cloud point, may result in the separation of a separate surfactant phase that can act as a foam breaker. Foaming decreases with increase in the length of the alkyl cap from CH_3 to C_4H_9 (Pryce, 1984). A fourth method is to put two bulky hydrophilic groups (e.g., POE chains) on the same carbon atom, thereby causing them to extend in different directions, increasing the area per molecule at the surface.

Structures of some very low-foaming surfactants are listed in Table 7-3. These materials all produce foam that disappears completely, or almost completely, within a few minutes.

IV. FOAM-STABILIZING ORGANIC ADDITIVES

The foaming properties of surfactant solutions can be modifed greatly by the presence or addition of other organic materials. Solutions that show excellent foaming properties can be converted to low- or nonfoaming material, and those that show poor foaming properties can be converted to nigh-foaming products by the addition of small amounts of the proper additive. Because of its practical importance, this method of modifying foaming properties has been extensively used and investigated.

Additives that increase the rate of attainment of surface tension equilibrium act as foam inhibitors by decreasing film elasticity, while those that decrease the rate of attainment of that equilibrium act as foam stabilizers. By decreasing the CMC of the surfactant solution and thereby lowering the activity of the monomeric surfactant in solution, an additive may decrease the rate of migration of the surfactant to the surface and the rate of attainment of surface tension equilibrium, with consequent increase in foam stability. On the other hand, additives that cause the breakdown of micelles, with the consequent increase in the activity of the monomeric surfactant, increase the rate of attainment of surface tension equilibrium and decrease foaming (Ross, 1958). Another mechanism by means of which additives can act as foam stabilizers is by increasing the mechanical strength of foam films. The surface films produced by solutions of highly purified surfactants are often weakly coherent, containing molecules that are relatively widely spaced because of the mutual repulsion of the oriented polar heads. These films are mechanically weak and nonviscous. When they constitute the interfacial film in the lamellae of a foam, liquid drains rapidly from the lamellae. The addition of the proper additive to this type of film can convert it to a closer-packed, more coherent one of high surface viscosity, which is slow-draining and produces a much more stable foam. Such slow-draining films can be produced by additives (e.g., linear alcohols of intermediate or long chain length) that form liquid-crystalline structures with the surfactant (Maner, 1982). On the other hand, additives that destroy liquid-crystalline structures (e.g., short- or branched-chain alcohols) promote drainage and decrease foam.

Since micelles can solubilize organic additives and thereby remove them from the interface, much larger amounts of foam-stabilizing additives are required to stabilize the foam of aqueous solutions above their CMC than below their CMC.

The most effective additives for increasing the stability of the foam produced by surfactant solutions appear to be long-chain, often water-insoluble, polar compounds with straight-chain hydrocarbon groups of approximately the same length as the hydrophobic group of the surfactant. Examples are lauryl alcohol for use with sodium dodecyl sulfate, *N*,*N*-bis(hydroxyethyl) lauramide for use with dodecylbenzenesulfonate, lauric acid for use with potassium laurate, and *N*,*N*-dimethyldodecylamine oxide for use with dodecylbenzenesulfonate and other anionics.

Studies of the effectiveness of these additives in stabilizing the foam of various types of anionic surfactants indicate that the foam produced by straight-chain surfactants is more susceptible to stabilization than that produced by branched-chain materials. The order of susceptibility to foam stabilization is as follows: primary alkyl sulfates > 2-*n*-alkanesulfonates > secondary alkyl sulfates > *n*-alkyl-benzene-sulfonates > branched-chain alkylbenzenesulfonates (Sawyer, 1958). This is exactly the order of decreasing van der Waals interaction with an adjacent compound containing a straight-chain hydrocarbon group. Moreover, the most effective foam-stabilizing compounds are those that lower the CMC of the surfactant solution considerably (Schick, 1957). Since the CMC of a surfactant in aqueous solution is not lowered significantly by solubilization of the material into the interior of the micelle, but only by solubilization between the surfactant molecules in the outer portion of the micellar core, the so-called palisade layer (Chapter 3, Sections IVC, IVD), it appears that the additive operates by penetrating into the surface film and organizing the surfactant molecules into a condensed structure by orienting itself between the molecules of surface-active agent in the film in a manner similar to that in the palisade layer of a micelle.

The increased cohesion of the resulting film may be due to the presence of a nonionic, polar "buffer" between the mutually repelling ionic heads of the surfactant molecules to which both ionic heads are attracted by ion–dipole interactions, whereas the hydrocarbon portions of all the molecules are held together by van der Waals forces. This would account for the greater susceptibility of surfactants having straight-chain, compared to branched-chain, hydrophobic groups to foam boosting and for the greater effectiveness of additives having straight-chain, compared to branched-chain, hydrophobic groups.

Polar additives may also increase foam stabilization by solubilizing foamicidal oils (Schick, 1957), since micelles containing solubilized polar additives (Chapter 4, Section IB4) have increased solubilization power for nonpolar materials.

The nature of the polar group in these additives is important. It has been found (Sawyer, 1958) that the order of effectiveness in these additives is *N*-polar substituted amides > unsubstituted amides > sulfolanyl ethers > glycerol ethers > primary alcohols. This order may be that of decreasing ability to form hydrogen bonds with the adjacent surfactant and water molecules since film viscosity increases greatly where hydrogen bonding between adjacent molecules is possible. The OH group in an alcohol is *not* capable sterically of forming direct bonds with adjacent molecules containing only OH groups, whereas the —CONH— group is capable of direct bonding with adjacent molecules. Also, foam stabilization is greater for those additives containing more than one polar group capable of forming hydrogen bonds. The explanation given for this is that the mutiple hydrogen bonds with water prevent the polar additives from being forced out from between the surfactant molecules and into the interior of the micelles in the bulk phase.

Another foam stabilizer for anionic surfactants, *N*,*N*-dimethyldodecylamine oxide, appears to operate in a somewhat different manner. Here it has been shown (Kolp, 1963; Rosen, 1964) that interaction occurs between the protonated amine oxide cation, $RN(CH_3)_2OH^+$, and the surfactant anion, yielding a product that has been isolated, $RN(CH_3)_2OH^+ \cdot {}^-O_3SR$, in which cation and anion are very strongly hydrogen-bonded via the H^+ of the cation. This compound is much more surface active than either the amine oxide or the anionic surfactant and adsorbs strongly at the air–water interface to form a closely packed film (Rosen, 1964). Similarly, salts of long-chain amines and alkyl sulfonates of equal chain length, for example, $C_{10}H_{21}SO_3^- \cdot {}^+N(CH_3)_3C_{10}H_{21}$, have been shown to produce unusually stable thin aqueous films because strong electrical attraction between the cationic and anionic surface-active ions promotes formation of a close-packed surface film (Corkill, 1963).

As described in Chapter 4, Section IB5, surfactants interact with polymers to form complexes, the strength of the surfactant–polymer interaction being dependent upon the chemical structures of the polymer and surfactant. These complexes adsorb at the air–aqueous solution interface, causing reduction in surface tension and increase in surface viscosity, with resulting changes in foaming effectiveness and foam stability.

The effect of the adsorbed surfactant–polymer complex on the rheology of the air–aqueous solution interface is easily detected by the '*talc particle*' test (Regismond, 1997). A small quantity of calcined talc powder is sprinkled on the surface of the aqueous solution in a 10-cm Petri dish. A gentle current of air is directed tangentially to the talc particles for 1–2 s and then removed. The observed movement is noted in the following categories: fluid (F), viscous (V), gel (G) (= almost no flow), solid (S) (= no flow), and viscoelastic (VE) (= net movement, with some recovery upon removal of air current).

The effect of interaction of sodium dodecyl sulfate with the polymer, polyvinylpyrrolidone, on the foaming of aqueous solutions of the former has been investigated by Folmer and Kronberg (2000). Depending upon the surfactant and polymer concentrations, the foaming can either be decreased or increased. Foaming increases when surface and/or bulk viscosities are increased by the surfactant–polymer concentration; it decreases when surfactant–polymer interaction in the bulk phase causes desorption of them from the air–aqueous solution interface.

V. ANTIFOAMING

When undesirable foaming of a solution cannot be reduced sufficiently by replacing the surfactant with a lower foaming one, or when the foam is caused partially or entirely by nonsurfactant components of the solution, then antifoaming agents are used to reduce the foam. Antifoaming agents act in various ways:

1. By removing surface-active material from the bubble surface. The decreased foaming shown by surfactant solutions in the presence of certain types of soil is often due to this mechanism: surfactant removal from the surface by adsorption onto or dissolution in the soil (Princen, 1972). Finely divided hydrophobic silica particles dispersed in silicone oil are effective anifoaming agents and are believed to act in this fashion by adsorbing surfactant molecules from the bubble surface and carrying them into the aqueous phase (Kulkarni, 1979). Hydrophobic particles also destabilize foam by forming lenses at the Plateau borders of the foam, promoting dewetting of the film lamellae and causing bubble coalescence (Wang, 1999).
2. By replacing the foam-producing surface film with an entirely different type of film that is less capable of producing foam. One method of doing this is by swamping the surface with rapidly diffusing noncohesive molecules of limited solubility in the solution. These must produce a surface tension low enough so that they can spread spontaneously over the existing film, (i.e., their spreading coefficient over the surface, $S_{LIS} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA}$ [equation 6.1], must be positive). The rapidly diffusing molecules at the surface

produce a surface film with little or no elasticity, since transient surface tension gradients producing film elasticity (Section I above) are rapidly destroyed by the fast-diffusing molecules. Some wetting agents with limited solubility in water, e.g., tertiary acetylenic glycols, act in this manner. Ethyl ether ($\gamma = 17$ dyn/cm) and isoamyl alcohol ($\gamma = 23$ dyn/cm) are believed to act as foam breakers by reducing the surface tension in local areas to exceptionally low values, thereby causing these areas to be thinned rapidly to the breaking point by the pull of the surrounding higher-tension regions (Okazaki, 1960). Another method is by replacing the elastic surface film with a brittle, close-packed surface film. Calcium salts of long-chain fatty acids (stearic and plamitic) do this with the foam of sodium dodecylbenzenesulfonate or sodium lauryl sulfate by displacing it from the surface film and replacing it wholely or in part by calcium soap molecules that form a "solid," brittle film having no elasticity. This calcium soap film consequently produces an unstable foam. If the calcium soap can form a true mixed film with the surfactant, the foam is *not* destroyed by the calcium soap (Peper, 1958).

3. By promoting drainage in the foam lamellae. Tributyl phosphate is believed to act as an antifoaming agent in this manner by reducing surface viscosity sharply. It has a large cross-sectional area at the aqueous solution–air interface. By intercalating between the surfactant molecules in the interfacial film it reduces the cohesive forces between them and consequently the surface viscosity. Symmetrical tetraalkylammonium ions may also act in this manner to destabilize the foam of sodium lauryl sulfate solutions. The surface viscosity decreases, accompanying increase in the area per surfactant molecule at the air–aqueous solution as the alkyl chain length of the quaternary ammonium ion increases, with resultant decrease in foam stability. Tetrapentylammonium bromide is particularly effective as a foam destabilizer (Blute, 1994).

VI. FOAMING OF AQUEOUS DISPERSIONS OF FINELY DIVIDED SOLIDS

When the aqueous system contains finely divided solids, then foaming of the system may be influenced greatly by the nature of the dispersed solid particles. If the particles have a surface that is hydrophobic, and if the particles are divided finely enough, then the particles may adsorb onto the surface of any air bubbles introduced into the system and stabilize them against coalescence. They adsorb at the air–solid interface from the aqueous system because their solid–aqueous solution interfacial tension, γSL, is high and their solid/(nonpolar) air interfacial tension, γSA, is low because of their nonpolar surface. Consequently, their contact angle, θ, with the aqueous phase, from equation 6.3

$$\gamma_{\mathrm{LA}} \cos \theta = \gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}}$$

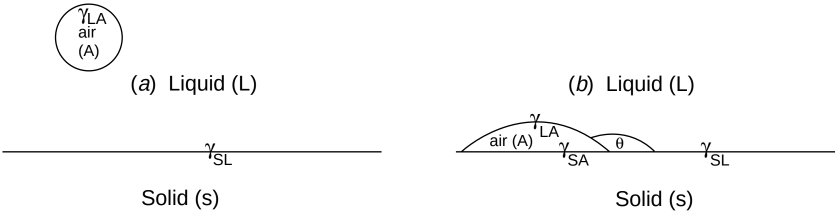


FIGURE 7-3 (*a*) Before adhesion of the solid to the air. (*b*) After adhesion of the solid to the air. Note the large value of θ measured in the liquid.

is high and their contact angle with the air is consequently low. The work of adhesion of the solid to the air

$$W_a = \gamma_{LA} + \gamma_{SL} - \gamma_{SA} \tag{7.7}$$

as shown in Figure 7-3, is consequently large and adhesion of the solid to the air is strong. The air bubbles in this case are stabilized not by a film of liquid, but by a film of adsorbed solid.

This type of adsorption is the basis for a number of important industrial processes, notably the separation of mineral ores by '*froth flotations*' (Somasundaran, 1979), the de-inking of waste paper (Turai, 1982), the ultrapurification of fine powders for the chemical and ceramic industries (Mougdil, 1991), and the production of "foamed" concrete. In the last case, for the concrete to entrain air, it is not even necessary for the liquid phase to show any foaming. In most of the processes used above, surfactants, such as salts of long-chain carboxylic acids or long-chain amines, that adsorb with their polar or ionic heads oriented toward the solid and their hydrophobic groups oriented away from it, are used to make the surface of the solid hydrophobic.

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PROBLEMS

1 Explain why film elasticity is greatest in the region of the CMC.

2 Discuss two properties of surfactants that account for the existence of film elasticity.

3 Describe two different mechanisms by means of which antifoams operate.

4 Give structural formulas for three different types of low-foaming surfactants, indicating the structural characteristics that cause them to foam poorly.

5 Calculate the time it would take for the surface concentration to reach a value of 2×10^{-10} mol/cm^2 from a 1×10^{-2} *M* solution of surfactant in the absence of stirring or an energy barrier to adsorption. Assume the bulk diffusion constant of the surfactant to be 2×10^6 cm^2/s.

6 Explain the observation that aqueous solutions of branched-chain surfactants show higher initial foam heights but poorer foam stability than their linear-chain isomeric surfactant based upon

(**a**) their equilibrium interfacial properties.

(**b**) their dynamic interfacial properties.

7 Aqueous solutions of some surfactants show good foaming at room temperature but very poor foaming at higher temperatures.

(**a**) Suggest a type of surfactant that shows this foaming behavior and explain the behavior.

(**b**) At what temperature would you expect to observe this behavior?

8 Emulsification by Surfactants

Emulsification—the formation of emulsions from two immiscible liquid phases—is probably the most versatile property of surface-active agents for practical applications and, as a result, has been extensively studied. Paints, polishes, pesticides, metal cutting oils, margarine, ice cream, cosmetics, metal cleaners, and textile processing oils are all emulsions or are used in emulsified form. Since there are a number of books and chapters of books devoted to emulsions and emulsification (Sjoblom, 1996; Solans and Kunieda, 1996; Becher, 2001), the discussion here covers only those aspects of emulsification that bear on the role of surfactants in this phenomenon.

An *emulsion* is a significantly stable suspension of particles of liquid of a certain size within a second, immiscible liquid. The term *significantly stable* means relative to the intended use and may range from a few minutes to a few years. Investigators in this field distinguish between three different types of emulsions, based upon the size of the dispersed particles: (1) *macroemulsions*, the most well-known type, opaque emulsions with particles >400 nm (0.4 μm), easily visible under a microscope; (2) *microemulsions*, transparent dispersions with particles <100 nm (0.1 μm) in size; and (3) *nanoemulsions* (*miniemulsions*), a type that is blue-white, with particle sizes between those of the first two types (100–400 nm [0.1–0.4 μm]. *Multiple emulsions* (Matsumoto, 1976), in which the dispersed particles are themselves emulsions, have been the subject of considerable investigation.

Two immiscible, pure liquids cannot form an emulsion. For a suspension of one liquid in another to be stable enough to be classified as an emulsion, a third component must be present to stabilize the system. The third component is called the *emulsifying agent* and it is usually a surface-active agent, although not necessarily of the type that is usually considered a surface-active agent (finely divided solids, for example, may act as emulsifying agents). The emulsifying agent, if of the conventional type, need not be an individual substance; in fact, the most effective emulsifying agents are usually mixtures of two or more substances, as we will see.

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

I. MACROEMULSIONS

Macroemulsions are of two types, based on the nature of the dispersed phase: oil-in-water (*O*/*W*) and water-in-oil (*W*/*O*). The *O*/*W* type is a dispersion of a water-immiscible liquid or solution, always called the *oil* (*O*), regardless of its nature, in an aqueous phase (*W*). The oil is, in this case, the "discontinuous" (inner) phase; the aqueous phase is the "continuous" (outer) phase. The *W*/*O* type is a dispersion of water or an aqueous solution (*W*) in a water-immiscible liquid (*O*). The type of emulsion formed by the water and the oil depends primarily on the nature of the emulsifying agent and, to some extent, on the process used in preparing the emulsion and the relative proportions of oil and water present. In general, *O*/*W* emulsions are produced by emulsifying agents that are more soluble in the water than in the oil phase, whereas *W*/*O* emulsions are produced by emulsifying agents that are more soluble in the oil than in the water phase. This is known as the *Bancroft rule* (Bancroft, 1913). *O*/*W* and *W*/*O* emulsions are not in thermodynamic equilibrium with each other; one type is usually inherently more stable than the other for a particular emulsifying agent at a given concentration under a given set of conditions. However, one type can be converted to the other by changing conditions. This is called *inversion* of the emulsion.

These two types of emulsions are easily distinguished: (1) An emulsion can readily be diluted with more of the outer phase, but not as easily with the inner phase. Consequently *O*/*W* emulsions disperse readily in water; *W*/*O* ones do not, but they do disperse readily in oil. This method works best on dilute emulsions. (2) *O*/*W* emulsions have electrical conductivities similar to that of the water phase; *W*/*O* emulsions do not conduct current significantly. (3) *W*/*O* emulsions will be colored by oil-soluble dyes, whereas *O*/*W* emulsions show the color faintly, if at all, but will be colored by water-soluble dyes. (4) If the two phases have different refractive indices, microscopic examination of the droplets will determine their nature. A droplet, on focusing upward, will appear brighter if its refractive index is greater than the continuous phase and darker if its refractive index is less than that of the continuous phase. This clearly identifies the substance in the droplet if one knows the relative refractive indices of the two phases. (5) In filter paper tests, a drop of an *O*/*W* emulsion produces an immediate wide, moist area; a drop of a *W*/*O* emulsion does not. If the filter paper is first impregnated with 20% cobaltous chloride solution and dried before the test, the area around the drop immediately turns pink if the emulsion is *O*/*W* and remains blue (shows no color change) if it is *W*/*O* (Tronnier, 1960).

There are three similarities between macroemulsions and foams: (1) They both consist of a dispersion of an immiscible state of matter in a liquid phase. Foams are dispersions of a gas in a liquid; emulsions are dispersions of a liquid in a second immiscible liquid. (2) The tension γ_I at the relevant interface is always greater than zero, and since there is a marked increase in interfacial area ΔA during the process (of emulsification or foaming), the minimum work involved is the product of the interfacial tension and the increase in interfacial area ($W_{\min} = \Delta A \times \gamma_I$. (3) The system will spontaneously revert to two bulk phases unless there is an interfacial film present that produces steric and/or electrical barriers to coalescence of the dispersed phase.

On the other hand, there are two significant differences between macroemulsions and foams: (1) The surfactants in the inter-facial film of a foam cannot dissolve in the dispersed (gas) phase, while in a macroemulsion the solubility of the surfactants in the liquid being dispersed is a major factor determining the stability of the emulsion. (2) In macroemulsions, both oil and water can serve as the continuous phase, i.e., both *O/W* and *W/O* emulsions are commonly encountered, while in foams, only the liquid acts as the continuous phase.

I.A. Formation

In the formation of macroemulsions, one of the two immiscible liquids is broken up into particles that are dispersed in the second liquid. Since the interfacial tension between two immiscible pure liquids is always greater than zero, this dispersion of the inner liquid, which produces a tremendous increase in the area of the interface between them, results in a correspondingly large increase in the interfacial free energy of the system. The emulsion produced is consequently highly unstable thermodynamically relative to the two bulk phases separated by a minimum area interface. It is for this reason that two immiscible liquids, when pure, cannot form an emulsion. The function of the emulsifying agent is to stabilize this basically unstable system for a sufficient time so that it can perform some function. This the emulsifying agent does by adsorption at the liquid–liquid interface as an oriented interfacial film. This oriented film performs two functions: (1) It reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases. (2) It decreases the rate of coalescence of the dispersed liquid particles by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one particle to another. The mechanical barrier increases the resistance of the dispersed particles to mechanical shock and prevents them from coalescing when they do collide. In the formation of macroemulsions, the reduction of interfacial tension reduces the amount of mechanical work required to break the inner phase into dispersed particles. In the case of microemulsions, the interfacial tension is reduced, at least temporarily, to such a low value that emulsification can occur spontaneously.

I.B. Factors Determining Stability

The term *stability*, when applied to macroemulsions used for practical applications, usually refers to the resistence of emulsions to the coalescence of their dispersed droplets. The mere rising or settling of the droplets (*creaming*) because of a difference in density between them and the continuous phase is usually not considered instability. Flocculation or coagulation of the dispersed particles, *without* coalescence of the liquid interior of the particles, although a form of instability, is not considered as serious a sign of instability as coalescence or *breaking* of the emulsion. The factors determining flocculation of the dispersed droplets in an emulsion are the same as those that bear on the flocculation of solid particles in a dispersion (Chapter 9). For a detailed discussion of flocculation in macroemulsions, see Kitchener (1968).

The rate of coalescence of the droplets in a macroemulsion is stated to be the only quantitative measure of its stability (Boyd, 1972). It can be measured by counting the number of droplets per unit volume of the emulsion as a function of time in a haemocytometer cell under a microscope (Sherman, 1968) or by means of a Coulter centrifugal photosedimentometer (Groves, 1964; Freshwater, 1966).

The rate at which the droplets of a macroemulsion coalesce to form larger droplets and eventually break the emulsion has been found to depend on a number of factors: (1) the physical nature of the interfacial film, (2) the existence of an electrical or steric barrier on the droplets, (3) the viscosity of the continuous phase, (4) the size distribution of the droplets, (5) the phase volume ratio, and (6) the temperature.

1. Physical Nature of the Interfacial Film The droplets of dispersed liquid in an emulsion are in constant motion, and therefore there are frequent collisions between them. If, on collision, the interfacial film surrounding the two colliding droplets in a macroemulsion ruptures, the two droplets will coalesce to form a larger one, since this results in a decrease in the free energy of the system. If this process continues, the dispersed phase will separate from the emulsion, and it will break. The mechanical strength of the interfacial film is therefore one of the prime factors determining macroemulsion stability.

For maximum mechanical stability, the interfacial film resulting from the adsorbed surfactants should be condensed, with strong lateral intermolecular forces, and should exhibit high film elasticity. The liquid film between two colliding droplets in an emulsion is similar to the liquid lamella between two adjacent air sacs in a foam (Chapter 7) and shows film elasticity for the same reasons (Gibbs and Marangoni effects).

Since highly purified surfactants generally produce interfacial films that are not close-packed (Table 2-2) and hence not mechanically strong, good emulsifying agents are usually a mixture of two or more surfactants rather than an individual surfactant. A commonly used combination consists of a water-soluble surfactant and an oil-soluble one. The oil-soluble surfactant, which generally has a long, straight hydrophobic group and a hydrophilic head that is only slightly polar, increases the lateral interaction between the surface-active molecules in the interfacial film and condenses it to one that is mechanically stronger than in its absence. Thus, the addition of an amount of lauryl alcohol sufficient to produce a close-packed monomolecular film increases the stability of sodium lauryl sulfate emulsions, as does the addition of NaCl, which, by compressing the electrical double layer, decreases the electrostatic repulsions between the ionic heads and allows the hydrophobic chains of the surfactant to approach each other more closely (Table 2-2). Consistent with this, POE alcohol emulsifying agents that have a broader distribution of POE chains produce more stable *O/W* emulsions than those with a narrower distribution. They also are stable over a larger temperature range (Saito, 1990).

An example of an oil-soluble surfactant and a water-soluble surfactant that are commonly used together as the emulsifying agent for many applications is a sorbitol ester (Span) and a POE sorbitol ester (Tween). Because of the greater interaction of the POE sorbitol derivative with the aqueous phase, its hydrophilic group extends further into the water than that of the nonoxyethylenated ester, and this is believed to permit the hydrophobic groups of the two materials to approach each other more closely in the interfacial film and to interact more strongly than when each surfactant is present by itself (Boyd, 1972). Figure 8-1 illustrates this complex formation at the interface.

Liquid-crystal formation can also stabilize the emulsion. By accumulating at the interface surrounding the dispersed particles, liquid crystals surround the particles with a high-viscosity region that resists the coalescence of individual droplets and also acts as a steric barrier (see Section B2 below) preventing the dispersed particles from approaching each other closely enough for van der Waals forces of attraction (Chapter 9, Section I) to operate (Friberg, 1976).

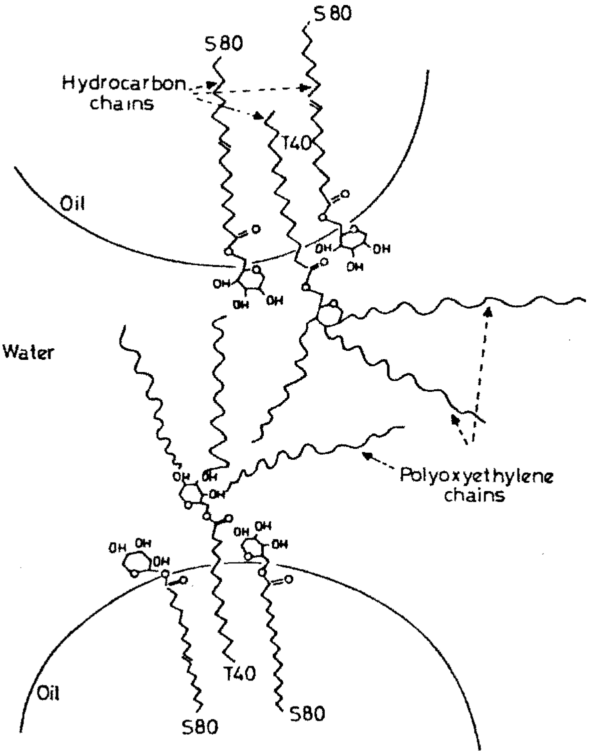


FIGURE 8-1 Complex formation between a Span (S80) and a Tween (T40) at the oil–water interface. Reprinted with permission from J. Boyd, C. Parkinson, and P. Sherman, *J. Colloid Interface Sci*, **41**, 359 (1972).

The films surround the droplets in *W/O* macroemulsions, in particular, must be very strong, and these films are believed to be of the solid-condensed type (Schulman, 1940; Ford, 1966) characterized by very strong lateral intermolecular forces and well-developed orientation of the film with respect to the interface, which confers a good deal of rigidity to the film. This type of film is necessary since the water droplets in a *W/O* emulsion carry little or no charge and therefore have no electrical barrier to coalescence (discussed in the following section). It is therefore mainly the mechanical strength of the interfacial film that prevents coalescence of the droplets in *W/O* macroemulsions, and to survive under the constant bombardment by neighboring droplets, the film must have unusual strength. The great rigidity of the film in these *W/O* emulsions is evidenced by the irregular shape of the water droplets in them, in contrast to the spherical shape of oil droplets in *O/W* emulsions.

2. Existence of an Electrical or Steric Barrier to Coalescence on the Dispersed Droplets The presence of a charge on the dispersed droplets constitutes an electrical barrier to the close approach of two particles to each other. This is believed to be a significant factor only in *O/W* emulsions. In *O/W* emulsions, the source of the charge on the dispersed droplets is the adsorbed layer of surfactant with its hydrophilic and oriented toward the water phase. In emulsions stabilized by ionic surfactants, the sign of the charge on the dispersed droplets is always that of the amphipathic ion. In emulsions stabilized by nonionic surfactants, the charge on the dispersed phase may arise either from adsorption of ions from the aqueous phase or from frictional contact between droplets and the aqueous phase. In the latter case, the phase with the higher dielectric constant is charged positively. In *W/O* emulsions, there is very little charge, if any, on the dispersed particles, and experimental data indicate no correlation between stability and any charge present. In fact, for water-in-benzene emulsions stabilized by oleate soaps of polyvalent metals, an *anticorrelation* was found between zeta potential and stability against coalescence. The true stabilizers in these systems are probably insoluble basic metal oleates produced by hydrolysis of the original metal oleates. Those metal oleates that do not stabilize water-in-benzene emulsions show no hydrolysis and have the highest zeta potentials. The hydrolysis products, if insoluble in both phases, accumulate at the interface and prevent the formation of an electrical double layer in the oil phase. Their accumulation at the interface stabilizes the *W/O* emulsion, since these basic metal oleates are preferentially wetted by the benzene and, in addition, form an interfacial film or layer that mechanically prevents coalescence of the water droplets (Albers, 1959). Hydrophobic solid particles stabilize *W/O* emulsions, while hydrophilic solid particles stabilize *O/W* emulsions (Aveyard and Clint, 2003).

The presence of groupings in the interfacial film that may be forced into higher energy arrangements by the close approach to each other of two dispersed droplets constitutes a steric barrier to such approach. Highly hydrated hydrophilic groups on the surfactants constituting the interfacial film in *O/W* emulsions, which may be forced to dehydrate on the close approach to each other of the two dispersed droplets, or long POE chains, which may be forced out of their usual coiled arrangement in water by such approach, may constitute such a barrier. In *W*/*O* emulsions, long alkyl groups extending into the oil phase from surfactants constituting the interfacial film may produce such a steric barrier.

3. Viscosity of the Continuous Phase An increase in the viscosity η of the continuous phase reduces the diffusion coefficient D of the droplets, since, for spherical droplets,

$$D = \frac{kT}{6\pi\eta a} \tag{8.1}$$

where k = the Boltzmann constant,
T = the absolute temperature,
a = the radius of the droplets.

As the diffusion constant is reduced, the frequency of collision of the droplets and their rate of coalescence are reduced. The viscosity of the external phase is increased as the number of suspended particles increases, and this is one of the reasons that many emulsions are more stable in concentrated form than when diluted. The viscosity of the external phase in emulsions is often increased by the addition of special ingredients for this purpose, such as natural and synthetic "thickening" agents. Friberg (1969) has pointed out the importance of the presence of liquid-crystalline phases (Chapter 3, Section IIc) in stabilizing emulsions. At certain concentrations of oil, water, and emulsifying agent, liquid-crystalline mesophases that increase the viscosity of the continuous phase may be formed. These can increase the stability of the macroemulsion greatly.

4. Size Distribution of Droplets A factor influencing the rate of coalescence of the droplets is the size distribution. The smaller the *range* of sizes, the more stable the emulsion. Since larger particles have less interfacial surface per unit volume than smaller droplets, in macroemulsions they are thermodynamically more stable than the smaller droplets and tend to grow at the expense of the smaller ones. If this process continues, the emulsion eventually breaks. An emulsion with a fairly uniform size distribution is therefore more stable than one with the same average particle size having a wider distribution of sizes.

5. Phase Volume Ratio As the volume of the dispersed phase in a macroemulsion increases, the interfacial film expands further and further to surround the droplets of dispersed material, and the basic instability of the system increases. As the volume of the dispersed phase increased beyond that of the continuous phase, the type of emulsion (*O*/*W*) or (*W*/*O*) becomes basically more and more unstable relative to the other type of emulsion, since the area of the interface that is now enclosing the dispersed phase is larger than that which would be needed to enclose the continuous phase. It often happens, therefore, that the emulsion inverts as more and more of the dispersed phase is added. If the emulsifying agent is so unbalanced as to strongly favor only the original type of emulsion, it may not invert, and may instead form a multiple emulsion, either *W/O/W* or *O/W/O*—the former type when it normally favors *W/O*, the latter type when it normally favors *O/W* (see Section ID below).

6. Temperature A change in temperature causes changes in the interfacial tension between the two phases, in the nature and viscosity of the interfacial film, in the relative solubility of the emulsifying agent in the two phases, in the vapor pressures and viscosities of the liquid phases, and in the thermal agitation of the dispersed particles. Therefore, temperature changes usually cause considerable changes in the stability of emulsions; they may invert the emulsion or cause it to break. Emulsifying agents are usually most effective when near the point of minimum solubility in the solvent in which they are dissolved, since at that point they are most surface-active. Since the solubility of the emulsifying agent usually changes with temperature change, stability of the emulsion usually also changes because of this. Finally, anything that disturbs the interface decreases its stability, and the increased vapor pressure resulting from an increase in temperature causes an increased flow of molecules through the interface, with a resulting decrease in stability.

A quantitative expression for the rate of coalescence of droplets in a macroemulsion, which includes most of the factors discussed previously, was developed by Davies and Rideal (1963), based on the von Smoluchowski (1916) theory of the coagulation of colloids.

The rate of diffusion-controlled coalescence of spherical particles in a disperse system as a result of collisions has been shown by von Smoluchowski to be proportional to the collision radius of the particles, the diffusion coefficient, and the square of the concentration of the particles:

$$\frac{-dn}{dt} = 4\pi D r n^2 \tag{8.2}$$

where D = diffusion coefficient,

r = collision radius (distance between centers when coale-scence begins),

n = number of particles per cm^3.

This assumes that every collision is effective in decreasing the number of particles. In the presence of an energy barrier to coalescence E, which is present in all dispersed systems,

$$\frac{-dn}{dt} = 4\pi D r n^2 e^{-E/kT} \tag{8.3}$$

On integration at constant temperature,

$$\frac{1}{n} = 4\pi D r t e^{-E/kT} + \text{constant} \tag{8.4}$$

From the Einstein equation,

$$D = \frac{kt}{6\pi\eta a} \tag{8.1}$$

where a is the average radius of the particles, and if we assume that coalescence occurs on contact (i.e., when $r = 2a$), then

$$\frac{1}{n} = 4\pi \frac{kT}{6\pi\eta a} 2ate^{-E/kT} + \text{constant} \tag{8.5}$$

$$= \frac{4kT}{3\eta} te^{-E/kT} + \text{constant} \tag{8.6}$$

A plot of $1/n$ versus t (n is determined by counting the particles per unit volume of the emulsion under a microscope) then permits the evaluation of E, since the slope of the curve equals

$$\frac{4kT}{3\eta} e^{-E/kT}$$

and k, T, and η are all known constants. It should be noted, however, that E may vary as the size or the number of particles in the emulsion changes.

If we define the mean volume of a particle $\bar{V} = V/n$, where $V =$ the volume fraction of the dispersed phase (i.e., the volume per cm^3 of the emulsion), then

$$\bar{V} = \frac{4}{3} \frac{VkT}{\eta} te^{-E/kT} + \text{constant} \tag{8.7}$$

Differentiating this expression yields an expression for the rate of coalescence of the particles and thus for the stability of the emulsion:

$$\frac{d\bar{V}}{dt} = \frac{4}{3} \frac{VkT}{\eta} e^{-E/kt} \tag{8.8}$$

$$= Ae^{-E/kt} \tag{8.9}$$

A is a constant for a particular system, called the *collision factor*. The effect of the surfactants used as the emulsifying agent is seen in the value of E, the energy barrier to coalescence, which includes both mechanical and electrical barriers.

I.C. Inversion

Macroemulsions may be changed from *W/O* to *O/W* and vice versa by varying some of the emulsification conditions: (1) the order of addition of the phases (by adding the water to the oil plus emulsifier a *W/O* emulsion may be obtained, whereas the addition of oil to the same emulsifier plus water may produce an *O/W* emulsion); (2) the nature of the emulsifier (making the emulsifier more oil-soluble tends to produce a *W/O* emulsion, whereas making it more water-soluble tends to produce an *O/W* emulsion); (3) the phase volume ratio (increasing the ratio of oil to water tends to produce a *W/O* emulsion and vice versa); (4) the phase in which the emulsifying agent is dissolved (placing the more hydrophilic of the surfactants used

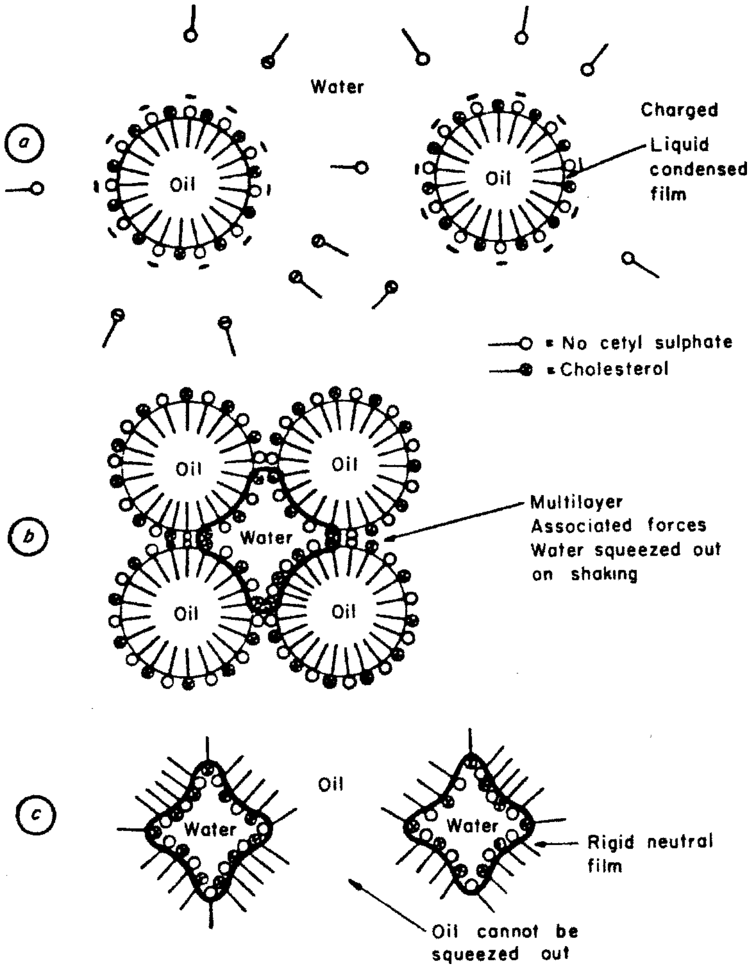


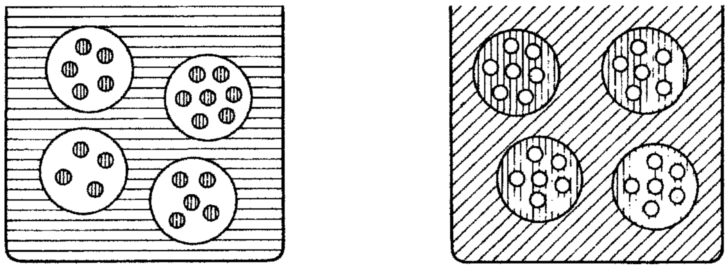
FIGURE 8-2 Inversion of an *O/W* emulsion stabilized by an interfacial film of sodium cetyl sulfate and cholesterol to a *W/O* emulsion upon addition of polyvalent cations. Adsorption of the cations neutralizes the negative charge on the oil droplets, thus allowing them to coalesce. Reprinted with permission from J.H. Schulman and E. G. Cockbain, *Trans. Faraday Soc.* **36**, 661 (1940).

as the emulsifying agent in the aqueous phase appears to favor *O/W* emulsion formation; (5) the temperature of the system (as the temperature of an *O/W* emulsion stabilized with a POE nonionic surfactant is increased, the surfactant becomes more hydrophobic and the emulsion may invert to *W/O*); on the other hand, some emulsions stabilized by ionic surfactants may invert to *W/O* on cooling; (6) the electrolyte or other additive content (the addition of strong electrolyte to *O/W* emulsions stabilized by ionic surfactants may invert them to *W/O* by decreasing the electrical potential on the dispersed particles and by increasing interaction between the surfactant ions and counter-ions (thereby making them less hydrophilic); the addition of long-chain alcohols or fatty acids may invert an *O/W* emulsion to *W/O* by making the combination of surfactants acting as emulsifying agents more hydrophobic).

