

Industrial Utilization of Surfactants

Principles and Practice

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Preface

There has been a plethora of books on surfactants, surfactant-containing products, and surfactant-related processes in recent years. In spite of this, the selections of surfactants for a particular application still is too often done on a trial-and-error basis. This is partly because the basic principles involved in surfactant utilization are often obscured by the mathematics required to apply these principles rigorously and partly because most real-life applications are too far removed from the simplified models of these applications to which these principles can be applied rigorously.

What the average technologist, who wishes to select in rational fashion a surfactant for use in some process or product, needs is information on the relationship between the *chemical structure of the surfactant and its performance* in that application. A knowledge of the mathematical equations is fundamental to an understanding of the relevant interfacial phenomena, but unless these equations lead to an understanding of how the chemical structure of the surfactant affects these phenomena, these equations have limited value to the technologist who must select a chemical, not an equation, from his laboratory shelf. Such chemical structure–performance property relationships are too often missing from most of the books published on surfactants.

The aims of this book are as follows:

- To provide this chemical structure–performance property information in the simplest possible terms.
- To provide the principles underlying the relationships of chemical structure to performance properties, so that the reader can understand why particular surfactant structures have certain performance properties.
- To give some examples of the application of these relationships to real-life uses of surfactants.

Those who would like to explore chemical structure–fundamental property relationships in somewhat greater depth might consult Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd edition, John Wiley, New York, 1989.

We have specifically omitted application areas, such as laundry detergents and cosmetics, in which considerable work has been published and instead have covered areas where much less information is available.

Milton J. Rosen
Manilal Dahanayake

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CHAPTER 1

General Principles

Which Surfactant Should I Use?

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Performance Properties That Involve Changing the Properties of Both the Interface(s) and the Solution Phase

Which Surfactant Should I Use?

A recent compilation of commercially available surfactants by trade name lists several thousand materials made in the United States alone (1). Undoubtedly, most of these are very similar products made by several different manufacturers. Even so, hundreds of different chemical structures can be found among these products. How does one decide which one to use for a particular application? Very often, the trial-and-error method is used: surfactants are picked at random from the shelf

in the laboratory, with the hope that one will do the job. At this stage in our knowledge of surfactant science, however, we should be able to do better than that. Although it is still impossible to pinpoint the *exact* surfactant chemical structure that is best for a particular process or product, selection in a rational, scientific manner of the proper structural types for a particular use is possible. The objective of this volume is to show how this selection can be done by describing the principles involved in surfactant utilization and then showing some applications of these principles to actual commercial use.

At the molecular level, a surfactant is an organic compound (Fig. 1.1) that contains at least one lyophilic ("solvent-loving") and one lyophobic ("solvent-fearing") group in the molecule. If the solvent in which the surfactant is to be used is water or an aqueous solution, the respective terms are hydrophilic and hydrophobic. When the surfactant is dissolved in a solvent, the presence of the lyophobic group distorts the normal structure of the solvent, increasing the free energy of the system, and the surfactant then spontaneously orients itself in some manner that will minimize contact between the solvent and the lyophobic group, thereby decreasing the free energy of the system. Thus in aqueous media, the surfactant molecules may migrate to the interfaces of the system and orient themselves there in such fashion as to minimize, as much as possible, contact between the water and their hydrophobic groups. This process is known as **adsorption**, and it changes the properties of the interfaces. This will be discussed in Chapter 2.

