SURFACTANTS AND INTERFACIAL PHENOMENA

FOURTH EDITION

Milton J. Rosen
Joy T. Kunjappu

WILEY

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PREFACE

Ever since surfactant science detached its umbilical cord from the body of colloid science and established its unique identity as an independent entity in the 1950s, great leaps in its theoretical and applied fronts have occurred. The real thrust of surfactant science and technology is centered on applications, although its importance in understanding frontline areas like the origin of life and soft matter (a subfield of condensed matter studies) technology is built upon the self-organizing power of surfactants into structures such as micelles or bilayers.

This book, when originally conceived in the 1970s, forecast the impending revolution that surfactant science was to witness in the future, and was developed to bridge the gap between fundamental knowledge and industrial applications. Later editions of the book incorporated advances in theory with a special link to end uses.

The importance of surfactants continues to emerge, as evidenced by the use of polymeric surfactants during the Gulf oil spill of 2010 to disperse the floating oil film in the ocean, in processing materials such as the silicon chip, and in the still emerging areas of *in vivo* biotechnology and *in vitro* nanotechnology.

The present edition has been updated to embrace these cutting-edge and state-of-the-art topics in surfactant application by the addition of three new chapters: Chapter 13, "Surfactants in Biology"; Chapter 14, "Surfactants in Nanotechnology"; and Chapter 15, "Surfactants and Molecular Modeling."

Most of the previously existing chapters have been revised with some new materials in the form of expanded, rewritten or new sections, and/or additional references and problems. Specifically, the following new sections (in **bold**) are added or existing ones revised (in *italics*): *environmental effects of surfactants*, **electronic searching of surfactant literature**, *zwitterioncs* (Chapter 1); *mechanism of adsorption and aggregation* (Chapter 2); **rheology of surfactant solutions** (Chapter 3); *solubilization* (Chapter 4); *accurate depiction of equations in film elasticity*, **foaming and antifoaming in organic media** (Chapter 7); *microemulsions*, *demulsification* (Chapter 8); *limitations of the DLVO theory*, **design**

of new dispersants (Chapter 9); **biosurfactants and enzymes in detergent formulations** (Chapter 10); and *problems* (Chapters 1, 2, 5–10, and 12).

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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 beneficiation of ores. The last decades have seen the extension of surfactant applications to such high-technology areas as electronic printing, magnetic recording, biotechnology, microelectronics, and viral research.

A surfactant (a contraction of the term ***surf**ace-**act**ive **a**g**ent***) 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; $W_{min} = \gamma_I \times \Delta_{\text{interfacial area}}$. 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.

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

I. 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.

II. 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 mol-

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

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

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

1. *Anionic.* The surface-active portion of the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

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

A. 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 (rosin is obtained from plant resins)
6. High-molecular-weight propylene oxide polymers (polyoxypropylene glycol derivatives)
7. Long-chain perfluoroalkyl groups
8. Polysiloxane groups
9. Lignin derivatives

B. General Effects of the Nature of the Hydrophobic Group

1. 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.

2. 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.

3. 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.

4. Polyoxypropylene or Polyoxyethylene (POE) Units Polyoxypropylene units increase the hydrophobic nature of the surfactant, its adsorption onto

polar surfaces, and its solubility in organic solvents. POE units decrease the hydrophobic character or increase the hydrophilicity of the surfactant.

5. 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 than 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; Section IIIA) and, for personal care products, skin irritation (Section IIIB) 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.

III. ENVIRONMENTAL EFFECTS OF SURFACTANTS

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, and of their biodegradation products to marine organisms and human beings.

Of late, these concerns in the public mind have become so serious that, to many people, the term "chemical" has become synonymous with "toxic chemical."* As a result, many manufacturers and users of chemicals, including

* One of the authors actually heard a college student, upon seeing "organic chemistry" written on a door, exclaim, "if it is organic, how can it be chemistry?"

surfactants, have paid serious attention to the biodegradability and toxicity of surfactants. In addition, they have sought new surfactants based upon renewable resources, so-called "green" surfactants (Section IVE, below).

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. Carboxylic acids have been identified as the metabolic end products of linear alcohol ethoxylates (AEs) and alkyl aryl sulfonates.

B. Surfactant Toxicity; Skin Irritation

Since surfactants are used in many products and formulations, such as cleaning solutions, cutting fluids, inks, and paints (Kunjappu, 2001), their skin irritability is important, and they can end up in aquifers and other water sources. **LD_{50}** (the *median lethal dose*—the dose required to kill half the members of a tested population) and **IC_{50}** (the *half maximal inhibitory concentration*—a measure of the effectiveness of a compound in inhibiting biological or biochemical function) data are used to represent the toxicity.

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 et al., 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 (LASs), with bioconcentration in fish (Rosen et al., 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 IVA 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.

Cationic surfactants are found to be more toxic than anionics, and the anionics are more toxic than the nonionics. Although anionic surfactants are more irritable to skin than nonionics, sodium dodecyl sulfate (SDS) is used in many personal care products. Sodium alkyl ether sulfates are much milder than alkyl sulfates, and are used in many hand dishwashing formulations. The widely distributed, negatively charged groups in lipids, proteins, and nucleic acids may be responsible for the higher toxicity of ionic surfactants because of possible electrostatic interaction, which may explain the acute toxicity and genotoxicity of some of these surfactants.

Even in small doses, some surfactants produce dermatological problems. EC_{50}, *half maximal effective concentration*, refers to the concentration of a drug, antibody, or toxicant that induces a response halfway between the baseline and maximum after some specified exposure time (for SDS, the $EC_{50} = 0.071\%$ w/v for the human epidermis (Cannon et al., 1994). Polyol surfactants like alkyl glucosides, and zwitterionics like betaines and amidobetaines are known to be mild toward skin. The biocidal effects are studied by the effect on mucous membrane and on the bacterial surface. Biological toxicity has also been evaluated from the partition of the surfactant between oil and water (Salager et al., 2000).

IV. 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 1.1 shows consumption of the various surfactant charge types by percentage (A) and the consumption of the five major types of surfactant by tonnage (B). The projected average increase in surfactant consumption is 2.4% annually, although exact updated numbers are not available at this point (see table source line).

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
Total	100
B. Major Surfactants, by Tonnage	
Surfactant	Thousand Metric Tons
Linear alkylbenzenesulfonates	420
Alcohol ethoxysulfates	380
Alcohol sulfates	140
Alcohol ethoxylates	275
Alkylphenol ethoxylates	225
Other	1625
Total	3065

Source: Colin A. Houston and Associates, Inc.

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 IVE).

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., SDS). 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 Fatty Alcohol Carboxylates (Alkyl Ether Carboxylates), $RO(CH_2CH_2O)_xCH_2COO^-M^+$ *(x = 4, Usually)* Products of the reaction of the terminal OH group of an 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

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, $AlCl_3$, 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 $AlCl_3$ 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 $AlCl_3$ 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. LAS 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 (ASs) and ether sulfates (see "Sulfuric Acid Ester Salts"), 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 is in dry cleaning, since it is hydrocarbon-soluble; and the

dimethylamine salt is 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, for example, for increasing the solubility of LAS and other ingredients in aqueous formulations, for thinning soap gels and detergent slurries.

Ligninsulfonates These are by-products 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* (oil-in-water) 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.