In the process of inverting an *O/W* emulsion to a *W/O* emulsion, any charge on the dispersed oil particles must be removed and an interlinked, solid condensed film formed from the original interfacial film. The process has been represented diagrammatically as shown in Figure 8-2 (Schulman, 1940). According to this mechanism, the charged film in the *O/W* emulsion is neutralized and the oil droplets tend to coagulate to form the continuous phase. The trapped water is surrounded by an interfacial film that realigns to form irregularly shaped droplets of water stabilized by a rigid, uncharged film. The result is a *W/O* emulsion.

I.D. Multiple Emulsions

There has been considerable interest in multiple emulsions, in part because of their potential as a means of (1) delivering drugs to specified targets in the body without the possible deleterious effects of these drugs on other organs and (2) prolonging the release of drugs that have a short biological half-life. Both *W/O/W* and *O/W/O* emulsions exist. In the first type (Figure 8-3*a*) the water-immiscible liquid (*O*) globules that are suspended in the aqueous (*W*) phase themselves contain dispersed globules of an aqueous solution; in *O/W/O* emulsions (Figure 8-3*b*), the globules of



(a) *(b)*

FIGURE 8-3 Multiple emulsions. (*a*) *W/O/W* emulsion: ▥, inner *W* phase; □, inner *O* phase; ▤, outer *W* phase. (*b*) *O/W/O* emulsion: □, inner *O* phase; ▥, inner *W* phase; ▨ outer *O* phase.

aqueous solution suspended in the oil phase contain dispersed oil particles. It is believed that *W/O/W* formation is a mesophase preceding complete inversion of *W/O* to *O/W* emulsions (Matsumoto, 1985).

Multiple emulsions of the *W/O/W* type are generally prepared by a two-step procedure (Matsumoto, 1976; Garti, 1983; Magdassi, 1984): a pre-formed *W/O* emulsion is added slowly, with stiring, to an aqueous solution containing a hydrophilic emulsifying agent. However, it is possible to form them by a one-step procedure (Matsumoto, 1983) if a dilute aqueous solution of the hydrophilic emulsifying agent (e.g., 1/20–1/50 the concentration of the lipophilic emulsifying agent) is used as the aqueous phase in forming the *W/O* emulsion. Inversion occurred at a water-to-oil volume ratio greater than 0.7, yielding a mixture of *O/W* and *W/O/W* emulsions. For the formation of *W/O/W* emulsions by this technique, a close-packed interfacial film in the *W/O* emulsion is needed.

In general, to obtain good yields of *W/O/W* emulsions, a high concentration of the lipophilic emulsifying agent in the oil phase during the preparation of the *W/O* emulsion and a low concentration of the hydrophilic emulsifier in the aqueous phase during the formation of the *W/O/W* emulsion are required. In some cases, to get >90% yields of *W/O/W* emulsions, the concentration of the lipophilic emulsifying agent in the oil phase had to exceed 30% and be 10–60 times that of the hydrophilic emulsifier (Matsumoto, 1976). The presence of anionic surfactant in the hydrophilic emulsifier produced greater stability in the *W/O/W* emulsion (Matsumoto, 1983; Garti, 1983), as did the addition of a protein (bovine serum albumin) to the aqueous inner phase (Omotosho, 1986).

I.E. Theories of Emulsion Type

1. Qualitative Theories All qualitative theories explaining the formation of *O/W* and *W/O* emulsions are based on the empirical Bancroft rule. Some investigators believe that the interfacial region produced by the adsorption and orientation of the surface-active molecules at the liquid–liquid interface can have different interfacial tensions (or interfacial pressures) on either of its two sides; that is, the interfacial tension between the hydrophilic ends of the surfactant molecules and the water phase molecules (or the interfacial pressure between the hydrophilic heads) can be different from the interfacial tension between the hydrophobic ends of the surfactant and the oil phase molecules (or the interfacial pressure between the hydrophobic ends). In the formation of the emulsion, the interfacial region would tend to curve so as to shorten the area of the side with the greater interfacial tension (or lower interfacial pressure), thus minimizing the interfacial free energy. If the oil-hydrophobic end tension were greater (or interfacial pressure lower) then the water-hydrophilic end tension, then the former side would be shortened, causing the film to be concave toward the oil, resulting in the enclosure of the oil by the water and therefore forming an *O/W* emulsion. On the other hand, if the water-hydrophilic end tension were greater (or interfacial pressure lower), then the oil-hydrophobic end tension, then the former side would be shortened, causing the film to be concave toward the water, forming a *W/O* emulsion. A preferentially oil-soluble

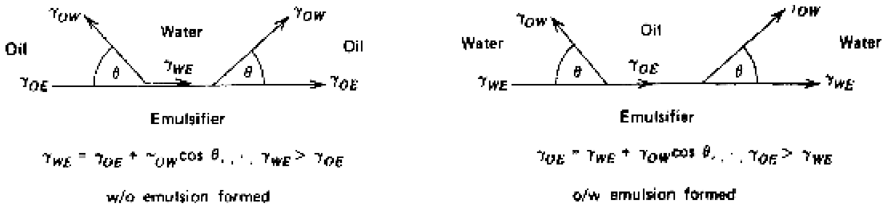


FIGURE 8-4 Effect of contact angle on emulsion type.

emulsifying agent would, of course, produce a lower interfacial tension (or greater interfacial pressure) at the oil interface, yielding a *W/O* emulsion; preferentially water-soluble emulsifying agent would produce a lower interfacial tension (or greater interfacial pressure) at the water interface, yielding an *O/W* emulsion.

Other investigators (Schulman, 1954) explain the formation of these two types of emulsions on the basis of the difference in contact angles at the oil–water–emulsifier boundary (Figure 8-4). If, at the contact between oil, water, and emulsifier, the oil contact angle (the contact angle, measured in the oil phase) is less than 90°, then the oil surface is concave toward the water, producing a *W/O* emulsion. On the other hand, if at the same oil–water–emulsifier contact, the water contact angle is less than 90°, then the water surfact is concave toward the oil, producing an *O/W* emulsion. Note, however, that if the oil contact angle is <90°, then $\gamma_{OE} < \gamma_{WE}$ (i.e., the emulsifier is more hydrophobic than hydrophilic). If the water contact angle is <90°, then $\gamma_{WE} < \gamma_{OE}$, and the emulsifying agent is more hydrophilic than hydrophobic. Thus, emulsifying agents with mainly hydrophilic character produce *O/W* emulsions, whereas those with mainly hydrophobic character produce *W/O* emulsions. This relation is *quantitatively* useful only for emulsifying agents, such as certain solids, that dissolve in neither the oil nor the water phase, or for emulsifying agents adsorbed on solids insoluble in both phases. If the emulsifying agent dissolves in either of the two phases, or in both, its contact angle with each phase in which it dissolves is nonexistent and therefore cannot be measured. Qualitatively, however, it follows that if an emulsifying agent is soluble in only one of the phases, its contact angle with that phase is zero, and therefore less than that which it makes with the phase in which it is not soluble; therefore, the phase in which it is soluble is the continuous phase in the emulsion. Thus, emulsifying agents that are predominantly oil-soluble form *W/O* emulsions, whereas those that are predominantly water-soluble form *O/W* emulsions.

This concept was tested (Schulman, 1954) for $BaSO_4$-stabilized emulsions containing surface-active agents. When the contact angle measured in the aqueous phase was slightly greater than 90°, a *W/O* emulsion was formed; when it was slightly less than 90°, an *O/W* emulsion was formed. If the angle was much greater than 90°, $BaSO_4$ particles dispersed in the oil phase; if much lower than 90°, they dispersed in the water phase. In the last two cases, the emulsions broke.

Studies on the coalescence of oil and water droplets at the oil–water interface confirm the conclusion that the dispersed phase will be the one that makes the higher contact angle with the emulsifier and have suggested still another factor in the formation of these two types of emulsions. It is believed that stability of the droplets in an external liquid medium is determined mainly by the ability or lack of ability of the material constituting the droplets to wet the adsorbed film between the droplets and the external medium (Cockbain, 1953). If the material in the droplets can wet the interfacial film (which means that a low contact angle exists between the emulsifier comprising the film and the material in the droplet), then the droplets will coalesce and the emulsion will be unstable. If the material in the droplets cannot wet the interfacial film (i.e., a high contact angle exists between emulsifier and material in the droplet), then it will be difficult for the droplets to coalesce, since it is difficult for the external phase to wet the area between the two droplets, and the emulsion will be stable. Therefore the more stable type of emulsion will be that in which the droplets contain the phase that wets the emulsifier less (i.e., the one that makes the higher contact angle with the emulsifier).

2. Kinetic Theory of Macroemulsion Type Davies (1957) developed a quantitative theory of macroemulsion type relating the type of emulsion formed to the kinetics of coalescence (equations 8.8 and 8.9) of the two types of droplets present: oil droplets and water droplets. According to this theory, the type of macroemulsion formed when oil and water are agitated together in the presence of an emulsifying agent is due to the relative rates of the two competing processes: (1) coalescence of oil droplets and (2) coalescence of water droplets. Agitation is presumed to break simultaneously both the oil and the water phases into droplets, with the emulsifying agent being adsorbed at the interface around these droplets. The phase that becomes the continuous one is that which has the faster rate of coalescence. If the rate of coalescence of the water droplets is much greater than that of the oil droplets, then an O/W emulsion forms; if the rate of coalescence of the oil droplets is much greater than that of the water droplets, than a W/O emulsion forms. When the rates of coalescence of the two phases are similar, the phase of larger volume becomes the outer phase.

In general, hydrophilic groups in the interfacial film constitute a barrier to the coalescence of oil droplets, whereas hydrophobic groups in the interfacial film constitute a barrier to the coalescence of water droplets. Hence an interfacial film that is predominantly hydrophilic tends to form O/W emulsions, whereas one that is predominantly hydrophobic tends to produce W/O emulsions.

According to Davies, a rate of 10^{-2} times the collision factor (i.e., $Ae^{-E/kT} = 10^{-2}A$ in equation 8.9) is a fast rate of coalescence, corresponding to complete coalescence of that phase within an hour, whereas a rate of $10^{-5}A$ is a very slow rate, corresponding to a stability of the order of several months for that phase in a dispersed form. Therefore, if the rate of coalescence of one phase is of the order of $10^{-5}A$ and the rate of coalescence of the other phase is considerably faster, then a stable emulsion will be formed with the phase having the slower rate as the dispersed phase. On the other hand, if the rate of coalescence of both phases is of the order of $10^{-2}A$, then both phases will coalesce rapidly and the emulsion will break, regardless of which phase has the slower rate.

If some substance is added to an emulsion or if some condition is varied, which changes the rates of coalescence of the two phases in such a manner that the rate of coalescence of the continuous phase is decreased very considerably (e.g., to the order of $10^{-5}A$) and the rate of coalescence of the dispersed phase is increased very considerably (e.g., to the order of $10^{-2}A$), then the emulsion, on agitation, inverts and the two phases switch roles in the emulsion.

II. MICROEMULSIONS

Although microemulsions (called *soluble oils* at that time) have been produced commercially since the 1930s, significant understanding of their nature has been acquired only during the past few decades, mainly as a result of the intense interest generated in them by laboratory and field tests that showed that they could increase the recovery of petroleum from reservoir rock. This is due to the ultralow interfacial tensions (Chapter 5, Section III*A*) attained at the microemulsions–petroleum interface, a prerequisite for the displacement of the residual petroleum in the capillaries of the rock. There has also been considerable recent interest in microemulsions of fluorocarbons as a result of the exceptionally high solubility of O_2 in these systems and their consequent potential as O_2 carriers in cases of circulatory disfunction (Mathis, 1984). In addition, microemulsions are used in the preparation of solid nanoparticles (Barette, 1992), in foods and beverages (Dungan, 1997), and as reaction media for organic syntheses (Schomacker, 1992).

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10–100 nm (0.01–0.1 μm) diameter that are generally obtained upon mixing the ingredients gently. They differ markedly from both macro- and miniemulsions in this respect, since these two types depend upon intense agitation for their formation. Microemulsions may be water-external (*O*/*W*), oil-external (*W*/*O*), or both.

Whether one considers a microemulsion to be a solution in one liquid of micelles swollen by a solubilized second liquid or a dispersion of tiny droplets of one liquid in a second liquid, the interfacial tension of the microemulsion against both of these liquids must be close to zero. In the first case the system is one-phase and therefore has no interface against either liquid as long as the micelles are capable of solubilizing more of the second liquid. In the second case the interfacial area is so large that an exceedingly low interfacial tension must be present to permit formation of the microemulsion with so little work. In addition, the interfacial region must be highly flexible, either to permit the large curvature required to surround exceedingly small particles or to allow the easy transition from oil-continuous to water-continuous structures that is characteristic of microemulsions.

It is generally accepted that the clear, fluid, middle (surfactant) phase between a nonpolar phase (*O*) and an aqueous phase (*W*) in a three-phase system (Chapter 5, Section III) is a microemulsion; if the concentration of surfactant is increased, the middle phase incorporates both the (oil and water) phases into a single (microemulsion) phase. As discussed in Chapter 5, Section III*A*, the guidelines for formation of this middle phase indicate the conditions for forming microemulsions. The Winsor R ratio (equation 5.2) measures the solubilization capacity for water relative to oil. Modification of that ratio by changing the structure of the surfactant, changing the temperature of the system, adding a cosurfactant, or adding electrolyte can change the solubilization capacity of the system for either water or oil, or both (Verzaro, 1984).

Microemulsions are generally prepared with more than one surfactant or with a mixture of a surfactant and a cosurfactant (e.g., a polar compound of intermediate chain length*), although cosurfactant-free microemulsions have been prepared (Holmberg, 1986). The combination is usually required to provide the proper balance between hydrophilic and lipophilic properties for the required oil and water phases under the conditions of use. This balance can be determined experimentally by mixing the oil and water phases in the desired proportions with the surfactant–cosurfactant combination and noting whether a Winsor Type I,II,III, or IV system (Figure 5-5) is obtained. It is advisable to use graduated vessels for this purpose so that the volumes of the phases can be measured. The surfactant–cosurfactant combination is then adjusted to bring the Winsor R value close to 1. If a three-phase system is finally obtained instead of a one-phase microemulsion, the concentration of surfactant–cosurfactant mixture can be increased until both water and oil phases disappear by solubilization into the surfactant phase.

As a result of the intensive research done on microemulsions in connection with enhancing the recovery of petroleum from oil reservoir rock, a number of methods have been developed for determining the conditions under which a microemulsion is formed. Thus, for microemulsions with anionic surfactants, equation 8.10 has been suggested (Salager, 1979) to develop the optimum formulation (when the equation equals zero):

$$\ln S - kACN - f(C_A) + \sigma - a_{\mathrm{T}}\Delta T = 0 \tag{8.10}$$

where S is the salinity of the aqueous phase in weight % NaCI,

ACN is the carbon number (or equivalent) of the alkane used,

$f(C_A)$ is a function of the alcohol concentration used as a cosurfactant,

σ is a parameter characteristic of the chemical structure of the surfactant used (which increases linearly with the hydrophilic chain length),

ΔT is the temperature deviation from a reference temperature (25°C),

k and a_T are empirical constants.

Equation 8.10 takes into consideration the formulation ingredients that may be necessary to produce a microemulsion with the ultralow interfacial tension (Chapter 5, Section IIIA) required for enhancing the recovery of petroleum from the reservoir rock.

From the equation, it is apparent that as the number of carbon atoms in the alkane (*ACN*) to be emulsified increases, or as the number of carbon atoms in the

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*Long-chain polar compounds are generally not desirable as cosurfactants since they tend to form liquid-crystalline structures that may increase the viscosity of the system and the rigidity of the interface.

hydrophobic group of the surfactant (σ) decreases, the salinity (S) of the solution must be increased to yield a microemulsion.

An analogous equation has been developed (Anton, 1997) for cationic surfactant-based microemulsions.

For POE nonionic surfactant-based microemulsions, equation 8.11 has been suggested (Bourrel, 1980):

$$\alpha - EON + bS - kACN - \phi(C_A) + a_T\Delta T = 0 \tag{8.11}$$

where α is characteristic of the surfactant hydrophobe (and increases with the number of carbons in it),

EON is the average number of oxyethylene groups in the surfactant hydrophilic group,

S, ACN, C_A, and ΔT are the same as in equation 8.10, and b, k, ϕ, and a_T are again empirical constants.

Here, it is apparent that as the number of oxyethylene groups (EON) in the surfactant molecule increases, the salinity (S) must be increased to yield a microemulsion. In contrast to equation 8.10, where the sign of the term $a_T\Delta T$ is negative, in equation 8.11 the sign of the $a_T\Delta_T$ term is positive. This is because ionic surfactants become more water-soluble (more hydrophilic) as the temperature is raised, and the left-hand side of equation 8.10 should reflect this by becoming less positive (or more negative) with temperature increase. On the other hand, POE nonionics, because of dehydration of their oxyethylene groups as the temperature increases (Chapter 4, Section IIIC), become less water-soluble (more hydrophobic) with this change, and the left-hand side of equation 8.11 should reflect this by becoming more positive.

The volume of the oil phase (in mL) solubilized per gram of surfactant used at the conditions where equations 8.10 or 8.11 are equal to zero (“optimum salinity”) is called the *solubilization parameter* at optimum formulation and symbolized by SP^*. The interfacial tension under these conditions, γ^*, is inversely proportional to the SP^*, and $\gamma^* = K/(SP^*)^2$ (Chun, 1979). Consequently, to obtain the lowest interfacial tension (Chapter 5, Section IIIA), the value of SP^* should be maximized.

Lipophilic linkers (Salager, 1998) and hydrophilic linkers (Uchiyama, 2000; Acosta, 2002) are used to increase the value of SP^* and decrease γ^*. Lipophilic linkers are long-chained alcohols (above C_8) and their low oxyethylenation products that increase the surfactant–oil interaction. The most effective ones have hydrophobic chain lengths that are an average of the hydrophobic chain length of the surfactant and the chain length of the alkane oil. Hydrophilic linkers increase the surfactant–water interaction. Examples are mono- and dimethylnaphthalene sulfonates and sodium octanoate

III. NANOEMULSIONS

These are also known as *miniemulsions* (Ugelstad, 1973; El-Asser, 1977, 1984; Grimm, 1983; Brouwer, 1986), *finely dispersed emulsions* (Sagitani, 1981), or *ultrafine emulsions* (Nakajima, 1993). They are blue-white semiopaque emulsions of 100–400 nm (0.1–0.4 μm) droplet size. The emulsifier is generally 1–3% of the oil phase, in contrast to the 15–30% in microemulsions, and is a mixture of an ionic surfactant and a cosurfactant, where the latter is generally a long-chain alcohol. The chain length of the cosurfactant is at least 12 carbons, in contrast to the considerably shorter lengths used in microemulsions. Nanoemulsions are used in the preparation of polymer latices, in cosmetics (where their translucent or transparent appearance makes them especially attractive), and in pharmaceutical drug delivery systems. Nanoemulsions of the *O*/*W* type are prepared by stirring a mixture of the surfactant and cosurfactant in water for at least an hour to produce a mixed micellar solution. The PIT method (Section IV B below) is commonly used for their preparation (Forster, 1997). The initial location of the (cosurfactant) fatty alcohol in the aqueous phase is essential for successful emulsification. The mechanism suggested for nanoemulsion formation is swelling of mixed micellar structures by solubilized solvent, followed by breakdown of these swollen structures to tiny droplets of <400 nm diameter. The gain in entropy of mixing during net transfer of fatty alcohol from aqueous phase to oil phase is suggested as the driving force for their formation (Brouwer, 1986). Nanoemulsions do not cream or settle because Brownian movement is larger than gravity effects on particles <1 μm.

For styrene nanoemulsions prepared with 10^{-2} *M* sodium lauryl sulfate and a 1:1 molar ratio of ionic surfactant:fatty alcohol, the order of decreasing stability with fatty alcohols of different chain length is $C_{16} > C_{18} > C_{14} > C_{12} > C_{10}$. For sodium lauryl sulfate-C_{16} alcohol mixtures, the order of decreasing stability with different sodium lauryl sulfate:fatty alcohol ratios is 1:3 > 1:2 > 1:1 > 1:6 > 1:0.5. The 1:3 and 1:2 ratios produce emulsions with stabilities > 1 month. The presence of rodlike liquid-crystalline structures at 1:1 to 1:3 ionic surfactant:fatty alcohol ratios is believed to be essential for the preparation of a stable nanoemulsion. (El-Aaser, 1984).

This method has been used to prepare nanoemulsions of such polymers as cellulose esters and epoxy resins, similar to latexes produced by emulsion polymerization. The nanoemulsions are prepared by direct emulsification of solutions of the polymers in organic solvents, followed by removal of the organic solvent by steam distillation under reduced pressure. The nanoemulsions produced in this fashion had stabilities > 1 year.

IV. SELECTION OF SURFACTANTS AS EMULSIFYING AGENTS

Correlations between the chemical structure of surface-active agents and their emulsifying power are complicated by the fact that both phases, oil and water, are of variable composition. This is in contrast to such phenomena as foaming or wetting, where one phase (the air) is more or less constant and some specific correlations can be made between structure and activity. Moreover, the concentration at which the emulsifying agent is used determines not only its emulsifying power, but even the type of emulsion (*O*/*W* or *W*/*O*) formed. As a result of this necessity of taking into consideration the composition of the two phases and the concentration of the emulsifying agent, it is not possible to rate specific surfactants as general emulsifying agents in any particular order. However, there are some general guidelines that can be helpful in the selection of surfactants as emulsifying agents. In general, for a surfactant to act as an emulsifier: (1) It must show good surface activity and produce a low interfacial tension *in the particular system in which it is to be used.* This means that it must have a tendency to migrate to the interface, rather than to remain dissolved in either one of the bulk phases. It must therefore have a balance of lyophilic and lyophobic groups such that it will distort the structure of both bulk phases to some extent, although not necessarily equally. Too great a solubility in either bulk phase will make its usefulness dubious. (2) It must form, at the interface, either by itself or with other adsorbed molecules that are present there, an interfacial film that is condensed because of lateral interactions between the molecules comprising the interfacial film. This means that for *O*/*W* macroemulsions the hydrophobic groups in the interfacial film should have strong lateral interactions; for *W*/*O* macroemulsions the hydrophilic groups should interact strongly. (3) It must migrate to the interface at a rate such that the interfacial tension is reduced to a low value in the time during which the emulsion is being produced. Since the rate of migration to the interface of a particular surfactant usually varies, depending on whether it is placed in the oil or in the water phase before the emulsification process, its emulsifying behavior often depends on the phase in which it is placed prior to emulsification.

Two other very general guidelines have already been established on the basis of the previous discussion: (1) Emulsifying agents that are preferentially oil-soluble form *W*/*O* emulsions and (2) a mixture of a preferentially oil-soluble surface-active agent and a preferentially water-soluble one often produces better and more stable emulsions than an individual surfactant. To these can be added a third guideline, which takes into consideration the nature of the oil phase: (3) The more polar the oil phase, the more hydrophilic the emulsifier should be; the more nonpolar the oil to be emulsified, the more lipophilic the emulsifier should be. This generalization is the basis for a number of methods of minimizing the work of selecting the most suitable emulsifying agent or combination of emulsifying agents for a particular system.

IV.A. The HLB Method

A frequently used method is known as the *HLB* (*hydrophile–lipophile balance*) *method*. In this method (Griffin, 1949), a number (0–40) indicative of emulsification behavior and related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule* has been assigned to many commercial emulsifying agents. (In some cases, the HLB number is calculated from the structure of the molecule; in other cases, it is based on experimental emulsification

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*Becher (1984) has pointed out the relation between the HLB number and the $V_H/l_c a_0$ parameter (Chapter 3, Section IIA).

data). In addition, a similar range of numbers has been assigned to various substances that are frequently emulsified, such as oils, lanolin, paraffin wax, xylene, carbon tetrachloride, and so on. These numbers are generally based on the emulsification experience* rather than on structural considerations. Then an emulsifying agent—or better still, a combination of emulsifying agents—is selected whose HLB number is approximately the same as that of the ingredients to be emulsified. If there are a number of ingredients to be emulsified simultaneously, the weighted average of the assigned numbers corresponding to the percentage composition of the mixture of ingredients is used. As in the case of the ingredients to be emulsified, when a combination of emulsifying agents of different HLB values is used, the HLB number of the mixture is the weighted average of the individual HLB numbers.

For example, if a mixture of 20% paraffin wax (HLB = 10) and 80% aromatic mineral oil (HLB = 13) is to be emulsified then the HLB number of the emulsifying agent combination should be $(10 \times 0.20) + (13 \times 0.80) = 12.4$. For this purpose a mixture of 60% of POE lauryl alcohol made from 23 mol of ethylene oxide (HLB = 16.9) and 40% POE of cetyl alcohol made from 2 mol of ethylene oxide (HLB = 5.3) could be tried:

$$\text{HLB} = (16.9 \times 0.60) + (5.3 \times 0.40) = 12.2$$

To determine the *optimum* emulsifier combination, however, various mixtures of other *types* of emulsifying agents with the same weighted average HLB number must then be tried to determine which structural types of emulsifying agents give the best results with this particular combination of emulsion ingredients, since the HLB number is indicative only of the type of emulsion to be expected, not the efficiency or effectiveness with which it will be accomplished (Griffin, 1954; Becher, 1973a). For *O/W* emulsions stabilized with POE nonionics, emulsion stability increases with increase in the length of the POE chain; for *W/O* emulsions, with length of the hydrophobic group (Shinoda, 1971).

As expected from the definition of the HLB value, materials with high HLB values are *O/W* emulsifiers and materials with low HLB value are *W/O* emulsifiers. An HLB value of 3–6 is the recommended range for *W/O* emulsification; 8–18 is recommended for *O/W* emulsification. Since the requirements for emulsification of a particular ingredient differ markedly, depending on whether the ingredient is the dispersed phase (*O/W* emulsion)or the continuous phase (*W/O* emulsion), each ingredient has a different HLB value, depending on which phase of the final emulsion it will become. Thus, paraffinic mineral oil has an HLB value of 11 for emulsification as the dispersed phase in an *O/W* emulsion and a value of 4 as the continuous phase in a *W/O* emulsion.

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*For determining the HLB of an oil of unknown HLB value, see Becher (1973b).

The HLB value for some types of nonionic surface-active agents can be calculated from their structural groupings (Griffin, 1954). Thus, for fatty acid esters of many polyhydric alcohols,

$$\text{HLB} = 20\left(1 - \frac{S}{A}\right) \tag{8.12}$$

where S is the saponification number of the ester and A is the acid number of the fatty acid used in the ester. For example, glyceryl monostearate has $S = 161$, $A = 198$, and hence HLB $= 3.8$. For esters for which good saponification data are not readily obtainable, the following formula can be used:

$$\text{HLB} = \frac{E + P}{5} \tag{8.13}$$

where E is the weight percentage of oxyethylene content and P is the weight percentage of polyol content. For materials where a POE chain is the only hydrophilic group, this reduces to

$$\text{HLB} = \frac{E}{5} \tag{8.14}$$

Thus, a POE cetyl alcohol made from 20 mol of ethylene oxide (77% oxyethylene) would have a calculated HLB of 15.4.

A commonly used general formula for nonionics is

$$20 \times \frac{M_H}{M_H + M_L} \tag{8.15}$$

Where M_H is the formula weight of the hydrophilic portion of the molecule and M_L is the formula weight of the lipophilic (hydrophobic) portion of the molecule.

The water solubility of the surfactant can be used to obtain a rough approximation of its HLB value (Becher, 2001)

Behavior in Water	HLB Range
No dispersibility	1–4
Poor dispersion	3–6
Milky dispersion after vigorous agitation	6–8
Stable milky dispersion (upper end almost translucent)	8–10
From translucent to clear	10–13
Clear solution	13+

There have been numerous attempts to determine HLB numbers from other fundamental properties of surfactants, e.g., from cloud points of nonionics (Schott, 1969), from CMCs (Lin, 1973), from gas chromatography retention times (Becher, 1964; Petrowski, 1973), from NMR spectra of nonionics (Ben-et, 1972), from partial molal volumes (Marszall, 1973), and from solubility parameters (Hayashi, 1967; McDonald, 1970; Beerbower, 1971). Although relations have been developed between many of these quantities and HLB values calculated from structural groups in the molecule, particularly in the case of nonionic surfactants, there are few or no data showing that the HLB values calculated in these fashions are indicative of actual emulsion behavior.

It has become apparent that although the HLB method is useful as a rough guide to emulsifier selection, it has serious limitations. Although, as mentioned previously, the HLB number of a surfactant is indicative of neither its efficiency (the required concentration of the emulsifying agent) nor its effectiveness (the stability of the emulsion), but only of the type of emulsion that can be expected from it, data have accumulated that show that even this is not reliably related to the HLB number. It has been pointed out (Shinoda, 1968; Boyd, 1972; Kloet, 2002) that a single surfactant can produce either an *O/W* or a *W/O* emulsion, depending on the temperature at which the emulsion is prepared, the shear rate, or, at high oil concentrations, on the ratio of surfactant to oil. *O/W* emulsions can be prepared with certain surfactants over the entire range of HLB numbers from 2 to 17.

IV.B. The PIT Method

A major disadvantage of the HLB method of selecting surfactants as emulsifying agents for a particular system is that it makes no allowance for the change in HLB value with change in the conditions for emulsification (temperature, nature of the oil and water phases, presence of cosurfactants or other additives). For example, we saw in Chapter 5, Section IIIA, that when the temperature is raised, the degree of hydration of a POE nonionic surfactant decreases and the surfactant becomes less hydrophilic. Consequently, its HLB must decrease. An *O/W* emulsion made with a POE nonionic surfactant may invert to a *W/O* emulsion when the temperature is raised; a *W/O* emulsion may invert to an *O/W* emulsion when the temperature is lowered. The temperature in the middle of the three-phase region at which inversion occurs is known as the *phase inversion temperature* (PIT) and is the temperature, as we have seen in Chapter 5, Section IIIA, at which the hydrophilic and lipophilic tendencies of the surfactant (or surfactant–cosurfactant mixture) “balance” in that particular system of oil and water phases. There is also a very good linear relationship between the PIT and the cloud points (Chapter 4, Section IIIB) of various types of POE nonionic surfactants when the system is saturated with the oil phase (Shinoda and Arai, 1964).

Since the oil–water interfacial tension is at a minimum at the PIT, emulsions made at this temperature should have the finest particle size. The minimum work needed to create the emulsions is the product of the interfacial tension and the increase in interfacial area ($W_{\min} = \gamma_I \times \Delta A$) and, for a given amount of mechanical work expended, ΔA should be a *maximum* at the temperature. Since the particle size diminishes as ΔA increases for a given amount of mechanical work expended, the particle size should be at a minimum at the PIT. This is the basis for a method of selecting surfactants as emulsifying agents for a particular system, the PIT method (Shinoda, 1964, 1965, 1968). This method is applicable only to emulsions that show inversion at a particular temperature.

According to this method, an emulsion made with equal weights of oil and aqueous phases and 3–5% of surfactant is heated and shaken at different temperatures and the temperature at which the emulsion inverts from *O*/*W* to *W*/*O*, or vice versa, is determined. A suitable emulsifier for an *O*/*W* emulsion should yield a PIT 20–60°C higher than the storage temperature of the emulsion; for a *W*/*O* emulsion, a PIT 10–40°C lower than the storage temperature is recommended (although PITs cannot be determined below 0°C).

For optimum stability, Shinoda and Saito (1969) suggest "emulsification by the PIT method," in which the emulsion is prepared at a temperature 2–4°C below the PIT and then cooled down to the storage temperature (for *O*/*W* emulsions). This is because an emulsion prepared near the PIT has a very fine average particle size but is not very stable to coalescence. Cooling it down to a temperature considerably below the PIT increases it stability without significantly increasing its average particle size.

The PIT is affected by the HLB and the concentration of the surfactant, the polarity of the oil phase, the phase ratio of the bulk phases and the presence of additives in them, and the distribution of POE chain lengths in POE nonionics (Shinoda, 1968; Mitsui, 1970). The PIT appears to be an almost linear function of the HLB value of the surfactant for a given set of emulsification conditions; the higher the HLB value, the greater the PIT. This is to be expected, since the larger the ratio of the hydrophilic to the lipophilic moiety in the surfactant molecule, the higher the temperature required to dehydrate it to the point where its structure is balanced. When the distribution of POE chain lengths in an emulsion stabilized by a POE nonionic surfactant is broad, its PIT is higher and its stability greater than when the distribution is narrow (Shinoda, 1971).

For a POE surfactant with a given HLB value, as the polarity of the oil phase decreases, the PIT increases. (The surfactant must be made more lipophilic to match the decreased polarity of the oil.) Thus, to keep the PIT constant (and hence a constant emulsifying power balance), the surfactant used must have a lower HLB value as the polarity of the oil phase decreases. The PIT of an emulsion made from binary mixture of oils is the weighted average, by volume, of the PITs of the emulsion made from the individual oils, using the same emulsifying agent (Arai, 1967):

$$\mathrm{PIT}_{(\mathrm{mix})} = \mathrm{PIT}_A \cdot \phi_A + \mathrm{PIT}_B \cdot \phi_B \tag{8.16}$$

where ϕ_A and ϕ_B are the volume fractions of oils A and B used in the emulsion.

The PIT appears to reach a constant value at 3–5% surfactant concentration when a POE nonionic containing a single POE chain length is used. When there is a distribution of POE chain lengths in the surfactant, the PIT decreases very sharply with increase in the concentration of the surfactant when the degree of oxyethylenation is low and less sharply when the degree of oxyethylenation is high.

As the oil–water ratio increases in an emulsion with a fixed surfactant concentration, the PIT increases. However, fixed ratios of surfactant to oil give the same PIT, even when the oil–water ratio varies. The higher the surfactant–oil ratio, the lower the PIT.

Additives, such a paraffin, that decrease the polarity of the oil phase increase the PIT, whereas those, such as oleic acid or lauryl alcohol, that increase its polarity lower the PIT. The addition of salts to the aqueous phase decreases the PIT of emulsions made with POE nonionics (Shinoda, 1970).

Since the PIT of a hydrocarbon–water emulsion stabilized with a POE nonionic surfactant is, as might be expected, related to the cloud point of an aqueous solution of the nonionic saturated with that hydrocarbon (Chapter 4), these effects on the PIT of emulsions stabilized by POE nonionics are readily understood. As mentioned in the discussion (Chapter 4, Section IIIB) of the effect of solubilizate on the cloud points of POE nonionics, long-chain aliphatic hydrocarbons that are solubilized in the inner core of the micelle increase the cloud point, whereas short-chain aromatic hydrocarbons and polar materials that are solubilized between the POE chains decrease it. They have the same effect on the PIT: long-chain aliphatic hydrocarbons increase the PIT and therefore tend to form stable *O/W* emulsions, whereas short-chain aromatics and polar additives decrease it and tend to form stable *W/O* emulsions (Shinoda, 1964). An increase in the length of the POE chain increases the cloud point and the PIT and consequently increases the tendency to form *O/W* emulsions, consistent with the generalization that the more water-soluble the emulsifier, the greater its tendency to form *O/W* emulsions.

IV.C. The HLD Method

The method developed originally for microemulsion formulation (Section II above) has been adapted (Salager, 1983, 2000) to macroemulsion formation. In this method, the value of the left-hand side of equation 8.10 or 8.11 is called the *hydrophilic-lipophilic deviation* (HLD). When the value equals zero, as in Section II, a microemulsion is formed; when the value is positive, a *W/O* macroemulsion is preferentially formed; when it is negative, an *O/W* macroemulsion is preferentially formed. The HLD is similar in nature to the Winsor *R* ratio (equation 5.2) in that when the HLD is larger than, smaller than, or equal to 0, *R* is larger than, smaller than, or equal to 1. The value of the HLD method is that, on a qualitative basis, it takes into consideration the other components of the system (salinity, cosurfactant, alkane chain length, temperature, and hydrophilic and hydrophobic groups of the surfactant). On the other hand, on a quantitative basis, it requires the experimental evaluation of a number of empirical constants.

V. DEMULSIFICATION

In some processes, the emulsification of two liquid phases is an undersirable phenonmenon. This often occurs when two immiscible phases are mixed together with considerable agitation, as in industrial extraction processes. However, probably the most important case of undersirable emulsification is in the recovery of petroleum from oil reservoirs. Crude oil always is associated with water or brine in the reservoir and also contains natural emulsifying agents, such as asphaltenes and resins. These, particularly the asphaltenes, together with other components in the petroleum, such as the resins and waxes, form a thick, viscous interfacial film around water droplets, with their polar groups oriented toward the water and their nonpolar groups toward the oil. This interfacial film is highly viscous, producing very stable, viscous *W/O* emulsions. To break these emulsions and separate the petroleum from the water in them, various techniques are used, notably the addition of surfactants called *demulsifiers* or *demulsifying agents*. Demulsification and demulsifiers in petroleum recovery have been discussed by Angle (2001) and Sjoblom (2001), respectively, but there have been few systematic studies (Shetty, 1992; Bhardwaj, 1993).

Mechanisms involved in the demulsification by surfactants of petroleum *W/O* emulsions include adsorption of the surfactant at the oil–water interface and reduction of the interfacial tension, change in the nature of the interfacial film from a highly hydrophobic one to a less hydrophobic one (and, consequently, one more wettable by water), reduction of the viscosity of the interfacial film by penetration into it of the surfactant, and displacement of the original *W/O* emulsion stabilizers, particularly the asphaltenes, from the interface into the oil phase.

Since the chemical composition of the crude oil and the natural emulsifying agents contained in it vary greatly, depending upon the material from which it was formed and the conditions of its formation, no one surfactant demulsifier can be used. Instead, a "chemical cocktail" is used, containing different surfactants to perform the required functions. These include wetting agents, such as di(2-ethylhexyl) sulfoscuccinate, and various polymeric surfactants, such as POE polyoxypropylenes and POE alkylphenol-formaldehyde polymers. The structure of the POE (and polyoxypropylenated) material can be "tailored" to meet the different composition of the petroleum.

