

# 1

## Types of Surfactants, their Synthesis, and Applications

### Definition of a Surfactant

Surfactant is a widely used contraction for surface active agent, which literally means active at a surface. The term *surface active* means that the surfactant reduces the free energy of surfaces and interfaces. Expressed differently, they reduce the surface and the interfacial tensions. This is not an unique quality, however. Most water-soluble organic compounds give a reduction of the surface and interfacial tensions when added to an aqueous solution but the effect is normally much less pronounced than for surfactants. The unique behavior of a surfactant is that it self-assembles at interfaces and forms tightly packed structures: monolayers at the air–water and the oil–water interface, and monolayers and aggregates at the solid–water interface. Such self-assembled layers drastically change the character of the interface. Surfactant self-assembly at the air–water interface, commonly referred to as the “surface,” is dealt with in Chapter 12; the assembling at the oil–water interface, which is key to formation of emulsions, is treated in Chapter 24; and assembly at the solid–water interface, *adsorption*, is described in depth in Chapter 8. Surfactants also self-assemble in water, usually forming *micelles* at very low concentration and other aggregates, called *surfactant liquid crystals*, at higher concentration. These are treated in Chapters 4 and 6, respectively.

The term surfactant is usually associated with relatively low molecular weight substances. The molecular weight is typically below 500 Da but may be larger for nonionic surfactants with long polyoxyethylene tails. There also exist polymeric surface active agents and these may be called polymeric surfactants. However, more often they are referred to as surface active polymers and that terminology is used in this book. Several chapters deal with surface active polymers.



**Figure 1.1** Schematic illustration of a surfactant

Surfactants are *amphiphilic* molecules. The word has a Greek origin with *amphi* meaning “both” and *phil* meaning “like”; that is, surfactants are molecules that like both a polar and a nonpolar environment. This is due to their structure. All surfactants have at least one polar headgroup that wants to be in water and at least one hydrophobic tail that prefers to be in an apolar environment; hence, the tendency to go to interfaces. Figure 1.1 shows the structure of a surfactant with one polar head group and one hydrophobic tail.

A surfactant may be viewed as a molecule consisting of a lyophilic and a lyophobic part. The lyophilic moiety is soluble in a specific fluid whereas the lyophobic moiety is insoluble in this fluid. When the fluid is water, which is usually the case, the terms hydrophilic and hydrophobic parts are normally used.

The term *amphiphile* or *amphiphilic compound* is sometimes used in the same sense as the word surfactant. Amphiphilic compounds are also very common in nature. All biological systems contain surface active substances. However, these molecules are usually called polar lipids rather than surfactants. Thus, implicit in the name is that a surfactant is a man-made compound in some sense, although the molecule may have a natural origin, as is discussed later in this chapter.

The hydrophobic tail is almost always based on one or more carbon chains and the chains may be linear, branched, or cyclic. The only exception to carbon chains as hydrophobic backbone is siloxane chains. There exist both high molecular weight and low molecular weight amphiphilic compounds based on the  $-\text{Si}-\text{O}-$  unit; these are discussed in Chapters 10 and 20, respectively.

## Surfactants Adsorb at Interfaces

The term interface denotes a boundary between any two immiscible phases; the term surface indicates that one of the phases is a gas, usually air. Altogether five different interfaces exist:

1. Solid–vapor *surface*
2. Solid–liquid
3. Solid–solid
4. Liquid–vapor *surface*
5. Liquid–liquid

The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface. The term interfacial tension is often used

**Table 1.1** Examples of interfaces involving at least one liquid phase

Interface	Type of system	Product
Solid–liquid	Suspension, sol, slurry	Solvent-borne paints, colloidal silica, cement slurries
Liquid–liquid	Emulsion	Bitumen emulsions, milk, cream
Liquid–vapor	Foam, aerosol	Shaving cream, fire fighting foams, clouds

instead of interfacial free energy per unit area. Thus, the surface tension of water is equivalent to the interfacial free energy per unit area of the boundary between water and the air above it. When that boundary is covered by surfactant molecules, the surface tension (or the amount of work required to expand the interface) is reduced. The denser the surfactant packing at the interface, the larger is the reduction in surface tension.

This book is concerned with events at interfaces that involve at least one liquid phase, which means three out of the five interfaces listed above. The liquid is usually, but not always, water. Phenomena occurring at these three interfaces, as well as in the bulk liquid, may be referred to as *wet surface chemistry*. *Dry surface chemistry* is also very important—heterogeneous catalysis is a prime example—but that science is not discussed here. Examples of the different “wet” interfaces and of products in which these interfaces are important are given in Table 1.1.

The systems indicated in Table 1.1 are all examples of dispersions, that is, systems with one phase, called the dispersed phase, finely distributed in another phase, the continuous phase. In many formulated products several types of systems are present at the same time. Water-based paints and paper coating formulations are examples of familiar but, from a colloidal point of view, very complicated systems, containing both solid–liquid (dispersed pigment particles) and liquid–liquid (latex or other binder droplets) interfaces. In addition, foam formation is a common (but unwanted) phenomenon at the application stage. All the interfaces are stabilized by surfactants.

As mentioned above, the tendency to accumulate at interfaces is a fundamental property of a surfactant. In principle, the stronger the tendency, the better is the surfactant. The tendency for a surfactant to accumulate at a boundary depends on the surfactant structure and also on the nature of the two phases that meet at the interface. Therefore, there is no universally good surfactant, suitable for all uses. The choice will depend on the application. A good surfactant should have low solubility in the bulk phases. Some surfactants (and several surface active macromolecules) are only soluble at the oil–water interface. Such compounds are difficult to handle but are very efficient in reducing the interfacial tension.

There is, of course, a limit to the surface and interfacial tension lowering effect by the surfactant. Usually that limit is reached when micelles start to form in the bulk solution. Table 1.2 illustrates what a good surfactant can do in terms of reducing surface and interfacial tensions. The values given are typical of what is attained by normal light-duty liquid detergents. With special formulations, so-called ultra-low interfacial tension, that is, values in the range of  $10^{-3}$  mN/m or below, can be obtained. An example of a system

**Table 1.2** Typical values of surface and interfacial tensions at room temperature (mN/m)

Water-air	72-73
10% aqueous NaOH-air	78
Aqueous surfactant solution-air	28-30
Decane-air	24
Benzene-air	29
Decane-water	51
Benzene-water	35
Hydrocarbon-aqueous surfactant solution	1-5

giving ultra-low interfacial tension is a three-phase system comprising a microemulsion in equilibrium with excess water and oil phases. Such systems are of interest in oil recovery and also in detergency; these are discussed in Chapter 25.

### Surfactants Aggregate in Solution and at Interfaces

As discussed, one characteristic feature of surfactants is their tendency to adsorb at interfaces. Another fundamental property of surface active agents is that unimers in solution tend to form aggregates, so-called micelles. (The free or unassociated surfactant is referred to in the literature either as *monomer* or *unimer*. In this text unimer is used and the term monomer is restricted to the polymer building block.) Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing the hydrophobic tail from contact with water, thereby reducing the free energy of the system. It is an important phenomenon, since surfactant molecules behave very differently when present in micelles than they do as free unimers in solution. Surface and interfacial tension lowering and dynamic phenomena, such as wetting and foaming, are governed by the concentration of free unimers in solution. The micelles can be seen as a reservoir for the surfactant unimers. The exchange of surfactant molecules between micelles and bulk solution is fast, with residence times in micelles typically much below milliseconds.

Micelles are generated already at a very low surfactant concentration in water. The concentration at which micelles start to form is called the critical micelle concentration (CMC) and is an important characteristic of a surfactant. A CMC of 10 mM, a reasonable value for an ionic surfactant, means that the unimer concentration will never exceed this value, regardless of the amount of surfactant added to the solution. Surfactant micellization is discussed in detail in Chapter 4.

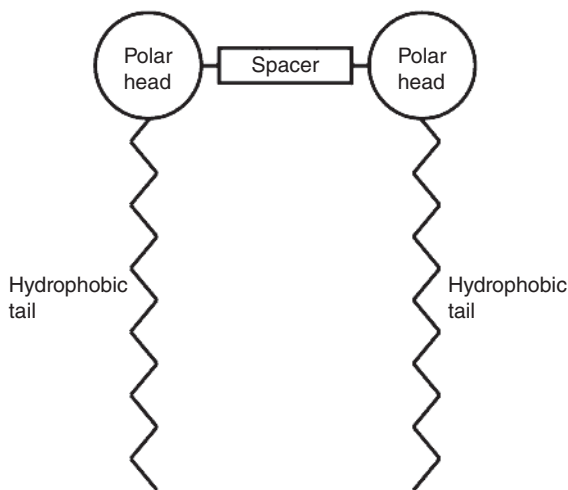
In a micelle, the surfactant hydrophobic tail is in the interior and the polar head group is directed towards the solvent. The micelle, therefore, is a polar aggregate of high water solubility and without surface activity. When a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic tail towards the surface and exposes its polar head group to the water. The surface has now become hydrophilic and, as a result, the interfacial tension between the surface and water has been reduced. Adsorption at hydrophilic surfaces often results in more complicated surfactant assemblies. Surfactant adsorption at hydrophilic and hydrophobic surfaces is discussed in Chapter 8.

## All Surfactants Contain at Least One Polar Head Group and at Least One Hydrophobic Tail

The hydrophobic part of a surfactant may be branched or linear, it may be cyclic and quite often it is an alkylaryl. The polar head group is usually, but not always, attached at one end of the alkyl chain. The number of carbon atoms in the hydrophobic tail is usually 8–18. The degree of chain branching, the position of the polar head group and the length of the chain are parameters of importance for the physicochemical properties of the surfactant.

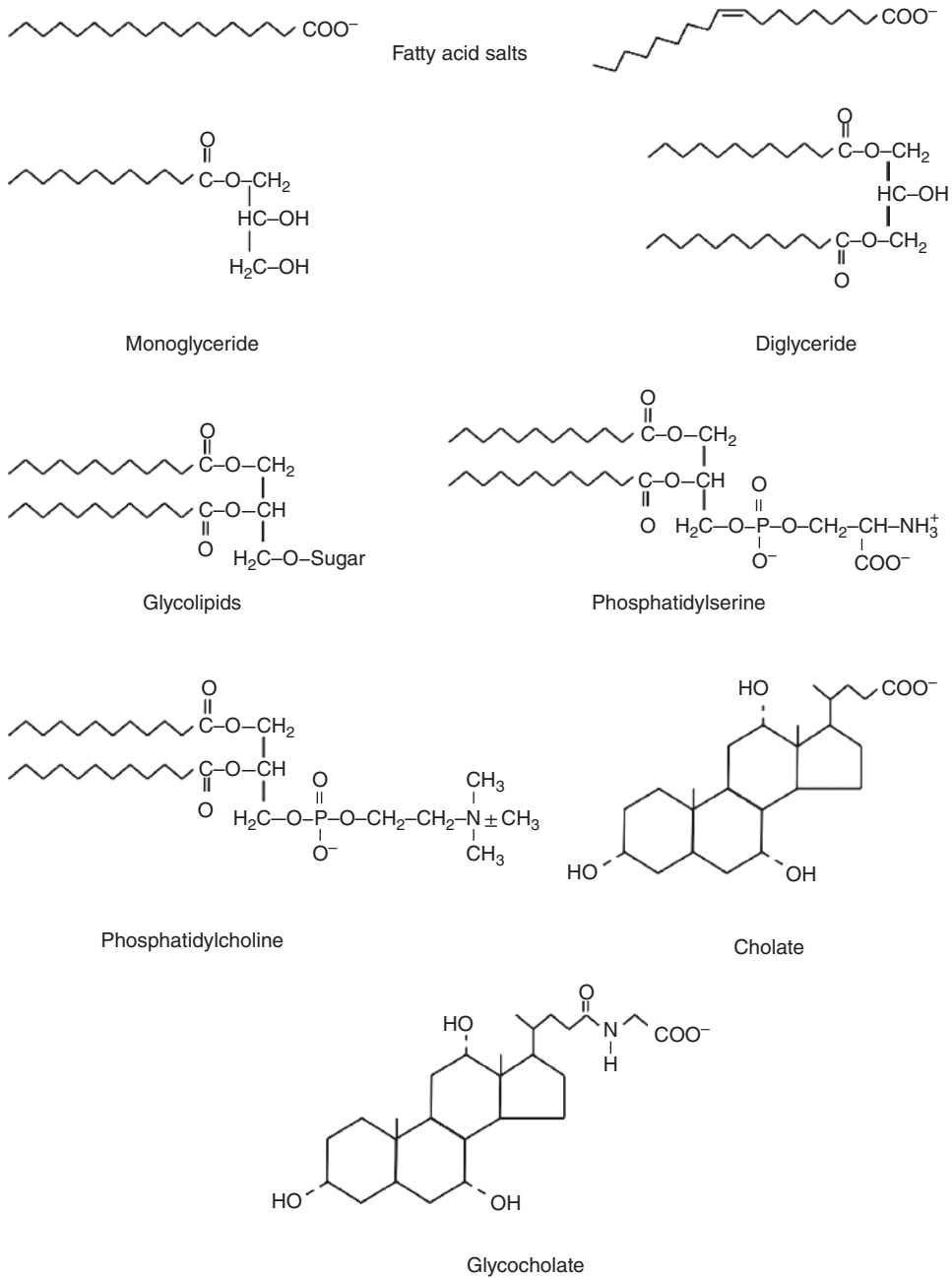
The polar part of the surfactant may be ionic or nonionic and the choice of polar head group determines the properties to a large extent. For nonionic surfactants the size of the head group can be varied at will; for the ionics the size is more or less a fixed parameter. As will be discussed many times throughout this book, the relative size of the hydrophobic tail and the polar head group, not the absolute size of either of the two, is decisive in determining the physicochemical behavior of a surfactant in water.