Another method of minimizing contact between the lyophobic group of the surfactant molecule and the solvent is by aggregating the

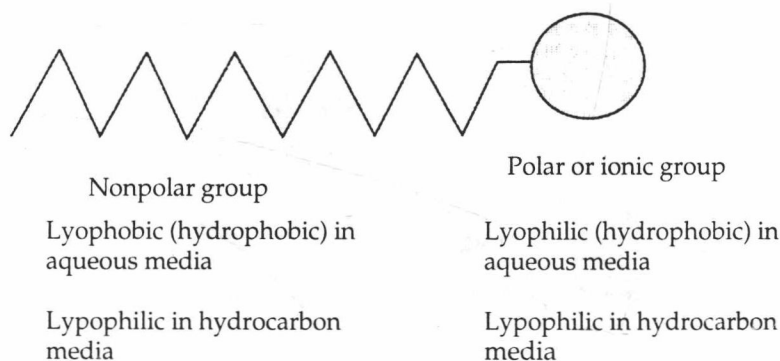


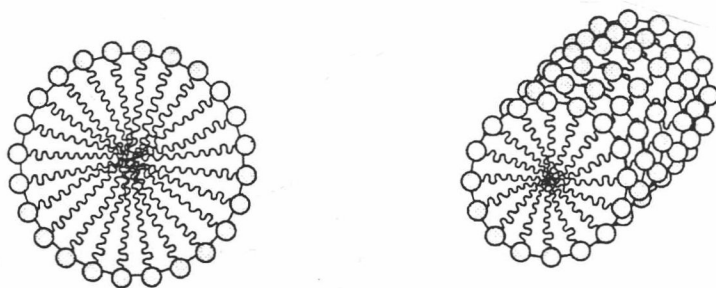
Figure 1.1. Generalized surfactant structure.

surfactant molecules into structures such as spheres, cylinders, or sheets, where the lyophobic groups are in the interior of the aggregate structure and the lyophilic groups are at the exterior, facing the solvent. Such a structure is called a **micelle** (Fig. 1.2). The process is called micellization and changes the properties of the solution phase. It will be discussed in Chapter 3.

The lyophilic group of the surfactant serves to keep it in solution. To retain those properties that are characteristic of surfactants—their **surface activity**—the surfactant must remain soluble in the solvent. For example, if the surfactant becomes insoluble in the solvent, it loses much if not all of its ability to cause the solution to wet surfaces or produce foam.

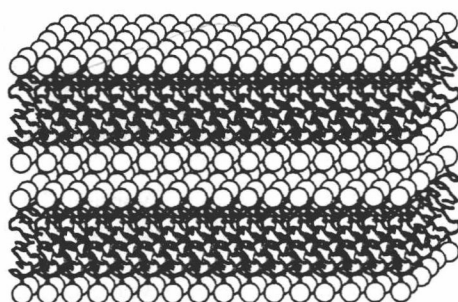
Surfactants, then, because of the presence of the lyophobic group in the molecule, produce two separate changes in the system: (i) they change the properties of the interfaces, and (ii) they change the properties of the solution phase.

Hydrophobic groups present in commercially available surfactants (Table 1.1) are usually either: (i) a hydrocarbon residue, (ii) a perfluoro-



Cross section of spherical micelle

Cylindrical



Lamellar

Figure 1.2. Micellar shapes.

TABLE 1.1

Some Hydrophobic Groups in Commercially Available Surfactants

Linear, saturated alkyl (n-dodecyl)	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2-$
Branched, saturated alkyl (2-ethylhexyl)	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_3\text{CHCH}_2- \\ \\ \text{CH}_2\text{CH}_3 \end{array}$
Linear, unsaturated alkyl (oleyl) $(\text{CH}_2)_7\text{CH}_2-$	$\text{cis-CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}$
Alkylbenzene (linear dodecylbenzene)	$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4-$
Alkyldiphenyl ether	$\text{C}_6\text{H}_5\text{O C}_6\text{H}_4(\text{R})-$
Polyoxypropylene	$-\text{[OCH}(\text{CH}_3)\text{CH}_2]_x-$
Polyoxybutylene	$-\text{[OCH}(\text{C}_2\text{H}_5)\text{CH}_2]_x-$
Polysiloxane	$\begin{array}{c} (\text{CH}_3)_3\text{Si}[\text{OSi}(\text{CH}_3)]_x\text{OSi}(\text{CH}_3)_3 \\ \end{array}$
Perfluoroalkyl	$\text{CF}_3(\text{CF}_2)_x\text{CF}_2-$
Lignin	Complex polymeric phenol