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PROBLEMS

1 List four different ways of distinguishing *O/W* from *W/O* macroemulsions.

2 Describe, or give the characteristic properties, of each of the following:

- **(a)** macroemulsion
- **(b)** nanoemulsion
- **(c)** microemulsion
- **(d)** multiple emulsion

3 Discuss the changes in interfacial tension that occur in the conversion of an *O/W* macroemulsion stabilized by a POE nonionic surfactant to a *W/O* macroemulsion upon raising the temperature above the cloud point.

4 Explain the relationship between γ_{OE}, γ_{WE}, spreading coefficient, and emulsion type.

5 An oil has an HLB of 10 for *O/W* emulsification. Calculate the percentages of $C_{12}H_{25}(OC_2H_4)_2OH$ and $C_{12}H_{25}(OC_2H_4)_8OH$ that should be used in attempting to emulsify this oil with a mixture of these two surfactants.

6 **(a)** Describe the effect of the following changes on the tendency of a system of a POE nonionic surfactant, an alkane, and water, to form an *O/W* emulsion:

1. Increase in the temperature from 25°C to 40°C
2. Change in the alkane from *n*-octane to *n*-dodecane
3. Increase in the number of carbon atoms of the hydrophobic group of the surfactant.

(b) Describe the effect in each case if the surfactant is an anionic surfactant.

7 Suggest and explain conditions under which the HLB value for a particular surfactant will vary

(a) for a POE nonionic surfactant

(b) for an ionic surfactant

9 Dispersion and Aggregation of Solids in Liquid Media by Surfactants

In many products and processes it is important to obtain significantly stable, uniform dispersions of finely divided solids. Paints, pharmaceutical preparations, drilling muds for oil wells, pigments, and dyestuffs are commonly used as suspensions of finely divided solids in some liquid medium.

However, when a preformed, finely divided solid is immersed in a liquid, it often does not form a stable dispersion. Many of the particles remain attached (aggregated) in the form of clumps, and those particles that do disperse in the liquid very often clump together again to form larger aggregates that settle out of the suspension. In addition, even when the particles do disperse in the liquid, the dispersion may be viscous or thin, the particles may remain dispersed for different lengths of time, and the sensitivity of the dispersions to molecular environmental conditions (pH, temperature, additives) may vary greatly. Before discussing the role of surfactants in these systems and the relation of the structure of the surfactant to its performance as a dispersing agent, it is necessary to review the forces between particles in these suspensions, since these forces, together with the particle size and shape and the volume of the dispersed phase, determine the properties of the suspension.

I. INTERPARTICLE FORCES

Tadros (1986) describes four types of interparticle forces: hard sphere, soft (electrostatic), van der Waals, and steric. Hard-sphere interactions, which are repulsive, become significant only when particles approach each other at distances slightly less than twice the hard-sphere radius. They are not commonly encountered.

I.A. Soft (Electrostatic) and van der Waals Forces: DLVO Theory

The soft (electrostatic) and van der Waals interparticle forces are described in the well-established theory of the stability of lyophobic dispersions (colloidal

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

dispersions of particles that are not surrounded by solvent layers). This theory was developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948) and therefore is called the *DLVO theory.* It assumes a balance between repulsive and attractive potential energies of interaction of the dispersed particles. Repulsive interactions are believed to be due either to the similarly charged electrical double layers surrounding the particles or to particle–solvent interactions. Attractive interactions are believed to be due mainly to the van der Waals forces between the particles. To disperse the particles, the repulsive interactions must be increased to the point where they overcome the attractive interactions; to aggregate the particles, the reverse must be done.

The total potential energy of interaction V is the sum of the potential energy of attraction V_A and that of repulsion V_R:

$$V = V_A + V_R \tag{9.1}$$

The potential energy of attraction in a vacuum for similar spherical particles of radius a whose centers are separated by a distance R is given by the expression (Hamaker, 1937)

$$V_A = \frac{-Aa}{12H} \tag{9.2}$$

where A is the Hamaker (van der Waals) constant and H is the nearest distance between the surfaces of the particles $(= R - 2a)$ when H is small $(R/a \leq 5)$. The attractive potential energy is always negative because its value at infinity is zero and decreases as the particles approach each other.

In a liquid dispersion medium, A must be replaced by an effective Hamaker constant,

$$A_{\text{eff}} = (\sqrt{A_2} - \sqrt{A_1})^2 \tag{9.3}$$

where A_2 and A_1 are the Hamaker constants for the particles and the dispersion medium, respectively (Vold, 1961). As the particles and the dispersion medium become more similar in nature, A_2 and A_1 become closer in magnitude and A_{eff} becomes smaller. This results in a smaller attractive potential energy between the particles.

The potential energy of repulsion V_R depends on the size and shape of the dispersed particles, the distance between them, their surface potential Ψ_0, the dielectric constant ε_r of the dispersing liquid, and the effectiveness thickness of the electrical double layer $1/\kappa$ (Chapter 2, Section I), where

$$1/\kappa = \left(\frac{\varepsilon_r \varepsilon_0}{4\pi F^2 \sum_i C_i Z_i^2} \right)^{1/2} \tag{2.1}$$

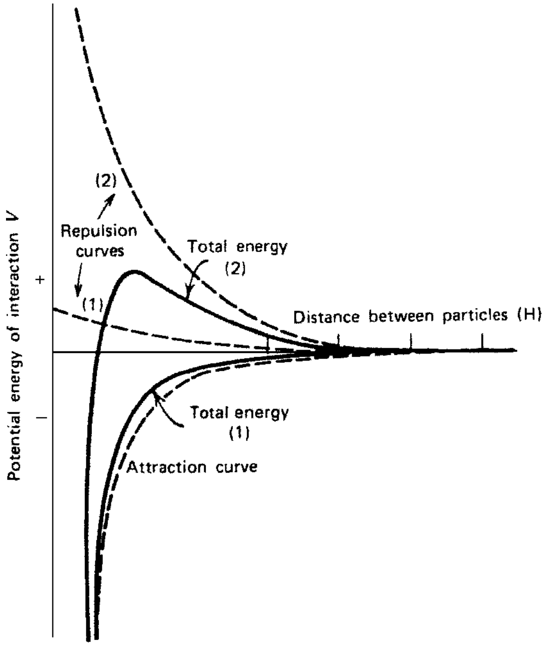

FIGURE 9-1 Total interaction energy curves (obtained by summation of attraction and repulsion curves) for two repulsion curves of different heights.

For two spherical particles (Lyklema, 1968) of radius a, when $a/(1/\kappa)$ $(=\kappa a) \ll 1$, i.e., small particles and a relatively thick electrical double layer,

$$V_R = \frac{\varepsilon_r a^2 \Psi_0^2}{R} e^{-\kappa H} \tag{9.4}$$

When $a/(1/\kappa)$ $(=\kappa a) \gg 1$, i.e., large particles and a relatively thin electrical double layer,

$$V_R = \frac{\varepsilon_r a \Psi_0^2}{2} \ln\left(1 + e^{-\kappa H}\right) \tag{9.5}$$

The potential energy of repulsion is always positive, since its value at infinity is zero and increases as the particles approach each other.

Typical plots of V_A and V_R as a function of the distance H between the particles are shown in Figure 9-1, together with the plot of the total energy of interaction V, the sum of V_A and V_R. The particles tend to aggregate at those distances where the attractive potential energy is greater than the repulsive energy and V becomes negative.

The form of the curve for the total potential energy of interaction V depends on the ratio of the particle size to the thickness of the electrical double layer

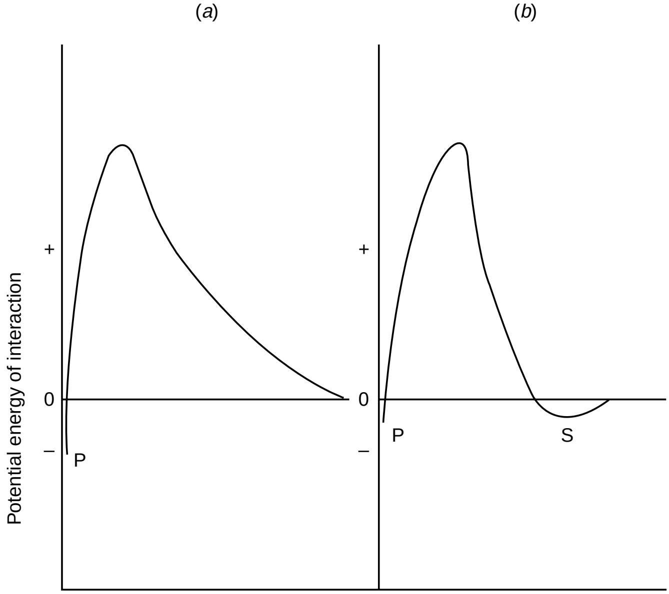

FIGURE 9-2 Potential energy of interaction as a function of distance of particle separation and ratio of particle size to thickness of the electrical double layer, $a/(1/\kappa) = \kappa a$. (a) $\kappa a \ll 1$; (b) $\kappa a \gg 1$.

$a/(1/\kappa) = \kappa a$ (Figure 9-2), the electrolyte concentration (Figure 9-3), and the surface potential Ψ_0 (Figure 9-4).

When $\kappa a \gg 1$ (i.e., when the ratio of particle size to thickness of the electrical double layer is very large), the curve for V (Figure 9-2*b*) shows a secondary minimum (S) at a relatively large distance of separation between the particles in addition to the primary minimum (P). Particles may therefore aggregate at a relatively large distance between the particles. This type of aggregation is sometimes called *flocculation* to distinguish it from aggregation in the primary minimum, which is termed *coagulation*. Since the depth of the secondary minimum is rather shallow, flocculation of this type is easily reversible and the particles can be freed by agitation. Particles larger than a few micrometers, especially flat ones, may show this phenomenon.

The effect on V of the addition of electrolyte to the (aqueous) dispersion medium and the consequent compression of the double layer is shown in Figure 9-3. With increase in the concentration of indifferent electrolyte, κ increases and the energy barrier to coagulation ($V_{\max}$) decreases and may even disappear, consistent with the known coagulation of lyophobic colloidal dispersions by electrolyte. Figure 9-4, illustrating the effect of the surface potential of the particles on V, indicates that the energy barrier to coagulation increases with increase in the surface potential. The effect of adsorption of surfactant ions onto the particle surface is apparent. When

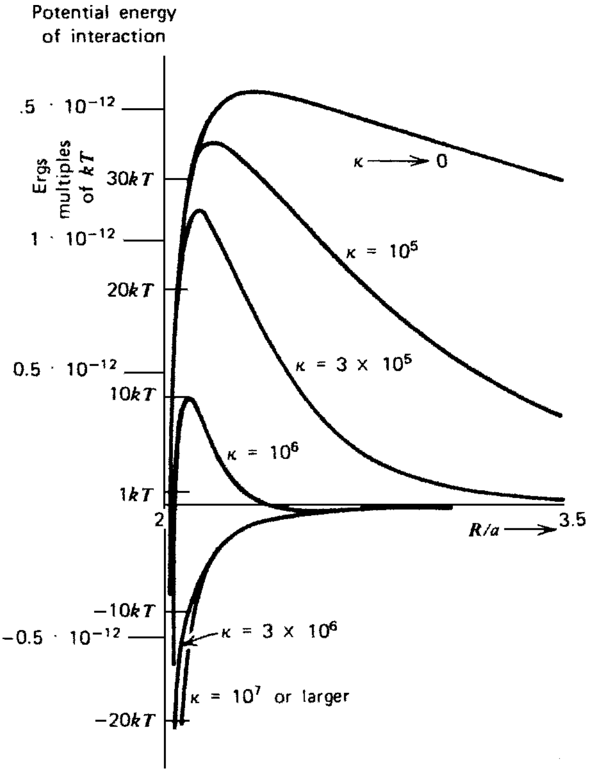

FIGURE 9-3 Influence of electrolyte concentration (as measured by κ) on the total potential energy of interaction of two spherical particles. Reprinted with permission from J. Th. G. Overbeek in *Colloid Science*, Vol. 1, H. Kruyt (Ed.), Elsevier, Amsterdam, 1952, Chap. 6, p. 276.

adsorption results in an increase in the potential of the particle at the Stern layer, the stability of the dispersion is increased; when it results in a decrease in that potential, the stability of the dispersion is lowered. Since the range of thermal energies for dispersed particles may go as high as $10\,kT$, an energy barrier of greater than $15\,kT$ is usually considered necessary for a stable dispersion.

The stability of a colloidal dispersion is usually measured by determining the rate of change in the number of particles n during the early stages of aggregation. The rate of diffusion-controlled coalescence of spherical particles in a disperse system as a result of collisions in the absence of any energy barrier to coalesence is given by the von Smoluchowski equation

$$\frac{-dn}{dt} = 4\pi D r n^2 \tag{8.2}$$

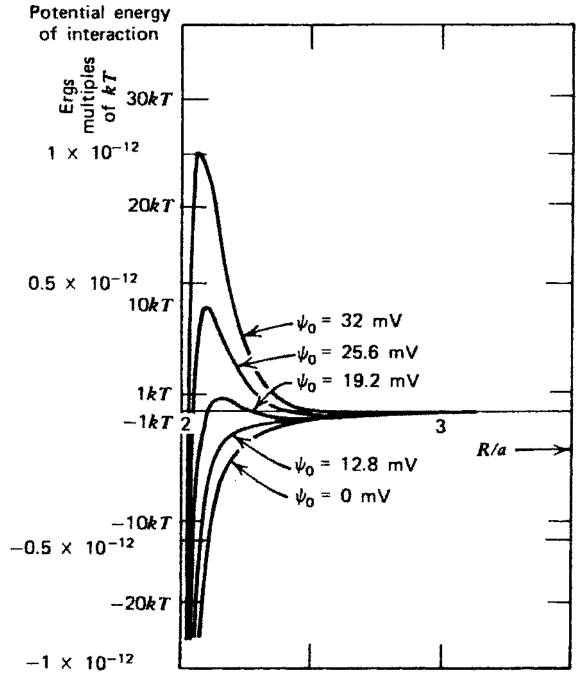

FIGURE 9-4 Influence of the surface potential ψ_0 on the total potential energy of interaction of two spherical particles. Reprinted with permission from J. Th. G. Overbeek in *Colloid Science*, Vol. 1, H. Kruyt (Ed.), Elsevier, Amsterdam, 1952, Chap. 6, p. 277.

Since, from the Einstein equation, $D = kT/6\pi\eta a$ (equation 8.1), and $r = 2a$,

$$\frac{-dn}{dt} = \frac{4kT}{3\eta} n^2 = K_0 n^2 \tag{9.6}$$

where K_0 is the rate (constant) for diffusion-controlled coalescence. Experimentally determined rate constants K_0 for coalescence in the absence of an electrical barrier to aggregation can be determined by adding electrolyte to the dispersion until no further rate increase is obtained (Parfitt, 1972).

In the presence of an energy barrier $V_{\max}$ to coalescence,

$$\frac{-dn}{dt} \propto K_0 n^2 e^{-V_{\max}/kT} = K n^2 \tag{9.7}$$

where K is the rate of (slow) coalescence in the presence of an energy barrier. The stability W of the dispersion is defined as the ratio of the rate constants in the absence and presence of an energy barrier, respectively:

$$W_{st} = \frac{K_0}{K} \propto e^{V_{\max}/kT} \tag{9.8}$$

Log W_{st} is therefore a linear function of $V_{\max}/kT$ and is usually plotted against some function of the concentration of an additive to show its effect on the energy barrier to aggregation and hence on the stability of the dispersion. From theoretical considerations, log W_{st} has been shown (Fuchs, 1934; Reerink, 1954) to be an approximately linear function of the log of the concentration of the electrolyte in the liquid phase during the initial phase of slow coagulation at constant surface potential. Values of W_{st} are usually calculated by determining the change in particle concentration with time during the initial period of aggregation, either directly by counting particles per unit volume under the microscope (Garvey, 1972) or ultramicroscope (Ottewill, 1966; Parfitt, 1972), in a manner similar to that used for determining the stability of emulsions (Chapter 8, Section IB), or indirectly from measurements of optical density using a spectrophotometer (Ottewill, 1960, 1966).

When absolute values of W_{st} are not required and the optical density D is proportional to n, measurements of optical density as a function of time may be used to show the effect of some additive on the stability of the dispersion. Thus $\log(dt/dD)_{t\to 0}$ is plotted versus the log of the concentration of added surfactants (Watanabe, 1960) to show their effect on some AgI sols. Values of $(dt/dD)_{t\to 0}$ are obtained from the reciprocal of the initial slope of a plot of D versus time. Alternatively, the rate constant K may be determined (McGown, 1966) from the slope of a linear plot of $1/n$ versus t (equation 8.4).

From the preceding discussion of the DLVO theory and equations 9.1–9.5 and 9.8, it is apparent that the stability of a lyophobic dispersion is a function of the particle radius and surface potential, the ionic strength and dielectric constant of the dispersing medium, the value of the Hamaker constant, and the temperature. Stability is increased by increase in the particle radius or surface potential or in the dielectric constant of the medium and by decrease in the effective Hamaker constant, the ionic strength of the dispersing liquid, or the temperature.

1. Limitations of the DLVO Theory The effect of a surfactant on the stability of a lyophobic dispersion, according to DLVO theory, is therefore limited to its effect on the surface potential of the dispersed particles, the effective Hamaker constant, and the ionic strength of the dispersing liquid (in the case of ionic surfactants). Since surfactants are generally used at very low concentrations, the main effect of ionic surfactants would be expected to be on the surface potential of the dispersed particles, and this is observed experimentally. The addition of an ionic surfactant to a dispersion and its adsorption onto the dispersed particles generally increases the stability of dispersions whose particles are of the same sign as the surfactant and decreases the stability of those whose particles are of opposite sign. However, the situation is sometimes considerably more complex (see below). In the case of nonionics, the DLVO theory limits their effect to a change in the effective Hamaker constant, and although this may account for part of their effect, it is probably insufficient to account for the very large increase in stability produced by many POE nomonics.

Therefore, although the DLVO theory is very useful in predicting the effect of ionic surfactants on electrical barriers to aggregation, to fully understand the effects of surfactants on dispersion stability, other factors must also be considered. They include the following: (1) Adsorption of the surfactant onto dispersed particles that are larger than colloidal in size may change the contact angle (Chapter 2, Section IIF) they make with the dispersing liquid. This change may affect the stability of the dispersion. An increase in the contact angle may cause the particles to flocculate from the dispersion or to float to the surface. A decrease in the contact angle may increase dispersibility (Parfitt, 1972). (2) Surfactants that are polymeric or that have long POE chains may form nonelectrical steric barriers to aggregation in aqueous media. The presence of these barriers, which are not covered by the DLVO theory, may increase the stability of dispersions, even when electrical barriers are reduced or absent. (3) In liquids of low dielectric constant, electrical barriers to aggregation are largely absent. In spite of this, stable dispersions of solids in these liquids can be prepared by use of surfactants that produce steric barriers to aggregation. (4) There is currently no accepted experimental method for measuring the potential at the Stern layer of the dispersed particles. The zeta potential, which is often used to estimate that potential, merely indicates the electrical potential at the plane of shear (the distance from the charged surface where the solvated particle and the solvent move with respect to each other). For highly solvated particles in particular this may be quite different from the Stern layer potential.

I.B. Steric Forces

As mentioned above, dispersions of solids in liquids can be stabilized by steric barriers and in the absence or presence of electrical barriers. Such barriers can be produced when portions (lyophilic chains) of molecules adsorbed onto the surfaces of the solid particles extend into the liquid phase and interact with each other. These interactions (Tadros, 1986) produce two effects: (1) a mixing effect and (2) an entropic effect. The mixing effect is due to solvent–chain interactions and the high concentration of chains in the region of overlap. This effect becomes significant when adjacent particles approach each other to slightly less than twice the thickness of the adsorbed layer on the particles. It depends greatly upon the relative strengths of solvent–chain and chain–chain interactions. When the solvent–chain interaction is stronger than the chain–chain interaction, the free energy of the system is increased when the regions containing the extended portions of the adsorbed molecules overlap, and an energy barrier is produced to a closer approach. When the chain–chain interaction is greater than the solvent–chain interaction, the free energy is decreased when the regions overlap, and attraction rather than repulsion occurs. The entropic effect is due to restriction of the motion of the chains extending into the liquid phase when adjacent particles approach each other closely. This effect becomes particularly important when the separation between particle surfaces becomes less than the thickness of the adsorbed layer.

Both effects increase with increase in the number of adsorbed chains per unit of surface area on the dispersed particles and with the length of the chains extending into the liquid phase. However, there is an optimum chain length for maximum stabilization, since the possibility of flocculation also increases with chain length. In cases where the nature of the liquid phase can be varied, steric stabilization is best when one group of the adsorbed molecule has only limited solubility in the liquid phase, thereby promoting its adsorption onto the solid to be dispersed, while the other (long) group has good compatibility or interaction with the liquid phase, assisting its extension into it (Lee, 1986). Some examples may serve to illustrate the application of both DLVO theory and steric factors to the explanation of stability changes in dispersions.

1. The addition of a cationic surfactant (Figure 9-5) to a negatively charged colloidal dispersion (Ottewill, 1960) at first decreased the zeta potential of the dispersed particles and the stability of the dispersion until the zeta potential and the potential at the Stern layer had been reduced to zero, at which point stability reached a minimum. With further addition of surfactant, however, the stability increased again. This was because further adsorption of surfactant by the dispersed particles beyond the point of zero charge caused them to acquire an electrical potential of positive sign. At still higher concentrations of the cationic surfactant, the stability of the dispersion decreased again, although the zeta potential continued to become more positive, the decrease in stability this time being due to compression of the electrical double layer by the increased concentration of ionic surfactant.

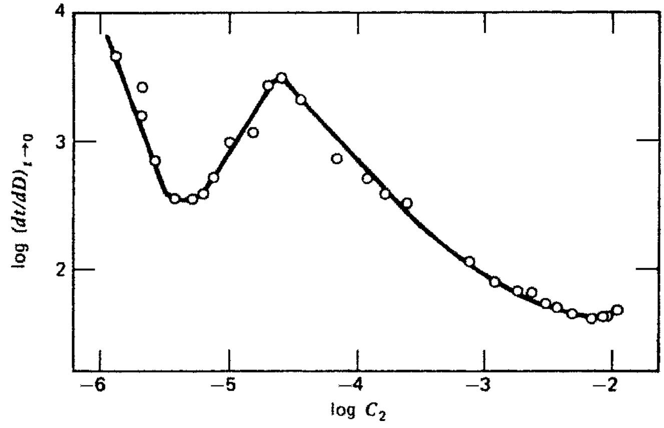

FIGURE 9-5 Stability $[\log(dt/dD)_{t\to 0}]$ of a negatively charged colloid dispersion of AgI as a function of log C_1, the concentration of added cationic surfactant, dodecylpyridinium bromide. Reprinted with permission from R. H. Ottewill and M. C. Rastogi, *Trans. Faraday Soc.* **56**, 866 (1960).

2. In another investigation (Garvey, 1972), adsorption of a polymeric ionic surfactant onto dispersed particles of the same sign initially caused an increase in both the stability of the dispersion and the zeta potential of the particles. Still higher concentrations of surfactant, however, resulted in a considerable decrease in the zeta potential of the particles. At these lower potentials, moreover, the stability of the dispersion showed a sharp increase. Here the explanation was that the decrease in the zeta potential was the result of a shift in the plane of shear (at which the zeta potential is measured) away from the surface of the particles resulting from the thicker layer of adsorbed polymeric surfactant at the higher liquid phase concentrations. This thicker adsorbed layer constituted a steric barrier to the aggregation of the particles and sharply increased the stability of the dispersion.
3. The addition of a POE nonionic surfactant to an aqueous dispersion whose particles carried a small negative charge increased the stability of the dispersion to flocculation by a polyvalent cation (Ottewill, 1968). The stability increased sharply as adsorption of the nonionic surfactant onto the particles approached a close-packed vertical monolayer. Stability at this point was very high even when the electrical double layer was compressed by large amounts of electrolyte or the charge removed by lowering the pH of the dispersion. The high stability at this point was attributed to the closely packed, strongly solvated POE chains. Close approach of the dispersed particles to each other would require desolvation of these chains, which consequently constituted an energy barrier to aggregation of the particles. This high stability may also be due, at least in part, to a decrease in the effective Hamaker constant (equation 9.3). The adsorption onto a dispersed particle of a layer that is chemically more similar to the solvent than to the particle itself causes a decrease in the effective Hamaker constant. The attraction between particles decreases rapidly with increase in the thickness of this adsorbed layer (Vold, 1961). Since the POE chain of the surfactant is highly hydrated, it is to be expected that adsorption of a POE nonionic surfactant onto the dispersed particles will decrease the effective Hamaker constant. As the adsorbed surfactant becomes more closely packed, the thickness of the adsorbed layer increases greatly and the attraction between the dispersed particles should show a sharp decrease. The stability of the dispersions at this point should consequently be very high.

II. ROLE OF THE SURFACTANT IN THE DISPERSION PROCESS

The dispersal of a solid in a liquid has been described as a three-stage process (Parfitt, 1968, 1972): (1) wetting the powder and displacing trapped air, (2) deaggregation or fragmentation of the particle clusters, (3) prevention of reaggregation of the dispersed particles.

II.A. Wetting of the Powder

For a liquid to disperse a finely divided solid, it must first wet each particle cluster completely. This will involve, at least in the final stages of wetting, a spreading type of wetting, in which the air is completely displaced from the surface by the wetting medium. The driving force for this process, as we have seen, is the spreading coefficient:

$$S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \tag{6.1}$$

and for spontaneously spreading wetting, this quantity must be positive, producing a contact angle of 0°. Wetting agents are therefore added to the liquid to lower γ_{SL} and/or γ_{LA} by adsorption at those interfaces, especially in those cases where a liquid of high γ_{LA}, such as water, is the dispersion medium. Reduction of the contact angle has been correlated with increased dispersibility in aqueous medium (Parfitt, 1972).

II.B. Deaggregation of Fragmentation of Particle Clusters

Once the particle clusters have been wet by the suspending liquid, they must be dispersed in it. This may be accomplished by the surface-active agent in two ways: (1) By being adsorbed in "microcracks" in the solid, it may reduce the mechanical work needed to fragment the particles of solid (Rebinder, 1947). These microcracks are believed to be formed in crystals under stress, but are self-healing and disappear when the stress is removed. The adsorption of surface-action agents onto the surfaces of these microcracks may increase their depth and reduce their self-healing ability and thus reduce the energy required to rupture solid particles mechanically. (2) The adsorption of an ionic surfactant onto the particles in a cluster may cause the individual particles in the cluster to acquire an electrical charge of similar sign, resulting in their mutual repulsion and dispersion in the liquid phase.

II.C. Prevention of Reaggregation

Once the solid has been dispersed in the liquid, it is necessary to prevent the individual dispersed particles from coming together once again to form aggregates. Reduction of the thermodynamic instability of the dispersion ($\gamma_{SL} \times \Delta A$, where ΔA is the increase in interfacial area as a result of the dispersion) relative to the aggregated state can be reduced, although probably not eliminated, by adsorption of surfactants there in such a fashion as to reduce γ_{SL}. In the case of aqueous dispersions, this means adsorption of the surfactant with the hydrophilic group oriented toward the aqueous phase. The tendency for the dispersed particles to aggregate can be further reduced by adsorption of surfactant onto the dispersed particles in such a fashion as to increase or produce energy barriers to aggregation. These energy barriers, examples of which have been described earlier, may be electrical or nonelectrical in nature. In both cases, solvation of the lyophilic heads probably plays an important, not fully understood role in stabilizing the dispersion.

III. COAGULATION OR FLOCCULATION OF DISPERSED SOLIDS BY SURFACTANTS

Surfactants may be used not only to disperse solids in liquid media, but also to coagulate or flocculate solids already dispersed in liquid media. This may be accomplished with surface-active agents by a number of different mechanisms.

III.A. Neutralization or Reduction of the Potential at the Stern Layer of the Dispersed Particles

Electrostatic attraction of surface-active ions to oppositely charged sites on the surface of the dispersed particles results in a lowering of the electrical energy barrier to the close approach of two particles to each other, thereby promoting coagulation. If the surfactant ion contains only one hydrophilic (ionic) group, electrostatic attraction of that group to the oppositely charged site on the surface of the particle may, in addition, result in adsorption of the surfactant ion with its hydrophobic group oriented toward the liquid phase. In aqueous media this will cause an increase in the solid–liquid interfacial tension and an increase in the contact angle that the liquid makes with the particle (increased water repellence), with the result that the solid tends either to flocculate from the medium or to be expelled to the air–solution interface. The concentrations of surfactants needed to coagulate hydrophobic colloidal dispersions are orders of magnitude less than those of inorganic ions of the same charge, longer-chain surfactants being more efficient than shorter-chain ones (Ottewill, 1960). On the other hand, orientation of the surfactant in this fashion may make the particles more dispersible in nonaqueous media (e.g., in the “flushing” of pigments [Moilliet, 1955]).

Surfactants that at low concentrations cause flocculation in aqueous media by this mechanism may act as deflocculators at higher concentrations. This phenomenon is due to adsorption of additional surfactant molecules by interaction of their hydrophobic groups with those of the previously adsorbed surfactant molecules and with their hydrophilic groups oriented toward the aqueous phase (Figure 2-12, Chapter 2, Section IIC). Adsorption of this additional surfactant probably occurs only after the potential at the Stern layer has been completely neutralized by adsorption of the oppositely charged surfactant (i.e., only after the point of zero charge has been reached). Adsorption of this additional surfactant consequently produces a potential of the same sign as the surfactant ion (opposite in sign to that of the original potential at the Stern layer), which helps to redisperse the particle. This additional adsorbed surfactant appears to be much more easily removed than the originally adsorbed layer by reducing the concentration of the surfactant in the dispersion. Dilution of the dispersion therefore may reaggregate the particles.

If the surfactant is one that has two or more hydrophilic (ionic) groups at different points in the molecule, then adsorption of the surfactant onto an oppositely charged surface may be with one hydrophilic group oriented toward the surface and with the other(s) oriented toward the aqueous phase. In this case, adsorption of the surfactant will neutralize or reduce the electrical potential of the surface but may not cause flocculation of the particles from the aqueous phase.

III.B. Bridging

Flocculation by a bridging mechanism may occur in two ways: (1) A long (usually polymeric) surfactant molecule containing functional groups at various points in the molecule that can adsorb onto sites on the surface of adjacent particles may attach itself to two or more dispersed particles, thereby binding them together in a loose arrangement. This type of bridging appears to occur when adsorption of the surfactant onto the surface of the dispersed particles is low, thus providing ample sites for attachment of surfactant molecules extending from other particles (Kitchener, 1972). Thus, adsorbed molecules that act as steric stabilizers when their particle surface coverage is high can act as flocculants when their surface coverage is low and surface sites for adsorption are available on adjacent particles. Bridging by this mechanism generally reaches a maximum at about one-half total surface coverage. (2) When surfactant molecules are adsorbed onto dispersed particles in such a fashion that the adsorbed molecules extend into the liquid phase and these extended portions are capable of interacting with each other, bridging may occur by interaction of the extended portions attached to different particles. This type of bridging may occur with long polymeric surfactant molecules when surface coverage by the adsorbed molecules is so high that sites for attachment by the previously described bridging mechanism are scarce. As mentioned above, this type of bridging is prone to occur when the liquid phase is not a good solvent for the portion of the adsorbed molecules extending into it and is minimized when there is strong interaction between those portions and the liquid phase. Therefore, it may also occur with the usual type of surfactant (containing one terminal hydrophilic group and a hydrophobic group) when adsorption onto the dispersed particles is with the hydrophobic groups oriented toward the aqueous phase and surface coverage is so high that the hydrophobic group is forced to extend into the aqueous phase. Under these conditions, hydrophobic groups from two dispersed particles may come together to reduce their surface energies, thereby bridging the two particles (Somasundaran, 1966). In either of these cases, the energy released upon bridging must be greater than the energy required to desolvate the bridging groups. Consequently, strong interaction of the extended groups with the solvent may inhibit bridging.

III.C. Reversible Flocculation

This technique is useful when it is desired to flocculate an aqueous dispersion temporarily (e.g., for ease in filtration, handling, or storage), but in a condition where it can readily be deflocculated. The particles are first treated with an ionic surfactant that imparts a potential to the particles sufficiently high to disperse them. Then the dispersion is treated with sufficient easily soluble electrolyte to compress the electrical double layer surrounding the particles to the point where flocculation occurs. Subsequent dilution of the flocculated material (and consequent reduction of the electrolyte concentration) redisperses it when desired (Stewart, 1935).

Reversible flocculation of aqueous dispersions stabilized sterically with POE nonionics can be accomplished by increasing the temperature. With increase in temperature, the hydrogen bonding of the POE chains to water is reduced and the chains tend to aggregate, flocculating the dispersion. Upon reducing the temperature, the chains hydrate again and the particles redisperse.

IV. THE RELATION OF SURFACTANT CHEMICAL STRUCTURE TO DISPERSING PROPERTIES

For the purpose of this discussion, the term *dispersing properties* is used for those properties of a surfactant that enable it to adsorb onto a solid particle and to produce by this adsorption energy barriers of sufficient height to disperse the particle in a (generally aqueous) liquid medium. Surfactants sharing these properties are termed *dispersing agents*. Thus, although wetting of the solid particle by the dispersing liquid is a necessary first step in the dispersion process, a surfactant that produces only wetting of the particle surface without raising energy barriers of sufficient height to disperse the particle is not demonstrating dispersing properties in this system. It is acting merely as a wetting agent. On the other hand, a surfactant that does not promote wetting of the particle surface yet produces energy barriers of sufficient height for dispersion of the particle is considered as demonstrating dispersion properties. Of course, there are surfactants that demonstrate both wetting and dispersing power in a particular system, but wetting agents are often added to dispersing agents to compensate for their lack of wetting power. This discussion is therefore restricted to those structural features that bear on the ability of the surfactant to form energy barriers to aggregation.

IV.A. Aqueous Dispersions

For the formation of electrical barriers to aggregation, ionic surfactants are generally used. When the solid to be dispersed is essentially nonpolar (e.g., hydrophobic carbon) and the dispersing medium is aqueous, conventional surfactants (containing one terminal hydrophilic group and a long hydrophobic group) may be used, since adsorption of the surface-active ion onto the essentially uncharged solid particles causes them all to acquire a charge of the same sign and to repel each other. An electrical barrier to aggregation will then have been formed. In addition, the adsorbed surfactant ions will be oriented with their hydrophobic groups toward the nonpolar particle and their hydrophilic heads toward the aqueous phase, producing a lowering of the solid–liquid interfacial tension. Since the efficiency of adsorption (Chapter 2, Section IID) in this case increases with increase in the length of the hydrophobic group, longer-chain compounds can be expected to be more efficient dispersing agents for this type of particle than shorter-chain ones.

When the solid to be dispersed is charged, however, conventional surfactants may not be useful. If a conventional surfactant of opposite charge is used, then flocculation rather than dispersion will probably occur until the charge on the particles has been neutralized. Only then may dispersion, caused by adsorption of additional surfactant ions onto the now uncharged particles, occur. Therefore, this is generally not an efficient method of forming the dispersion. On the other hand, if a conventional surfactant of the same sign as the particle is used, the situation is not improved much. Although adsorption of the surfactant ion may increase the electrical energy barrier to aggregation, and generally occurs with the ionic hydrophilic head oriented away from the similarly charged particle surface (and hence oriented toward the aqueous phase), repulsion between the adsorbing surfactant ion and the similarly charged particle inhibits adsorption. Only at relatively high concentrations of the surfactant in the aqueous phase is adsorption sufficiently high to stabilize the dispersion.

As a result, ionic dispersing agents for use with charged or polar solids in aqueous medium usually have ionic groups at various positions in the surfactant molecule and hydrophobic groups containing polarizable structures such as aromatic rings or ether linkages rather than saturated hydrocarbon chains. The multiple ionic groups probably serve a number of purposes: (1) They inhibit adsorption of the surfactant molecule with the hydrophobic group facing the aqueous phase. On oppositely charged particles, one of the multiple ionic groups in the surfactant molecule can be adsorbed onto an oppositely charged site while another may be oriented toward the aqueous phase, thus preventing adsorption of the surfactant with its hydrophobic group facing the aqueous phase and the consequent tendency of the dispersion to flocculate. (2) They increase the efficiency of the surfactant molecule in producing an electrical barrier to aggregation. The larger the number of ionic charges of similar sign per molecule, the greater the increase in the electrical barrier per adsorbed molecule on similarly charged particles and the greater the neutralization of charge leading to formation of an electrical barrier of sign similar to that of the surfactant on oppositely charged particles. (3) They permit extension of the surfactant molecule into the aqueous phase (thus creating a steric barrier to coalescence) without an increase in the free energy of the system. The decrease in free energy resulting from hydration of the ionic hydrophilic groups may compensate for the free energy increase due to the increased contact of the hydrophobic group with the aqueous phase.

The difference in the properties of aqueous dispersions treated with oppositely charged surfactants containing a single hydrophilic group and a hydrophobic group or containing two hydrophilic groups at opposite ends of the hydrophobic group has been discussed by Esumi (1986). The dispersions were, in all cases, flocculated by the addition of the oppositely charged surfactant. However, when the surfactant used had a single hydrophilic group the flocculated particles were easily dispersed (“flushed”) into toluene. When it had two hydrophilic groups at opposite ends of the hydrophobic group the flocculated material could not be dispersed in toluene, but formed a film at the toluene–water interface. In the first case the flocculated particles were lipophilic because of the orientation of the hydrophobic groups of the adsorbed surfactant molecules toward the aqueous phase; in the second case each hydrophobic group extending into the aqueous phase had a terminal hydrophilic group which prevented the particles from becoming lipophilic.

The polarizable structures in the hydrophobic group of the dispersing agent offer sites by means of which the surfactant can interact with charged sites on the particle size and consequently adsorb via its hydrophobic group. It has been shown, for example, that alumina adsorbs surfactants onto its surface by polarization of the π electrons in the adsorbate (Snyder, 1968). This gives the adsorbed surfactant molecules the proper orientation for acting as dispersing agents in aqueous media.

The adsorption from aqueous solution of surfactants with two hydrophilic and two hydrophobic groups (gemini surfactants, Chapter 12) onto oppositely charged sites on solid particle surfaces—cationic geminis onto clay particles (Li, 2000), anionic geminis onto limestone particles (Rosen, 2001)—results in one hydrophilic group oriented toward the solid surface and the second oriented toward the aqueous phase. The solid particles are dispersed in both cases.

Examples of commonly used dispersing agents containing multiple ionic groups and aromatic hydrophobic groups are β-naphthalene–sulfonic acid–formaldehyde condensates and ligninsulfonates (Chapter 1, Section IA2).