The vast majority of surfactants contains only one polar head group. Recently, there has been considerable research interest in certain dimeric surfactants, containing two hydrophobic tails and two head groups linked together via a short spacer. These species, generally known under the name *gemi*ni (Latin for “twin”) surfactants, are not yet of commercial importance. They show several interesting physicochemical properties, such as very high efficiency in lowering surface tension and very low CMC. The low CMC values of gemini surfactants can be illustrated by a comparison of the value for the conventional cationic surfactant dodecyltrimethylammonium bromide (DTAB) (16 mM) and that of the corresponding gemini surfactant, having a two carbon linkage between the monomers (0.9 mM). The difference in CMC between monomeric and dimeric surfactants could be of considerable practical importance. A typical gemini surfactant is shown in Figure 1.2. Gemini surfactants are further discussed in a separate section of this chapter.



**Figure 1.2** A gemini surfactant

6 Surface Chemistry of Surfactants and Polymers



**Figure 1.3** Examples of polar lipids

## Surface Active Compounds are Plentiful in Nature

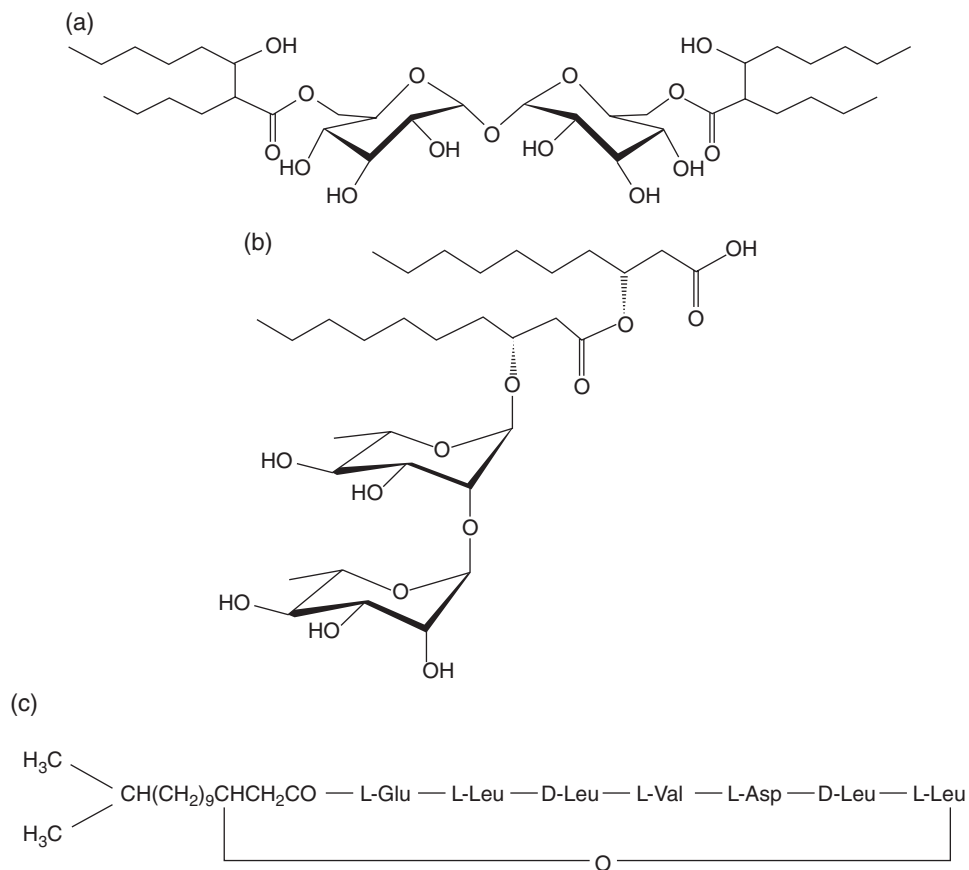
Nature's own surfactants are usually referred to as polar lipids. These are abundant in all living organisms. In biological systems the surface active agents are used in very much the same way as surfactants are employed in technical systems: to overcome solubility problems, as emulsifiers, as dispersants, to modify surfaces, and so on. There are many good examples of this in biological systems: bile salts are extremely efficient solubilizers of hydrophobic components in the blood, while mixtures of phospholipids pack in ordered bilayers of surfactant liquid crystal type and such structures constitute the membranes of cells. Figure 1.4 gives examples of important polar lipids. The only important example of a surfactant being obtained directly, without chemical conversion, from nature is lecithin. (The term lecithin is not used in a strict way in the surfactant literature. It is sometimes used synonymously with phosphatidylcholine and it sometimes refers to phospholipids in general.) Lecithin is extracted from phospholipid-rich sources such as soybean and egg.

Microorganisms are sometimes efficient producers of surface active agents. Both high molecular weight compounds, for example, lipopolysaccharides, and low molecular weight polar lipids can be produced in good yields, particularly when the microorganism is fermented on a water-insoluble substrate. Surface active polymers of this type are dealt with in Chapter 10. Figure 1.4 gives the structures of a low molecular weight acylated sugar, a trehalose lipid obtained from the cell walls of *Mycobacterium tuberculosis*, a glycolipid from *Pseudomonas aeruginosa* called rhamnolipid (or more specifically, a di-rhamnolipid), and a surface active polypeptide derivative produced from *Bacillus subtilis*. These and several other low molecular weight amphiphilic lipids have proven to be effective surfactants. Surface active agents produced from bacteria and yeasts have attracted considerable interest in recent years and much effort has been directed towards improving the fermentation and, not least, the work-up procedure. Although considerable process improvements have been made, commercial use of these products is still limited due to their high price. Their main use is in the cosmetics sector.

## Surfactant Raw Materials may be Based on Petrochemicals or Oleochemicals

For many years there has been a strong trend towards *green surfactants*, particularly for the household sector. In this context, the term *natural surfactant* is often used to indicate some natural origin of the compound. However, no surfactants used in any substantial quantities today are truly natural. With few exceptions they are all manufactured by organic synthesis, usually involving rather hard conditions, which inevitably give by-products. For example, monoglycerides are certainly available in nature but the surfactants sold as monoglycerides are prepared by glycerolysis of triglyceride oils at temperatures well above 200°C, yielding di- and triglycerol derivatives as by-products. Alkyl glucosides are abundant in living organisms but the surfactants of this class, often referred to as APGs (alkyl polyglucosides), are made in several steps that by no means are natural.

A more adequate approach to the issue of origin is to divide surfactants into oleochemically based and petrochemically based. Surfactants based on oleochemicals are made from



**Figure 1.4** Examples of surface active polar lipids produced by fermentation: (a) a trehalose lipid; (b) a rhamnolipid; and (c) a cyclic polypeptide derivative. (The hydrocarbon chains in structures (a) and (b) are only schematic; in reality they are longer than shown here.)

renewable raw materials, most commonly vegetable oils. Surfactants from petrochemicals are made from small building blocks, such as ethylene, produced by cracking of naphtha. Quite commonly, a surfactant may be built up by raw materials from both origins. Fatty acid ethoxylates are one example out of many.

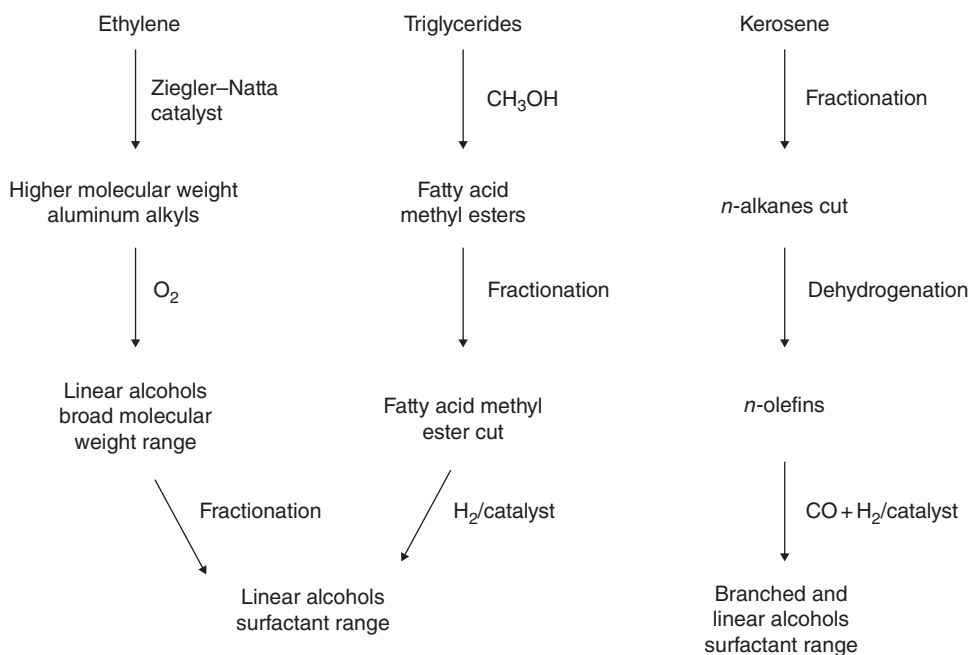
Sometimes the oleochemical and the petrochemical pathways lead to essentially identical products. For example, linear alcohols in the  $\text{C}_{10}$ – $\text{C}_{14}$  range, which are commonly used as hydrophobes for both nonionics (alcohol ethoxylates) and anionics (alkyl sulfates, alkyl phosphates, etc.), are made either by hydrogenation of the corresponding fatty acid methyl esters or via Ziegler–Natta polymerization of ethylene using triethyl aluminum as catalyst. Both routes yield straight-chain alcohols and the homologue distribution is not very different, since it is largely governed by the distillation process. Both pathways are used in very large scale operations.



It is not obvious that the oleochemical route will lead to a less toxic and more environmentally benign surfactant than the petrochemical route. By-products that may be allergenic or toxic to aquatic organisms can be generated by both routes. However, from the carbon dioxide cycle point of view, chemical production based on renewable raw materials is always preferred. In terms of *Carbon Footprint*, that is, the amount of greenhouse gas emissions caused by a product, today a popular measure of the impact made on the environment, oleochemically-based surfactants are preferred.

Linear long-chain alcohols are often referred to as fatty alcohols, regardless of their source. Branched alcohols are also of importance as surfactant raw material. They are invariably produced by synthetic routes, the most common being the so-called Oxo process, in which an olefin is reacted with carbon monoxide and hydrogen in the presence of a soluble rhodium catalyst to give an aldehyde (the hydroformylation reaction), which is subsequently reduced to the alcohol by catalytic hydrogenation. Recent advances in the process technology have made it possible to obtain tailor-made higher olefin fractions from lower and higher linear alpha olefins via isomerization and disproportionation. A mixture of branched and linear alcohols is obtained and the ratio between the two can be varied to some extent by the choice of catalyst and reaction conditions.

The different routes to higher molecular weight primary alcohols are illustrated in Figure 1.5.



**Figure 1.5** Different pathways for preparation of primary alcohols of interest as surfactant building block; from left to right: Ziegler-Natta polymerization of ethylene; reduction of fatty acid methyl esters; hydroformylation of higher olefins (the Oxo process)

## Surfactants are Classified by the Polar Head Group

The primary classification of surfactants is made on the basis of the charge of the polar head group. It is common practice to divide surfactants into the classes anionics, cationics, nonionics, and zwitterionics. Surfactants belonging to the latter class contain both an anionic and a cationic charge under normal conditions. In the literature they are often referred to as amphoteric surfactants but the term *amphoteric* is not always correct and should not be used as synonymous to *zwitterionic*. An amphoteric surfactant is one that changes its state of ionization with pH. Among normal organic substances, simple amino acids are well-known examples of amphoteric compounds. However, many of the amino acid-based surfactants, nowadays of increasing interest because of their natural origin, are not amphoteric. They are N-acyl derivatives of the amino acid, which means that the basic character of the  $\alpha$ -amino group is lost. Thus, they are anionic surfactants unless they are based on lysine or some other dibasic amino acid, in which case they become amphoteric. Some zwitterionic surfactants retain their charges over the whole pH range. Surfactants with a quaternary ammonium as the cationic group and a sulfonate salt as the anionic group, such as the sulfobetaines, are examples of that. Normal betaine surfactants (see below), on the other hand, are based on a quaternary ammonium group and a carboxylate group, the latter becoming protonated at low pH. Thus, a betaine surfactant is zwitterionic at high and medium pH but cationic at low pH.

Most ionic surfactants are monovalent but there are also important examples of divalent anionic amphiphiles. For the ionic surfactants the choice of counterion plays a role in determining the physicochemical properties. Most anionic surfactants have sodium as counterion but other cations, such as lithium, potassium, calcium, protonated amines, and quaternary ammonium compounds, are used as surfactant counterions for specific purposes. For example, potassium or ammonium as the counterion instead of sodium gives higher solubility in organic solvents, which is sometimes an advantage. The counterion of cationic surfactants is usually a halide, acetate, or methyl sulfate. The counterion used with a cationic surfactant often plays an important role for the physicochemical properties of a formulation. Large polarizable ions, that is, singly charged ions with low charge density ("soft" or *chaotropic* ions) such as iodide or thiocyanate, interact much more strongly with interfaces than do small or multiply charged ions ("hard" or *kosmotropic* ions) such as chloride, acetate, and sulfate. This effect is related to the *Hofmeister series* in which electrolytes are ordered according to their ability to *salt in* or *salt out* a solute. The relation between the Hofmeister series and solubility of a solute in aqueous solution is further discussed on page 25.

The hydrophobic group is normally a hydrocarbon (alkyl or alkylaryl) but may also be a polydimethylsiloxane or a fluorocarbon. The two latter types of surfactants are particularly effective in nonaqueous systems.