hydrocarbon residue, (iii) a siloxane residue, or (iv) a polyoxypropylene or polyoxybutylene residue. The hydrocarbon residue may be straight alkyl chain, branched alkyl chain, saturated, unsaturated, partly cyclic, or aromatic. The perfluorohydrocarbon residue may be straight chain or branched chain, completely perfluorinated, or attached to a hydrocarbon residue. Siloxane residues are often attached *via* short alkyl chains to the lyophilic group.

The hydrophilic group (Table 1.2) attached to the hydrophobic group may be: (i) negatively charged, in which case the surfactant is anionic, e.g., $\text{C}_{12}\text{H}_{25}\text{SO}_4^-$; (ii) positively charged, in which case the surfactant is cationic, e.g., $\text{C}_{10}\text{H}_{33}\text{N}(\text{CH}_3)_3^+$; (iii) both positively and negatively charged, i.e., a zwitterion, often called an ampholyte (i.e., an amphoteric surfactant), e.g., $\text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$; or (iv) without formal charge, i.e., a nonionic surfactant, e.g., $\text{C}_{12}\text{H}_{25}(\text{OC}_2\text{H}_4)_8\text{OH}$.

Whether a group is lyophilic or lyophobic depends on the nature of the solvent in which the surfactant is dissolved for use. Thus in water solution, an alkyl chain is lyophobic (hydrophobic) and an ionic group is lyophilic (hydrophilic). On the other hand, in hydrocarbon solution, the alkyl chain is lyophilic (compatible with the hydrocarbon solvent), whereas the ionic group is lyophobic (causing distortion of the hydrocarbon structure). The nature of the solvent used must therefore be considered in determining which group is lyophilic and which is lyophobic.

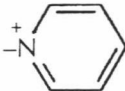
TABLE 1.2

Some Hydrophilic Groups in Commercially Available Surfactants

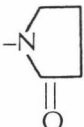
Anionics

Sulfate	$-\text{OSO}_2\text{O}^-$
Sulfonate	$-\text{SO}_2\text{O}^-$
Phosphated ethoxylates	$-\text{[(OC}_2\text{H}_4)_x]_2 \text{P(O)O}^-$ $-\text{[(OC}_2\text{H}_4)_x] \text{P(O)(O}^-\text{)}_2$
Carboxylate	$-\text{COO}^-$

Cationics

Ammonium, primary	$-\text{NH}_3^+$
Ammonium, secondary	$\begin{array}{c} \\ -\text{NH}_2^+ \end{array}$
Ammonium, tertiary	$\begin{array}{c} \\ -\text{NH}^+ \\ \end{array}$
Ammonium, quaternary	$\begin{array}{c} \\ -\text{N}^+- \\ \end{array}$
Pyridinium	

Nonionics

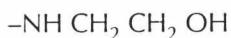
Polyoxyethylene (ethoxylate)	$-(\text{OCH}_2\text{CH}_2)_x\text{OH}$
Monoglyceride	$-\text{OCH}_2\text{CHOHCH}_2\text{OH}$
Diglyceride	$-\text{OCH}_2\text{CH(O-)}\text{CH}_2\text{OH}$ $-\text{OCH}_2\text{CHOHCH}_2\text{O-}$
Acetylenic glycol	$\begin{array}{c} \quad \quad \\ -\text{C}-\text{C} \equiv \text{C}-\text{C}- \\ \quad \quad \\ \text{OH} \quad \text{OH} \end{array}$
Pyrrolidinone	

(continued)

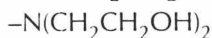
TABLE 1.2
(Continued)

Nonionics (continued)