Polyelectrolytes prepared from ionic monomers are often excellent dispersing agents for solids in aqueous media. Their multiple ionic groups can impart high surface charges to the solid particles onto which they adsorb. When the tendency to adsorb onto the surface of a solid particle of an individual functional group attached to the backbone of the polymer is low, the number of such groups in the macromolecule must be large enough that the total adsorption energy of the molecule is sufficient to anchor it firmly to the particle surface. Homopolymers, consequently, are not as versatile as copolymers, since the former have a more limited range of substrates to which they anchor well, especially when the molecular weight of the polymer is low. Copolymers of monomers with different structural characteristics yield products that can adsorb strongly to a wider variety of substrates. Thus, acrylic acid or maleic anhydride copolymerized with styrene yields dispersing agents, with aromatic nuclei attached to the backbone of the polymer, that can adsorb onto a wide range of substrates. For nonpolar substrates, short-chain monomers, such as acrylic acid, are copolymerized with long-chain monomers, e.g., lauryl methacrylate, to increase the binding energy of the dispersing agent to the particle surface (Buscall, 1986).

With increase in the number of hydrophilic groups per molecule of dispersing agent, there is often an increase in its solubility in water and this may cause a decrease in its adsorption onto a particular particle surface (Garvey, 1972), especially when the interaction between the surfactant and the particle surface is weak. In some cases, therefore, the adsorption of the dispersing agent onto a particle surface and its dispersing power for it may go through a maximum, with increase in the number of ionic groups in the surfactant molecule. Thus, in the preparation of aqueous dispersions of dyestuffs (Prazak, 1970), hydrophobic dyestuffs, which would be expected to interact strongly with the hydrophobic groups of ligninsulfonate dispersing agents, produce dispersions that are stable to heat when the ligninsulfonate is highly sulfonated. Hydrophilic dyestuffs, on the other hand, which would not be expected to interact strongly with this type of dispersing agent, form dispersions with it that are not stable to heating. A less highly sulfonated ligninsulfonate, however, produces dispersions that are heat stable with these hydrophilic dyestuffs. Presumably, the high solubility of the highly sulfonated dispersing agent at the elevated temperature removes it from the surface of the hydrophilic, but not the hydrophobic, dyestuff. In order to get equal heat stability with the hydrophilic dyestuffs, a less soluble (less sulfonated) dispersing agent must be used.

Particles can also be dispersed in the aqueous medium by the use of steric barriers. For this purpose, both ionic and nonionic surfactants can serve as steric stabilizers. As discussed previously, steric barriers to aggregation are produced when the adsorbed surfactant molecules extend chains into the aqueous phase and inhibit the close approach of two particles to each other. As mentioned in Section IB above, steric stabilization increases with increase in the length of the chains extending into the liquid phase. Consequently, polymeric surfactants, both ionic and nonionic, are commonly used as steric stabilizers since the length of the chain extending into the liquid phase can often be increased conveniently by increasing the degree of polymerization. Surfactants with ionic groups distributed along the length of molecule can, as mentioned previously, produce such steric barriers, and their effectiveness in doing so increases with the distance into the aqueous phase to which the molecules can extend. Hence longer compounds are more effective than shorter ones (Garvey, 1972), provided that increased solubility in the aqueous phase does not decrease their adsorption onto the particle surface significantly. Nonionic surfactants of the POE type are excellent dispersing agents for many purposes because their highly hydrated POE chains extend into the aqueous phase in the form of coils that present excellent steric barriers to aggregation. In addition, the thick layer of hydrated oxyethylene groups similar in nature to the aqueous phase would be expected to produce a considerable decrease in the effective Hamaker constant (equation 9.3) and a consequent sharp decrease in the van der Waals attraction between particles. For the adsorbed layer to be an effective steric barrier, its thickness must generally exceed 25 Å. For a POE chain in aqueous medium, this is usually attained when there are more than 20 EO units in the chain, although stable aqueous dispersion of solid particles by POE nonionics with much smaller POE chains has been observed. Thus, ferric oxyhydroxide (β-FeOOH), precipitated by the hydrolysis of ferric chloride in the presence of a POE C_{12}–C_{15} alcohol with an average of 4 oxyethylene units, was obtained as a dispersion of nano-sized particles stable for several months (O'Sullivan, 1994).

Block and graft polymers are widely used as steric stabilizers. Since the two blocks are separated in the molecule, they can be designed chemically, by use of the proper functional groups and degree of polymerization, for optimum efficiency and effectiveness. One block should be designed to adsorb strongly onto the particle surface (and also have limited solubility in the liquid phase), the other block(s) to extend into the liquid phase (good compatibility with and/or interaction with the liquid phase). One commonly used type is the polyoxyethylene–polyoxypropylene

(POE–POP) block copolymer, made from ethylene oxide and propylene oxide. For dispersions in aqueous media, products of structure

$$H(OCH_2CH_2)_x[OCH(CH_3)CH_2]_y(OCH_2CH_2)_zOH$$

are used. The central POP block, $[OCH(CH_3)CH_2]_y$, which is not soluble in water, is attached to the surface of the solid particle, while the water-soluble POE chains extend into the aqueous phase as random coils and produce a steric barrier to the close approach of adjacent particles. Another type that is used has the structure

$$H[OCH(CH_3)CH_2]_x(OCH_2CH_2)_y[OCH(CH_3)CH_2]_zOH$$

Here, the POE block is central, surrounded by POP chains. This type is most effective in nonaqueous liquids in which the POE block has limited solubility and the POP blocks have good solubility, causing the former to adsorb efficiently onto the solid particles, while the latter extend into the liquid phase to produce the steric barrier. In both of these types, steric stabilization increases with increase in the length of the chain extending into the liquid phase. The increase in solubility with increase in the length of the POE chain can, in this type of compound, readily be compensated for by increasing the length of the POP hydrophobic groups. Thus the most effective dispersing agents of this type would be expected to be those in which both the POE and POP chains are long.

When the particles to be dispersed are hydrophilic, then adsorption of conventional POE nonionic surfactants occurs with the POE chains oriented toward the hydrophilic particle surface and the hydrophobic chains oriented toward the aqueous phase (Glazman, 1986). Stabilization of the dispersion is then achieved by bilayer formation, with the hydrophobic groups of the two surfactant layers oriented toward and associated with each other, while the POE chains of the second layer are oriented toward the aqueous phase. Consistent with this explanation is the lack of any stabilization effect until the surfactant concentration in the aqueous phase is considerably above the concentration required for hydrophobic group association, i.e., the CMC.

IV.B. Nonaqueous Dispersions

In nonaqueous media of low dielectric constant, electrical barriers to aggregation are usually ineffective and steric barriers are generally required to disperse solid particles. As the dielectric constant of the dispersing medium increases, electrical barriers become more significant. The steric barriers may arise either from the energy required to desolvate, as the particles approach each other, the portions of the adsorbed surfactant molecules extending into the dispersing medium, or from the decrease in the entropy of the system as these portions of the adsorbed molecules are restricted in their movement or arrangement by the close approach of two particles. The effective Hamaker constant and the consequent attraction between particles can also be reduced by the use of molecules that, on adsorption, extend out from the particle surface lyophilic groups of a nature similar to that of the dispersing liquid.

Thus, the dispersion of carbon in aliphatic hydrocarbons is improved by the addition of alkylbenzenes (van der Waarden, 1950, 1951). The benzene rings are presumably adsorbed onto the surface of the carbon and the aliphatic chains extend into the dispersing liquid. Increase in the length and the number of alkyl groups attached to the benzene nucleus increases the stability of the dispersion. In somewhat similar fashion, the dispersion of two ionic solids (halite and sylvite) in nonpolar solvents was improved by the addition of long-chain amines (Bischoff, 1960). An increase in the chain length of the amine increased its efficiency as a dispersing agent.

A mechanism for electrical charging of solid particles in nonaqueous media has been proposed by Fowkes (1982), involving acid–base interaction between neutral particle and neutral adsorbed dispersing agent. Charge separation between them occurs when the charged dispersing agent is desorbed and incorporated into bulky reverse micelles in the nonaqueous phase with the charged sites in the interior of the micelle. Acidic or basic polymers are consequently effective dispersing agents for solid particles in nonaqueous media.

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PROBLEMS

1 List three different ways of increasing the stability of a dispersion of an ionic solid in a liquid.

2 Discuss two different mechanisms by which the POE chain in a nonionic surfactant adsorbed on a finely divided hydrophobic substance can help stabilize a dispersion of that substance in water.

3 Explain why Ca^{2+} is much more effective than Na^{+}, at the same molar concentration in the solution phase, as a flocculant for an aqueous dispersion stabilized by an anionic surfactant.

4 Which one of the following, at the same molar concentration in the solution phase, would be expected to be the most effective stabilizer for a dispersion of a positively charged hydrophilic solid in heptane?

(a) $C_{12}H_{25}(OC_2H_4)_2OH$

(b) $C_{12}H_{25}(OC_2H_4)_8OH$

(c) $C_{12}H_{25}N^{+}(CH_3)_3Cl^{-}$

(d) Sodium ligninsulfonate

5 A dispersion of an ionic solid in aqueous medium is precipitated by small amounts of $C_{12}H_{25}SO_4^-Na^+$ or $C_{12}H_{25}(OC_2H_4)_{10}OH$ but is unaffected by the addition of $C_{12}H_{25}N^+(CH_3)_3Cl^-$. What conclusions regarding the solid can be drawn from these data?

6 Discuss the effect of the following surfactants on an aqueous dispersion of a water-insoluble salt of a polyvalent metal whose particles are positively charged:

(a) A small amount of $C_{12}H_{25}SO_4^-Na^+$

(b) A small amount of $C_{12}H_{25}(OC_2H_4)_{10}OH$

(c) A small amount of $C_{12}H_{25}N^+(CH_3)_3Cl^-$

(d) A large amount of $C_{12}H_{25}C_6H_4SO_3^-Na^+$

7 Explain why a gemini surfactant (with two hydrophobic and two hydrophilic groups in the molecule, Chapter 12) is a much better dispersing agent than a similar surfactant with only one hydrophobic and one hydrophilic group in the molecule for oppositely charged solids but not much better for similarly charged solids.

10 Detergency and Its Modification by Surfactants

Since detergency is by far the largest single use for surfactants, there is a voluminous literature on the subject. In spite of that, it is only in recent years that a real understanding of the factors involved in the cleaning process has started to emerge and a great deal about the subject still remains obscure. This is undoubtedly due to the complexity of the cleaning process and the large variations in soils and substrates encountered. Since several books have been devoted to various aspects of detergency (Cutler, 1986; Lai, 1997; Showell, 1998; Broze, 1999; Friedli, 2001a), this discussion will cover only those areas that are pertinent to the role of surfactants in the cleaning process.

The term *detergency*, as used to describe a property of surface-active agents, has a special meaning. As a general term, it means cleaning power, but no surfactant by itself can clean a surface. The term *detergency*, when applied to a surface-active agent, means the special property it has of enhancing the cleaning power of a liquid. This it accomplishes by a combination of effects involving adsorption at interfaces, alteration of interfacial tensions, solubilization, emulsification, and the formation and dissipation of surface charges.

I. MECHANISMS OF THE CLEANING PROCESS

Three elements are present in every cleaning process: (1) the substrate (the surface that is to be cleaned), (2) the soil (the material that is to be removed from the substrate in the cleaning process), and (3) the cleaning solution or "bath" (the liquid that is applied to the substrate to remove the soil). The difficulty in developing a unified mechanism for the cleaning process lies in the almost infinite variety of the first two elements—the substrate and the soil. The substrate may vary from an impervious, smooth, hard surface like that of a glass plate to a soft, porous, complex surface like that of a piece of cotton or wool yarn. The soil may be liquid or solid (usually a combination of both), ionic or nonpolar, finely or coarsely ground, inert or reactive toward the cleaning bath. As a result of this great variability of substrate and soils, there is no one single mechanism of detergency, but rather a number of different mechanisms, depending on the nature of substrate

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ISBN 0-471-47818-0

and soil. The bath used is generally a solution of various materials, collectively called the *detergent*, in the cleaning liquid. Except in the case of dry cleaning, which is covered later in this section, the liquid in the bath is water.

In general, cleaning consists essentially of two processes: (1) removal of the soil from the substrate and (2) suspension of the soil in the bath and prevention of its redeposition. This second process is just as important as the first, since it prevents redeposition of the soil onto another part of the substrate.

I.A. Removal of Soil from Substrate

Soils are attached to substrates by various types of forces and as a result are removed from them by different mechanisms. This discussion is restricted to the removal of soils by mechanisms in which surfactants play a major role; it will not cover the removal of soil by mechanical work, or chemical reagents such as bleaches, reducing agents, or enzymes. Substances that are chemisorbed via covalent bond formation can generally be removed only by chemical means that destroy those bonds (e.g., by use of oxidizing agents or enzymes); soils that can be removed by the use of surfactants are generally attached by physical adsorption (van der Waals forces, dipole interactions) or by electrostatic forces. The removal of soil by surfactants generally involves their adsorption onto the soil and substrate surfaces from the cleaning bath (Schwuger, 1982). This adsorption changes interfacial tensions and/or electrical potentials at the soil–bath and substrate–bath interfaces in such a manner as to enhance the removal of the soil by the bath.

Soils whose removal from substrates can be enhanced by the presence of surfactants in the cleaning bath are generally classified according to the mechanisms by which they are removed. Liquid soils, which may contain skin fats (sebum), fatty acids, mineral and vegetable oils, fatty alcohols, and the liquid components found in cosmetic materials, are generally removed by the *roll-back* mechanism. Solid soils may consist either of organic solids, such as mineral or vegetable waxes, that can be liquefied by the application of heat or the action of additives, or of particulate matter, such as carbon, iron oxide, or clay particles, that cannot be liquefied. The former are generally removed, after liquefaction, by the roll-back mechanism; the latter, by the production of repulsive electrical potentials on soil and substrate surfaces.

Evidence is accumulating that maximum detergency may be associated with the presence of an insoluble, surfactant-rich phase—the middle phase discussed in Chapter 5, Section III. Thus, soap forms dispersed particles of an insoluble surfactant-rich product in hard water in the presence of certain surfactants known as *lime soap dispersing agents* agents (LSDA), described in Section II below. This product, although insoluble in the cleaning bath, shows high surface activity and high detergency (Weil, 1976). Commercial linear alkylbenzenesulfonate (LAS) in hard water in the presence of certain POE nonionics forms a suspension of insoluble particles that solubilizes mineral oil (Smith, 1985). The suspension shows better detergency than LAS by itself in water of the same hardness (Smith, 1985). In oily soil detergency by POE nonionics (Section IB2 below), maximum detergency is obtained 15–30°C above the cloud point of the nonionic, where particles of a surfactant-rich phase are present in the cleaning bath.

1. Removal of Liquid Soil Removal of liquid (oily) soil by aqueous baths is accomplished mainly by a *roll-back* or *roll-up* mechanism in which the contact angle that the liquid soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath.

Figure 6-3 illustrates the situation of a liquid soil adhering to a substrate in the presence of air. The reversible work to remove the liquid oily soil O from the substrate, the work of adhesion W_a (equations 6.12 and 6.13) is given by the expressions

$$W_{O/S(A)} = \gamma_{SA} + \gamma_{OA} - \gamma_{SO} \tag{10.1}$$

$$= \gamma_{OA}(\cos\theta + 1) \tag{10.2}$$

where θ is the contact angle, measured in the liquid soil phase, at the soil–substrate–air junction. Figure 10-1 illustrates the situation where the air is replaced by a cleaning bath. The work of adhesion of the liquid soil for the substrate is now given by the expression

$$W_{O/S(B)} = \gamma_{SB} + \gamma_{OB} - \gamma_{SO} \tag{10.3}$$

$$= \gamma_{OB}(\cos\theta + 1) \tag{10.4}$$

and the contact angle by the expression

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} \tag{10.5}$$

When surfactants of the proper structure are present in the bath, they will adsorb at the substrate–bath (*SB*) and liquid soil–bath (*OB*) interfaces in such a fashion (i.e., with the hydrophilic group oriented toward the aqueous bath) as to reduce γ_{SB} and γ_{OB}, with consequent reduction in the work to remove the soil from the substrate. Reduction in γ_{SB} will also cause a decrease in cos θ and an increase in θ, resulting in the observed roll-back of the liquid soil. Many investigators of oily soil removal,

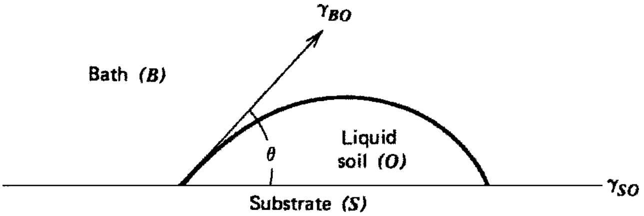


FIGURE 10-1 Contact angle at the bath–liquid soil–substrate junction.

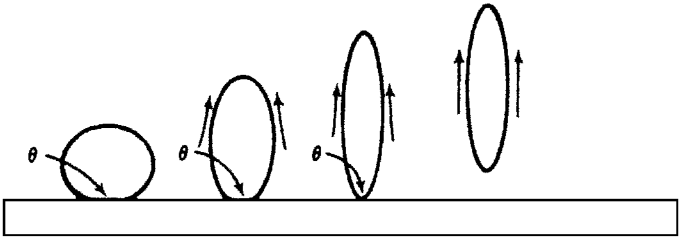


FIGURE 10-2 Complete removal of oil droplets from substrate by hydraulic currents (arrows) when θ remains constant at >90°. Reprinted with permission from A. M. Schwartz, in *Surface and Colloid Science*, Vol. 5, E. Matijevic (Ed.), Wiley, New York, 1972, p. 212.

both on textile and hard surfaces, have found that reduction of γ_{OB} (Dillan, 1979, 1984; Matson, 1980; Pierce, 1980; Aronson, 1983) and/or increase in θ, measured in the oily soil phase (Rubingh, 1982), correlates well with increase in detergency. In some cases, this low γ_{OB} value may be associated with the separation of an insoluble surfactant-rich phase (Chapter 5, Section III). In many cases, γ_{SB} is reduced to tht point where $\gamma_{SB} - \gamma_{SO}$ is negative, with resulting increase in θ to a value greater than 90°. Such a situation is illustrated in Figure 10-2.

If the contact angle is 180°, the bath will spontaneously completely displace the liquid soil from the substrate; if the contact angle is less than 180° but more than 90°, the soil will not be displaced spontaneously but can be removed by hydraulic currents in the bath (Figure 10-2) (Schwartz, 1972). When the contact angle is less than 90°, at least part of the oily soil will remain attached to the substrate, even when it is subjected to the hydraulic currents of the bath (Figure 10-3) (Schwartz, 1971, 1972), and mechanical work or some other mechanism (e.g., solubilization, see below) is required to remove the residual soil from the substrate.

In high-speed spray cleaning, a critical factor is the dynamic surface tension reduction of the surfactant solution (Chapter 5, Section IV), rather than its

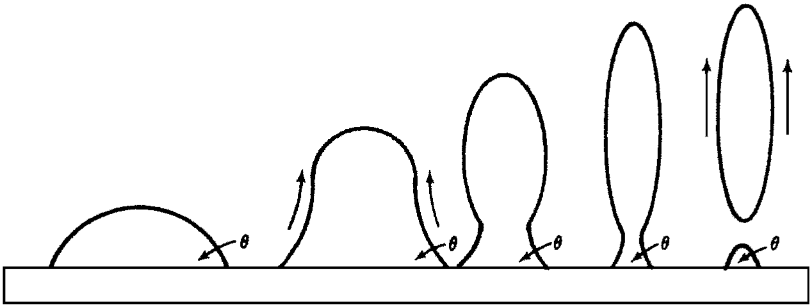


FIGURE 10-3 Rupture and incomplete removal of large oil droplets by hydraulic currents (arrows) when θ remains constant at <90°. A small droplet remains attached to the substrate. Reprinted with permission from A. M. Schwartz, in *Surface and Colloid Science*, Vol. 5, E. Matijevic (Ed.), Wiley, New York, 1972, p. 211.

equilibrium surface tension value, since under these cleaning conditions equilibrium values are not attained. Suifactants that reduce the surface tension to the lowest values in short times exhibit the best soil removal (Prieto, 1996).

2. Removal of Solid Soil

Liquefiable Soil The first stage in the removal of this type of soil is believed to be liquefaction of the soil (Cox, 1986). Penetration of the soil by surfactant (and associated water molecules) from the cleaning bath with resulting liquefaction may be a key process in the removal of this type of soil (Cox, 1984). In cases where penetration of the solid soil by surfactants or other additives does not occur, an increase in the temperature of the cleaning process may result in its liquefaction. The liquefied soil is then removed by the roll-back mechanism described above (Cox, 1987).

Particulate Soil Removal of particulate solid soil by aqueous baths is accomplished by the following mechanisms:

1. *Wetting of the substrate and the soil particles by the bath.* Adhesion of small solid particles to solid substrate is greatly diminished by immersion in water because of interaction of the water with substrate and particles. The presence of water results in the formation of electrical double layers at the substrate–liquid and particle–liquid interfaces. These electrical double layers almost always result in charges of similar sign on substrate and particle with a resulting mutual repulsion that, when superimposed on the preexisting van der Waals attraction, causes a diminution of the net adhesion (Chapter 9). In addition, water may cause the substrate surface, especially if it is of a fibrous nature, to hydrate and swell, resulting in an increase in the distance between particle and substrate.

The tendency of the bath B to spread over the soil particle P or the substrate S is given by the spreading coefficients (Chapter 6), $S_{B/P}$ and $S_{B/S}$, respectively, where

$$S_{B/P} = \gamma_{PA} - \gamma_{PB} - \gamma_{AB} \tag{10.6}$$

and

$$S_{B/S} = \gamma_{SA} - \gamma_{SB} - \gamma_{AB} \tag{10.7}$$

(Subscripts PA, SA, and AB refer to the particle–air, substrate–air, and air–bath interfaces, respectively.) If the spreading coefficient is positive, then spreading occurs spontaneously; if not, mechanical work must be done to wet the surface completely. Adsorption of surfactant from the bath at the air–bath interface or onto soil or substrate (with the hydrophilic group oriented toward the bath) can reduce γ_{AB}, γ_{PB}, or γ_{SB}, respectively, and thereby increase the tendency to wet the soil and/or substrate. Since the soil particle or the substrate is often hydrophobic, with the consequence that γ_{PA} or γ_{SA}, respectively, is low, mechanical work is often necessary to wet both the soil and the substrate completely with the bath. This is one of the reasons that washing is always accompanied by some mechanical work.

2. *Adsorption of surfactant and other bath components (e.g., inorganic ions) at the substrate–liquid and particle–liquid interfaces.* This causes a decrease in the work required to remove the particle from the substrate, since the free energy change per unit area involved in this process is the work of adhesion W_a (Chapter 6, Section IB), given in this case by the expression

$$W_a = \gamma_{SB} + \gamma_{PB} - \gamma_{SP} \tag{10.8}$$

Adsorption of surfactants at these interfaces can result in a decrease in γ_{SB} and γ_{PB}, with a consequent decrease in the work required to cause removal of the particle from the substrate.

3. However, the major mechanism by means of which particulate soil is removed from the substrate by nonmechanical means is probably through the increase *in the negative electrical potentials at the Stern layers* (Chapter 2, Section I, and Chapter 9) *of both soil and substrate on adsorption onto them of anions from the bath.* As might be expected, anionic surfactants in the bath are particularly effective for increasing negative potentials on both substrate and particulate soil, although inorganic anions in the bath, especially polyvalent ones, are also useful for this purpose. This increase in the negative potentials of both substrate and soil increases their mutual repulsion (i.e., the energy barrier for removal of the soil from the substrate is decreased and, at the same time, the energy barrier for soil redeposition is increased [Kling and Lange, 1960]).

Since the adsorption of nonionics onto soil or substrate does not significantly increase its electrical potential at the Stern layer, this mechanism of soil removal is probably not a major one for nonionics, and nonionics are generally not as effective as anionics for the removal of particulate soil (Albin, 1973). On the other hand, they appear to be very effective for producing steric barriers (see below) for the prevention of soil redeposition.

The reduced work of adhesion between soil and substrate caused by adsorption onto them of surfactant molecules with their hydrophulic groups oriented toward the bath, the reduced van der Waals attraction resulting from hydration of these hydrophulic groups (Chapter 9), and the increased electrostatic repulsion caused by the increase in magnitude of the electrical potentials of similar sign on soil and substrate all facilitate the separation of soil and substrate. However, mechanical work is almost always required to remove solid soil from the substrate. Larger particles are removed more readily than smaller particles. In small particles the ratio of the area of true contact A_0 of the particle with the substrate to total surface area A is high. Any noninertial force tending to remove the particle is proportional to $A - A_0$, whereas the force holding the particle to the substrate is proportional to A_0 (Schwartz, 1972). Thus, a greater force per unit area is required to remove a small particle than a large one. In addition, the streaming velocity resulting from mechanical agitation approaches zero near the surface of the substrate, and therefore small particles encounter only the smaller velocities. Soil particles smaller than 0.1 μm cannot be removed from fibrous textile material at all (Lange, 1967).

I.B. Suspension of the Soil in the Bath and Prevention of Redeposition

Suspension of the soil in the bath and the prevention of redeposition are also accomplished by different mechanisms, depending on the nature of the soil.

1. Solid Particulate Soil: Formation of Electrical and Steric Barriers; Soil Release Agents The formation of electrical and steric barriers is probably the most important mechanism by which solid soil is suspended in the bath and prevented from redepositing on the substrate. Adsorption of similarly charged (almost always negative) surfactant or inorganic ions from the bath onto the detached soil particles increases their electrical potentials at the Stern layer, causing mutual repulsions and preventing agglomeration (Chapter 9, Section IA). Adsorption of POE nonionic surfactants with their hydrated POE chains oriented toward the bath also prevents agglomeration of soil particles by reducing van der Waals attraction between them and by producing a steric barrier to their close approach to each other (Chapter 9, Section IB).

Adsorption in similar fashion of other bath components onto the substrate or soil can also produce electrical and steric barriers to the close approach of soil particles to the substrate, thus inhibiting or preventing the redeposition of soil particles. Special components, called *soil release agents* or *antiredeposition agents*, are often added to the bath for this purpose. These are generally polymeric materials that by adsorption onto the fabric or soil produce a steric and sometimes also an electrical barrier to the close approach of soil particles (Trost, 1963).

Thus, sodium carboxymethylcellulose, used in laundry detergents, adsorbs onto cotton and increases its negative charge, thereby enhancing its repulsion of (negatively charged) soil. Polyacrylates are also used for this purpose (Bertleff, 1998). POE terephthalate polyesters are used for polyester fabrics. They adsorb on the (hydrophobic) polyester with their POE groups oriented towards the aqueous bath phase, making the fabric surface hydrophilic and causing it to repel oily soil particles (O'Lenick, 1999). For polyester or polyester/cotton fabrics, methylhydroxyethylcellulose is also very effective (Carrion Fite, 1992).

2. Liquid Oily Soil

Solubilization Solubilization has long been known to be a major factor in the removal of oily soil and its retention by the bath. This is based upon the observation (Ginn, 1961; Mankowich, 1961) that oily soil removal from both hard and textile surfaces becomes significant only above the CMC for nonionics and even for some anionics having low CMCs, and reaches its maximum only at several times the CMC. A considerable amount of research has been devoted to the removal of oily soil by POE nonionic surfactants, particularly from polyester or polyester/cotton (Benson, 1982, 1985, 1986; Dillan, 1979, 1984; Pierce, 1980; Raney, 1987; Miller, 1993). Optimal oily soil detergency has been correlated (Benson, 1986; Raney, 1990, 1991) with the PIT (Chapter 8, Section IVB), both for POE nonionic surfactants and for POE nonionic–anionic mixtures. As discussed in Chapter 5, Section III, γ_{OW} reaches its minimum value at the PIT. Moreover, the solubilization of nonpolar material (Chapter 4, Section IB7) increases markedly with separation of the surfactant-rich middle phase. Thus, conditions are optimum at the PIT for the removal of oily soil by the roll-back mechanism and its retention in the bath via solubilization. On the other hand, a relationship has been found between the interfacial tension in the *supersolubilization region*, i.e., in the oil-swollen aqueous micellar region close to the three-phase region (Figure 5-5), and oily soil detergency (Tongcumpou, 2003). Although the interfacial tension is not at its minimum and the solubilization parameter (Chapter 8, Section II) is not at its maximum at that point, the removal of the oily soil investigated was close to the maximum and avoided the complications of a three-phase system.

Liquid-crystalline phase or microemulsion formation between surfactant, water, and oily soil accompanies oily soil removal from hydrophobic fabrics such as polyester (Raney, 1987; Yatagai, 1990). It has been suggested (Miller, 1993) that maximum soil removal occurs not by solubilization into ordinary micelles, but into the liquid-crystal phases or microemulsions that develop above the cloud point of the POE nonionic.

The extent of solubilization of the oily soil depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature (Chapter 4, Section IB). At low bath concentrations only a relatively small amount of oily soil can be solubilized, whereas at high surfactant concentrations (10–100 times the CMC), solubilization is more similar to microemulsion formation (Chapter 8, Section II) and the high concentration of surfactant can accommodate a much larger amount of oily matter (Schwartz, 1972). With ionic surfactants, the use concentration is generally not much above the CMC; consequently, solubilization is almost always insufficient to suspend all the oily soil. When insufficient surfactant is present to solubilize all the oily soil, the remainder is probably suspended in the bath by macroemulsification Antiredeposition agents, such as the POE terephthate polyesters mentioped in Section 1 above, help prevent redeposition of suspended oily soil particles.

Macroemulsification For macroemulsification to be important, it is imperative that the interfacial tension between oily soil droplets and bath be low, so that emulsification can be accomplished with very little mechanical work. Here adsorption of surfactants at the oily soil–bath interface, with consequent lowering of the interfacial tensions, may play an important role. Emulsification was found to become a major factor when alkaline builders were added to a cleaning bath containing POE nonionic surfactant and the soil was mineral oil containing 5% oleic acid (Dillan, 1979). It is also involved in the suspension of liquefiable solid soil (Cox, 1987).

The ability of the bath to emulsify the oily soil is, however, in itself insufficient to keep all the soil from redepositing on the substrate (Schwartz, 1972). When the emulsified oil droplets impinge on the substrate, some of them may adhere to it in part, with the adhering portion tending to assume the equilibrium contact angle, unless the latter is 180° (i.e., unless complete oily soil removal by roll-back has been attained). This is in contrast to solubilization, which can result in complete removal of the oily soil from the substrate.

Mere dispersion of soil particles in the bath appears to be insufficient to accomplish effective cleaning. There appears to be no correlation between detergency and dispersing power of the bath. Surfactants with excellent dispersing powers are often very poor detergents and vice versa. On the other hand, increased adsorption onto substrate and soil, in the case of anionics and nonionics, and solubilizing power, in the case nonionics and fatty soil, appear to correlate well with detergency.

I.C. Skin Irritation

Skin irritation is an important factor in the selection of surfactants for use in cleaning materials that may contact the skin. The adsorption of monomeric surfactant from the cleaning product onto charged sites on the skin results in protein denaturation. All types of surfactants have been shown to produce skin protein denaturation in the order anionics > cationics > zwitterionics > amine oxides > POE nonionics (Miyazawa, 1984; Ohbu, 1984; Rhein, 1986). The order for anionics is sodium lauryl sulfate > C_{12}LAS > sodium laurate > AOS ≈ NaC_{12} AES (Kastner, 1980). No denaturation occurs with $C_{12}H_{25}(OC_2H_4)_6SO_4Na$ or $C_{12}H_{25}(OC_2H_4)_8OH$ (Ohbu, 1984).

The skin irritancy of anionics can be diminished by the addition of positively charged materials such as protein hydrolysates (Taves, 1986) or long-chain amine oxides that interact with the anionic and decrease its tendency to adsorb onto the skin, or by polymers that interact with them (Chapter 5, Section 1B5) to reduce the CMC and, consequently, the concentration of monomeric anionic surfactant (Goddard, 1994), since it is the latter that produces the skin irritation.

I.D. Dry Cleaning

Here the bath liquid used is not water but a hydrocarbon or chlorinated hydrocarbon. However, water in small amounts is always present in these systems and is a most essential ingredient.

Since oily soil is completely removed by the solvent, the main task for surfactants and other components of the bath is probably that of inhibiting redeposition of solid soil particles that are freed from the substrate when oily soil binding them to it is dissolved by the bath liquid. The rather high interfacial tension between textile fibers and the solvents used in dry cleaning promotes such soil redeposition. No clear generalizations have been deduced regarding the influence of type or concentration of surfactant on this process (Lange, 1967). Charge on the particles appears to play no role in the stabilization of the dispersion, probably because the potentials in the electrical double layers adjacent to the surfaces decay very rapidly in the nonpolar solvent. (Because of the very low dielectric constant, counterions are held very close to the surfaces.) However, there seems to be a correlation between adsorption of the surfactants present onto the substrate and soil particles and the prevention of redeposition of solid soil (von Hornuff, 1972). Surfactants are probably adsorbed with polar heads oriented toward the substrate and soil and hydrophobic chains oriented toward the nonpolar solvent. This manner of adsorption produces a steric barrier to agglomeration or redeposition of the particles, since any close approach to another surface will constrain the free mobility of the hydrophobic chains. This adsorption of surfactants appears to be increased by small amounts of water in the solvent that hydrate soil and substrate surfaces.

Water-soluble soil (sodium chloride, sugar) appears to be removed by solubilization (Chapter 4, Section II) into free water in the interior of surfactant micelles in the solvent. Surfactant micelles in nonpolar solvents are formed with the polar heads oriented into the interior of the micelle. Water is added to the dry-cleaning solvent and is solubilized into the interior of these micelles. Some of this water in the interior is bound strongly to the polar heads of the surfactants in the interior of the micelle and some is essentially free water. Studies (Aebi, 1959) have shown that it is the free water that dissolves water-soluble soil rather than the bound water. In the absence of any free water in the solvent, water-soluble soil is not removed to any significant extent. The water-soluble soil appears to be removed from fibrous surfaces by a process involving hydration of the soil followed by solubilization (Mönch, 1960; Rieker, 1973).

II. EFFECT OF WATER HARDNESS

The presence of polyvalent cations, notably Ca^{2+} and Mg^{2+}, in the bath water is invariably detrimental to the cleaning process for a number of reasons:

1. Adsorption of polyvalent cations onto the negatively charged substrate and soil reduces their electrical potentials, thus impeding soil removal and facilitating its redeposition. The detrimental effect attributed to this has been noted also in detergency studies involving only nonionic surfactants (Porter, 1967; Schwuger, 1971).
2. Polyvalent cations can act as linkages between negatively charged substrate and negatively charged soil, thus promoting soil redeposition (deJong, 1966). They can also act as linkages between the negatively charged hydrophilic groups of anionic surfactants and the negatively charged soil or substrate, causing adsorption of the former with their hydrophilic groups oriented toward the latter and their hydrophobic groups toward the bath. Adsorption with this orientation results in increases in γ_{SB} and γ_{PB}, the interfacial tensions at the substrate–bath and soil–bath interfaces, increasing the work of adhesion and impeding wetting and oily soil roll-back.

3. Adsorption of polyvalent cations onto solid soil particles dispersed in the bath can reduce their (negative) electrical potentials and cause them to flocculate and redeposite onto the substrate.
4. At high polyvalent cation concentrations, the corresponding metal salts of anionic surfactants and other anions (e.g., phosphates, silicates) in the bath may precipitate onto the substrate. In some cases, this may mask the presence of soil on the substrate (Rutkowski, 1971) or produce other deleterious effects (Vance, 1969; Brysson, 1971).

II.A. Builders

In addition to surfactants, a number of other materials are present in formulated laundry detergents. Among these are materials called builders. Their main purpose is to counter the detrimental effects of polyvalent cations on detergency. Polyvalent cations are introduced into the wash bath mainly by water hardness but may also come from soil or substrate. In addition, builders serve to increase the detersive effidency and effectiveness of surfactants and to supplement their beneficial effects on soil removal.

Builders perform the following primary functions, in order of decreasing importance:

1. *Sequestration, Precipitation or Ion Exchange*. These are the three mechanisms by which builders reduce the concentration of polyvalent cations in the wash bath. Excellent sequestration is provided by sodium and potassium polyphosphates, especially the tripolyphosphates which for decades were the builders of choice in laundry detergents. However, they are responsible for *eutrophication* (overfertilization of stagnant bodies of water) with adverse effects on aquatic organisms. As a result, use of polyphosphates in U.S. household detergents is limited to automatic dishwashing detergents. Precipitation by sodium carbonate effectively removes polyvalent cations from the wash liquor, but the insoluble calcium compounds which result can present an unsightly precipitate on washed goods. Sodium aluminosilicates (e.g., Zeolite A) physically trap polyvalent cations and exchange them for sodium ions. This builder is insoluble in water and is not suitable for liquid detergents. At present, the builder system in powdered laundry detergents consists of zeolite, carbonate, and low levels of polycarboxylate cobuilders.

Interest in effective biodegradable, nonphosphate sequestering builders that can also be used in liquid detergents continues to be active. Sodium citrate is the principal small-molecule commercial polycarboxylate builder at present even though it is only moderately effective. Other small molecules—polycarboxylates, ethylenediamino disuccinate, and tartrate mono/disuccinate—have been tested but have not attained large-scale usage.

Polymeric polycarboxylates, such as polyacrylates and acrylate–maleate copolymers, are finding usage as cobuilders in zeolite–carbonate builder systems. Polymers are finding increasing application in detergent formulations as dispersing agents, soil release agents, antiwrinkling additives, dye transfer inhibitors, fabric care additives, and other functionalities (Bertleff, 1998).

2. *Deflocculation and Dispersion of Particulate Soils.* This is accomplished by adsorption of the builder onto soil particles with a consequent increase in their negative electrical potentials, thus increasing their mutual repulsion. For this purpose polyphosphate and polycarboxylate ions, with their multiple negative charges, are particularly suited. Inorganic salts, in general, by decreasing the solubility of surfactants in the bath, promote their adsorption onto substrate and soil particles, and thereby increase their efficiency and effectiveness as soil dispersants.

3. *Alkalinity and Buffering.* High pH increases the negative potentials at soil and substrate and promotes cleaning. Buffering is necessary to prevent soil and substrate components from lowering the pH, with consequent lowering of surface potentials. Sodium carbonate is particularly effective for this purpose.

Current laundry detergents in powder form contain 8–25% surfactant and 30–80% builders. The builders are mainly inorganic salts, used at fairly high percentages, but a few organic polymeric materials are also used, at low percentages. Sodium polyacrylates have been recommended for use with sodium carbonate as builder. The polyacrylates prevent precipitation of insoluble carbonates (Nagarajan, 1985).