For a few surfactants there is some ambiguity as to classification. For example, amine oxide surfactants are sometimes referred to as zwitterionics, sometimes as cationics, and sometimes as nonionics. Their charge is pH dependent and in the net neutral state they may either be seen as having distinct anionic and cationic charges or as dipolar nonionic compounds. Fatty amine ethoxylates, which contain both an amino nitrogen atom (cationic polar group) and a polyoxyethylene chain (nonionic polar group), may be included in either the cationics or the nonionics class. The nonionic character dominates when the

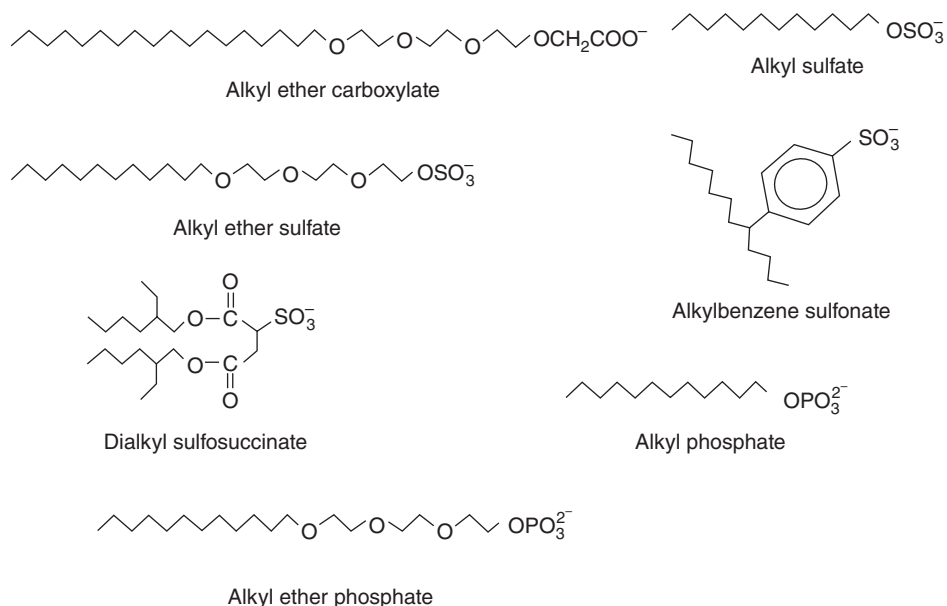
polyoxyethylene chain is very long, whereas for medium and short chains the physicochemical properties are mainly those of cationic surfactants. Surfactants containing both an anionic group, such as sulfate, phosphate, or carboxylate, and a polyoxyethylene chain are also common. These surfactants, known as ether sulfates and so on, usually contain short polyoxyethylene chains, typically two or three oxyethylene units, and are therefore categorized as anionics.

## Anionics

Carboxylate, sulfate, sulfonate, and phosphate are the polar groups found in anionic surfactants. Figure 1.6 shows structures of the more common surfactant types belonging to this class.

Anionics are used in a larger volume than any other class of surfactant. A rough estimate of the worldwide surfactant production is 20 million metric tons per year. Soap is the largest single surfactant followed by linear alkylbenzene sulfonate. Anionics in total represent roughly 70% of the surfactant consumption. Even if soap is excluded, as is often the case in the statistics, anionics is still the dominating class. One reason for their popularity is the ease and low cost of manufacture. Anionics are used in most detergent formulations and the best detergency is obtained by alkyl and alkylaryl chains in the  $C_{12}$ – $C_{18}$  range.

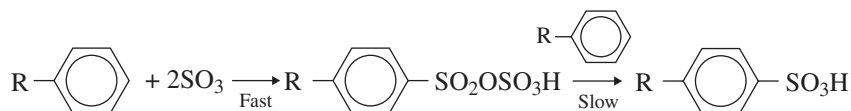
The counterions most commonly used are sodium, potassium, ammonium, calcium, and various protonated alkyl amines. Sodium and potassium impart water solubility, whereas calcium and magnesium promote oil solubility. Amine/alkanol amine salts give products with both oil and water solubility.



**Figure 1.6** Common anionic surfactants

As mentioned above, soap is still the largest single type of surfactant. It is produced by saponification of natural oils and fats. Soap is a generic name representing the alkali metal salt of a carboxylic acid derived from animal fats or vegetable oils. Soap bars are usually based on mixtures of fatty acids obtained from tallow, coconut, and palm oil. Under the right conditions soaps are excellent surfactants. Their sensitivity to hard water is a major drawback, however, and has constituted a strong driving force for the development of synthetic surfactants. The vast majority of soap produced goes into soap bars but soap also has specific niche applications. One important such application is as foam control agent in laundry detergents, where it suppresses the foam produced by the regular surfactants in the formulation, typically a combination of an alkylbenzene sulfonate and a fatty alcohol ethoxylate. A very specific use of the lithium salt of a fatty acid, that is, lithium 12-hydroxystearic acid, is as the major constituent of greases.

Alkylbenzene sulfonates is the largest class of synthetic surfactants. They are widely used in household detergents, as well as in a variety of industrial applications. They are made by sulfonation of alkylbenzenes. In large-scale synthesis, sulfur trioxide is the sulfonating agent of choice but other reagents, such as sulfuric acid, oleum ( $\text{H}_2\text{SO}_4 \cdot n\text{SO}_3$ ), chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ), or amidosulfonic acid (sulfamic acid,  $\text{H}_2\text{NSO}_3\text{H}$ ), may also be used and may be preferred for specific purposes. Industrial synthesis is usually carried out in a continuous process, using a falling film reactor. The first step of the synthesis results in the formation of the pyrosulfonic acid, which slowly and spontaneously reacts further to give the sulfonic acid:



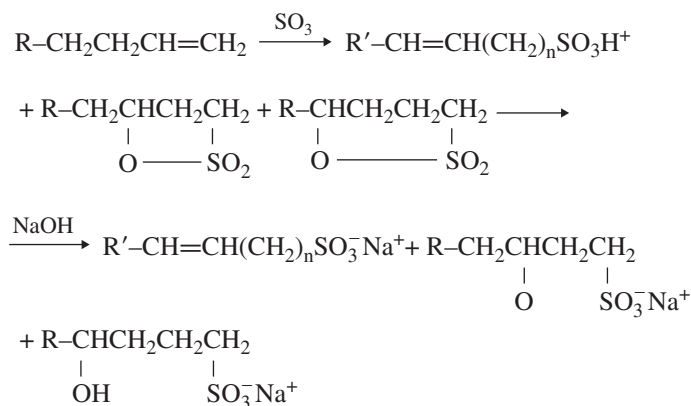
The sulfonic acid is subsequently neutralized, usually by caustic soda, to give the surface active alkylbenzene sulfonate salt. Due to the bulkiness of the alkyl substituent, the process gives almost exclusively *p*-sulfonation. R in the scheme above is typically an alkyl group of 12 carbon atoms. Originally, alkylbenzenes as surfactant intermediates were based on branched alkyls but these have now almost entirely been replaced by their linear counterparts, thus giving the name linear alkylbenzene sulfonate (LABS or LAS). Faster biodegradation has been the main driving force for the transition to chains without branching. Alkylbenzenes are made by alkylation of benzene with an *n*-alkene or with alkyl chloride using HF or  $\text{AlCl}_3$  as catalyst. The reaction yields a mixture of isomers with the phenyl group attached to one of the nonterminal positions of the alkyl chain.

Sulfonation with sulfur trioxide as reactant, together with the closely related sulfation process to make sulfated alcohols, see below, is one of the largest chemical operations worldwide. The total annual production of sulfonated/sulfated surfactants is around five million metric tons. The second largest process for making surfactants is ethoxylation, the key step in the production of nonionic surfactants.

Other sulfonate surfactants that have found use in detergent formulations are paraffin sulfonates and  $\alpha$ -olefin sulfonates, the latter often referred to as AOSs. Both are complex mixtures of compounds with varying physicochemical properties. Paraffin sulfonates, or secondary *n*-alkane sulfonates, are usually prepared by sulfoxidation of paraffin hydrocarbons with sulfur dioxide and oxygen under UV (ultraviolet) irradiation. In an

older process, which is still in use, paraffin sulfonates are made by sulfochlorination. Both processes are free radical reactions and, since secondary carbon atoms give much more stable radicals than primary carbon atoms, the sulfonate group will be introduced more or less randomly on all nonterminal carbon atoms along the alkane chain. A C<sub>14</sub>–C<sub>17</sub> hydrocarbon cut, sometimes called the *Euro cut* because paraffin sulfonates have by tradition mainly been produced in Europe, is normally used as hydrophobe raw material. Thus, the product obtained will be a very complex mixture of both isomers and homologues.

$\alpha$ -Olefin sulfonates are prepared by reacting linear  $\alpha$ -olefins with sulfur trioxide, typically yielding a mixture of alkene sulfonate (60–70%), 3- and 4-hydroxyalkane sulfonates (around 30%) and some disulfonate and other species. The two main  $\alpha$ -olefin fractions used as starting material are C<sub>12</sub>–C<sub>16</sub> and C<sub>16</sub>–C<sub>18</sub>. The ratio of alkene sulfonate to hydroxyalkane sulfonate is to some degree governed by the ratio of SO<sub>3</sub> to olefin: the higher the ratio, then the more alkene sulfonic acid will be formed. Formation of hydroxyalkane sulfonic acid proceeds via a cyclic sultone, which is subsequently cleaved by alkali. The sultone is toxic and it is important that its concentration in the end product is very low. The route of preparation can be written as follows:



An important alkyl sulfonate surfactant is sodium di(2-ethylhexyl)sulfosuccinate, often referred to by its American Cyanamid trade name Aerosol OT, or AOT. This surfactant, with its bulky hydrophobe structure (Figure 1.6), is particularly useful for preparation of water-in-oil microemulsions, as discussed in Chapter 17. Isethionate surfactants, with the general formula R–COOCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>–</sup>Na<sup>+</sup>, are fatty acid esters of the isethionic acid salt. They are among the mildest sulfonate surfactants and are used in cosmetics formulations.

Very crude sulfonate surfactants are obtained by sulfonation of lignin, petroleum fractions, alkylnaphthalenes or other low-cost hydrocarbon fractions. Such surfactants are used in a variety of industrial applications as dispersants, emulsifiers, demulsifiers, defoamers, wetting agents, and so on.

Sulfated alcohols and sulfated alcohol ethoxylates constitute another important group of anionics, widely used in detergent formulations. They are monoesters of sulfuric acid and the ester bond is a labile linkage, which splits with particular ease at low pH where the hydrolysis is autocatalytic. Both linear and branched alcohols, typically with 8–16 carbon atoms, are used as raw material. The linear 12-carbon alcohol leads to the dodecylmonoester of sulfuric acid and, after neutralization with caustic soda, to sodium dodecyl sulfate (SDS),

which is by far the most important surfactant within this category. The alcohol ethoxylates used as intermediates are usually fatty alcohols with two or three oxyethylene units. The sulfation process is similar to the sulfonation discussed above. Sulfur trioxide is the reagent used for large-scale production and, analogous to sulfonation, the reaction proceeds via an intermediate pyrosulfate:



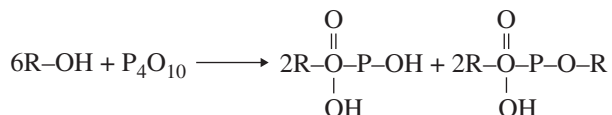
Synthesis of sulfate esters of ethoxylated alcohols proceeds similarly. In this reaction, 1,4-dioxane is usually formed in non-negligible amounts. Since dioxane is toxic, its removal by subsequent evaporation is essential. These surfactants are usually referred to as ether sulfates. Such surfactants are good at producing foams and have low toxicity to the skin and eye. They are popular in hand dishwashing and shampoo formulations.

Ethoxylated alcohols may also be transformed into carboxylates, that is, to give ether carboxylates. These have traditionally been made from sodium monochloroacetate using the Williamson ether synthesis:



The Williamson synthesis usually does not proceed quantitatively. A more recent synthetic procedure involves oxygen or peroxide oxidation of the alcohol ethoxylate in alkaline solution using palladium or platinum catalyst. This reaction gives conversion of the ethoxylate in very high yield, but may also lead to oxidative degradation of the polyoxyethylene chain. Ether carboxylates have found use in personal care products and are also used as a cosurfactant in various liquid detergent formulations. Like ether sulfates, ether carboxylates are very tolerant to high water hardness. Both surfactant types also exhibit good lime soap dispersing power, which is an important property for a surfactant in personal care formulations. Lime soap dispersing power is usually defined as the number of grams of surfactant required to disperse the lime soap formed from 100 g of sodium oleate in water with a hardness equivalent of 333 ppm of calcium carbonate ( $\text{CaCO}_3$ ).