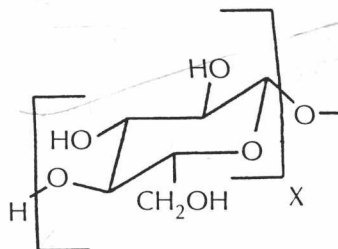
Monethanolamide



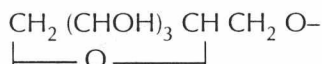
Diethanolamide



Polyglycoside

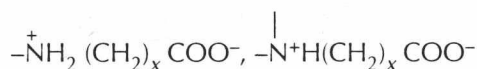


Sorbide

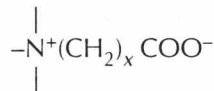


Zwitterionics^a

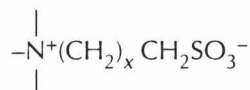
Aminocarboxylates



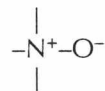
Betaine



Sulfobetaine



Amine oxide



^aOften called ampholytic or amphoteric (incorrectly, in the case of betaines and sulfobetaines).

Which Surfactant Is "Best"?

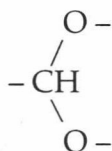
What Do We Mean by "Best"? Before trying to answer that question, we must first decide what we mean by "best." Do we mean the level of performance the surfactant can make available (its effectiveness), do we mean how much surfactant is needed to attain the desired level of performance (its efficiency), or do we mean how fast the surfactant can make available the desired level of performance (its speed of action)?

These all depend on different properties of the surfactant. Thus the efficiency and effectiveness of the surfactant, as we shall see, depend on its equilibrium properties, whereas its speed of action often depends on its dynamic (nonequilibrium) properties.

Other considerations also determine which surfactant is best for a particular use, some physico-chemical, some not.

Chemical Stability. The chemical stability of the surfactant in the system in which it is to be used is generally an important consideration. In some cases, instability is desired. For example, in formulating coatings with a surfactant, it is often desirable for the surfactant to lose its hydrophilic properties during drying of the film, in order that the final film not be sensitive to moisture in the air or water. On the other hand, in formulating a cosmetic emulsion that may be used over a time of considerable length, it is necessary that the surfactant(s) used not hydrolyze or undergo any other decomposition that may result in demulsification of any of the ingredients.

Ester linkages, $-C(O)-OR$, found in glycerol, sorbitol, polyglycol, polysaccharide, and other polyol esters, hydrolyze in both aqueous alkaline and acidic media, whereas organic sulfate linkages, $-COSO_3^-$, found in sulfated alcohols and sulfated ethoxylated alcohols, are stable in alkaline media but hydrolyze in aqueous acidic media. The acetal



linkage, found in alkyl polyglycosides, is also stable in aqueous alkaline media, but hydrolyzes in aqueous acidic media:

The anionic hydrophilic carboxylate group, $-COO^-$, is converted to the less water-soluble nonionic carboxylic acid group, $-C(O)-OH$, in acid media, whereas the cationic (RNH_3^+ , $R_2NH_2^+$, and R_3NH^+) ammonium salts are transformed to their corresponding less water-soluble nonionic free amines in basic media. Surfactants containing chemical groups (e.g., 1 and 2° hydroxyl, sulfide, amino, and benzylic hydrogen groups) that are sensitive to oxidizing agents cannot be used with oxidizing ingredients such as hypochlorite bleach (unless these groups are sterically blocked from reacting).

Environmental Impact. A major concern at present is the effect of chemicals on the environment, and this extends also to surfactants. Consequently, in deciding which surfactant to use for a particular purpose, one of the considerations may be its environmental impact. Here, the relevant properties are: (i) its biodegradability, and (ii) its toxicity to beneficial organisms it may encounter, both in its use and in its disposal. Generally, the greater the rate of biodegradation to innocuous products, the less important is the toxicity of the undegraded surfactant and its degradation products. The volume of surfactant used may also determine the importance of biodegradation and toxicity. Surfactants used in small volume for specialized purposes can be expected to have less environmental impact than those used in large amounts.