In addition to these primary functions, some builders are used for special purposes. Sodium silicates are used to prevent corrosion of aluminium parts in washing machines (they form a protective aluminium silicate coating), to prevent overglaze corrosion on china and, in powder detergents, as a structural agent to yield a crisp, nonsticky product. Organic polymers called *antiredeposition agents* are used, at low concentrations, to prevent redeposition of soil onto the substrate. Sodium carboxymethylcellulose is used at concentrations below 2% and in alkaline medium to prevent redeposition of soil onto cellulosic fibers. It adsorbs via H bonding to the cellulosic material and produces a (negatively charged) electrical barrier to the deposition of soil. It performs poorly on more hydrophobic synthetic fabrics, such as polyester, presumably because of poor adsorption. On such substrates nonionic cellulose derivatives, such as hydroxyethyl-, 2-hydroxypropyl-, and 3-hydroxybutylcellulose have been suggested as antiredeposition agents. The latter compound was reported to be the best of the three for use on polyester (Greminger, 1978). POE–polyoxypropylene copolymers (Chapter 9, Section VA) can also be used as antiredeposition agents on polyester. To be effective for this purpose, the molecules must adsorb onto the polyester via the polyoxypropylene group, leaving the POE chains free to extend into the aqueous phase and form a steric barrier against soil redeposition. For effective protection, the thickness of the adsorbed layer should exceed 25 Å (Gresser, 1985).

II.B. Lime Soap Dispersing Agents

Lime soap dispersing agents (LSDA) are surfactants that enable soap to act as an effective laundry detergent in hard water without the deposition of insoluble calcium soap. For a surfactant to act as an LSDA, it must possess a bulky hydrophilic group (e.g., an ester, ether, amido, or amino linkage between the terminal hydrophilic group and the hydrophobic group) and a straight-chain hydrophobic group. It is believed that, in the presence of hardness ions (Ca^{2+}, Mg^{2+}), the soap and LSDA form a mixed micelle that shows high surface activity, including detergency. The bulky hydrophilic group of the LSDA forces the mixed micelle, with its hydrophilic groups oriented toward the aqueous phase, to retain its convex curvature (Linfield, 1978) toward the water. Soap micelles by themselves are believed to invert in hard water, with their hydrophobic groups oriented toward the aqueous phase, producing insoluble lime soaps (Stirton, 1965).

An extensive investigation of tallow-derived surfactants as LSDA in soap formulations for laundry detergents revealed (Linfield, 1978) that anionic and particularly zwitterionic surfactants are the best surfactant types for use as LSDA. POE nonionics are very effective LSDA but have a deleterious effect on the detergency of soap, while cationics form water-insoluble salts with soap. Among the anionics, an *N*-methyl tauride, $RCON(CH_3)CH_2CH_2SO_3Na$ (Noble, 1972), a sulfated alkanolamide, $RCONHCH_2CH_2OCH_2CH_2OSO_3Na$ (Weil, 1970), and a sulfated POE alcohol, $R(OCH_2CH_2)_3OSO_3Na$ (Weil, 1966; Bistline, 1972), all based on a tallow-derived hydrophobic group, were found to be the most effective. Zwitterionic surfactants of the sulfobetaine type were found to be even more effective LSDA. Although a simple betaine, $RN(CH_3)_2CH_2COO^-$, showed only fair lime soap dispersing properties and poor detergency in a soap formulation, an amidosulfobetaine, $RCONH(CH_2)_3N^+(CH_3)_2CH_2CH_2CH_2SO_3{}^-$ (Parris, 1973, 1976), was the best LSDA among the materials studied. The corresponding sulfated material, $RCONH(CH_2)_3N^+(CH_3)_2CH_2CH_2CH_2OSO_3^-$ (Parris, 1976), and *N*-alkylsulfobetaine, $RN^+(CH_3)_2CH_2CH_2CH_2SO_3^-$ (Parris, 1973), were also very effective LSDA and showed even better detergency in a soap formulation. A coconut oil-derived amido hydroxysulfobetaine $RCONH(CH_2)_3N^+(CH_3)_2CH_2CHOHCH_2$-$SO_3^-$, showed excellent detergency in soap formulations in water of 1000 ppm hardness (Noble, 1980).

III. FABRIC SOFTENERS

Fabric softeners have two major functions: (1) to impart a soft *feel* to dried fabrics and (2) to reduce static cling. They also reduce drying time and thus extend the life of tumble-dried garments by reducing mechanically induced fiber damage. Their development, including environmental considerations and chemical structures, has been reviewed by Levinson (1999). Originally designed for use in the final rinse cycle of washing machines, fabric softeners have been modified for use in the drying cycle of automatic dryers. They impart softness by adsorbing onto the (negatively charged) fabrics via their positively charged hydrophilic head groups, with their hydrophobic groups oriented away from the surface, reducing γ_{SA} and the work of adhesion of water to the substrate. This reduces the shrinkage (reduction of substrate surface area) and resulting hard feel that accompanies the removal of water from the substrate. They reduce static cling by reducing the negative static charge present on most surfaces.

Currently used fabric softeners are all cationic surfactants of structural types (Puchta, 1993; Levinson, 1999; Friedli, 2001b, 2002):

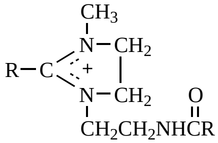
I. *Dialkyl Dimethylammonium Salts*

$$R_2N^+(CH_3)_2X^- \qquad (X^- \text{ is } Cl^- \text{ or } CH_3SO_4^-)$$

II. *Polyethenoxylated Diamido Quaternary Ammonium Salts*

$$(RCONHCH_2CH_2)_2N^+(CH_3)(CH_2CH_2O)_xHX^- \qquad (X^- \text{ is usually } CH_3SO_4^-)$$

III. *Amido Imidazolinium Salts*



X^- (X^- is usually $CH_3SO_4^-$)

IV. *Ester Quaternary Ammonium Salts (Ester Quats)*
  A. $(RCOOCH_2CH_2)_2N^+(CH_3)(CH_2CH_2OH)\cdot CH_3SO_4^-$
  B. $RCOOCH_2CH(OOCR)CH_2N^+(CH_3)_3Cl^-$

V. *Amidoester Quaternary Ammonium Salts (Amidoester Quat)*

$$RCOOCH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2NHCORCl^-$$

R is based upon tallow or hydrogenated tallow.

All of the above types are used as rinse cycle additives. Shorter-chain hydrophobic groups show little softening and unsaturated chains produce a dry, rather than a slick, feel. The Type I materials with saturated tallow chains give excellent softening performance but are now not used in Europe because of biodegradability considerations. For use in automatic clothes dryers, Type I in the form of the $CH_3SO_4^-$ salt is generally used, since the Cl^- may release corrosive hydrogen chloride. Type III materials are often used as drying cycle additives because of the difficulty of formulating them as rinse cycle additives. Type IV materials (ester quats) are now commonly used in Europe because of their excellent biodegradability. It appears that two ester groups are needed for ready biodegradability (Friedli, 2001b). Palm stearine fatty acids (60% C_{16} and 40% C_{18}) were found to give softening performance similar to that of tallow acids in IV A-type (triethanolamine-based) ester quat formulations. The addition of monoalkyl trimethylammonium halides increased the dye transfer inhibition properties of the formulation (Friedli, 2002).

Since these materials are all cationics that operate by adsorbing strongly onto fabric surfaces via their positively charged hydrophilic groups, when formulated with anionic surfactants for use in the wash cycle, both the softening properties of the cationic and the detergency properties of the anionic are reduced because of anionic–cationic interaction. When formulated with POE nonionics, the detergency of the POE nonionic appears not to be impaired, but the softening properties of the cationic are significantly reduced (Williams, 1981). An investigation of the use of alkyldimethylamine oxides as additives to ditallowdimethylammonium chloride fabric softeners found that octadecyldimethylamine oxides exhibited synergistic behavior with the quaternary ammonium compound in its softening effect on cotton towels and its prevention of static buildup on polyester fabrics (Crutcher, 1992). For fabric softening, the order of decreasing effectiveness is, consequently, rinse cycle > dryer cycle > wash cycle addition. Rinse cycle additives of Type I based upon hydrogenated tallow are the most effective. For static control, the order of decreasing effectiveness is dryer cycle > wash cycle > rinse cycle.

IV. THE RELATION OF THE CHEMICAL STRUCTURE OF THE SURFACTANT TO ITS DETERGENCY*

Correlations between the chemical structure of the surfactant and its detergency are complicated by the differing soils and substrates to be cleaned, by the amount and nature of builders present, by the temperature and hardness of the water used in the bath, and by the different mechanisms by means of which soils are removed. Correlations are therefore valid only when many of these variables are specified and controlled.

IV.A. Effect of Soil and Substrate

1. Oily Soil Nonpolar soil has been found to be removed from hydrophobic substrates (e.g., polyester) more effectively by POE nonionics than by anionics (Fort, 1968; McGuire, 1975), and investigations of this type of soil removal have concentrated on the use of POE nonionics. POE nonionics have also been found (Rutkowski, 1971) to remove oily soils and prevent their redeposition at lower bath concentrations than anionics (i.e., nonionic surfactants are more efficient for these purposes than anionics). The greater efficiency of nonionics in soil removal is presumably due to their lower CMCs; in the prevention of soil redeposition it is probably due to their greater surface coverage per molecule when adsorbed on substrate and soil.

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*AS mentioned previously, the term *detergency* as used here refers to the power of the surfactant to enhance the cleaning power of the bath liquid. Except for dry cleaning (Section IVD below), the bath liquid referred to in this discussion is water.

As mentioned above, maximum oily soil removal from polyester substrates by POE nonionics is obtained when the PIT of the surfactant in the presence of that soil is close to the wash temperature. Since the PIT decreases with decrease in the EO content of the POE nonionic surfactant, it is to be expected that as the wash temperature is decreased, the EO content of the surfactant showing optimum oily soil removal will decrease. Thus, for single homogeneous surfactants, $C_{12}H_{25}(OC_2H_4)_xOH$, maximum cetane detergency at 30°C was shown by the 4EO compound (PIT = 30°C), at 50°C by the 5EO compound (PIT = 52°C), and at 65°C by the 6EO compound (Benson, 1986). The detergency of the 5EO compound at 30°C could be increased by additives that decreased its cloud point (and PIT).

In addition, as the wash temperature decreases, the chain length of the hydrophobic group for optimum oily soil removal appears to decrease. Thus, for oily soil removal from polyester/cotton by blends of homogeneous 3EO and 8EO nonionics having similar cloud points, the order of maximum oil removal at 70° was $C_{14} = C_{12} > C_{10}$, at 38°C it was $C_{10} = C_{12} > C_{14}$, and at 24°C it was $C_{10} > C_{12} > C_{14}$. The difference has been ascribed to the rate of solubilization of the soil, since the rate for these surfactant blends decreases with increase in the length of the hydrophobe (Benson, 1982).

For commercial POE nonionics with different types of hydrophobic groups of approximately equivalent chain length and the same degree of oxyethylenation (9 mol EO), the order of decreasing nonpolar soil removal from polyester/cotton was nonylphenol adduct > secondary $C_{11} - C_{15}$ alcohol adduct > linear primary $C_{12} - C_{15}$ alcohol adduct. This was the order of decreased effectiveness of equilibrium γ_{OW} reduction and of reduced rate of γ_{OW} reduction (Dillan, 1984).

Nonionics have been shown also to be more effective than ionics in the removal of oily soil from relatively nonpolar substrates (polyester, nylon). On cotton, however, a relatively hydrophilic fiber, anionics can outperform nonionics in detergency, and both of these are superior to cationics (Fort, 1968). The effects here may be due to differences in the orientation of adsorption of the different types of surfactants on the different substrates. On nonpolar substrates and soils, POE nonionics are adsorbed (Chapter 2) from aqueous solution via dispersion forces or hydrophobic bonding with their hydrophobic POE groups oriented toward the adsorbent and their hydrophilic POE groups toward the bath. Adsorption of the surfactant in this fashion on the substrate lowers the substrate–bath interfacial tension γ_{SB} and facilitates soil removal (equation 10.3); adsorption in this fashion on both substrate and soil produces a steric barrier that inhibits soil redeposition.

On a cellulose substrate, on the other hand, adsorption–desorption data (Waag, 1968) indicate that POE nonionics can be adsorbed, at least partly, by hydrogen bonding between the hydroxyl groups of the cellulose and the ether linkages of the hydrophilic POE chain. This results in orientation of the surfactant with its hydrophilic group toward the substrate and its hydrophobic group toward the bath. Adsorption of the surfactant onto the cellulose substrate in this fashion makes the latter more hydrophobic and increases γ_{SB}, impeding removal of oily soil and facilitating its redeposition. This may account for the poorer washing performance of nonionics on cotton than on nonpolar substrates.

This unfavorable orientation of adsorption may also account for the even poorer performance of cationics on cotton. Since cotton acquires a negative charge at neutral or alkaline pHs, cationic surfactants may be adsorbed onto it by electrostatic attraction between the negatively charged sites on the fiber and the positively charged hydrophilic groups of the surfactant, with the hydrophobic groups of the adsorbed surfactant molecules oriented toward the bath. This orientation of the cationic surfactant onto the cotton will make it more hydrophobic and increase γ_{SB}, impeding the removal of oily soil and facilitating its redeposition.

Anionic surfactants, by contrast, although not adsorbed well onto negatively charged cotton except at relatively high bath concentrations of surfactant, can adsorb onto it only with their negatively charged hydrophilic groups oriented away from the similar charged substrate, and toward the bath, thereby increasing its hydrophilic character and decreasing γ_{SB}, facilitating soil removal and inhibiting soil redeposition. These considerations may underlie the observation by several investigators (Fort, 1966; Gordon, 1967; Spangler, 1967; Rutkowski, 1971) that for the removal of oily soil, nonionics are best for nonpolar substrates and anionics are best for cellulose substrates.

Geol (1998) has suggested guidelines for the optimal removal of oily soil from 65:35 polyester/cotton fabric by POE nonionic–anionic mixtures, based on the observation that maximum oily soil removal from this type of substrate is obtained at the PIT of the system, where the oil–water interfacial tension is at a minimum. Since the addition of anionic surfactant or increase in the POE content of the nonionic produces an increase in the PIT of the system, while the addition of salting-out electrolyte (NaCl, Na_2CO_3, $Na_5P_3O_{10}$) or decrease in the POE content of the nonionic reduces the PIT, these two opposing tendencies can be used to "tune" the system so that the PIT approximates the wash temperature. Thus, at a fixed level of electrolyte in the system, increase in the anionic/nonionic ratio, which increases the PIT, can be compensated for by use of a nonionic with a lower POE content. Increase in the electrolyte content, which decreases the PIT, can be compensated for by increase in the POE content of the nonionic or by increase in the anionic/nonionic ratio. Detergency results with C_{12} linear alkylbenzenesulfonate–POE lauryl alcohol mixtures in the presence of $Na_2CO_3/Na_5P_3O_{10}$ mixtures, using artificial sebum as oily soil, were in accordance with these concepts.

Studies of solid hydrophobic soil removal from hard surfaces (Cox, 1984, 1986, 1987) indicate that liquefaction of the soil, involving penetration by surfactant and associated water molecules, is a key step in the removal of this type of soil. POE nonionics with short-chain (C_6, C_8) hydrophobic groups gave better performance than longer-chain (C_{12}) materials with the same percentage of EO. Performance also increased with decrease in EO content, in the 50–80% range. These effects are believed to be due to faster penetration by the shorter-chain materials. A C_{13} LAS performed better than shorter-chain homologs and its performance was improved in the presence of Mg^{2+}. The effects here are ascribed to better soil emulsification by the longer-chain LAS and better penetration in the presence of Mg^{2+}.

2. Particulate Soil Particulate soil is removed better from both cotton and Dacron–cotton blends by anionics than by nonionics (Albin, 1973). Here increase in the electrical potentials on soil and substrate is probably the major mechanism by which this type of soil is removed and dispersed in the bath. Nonionics are consequently frequently less effective for removing this soil from the substrate, although they may be as effective and generally are more efficient than anionics in preventing its redeposition onto substrates (Rutkowski, 1968; Schott, 1968). Optimum particulate soil removal by POE nonionics from polyester/cotton requires a longer chain hydrophobic group and a higher EO content than oily soil removal (Vreugdenhil, 1984). Schwuger (1982) has pointed out that surfactants that adsorb equally well onto a hydrophobic soil and show equal detergency for this type of soil may show differences in adsorption for a hydrophilic soil. This may account for differences in detergency shown for this latter type of soil or for mixed soil (below).

Cationics, again, show poor detergency, since most substrates and particulate soils acquire negative potentials when contacted with aqueous baths at neutral or alkaline pHs. Adsorption of the positively charged surfactant ions onto substrate and soil decreases their (negative) electrical potentials, making more difficult the removal of soil and facilitating its redeposition.

3. Mixed Soil Mixed soil, which contains both oily and particulate matter, is commonly used in laundering investigations, since it approximates the composition of the soil found in clothing. A comparison of the washing performance of sodium alkyl sulfates and sodium methyl α-sulfocarboxylates has indicated that oniy when two different surfactants show equally good adsorption onto the fabric and all the components of the soil do they show similar washing properties. Surfactants that adsorb less strongly than others onto the textile fiber or onto some major component of the soil show poorer detergency (Schwuger, 1971). However, good adsorption by the surfactant onto a substrate and soil is not sufficient to ensure good washing properties. The surfactant must also be adsorbed with the proper orientation for soil removal, with its hydrophilic group oriented toward the aqueous bath phase. Thus, in a study comparing the laundering properties at 49°C of unbuilt sodium dodecylbenzenesulfonate with those of a nonionic POE isooctylphenol using a mixed soil, it was found (Rutkowski, 1971) that the nonionic was more efficient than the anionic both in removing soil from polyester fabric and in preventing soil redeposition on it, but it was not more effective than the anionic at higher concentrations in either respect. On cotton, however, although the nonionic was still somewhat more efficient but not more effective than the anionic in removing soil, it was not more efficient and was considerably less effective than the anionic in preventing soil redeposition. The poorer performance of the nonionic in preventing soil redeposition on the cotton may again be due to its adsorption, at least in part, onto the fiber via hydrogen bonding of the POE group with the hydrophobic groups oriented toward the bath, thus providing sites for soil redeposition.

In some cases, this orientation may be difficult to predict. Thus, a study of the adsorption of a series of *n*-alkyl sulfates and POE nonylphenols onto isotactic polypropylene fiber and of the washing properties of the same surfactants for the fiber using a mixed soil indicated that, although the adsorption of sodium hexadecyl sulfate onto the fiber was greater than that of a POE nonylphenol with a chain of 10 oxyethylene groups, the detergency of the former for the fiber was much lower. This was in spite of the fact that both compounds have equally good, similar emulsifying and solubilizing properties for this soil. Closer investigation of the adsorption of the two surfactants revealed that the anionic was adsorbed by strong, essentially irreversible interaction of its hydrophilic group with sites on the fiber (possibly polyvalent cations from the catalyst used in the polymerization), whereas the nonionic was adsorbed in normal, reversible fashion via its hydrophobic group (Schwuger, 1971).

IV.B. Effect of the Hydrophobic Group of the Surfactant

Since both the extent of adsorption of the surfactant onto substrate and soil and its orientation with the hydrophobic group toward the adsorbents are of major importance in both soil removal and the prevention of soil redeposition, it is to be expected that changes in the length of the hydrophobic group will result in changes in detergency. Since an increase in the length of the hydrophobic group results in an increase in its efficiency of adsorption from aqueous solution (Chapter 2, Section II) and an increase in its tendency to adsorb via its hydrophobic group, whereas branching of the hydrophobic group or a centrally located hydrophilic group decreases the efficiency of adsorption, these probably account for the general observation that good detergents generally have a long, straight hydrophobic group and a hydrophilic group that is located either terminally or close to one end of the surfactant molecule. Numerous studies have indicated that detergency increases with increase in the length of the hydrophobic group, subject to solubility limits, and with movement of the hydrophilic group from a central to a more terminal position in the molecule (Kölbel, 1959; Burgess, 1964; Hellsten, 1965; Finger, 1967; Schwuger, 1982). Thus, in distilled water, compounds with straight hydrophobic groups are letter detergents than their branched-chain isomers, fatty acid soaps generally are better than rosin soaps, and C_{16} and C_{18} fatty acid soaps are better than C_{12} and C_{14} soaps. The same effects are noticed in the alkyl sulfate and alkylbenzenesulfonate series in distilled water. In the latter series, parasulfonates appear to be better than ortho and monoalkyl better than isomeric dialkyl (Ginn and Harris, 1961; Kölbel, 1960).

There is one very important limitation on this increase of detergency with hydrophobic chain length, and that is the solubility of the surfactant in the cleaning bath. Particularly for ionic-type surfactants, the solubility of the surfactant in aqueous media decreases rapidly with increased length of the hydrophobic portion. of the molecule, and precipitation of the surfactant, especially by any polyvalent cations present in the system, causes a marked decrease in detergency. Thus, optimum detergency is generally shown by the longest straight-chain surfactants whose solubility in the aqueous bath *under use conditions* is sufficient to prevent their precipitation onto the substrate in the presence of polyvalent cations. As the hardness of the bath water increases, optimum detergency appears to shift to shorter-chain homologs. Since solubility of ionic straight-chain surfactants in water generally increases with movement of the hydrophilic group from a terminal to a more central position in the molecule, when the surfactant with terminal hydrophilic group is either too insoluble or too sensitive to polyvalent cations for effective detergency, isomers with centrally located hydrophilic groups may show superior detergency (Rubinfeld, 1965). Thus, commercial linear dodecylbenzenesulfonate, which is produced with the phenylsulfonate group at the 2-, 3-, and other internal positions of the dodecyl group, rather than at the 1-position, is superior to the latter in detergency. 1-Phenylsulfonate, although superior to the other isomers in hot distilled water, has so slight a solubility at ordinary temperatures and is so sensitive to the presence of hard water cations (Ca^{2+}, Mg^{2+}) that it is not usable under normal washing conditions. As the bath temperature increases and the solubility of ionic surfactants in the bath increases, the length of the hydrophobic chain for optimum detergency increases (Matson, 1963).

In POE nonionics containing the same number of oxyethylene units, increase in the length of the hydrophobic group increases the efficiency of oily soil removal by decreasing the CMC and hence the concentration at which solubilization commences. Optimum detergency increases with increase in the chain length of the hydrophobe to a maximum that again is dependent on the temperature of the bath.

IV.C. Effect of the Hydrophilic Group of the Surfactant

From our previous discussion, it is apparent that the charge on an ionic surfactant plays an important role in detergency. Because of the unfavorable (for detergency) orientation of the surfactant resulting from electrostatic attraction of its hydrophilic group to oppositely charged sites on the substrate or soil, ionic surfactants cannot be used efficiently for the removal of soil from oppositely charges substrates. Thus, cationics perform poorly on negatively charged substrates, especially at alkaline pHs, whereas anionics would not be expected to perform as well as cationics for the removal of soil from positively charged substrates at acidic pHs.

In POE nonionics, an increase in the number of oxyethylene groups in the hydrophilic POE chain appears to decrease the efficiency of adsorption of the surfactant onto most materials (Chapter 2), and this is sometimes accompanied by a decrease in detergency. For example, the detergency of wool at 30°C by a fixed molar concentration of POE nonylphenol in distilled water decreases with increase in the number of oxyethylene groups from 9 to 20 (Schwuger, 1971). This is consistent with adsorption studies that show that the greater the adsorption of these nonionics on wool, the greater the detergency (Kame, 1963).

On the other hand, the detergency of isotactic polypropylene at 90°C by these same surfactants in distilled water increases with increase in the number of oxyethylene units in the POE chain to a maximum at 12 and then decreases (Schwuger, 1971) . The major factor involved here is probably the PIT of the surfactant , which increases with increase in the number of oxyethylene groups in the molecule. Detergency is optimum in the vicinity of the PIT, presumably because solubilization of oily soil by the surfactant increases markedly there.

A similar detergency maximum at almost the same oxyethylene content has been observed in the removal of oily soil from metal surfaces using similar surfactants in an alkaline, built formulation (Komor, 1969). The maximum here is at 68% oxyethylene (about 11 oxyethylene units per nonylphenol) at bath temperatures from 40 to 80°C. For a series of polyoxyethylenated nonrandom linear alkylphenols with C_8–C_{18} alkyl chains, optimum removal of sebum soil from cotton at 49°C and 50 and 300 ppm water hardness was obtained at 63–68% oxyethylene content (Smithson, 1966). A study of the removal of oily soil from cotton and permanent press cloths, and of clay from permanent press cloths by commercial POE alcohols, showed that POE C_{12}–C_{14} alcohols with 60% or greater ethylene oxide content achieved the best soil removal (Cox, 1989).

Studies of the soil removal properties of polyoxyethylenated straight-chain primary alcohols on cotton and Dacron–cotton permapress fabric indicate that this detergency maximum with change in the number of oxyethylene units in the POE chain is also shown on these fabrics. In liquid no-phosphate formulations built only with diethanolamine to provide an alkaline pH, optimum removal of both sebum and clay soils from Dacron–cotton permapress at 49°C in 150 ppm hard water occurs with about 5, 9, and 10 oxyethylene units for POE C_{9-11}, C_{12-15}, and C_{16-18} alcohol mixtures, respectively. For removal of the same soils from cotton at the same temperature, the optimum POE chain lengths are about two oxyethylene units larger (Albin, 1973).

The effect of changing the hydrophilic group from nonionic to anionic can be seen by comparing the soil removal properties of these same POE alcohols with two series of anionics made from the same hydrophobes, either by sulfating the alcohol mixture directly or after polyoxyethylenation with 3 or 6 mol of ethylene oxide. Using the same liquid no-phosphate formulation and the same laundering conditions at 49°C in 150 ppm hard water, the following results were obtained (Albin, 1973):

1. Both series of anionics made from the C_{12-15} alcohol mixture showed better detergency than the corresponding surfactants made from the C_{16-18} alcohol mixture; the corresponding materials made from the C_{9-11} alcohol mixture were poorest.
2. The directly sulfated materials (alkyl sulfates) made from the C_{9-11} and C_{16-18} alcohol mixtures were always poorer, in most cases considerably poorer, than the best nonionics made from the same alcohol mixtures.
3. Generally, there was no significant difference in the performance of sulfated surfactants polyoxyethylenated with 3 mol of ethylene oxide and the corresponding materials with six oxyethylene units.
4. Polyoxyethylenation of the C_{9-11} and C_{16-18} alcohol mixtures prior to sulfation generally improved their detergency considerably; in the case of the C_{12-15} alcohol mixture, polyoxyethylenation prior to sulfation reduced its performance on Dacron–cotton permapress slightly and improved its performance on cotton.

5. The best nonionics (made from the C_{12-15} alcohol mixture) were better than any of the anionics for both sebum and clay removal from Dacron–cotton permapress, but were not as good as the best anionics (sulfated POE C_{12-15} alcohols) for sebum or clay removal from cotton.

Comparable results were obtained in formulations containing sodium silicate as a builder together with 0–45% sodium tripolyphosphate, using 250 ppm hard water and a bath temperature of 49°C (Illman, 1971). A nonionic surfactant prepared by polyoxyethylenation of a C_{12-15} alcohol mixture with 9–11 mol of ethylene oxide generally showed similar detergency to an anionic prepared by sulfation of a C_{12-15} alcohol mixture previously polyoxyethylenated with 3 mol of ethylene oxide at all percentages of sodium tripolyphosphate, and both were considerably superior to a linear tridecylbenzenesulfonate and a sulfated C_{16-18} alcohol mixture. The nonionic was somewhat better than the sulfated POE alcohol for removing nonpolar fatty soil from Dacron–cotton permapress, and the reverse was true for the removal of polar soil from Dacron–cotton permapress and carbon soil from cotton, but similar results for the two surfactants were obtained for clay removal from both Dacron–cotton permapress and cotton, and polar and nonpolar fatty soil from cotton.

IV.D. Dry Cleaning

Surfactants used as detergents in dry cleaning must, of course, be soluble in the solvent used as the bath liquid. They are often added as solutions in some suitable solvent. Surfactants used for this purpose include solvent-soluble petroleum sulfonates, sodium and amine salts of alkylarylsulfonates, sodium sulfosuccinates, POE phosphate esters, sorbitan esters, POE amides, and POE alkylphenols (Martin, 1965).

There seem to have been few systematic investigations of the effect of the chemical structure of the surfactant on the cleaning properties of the bath. The hydrophilic group of the surfactant appears to play a more important role than the hydrophobic (Kajl, 1960; Lange, 1967). In view of the two main mechanisms by means of which surfactants aid the cleaning process—(1) adsorption via the hydrophilic group onto soil and substrate to prevent redeposition of solid soil and (2) solubilization of water-soluble soil by water held between the hydrophilic groups in the interior of the micelles (Chapter 4, Section II)—the importance of the hydrophilic group is not unexpected. The function of the hydrophobic group appears to be that of producing the steric barrier to the aggregation of solid soil particles dispersed in the bath. Consistent with this, C_{16-18} straight chains appear to be the most effective for this purpose Wedell, 1960).

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PROBLEMS

1 Explain why cationic surfactants, which ordinarily show poor detergency in aqueous media, can be used successfully as detergents at low pH.

2 Explain how the addition of a small amount of a cationic surfactant can increase the efficiency of an alkaline solution of an anionic surfactant in soil removal from a textile surface.

3 **(a)** What effect would adsorption of a surfactant onto a textile surface via its hydrophilic head have on the spreading coefficient of the bath on the textile surface?

(b) List two cases where this may occur.

4 Sodium sulfate is often found in laundry detergent powders based on sodium linear alkylbenzenesulfonate. Aside from acting as an inexpensive "filler," suggest other reasons for its presence and possible useful functions.

11

Molecular Interactions and Synergism in Mixtures of Two Surfactants

In most practical applications, mixtures of surfactants, rather than individual surfactants, are used. In some cases, this is involuntary, since the commercial surfactants used, even when designated by the name of an individual surfactant, e.g., sodium lauryl sulfate, are mixtures of surface-active materials as a result of the nonhomogeneous raw materials used in their manufacture and/or the presence of unreacted raw materials and manufactured by-products. In other cases, different types of surfactants are purposely mixed to improve the properties of the final product.

In most cases, when different types of surfactants are purposely mixed, what is sought is *synergism*, the condition in which the properties of the mixture are better than those attainable with the individual components by themselves. For example, a long-chain amine oxide is often added to a formulation based upon an anionic surfactant because the foaming properties of the mixture are better than those of either surfactant by itself.

Although the existence of synergistic relations between certain types of surfactants has been known and utilized for many years, the investigation of synergism in *quantitative* terms is a recent development based upon a simple, convenient method for measuring molecular interactions between surfactants. The molecular interactions between two different surfactants adsorbed at various interfaces are measured by a parameter, β, that indicates the nature and strength of those interactions. The value of the β parameter is related to the free energy change upon mixing of the two surfactants $[\Delta G_{\text{mix}} = \beta X(1 - X)RT]$, where X is the mole fraction of the first surfactant in the mixture (on a surfactant-only basis) adsorbed at the interface and $(1 - X)$ is the mole fraction of the second surfactant.

The *regular solution* equation (Rubingh, 1979) for β, is $\beta = [W_{AB} - (W_{AA} + W_{BB}/2]RT$, where W_{AB} is the molecular interaction energy between the mixed surfactants, W_{AA} is the molecular interaction energy between the first surfactant before mixing with the second, W_{BB} is the molecular interaction energy between the second surfactant before mixing with the first, R is the gas constant, and T, the absolute temperature, is a convenient way of understanding its meaning. For

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Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

attractive interaction, the sign of W is negative; for repulsive interaction, it is positive. Thus, a negative β value indicates that, upon mixing, the two surfactants experience either greater attraction or less repulsion than before mixing; a positive β value, less attraction or greater repulsion upon mixing than before mixing. A value close to zero indicates little or no change in interactions upon mixing. Since, in ionic surfactant-containing mixtures, there is always repulsive interaction between the ionic surfactant molecules before mixing, the β parameter is almost always negative, if only because of the dilution effect upon mixing with a second surfactant, except for anionic–anionic mixtures. Steric effects contribute to the value of the β parameter when there are variations in the size of the hydrophilic head group or in the branching of the hydrophobic groups of the two surfactants (Zhou, 2003). From the relevant properties of the individual surfactants and the values of the molecular interaction parameters, it is possible to predict whether synergism will exist in a mixture of surfactants and, if so, the ratio of the materials at which synergism will be a maximum and the optimum value of the relevant surface property at that point. At the present time, mixtures containing only two surfactants have been investigated, although the method is theoretically (Holland, 1983) capable of handling any number of components. However, in any multi-component system, the strongest interaction between two surfactants usually determines the properties of the entire system and evaluation of that one interaction will probably be sufficient to allow prediction of the properties of the mixture.

I. EVALUATION OF MOLECULAR INTERACTION PARAMETERS

The two fundamental properties of surfactants are monolayer formation at interfaces and micelle formation in solution; for surfactant mixtures, the characteristic phenomena are mixed monolayer formation at interfaces (Chapter 2, Section IIIG) and mixed micelle formation in solution (Chapter 3, Section VIII). The molecular interaction parameters for mixed monolayer formation by two different surfactants at an interface can be evaluated using equations 11.1 and 11.2 which are based upon the application of nonideal solution theory to the thermodynamics of the system (Rosen, 1982):

$$\frac{X_1^2 \ln(\alpha C_{12}/X_1 C_1^0)}{(1 - X_1)^2 \ln[(1-\alpha)C_{12}/(1 - X_1)C_2^0]} = 1 \tag{11.1}$$

$$\beta^\sigma = \frac{\ln(\alpha C_{12}/X_1 C_1^0)}{(1 - X_1)^2} \tag{11.2}$$

where α is the mole fraction of surfactant 1 in the total surfactant in the solution phase, i.e., the mole fraction of surfactant 2 equals $1 - \alpha$; X_1 is the mole fraction of surfactant 1 in the total surfactant in the mixed monolayer; C_1^0, C_2^0, and C_{12} are the solution phase molar concentrations of surfactants 1,2, and their mixture, respectively, required to produce a given surface tension value; and β^σ is the molecular interaction parameter for mixed monolayer formations at the aqueous solution–air interface.

For evaluating the molecular interaction parameters for mixed micelle formation by two different surfactants, equations 11.3 and 11.4 (Rubingh, 1979) are used.

$$\frac{(X_1^M)^2 \ln(\alpha C_{12}^M / X_1^M C_1^M)}{(1 - X_1^M)^2 \ln[(1-\alpha)C_{12}^M/(1 - X_1^M)C_2^M]} = 1 \tag{11.3}$$

$$\beta^M = \frac{\ln(\alpha C_{12}^M / X_1^M C_1^M)}{(1 - X_1^M)^2} \tag{11.4}$$

where C_1^M, C_2^M, and C_{12}^M are the CMCs of individual surfactants 1 and 2 and their mixture at a given value of α, respectively; X_1^M is the mole fraction of surfactant 1 in the total surfactant in the mixed micelle; and β^M is a parameter that measures the nature and extent of the interaction between the two different surfactant molecules in the mixed micelle in aqueous solution. Equation 11.1 (or 11.3) is solved numerically for X_1 (or X_1^M), and substitution of this in equation 11.2 (or 11.4) yields the value of β^σ (or β^M).

The determination of β^σ and β^M experimentally is shown in Figure 11-1. Surface tension–log surfactant concentration curves for each of the two individual suractants in the system and at least one mixture of them at a fixed value of α must be determined. For calculating β^σ (the molecular interaction parameter for mixed monolayer formation at the aqueous solution–air interface), C_1^0, C_2^0 and C_{12}^0 are required; for β^M, the CMCs, C_1^M, C_2^M, and C_{12}^M, are needed.

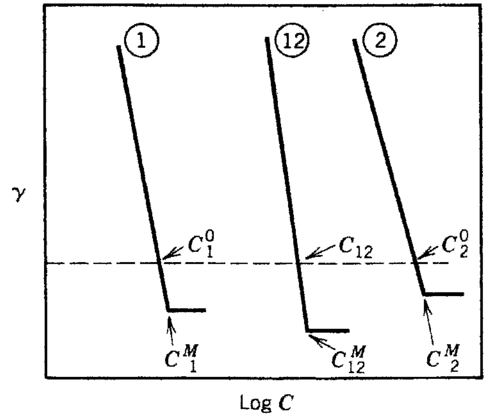

FIGURE 11-1 Experimental evaluation of β^σ or β^M. ① Individual surfactant 1; ② Individual surfactant 2; ⑫ Mixture of surfactants 1 and 2 at a fixed mole fraction α in solution. Reprinted with permission from M. J. Rosen in *Phenomena in Mixed Surfactant Systems*, J. F. Scamehorn (Ed.), ACS Symp. Series 311, American Chemical Society Washington, DC, 1986, p. 148.

I.A. Notes on the Use of Equations 11.1–11.4

In order to obtain valid β parameter values, i.e., values that do not change significantly with change in the ratio of the surfactant in the mixture, the following conditions must be met:

1. The two surfactants must be molecularly homogeneous and free from surface-active impurities.
2. Since equations 11.1–11.4 neglect countenon effects, all solutions containing ionic surfactants should have the same total ionic strength, with a swamping excess of any counterions.
3. Since the derivation of these equations is based upon the assumption that the mixed micelle or monolayer can be considered to contain only surfactants, these structures are considered to contain no free water. This is reasonable when the surfactant molecules are so closely packed (e.g., at their maximum surface excess concentration in the monolayer) that all the water present can be considered to be bound to the hydrophilic head groups. Because of this and because surfactant mixtures are generally used above their CMC, it is advisable to determine β^{σ} using C_1^0, C_2^0, and C_{12} values taken from the γ–$\log C$ plots at such a value of γ that the slopes are all linear or almost so, and preferably at the lowest possible γ value. For this purpose it is permissible to extend the γ–$\log C$ plot to values above the CMC of one of the surfactants (see Figure 11-8*a*) by extrapolating linearly the portion of maximum slope just below the CMC. If the plot shows a decrease in slope close to the CMC, that portion should be ignored in extending the plot.

   Since equations 11.1 and 11.3 contain the terms $((X_1)^2/(1-X_1)^2)$ and $((X_1^M)^2/(1-X_1^M)^2)$, respectively, which change rapidly in value when X approaches 1 or 0, it is advisable to use for the surfactant mixtures α values that yield X_1 or X_1^M values between 0.2 and 0.8. When the value is beyond these limits, small experimental errors may cause large errors in calculating X_1 or X_1^M, with consequent large deviations in the value of β^{σ} or β^M. Values of X_1 approximating 0.5 can be obtained by using an α value equal to the ratio $C_1^0/(C_1^0 + C_2^0)$, and values of X_1^M approximating 0.5 can be obtained by using an α value equal to $C_1^M/(C_1^M + C_2^M)$.

The interaction parameters in the presence of a second liquid (hydrocarbon) phase, β_{LL}^{σ} and β_{LL}^{M}, for mixed monolayer formation at the aqueous solution–hydrocarbon interface and for mixed micelle formation in the aqueous phase, respectively, can be evaluated (Rosen, 1986) by equations analogous to 11.1, 11.2 and 11.3, and 11.4, respectively. The necessary data are obtained from interfacial tension–concentration curves.