Phosphate-containing anionic surfactants, both alkyl phosphates and alkyl ether phosphates, are made by treating the fatty alcohol or fatty alcohol ethoxylate with a phosphorylating agent, usually phosphorus pentoxide ( $\text{P}_4\text{O}_{10}$ ). The reaction yields a mixture of mono- and diesters of phosphoric acid, and the ratio between the esters is governed by the ratio of the reactants and the amount of water in the reaction mixture:



All commercial phosphate surfactants contain both mono- and diesters of phosphoric acid but the relative amounts vary from one producer to another. Since the physicochemical properties of the alkyl phosphate surfactants depend on the ratio of the esters, alkyl phosphates from different suppliers are less interchangeable than other surfactants. Phosphorus oxychloride ( $\text{POCl}_3$ ) can also be used as a phosphorylating agent to produce

**Box 1.1 Important facts about anionic surfactants**

- They constitute the largest class of surfactant
- They have limited compatibility with cationic surfactants (shorter surfactants have better compatibility)
- They are generally sensitive to hard water and the sensitivity decreases in the order carboxylate > phosphate > sulfate  $\cong$  sulfonate
- A short polyoxyethylene chain between the anionic group and the hydrophobic tail improves hard water tolerance
- A short polyoxypropylene chain between the anionic group and the hydrophobic tail improves solubility in organic solvents (but may reduce the rate of biodegradation)
- Alkyl sulfates are rapidly hydrolyzed at low pH in an autocatalytic process. The other types are hydrolytically stable unless extreme conditions are used

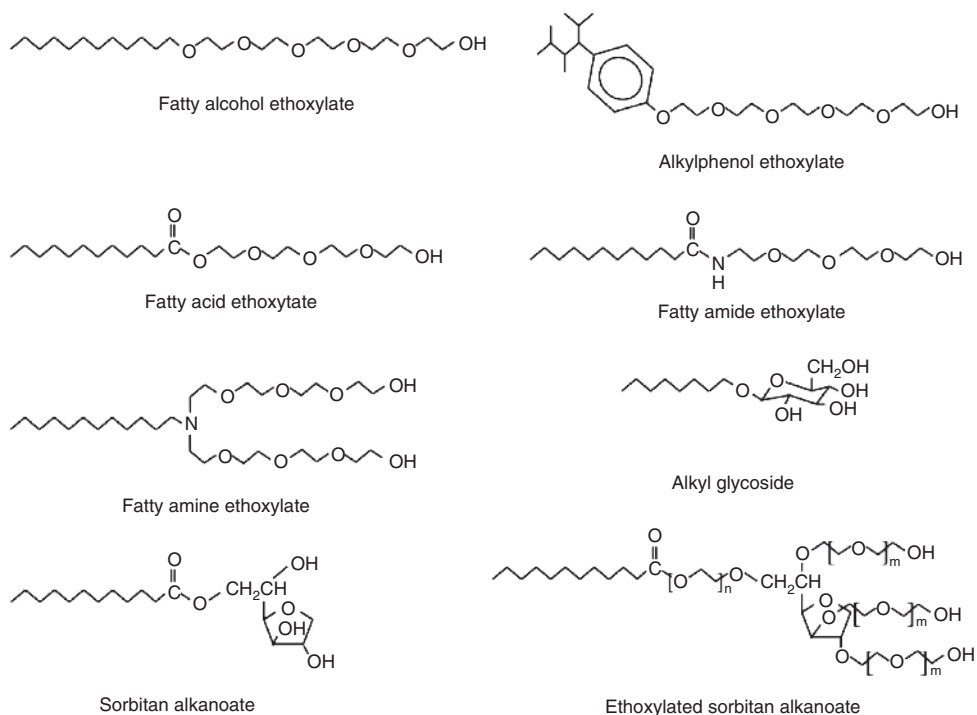
alkyl phosphate surfactants. Also with  $\text{POCl}_3$ , a mixture of mono- and diesters of phosphoric acid is obtained.

Phosphate surfactants are used in the metal working industry, where advantage is taken of their anticorrosive properties. They are also used as emulsifiers in plant protection formulations. Finally, some important facts about anionic surfactants are given in Box 1.1.

**Nonionics**

Nonionic surfactants have either a polyether or a polyhydroxyl unit as the polar group. Polyether-based surfactants dominate and the polyether consists of oxyethylene units made by polymerization of ethylene oxide (EO). Strictly speaking, the prefix “poly” is a misnomer. The typical number of oxyethylene units in the polar chain is 5–10, although some surfactants, for example, those used as dispersants, often have much longer oxyethylene chains. Ethoxylation is usually carried out under alkaline conditions. Any material containing an active hydrogen can be ethoxylated. The most commonly used starting materials are fatty alcohols, alkylphenols, fatty acids, and fatty amines. Esters, for example, triglyceride oils, may be ethoxylated in a process that in a one-pot reaction involves alkaline ester hydrolysis followed by ethoxylation of the acid and alcohol formed and subsequent partial condensation of the ethoxylated species. Castor oil ethoxylates, used for animal feed applications, constitute an important example of triglyceride-based surfactants.

Examples of polyhydroxyl-based (polyol-based) surfactants are sucrose esters, sorbitan esters, alkyl glucosides, and polyglycerol esters, the latter type actually being a combination of polyol and polyether surfactant. Polyol surfactants may also be ethoxylated. A common example is fatty acid esters of sorbitan (known under the trade name of Span) and the corresponding ethoxylated products (known as Tween). The five-membered ring structure of sorbitan is formed by dehydration of sorbitol during manufacture. The sorbitan ester surfactants are edible and, hence, useful for food and drug applications. Acetylenic glycols, surfactants containing a centrally located acetylenic bond and hydroxyl groups at the adjacent carbon atoms, constitute a special type of hydroxyl-based surfactant that have found use as antifoam agent, particularly in coatings applications.



**Figure 1.7** Common nonionic surfactants

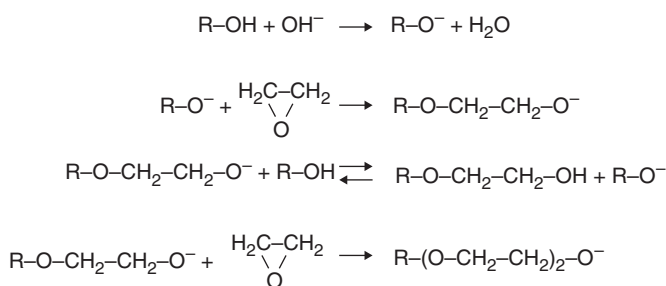
Figure 1.7 gives structures of the more common nonionic surfactants. As is discussed below, a commercial oxyethylene-based surfactant consists of a very broad spectrum of compounds, broader than for most other surfactant types. Fatty acid ethoxylates constitute particularly complex mixtures with high amounts of free poly(ethylene glycol) (PEG) and fatty acid as by-products. The single most important type of nonionic surfactant is fatty alcohol ethoxylates. They are used in liquid and powder detergents, as well as in a variety of industrial applications. They are frequently used to stabilize oil-in-water emulsions and their use as emulsifier is discussed in some detail in Chapter 24. Fatty alcohol ethoxylates can be regarded as hydrolytically stable in the pH range 3–11. They undergo a slow oxidation in air, however, and some oxidation products, such as aldehydes and hydroperoxides, are more irritating to the skin than the intact surfactant. Throughout this text fatty alcohol ethoxylates are referred to as  $C_m E_n$  with  $m$  being the number of carbon atoms in the alkyl chain and  $n$  being the number of oxyethylene units. Some important facts about nonionic surfactants are given in Box 1.2.

Polyoxyethylene-based surfactants can be tailor-made with high precision with regard to the average number of oxyethylene units added to a specific hydrophobe, for example, a fatty alcohol. However, the ethoxylation invariably gives a broad distribution of chain lengths. If all hydroxyl groups, that is, those of the starting alcohol and of the glycol ethers formed, had the same reactivity, a Poisson distribution of oligomers would be obtained. Since the starting alcohol is slightly less acidic than the glycol ethers, its deprotonation is disfavored, leading to a lower probability for reaction with ethylene oxide. The reaction scheme is given in Figure 1.8.



**Box 1.2 Important facts about nonionic surfactants**

- They are the second largest class of surfactant
- They are normally compatible with all other types of surfactants
- They are not sensitive to hard water
- Contrary to ionic surfactants, their physicochemical properties are not markedly affected by electrolytes
- The physicochemical properties of ethoxylates are very temperature dependent. Contrary to most organic compounds they become less water soluble – more hydrophobic – at higher temperatures. The reason for this unusual behavior is discussed in Chapter 7. Polyol-based nonionics exhibit the normal temperature dependence, that is, their solubility in water increases with temperature.

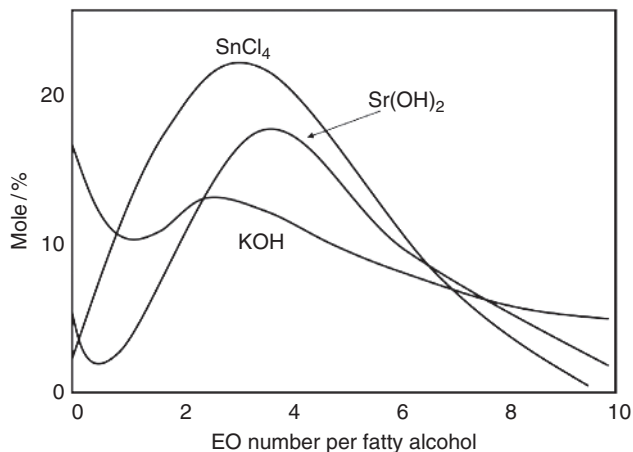


**Figure 1.8** Base catalyzed ethoxylation of a fatty alcohol, R-OH

Hence, a considerable amount of unethoxylated alcohol will remain in the reaction mixture, also with relatively long ethoxylates. This is sometimes a problem and considerable efforts have been made to obtain a narrower homologue distribution. The distribution can be affected by the choice of ethoxylation catalyst and it has been found that alkaline earth hydroxides, such as Ba(OH)<sub>2</sub> and Sr(OH)<sub>2</sub>, give a much narrower distribution than KOH, probably due to some coordination mechanism. Also Lewis acids, for example, SnCl<sub>4</sub> and BF<sub>3</sub>, give narrow distributions. Acid catalyzed ethoxylation suffers, however, from the drawback of 1,4-dioxane being formed in considerable quantities as by-product. Therefore, this process can only be used to prepare short ethoxylates. In Figure 1.9 the homologue distribution of a conventional alcohol ethoxylate, using KOH as catalyst, is compared with ethoxylates prepared using a Lewis acid and an alkaline earth hydroxide as catalyst.

So-called *peaked ethoxylates* have a growing share of the market. Typical advantages of ethoxylates with peaked distribution are that:

1. The low content of free alcohol reduces smell.
2. The low content of free alcohol reduces “pluming” during spray drying.
3. The low content of low oxyethylene homologues increases solubility.
4. The low content of high oxyethylene homologues reduces viscosity.
5. In alkyl ether sulfates, the low content of alkyl sulfate reduces skin irritation.



**Figure 1.9** Typical homologue distribution of a fatty alcohol reacted with four moles of EO using different ethoxylation catalysts

Ethoxylated alkylphenols have a narrower homologue distribution than the alcohol ethoxylates. The phenolic hydroxyl group is a considerably stronger acid than the alcoholic hydroxyl of the first ethoxylate formed. This means that the phenolic hydroxyl will be preferentially deprotonated, which, in turn, means that there is virtually no unreacted alkylphenol left even in alkylphenol ethoxylates with only few oxyethylene units.

As mentioned in Box 1.2, nonionic surfactants containing polyoxyethylene chains exhibit reverse solubility versus temperature behavior in water. On raising the temperature two phases eventually appear. The temperature at which this occurs is referred to as the cloud point, alluding to the fact that the solution becomes turbid. The cloud point depends on both the hydrophobe chain length and the number of oxyethylene units; it can be determined experimentally with high accuracy. In the manufacture of polyoxyethylene-based surfactants, cloud point determination is used as a way to monitor the degree of ethoxylation. The onset of turbidity varies somewhat with surfactant concentration and in the official test method the cloud point is determined by heating a 1% aqueous solution to above clouding and then monitoring the transition from turbid to clear solution on slow cooling of the sample. For surfactants with long polyoxyethylene chains, the cloud point may exceed 100°C. For such surfactants determinations are often made in electrolyte solutions, since most salts lower the cloud point. Clouding of nonionic surfactants is discussed in detail in Chapter 7.

Ethoxylated triglycerides, for example, castor oil ethoxylates, have an established position on the market and are often regarded as *semi-natural surfactants*. A niche type of product is the fatty acid methyl ester ethoxylates, made from the fatty acid methyl ester by ethoxylation, usually using hydrotalcite, a magnesium–aluminum hydroxycarbonate, as catalyst. The methyl ester ethoxylates have the advantage over alcohol ethoxylates of being much more soluble in aqueous solution. Surfactants that combine high water solubility with proper surface activity are needed in various types of surfactant concentrates.



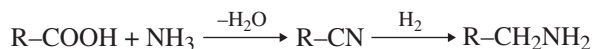
Alcohol ethoxylates with the terminal hydroxyl group replaced by a methyl or ethyl ether group constitute another category of niche products. Such *end-capped nonionics* are made by O-alkylation of the ethoxylate with alkyl chloride or dialkyl sulfate or by hydrogenation of the corresponding acetal. Compared with normal alcohol ethoxylates, the end-capped products are more stable against strong alkali and against oxidation. They are also low foaming, which is important in many applications.

### Cationics

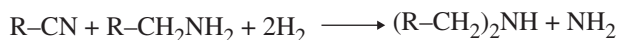
The vast majority of cationic surfactants are based on the nitrogen atom carrying the charge. Both amine and quaternary ammonium-based products are common. The amines only function as a surfactant in the protonated state; therefore, they cannot be used at high pH. Quaternary ammonium compounds, *quats*, on the other hand, are not pH sensitive. Nonquaternary cationics are also much more sensitive to polyvalent anions. As discussed previously, ethoxylated amines (Figure 1.7) possess properties characteristic of both cationics and nonionics. The longer the polyoxyethylene chain, then the more nonionic is the character of this surfactant type.

Figure 1.10 shows the structures of typical cationic surfactants. The diester quat represents an environmentally friendly type, which during the 1980s and 1990s almost completely replaced dialkyl quats as textile softening agents. The diester quats most commonly used for fabric softening generally show very limited water solubility and form lamellar phases and liposomes at low concentration. The low water solubility in combination with the hydrolytic instability makes formulation of softener products a demanding task. Diester quats used as rinse cycle softeners are usually formulated together with additives such as a hydrophilic alcohol ethoxylate and/or a water miscible solvent, such as isopropanol.

