

# **SURFACTANTS**

## **and INTERFACIAL PHENOMENA**

*THIRD EDITION*



**MILTON J. ROSEN**

# SURFACTANTS AND INTERFACIAL PHENOMENA

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THIRD EDITION

**Milton J. Rosen**

*Surfactant Research Institute*

*Brooklyn College*

*The City University of New York*



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# **SURFACTANTS AND INTERFACIAL PHENOMENA**

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# Preface

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

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

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

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

*Great Neck, New York*

MILTON J. ROSEN

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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, 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  $\gamma_I$  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

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,  $\text{RCOO}^-\text{Na}^+$  (soap),  $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$  (alkylbenzene sulfonate).
2. *Cationic*. The surface-active portion bears a positive charge, for example,  $\text{RNH}_3^+\text{Cl}^-$  (salt of a long-chain amine),  $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$  (quaternary ammonium chloride).
3. *Zwitterionic*. Both positive and negative charges may be present in the surface-active portion, for example,  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid),  $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  (sulfobetaine).
4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example,  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride of long-chain fatty acid),  $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$  (polyoxyethylenated alkylphenol),  $\text{R}(\text{OC}_2\text{H}_4)_x\text{OH}$  (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. Alkyl-naphthalene 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