Interaction parameters for mixed monolayer formation at the aqueous solution–solid interface (β_{SL}^{σ}) can also be evaluated (Rosen, 1987), *in the case where the solid has a low-energy (hydrophobic) surface*, by equations analogous to 11.1 and 11.2. In this case, quantities C_1^0, C_2^0, and C_{12} are the concentrations in aqueous solutions of surfactant 1, surfactant 2, and their mixture, respectively, *at the same value of the adhesion tension*, γ_{LA} cos θ, where γ_{LA} is the surface tension of the surfactant solution and θ its contact angle measured in the aqueous phase on a smooth, nonporous planar surface of the hydrophobic solid (Figure 6-2). Alternatively, β^{σ}_{SL} values can be obtained from the adsorption isotherms of solutions of surfactant 1, surfactant 2, and at least one mixture of them at a fixed equilibrium value of α on the finely divided solid (Chapter 2, Section IIB).

From equation 2.19a, $d_{\gamma_{SL}} = -nRT\Gamma_{SL} d\ln C$, and, integrating both sides of the equation,

$$\int_{\gamma_{SL}}^{\gamma^0_{SL}} d\gamma_{SL} = \gamma^0_{SL} - \gamma_{SL} = \Pi_{SL} = RT\int_c^0 \Gamma_{SL} \cdot d\ln C \qquad (11.5)$$

Integrating the area under the plot of adsorption, Γ_{SL} versus ln C (or log C) (Figure 11-2) below the CMCs of the respective solutions, yields the value of Π_{SL}, the amount of solid–aqueous solution interfacial tension reduction. This is plotted (Figure 11-3) against ln (or log) C and values of C^0_1, C^0_2, and C_{12} selected, at the largest common value of Π_{SL}, for substitution into equations 11.1 and 11.2 to evaluate β^{σ}_{SL}. Π_{SL} can also be evaluated (Zhu, 1991) directly from adsorption isotherm data by use of equations

$$\Pi_{SL} = \Gamma_{\infty} RT \ln(1 + C_1/a) \qquad (11.6)$$

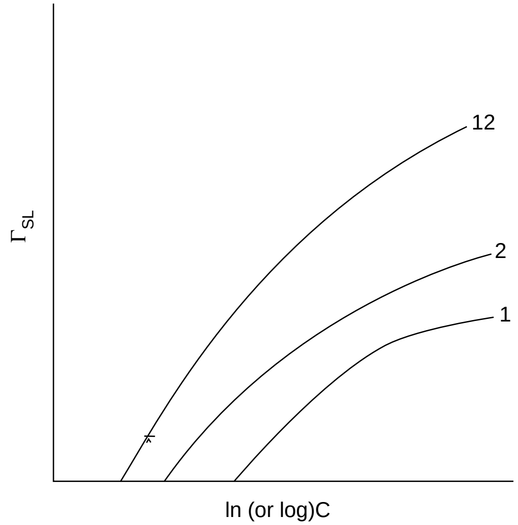

FIGURE 11-2 Plots of adsorption (Γ_{SL}) on a powdered, finely divided solid versus ln (or log) total surfactant concentration, C, of aqueous solutions of surfactants 1, 2, and a mixture of them, 12, at a fixed value of α, for evaluation of Π_{SL}.

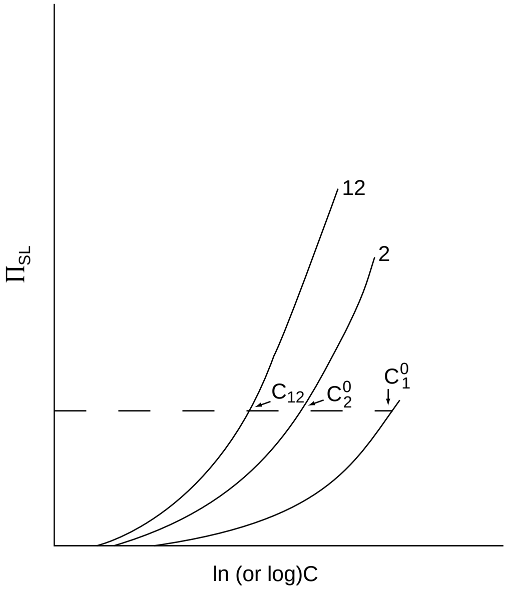

FIGURE 11-3 Plots of Π_{SL} versus ln (or log) C for evaluation of β_{SL} from adsorption isotherm data below the CMCs of the aqueous solutions of surfactants 1, 2, and a mixture of them (12) at a fixed value of α.

for monolayer adsorption and

$$\Pi_{SL} = \Gamma_{\infty}^{S}/nRT\ln(1 + C_1^n/a) \qquad (11.7)$$

for adsorption with surface aggregates, by use of equations 2.7 or 2.8 to evaluate a and Γ_M^S and equation 2.12 to evaluate K $(= 1/a)$ and n.

The molecular interaction parameters evaluated using equations 11.1–11.4, together with the properties of the individual surfactants (see Section III below), are used to predict whether synergism of a particular type will occur when the two surfactants are mixed and, if so, the molar ratio of the two surfactants at which maximum synergism will exist and the relevant property of the mixture at that point. The particular interaction parameters used depend upon the nature of the interfacial phenomenon involved as described below.

II. EFFECT OF CHEMICAL STRUCTURE AND MOLECULAR ENVIRONMENT ON MOLECULAR INTERACTION PARAMETERS

A considerable number of molecular interaction parameters on well-characterized surfactant pairs have been measured during the past two decades. In addition, information on how the parameters change with variation in the chemical structures of the two surfactants and in their molecular environment (pH, temperature, ionic strength of the solution) has accumulated. This permits the estimation of these parameters when it may not be convenient to determine them experimentally.

Table 11-1 lists values of the various types of molecular interaction parameters. Almost all of the mixtures show negative β values, indicating more attraction (or less repulsion) after mixing than before. The only examples observed to date of surfactant pairs with positive β values (greater repulsion or smaller attraction of the two components after mixing than before) are (1) anionic–anionic mixtures of sodium soaps ($\overline{>}C_{14}$) with either commercial dodecylbenzenesulfonate (LAS) or sodium hexadecanesulfonate (Rosen, 1989) and (2) mixtures of hydrocarbon-chain and perfluorocarbon-chain surfactants of the same charge type (Zhao, 1986). These latter types have been shown to form aggregated separate domains rather than mixed films or mixed micelles upon mixing (Kadi, 2002).

The interaction between the two surfactants is mainly due to electrostatic forces. The strength of attractive electrostatic interaction decreases in the order anionic–cationic > anionic–zwitterionic capable of accepting a proton > cation–zwitterionic capable of losing a proton > anionic–POE nonionic > cationic–POE nonionic. Mixtures of surfactants of the same charge type (anionic–anionic, cationic–cationic, nonionic–nonionic, zwitterionic–zwittenonic) show only very weak interaction (negative β values of 1 or less) at the aqueous solution–air interface, although they can show significant interaction at other interfaces.

The large negative β values observed in the cases of two oppositely charged surfactants are consequently due to the attractive electrostatic interaction they experience after mixing. In the case of ionic–nonionic mixtures, however, where attractive electrostatic interaction after mixing may be expected to be weak, a major contribution to the negative β values observed may be the reduction after mixing with the nonionic of the self-repulsion of the ionic surfactant before mixing, i.e., a dilution effect (Zhou, 2003).

Except for some mixtures of anionics with POE nonionics that have about six or more oxyethylene groups, β^m values are less negative, at best equally negative, compared to their β^σ values for the same surfactant under the same conditions. This may be due to the greater difficulty of accommodating hydrophobic groups in the interior of a convex micelle compared to a planar interface.

Steric effects appear when either surfactant molecule of the mixture varies in the size of the head group or in the branching of the hydrophobic group. Thus, sodium tertiary butylbenzenesulfonate interacts less strongly with cetyl trimethylammonium bromide than isobutylbenzenesulfonate, which in turn interacts less strongly than normal butylbenzenesulfonate (Bhat, 1999).

Branching near the hydrophilic head group, or increase in its size, decreases the negative values of both β^σ and β^M, with greater effect on β^M than on β^σ. Branching in the hydrophobic group appears to reduce the negative value mainly of β^M. On the other hand, increase in the number of oxyethylene groups in a POE nonionic increases sharply the negative value of β^M in sodium anionic–POE nonionic mixtures. This effect is not seen in cationic–POE nonionic mixtures and may be due to the acquisition of a positive charge by the POE chain when it is large enough to complex the Na^+ of the anionic (Matsubara, 1999, 2001; Liljekvist, 2000; Rosen,

TABLE 11-1 Values of Molecular Interaction Parameters

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
	Anionic–Anionic Mixtures			
$C_{13}COO^{-}Na^{+}$–$LAS^{-}Na^{+a}$ (0.1 *M* NaCl, pH 10.6)	60	+0.2	−0.6	Rosen, 1989d
$C_{15}COO^{-}Na^{+}$–$C_{12}SO_3^{-}Na^{+}$ (0.1 *M* NaCl, pH 10.6)	60	−0.01	+02	Rosen, 1989d
$C_{15}COO^{-}Na^{+}$–$LAS^{-}Na^{+a}$ (0.1 *M* NaCl, pH 10.6)	60	+1.4	+0.7	Rosen, 1989d
$C_{15}COO^{-}Na^{+}$–$C_{16}SAS^{-}Na^{+b}$ (0.1 *M* NaCl, pH 10.6)	60	−0.1	−0.7	Rosen, 1989d
$C_{15}COO^{-}Na^{+}$–$C_{16}SO_3^{-}Na^{+}$ (0.1 *M* NaCl, pH 10.6)	60	+0.7	+0.7	Rosen, 1989d
$C_7F_{15}COO^{-}Na^{+}$–$C_{10}SO_4^{-}Na^{+}$ (0.1 *M* NaCl, heptane–H_2O)	30	+0.8(β^{σ}_{LL})	+0.3	Zhao, 1986
$C_7F_{15}COO^{-}Na^{+}$–$C_{12}SO_4^{-}Na^{+}$ (0.1 *M* NaCl)	30	+2.0	—	Zhao, 1986
$C_{12}SO_3^{-}Na^{+}$–$LAS^{-}Na^{+a}$ (0.1 *M* NaCl)	25	−0.3	−0.3	Rosen, 1989d
$C_{12}SO_3^{-}Na^{+}$–$AOT^{-}Na^{+c}$ (0.1 *M* NaCl)	25	−0.3	−0.5	Rosen, 1989d
	Anionic–Cationic Mixtures			
$C_7F_{15}COO^{-}Na^{+}$–$C_7N^{+}Me_3Br^{-}$ (0.1 *M* NaCl)	30	−15.0	—	Zhao, 1986
$C_5SO_3^{-}Na^{+}$–$C_{10}Pyr^{+}Cl^{-d}$ (0.01 *M* NaCl)	25	$-11._8$	—	Goralczyk, 2003
$C_5SO_3^{-}Na^{+}$–$C_{10}Pyr^{+}Cl^{-d}$ (0.03 *M* NaCl)	25	$-10._8$	—	Goralczyk, 2003
$C_5SO_3^{-}Na^{+}$–$C_{10}Pyr^{+}Cl^{-d}$ (0.03 *M* NaBr)	25	−8.2	—	Goralczyk, 2003
$C_5SO_3^{-}Na^{+}$–$C_{10}Pyr^{+}Cl^{-d}$ (0.03 *M* NaI)	25	−5.5	—	Goralczyk, 2003
$C_7SO_3^{-}Na^{+}$–$C_{10}Pyr^{+}Cl^{-d}$ (0.01 *M* NaCl)	25	$-15._4$	—	Goralczyk, 2003
$C_8SO_3^{-}Na^{+}$–$C_{14}N^{+}Me_3Br^{-}$ (0.1 *M* NaBr (aq.)–air)	25	$-13._5$	—	Gu, 1989
$C_8SO_3^{-}Na^{+}$–$C_{14}N^{+}Me_3Br^{-}$ (0.1 *M* NaBr (aq.)–PTFE^{e})	25	$-10._8$ (β^{σ}_{SL})	—	Gu, 1989
$C_8SO_3^{-}Na^{+}$–$C_{14}N^{+}Me_3Br^{-}$ (0.1 *M* NaBr (aq.)–Parafilm)	25	$-11._2$ (β^{σ}_{SL})	—	Gu, 1989
$C_{10}SO_3^{-}Na^{+}$–$C_{12}N^{+}Me_3Br^{-}$	25	$-35._6$	—	Rodakiewicz-Nowak, 1982
$C_{10}SO_3^{-}Na^{+}$–$C_{12}N^{+}Me_3Br^{-}$ (H_2O–PTFE^{e})	25	$-28._8$ (β^{σ}_{SL})	—	Gu, 1989
$C_{10}SO_3^{-}Na^{+}$–$C_{12}N^{+}Me_3Br^{-}$ (H_2O–polyethylene)	25	$-26._6$ (β^{σ}_{SL})	—	Gu, 1989
$C_{10}SO_3^{-}Na^{+}$–$C_{12}N^{+}Me_3Br^{-}$ (0.1 *M* NaBr (aq.)–air)	25	$-19._6$	—	Gu, 1989

$C_{10}SO_3^-Na^+$–$C_{12}N^+Me_3Br^-$ (0.1 *M* NaBr (aq.)–PTFE^e)	25	$-14._1$	—	Gu, 1989
$C_{10}SO_3^-Na^+$–$C_{12}N^+Me_3Br^-$ (0.1 *M* NaBr (aq.)–Parafilm)	25	$-15._3$	—	Gu, 1989
$C_{10}SO_3^-Na^+$–$C_{12}Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–air)	25	$-19._7$	—	Gu, 1989
$C_{10}SO_3^-Na^+$–$C_{12}Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–PTFE^e)	25	$-14._2$ (β^{σ}_{SL})	—	Gu, 1989
$C_{10}SO_3^-Na^+$–$C_{12}Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–Parafilm)	25	$-15._5$ (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_8Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–air)	25	$-19._5$	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_8Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–PTFE^e)	25	$-14._1$ (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_8Pyr^+Br^{-d}$ (0.1 *M* NaBr (aq.)–Parafilm)	25	$-15._3$ (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_{10}Pyr^+Cl^{-d}$ (0.1 *M* NaCl)	25	$-33._2$	—	Liu, 1996
$C_8SO_4^-Na^+$–$C_8N^+Me_3Br^-$	25	$-14._2$	$-10._2$	Zhao, 1980
$C_8SO_4^-Na^+$–$C_8N^+Me_3Br^-$ (0.1 *M* NaBr)	25	−14	−10	Liu, 1996
$C_8SO_4^-Na^+$–$C_8Pyr^+Br^{-d}$	25	—	$-10._7$	Li, 1992
$C_8SO_4^-Na^+$–$C_8(OE)_3Pyr^+Cl^{-d}$	25	—	$-6._3$	Li, 1992
$C_8OESO_4^-Na^+$–$C_8Pyr^+Br^{-d}$	25	—	$-8._1$	Li, 1992
$C_8(OE)_3SO_4^-Na^+$–$C_8Pyr^+Br^{-d}$	25	—	$-4._4$	Li, 1992
$C_8(OE)_3SO_4^-Na^+$–$C_8(OE)_3Pyr^+Cl^{-d}$	25	—	$-3._9$	Li, 1992
$C_8(OE)_3SO_4^-Na^+$–$C_{10}Pyr^+Cl^{-d}$	25	—	$-8._1$	Li, 1992
$C_8(OE)_3SO_4^-Na^+$–$C_{12}Pyr^+Br^{-d}$	25	—	$-10._4$	Li, 1992
$C_8(OE)_3SO_4^-Na^+$–$C_{14}Pyr^+Br^{-d}$	25	—	$-11._4$	Li, 1992
$C_{10}SO_4^-Na^+$–$C_{10}N^+Me_3Br^-$	25	—	$-18._5$	Corkill, 1963
$C_{10}SO_4^-Na^+$–$C_{10}N^+Me_3Br^-$ (0.05 *M* NaBr)	23	—	$-13._2$	Holland, 1983
$C_{12}SO_4^-Na^+$–$C_{12}N^+Me_3Br^-$	25	−27.8	$-25._5$	Lucassen-Reynders, 1981
$C_{12}SO_4^-Na^+$–$C_{12}N^+Me_3Br^-$ (H_2O–PTFE^e)	25	−30.6 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_4^-Na^+$–$C_{12}N^+Me_3Br^-$ (H_2O–polyethylene)	25	−26.7 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}(OE)_3SO_4^-Na^+$–$C_{16}N^+Me_3Cl^-$	25	—	$-23._1$	Esumi, 1994
$C_{12}(OE)_5SO_4^-Na^+$–$C_{16}N^+Me_3Cl^-$	25	—	$-16._8$	Esumi, 1994
$C_{12}(OE)_3SO_4^-Na^+$–$C_8F_{17}CH_2CH(OH)CH_2N^+(CH_3)$-$(C_2H_4OH)_2 \cdot Cl^-$	25	—	$-17._1$	Esumi, 1994
$C_{12}(OE)_5SO_4^-Na^+$–$C_8F_{17}CH_2CH(OH)CH_2N^+$-$(CH_3)(C_2H_4OH)_2 \cdot Cl^-$	25	—	$-10._7$	Esumi, 1994

(*Continued next page*)

TABLE 11-1 (*Continued*)

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
$C_4H_9\phi SO_3^-Na^+–C_{16}N^+Me_3Br^-$	27	-9.9_5	—	Bhat, 1999
$(CH_3)_2CHCH_2\phi SO_3^-Na^+–C_{16}N^+Me_3Br^-$	27	−9.4	—	Bhat, 1999
$(CH_3)_3C\phi SO_3^-Na^+–C_{16}N^+Me_3Br^-$	27	−8.2	—	Bhat, 1999
C_{16}-2-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−19.4	Bourrel, 1984
C_{16}-4-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−17.2	Bourrel, 1984
C_{16}-6-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−16.1	Bourrel, 1984
C_{16}-8-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−15.3	Bourrel, 1984
C_{14}-7-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−17.3	Bourrel, 1984
C_{12}-6-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−18.7	Bourrel, 1984
C_{10}-5-ϕ-$SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−19.9	Bourrel, 1984
$C_{12}SO_3^-Na^+–C_{14}N^+Me_3Br^-$	50	—	−20.0	Bourrel, 1984
Anionic–Nonionic Mixtures				
$C_7F_{15}COO^-Na^+–C_8SOCH_3$	25	−4.7	−3.2	Zhao, 1986
$C_7F_{15}COO^-Li^+–C_8$-β-D-glucoside	25	—	−1.9	Esumi, 1996
$C_{10}SO_3^-Na^+$–1,2-C_{12} diol (0.1 *M* NaCl)	25	−2.4	—	Rosen, 1983
$C_{12}SO_3^-Na^+$–1,2-C_{10} diol (0.1 *M* NaCl)	25	-2.7_5	−1.3	Zhou, 2003
$C_{12}SO_3^-Na^+$–1,2-C_{12} diol (0.1 *M* NaCl)	25	−3.0	−1.45	Rosen, 1983
$C_{12}SO_3^-Na^+$–4,5-C_{10} diol (0.1 *M* NaCl)	25	−3.2	—	Zhou, 2003
$C_{14}SO_3^-Na^+$–1,2-C_{12} diol (0.1 *M* NaCl)	25	−2.6	—	Rosen, 1983
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (H_2O–air)	25	−2.6	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (H_2O–Parafilm)	25	−2.1 (β^{σ}_{SL})	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (H_2O–PTFE[e])	25	−2.0 (β^{σ}_{SL})	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (0.1 *M* NaCl (aq.)–air)	25	−3.1	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (0.1 *M* NaCl (aq.)–Parafilm)	25	−2.9 (β^{σ}_{SL})	—	Rosen, 1989b

$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (0.1 *M* NaCl (aq.)–PTFE^{-e})	25	−2.5 (β^{σ}_{SL})	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-decyl-2-pyrrolid(in)one (0.1 *M* NaCl (aq.)–hexadecane)	25	−1.7 (β^{σ}_{LL})	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–*N*-octyl-2-pyrrolid(in)one (0.1 *M* NaCl (aq.)–hexadecane)	25	−2.3 (β^{σ}_{LL})	—	Rosen, 1989b
$C_{12}SO_3^-Na^+$–$C_{11}H_{23}CON(CH_3)CH_2(CHOH)_4CH_2OH$ (0.1 *M* NaCl)	25	−2.8	−1.8	Zhou, 2003
$C_{12}SAS^-Na^{+b}$–$C_{12}(OE)_7OH$	25	−0.2	−1.0	Zhu, 1987
$C_{10}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−2.2	—	Rosen, 1983
$C_{12}SO_3^-Na^+$–TMN6^f (0.1 *M* NaCl)	25	−1.7	−2.1	Zhou, 2003
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl)	25	−1.6	−0.8	Zhou, 2003
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_7OH$ (0.1 *M* NaCl)	25	−1.7	−2.4	Zhou, 2003
$C_{12}SO_3^-Na^{+b}$–$C_{12}(OE)_8OH$	25	−1.5	−3.4	Rosen, 1983
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−2.6	−3.1	Rosen, 1983
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.5 *M* NaCl)	25	−2.0	—	Rosen, 1983
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl (aq.)–PTFE^e)	25	−2.1 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.5 *M* NaCl (aq.)–PTFE^e)	25	−1.7 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_{14}(OE)_4OH$ (0.1 *M* NaCl)	25	−1.1	−0.5	Zhou, 2003
$C_{12}SO_3^-Na^+$–$C_{14}(OE)_8OH$ (0.1 *M* NaCl)	25	−1.4	−2.0	Zhou, 2003
$C_{14}SO_3^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−2.3	—	Rosen, 1983
$C_{10}SO_4^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−3.2	—	Rosen, 1983
$C_{12}SO_4^-Na^+$–$C_8(OE)_4OH$	25	—	−3.1	Lange, 1973
$C_{12}SO_4^-Na^+$–$C_8(OE)_6OH$	25	—	−3.4	Lange, 1973
$C_{12}SO_4^-Na^+$–$C_8(OE)_{12}OH$	25	—	−4.1	Lange, 1973
$C_{12}SO_4^-Na^+$–$C_{10}(OE)_4OH$ (5×10^{-4} *M* Na_2CO_3)	23	—	−3.6	Holland, 1983
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl)	25	−3.0	—	Huber, 1991
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl–PTFE^e)	25	−2.1 (β^{σ}_{SL})	—	Huber, 1991

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TABLE 11-1 (*Continued*)

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_6OH$ (0.1 *M* NaCl)	25	−2.5	−3.4	Penfold, 1995; Goloub, 2000
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_8OH$	25	−2.7	−4.1	Rosen, 1983
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−3.5	—	Rosen, 1983
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl–PTFE[e])	25	−2.9 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_4^-Na^+$–$C_{14}(OE)_8OH$ (0.5 *M* NaCl)	25	−3.3, 3.1	−3.0	Ingram, 1980; Rosen, 1983
$C_{12}SO_4^-Na^+$–$C_{12}(OE)_8OH$ (0.5 *M* NaCl–PTFE[e])	25	−2.7 (β^{σ}_{SL})	—	Gu, 1989
$C_{12}SO_4^-Na^+$–$C_{16}(OE)_{10}OH$[g]	30	−4.3	−6.6	Ogino, 1986
$C_{12}SO_4^-Na^+$–$C_{16}(OE)_{20}OH$[g]	30	—	−6.2	Ogino, 1986
$C_{12}SO_4^-Na^+$–$C_{16}(OE)_{30}OH$[g]	30	—	−4.3	Ogino, 1986
$C_{14}SO_4^-Na^+$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−3.2	—	Rosen, 1983
$C_{12}(OE)SO_4^-Na^+$–C_{10}-β-glucoside (0.1 *M* NaCl, pH 5.7)	25	−1.8	−1.4	Rosen, 2001a
$C_{12}(OE)SO_4^-Na^+$–C_{10}-β-maltoside (0.1 *M* NaCl, pH 5.7)	25	−1.5	−1.2	Rosen, 2001a
$C_{12}(OE)SO_4^-Na^+$–C_{12}-β-maltoside (0.1 *M* NaCl, pH 5.7)	25	−1.4	−1.3	Rosen, 2001a
$C_{12}(OE)SO_4^-Na^+$–C_{12}-2:1 (molar) C_{12} maltoside, C_{12} glucoside (0.1 *M* NaCl, pH 5.7)	25	−3.2	−3.2	Rosen, 2001a
$C_{12}(OE)_2SO_4^-Na^+$–1,2-C_{10} diol (0.1 *M* NaCl)	25	−1.4	∼0	Zhou, 2003
$C_{12}(OE)_2SO_4^-Na^+$–$C_{11}H_{23}CON(CH_3)$-$CH_2(CHOH)_4OH$ (0.1 *M* NaCl)	25	−1.8	−1.2	Zhou, 2003
$C_{12}(OE)_2SO_4^-Na^+$–$C_8(OE)_4OH$	25	—	−1.6	Holland, 1984
$C_{12}(OE)_2SO_4^-Na^+$–TMN6[f] (0.1 *M* NaCl)	25	−1.6	−0.9	Zhou, 2003
$C_{12}(OE)_2SO_4^-Na^+$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl)	25	−1.4	−0.9	Zhou, 2003
$C_{12}(OE)_2SO_4^-Na^+$–$C_{12}(OE)_6OH$ (0.1 *M* NaCl)	25	−1.5	-1.9_5	Zhou, 2003
$C_{12}(OE)_2SO_4^-Na^{+}$[b]–$C_{12}(OE)_{10}OH$[b] (0.1 *M* NaCl)	25	−2.1	−2.3	Rosen 1988
C_{10}-3$\phi SO_3^-Na^+$–$C_9\phi(OE)_{10}OH$ (0.17 *N* NaCl)[g]	27	—	−1.5	Osborne-Lee, 1985
LAS^-Na^{+}[a]–C_{10}-β-maltoside (0.01 *M* NaCl)	22	−1.9	−2.1	Liljekvist, 2000

LAS^-Na^{+a}–$C_{11}CON(C_2H_4OH)_2$ (0.1 *M* NaCl)	25	−2.4	−1.5	Rosen, 1988
LAS^-Na^{+a}–*N*-Octyl-2-pyrrolid(in)one (0.005 *M* NaCl (aq.)–air)	25	−3.8	−2.3	Zhu, 1989
LAS^-Na^{+a}–*N*-Dodecyl-2-pyrrolid(in)one (0.005 *M* NaCl (aq.)–air)	25	−3.1	−1.7	Zhu, 1989
LAS^-Na^{+a}–$C_{10}(OE)_8OH$ (0.1 *M* NaCl)	22	−4.8	−3.3	Liljekvist, 2000
LAS^-Na^{+a}–$C_{12}(OE)_{10}OH$ (0.1 *M* NaCl)	25	−2.4	−2.7	Rosen, 1988
C_{12}-2-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$	25	−3.1	−5.2	Utarapichart, 1987
C_{12}-2-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.005 *N* NaCl)	25	−4.0	−5.8	Utarapichart, 1987
C_{12}-2-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.01 *N* NaCl)	25	−4.3	−5.4	Utarapichart, 1987
C_{12}-2-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.01 *N* NaCl)	40	−3.4	−3.8	Utarapichart, 1987
C_{12}-4-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$	25	−2.3	−5.1	Utarapichart, 1987
C_{12}-4-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.005 *N* NaCl)	25	−3.9	−5.5	Utarapichart, 1987
C_{12}-4-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.01 *N* NaCl)	25	−3.9	−5.0	Utarapichart, 1987
C_{12}-4-$\phi SO_3^- Na^+$–$C_{12}(OE)_8OH$ (0.1 *N* NaCl)	25	−3.5	−3.9	Utarapichart, 1987
C_{12}-4-$\phi SO_3^- Na^+$–$C_9\phi(OE)_{50}OH^b$ (0.17 *N* NaCl)	27	—	−2.6	Osborne-Lee, 1985
AOT^c-1,2-C_{10} diol (0.1 *M* NaCl)	25	−1.3	−1.2	Zhou, 2003
AOT^c–$TMN6^f$ (0.1 *M* NaCl)	25	−0.5	−0.5	Zhou, 2003
AOT^cNa^+–$C_{12}(OE)_5OH$	25	−0.9	−1.2	Chang, 1985
AOT^c–$C_{12}(OE)_6OH$ (0.1 *M* NaCl)	25	−1.6	−1.5	Zhou, 2003
AOT^cNa^+–$C_{12}(OE)_7OH$	25	−1.6	−1.9	Chang, 1985
AOT^cNa^+–$C_{12}(OE)_8OH$	25	−2.6	−2.0	Utarapichart, 1987
AOT^cNa^+–$C_{12}(OE)_8OH$ (0.05 *N* NaCl)	25	−1.7	−3.6	Utarapichart, 1987
AOT^c–$C_{14}(OE)_8OH$ (0.1 *M* NaCl)	25	-2.0_5	−0.2	Zhou, 2003
$C_{12}H_{25}CH(SO_3^- Na^+)COOCH_3$–$C_9H_{19}CON(CH_3)$-$CH_2(CHOH)_4CH_2OH$	30	—	−2.1	Okano, 2000
	Anionic–Zwitterionic Mixtures			
$C_8F_{17}SO_3^- Li^+$–$C_6F_{13}C_2H_4SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COO^-$	25	—	−8.3	Esumi, 1993

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TABLE 11-1 (*Continued*)

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
$C_{12}SO_3^-Na^+$–$C_{12}N^+H_2(CH_2)_2COO^-$ (0.1 *M* NaBr (aq.)–air, pH 5.8)	25	−4.2	−1.2	Rosen, 1991a
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)Me)CH_2COO^-$ (pH 5.0)	25	−6.9	−5.4	Rosen, 1984
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)Me)CH_2COO^-$ (pH 6.7)	25	−4.9	−4.4	Rosen, 1984
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)Me)CH_2COO^-$ (pH 9.3)	25	−2.9	−1.7	Rosen, 1984
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)Me)CH_2COO^-$ (0.1 *M* NaBr-PTFE^e, pH 5.8)	25	−6.2	—	Rosen, 1987
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (0.1 *M* NaBr–Parafilm, pH 5.8)	25	−6.9	—	Gu, 1989
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), hexadecane–water	25	−5.2 (β^{σ}_{LL})	−4.0(β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), dodecane–water	25	−4.8 (β^{σ}_{LL})	−3.6(β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), heptane–water	25	−4.7 (β^{σ}_{LL})	−4.0(β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), isooctane–water	25	−4.4 (β^{σ}_{LL})	−4.0(β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), cyclohexane–water	25	−5.0 (β^{σ}_{LL})	−4.2(β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{12}N^+(B_z)(Me)CH_2COO^-$ (pH 5.8), toluene–water	25	−3.2 (β^{σ}_{LL})	−2.1 (β^{M}_{LL})	Rosen, 1989c
$C_{12}SO_3^-Na^+$–$C_{10}N^+(B_z)(Me)C_2H_4SO_3^-$ (pH 6.6)	25	−2.5	—	Rosen, 1984
$C_{12}SO_3^-Na^+$–$C_{14}N^+(CH_3)_2O^-$ (0.1 *M* NaCl (aq.)–air, pH 5.8)	25	−10.3	−7.8	Rosen, 1994
$C_{12}SO_3^-Na^+$–$C_{14}N^+(CH_3)_2O^-$ (0.1 *M* NaCl (aq.)–air, pH 2.9)	25	−13.5	—	Rosen, 1994
$C_{10}SO_4^-Na^+$–$C_{12}N^+H_2(CH_2)_2COO^-$	30	−13.4	−10.6	Tajima, 1979

$C_{10}SO_4^-Na^+$–$C_{10}S^+(Me)O^-$	25	−4.3	−4.3	Zhu, 1988
$C_{12}SO_4^-Na^+$–$C_{12}N^+H_2(CH_2)_2COO^-$	30	−15.7	−14.1	Tajima, 1979
$C_{12}SO_4^-Na^+$–$C_{12}N^+(CH_3)_2O^-$	23	—	−7.0	Goloub, 2000
$C_{12}SO_4^-Na^+$–$C_{10}S^+(Me)O^-$ (1×10^{-3} *M* Na_2CO_3)	24	—	−2.4	Holland, 1983
$C_{12}SO_4^-Na^+$–$C_{10}P^+(Me)_2O^-$ (1×10^{-3} *M* Na_2CO_3)	24	—	−3.7	Holland, 1983
$C_{12}SO_4^-Li^+$–$C_6F_{13}C_2H_4SO_2NH(CH_2)_3N^+(CH_3)_2CH_2$-$COO^-$	25	—	0	Esumi, 1993
$C_{14}SO_4^-Na^+$–$C_{12}N^+H_2(CH_2)_2COO^-$	30	−15.5	−15.5	Tajima, 1979
LAS^-Na^{+a}–$C_{12}N^+(Me)_2CH_2COO^-$ (0.1 *N* NaCl, pH 5.8)	25	−3.8	−2.9	Rosen, 1988
LAS^-Na^{+a}–$C_{12}N^+(Me)_2CH_2COO^-$ (0.1 *N* NaCl, pH 9.3)	25	−2.8	−1.7	Rosen, 1988
	Cationic–Cationic Mixtures			
$C_{12}N^+Me_3Cl^-$–$C_{14}N^+Me_3Cl$	30	—	−0.8	Filipovic-Vincekovic, 1997
	Cationic–Nonionic Mixtures			
$C_{10}N^+Me_3Br^-$–C_{10}-β-glucoside (0.1 *M* NaCl, pH 9.0)	25	−1.2	−1.2	Rosen, 2001a
$C_{10}N^+Me_3Br^-$–C_{10}-β-maltoside (0.1 *M* NaCl, pH 9.0)	25	−0.3	−0.3	Rosen, 2001a
$C_{12}N^+Me_3Cl^-$–C_{12}-β-maltoside (0.1 *M* NaCl, pH 5.7)	25	−1.0	−0.8	Rosen, 2001a
$C_{12}N^+Me_3Cl^-$–C_{12}-β-maltoside (0.1 *M* NaCl, pH 9.0)	25	−1.9	−1.5	Rosen, 2001a
$C_{12}N^+Me_3Cl^-$–2:1 (molar) C_{12} maltoside, C_{12} glucoside (0.1 *M* NaCl, pH 9.0)	25	−2.8	−2.8	Rosen, 2001a
$C_{14}N^+Me_3Br^-$–C_{12}-β-maltoside (0.1 *M* NaCl, pH 9.0)	25	−1.8	−1.3	Rosen, 2001a
$C_{10}N^+Me_3Br^-$–$C_8(OE)_4OH$ (0.05 *M* NaBr)	23	—	−1.8	Holland, 1983
$C_{12}N^+Me_3Cl^-$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl)	25	−1.8	-0.3_5	Zhou, 2003
$C_{12}N^+Me_3Cl^-$–$C_{12}(OE)_5OH$	25	—	−1.0	Rubingh, 1982
$C_{12}N^+Me_3Cl^-$–$C_{12}(OE)_7OH$ (0.1 *M* NaCl)	25	−1.8	−1.2	Zhou, 2003
$C_{16}N^+Me_3Br^-$–$C_{12}(OE)_5OH$	25	—	−3.0	Rubingh, 1982
$C_{16}N^+Me_3Cl^-$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	—	−3.1	Lange, 1973

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TABLE 11-1 (*Continued*)

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
$C_{20}N^+Me_3Cl^-$–$C_{12}(OE)_8OH$	25	—	−4.6	Lange, 1973
$C_{12}Pyr^+Br^{-d}$-*N*-octylpyrrolid(in)one (0.1 *M* NaBr, ph 5.9)	25	−1.6	—	Rosen, 1991a
$C_{12}Pyr^+Br^-$–$C_{12}(OE)_8OH$	25	−1.0	—	Hua, 1982a
$C_{12}Pyr^+Br^-$–$C_{12}(OE)_8OH$ (0.1 *M* NaBr)	25	−0.8	—	Rosen, 1982
$C_{12}Pyr^+Cl^-$–$C_{12}(OE)_8OH$	25	−2.8	—	Rosen, 1983
$C_{12}Pyr^+Cl^-$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	10	−2.5	—	Rosen, 1983
$C_{12}Pyr^+Cl^-$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−2.2	—	Rosen, 1983
$C_{12}Pyr^+Cl^-$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	40	−2.0	—	Rosen, 1983
$C_{12}Pyr^+Cl^-$–$C_{12}(OE)_8OH$ (0.5 *M* NaCl)	25	−1.5	—	Rosen, 1983
$(C_{12})_2N^+Me_2Br^-$–$C_{12}(OE)_5OH$	25	—	−1.6	Rubingh, 1982
Cationic-Zwitterionic Mixtures				
$C_{10}N^+Me_3Br^-$–$C_{10}S^+MeO^-$, pH 5.9	25	−0.6	−0.6	Zhu, 1988
$C_{12}N^+Me_3Br^-$–$C_{12}N^+(Bz)(Me)CH_2COO^-$, pH 5.8	25	−1.3	−1.3	Rosen, 1984
$C_{12}Pyr^+Br^{-d}$–$C_{12}N^+H_2CH_2CH_2COO^-$ (0.1 *M* NaBr (aq.), pH 5.8)	25	−4.8	−3.4	Rosen, 1991a
Nonionic–Nonionic Mixtures				
C_{10}-β-glucoside–C_{10}-β-maltoside (0.1 *M* NaCl, pH 9.0)	25	−0.3	−0.2	Rosen, 2001a
C_{10}-β-glucoside–$C_{12}(OE)_7OH$	25	—	-0.0_4	Sierra, 1999
C_{10}-β-maltoside–$C_{10}(OE)_8OH$ (0.1 *M* NaCl)	22	−0.5	−0.3	Liljekvist, 2000
C_{12}-β-maltoside–$C_{12}(OE)_7OH$ (0.1 *M* NaCl, pH 5.7)	25	−0.7	-0.0_5	Rosen, 2001a
$C_{12}(OE)_3OH$–$C_{12}(OE)_8OH$	25	−0.2	—	Rosen, 1982
$C_{12}(OE)_3OH$–$C_{12}(OE)_8OH$ (H_2O–hexadecane)	25	$-0.7(\beta^{\sigma}_{LL})$	$-0.2\ (\beta^{M}_{LL})$	Rosen, 1991b
$C_{12}(OE)_4OH$–$C_{12}(OE)_8OH$ (0.1 *M* NaCl)	25	−0.3	—	Huber, 1991
$C_{12}(OE)_8OH$–$C_{12}(OE)_4OH$ (0.1 *M* NaCl–PTFE^e)	25	$0.0\ (\beta^{\sigma}_{SL})$	—	Huber, 1991

$C_{10}F_{19}(OE)_9OH$–t-$C_8H_{17}C_6H_4(OE)_{10}OH$	25	+0.8	—	Zhao, 1986
N-butyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, pH 7.0	25	−0.4	—	Wu, 2002
N-butyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, on polyethylene, pH 7.0	25	$-3.5\beta^{\sigma}_{SL}$	—	Wu, 2002
N-hexyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, pH 7.0	25	−0.8	—	Wu, 2002
N-hexyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, on polyethylene, pH 7.0	25	$-5.9\beta^{\sigma}_{SL}$	—	Wu, 2002
N-(2 ethylhexyl)-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, pH 7.0	25	−0.7	—	Wu, 2002
N-(2 ethylhexyl)-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, on polyethylene, pH 7.0	25	$-6.7\beta^{\sigma}_{SL}$	—	Wu, 2002
N-octyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, pH 7.0	25	−0.4	—	Wu, 2002
N-octyl-2-pyrrolid(in)one–$C_{12}(OE)_8OH$ (H_2O–hexadecane)	25	−0.5 (β^{σ}_{LL})	−0.1 (β^{M}_{LL})	Rosen, 1991b
N-octyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, on polyethylene, pH 7.0	25	−5.4 (β^{σ}_{SL})	—	Wu, 2002
N-decyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, pH 7.0	25	+0.1	—	Wu, 2002
N-decyl-2-pyrrolid(in)one–$(CH_3)_3SiOSi(CH_3)$-$[CH_2(CH_2CH_2O)_{8.5}CH_3]OSi(CH_3)_3$, on polyethylene, pH 7.0	25	+1.2 (β^{σ}_{SL})	—	Wu, 2002
N-dodecyl-2-pyrrolid(in)one–$C_{12}(OE)_8OH$ (H_2O–hexadecane)	25	−2.0 (β^{σ}_{LL})	−1.4 (β^{M}_{LL})	Rosen, 1991b

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TABLE 11-1 (*Continued*)

Mixture	Temp. (°C)	β^{σ}	β^{M}	Reference
	Nonionic–Zwitterionic Mixtures			
C_{12}-β-maltoside–$C_{12}N^{+}(Bz)(Me)CH_2COO^{-}$ (0.1 *M* NaCl, ph 5.7)	25	−1.7	−1.1	Rosen, 2001a
2:1 (molar) C_{12} maltoside-C_{12} glucoside–$C_{12}N^{+}(Bz)MeCH_2COO^{-}$ (0.1 *M* NaCl, pH 5.7)	25	−2.7	−2.7	Rosen, 2001a
$C_{10}(EO)_4OH$–$C_{12}N^{+}(Me)_2O^{-}$ (5×10^{-4} Na_2CO_3)	23	—	−0.8	Holland, 1983
$C_{12}(EO)_6OH$–$C_{12}N^{+}(Me)_2O^{-}$ (pH 2)	23	—	−1.0	Goloub, 2000
$C_{12}(EO)_6OH$–$C_{12}N^{+}(Me)_2O^{-}$ (pH 8)	23	—	−0.3	Goloub, 2000
$C_{12}(EO)_8OH$–$C_{12}N^{+}(Bz)(Me)CH_2COO^{-}$	25	−0.6	−0.9	Rosen, 1984

[a] $LAS^{-}Na^{+}$ = commercial sodium C_{12} benzenesulfonate.