The main synthesis procedure for nonester quaternary ammonium surfactants is the nitrile route. A fatty acid is reacted with ammonia at high temperature to yield the corresponding nitrile, a reaction that proceeds via an intermediate amide. The nitrile is subsequently hydrogenated to primary amine using a cobalt or nickel catalyst:



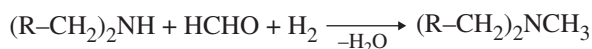
Secondary amines can be produced either directly from the nitrile or in a two-stage reaction from the primary amine. In the one-stage route, which is believed to proceed via an intermediate imine, ammonia is continuously removed from the reaction in order to promote secondary amine formation:

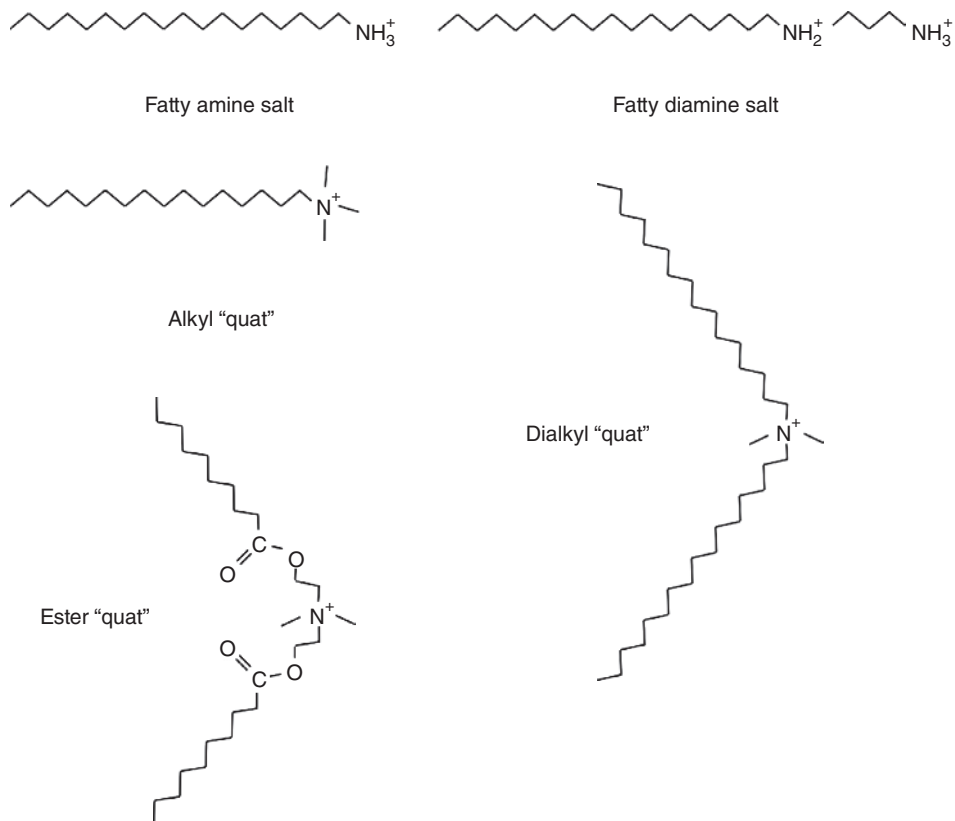


Primary amines can be converted to long-chain 1,3-diamines by cyanoethylation followed by hydrogenation:



Primary or secondary long-chain alkyl amines can be methylated to tertiary amines, for example, by reaction with formaldehyde under reducing conditions:





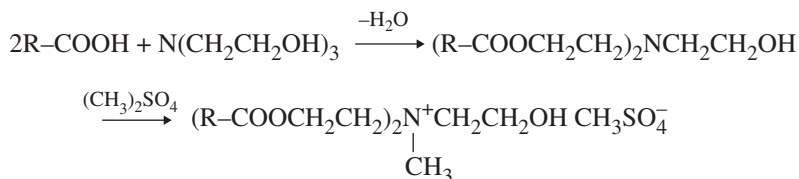
**Figure 1.10** Common cationic surfactants

Ethylene oxide can also be used as an alkylating agent to convert primary or secondary amines to tertiary amines with the general structures  $\text{R}-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$  and  $(\text{R}-\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}$ , respectively.

Quaternary ammonium compounds are usually prepared from the tertiary amine by reaction with a suitable alkylating agent, such as methyl chloride, methyl bromide, or dimethyl sulfate, the choice of reagent determining the surfactant counterion:



Ester-containing quaternary ammonium surfactants, *ester quats*, are prepared by esterifying a fatty acid (or a fatty acid derivative) with an amino alcohol followed by N-alkylation as above. The process is illustrated here for triethanolamine as the amino alcohol and dimethyl sulfate as methylating agent:



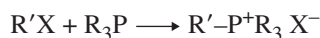
**Table 1.3** Applications of cationic surfactants related to their adsorption at surfaces

Surface	Application
Steel	Anticorrosion agent
Mineral ores	Flotation collector
Stones	Road surfacing with bitumen emulsion
Inorganic pigments	Dispersant
Plastics	Antistatic agent
Fibers	Antistatic agent, fabric softener
Hair	Conditioner
Fertilizers	Anticaking agent
Bacterial cell walls	Bactericide

**Box 1.3 Important facts about cationic surfactants**

- They are the third largest class of surfactant
- They have limited compatibility with anionics (shorter surfactants have better compatibility)
- Hydrolytically stable cationics show higher aquatic toxicity than most other classes of surfactants
- They adsorb strongly to most surfaces and their main uses are related to this interaction

Nitrogen-based compounds constitute the vast majority of cationic surfactants. However, phosphonium, sulfonium, and sulfoxonium surfactants also exist. The first two are made by treatment of an alkyl chloride with trialkyl phosphine or dialkyl sulfide, respectively, as is shown here for phosphonium surfactant synthesis:



Sulfoxonium surfactants are prepared by hydrogen peroxide oxidation of the sulfonium salt. The industrial use of non-nitrogen cationic surfactants is small, since only rarely do they give performance advantages over their less expensive nitrogen counterparts. Phosphonium surfactants carrying one long-chain alkyl and three methyl groups have found use as biocides.

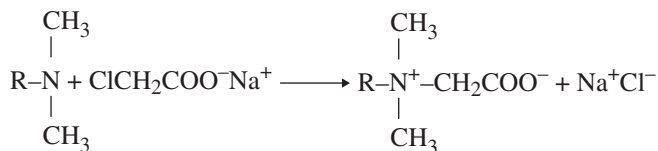
The majority of surfaces, metals, minerals, plastics, fibers, cell membranes, and so on, are negatively charged. The prime uses of cationics relate to their tendency to adsorb at these surfaces. In doing so, they change the character of the surface. Some examples are given in Table 1.3, while some important facts about cationic surfactants are given in Box 1.3.

**Zwitterionics**

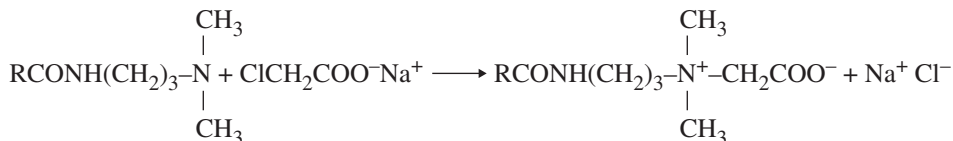
Zwitterionic surfactants contain two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to as *amphoterics*, but as was pointed out on page 10, the terms are not identical.

The change in charge with pH of the truly amphoteric surfactants naturally affects properties such as foaming, wetting, detergency, and so on. These will, therefore, depend strongly on the solution pH. At the isoelectric point the physicochemical behavior often resembles that of nonionic surfactants. Below and above the isoelectric point there is a gradual shift towards the cationic and anionic character, respectively. Surfactants based on sulfate or sulfonate (and a quaternized nitrogen as positive charge) remain zwitterionic down to very low pH values due to the very low  $pK_a$  values of the monoalkyl ester of sulfuric acid and of the alkyl or alkylaryl sulfonic acid, respectively.

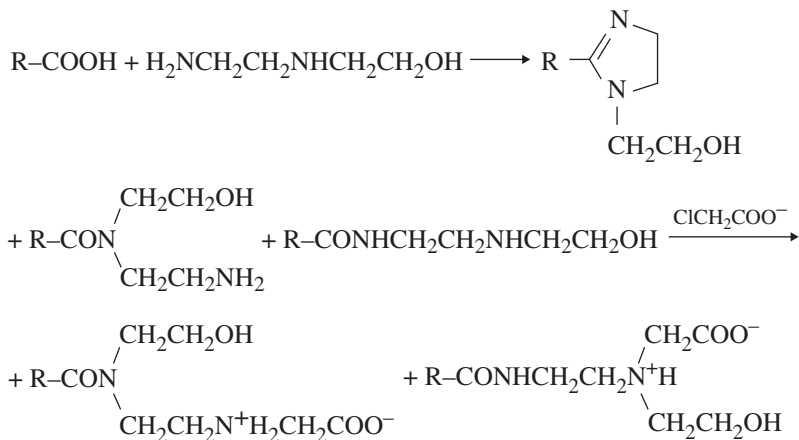
Common types of zwitterionic surfactants are N-alkyl derivatives of simple amino acids, such as glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), betaine ( $(\text{CH}_3)_2\text{NCH}_2\text{COOH}$ ) and amino propionic acid ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$ ). They are usually not prepared from the amino acid, however, but by reacting a long-chain amine with sodium chloroacetate or a derivative of acrylic acid, giving structures with one and two carbons, respectively, between the nitrogen and the carboxylate group. As an example, a typical betaine surfactant is prepared by reacting an alkyl dimethyl amine with sodium monochloroacetate:

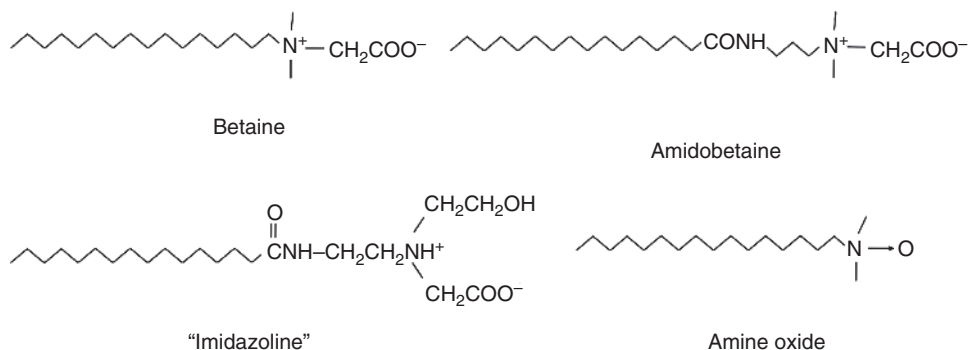


Amidobetaines are synthesized analogously from an amidoamine:



Another common type of zwitterionic surfactant, usually referred to as an imidazoline, is synthesized by reaction of a fatty acid with aminoethylethanolamine followed by treatment with chloroacetate. The nomenclature for this surfactant type is a bit confused; it was believed that the products contained an imidazoline ring, but later investigations have shown that the five-membered ring is cleaved during the second synthesis step. A typical reaction sequence is:





**Figure 1.11** Common zwitterionic surfactants. The arrow from the nitrogen to the oxygen atom in the formula of the amine oxide indicates that electrons are pulled away from the nitrogen atom. Sometimes the formula is written with a normal bond between the two heteroatoms, in which case there is a positive sign on the nitrogen and a negative sign on the oxygen

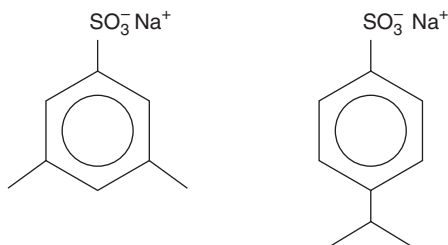
#### Box 1.4 Important facts about zwitterionic surfactants

- They are the smallest class of surfactant (partly due to high price)
- They are normally compatible with all other types of surfactants
- They are not sensitive to hard water
- They are generally stable in acids and bases. The betaines, in particular, retain their surface activity at high pH, which is unusual
- Most types show very low eye and skin irritation. They are, therefore, well suited for use in shampoos and other personal care products

Zwitterionics as a group are characterized by having excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other cosmetic products. Since they possess no net charge, zwitterionics, similar to nonionics, function well in high electrolyte formulations. A traditional use of the products has been in alkaline cleaners. Figure 1.11 shows examples of typical zwitterionics and Box 1.4 summarizes some general information about the surfactant class. As mentioned previously, amine oxide surfactants, or more correctly N-oxides of tertiary amines, are sometimes categorized as zwitterionics, sometimes as nonionics, and sometimes as cationics. They basically behave as nonelectrolytes but at low pH or in the presence of an anionic surfactant an amine oxide surfactant will pick up a proton and behave as a cationic surfactant. A 1:1 salt will form between the anionic surfactant and the protonated amine oxide and this salt is very surface active. Amine oxides are prepared by hydrogen peroxide oxidation of the corresponding tertiary amine. They are good foam boosters and frequently used in cleaning formulations.

## Hydrotropes and Solubilization

Hydrotropes are substances that increase the solubility of sparingly soluble organic molecules in water. The term, which was coined almost 100 years ago, is widely used in connection with liquid formulations but the meaning of the term differs depending on the application. In cleaning



**Figure 1.12** Sodium xylene sulfonate (left) and sodium cumene sulfonate (right)

formulations, which volume-wise may be the most important, the term hydrotrope has a very broad meaning, ranging from cosolvents, such as glycol ethers, to hydrophilic surfactants, such as medium-chain alkyl phosphates or short alkyl glucosides. In a stricter sense a hydrotrope is a compound that shows some amphiphilicity, yet does not exhibit the distinct break on the surface tension versus concentration plot that is indicative of a cooperative self-assembly process in solution. Thus, by the definition of a surfactant mentioned at the beginning of this chapter, a true hydrotrope is not a surfactant. The most common traditional hydrotropes are short-chain alkylbenzene sulfonates. Two representative examples of such compounds are shown in Figure 1.12. Both sodium cumene sulfonate and sodium xylene sulfonate decrease the surface tension to approximately 40 mN/m but they do not self-assemble into micelles. When the alkyl chain of a sodium alkylbenzene sulfonate has four or more carbon atoms a distinct self-association at a certain concentration can be detected by techniques such as light scattering or NMR diffusometry. Such compounds should be regarded as surfactants.

Alkyl-naphthalene sulfonates are alternatives to alkylbenzene sulfonates and give approximately the same effect. Aromatic carboxylic acids are also used as hydrotropes. Sodium salicylate is a typical example of such a compound.

