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 AlC13 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.

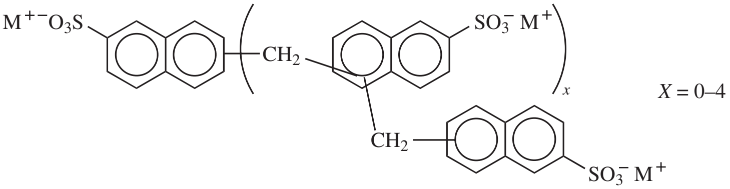
ADVANTAGES. NaOCl shows good stability in solutions of DPES.

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 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).

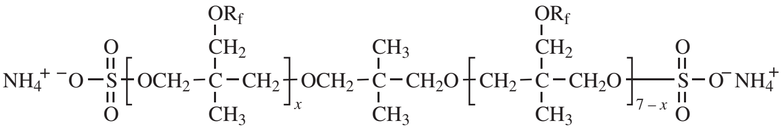
The nonoxyethylenated monoalkyl phosphates cause little skin irritation and are used in personal care products. The sodium salt of monododecyl phosphate, unlike soap, works in a weakly acidic medium and can therefore be used as a detergent in face cleaners and cleansers and in body shampoos. The potassium 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



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

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

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 bola-amphiphile.

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*

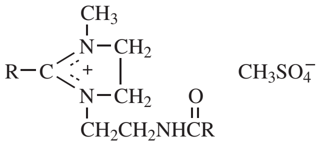
ADVANTAGES. Electrical charge on the molecule is unaffected by pH changes—positive charge remains in acidic, neutral, and alkaline media.

DISADVANTAGES. Since water solubility is retained at all pHs, they are more easily removed from surfaces onto which they may be adsorbed (insolubility of nonquaternary 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 $\leftarrow\!\!\!\left(CH_2CH(CH_3)O \right)\!\!\!\rightarrow_x$ 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,’’ $R_1R_2C[(OC_2H_4)_xOH]C{\equiv}CC[(OC_2H_4)_xOH]R_1R_2$

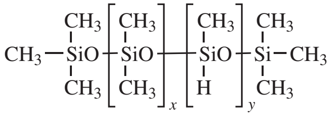
ADVANTAGES OF THE GLYCOLS. Excellent wetting agents at low concentrations and nonfoaming; nonwaxy solids (rare among nonionics); volatile with steam, thus readily removed from system after use.

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.

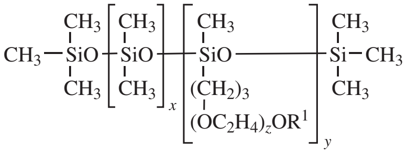
USES. Wetting agents for use in powdered solids (dyestuffs, wettable pesticide powders); synergistic with anionics and nonionics to decrease foam, reduce viscosity, and increase wetting in aqueous solution; rinse aids in dishwashing; wetting agents in emulsion paits.

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



$$CH_3-Si(CH_3)_2O-\left[Si(CH_3)_2O\right]_x-\left[Si(CH_3)(H)O\right]_y-Si(CH_3)_3$$

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

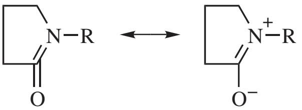


$$CH_3-Si(CH_3)_2O-\left[Si(CH_3)_2O\right]_x-\left[Si(CH_3)\left((CH_2)_3(OC_2H_4)_zOR^1\right)O\right]_y-Si(CH_3)_3$$

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

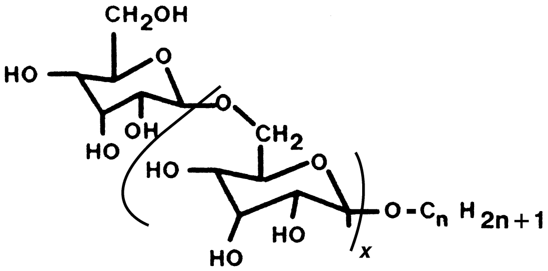


FIGURE 1-1 Alkylpolyglycoside.

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.

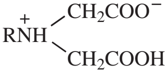
DISADVANTAGES. Often insoluble in most organic solvents, including ethanol.

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,

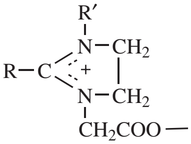


$$R\overset{+}{N}H\begin{cases} CH_2COO^- \\ CH_2COOH \end{cases}$$

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., L. Fei, and S. W. Morrall, *J. Surfactants Detgts.* **2**, 343 (1999).
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.