[b] SAS = commercial secondary alkanesulfonate.

[c] $AOT^{-}Na^{+}$ = sodium di(2-ethylhexyl)sulfosuccinate.

[d] Pyr^{+} = pyridinium.

[e] PTFE = polytetrafluoroethylene.

[f] TMN6 = commercial 2,4,8-trimethyl-nonanol $(OC_2H_4)_8OH$.

[g] Commercial materials.

2001b; Zhou, 2003). Also, it has been observed that bulky head groups in a surfactant are more readily accommodated at the surface of a convex micelle than at the planar air–solution interface (Matsuki, 1997).

The values of both β^{σ} and β^{M} become more negative as the chain lengths of the alkyl groups on the surfactants are increased. The negative value of β^{σ} appears to become larger as the alkyl chains approach each other in length. This appears not to be true for β^{M}, which becomes more negative with increase in the total number of carbon atoms in the alkyl chains of the two surfactants. Zwitterionics that are capable of accepting a proton (amino carboxylates, amine oxides) interact with anionics by acquiring a net positive charge through acceptance of a proton from the water. The resulting cationic conjugate acid interacts electrostatically with the anionic surfactant. An increase in the pH of the aqueous phase consequently causes a reduction in the strength of the attractive interaction between the two surfactants, as illustrated by the $C_{12}SO_3^-Na^+ - C_{12}N^+(B_z)(Me)CH_2COO^-$ system. Decrease in the basicity of the zwitterionic, e.g., $[C_{10}N^+(B_z)(Me)CH_2CH_2SO_3^-$ vs. $C_{12}N^+(B_z)(Me)CH_2COO^-]$ at constant pH, also decreases the attractive interaction with an anionic. Zwitterionics that are capable of losing a proton and acquiring a negative charge interact significantly with cationic surfactants. *N*-Alkyl-*N*, *N*-dimethylamine oxides and *N*-alkyl-*N*-methylsulfoxides interact with anionic surfactants in a manner similar to that of other zwitterionics by accepting a proton from the water to form the cationic conjugate acid. Their interaction with cationic surfactants is far weaker (Zhu, 1988) since these compounds cannot become solely anionic in nature.

In general, an increase in the elecrolyte content of the aqueous phase produces a decrease in the negative value of β^{σ}. This is true even for ionic–POE nonionic mixtures, indicating that interaction between them is, at least partly, electrostatic. For anionic–cationic mixtures, the decrease in the negative value of β^{σ} upon addition of sodium halides was found to be NaI > NaBr > NaCl (Goralczyk, 2003), reflecting the order of decreasing tendency to neutralize the charge of the cationic surfactant (and, consequently, its attraction for the anionic). However, in the case of anionic–POE nonionic mixtures, an initial *increase* in the negative value of β^{σ} is observed when NaCl is added to the salt-free mixture. This has been attributed (Rosen, 1983) to complex formation between the Na^+ and the ether oxygens of the POE chain, resulting in its acquiring a positive charge that increases the strength of its interaction with anionic surfactant. This effect is not observed in cationic–POE nonionic mixtures (acquisition of a positive charge by the POE chain would not increase its interaction with a cationic surfactant).

Temperature increase in the 10–40°C range generally causes a decrease in attractive interaction.

III. CONDITIONS FOR THE EXISTENCE OF SYNERGISM

Based upon the same nonideal solution theory used in the evaluation of molecular interaction parameters above, the conditions for the existence of synergism in various fundamental interfacial phenomena, i.e., reduction of surface or interfacial tension, mixed micelle formation, have been derived mathematically. When synergism exists, the conditions at the point of maximum synergism, such as α^* (the mole fraction of surfactant 1 in the total surfactant in the solution phase), X^* (the mole fraction of surfactant 1 in the total surfactant at the interface), $C_{12,\min}^{M}$ (the minimum CMC of the mixture), and $\gamma_{\mathrm{CMC}}^{*}$ (the minimum surface tension of the mixture at its CMC), can all be determined from the values of the relevant molecular interaction parameters and properties of the individual surfactants.

However, it should be understood that, because of the assumptions and approximations used in the nonideal solution theory upon which these relations are based, the calculated values for conditions at the point of maximum synergism may only approximate the values found under experimental conditions and should be used mainly for estimation purposes. This is especially true when commercial surfactants are used that may contain surface-active materials (impurities) of a type different from that of the nominal surfactant. These may cause the molecular interaction parameters to have values somewhat different from those listed in Table 11-1 for the nominal surfactant. When such impurities are suspected, it is advisable to determine experimentally the values of the interaction parameters.

III.A. Synergism or Antagonism (Negative Synergism) in Surface or Interfacial Tension Reduction Efficiency

The efficiency of surface (or interfacial) tension reduction by a surfactant has been defined (Chapter 5, Section I) as the solution phase surfactant concentration required to produce a given surface (or interfacial) tension (reduction). Synergism in this respect is present in an aqueous system containing two surfactants when a given surface (or interfacial) tension can be attained at a total mixed surfactant concentration lower than that required of either surfactant by itself. Antagonism (negative synergism) is present when it is attained at a higher mixed surfactant concentration than that required of either surfactant by itself. Synergism and antagonism are illustrated in Figure 11-4.

From the relations upon which equations 11.1 and 11.2 are based and the definition for synergism or antagonism (negative synergism) of this type, it has been shown mathematically (Hua, 1982b, 1988) that the conditions for synergism or antagonism, in surface tension reduction efficiency to exist are:

Synergism	Antagonism
1. β^{σ} must be negative	1. β^{σ} must be positive
2. $\lvert\beta^{\sigma}\rvert > \lvert\ln(C_1^0/C_2^0)\rvert$	2. $\beta^{\sigma} > \lvert\ln(C_1^0/C_2^0)\rvert$

It is apparent from condition 2 that to increase the probability of synergism existing, the two surfactants selected for the mixture should have C_1^0 and C_2^0 values as close to each other as possible. When the values are equal, *any* value of β^{σ} (other than 0) will produce synergism or antagonism.

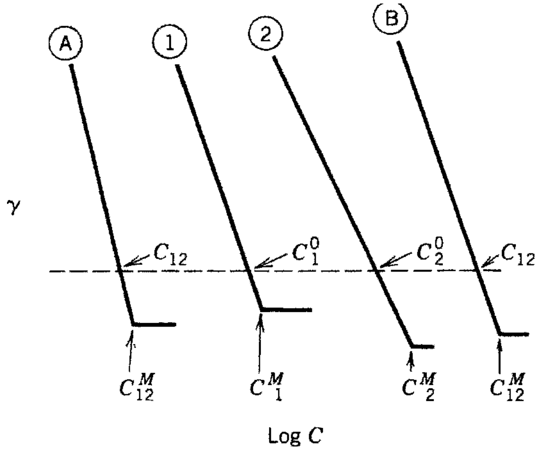

FIGURE 11-4 Synergism or antagonism (negative synergism) in surface tension reduction efficiency or in mixed micelle formation. (1) Pure surfactant 1; (2) pure surfactant 2; (*A*) mixture of surfactants 1 and 2 at a given mole fraction α in the aqueous phase showing synergism ($C_{12} < C_1^0$, C_2^0 or $C_{12}^M < C_1^M$, C_2^M); (*B*) mixture of surfactants 1 and 2 at a given mole fraction α in the solution phase showing antagonism (negative synergisn) ($C_{12} > C_1^0$, C_2^0 or $C_{12}^M > C_1^M$).

At the point of maximum synergism or maximum antagonism, i.e., at the minimum or maximum aqueous phase total molar concentration, respectively, of mixed surfactant to produce a given surface tension, the mole fraction α^* of surfactant 1 in the solution phase (on a surfactant-only basis) equals its mole fraction X_1^* at the interface and is given by the relation.

$$\alpha^* = \frac{\ln(C_1^0/C_2^0) + \beta^\sigma}{2\beta^\sigma}$$

The minimum (or maximum) aqueous phase total molar concentration of mixed surfactants in the system to produce a given surface tension is

$$C_{12,\min} = C_1^0 \exp\left\{\beta^\sigma\left[\frac{\beta^\sigma - \ln(C_1^0/C_2^0)}{2\beta^\sigma}\right]^2\right\}$$

From the above relation, the larger the negative value of β^σ, the smaller will be the value of $C_{12,\min}$; the larger its positive value, the greater the value of $C_{12,\max}$. Figure 11-5 illustrates the relations between log C_{12} and α in systems showing synergism or antagonism in surface tension reduction efficiency.

Analogous expressions have been derived for the existence of synergism in interfacial tension reduction efficiency at the liquid–liquid interface (Rosen, 1986)

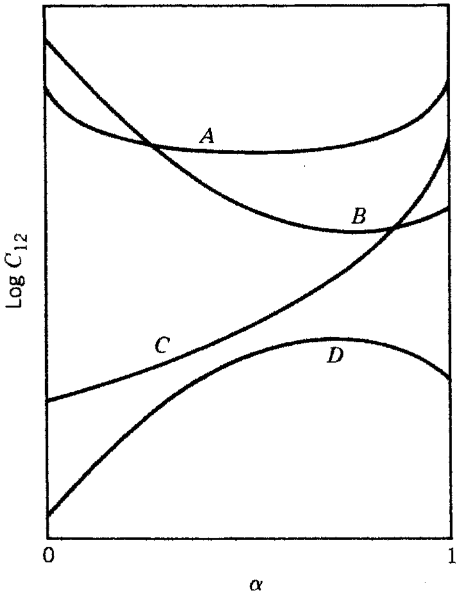

FIGURE 11-5 Synergism and antagonism (negative synergism) in surface tension reduction efficiency. LogC_{12} vs. α curves illustrating (*A*) synergism when $\beta^{\sigma} < 0,|\ln C_1^0|C_2^0 \approx 0|$; (*B*) synergism when $\beta^{\sigma} < 0$, $|\beta^{\sigma}| > \ln C_1^0|C_2^0| > 0$; (*C*) no synergism when $\beta^{\sigma} < 0$, $|\beta^{\sigma}| < |\ln C_1^0|C_2^0|$; (*D*) antagonism when $\beta^{\sigma} > 0$, $|\beta^{\sigma}| > |\ln C_1^0|C_2^0|$.

and at the liquid–hydrophobic solid interface (Rosen, 1987), and for the conditions at the point of maximum synergism.

III.B. Synergism or Antagonism (Negative Synergism) in Mixed Micelle Formation in Aqueous Medium

Synergism in this respect is present when the CMC in aqueous medium of any mixture of two surfactants is smaller than that of either individual surfactant. Antagonism in this respect is present when the CMC of the mixture is larger than the CMC of either surfactant of the mixture. These are illustrated in Figure 11-4. From equations 11.3 and 11.4 and the definition for this type of synergism or antagonism, the conditions for synergism or antagonism in this respect in a mixture containing two surfactants (in the absence of a second liquid phase) have been shown mathematically (Hua, 1982b, 1988) to be

Synergism	Antagonism
1. β^M must be negative	1. β^M must be positive
2. $\lvert\beta^M\rvert > \lvert\ln(C_1^M/C_2^M)\rvert$	2. $\lvert\beta^M\rvert > \lvert\ln(C_1^M/C_2^M)\rvert$

At the point of maximum synergism or antagonism, i.e., where the CMC of the system is at a minimum or maximum, respectively, the mole fraction α^* of surfactant 1 in the solution phase (on a surfactant-only basis) equals its mole fraction $X_1^{M,*}$ in the mixed micelle and is given by the relation

$$\alpha^* = \frac{\ln(C_1^M/C_2^M) + \beta^M}{2\beta^M}$$

The minimum (or maximum) CMC of the mixture is

$$C_{12,\min}^M = C_1^M \exp\left\{ \beta^M \left[\frac{\beta^M - \{\ln C_1^M/C_2^M\}}{2\beta^M} \right]^2 \right\}$$

Figure 11-6 illustrates the relation of log C_{12}^M to α in some systems showing synergism in mixed micelle formation.

Analogous expressions have been derived (Rosen, 1986) for the existence of synergism in mixed micelle formation in the presence of a second liquid phase and for the conditions at the point of maximum synergism.

III.C. Synergism or Antagonism (Negative Synergism) in Surface or Interfacial Tension Reduction Effectiveness

Synergism of this type exists when the mixture of two surfactants at its CMC reaches a lower surface (or interfacial) tension γ_{12} value than that attained at the CMC of either individual surfactant (γ_1^{CMC}, γ_2^{CMC}); antagonism exists when it reaches a higher surface (or interfacial) tension $\gamma_{12}^{\mathrm{CMC}}$ value. These are illustrated in Figure 11-7. The conditions for synergism or antagonism in surface tension reduction effectiveness to occur (Hua, 1988) are

Synergism	Antagonism
1. $\beta^\sigma - \beta^M$ must be negative	2. $\beta^\sigma - \beta^M$ must be positive
2. $\lvert\beta^\sigma - \beta^M\rvert > \left\lvert \ln\left(\frac{C_1^{0,\mathrm{CMC}} C_2^M}{C_2^{0,\mathrm{CMC}} C_1^M}\right) \right\rvert$	2. $\beta^\sigma - \beta^M > \left\lvert \ln\left(\frac{C_1^{0,\mathrm{CMC}} C_2^M}{C_2^{0,\mathrm{CMC}} C_1^M}\right) \right\rvert$

where $C_1^{0,\mathrm{CMC}}$ and $C_2^{0,\mathrm{CMC}}$ are the molar concentrations of surfactants 1 and 2, respectively, required to yield a surface tension equal to that of any mixture at its CMC.

It is apparent from condition 1 that synergism in surface tension reduction effectiveness can occur only when the attractive interaction between the two surfactants in the mixed monolayer at the aqueous solution–air interface is stronger than that in the mixed micelle in the solution phase. When the attraction between

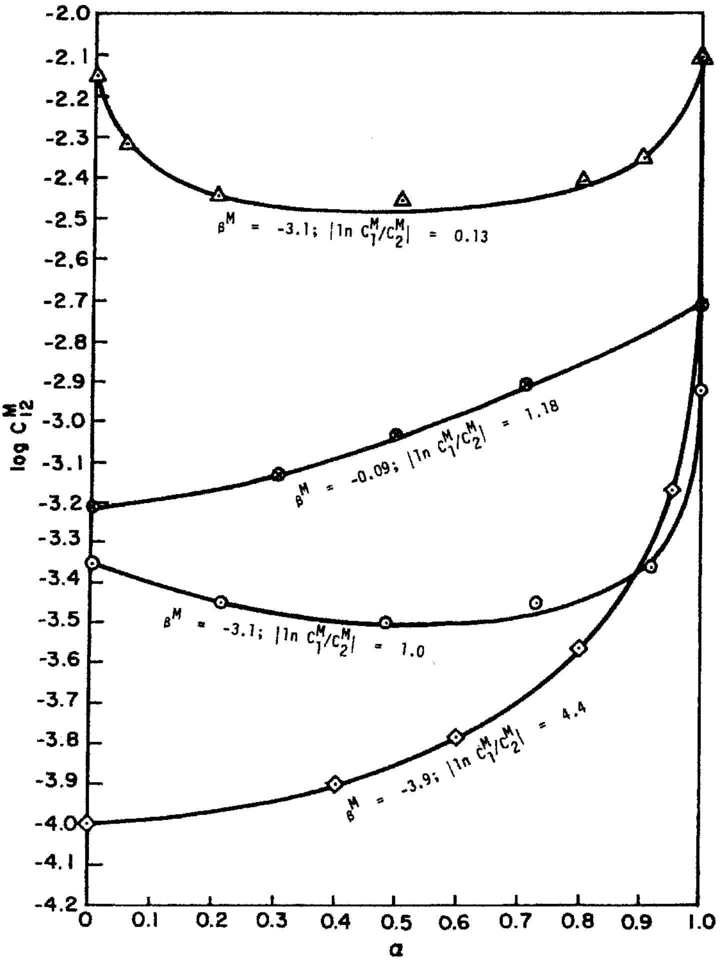

FIGURE 11-6 Synergism in mixed micelle formation for some binary surfactant mixtures. ◇, $C_{12}H_{25}SO_4Na/C_{12}H_{25}(OC_2H_4)_8OH$ mixtures in water at 25°C, showing no synergism; △, $C_{12}H_{25}SO_4Na/C_8H_{17}(OC_2H_4)_7OH$ mixtures in water at 25°C, showing synergism. Data from H. Lange and K. H. Beck, *Kolloid Z. Z. Polym.* **251**, 424 (1973). ○, $(C_{12}H_{25}SO_4)_2M/C_{12}H_{25}(OC_2H_4)_{49}OH$ ($M = Zn^{2+}, Mn^{2+}, Cu^{2+}, Mg^{2+}$) mixtures in water at 30°C, showing synergism. Data from N. Nishioka, *J. Colloid Interface Sci.* **60**, 242 (1977). ⊗, $C_{10}H_{21}S(O)CH_3/C_{10}H_{21}(OC_2H_4)_3$ mixtures at 25°C, showing no synergism. Data from B. T. Ingram, and A. H. W. Luckhurst, in *Surface Active Agents*, Soc. Chem. Ind., London, 1979, p. 89. Adapted with permission from Ref. 3. Copyright 1982, American Oil Chemists' Society. (From M. J. Rosen, in *Phenomena in Mixed Surfactant Systems*, J. F. Scamehern [Ed.], ACS Symp. Series 311, American Chemical Society, Washington, DC, 1986, p. 144.).

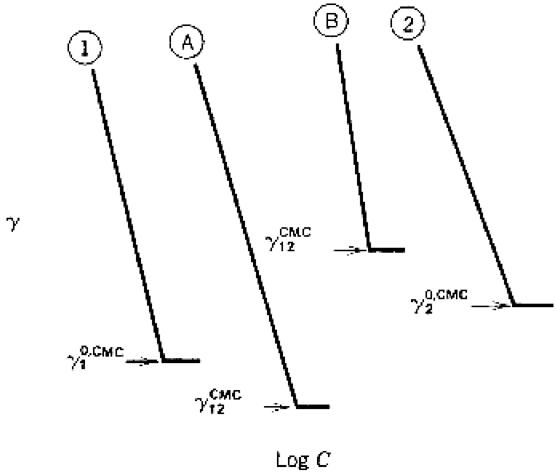

FIGURE 11-7 Synergism or, antagonism (negative synergism) in surface tension reduction effectiveness.(1) Pure surfactant 1; (2) pure surfactant 2; (*A*) mixture of surfactants 1 and 2 at a given mole fraction α in the solution phase showing: synergism ($\gamma_{12}^{\mathrm{CMC}} < \gamma_1^{\mathrm{CMC}}, \gamma_2^{\mathrm{CMC}}$); (*B*) Mixture of surfactants 1 and 2 at a given mole fraction α in the solution phase showing antagonism ($\gamma_{12}^{\mathrm{CMC}} > \gamma_1^{\mathrm{CMC}}, \gamma_2^{\mathrm{CMC}}$).

the two surfactants in the mixed micelle is stronger than in the mixed monolayer, it is possible for antagonism of this type to occur.

When, from the values of β^{σ} and β^{M}, it is possible that the system may show synergism of this type, it is advisable (for the purpose of determining the values of $C_1^{0,\mathrm{CMC}}$ and $C_2^{0,\mathrm{CMC}}$ for testing condition 2 above) to extend the γ–log C plot of the surfactant having the larger γ_{CMC} value down to a γ value equal to that of the other surfactant (with the smaller γ_{CMC}). To do this, the linear (or almost linear) portion of maximum slope below the CMC is extended downward (see Figure 11-8a); any portion of the plot close to the CMC showing a decrease in slope is ignored. The quantity $|\ln(C_1^{0,\mathrm{CMC}}/C_2^{0,\mathrm{CMC}})(C_2^{M}/C_1^{M})|$ then equals $\ln(C^{0,\mathrm{CMC}}/C^{M})$ for the surfactant whose plot has been extended.

When it is possible that the system may show antagonism (negative synergism) (from the values of β^{σ} and β^{M}), it is advisable to use values of $C_1^{0,\mathrm{CMC}}$ and $C_2^{0,\mathrm{CMC}}$ at the γ_{CMC} of the surfactant having the larger surface tension value at its CMC (see Figure 11–8*b*). In this case, the quantity $|\ln(C_1^{0,\mathrm{CMC}}/C_2^{0,\mathrm{CMC}})(C_2^{M}/C_1^{M})|$ equals $\ln C^{M}/C^{0,\mathrm{CMC}}$ for the surfactant having the smaller surface tension value at its CMC.

At the point of maximum synergism or maximum antagonism in surface or interfacial tension reduction effectiveness, the composition of the mixed interfacial layer equals the composition of the mixed micelle, i.e., $X_1^{*,E} = X_1^{M,*,E}.\alpha^{*,E}$, the mole fraction of surfactant 1 in the solution phase (on a surfactant-only basis) at this

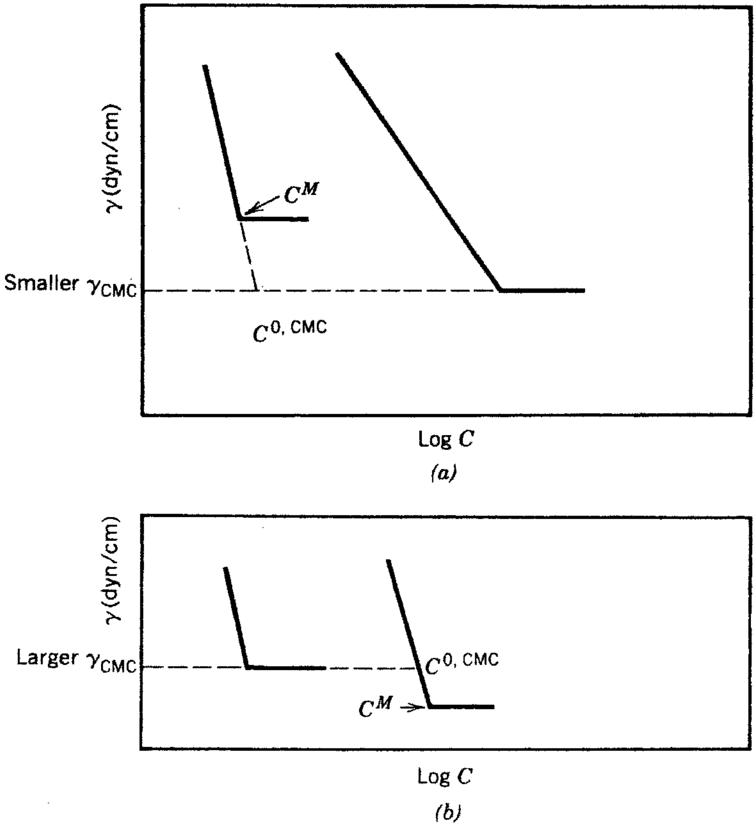

FIGURE 11-8 Evaluation of $[(C_1^{0.CMC}/C_2^{0.CMC})(C_2^M/C_1^M)]$ (*a*) for systems that may show synergism; (*b*) for systems that may show antagonism.

point is obtained (Hua, 1988) by solving equation 11.5 numerically for $X_1^{*,E}$ and substituting that value in equation 11.6:

$$\frac{\gamma_1^{0,CMC} - K_1(\beta^\sigma - \beta^M)(1 - X_1^*)^2}{\gamma_2^{0,CMC} - K_2(\beta^\sigma - \beta^M)(1 - X_1^*)^2} = 1, \qquad (11.5)$$

$$\alpha^{*,E} = \frac{\dfrac{C_1^M}{C_2^M} \cdot \dfrac{X_1^*}{1 - X_1^*} \exp[\beta^M\ (1 - 2X_1^*)]}{1 + \dfrac{C_1^M}{C_2^M} \cdot \dfrac{X_1^*}{1 - X_1^*} \exp[\beta^M\ (1 - 2X_1^*)]}, \qquad (11.6)$$

where K_1, K_2 are the slopes of the $\gamma - \ln C$ plots of the aqueous solutions of surfactant 1 and 2, respectively; $\gamma_1^{0,CMC}$, $\gamma_2^{0,CMC}$ are the surface or interfacial tensions of surfactants 1 and 2, respectively, at their respective CMCs.

III.D. Selection of Surfactant Pairs for Optimal Interfacial Properties

(Rosen, 1989a)

1. *For Maximum Reduction of the CMC.* Select surfactant pairs with the largest negative β^M values (strongest attractive interaction in mixed micelle formation). When interaction between the two surfactants is weak, i.e., β^M is a small negative number, select a pair with approximately equal CMC values. The surfactant with the smaller CMC should always be used in larger quantity than the one with the larger CMC.
2. *For Maximum Efficiency in Surface (or Interfacial) Tension Reduction.* Select surfactant pairs with the largest negative β^σ (or β^σ_{SL} or β^σ_{LL}) values. If one of the surfactants in the formulation is specified, then the second surfactant should, if possible, have a larger pC_{20} value (be more efficient) than the first. If β^σ (or β^σ_{SL} or β^σ_{LL}) for the surfactant pair is a small negative number (attractive interaction between them is weak), select surfactants with approximately equal pC_{20} values. If β^σ (or β^σ_{SL} or β^σ_{LL}) is a large negative number, use equimolar amounts of each surfactant to achieve maximum efficiency; otherwise, use a larger quantity of the more efficient surfactant (i.e., the one with the larger pC_{20} value).
3. *For Maximum Reduction of Surface (or Interfacial) Tension.* Select surfactant pairs with the largest negative β^σ (or β^σ_{SL} or β^σ_{LL}) $- \beta^M$ values. If this quantity is only a small negative number, use, if possible, two surfactants with approximately equal γ values at their CMC. When this is not possible, the surfactant with the higher γ value at its CMC should, preferably, have the smaller area/molecule at the interface.

IV. THE RELATION BETWEEN SYNERGISM IN FUNDAMENTAL SURFACE PROPERTIES AND SYNERGISM IN SURFACTANT APPLICATIONS

The relations between synergism (or antagonism) in the fundamental properties of mixed monolayer formation at an interface or mixed micelle formation in solution and synergism in various practical applications of surfactants is still a relatively unexplored area. Some studies have probed this area, but much remains to be known.

A study that investigated a number of applications was of aqueous mixtures of commercial sodium dodecylbenzenesulfonate (LAS) and sulfated POE dodecyl alcohol. These mixtures show synergism in interfacial tension reduction effectiveness (both static and dynamic) against olive oil, with the degree of synergism increasing with increase in the number of oxyethylene groups from one to four (Figure 11-9). When the sulfated alcohol is not oxyethylenated, i.e., in LAS–sodium dodecyl sulfate mixtures, no synergistic interaction is observed. Synergism for these mixtures was observed in wetting of polyester, in emulsification of olive oil, in dishwashing, and in soil removal from wool (Figures 11-10 and 11-11), with

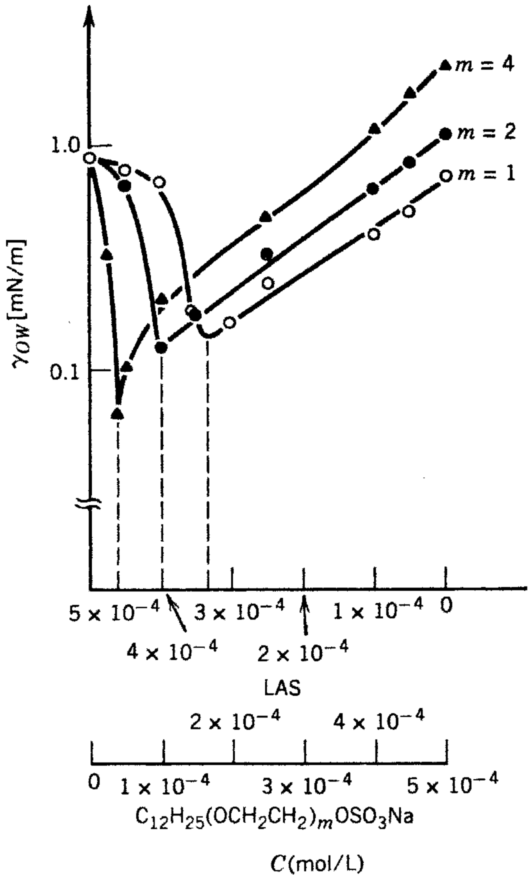

FIGURE 11-9 Olive oil–water interfacial tension for LAS–alkylether sulfate mixtures (purity: LAS, technical product; ether sulfates, 98.0–99.5%) Reprinted with permission from M. J. Schwuger in *Structure/Performance Relationships in Surfactants* M. J. Rosen (Ed.), ACS Symp. Senes 253, American Chemical Society, Washington, DC, 1984, p. 22.

the point of maximum synergism in all these phenomena being at approximately the same surfactant ratio as that observed for synergism in interfacial tension reduction effectiveness (Schwuger, 1984).

An investigation of synergism in foaming in aqueous media and its relation to synergism in the fundamental properties of surface tension reduction and mixed micelle formation showed that synergism (or negative synergism) in foaming effectiveness, measured by initial foam heights by the Ross–Miles technique (Chapter 7, Section III), is related to synergism (or antagonism) in surface tension reduction effectiveness (Rosen, 1988). Binary mixtures of surfactants that lowered the surface tension to values below that attainable with the individual surfactants

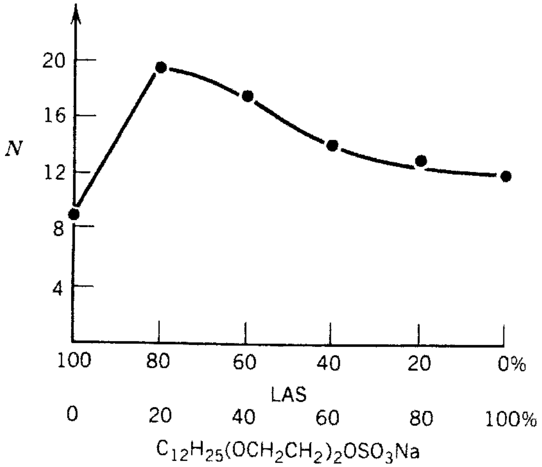

FIGURE 11-10 Dishwashing by LAS–dodecyl 2 EO sulfate mixtures. *N*, number of plates washed at 45°C (technical surfactants). Reprinted with permission from M. J. Schwuger in *Structure/Performance Relationships in Surfactants*, M. J. Rosen (Ed.), ACS Symp. Senes 253, American Chemical Society, Washington, DC, 1984, p. 23.

showed higher initial foam heights than those produced by the individual surfactants (Figure 11-12*a*). Maximum foam height was obtained at approximately the same mole ratio of the two surfactants that produced maximum synergism in surface tension reduction, and this ratio was in agreement with that calculated by the equations in Section III above. A surfactant mixture that showed antagonism in surface tension reduction effectiveness (higher surface tension at the CMC of the mixture than observed at the CMC of the individual surfactants by themselves) showed lower initial foam height than that produced by the individual surfactants (Figure 11-12*b*) at the same total surfactant concentration. There appeared to be no relation between synergism in surface tension reduction efficiency or mixed micelle formation and foaming efficiency (surfactant concentration to produce a given amount of initial foam height).

Various mixtures of anionic and cationic surfactants, which interact strongly and show marked synergism in surface tension reduction efficiency, mixed micelle formation, and surface tension reduction effectiveness, show synergism in wetting at various interfaces. Thus, mixtures of sodium *n*-octyl sulfate and octyltrimethylammonium bromide, which interact very strongly in aqueous media (Table 11-1), show much better wetting properties for paraffin wax than the individual surfactants by themselves (Zhao, 1980). Aqueous solutions of mixtures of sodium perfluorooctanoate and octyltrimethylammonium bromide, which show synergism in the three fundamental properties mentioned above, spread readily over kerosene and *n*-heptane surfaces, although aqueous solutions of the individual surfactants by themselves do not (Zhao, 1983).

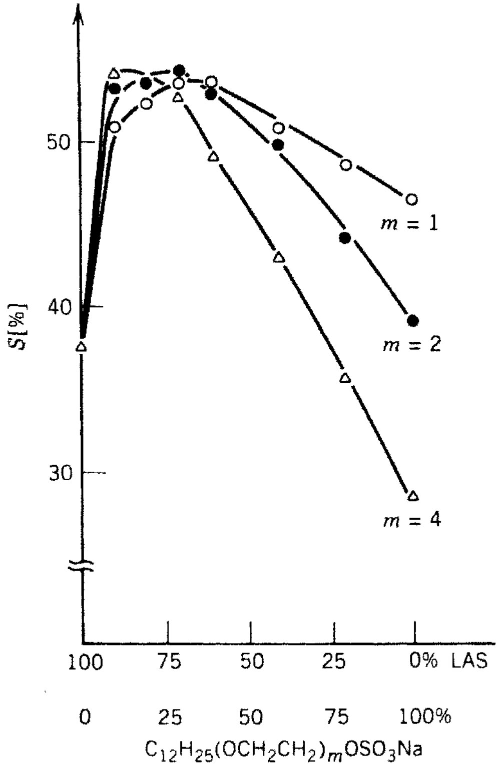

FIGURE 11-11 Soil removal from wool by LAS–alkylether sulfate mixtures (technical surfactants). Test conditions: 30°C; total surfactant concentration 5×10^{-3} mol/L; sebum–pigment mixture soil. Reprinted with permission from M. J. Schwuger in *Structure/Performance Relationships in Surfactants*, M. J. Rosen (Ed.), ACS Symp. Senes 253, American Chemical Society, Washington, DC, 1984, p. 24.

Interaction between the surface-active components in surfactant mixtures and with the solubilizate can both increase and decrease solubilization into the mixed micelles. Thus, the addition of small quantities of sodium dodecyl sulfate sharply decreases the solubilization of Butobarbitone by micellar solutions of a commercial POE nonionic, $C_{12}H_{25}(OC_2H_4)_{23}OH$. The competitive interaction of the sodium dodecyl sulfate with the oxyethylene groups on the surface of the micelles of the nonionic surfactant is believed to be the cause of this phenomenon (Treiner, 1985). On the other hand, a mixture of sodium dodecyl sulfate and sorbitan monopalmitate in aqueous solution (Span 40) solubilized dimethylaminoazobenzene more than either surfactant by itself, with maximum solubilization observed at a 9:1 molar ratio of the anionic to the nonionic (Fukuda, 1958).

The solubilizing power of a tetradecylammonium bromide–sodium octane sulfonate mixture for equal amounts of water and hydrocarbon at 50°C is less than that of the individual components and decreases sharply as the surfactant

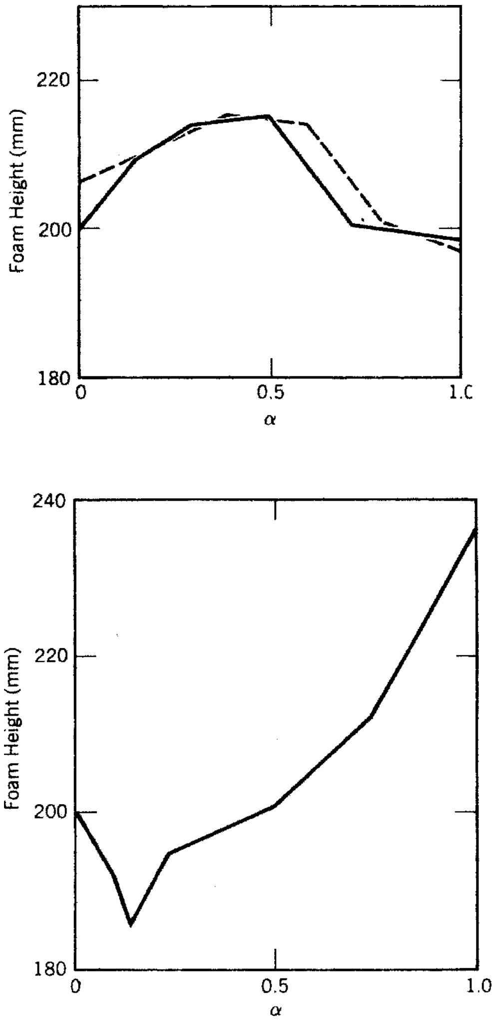

FIGURE 11-12 (*a*) Initial form height vs. mole fraction α of commercial sodium linear alkylbenzensulfonate (LAS) in the total surfactant in the aqueous phase in 0.25% LAS–dodecylbetaine mixtures (60°C, 0.1 *M* NaCl).—, pH 5.8; —, pH 9.3. (*b*) Initial foam height vs. mole fraction α of C_{16} sodium soap in the total surfactant in the aqueous phase of 0.25% C_{16} soap–LAS mixtures (60°C, 0.1 *N* NaCl, pH 10.6). From M. J. Rosen and Z. H. Zhu, *J. Am. Oil Chem. Soc.* **65**, 663 (1988).

proportions approach a 1:1 molar ratio. Here, the interaction between the two surfactants produces antagonism.

The proposed explanation is based upon the Winsor *R* concept (Chapter 5, Section III), with the interaction between the surfactants producing a pseudo-nonionic complex that decreases the A_{CW} value in the denominator of the *R* ratio, with consequent decrease in the solubilization power (Bourrel, 1984).