Transfer of a poorly water soluble substance into an aqueous formulation is a very important issue in formulation science and the use of a hydrotrope is not the only way to do this. There are three main approaches:

1. Formulation of a dispersed system, such as an oil-in-water emulsion or a solid suspension. Emulsions and suspensions are dealt with in Chapters 21 and 24.
2. Formulation of a microemulsion, that is, a macroscopic one-phase system that on the microscopic level exhibits distinct hydrophilic and hydrophobic domains. Microemulsions are presented in Chapter 17.
3. Formulation of a system that is homogeneous on both the macroscopic and the microscopic level. Use of a water-miscible organic solvent to improve the solubility of a lipophilic compound is the prime example.

Use of a hydrotrope may relate to either approach 2 or approach 3 depending on in how broad a sense the term is used. A hydrophilic surfactant, often referred to as a cosurfactant, is commonly used for formulating a microemulsion, that is, a system of type 2 above. The cosurfactant can be seen as a hydrotrope in that formulation. Use of a cosolvent such as a glycol ether falls within category 3 and the glycol ether may also be regarded as a hydrotrope. A classical hydrotrope such as xylene or cumene sulfonate is a borderline case and may be classified into either type 2 or type 3 of the formulation approaches listed above. The term *coupling agent* is sometimes used synonymously with hydrotrope.



Apart from the ways to improve the aqueous solubility mentioned above, that is, use of a cosolvent, a classical hydrotrope or a hydrophilic surfactant, one must be aware of yet another parameter of importance: the electrolyte. An electrolyte can be either *salting in* or *salting out*. Salting in electrolytes help solubilize poorly soluble organic substances in water and the effect can be substantial. The order in which salts appear on this scale is given by the Hofmeister series, named after a famous paper from the late 1800s in which ions were classified in order of their ability to salt out proteins. The Hofmeister series for anions is:



For cations it is:

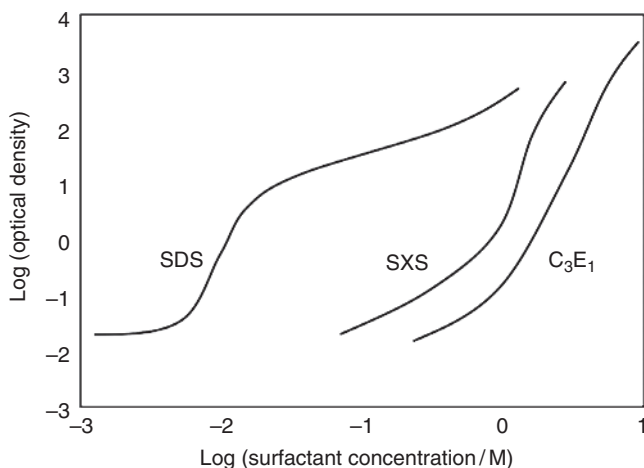


The further to the right in the two series, the more beneficial is the ion for solubilization of an organic compound. A common example of the use of the Hofmeister series is in biochemistry, where proteins are made to precipitate from an aqueous solution by addition of ammonium sulfate, the salt of the two ions furthest to the left in the two series. Salts of ions at the right end of the series are good at increasing the solubility of a protein. However, such salts, for example, guanidinium thiocyanate, are so efficient structure breakers that they may disrupt the intramolecular noncovalent interactions, which means that the protein loses its secondary structure and becomes randomly coiled. (Urea, a small, uncharged molecule, behaves in the same way as guanidinium salts; also, nonionic molecules can act as salting in reagents.)

Cosolvents such as glycol ethers are needed in large amounts in order to give proper effect. Also hydrotropes of the type shown in Figure 1.12 have to be added in relatively large amounts in order to solubilize a hydrophobic organic substance. Typical hydrotrope concentrations are 1 M and the cosolvents are used in even higher concentrations. Surfactants, on the other hand, are effective as solubilizers at concentrations several orders of magnitude lower. Figure 1.13 shows solubilization of a hydrophobic organic dye using either a surfactant, a classical hydrotrope or a glycol ether as additive. The order of efficacy is very clear: surfactant > hydrotrope > cosolvent.

The mechanism of solubilization is clearly different for a cosolvent and for a surfactant. The cosolvent changes the solvency by affecting the character of the solvent. The change may be quantified by the use of solubility parameters. Replacing water by a water–glycol ether mixture leads to a reduction of the hydrogen bonding and the polar contributions of the solubility parameter, which, in turn, means that the dispersion contribution gains in importance. This is favorable for dissolution of most hydrophobic organic compounds.

Hydrotropes destroy the ordered packing of self-aggregated surfactants just as urea and chaotropic ions do with proteins, as discussed above. Thus, cumene sulfonate and other traditional hydrotropes are very efficient in reducing the extension of liquid crystalline phases that often appear in concentrated surfactant solutions (Chapter 6). The liquid crystalline phases are highly viscous and difficult to handle, so addition of a hydrotrope is common in many cleaning formulations. Another important use of hydrotropes in surfactant-based formulations is to raise the cloud point of long-chain fatty alcohol ethoxylates. These hydrophobic nonionic surfactants are very effective in removing oily soil but



**Figure 1.13** Solubilization of an organic dye (Disperse Red 13) in aqueous solution as a function of amount of added SDS (left), sodium xylene sulfonate (middle) and ethylene glycol monopropyl ether (right). The solubilization is quantified by the optical density given on the y-axis. (Adapted with permission from Bauduin, P., Renoncourt, A., Kopf, A., et al. (2005) Unified concept of solubilization in water by hydrotropes and cosolvents. *Langmuir*, 21, 6769–6775. Copyright © 2005, American Chemical Society.)

**Table 1.4** Cloud point (°C) of solutions of 1% alcohol ethoxylate with addition of 1% hydrotrope

Fatty alcohol ethoxylate	No hydrotrope	Butyl glucoside	Octyl glucoside	Decyl glucoside	Undecyl glucoside	Sodium toluene sulfonate
$C_{11}E_5$	27	28	59	52	35	36
$C_{13}E_6$	<0	9	48	37	9	9

(From Matero, A., Mattsson, Å. and Svensson, M. (1998) APGs as hydrotropes. *Journal of Surfactants and Detergents*, 1, 485–489.)

the best surfactants often have very low cloud points. The role of the hydrotrope in such formulations is to bring the cloud point to above working temperature. Cumene sulfonate and similar compounds are efficient in doing so but hydrophilic surfactants, such as short-chain alkyl phosphates and hydrophilic alkyl glucosides, are often even more efficient. The hydrophilic surfactant in such a formulation is usually termed a *cosurfactant* but it clearly acts as a hydrotrope. As is illustrated in Table 1.4, the cosurfactant needs to be fine-tuned for the specific application.

## Gemini Surfactants have Special Features

A gemini surfactant may be viewed as a surfactant dimer, that is, consisting of two amphiphilic molecules connected by a spacer. The general structure is shown in Figure 1.2. Gemini surfactants are also referred to as twin surfactants, dimeric surfactants, or bis-surfactants.

The spacer chain, which can be hydrophilic or hydrophobic, rigid or flexible, should bind the two moieties together at, or in close proximity to, the head groups. Connecting two surfactant moieties towards the end of their hydrophobic tails results in a so-called *bola-form* surfactant and the physicochemical properties of such species are very different from those of gemini surfactants. Most gemini surfactants are composed of two identical halves, but unsymmetrical geminis have also been synthesized, either having different hydrophobic tail lengths or different types of polar groups (*heterogemini surfactants*), or both. Higher oligomers of single surfactants, that is, tris-surfactants, tetra-surfactants, and so on have also been synthesized. These are difficult to prepare, however, and may not be so practically interesting.

Gemini surfactants have not yet reached the market in large-scale quantities. They are, however, attracting considerable attention, both in industry and in academia. Some gemini surfactants, in particular symmetrical cationic ones, are made from readily available raw materials by a straightforward synthesis, as is discussed here.

Figure 1.14 shows examples of gemini surfactants. Compounds I–III are cationics differing in the type of spacer unit connecting the two ionic moieties. The spacer of compound I is hydrophobic and flexible, that of compound II is hydrophilic and flexible, and that of compound III is hydrophobic and rigid. Compound IV is an ester-containing cationic gemini surfactant and compound V is an anionic one. Finally, compounds VI and VII are examples of heterogemini surfactants. For the regular cationic gemini surfactants, such as compound I, which by far are the most studied, the nomenclature used in the literature is *m-n-m*, where *m* is the number of carbons in the hydrophobic tails and *n* the number of carbons in the spacer unit.

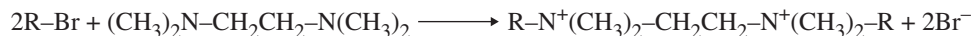
## Synthesis

Regular cationic geminis, such as compounds I–III of Figure 1.14, are conveniently prepared by reacting an alkyldimethylamine with an  $\alpha,\omega$ -dihalo compound. Dibromo reagents are very reactive and are usually employed in laboratory synthesis but the corresponding dichloro compounds may be preferred in large-scale preparation:

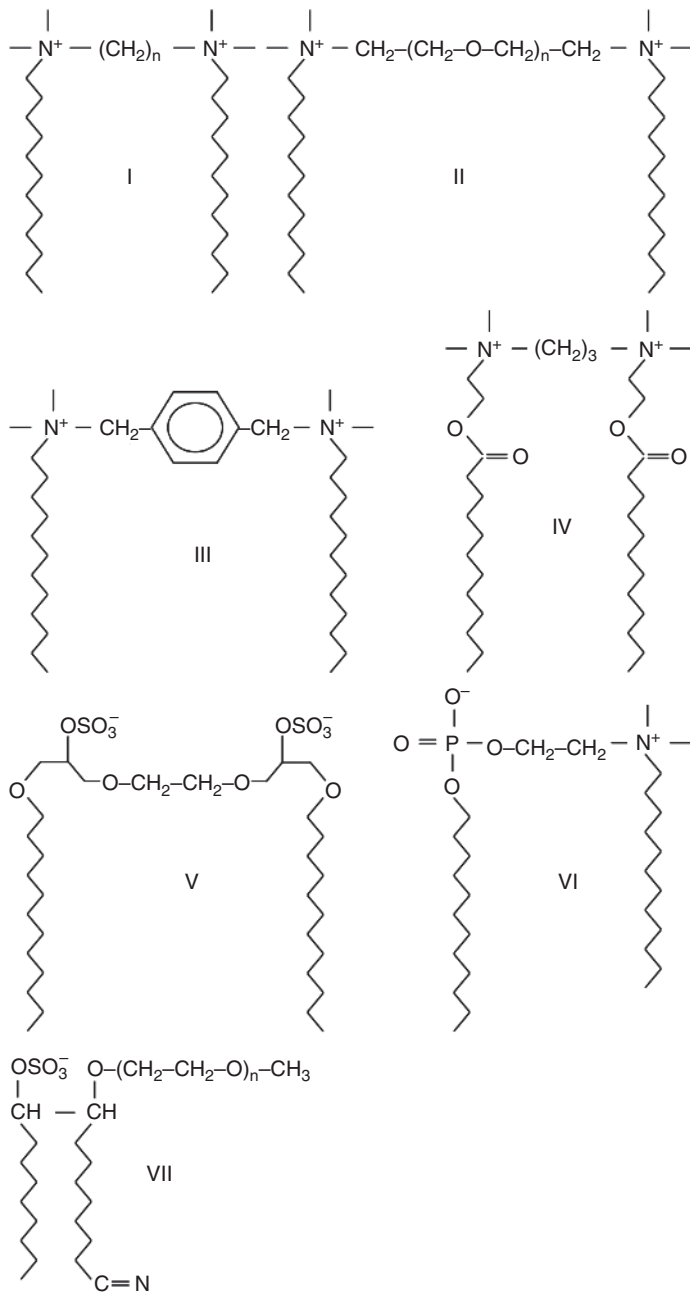


where R is an alkyl of normal surfactant chain length such as  $\text{C}_{12}\text{H}_{25}$ . X can be alkylene to give a hydrophobic, flexible spacer,  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$  or  $\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2$  to give a hydrophilic flexible spacer, or  $\text{CH}_2\text{-}\Phi\text{-CH}_2$  to give a hydrophobic, rigid spacer ( $\Phi$  denotes a phenyl ring, i.e., in the simplest case  $\text{C}_6\text{H}_4$ ).

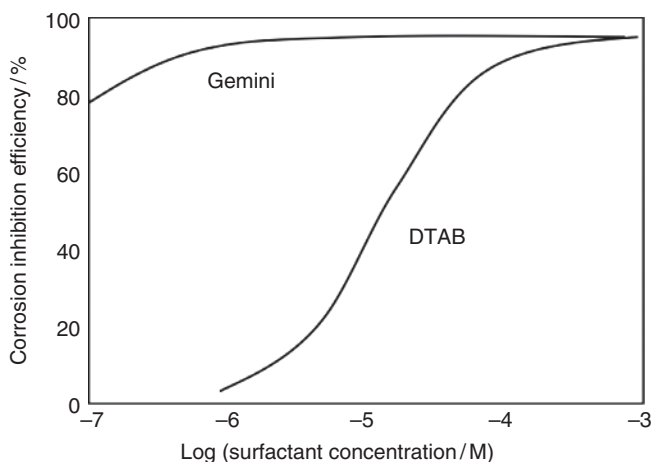
For the specific (but important) case when X equals  $\text{CH}_2\text{CH}_2$  in the formula above the dihalo compound is not reactive enough. The preferred synthesis route is then:



Ester-containing gemini surfactants, such as compound IV of Figure 1.14, are of interest because the ester bond is easily hydrolyzed in the sewage plant. Their preparation route is analogous to that of the stable gemini surfactants with the alkyldimethyl reactant ( $\text{R-N}(\text{CH}_3)_2$  in the formula above) replaced by the *N,N*-dimethylaminoethyl ester of a fatty acid ( $\text{R-COO-CH}_2\text{CH}_2\text{-N}(\text{CH}_3)_2$ ).