Biodegradability (2). Surfactants containing alkyl groups that are branched are more resistant to biodegradation than those containing straight alkyl chains, particularly if the branching is adjacent to the terminal methyl group of the chain. A general principle appears to be that increased distance between the hydrophilic group and the far end of the hydrophobic group increases the speed of biodegradation. The speed of degradation decreases with an increase in the number of methyl groups on the alkyl chain and with the number of alkyl chains in the molecule. The ease of biodegradability also decreases with an increase in the number of oxyethylene groups in ethoxylated surfactants. Secondary alcohol ethoxylates degrade more slowly than primary alcohol ethoxylates, even when the former alcohol is linear. The replacement of oxyethylene groups by oxypropylene or oxybutylene groups also decreases biodegradability.

Toxicity. The toxicity of surfactants depends on both their tendency to adsorb onto organisms and the ease with which the surfactant molecule can penetrate cell membranes (3): tendency to adsorb onto organisms appears to increase with tendency of the surfactant to adsorb onto related interfaces (see Chapter 2, Adsorption onto Insoluble Solids and Liquids from Nonaqueous Solutions of Surfactants), whereas ease of penetration appears to decrease with an increase in the area occupied by the surfactant at the interface (see Chapter 2, Adsorption onto Insoluble Solids or Liquids from Aqueous Solutions of Surfactants). Another property related to its environmental impact is the aqueous solubility of the surfactant in the presence of other water-soluble or water-dispersible substances with which it may come in contact, since often the effect of a surfactant on other organisms depends on its concentration in aqueous media that contact the organisms. For example, hardness (Ca^{2+} , Mg^{2+}) in the water may precipitate an anionic surfac-

tant from its solution in a waste water stream and consequently reduce its environmental impact.

Skin Irritation. In products that may come in contact with the skin, skin irritation by the surfactant, *in the formulation in which it contacts the skin*, is a major factor in deciding which surfactant to use. Protein denaturation, as a result of adsorption of the surfactant onto charged sites on the skin, is believed to be one of the major causes of skin irritation. Here, as in the preceding discussion of toxicity, the tendency of the surfactant to adsorb onto the skin and the ease with which it can penetrate the cell membranes appear to determine skin irritation. Studies of protein denaturation by surfactants indicate that both anionic and cationic surfactants may produce considerable denaturation of proteins. In general, the order of denaturation is: anionics, cationics > amphoterics, amine oxides > ethoxylated nonionics (4–6). For anionic surfactants with C_{12} alkyl chains, the order is: alkylbenzenesulfonate > alcohol sulfate > alpha olefin sulfonate > ethoxylated alcohol sulfate. For the series $C_{12}H_{25}(OC_2H_4)_xSO_4Na$, no denaturation occurs when $x = 6$ or 8 (6).

The addition of positively charged organic material (surface-active or otherwise) that interacts with anionic surfactants can decrease the skin irritation of the latter. This is probably because the positively charged material interacts with the anionic surfactant and decreases its tendency to adsorb onto positively charged sites on the skin. The greater the positive charge of the additive, the greater its protective action on the skin. Thus, positively charged protein hydrolysates, when added to anionic detergents, protect the skin from irritation (7). The addition also of cationic surfactants or long-chain amine oxides to anionic surfactants decreases the irritation of the skin.

Finally, economic considerations, such as cost of the surfactant and the final product or process in which it appears, are of major importance in determining which surfactant to use. These are outside the scope of this book, however.

What Do I Want the Surfactant(s) to Do?

As mentioned in the preceding discussion, surfactants have two sets of properties: (i) they adsorb at interfaces and, as a result of this adsorption, change the properties of those interfaces; and (ii) they aggregate in the solvent in which they are dissolved and, as a result of this aggregation, change the properties of the solution phase. In order to decide