Interaction between the two surfactants has also been shown both to increase and decrease their adsorption at various interfaces. The addition of a small amount (<20 mol%) of a POE nonionic to an anionic surfactant, sodium dodecyl sulfate, increased the adsorption of the anionic onto carbon at low surfactant concentrations. As the ratio of nonionic to anionic increased this effect was diminished, and at a 1:1 molar ratio the anionic was scarcely adsorbed. It was suggested that inclusion of the POE nonionic in the adsorbed film on the carbon reduces electrical repulsion between adsorbed surfactant molecules and also between them and the negatively charged carbon surface. Increased solution concentration of POE nonionic caused displacement of the anionic from the adsorbed film by the more surface-active nonionic (Schwuger, 1977).

Interaction between two surfactants in aqueous solution producing synergism in foaming and decreased adsorption onto solid surfaces has been used to advantage in the separation of minerals. An alkyl sulfosuccinate–POE nonionic mixture that shows synergism in foaming and whose interaction results in decreased adsorption onto scheelite and calcite surfaces produced enhanced selectivity and recovery of scheelite by the flotation process (von Rybinski, 1986).

The addition of a second surfactant that interacts with the first surfactant to change various fundamental interfacial properties has been shown to affect detergency in several recent investigations (Schwuger, 1982; Aronson, 1983; Matson, 1984; Cox, 1985; Smith, 1985). Both synergistic and antagonistic effects were observed. Thus, significant improvement in the detergency by LAS of sebum soiled permanent press and cotton cloth at water hardness > 100 ppm Ca^{2+} was obtained by replacing a portion of the LAS by a POE nonionic (Cox, 1985). Optimum detergency at 100°F was obtained with a C_{12}–C_{14} nonionic containing 70% EO at a 1:4 nonionic–LAS ratio. Calculation of the mole fraction of the nonionic in the mixed micelle (by equation 11.3) for this 1:4 nonionic–LAS mixture showed that the mixed micelle formed consisted predominantly of the nonionic. The improved detergency is consequently believed to be due to the nonionic acting as a micelle promotion agent, incorporating LAS into the mixed micelle and Ca^{2+} by counterion binding to the micellar surface, thus reducing the formation of Ca $(LAS)_2$ in the solution phase. The free LAS, on the other hand, is believed to be mainly responsible for the interfacial and detergency properties of the mixture.

On the other hand, the addition of minor amounts of LAS to a POE nonionic solution that showed rapid removal of mineral oil soil from a polyester surface decreased the rate of removal or inhibited its removal completely. The effect appeared to be related to its effect on the mineral O/W interfacial tension: As the O/W interfacial tension increased, removal time of the oily soil increased; when the O/W interfacial tension exceeded a critical value, removal was completely inhibited (Aronson, 1983).

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PROBLEMS

1 **(a)** Surfactant *A* has a pC_{20} value of 3.00 in 0.1 *M* NaCl (aq.); surfactant B has a pC_{20} value of 3.60 in the same medium. The β^{σ} value for the mixture in 0.1 *M* NaCl is −2.80. Will a mixture of surfactants A and B in 0.1 *M* NaCl show synergism in surface tension reduction efficiency?

(b) If this system does show synergism of this type, calculate the values of α^* (the mole fraction of surfactant A in the mixture, on a surfactant-only basis, at the point of maximum synergism) and $C_{12,\min}$ (the minimum total molar surfactant concentration to yield a 20 dyn/cm reduction in the surface tension of the solvent).

2 Surfactants C and D have CMC values of 1.38×10^{-4} and 4.27×10^{-4} mol/L, respectively, in aqueous 0.1 *M* NaCl. This mixture, in the same medium, has a CMC value of 3.63×10^{-4} mol/L when the mole fraction α of surfactant C in the mixture is 0.181 (on a surfactant-only basis).

(a) Calculate β^{M} for a mixture of surfactants A and B.

(b) Will this mixed system exhibit synergism or antagonism in mixed micelle formation? If so, calculate the values of α^* and $C^{M}_{12,\min(\max)}$.

3 Surfactants C and D of Problem 2 individually reduce the surface tension of an aqueous 0.1 *M* NaCl solution to 30 dyn/cm when their respective molar concentrations are 9.1×10^{-4} and 3.98×10^{-4}. The mixture of them at $\alpha = 0.181$ in Problem 2 has a surface tension value of 30 dyn/cm when the total molar surfactant concentration is 3.47×10^{-4}. Will a mixture of surfactants C and D exhibit synergism or antagonism in surface tension reduction effectiveness?

4 Without consulting tables, place the following mixtures in order of increasing attractive interaction (increasing negative β^{σ} value) at the aqueous solution–air interface:

(a) $C_{12}H_{25}(OC_2H_4)_6OH$–$C_{12}H_{25}SO_3^-Na^+(H_2O)$

(b) $C_{12}H_{25}(OC_2H_4)_6OH$–$C_{12}H_{25}(OC_2H_4)_{15}OH$(0.1 *M* NaCl, H_2O)

(c) $C_{12}H_{25}SO_3^-Na^+$–$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-(H_2O)$

(d) $C_{12}H_{25}N^+(CH_3)_3Cl^-$–$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-(H_2O)$

5 Explain the β values obtained for the following mixtures:

(a) $C_7F_{15}COO^-Na^+$–$C_{12}H_{25}SO_4^-Na^+$ (0.1 *M* NaCl, 30°), $\beta^{\sigma} = +2.0$

(b) $C_5H_{11}SO_3^-Na^+$–$C_{10}H_{21}Pyr^+Cl^-$ (0.03 *M* NaCl, 25°), $\beta^{\sigma} = -10.8$; $C_5H_{11}SO_3^-Na^+$–$C_{10}H_{21}Pyr^+Cl^-$ (0.03 *M* NaI, 25°), $\beta^{\sigma} = -5.5$

(c) $C_{12}H_{25}SO_3^-Na^+$–$C_{12}H_{25}N^+(Bz)(Me)CH_2COO^-$ (pH 5.0, 20°), $\beta^M = -5.4$; $C_{12}H_{25}SO_3^-Na^+$–$C_{12}H_{25}N^+(Bz)(Me)CH_2COO^-$ (pH 9.3, 25°), $\beta^M = -1.7$

(d) $C_{10}H_{21}SO_3^-Na^+$–$C_{12}H_{25}N^+(Me)_3Br^-$ (H_2O, 25°), $\beta^\sigma = -35.6$;
$C_{10}H_{21}SO_3^-Na^+$–$C_{12}H_{25}N^+(Me)_3Br^-$ (0.1 *M* NaBr, 25°), $\beta^\alpha = -19.6$

(e) $C_{10}H_{21}S^+(CH_3)O^- + C_{10}H_{21}SO_4^-Na^+$ (pH = 5.9), $\beta^\sigma = -4.3$;
$C_{10}H_{21}S^+(CH_3)O^- + C_{10}H_{21}N(CH_3)_3{}^+Cl^-$ (pH = 5.9), $\beta^\sigma = -0.6$

(f) $C_{12}H_{25}N^+H_2CH_2CH_2COO^- + C_{12}H_{25}SO_3^-Na^+$ (pH = 5.8), $\beta^\sigma = -4.2$;
$C_{12}H_{25}N^+H_2CH_2CH_2COO^- + C_{12}H_{25}Pyr^+Br^-$ (pH = 5.8), $\beta^\sigma = -4.8$

12 Gemini Surfactants

Gemini surfactants, sometimes also called *dimeric surfactants*, contain two hydrophobic groups (sometimes three) and two hydrophilic groups in the molecule, connected by a linkage close to the hydrophilic groups (Figure 12-1).* They therefore have three structural elements—a hydrophilic group, a hydrophobic group, and their linkage—that may be varied to change the properties of the surfactant. There has been considerable interest in these compounds, both academic and industrial, since it was pointed out (Rosen, 1993a) that the interfacial properties of these surfactants in aqueous media can be orders of magnitude greater than those of comparable conventional surfactants (i.e., surfactants with single but similar hydrophilic and hydrophobic groups). Hundreds of scientific papers and patents have appeared in the literature in the past decade and have been reviewed (Rosen, 1998; Menger, 2000a; Zana, 2002). All charge types of geminis have been synthesized and investigated: anionics, including dicarboxylates, disulfates, disulfonates, and diphosphates (e.g., Zhu, 1990; Menger, 1991; Rosen, 1992; Duivenwoorde, 1997); cationics (e.g., Devinsky, 1985; Zana, 1991); nonionics (e.g., Eastoe, 1994; Paddon-Jones, 2001); zwitterionics (e.g., Seredyuk, 2001); and a variety of structural types: alkylglucoside-based (Castro, 2002), arginine-based (Pinazo, 1999), glucamide-based (Eastoe, 1996), sugar-based (Johnsson, 2003), with unsaturated linkages (Menger, 2000b; Tatsumi, 2001), hydrolyzable (Tatsumi, 2000), and with nonidentical headgroups (Alami, 2002).

I. FUNDAMENTAL PROPERTIES

Some examples of geminis, their C_{20} and CMC values, and those of comparable conventional surfactants, are shown in Table 12-1.

As can be seen from the data in Table 12-1, the C_{20} values, a measure of the efficiency of adsorption of the surfactant at the interface (Chapter 2, Section IIIE), can be two to three orders of magnitude smaller than the C_{20} values of comparable conventional surfactants, and their CMCs (Chapter 3, Section I) can be one to two orders of magnitude smaller than those of comparable conventional surfactants. The

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*If the linkage is not close to the hydrophilic groups, the unique properties mentioned below are not observed.

Surfactants and Interfacial Phenomena, Third Edition. Milton J. Rosen
ISBN 0-471-47818-0

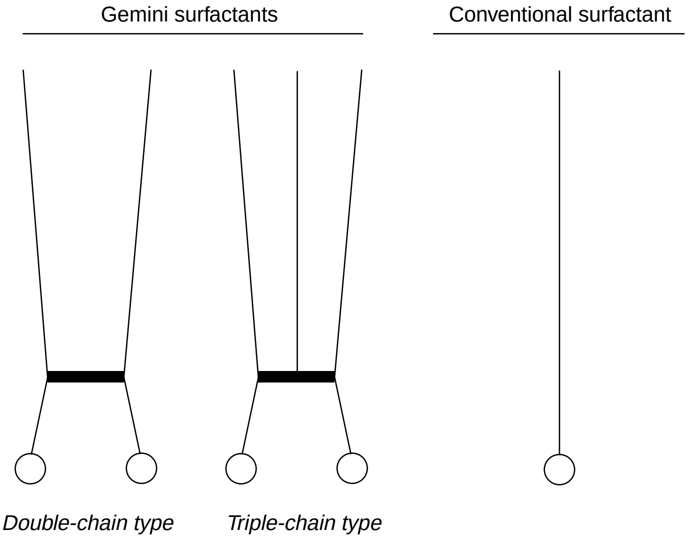

FIGURE 12-1 Conventional and gemini surfactants. ———, hydrophobic group; ▬, connecting group; ○, hydrophilic group.

reason for this greater surface activity of geminis, compared to comparable conventional surfactants, is the larger total number of carbon atoms in the hydrophobic chains of the geminis. The larger the total number of carbon atoms in the surfactant molecule, the greater the distortion of the water structure of the aqueous phase and the greater the tendency to adsorb at the interfaces surrounding the aqueous phase or to form micelles in the aqueous phase, i.e., greater surface activity (Chapter 1, Section B). This results in smaller C_{20} values (Chapter 2, Section IIIE) and smaller CMC values (Chapter 3, Section IV).

On the other hand, increase in the total number of carbon atoms in the hydrophobic chain(s) of the surfactant molecule decreases the solubility of the surfactant in water and limits its surface activity. When the surfactant contains two hydrophilic groups, however, its solubility in water increases and the molecule can accommodate more carbon atoms in the hydrophobic groups without becoming water-insoluble. Consequently, gemini surfactants are much more surface-active than their comparable conventional surfactants, which have only half the number of carbon atoms in the molecule. In addition, geminis are more water-soluble than comparable conventional surfactants and have much lower Krafft points (Chapter 5, Section IIA).

Trimeric and oligomeric surfactants have also been prepared (Zana, 1995; Sumida, 1998; In, 2000; Onitsuka, 2001). Their CMC values are even smaller than those of the analogous geminis. As the number of hydrophobic groups per molecule increases for gemini quaternary C_{12} ammonium compounds with polymethylene $-(CH_2)_n-$ spacers, their surface layers become more dense, their micellar microviscosity increases, and their micellar shape changes from spherical to wormlike, to

TABLE 12-1 C_{20} and CMC Values of Gemini and Comparable Conventional Surfactants at 25°C

Compound	Medium	C_{20} (10^{-6}) M	CMC ($10^{-6}M$)	Reference
$[C_{10}H_{21}OCH_2CH(OCH_2COO^-Na^+)CH_2]_2O$	H_2O	4	84	Zhu, 1993
$C_{11}H_{23}COO^-Na^+)$	H_2O	5,000	20,000	Zhu, 1993
$[C_{10}H_{21}OCH_2CH(OCH_2CH_2CH_2SO_3^-Na^+]_2O$	H_2O	8	33	Zhu, 1991
$C_{12}H_{25}SO_3^-Na^+$	H_2O	4,400	9,800	Zhu, 1991
$[C_{10}H_{21}OCH_2CH(SO_4^-Na^+)CH_2OCH_2]_2$	H_2O	1	13	Zhu, 1990
$C_{12}H_{25}SO_4^-Na^+$	H_2O	3,100	8,200	Zhu, 1990
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2 \cdot 2Br^-$	H_2O	—	840	Zana, 1991
$[C_{12}H_{25}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$	H_2O	129	700	Rosen, 1996
$C_{12}H_{25}N^+(CH_3)_3 \cdot Br$	H_2O	8,000	16,000	Rosen, 1996
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Cl^-$	0.1 M NaCl	0.9	9.6	Song, 1996
$[C_{12}H_{25}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$	0.1 M NaCl	0.9	21	Rosen, 1996
$C_{12}H_{25}N^+(CH_3)_3 \cdot Cl^-$	0.1 M NaCl	1,950	5,760	Li, 2001
$(C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]CONHCH_2)_2 \cdot 2Cl^-$	H_2O	1.9	9.5	Perez, 1998
$C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]COOCH_3 \cdot Cl^-$	H_2O	630	6,000	Perez, 1998
$\{C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]CONHCH_2\}_2 \cdot 2Cl^-$	0.01 M NaCl	1	9.2	Perez, 1998
$C_{11}H_{23}CONHCH[(CH_2)_3NHC(NH_2)_2^+]COOCH_3 \cdot Cl^-$	0.01 M NaCl	50	270	Perez, 1998

branched worm-like, to ring-like. Zero-shear viscosity increases very rapidly to a maximum with increase in the number of oligomers (In, 2000).

As in conventional surfactants, the C_{20} and CMC values decrease with increase in the total number of carbon atoms in the molecule. However, unlike this behavior in conventional surfactants, when the number of carbon atoms in the alkyl chains of the geminis exceeds a certain value (about 14 carbon atoms per chain, the exact number dependent upon gemini structure, temperature, and the electrolyte content of the aqueous phase), the linear relationship with the log of the C_{20} value (Chapter 2, Section IIIE) or with the log of the CMC (Chapter 3, Section IVA4) breaks down. The log C_{20} or log CMC values start to deviate more and more from this linear relationship, with the C_{20} and CMC values becoming larger than expected, i.e., in the direction of decreased surface activity and micellization tendency. This deviation becomes larger and larger with increase in the number of carbon atoms in the alkyl chains until the C_{20} and CMC values actually increase with this change. This behavior has been attributed (Menger, 1991) to the formation of small, non-surface-active aggregates (dimers, trimers, etc.) in the aqueous phase below the CMC, decreasing the concentration of the surface-active monomeric species and, consequently, the surface activity and micellization tendency. This has been confirmed by calculation of the equilibrium constants for this self-association (Rosen, 1996; Song, 1996) and by fluorescence spectroscopy (Mathias, 2001). This self-aggregation below the CMC to form small, non-surface-active aggregates when the alkyl chains of the geminis are long may be due to the exceptionally large free energy decrease resulting from hydrophobic bonding between adjacent gemini molecules, each containing two (or three) long hydrophobic chains.

The flexibility, length, and hydrophobicity (or hydrophilicity) of the linkage between the two hydrophilic groups of the gemini affect such properties as the C_{20}, CMC, and area/molecule at the air–aqueous solution interface values, sometimes considerably. For cationic geminis with the flexible, hydrophobic polymethylene, $\leftarrow CH_2 \rightarrow_n$, linkage, the value of the CMC increases with increase in the number of methylene groups to a maximum in the neighborhood of 6 (Devinsky, 1991; Zana, 1991) and the area/molecule at the air–aqueous solution interface to a maximum in the neighborhood of 10 methylene groups (Alami, 1993; Espert, 1998), and then they both decrease. This is believed to be due to the unfavorable orientation of the hydrophobic polymethylene linkage when it is in contact with the aqueous phase. Consequently, it is believed to penetrate into the micellar interior (in the case of the CMC) or loop into the air (in the case of the area/molecule at the air–aqueous solution interface) when the linkage is sufficiently long. This decreases the CMC and the area/molecule at the interface, respectively. A rigid linkage, e.g., $-CH_2C_6H_4CH_2-$, $-CH_2C{\equiv}C-CH_2-$, prevents this and consequently increases the CMC and the area/molecule at the interface. The smallest CMC, C_{20}, and area/molecule values are obtained when the linkage is short, flexible, and slightly hydrophilic. However, Zhu and coworkers (1993), Dreja and coworkers (1999), and Wettig and coworkers (2003), investigating the properties of geminis with hydrophilic spacers, have observed a monotonic increase in the area/molecule of the gemini at the air/aqueous solution interface with increase in the length of the hydrophilic spacer, presumably due to the compatibility of the linkage with the aqueous phase.

A very useful property of geminis is their packing at various interfaces. At the air–aqueous solution interface, when the linkage between the two hydrophilic groups is small or hydrophilic and close to the hydrophilic groups, the hydrophobic groups of the gemini can be more closely packed (In, 2000) than those of the comparable conventional surfactant under the same conditions (temperature, ionic strength) in the aqueous phase. The packing of the chains is so close in some cases (Rosen, 1999; Onitsuka, 2001; Seredyuk, 2001; Tsubone, 2003a) that it appears that multilayers are formed. This closer packing makes the interfacial film of the geminis more coherent, and this is reflected in their superior foaming (Zhu, 1991; Ono, 1993; Zhu, 1993) and their superior emulsifying properties (Briggs, 1990; Dreja, 1998). This close packing of the hydrophobic groups, in geminis with short linkages close to their hydrophilic groups (indicated by small area/molecule values at the air–aqueous solution interface), results in a packing parameter (Chapter 3, Section II) indicative of cylindrical micelle formation in aqueous media and may account for the unusually high viscosities shown by some geminis (Zana, 1993; Schmitt, 1995). The geminis $[C_{12}H_{25}N^+(CH_3)_2CH_2]_2 \cdot 2Br^-$ and $[C_{12}H_{25}N(CH_3)_2CH_2]_2CH_2 \cdot 2Br^-$ have been shown (Zana, 1993; Danino, 1995) to have long, wormlike micelles in aqueous solution. The entanglement of these wormlike micelles produces the high viscosity of the aqueous phase.

Gemini surfactants also show unique adsorption at oppositely charged solid surfaces from aqueous media. Whereas conventional surfactants adsorb onto this type of solid from aqueous media with their hydrophilic groups oriented toward the oppositely charged solid surface (Figure 2-12) and their hydrophobic groups oriented toward the aqueous phase, making the solid, at least initially, more hydrophobic, geminis with short linkages adsorb onto these surfaces with one hydrophilic group oriented toward the solid and the other oriented toward the aqueous phase (Li, 2000; Rosen, 2001), retaining the hydrophilic character of the solid. One of the effects of this is to make the solid more dispersible in the aqueous phase.

A standard free energy change upon micellization for ionic gemini surfactants with two hydrophilic groups and monovalent counterions can be calculated (Zana, 1996) by taking into account the degree of binding $(1 - \alpha)$ of the counterions to the micelle,

$$\begin{aligned} \Delta G^\circ_{\text{mic}} &= RT[1 + 2(1 - \alpha)] \ln X_{\text{CMC}} \\ &= 2.3RT(3 - 2\alpha) \log X_{\text{CMC}} \end{aligned}$$

where α is the degree of ionization of the gemini surfactant, measured by the ratio of the slopes of the plot of specific conductivity vs. C above and below the CMC (Chapter 3, Section IVA3), and X_{CMC} is the mole fraction of the surfactant in the liquid phase at the CMC. The degree of binding of cationic geminis appears to be similar to those of comparable conventional surfactants (Zana, 1995) (Table 3-3).

II. INTERACTION WITH OTHER SURFACTANTS

Because of the double charge on ionic geminis, they interact more strongly with oppositely charged surfactants at interfaces or in mixed micelles than do singly charged (conventional) surfactants. The strength of the interaction between two different types of surfactants, both conventional and gemini, is measured by the so-called β parameter (Chapter 11, Section I). The numerical value of the β parameter (which is negative when greater attractive [or less repulsive] interaction occurs after mixing and is positive when there is greater repulsion [or less attraction] between the two different surfactants after mixing) depends upon the nature of the interface (liquid–air, liquid–liquid, or liquid–solid) at which they interact and also upon whether the interaction is between the different surfactants adsorbed in a mixed monolayer at an interface (β^{σ}) or between them in a mixed micelle in aqueous medium (β^{M}). The nature and strength of the interactions between the two different surfactants determine whether the mixtures of the two surfactants will exhibit synergism, antagonism (negative synergism), or ideal behavior in their interfacial properties (Chapter 11, Section III). Interaction parameters for mixtures of gemini surfactants or conventional surfactants with the same second surfactant indicate that the interactions are much stronger for the gemini surfactants than for their comparable conventional surfactants (Rosen, 1993a,b; Liu, 1996; Li, 2001). Some data are shown in Table 12-2 together with interaction parameters for some comparable conventional surfactant mixtures. The data also indicate that interaction between the two different types of surfactants is much stronger in the mixed monolayer at the planar air–aqueous solution interface than in the convex mixed micelle. This is believed to be due to the greater difficulty of accommodating the two hydrophobic groups of the gemini in the interior of the convex micelle. This may also account for the observation mentioned above that, whereas the C_{20} values of gemini are often two to three orders of magnitude smaller than those of comparable conventional surfactants, their CMC values are only one to two orders of magnitude smaller.

An unexpected aspect of these interactions for ionic geminis, both in mixed monolayers and in mixed micelles, is that 1 mol of the doubly charged molecule interacts with only 1 mol of the second surfactant, even when the second surfactant is singly and oppositely charged, contrary to the expected 1:2 molar ratio. This is in contrast to what is observed with conventional surfactants, where they interact with oppositely charged surfactants in the expected 1:1 molar ratio and generally produce a water-insoluble product with no charge and little surface activity. The 1:1 interaction product of the doubly charged gemini and an oppositely singly charged conventional surfactant, on the other hand, has a net charge (of the same type as the gemini), is water-soluble, and retains high surface activity. Gemini surfactants also interact more strongly than do their comparable conventional surfactants with water-soluble polymers. This is true for both neutral and oppositely charged polymers (Kastner, 1999; Pisarcik, 2000).

This much stronger interaction of geminis with other surfactants in mixed monolayers than in mixed micelles means that there is a strong possibility of

TABLE 12-2 Interaction Parameters of Gemini Surfactants with Conventional Surfactants at 25°C

System	Medium	β^σ	β^M	Reference
Anionic–Cationic Mixtures				
$[C_8H_{17}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaBr	−26	−12	Liu, 1996
$[C_8H_{17}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaBr	−30	−13	Liu, 1996
$C_8Pyr^+Br^-$–$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaBr	−19.5	—	Gu, 1989
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{10}H_{21}SO_3^-Na^+$	0.1 *M* NaBr	−34	−14	Liu, 1996
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaBr	−34	−18	Liu, 1996
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{12}H_{25}SO_3^-Na^+$	0.1 *M* NaCl	−40	−19	Liu, 1996
$[C_8H_{17}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{12}H_{25}(OC_2H_4)_4SO_4^-Na^+$	0.1 *M* NaBr	−28	—	Liu, 1996
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–$C_{12}H_{25}(OC_2H_4)_4SO_4^-Na^+$	0.1 *M* NaBr	−31	−11	Liu, 1996
Anionic–Nonionic Mixtures				
$(C_{10}H_{21})_2C_6H_2(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$–$C_{12}H_{25}(OC_2H_4)_7OH$	0.1 *M* NaCl	−6.9	−0.8	Rosen, 1993b
$C_{10}H_{21}C_6H_3(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$–$C_{12}H_{25}(OC_2H_4)_7OH$	0.1 *M* NaCl	−1.8	−0.9	Rosen, 1993b
Anionic–Zwitterionic Mixtures				
$(C_{10}H_{21})_2C_6H_2(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$–$C_{14}H_{29}N(CH_3)_2O$, pH = 6.0	0.1 *M* NaCl	−7.3	−2.4	Rosen, 1994
$C_{10}H_{21}C_6H_3(SO_3^-Na^+)OC_6H_5$–$C_{14}H_{29}N(CH_3)_2O$, pH = 5.8	0.1 *M* NaCl	−4.7	−3.2	Rosen, 1993b
Cationic–Nonionic Mixtures				
$[C_{10}H_{21}N^+(CH_3)_2CH_2CH_2]_2 \cdot 2Br^-$–decyl-β-glucoside (pH = 9)	0.1 *M* NaCl	−4.0	−1.9	Li, 2001
$2C_{10}H_{21}N^+(CH_3)_3 \cdot 2Br^-$–decyl-β-glucoside (pH = 9)	0.1 *M* NaCl	−1.2	−1.2	Rosen, 2001

(*Continued next page*)

TABLE 12-2 (*Continued*)

System	Medium	β^{σ}	β^{M}	Reference
$[C_{10}H_{21}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Br^-$–decyl-β-glucoside (pH = 9)	0.1 *M* NaCl	−4.2	−1.2	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2CH_2]_2 \cdot 2Br^-$–decyl-β-maltoside	0.1 *M* NaCl	−2.7	−1.9	Li, 2001
$C_{10}H_{21}N^+(CH_3)_3 \cdot Br^-$–decyl-β-maltoside	0.1 *M* NaCl	−0.3	−0.3	Rosen, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Br^-$–decyl-β-glucoside	0.1 *M* NaCl	−4.2	−1.2	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2]_2CHOH \cdot 2Br^-$–decyl-β-maltoside	0.1 *M* NaCl	−2.9	−1.4	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–decyl-β-glucoside	0.1 *M* NaCl	−3.1	−1.4	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$–decyl-β-maltoside	0.1 *M* NaCl	−2.0	−1.7	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2CH_2]_2O \cdot 2Br^-$–decyl-β-glucoside	0.1 *M* NaCl	−3.3	−1.5	Li, 2001
$[C_{10}H_{21}N^+(CH_3)_2CH_2CH_2]_2O \cdot 2Br^-$–decyl-β-maltoside	0.1 *M* NaCl	−2.3	−1.7	Li, 2001
$[C_{12}H_{25}N^+(CH_3)_2CH_2CH_2]_2 \cdot 2Br^-$–dodecyl-β-maltoside	0.1 *M* NaCl	−3.0	−2.2	Li, 2001
$[C_{12}H_{25}N^+(CH_3)_2CH_2]_2 \cdot 2Br^-–C_{12}(OC_2H_4)_6OH$	H_2O	—	−2.2	Esumi, 1998
$[C_{12}H_{25}N^+(CH_3)_3 \cdot Cl^-–C_{12}(OC_2H_4)_5OH$	H_2O	—	−1.0	Rubingh, 1982

synergism existing between them in effectiveness of surface or interfacial tension reduction since that is one of the requirements for synergism of this type (Chapter 11, Section IIIC). Synergism in surface or interfacial tension reduction effectiveness is very important in enhancing such performance properties as detergency, foaming, and wetting.

In a manner similar to the self-aggregation of geminis below their CMC to form small, non-surface-active aggregates when the alkyl chain exceeds a critical number of carbon atoms, described above, the interaction of ionic geminis with oppositely charged surfactants produces a marked decrease in surface activity when the combined alkyl carbon number of the two interacting surfactants (32 in the cases studied) exceeds a critical value (Liu, 1996). Again, this is attributed to the formation of small, non-surface-active aggregates, in this case involving both oppositely charged surfactants. As with the shorter-chain geminis, the interaction product of the doubly charged gemini and the singly charged conventional surfactant is again 1:1 molar and water-soluble.

Because of this interaction of only one of the ionic groups of the gemini with an oppositely charged conventional surfactant, tiny amounts of the gemini can be used to promote substantial growth of oppositely charged micelles by crosslinking them (Menger, 1995).

III. PERFORMANCE PROPERTIES

The unique physicochemical properties described above result in gemini surfactants exhibiting some very desirable performance properties. Their very low C_{20} values make them remarkably efficient in reducing equilibrium surface tension, while their very low CMC values make them very efficient solubilizers (Chapter 4) of water-insoluble material, since solubilization occurs only above the CMC. Thus, cationic geminis of structure $[C_{12}H_{25}N(CH_3)_2]_2(CH_2)_n \cdot 2Br^-$ have been observed to solubilize more toluene, *n*-hexane, or styrene into water than their comparable conventional surfactants, particularly when *n* is small (Dam, 1996; Dreja, 1998), and disodium didecyl diphenyl ether disulfonate has been found to solubilize water-insoluble nonionic surfactants more efficiently and more effectively than monosodium monodecyl diphenyl ether monosulfonate (Rosen, 1992). Their low CMC values also cause them to show very low skin irritation (which is associated with the concentration of monomeric surfactant in the aqueous phase) (Diz, 1994; Kitsubi, 1997; Li, 1997; Okano, 1997; Tracy, 1998). The double charge on the molecules of ionic geminis also make them better dispersing agents for finely divided solids in aqueous media (Chapter 9) than their comparable conventional surfactants.

When the alkyl chains of geminis are short and branched and the group linking the hydrophilic groups is short, geminis show excellent wetting properties. Tertiary acetylenic glycols of structure $R_1R_2C(OH)C{\equiv}CC(OH)R_1R_2$, where R_1 is CH_3 and R_2 is an alkyl chain with two to four carbon atoms, and which are gemini-type surfactants that have been commercialized for decades, are excellent wetting agents. Gemini diamides of structure $\{RN[(C_2H_4O)_xH]CO\}_2R^1$, where R is

2-ethylhexyl, $x = 4$, and R^1 is either $-(CH_2)_2-$ or $-CH{=}CH-$, have been reported (Micich, 1988) to be excellent hydrophobic soil wetting and rewetting agents.

As a result of the tighter packing of the hydrophobic groups of geminis when the linkage between the hydrophilic groups is small, mentioned above, and the resulting more coherent surface film, the foaming of aqueous solutions of geminis of this type has been found in many cases to be superior to that of their comparable conventional surfactants (*monomers*). Both initial foam height and foam stability have been found to be significantly greater in several series of anionic geminis (Zhu, 1991; Ono, 1993; Zhu, 1993; Kitsubi, 1998). Although conventional cationic surfactants of alkyl trimethylammonium chloride structure show very little foam in aqueous solution, the analogous geminis, $[RN^+(CH_3)_2]_2(CH_2)_n \cdot 2Cl^-$, where $n = 2$ or 3 and R is $C_{12}H_{25}$ or $C_{14}H_{29}$, show very high foam (Kim, 1996). When the length of the linkage between the hydrophilic groups was increased, both initial foam and foam stability decreased.

Studies of the removal of some pollutants from water by anionic and cationic geminis adsorbed on soil solids showed that they are both more efficient and more effective at removing the pollutants than their comparable conventional surfactants (Li, 2000; Rosen, 2001). Quaternary ammonium surfactants often show strong antimicrobial activity, and an extensive study was made (Pavlikova, 1995) of the geminis of structure $[RN^+(CH_3)_2CH_2OC(O)]_2(CH_2)_n$ to determine their activity. Maximum activity was shown when R is $C_{12}H_5-$ and $n = 2$, and antimicrobial activity of this gemini was far superior to the activity of single-chain commercial antimicrobials such as benzyldodecyldimethylammonium bromide. Another study (Diz, 1994) showed that diquaternary geminis of structure $[C_{12}H_{25}N^+(CH_3)_2CH_2C(O)NHCH_2CH_2]_2 \cdot 2Cl^-$ or $[C_{12}H_{25}N^+(CH_3)_2CH_2C(O)NH(CH_2)S)_2 \cdot 2Cl^-$ showed greater antimicrobial activity against both gram-positive and gram-negative organisms and against *Candida albicans* than did hexadecyltrimethylammonium bromide. A gemini-type surfactant, *N*,*N*-di *n*-hexadecyl-*N*,*N*-dihydroxyethylammonium bromide, was found (Banerjee, 1999) to be a more effective transfection (gene-delivering) agent than either the mono hexadecyl or mono hydroxyethyl analog.

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PROBLEMS

Explain the following observations regarding the properties of geminis, compared to those of conventional surfactants having similar, but single, hydrophilic and hydrophobic groups:

1 Their C_{20} values are generally two or three orders of magnitude smaller than those of the latter.

2 Their CMC values are generally one or two orders of magnitude smaller than those of the latter, not the two or three orders of magnitude observed in (1) (above) for the C_{20} values.

3 They wet substrates less rapidly than the latter.

4 They are better foaming and emulsifying agents than the latter.

5 They are better dispersing agents for oppositely charged, finely divided solids than the latter.

Answers to Selected Problems

Chapter 1

1 $RCOO^-Me^+$; $ROSO_2O^-Me^+$

2 $RCOOCH_2CHOHCH_2OH$

3 $RN(CH_3)_3^+X^-$

4 $C_{12}H_{25}C_6H_5SO_3^-Na^+$

5 $H(OC_2H_4)_x[OCH(CH_3)CH_2]_y(OC_2H_4)_zOH$

6 $RN^+(CH_3)_2(CH_2)_xSO_3^-$

7 $H(OC_2H_4)_x[OCH(CH_3)CH_2]_y(OC_2H_4)_zOH$

8 $RCOOCH_2CH_2SO_3^-Na^+$

Chapter 2

1 **(a)** 4.54×10^{-10}mol cm^{-2}
  (b) 36.6 Å^2
  (c) -47.4 kJmol^{-1}

2 $\mathbf{d} < \mathbf{c} < \mathbf{a} < \mathbf{b} < \mathbf{e}$

4 5.8 Å

5 60. Å^2

6 $X_1 = 0.40$

7 **(a)** 7×10^{-6} M.
  (b) Soak glass beaker in cationic surfactant solution overnight. Replace solution with fresh one.

Chapter 3

1 Cylindrical; $V_H/l_c.a_o = 0.44$

4 -29.5 kJ mol^{-1}

7 $\mathbf{e} > \mathbf{c} > \mathbf{a} \simeq \mathbf{d} > \mathbf{b}$

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Chapter 4

4 Micellar catalysis of acid hydrolysis of the ester linkage may occur.

Chapter 5

2 **a**, **d**, **e** cause increase; **b**, **c** cause decrease.

4 **(a)** 34.6 mN/m
  (b) 31.3 mN/m

Chapter 6

1 **(a)** Weak interaction; $\phi = 0.62$
  (b) 7 dynes/cm

2 Since $\gamma_c = \gamma_{LA}$ of the wetting liquid and $\cos\theta = 1$, then $\gamma_{SL} = 0$ (Eq. 6.3).

3 Increase of 17.6 ergs/cm^2

4 On cellulosic substrates, the POE nonionics may initially be adsorbed via hydrogen bonding of the POE chain to the surface, making the latter less wettable momentarily.

5 **c** > **b** > **e** > **a** > **d**

6 **(a)** Hydrocarbon-chain surfactants and hydrocarbon substrates (e.g., paraffin, polyethylene)
  (b) Siloxane-chain surfactants and hydrocarbon substrates

Chapter 7

1 See equation 7.3. Γ and C_s reach maximum values near the CMC.

5 1.6×10^{-4} s

7 **(a)** POE nonionic
  (b) Cloud point

Chapter 8

5 61% $C_{12}H_{25}(OC_2H_4)_2$; 39% $C_{12}H_{25}(OC_2H_4)_8OH$, using the relationship 2O $M_H/(M_H + M_L)$

6 See equations 8.10 and 8.11

7 **(a)** Temperature change
  (b) Electrolyte addition to the solution

Chapter 9

1 Increase the dielectric constant of the dispersing liquid; increase the surface potential of the solid; increase the thickness of the electrical double layer.

2 **(a)** Reduction of the effective Hamaker constant; **(b)** production of steric barrier.

3 It produces a greater reduction of $1/\kappa$.

4 Answer – **B** is correct. **A** is too soluble in heptane to adsorb efficiently; $C_{12}H_{25}N^+(CH_3)_3$ would not adsorb; the ligninsulfonate group would not produce an effective steric barrier.

5 It is a positively charged solid, probably with polyvalent cation sites, as evidenced by precipitation with POE nonionic.

6 **(a)** and **(b)** flocculation
(c) no effect
(d) flocculation, followed by redispersion.

Chapter 10

1 Substrate and soil may both acquire a positive charge that prevents adsorption of the cationic onto them via its hydrophilic head.

2 Neutralization of negative charge of textile surface by cationic surfactant enhances adsorption onto it of anionic surfactant.

3 **(a)** Spreading coefficient will decrease because γ_{SB} is increased.
(b) 1 Cationic surfactant on negatively charged textile surface
2 POE nonionic on hydroxylated (e.g., cellulose) surface

Chapter 11

1 **(a)** From their pC_{20} values, $|\ln C_A/C_B| = 1.39$. Thus, synergism of this type should exist in the mixture.
(b) $\alpha^* = 0.25$ (for surfactant A); $C_{12,\min} = 2.1 \times 10^{-4}$ molar (for $\pi = 20$ dyn/cm).

2 **(a)** $\beta^M = +0.7$
(b) No. $|\ln C_1^M/C_2^M| = 1.13$

3 $\beta^\sigma = +1.4$; $\beta^\sigma - \beta^M$ consequently $= +0.7$. Since $|\ln C_1^{0,\mathrm{CMC}}/C_2^{0,\mathrm{CMC}} \cdot C_2^M/C_1^M| = 0.35$, the system will exhibit antagonism in surface tension reduction effectiveness.

4 **(b)** $=$ least negative β^σ value; **(d)**; **(a)**; **(c)** $=$ most negative β^σ value.

Chapter 12

1 Increased distortion of solvent by double (or triple) the number of hydrophobic groups in the molecule

2 Greater difficulty of accommodating two (or three) hydrophobic groups in the interior of a spherical or cylindrical micelle than at a planar surface

3 Larger molecular size of the gemini, hence a smaller diffusion rate.

4 Closer packing of the hydrophobic groups of the gemini at the relevant interface

5 Geminis can adsorb with one hydrophilic group facing the solid and the second facing the aqueous phase, producing a hydrophilic surface. The first layer of a conventional surfactant adsorbs to produce a hydrophobic surface.

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