**Figure 1.14** Structures of gemini surfactants. Compounds I–IV are cationic gemini surfactants, compound V is an anionic gemini surfactant, and compounds VI and VII are examples of heterogemini surfactants



**Figure 1.15** Comparison between a regular cationic surfactant, DTAB, and a gemini surfactant with C12 hydrophobic tails and a tetramethylene spacer (12-4-12) with respect to efficiency to protect mild steel being exposed to 1 M HCl solution for 4 h. (Adapted with permission from Mahdavian, M., Tehrani-Bagha, A.R. and Holmberg, K. (2011) Comparison of a cationic gemini surfactant and the corresponding monomeric surfactant for corrosion protection of mild steel in hydrochloric acid. *Journal of Surfactants and Detergents*, **14**, 605–613. Copyright © 2011, Springer.)

### Gemini Surfactants are More Efficient

As mentioned on page 5, gemini surfactants self-assemble at very low concentrations compared to the corresponding monomeric surfactants. The low CMC values of gemini surfactants are an indication that they can be used in lower concentration than normal surfactants of the same hydrophobic tail length. This is indeed the case and has been demonstrated for a variety of applications. A striking example, illustrated in Figure 1.15, is in corrosion protection. As the curves show, both a regular cationic surfactant and the gemini surfactant can provide very effective corrosion protection but the gemini surfactant can be used in several orders of magnitude lower amount.

## Cleavable Surfactants are Attractive from an Environmental Point of View

### Background

The term *cleavable surfactant* generally refers to a surfactant with a labile bond intentionally included in the molecular structure. Traditionally, the presence of an inherently labile bond in a surfactant was considered a substantial disadvantage but, much due to the increased concern for the environment, the negative attitude towards surfactants that contain a labile bond has changed. Among the surfactant workhorses—anionics such as alkylbenzene sulfonates and alkyl sulfates, nonionics such as fatty alcohol ethoxylates and alkylphenol ethoxylates, and cationics such as alkyl quats and dialkyl quats—only alkyl

sulfates are not chemically stable under normal conditions. Alkyl sulfates are monoesters of sulfuric acid, which are readily hydrolyzed under acidic conditions to release sulfuric acid. The produced acid will, in turn, accelerate breakdown of the surfactant. This autocatalytic degradation of a surfactant such as SDS is well known among those who formulate surfactant-containing products and has often been regarded as a substantial disadvantage with this specific surfactant. The general attitude used to be that weak bonds in a surfactant may cause handling and storage problems and should, therefore, be avoided.

For a couple of decades, environmental concern has been one of the main driving forces for the development of new surfactants and their rate of biodegradation is a major issue. One of the main approaches taken to produce readily biodegradable surfactants is to build into the structure a bond with limited stability. For practical reasons the weak bond is usually the bridging unit between the polar head group and the hydrophobic tail of the surfactant, which means that the degradation immediately leads to destruction of the surface activity of the molecule, an event usually referred to as the *primary degradation* of the surfactant. Biodegradation then proceeds along various routes depending on the type of primary degradation product. The ultimate decomposition of the surfactant, often expressed as amount of carbon dioxide evolved during four weeks exposure to appropriate microorganisms, counted as a percentage of the amount of carbon dioxide that could theoretically be produced, is the most important measure of biodegradation (page 53).

There are many possible types of cleavable bonds and a wide range of cleavable surfactants can be designed with respect to stability and cleavage properties. The majority of cleavable surfactants contain a hydrolyzable bond, for which the breakdown can be induced by a change in pH. In the environment bonds susceptible to hydrolysis are often degraded by enzymatic catalysis but only few published investigations deal with the breakdown of cleavable surfactants *in vitro*. Cleavable surfactants with the bond breakage induced by other triggers, such as UV light, ozone, or an increase in temperature, have also been developed.

Environmental concern is the main driving force behind the concept of cleavable surfactants but there are also other incentives. The use of a cleavable surfactant can be a way to avoid complications, such as foaming or formation of unwanted, stable emulsions, that may occur in industrial processes involving surfactant-based formulations. If the weak bond is present between the polar and the apolar part of the molecule, cleavage will lead to one water-soluble and one water-insoluble product. Both moieties can usually be removed by standard work-up procedures. This approach has been of particular interest for surfactants used in preparative organic chemistry and in various biochemical applications. A related application is the use of a cleavable cationic surfactant as a transient biocide.

Another use of surfactants with limited stability is to have the cleavage product impart a new function. For example, a surfactant used in personal care formulations may decompose on application to form products beneficial to the skin. A surfactant used for cleaning of rain clothes, tents, and so on may decompose during the washing process and the hydrophobic moiety released, for example a fatty alcohol, will deposit on the textile and act as a hydrophobizing agent. Surfactants that after cleavage impart a new function are sometimes referred to as *functional surfactants*.

Finally, surfactants that in a controlled way break down into nonsurfactant products may find use in specialized applications, for example in the biomedical field. For instance, cleavable surfactants that form vesicles or microemulsions can be of interest for drug delivery, provided the metabolites are nontoxic.

## Alkali-Labile Surfactants

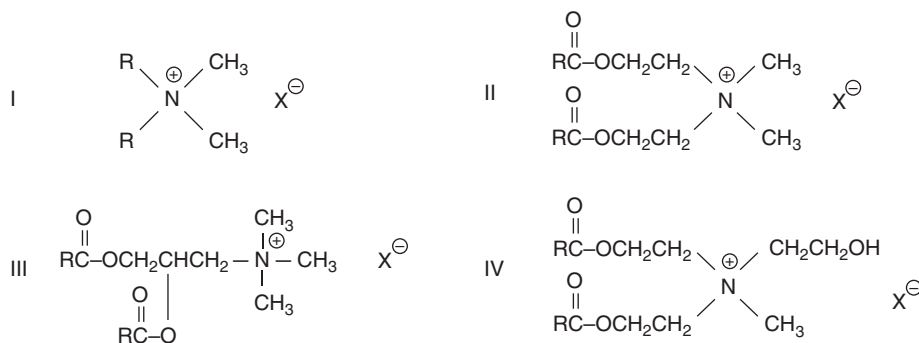
The ester bond is the typical linkage to use in the design of alkali-labile surfactants. The concept is by no means new. PEG esters of fatty acids, also referred to as fatty acid ethoxylates, have been commercially available for a long time. This surfactant class has an ester group between the polar head group and the hydrophobic tail. Fatty acid esters of sugars constitute another established type of ester surfactants. Sorbitan esters of fatty acids, known under their trade name Span, are one well-known example and sucrose esters are another. Other established ester-containing surfactants are dialkylsulfosuccinates,  $\alpha$ -sulfo fatty acid methyl esters, methyl ester ethoxylates, ethoxylated triglycerides, and sulfated triglycerides.

## Normal Ester Quats

Cationic surfactants have traditionally been stable molecules. However, when environmental concern became an important issue it soon became clear that the traditional “quats,” with a large use as fabric softeners, exhibited a slow rate of biodegradation and considerable aquatic toxicity. The toxicity is not unexpected considering that cationic surfactants in general are potent microbicides and frequently used as such. The response from the industry was to change the surfactant used in fabric softener formulations from normal stable “quats” to “ester quats.” The structures of both can be found in Figure 1.10.

What is meant by ester quats are surfactants based on esters between one or more fatty acids and a quaternized amino alcohol. Figure 1.16 shows examples of three different ester quats, all containing two long-chain and two short substituents on the nitrogen atom. The figure also shows the “parent,” noncleavable quat. As can be seen, the ester-containing surfactants contain two carbon atoms between the ester bond and the nitrogen that carries the positive charge. Cleavage of the ester bonds of surfactants II–IV yields a fatty acid soap in addition to a highly water-soluble quaternary ammonium diol or triol. These degradation products exhibit low fish toxicity and are degraded further by established metabolic pathways. The overall ecological characteristics of ester quats are much superior to those of traditional quats as represented by compound I of Figure 1.16.

The switch from stable dialkyl quats to dialkylester quats in softener formulations, which mainly took place during the 1990s, may represent the most dramatic change of product



**Figure 1.16** Structures of one conventional quaternary ammonium surfactant (I) and three ester quats (II–IV). *R* is a long-chain alkyl and *X* is Cl, Br, or  $\text{CH}_3\text{SO}_4^-$

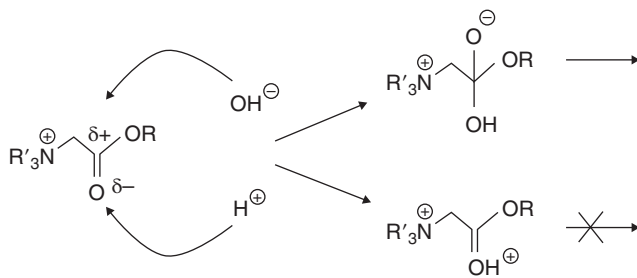
type in the history of surfactants and was entirely environment-driven. Ester quats have also fully or partially replaced traditional quats in other applications of cationic surfactants, such as hair care products and various industrial formulations.

The cationic charge close to the ester bond renders normal ester quats unusually stable to acid and labile to alkali. The hydrolysis rate is at minimum at pH 3–4 and accelerates strongly above pH 5–6. Formulations containing ester quats must, therefore, be maintained at low pH. The pH dependency of the hydrolysis rate is even more pronounced for betaine esters, for which the mechanism of hydrolysis is discussed in more detail in the following section.

### Betaine Esters

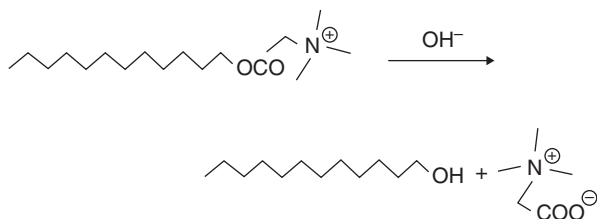
The rate of alkali-catalyzed ester hydrolysis is influenced by adjacent electron-withdrawing or electron-donating groups. A quaternary ammonium group is strongly electron withdrawing. The inductive effect will lead to a decreased electron density at the ester bond; hence, alkaline hydrolysis, which starts by a nucleophilic attack by hydroxyl ions at the ester carbonyl carbon, will be favored. Compounds II–IV of Figure 1.16 all have two carbon atoms between the ammonium nitrogen and the –O– oxygen of the ester bond. Such esters undergo alkaline hydrolysis at a faster rate than esters lacking the adjacent charge but the difference is not very large. If, on the other hand, the charge is at the other side of the ester bond, the rate enhancement is much more pronounced. Such esters are extremely labile on the alkaline side but very stable even under strongly acidic conditions. The large effect of the quaternary ammonium group on the alkaline and acid rates of hydrolysis is due to a stabilization/destabilization of the ground state, as illustrated in Figure 1.17. The charge repulsion, involving the carbonyl carbon atom and the positive charge at the nitrogen atom, is relieved by hydroxide ion attack but augmented by protonation. The net result is that, compared with an ester lacking the cationic charge, the rate of alkaline hydrolysis is increased 200-fold whereas the rate of acid hydrolysis is decreased 2000-fold. For surface active betaine esters based on long-chain fatty alcohols the rate of alkaline hydrolysis is further accelerated due to micellar catalysis, as is discussed later in this chapter. The presence of large, polarizable counterions, such as bromide, can completely outweigh the micellar catalysis, however.

The extreme pH dependence of surface active betaine esters makes them interesting as cleavable cationic surfactants. The shelf life is long when stored under acidic conditions and the hydrolysis rate will subsequently depend on the pH at which they are used. Single chain surfactants of this type have been suggested as *temporary bactericides* for use in



**Figure 1.17** Mechanisms for acid- and base-catalyzed cleavage of a betaine ester





**Figure 1.18** Alkaline hydrolysis of a betaine ester surfactant into a fatty alcohol and betaine

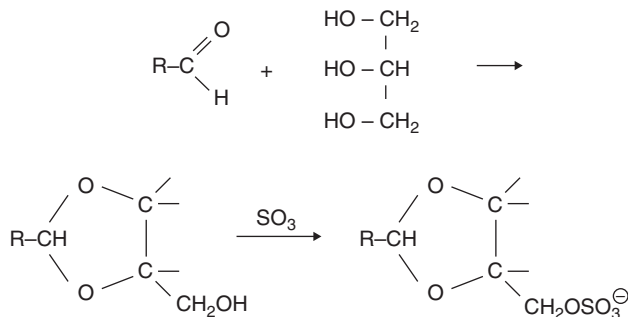
hygiene products, for disinfection in the food industry, and in other applications where only a short-lived bactericidal action is wanted. Figure 1.18 illustrates the breakdown of a betaine ester with bactericidal action into harmless products, fatty alcohol, and betaine, an amino acid. The concept is also of interest for formulations in the cosmetics area, where the skin irritation of stable quats can be a problem. A possible medical application of betaine ester surfactants that is described in the literature is for DNA compaction, that is, folding of the large DNA molecule so that it can pass through a cell membrane. Normal cationic surfactants are effective for this purpose but their toxicity limits their *in vivo* use. Betaine ester surfactants have also been evaluated for emulsion polymerization. The subsequent decomposition of the surfactant is a way to produce emulsifier-free latex. The patent literature also contains examples of betaine esters containing two long tails for use as fabric softeners.

### Acid-Labile Surfactants

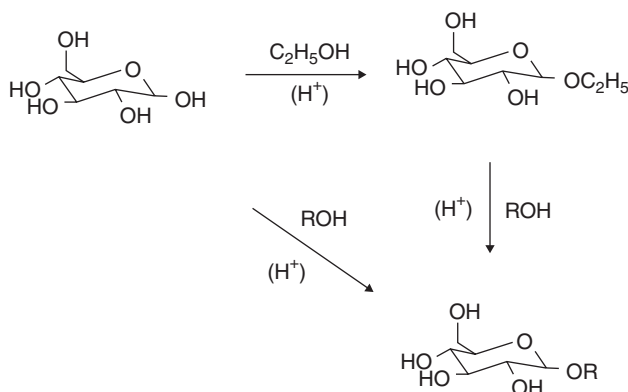
As mentioned above, SDS is labile on the acidic side and relatively stable at high pH. However, SDS was developed long before the concept of “cleavable surfactants” was introduced. In more recent times a number of surfactants have been developed, and reached the market, where the intention has been to design a surfactant that is stable under the normal alkaline conditions of the washing process but breaks down at low pH. However, none of these research lines have resulted in a dramatic change of a product class, as was the case when the stable quats were replaced by ester quats.

