SURFACTANTS AND INTERFACIAL PHENOMENA

THIRD EDITION

Milton J. Rosen
Surfactant Research Institute
Brooklyn College
The City University of New York

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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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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), $R(OC_2H_4)_x$ OH(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.

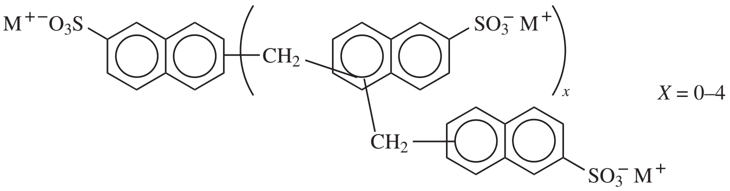
ADVANTAGES. NaOCl shows good stability in solutions of DPES.

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, $RCONHCH_2CH_2O(CH_2CH_2O)_3SO_3Na$ RCO is usually derived from coconut oil. Produced by