### Acetals

Surfactants containing an acetal or a ketal linkage between the polar head group and the hydrophobic tail are well known on the market. They may be cyclic, as the compound in Figure 1.19, or acyclic, as in APGs (Figure 1.20). Both acetal and ketal surfactants are very stable in an alkaline environment but break down relatively easily under acidic conditions. The cyclic compounds are more susceptible to acid hydrolysis than the acyclic ones and ketal surfactants are, in general, more labile than the corresponding acetal surfactants. As an example, a ketal surfactant kept at pH 3.5 was cleaved to the same extent as an acetal surfactant of similar structure kept at pH 3.0. The lower stability of the ketal linkage is due to the greater stability of the carbocation formed during ketal hydrolysis compared to that formed during acetal hydrolysis. However, the biodegradation of acetal surfactants has been found to be faster than for ketal surfactants of similar structure.



**Figure 1.19** Preparation of a sulfated acetal surfactant from a fatty aldehyde and glycerol

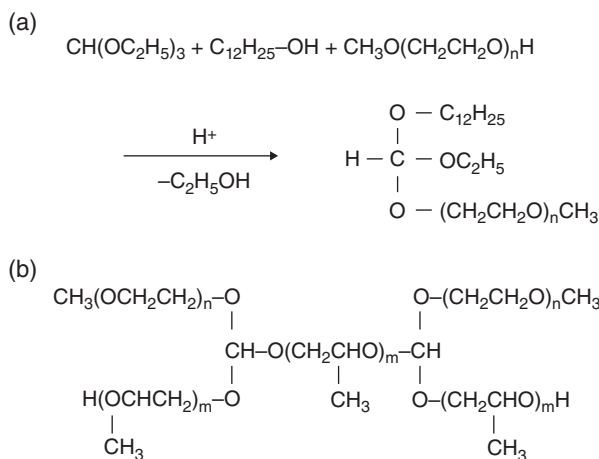


**Figure 1.20** Preparation of alkyl glucoside surfactants

Both acetal and ketal surfactants may be cationic, anionic, or nonionic. It has been found that the 1,3-dioxolane ring, which is present in cyclic acetal and ketal surfactants, corresponds to approximately two oxyethylene units with regard to effect on the CMC and adsorption characteristics. Thus, when an acetal surfactant is made from glycerol and the remaining hydroxyl group subsequently sulfated, the physicochemical properties resemble those of the well-known ether sulfates of the general formula  $\text{R}-(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3\text{Na}$ . This is interesting since commercial alkyl ether sulfates typically contain two to three oxyethylene units.

The acyclic acetal surfactant APG is synthesized by direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Alternatively, it is made by transacetalization of a short-chain alkyl glucoside, such as ethyl or butyl glucoside, with a fatty alcohol. The latter procedure is used for APGs with longer alkyl tails. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction is used as starting material. Figure 1.20 illustrates the synthesis.

Alkyl glucosides can also be made by enzymatic synthesis, using  $\beta$ -glucosidase as catalyst, which yields only the  $\beta$ -anomer (and gives low yield). The corresponding  $\beta$ -anomer can be obtained by  $\beta$ -glucosidase catalyzed hydrolysis of the racemate. There are considerable differences between the  $\alpha,\beta$ -mixture obtained by organic synthesis and the pure enantiomers



**Figure 1.21** (a) Synthesis of an ortho ester-based surfactant; (b) structure of an ortho ester-based block copolymer

obtained by the bio-organic route. The  $\beta$ -anomer of *n*-octyl glucoside has found use as a surfactant in biochemical work.

### Ortho Esters

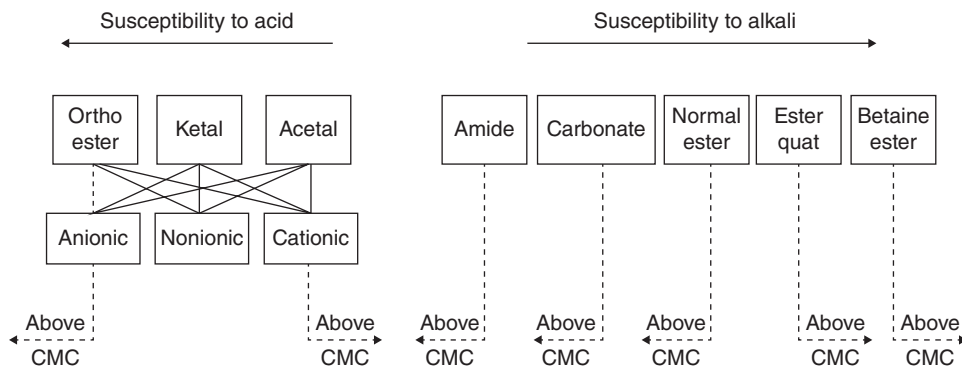
Surfactants containing the ortho ester bond have been explored in recent years. They are typically prepared by transesterification of a low molecular weight ortho ester (such as triethyl orthoformate) with a fatty alcohol and a methyl-capped PEG. Due to the trifunctionality of the ortho ester, a complex mixture of species is obtained. The synthesis is shown in Figure 1.21.

Furthermore, if the reactant alcohol is difunctional, cross-linking will occur and a large network will be formed. An example based on poly(propylene glycol) (PPG) and PEG is also shown in Figure 1.21. Such PEG-PPG block copolymers exhibit higher biodegradation rates than conventional block copolymers without ortho ester linkages between the segments. By varying the number and types of substituents (fatty alcohol, alkyleneoxy group, end blocking), the properties of the ortho ester-based surfactant or block copolymer can be tailor-made.

Hydrolysis of ortho esters occurs by a mechanism analogous to that of acetals and ketals and gives rise to one mole of formate and two moles of alcohol. Ortho ester-based surfactants undergo acid-catalyzed cleavage much more readily than acetal-based surfactants under the same conditions. For instance, a water-soluble ortho ester based on octanol and monomethyl-PEG is hydrolyzed to 50% in two hours at pH5. The structure of the surfactant has been found to influence the hydrolysis rate and, in general, a more hydrophilic surfactant has a higher decomposition rate.

### Overview

As illustrated by the discussion above, there exists a wide range of cleavable surfactants suitable for different applications. One of the most decisive factors for choosing surfactant type is the pH required for the application in question. Figure 1.22 summarizes the susceptibility



**Figure 1.22** Hydrolysis characteristics of different types of hydrolysable surfactants. (Redrawn from Stjern Dahl, M. (2005) *Biodegradable surfactants containing hydrolyzable bonds*. PhD thesis. Chalmers University of Technology, Göteborg, Sweden.)

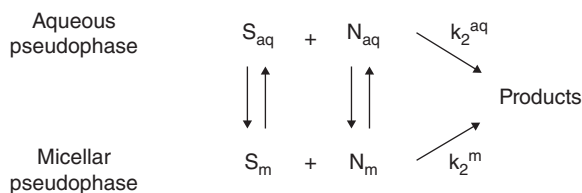
to acid and alkaline hydrolysis of the different types of surfactants discussed above, as well as some more types, including the effects of surfactant aggregation on the hydrolysis rate. This effect is further discussed and illustrated in the next section of this chapter. The figure is based on collected data from the literature and on assumptions based on extrapolation of such data.

### Self-Aggregation of a Surfactant may Increase or Decrease the Hydrolysis Rate of Surfactants Containing a Labile Bond

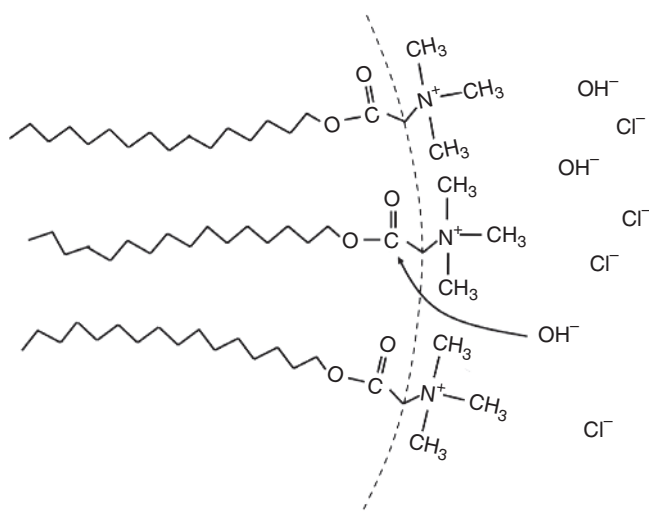
Surfactants aggregate to form micelles and the concentration at which the first micelle is formed is called the CMC. A micellized surfactant will experience a different environment than a surfactant unimer in solution. As will be seen, micellization may cause either an increase or a decrease in the rate at which a cleavable surfactant degrades by hydrolysis. An increase in reaction rate is often referred to as *micellar catalysis*. The opposite behavior could, correspondingly, be called *micellar inhibition*.

Most quantitative treatments of micellar rate effects are based on the so-called pseudophase model. In this model, the surfactant aggregates and the bulk aqueous solution are regarded as distinct reaction regions, or pseudophases. Provided that the exchange of material between the bulk and the micellar pseudophase is fast enough that the reaction does not disturb the equilibrium distribution of the reactants, which is true for most thermal reactions, the observed reaction rate will be the weighted sum of the rates in the micellar and the aqueous pseudophases. A schematic representation of the pseudophase model of a bimolecular reaction is shown in Figure 1.23.

Since a cleavable surfactant is itself one of the reactants, the influence of micelle formation on the degradation of such a surfactant constitutes a special case of micellar catalysis (or inhibition). Depending on their molecular structures, the cleavage products might gradually change the properties of the system as the reaction proceeds; for example, the effective CMC of the surfactant, and thus the fraction of aggregated molecules, may be raised or lowered. The character of the aggregates with respect to shape, charge, or lifetime may also change. Such variations with time may influence the reaction kinetics significantly.



**Figure 1.23** Schematic illustration of the two-site principle of the pseudophase model.  $S$  and  $N$  represent the reactants and indices  $aq$  and  $m$  denote the aqueous and micellar pseudophases, respectively.  $k_2^{aq}$  and  $k_2^m$  are the rate constants in the respective pseudophases. (With permission from Bunton, C.A., Nome, F., Quina, F.H. and Romsted, L.S. (1991) Ion binding and reactivity at charged aqueous interfaces. *Accounts of Chemical Research*, **24**, 357–364. Copyright 1991, American Chemical Society.)

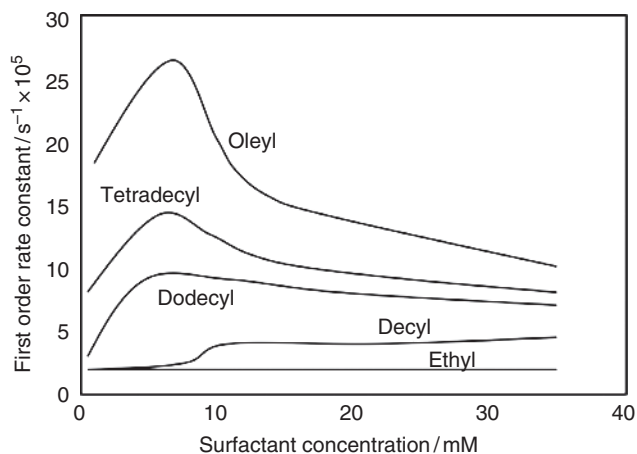


**Figure 1.24** Micellar catalysis is caused by an increased concentration of hydroxyl ions in the vicinity of the surface of the cationic micelle. If chloride as counterion is replaced by a more polarizable anion, such as bromide, access of the hydroxyl ion will be more limited and the rate of hydrolysis will decrease

### Increased Hydrolysis Rate—Micellar Catalysis

Cationic ester-containing surfactants, such as ester quats and betaine esters, are subject to micellar catalysis and hydrolyze faster when present in micelles than as free unimers in solution. This is due to an increased hydroxyl ion concentration around the micelle, that is, the local effective pH in the vicinity of the micelle surface is higher than in the bulk. Figure 1.24 illustrates the phenomenon for a betaine ester surfactant.

Figure 1.25 shows the pseudo-first-order rate constants for alkaline hydrolysis of a series of betaine esters with different lengths of the alkyl tail. The observed pronounced concentration dependence of the hydrolysis rate can be explained by micellar catalysis, that is, by

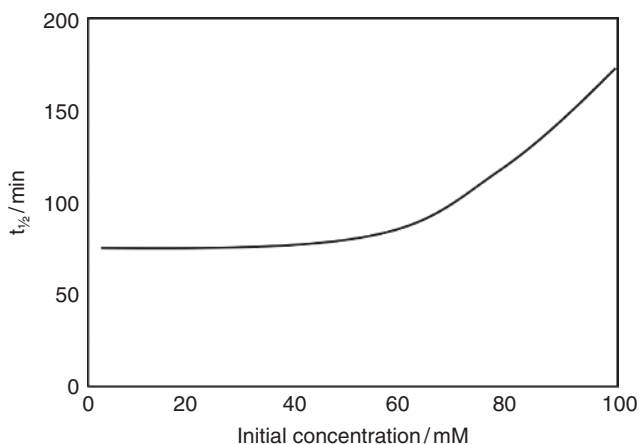


**Figure 1.25** Concentration dependence of the pseudo-first-order rate constants in a 100 mM phosphate buffer at pH 7.5 and 37°C for surface active betaine esters with hydrophobic tails of different sizes. For comparison, the rate constant for a non-surface active betaine ester (ethyl betainate) is included. (Reprinted with permission from Lundberg, D. and Holmberg, K. (2004) NMR studies on hydrolysis kinetics and micellar growth in solutions of surface-active betaine esters. *Journal of Surfactants and Detergents*, 7, 239. Copyright © 2004, Springer.)

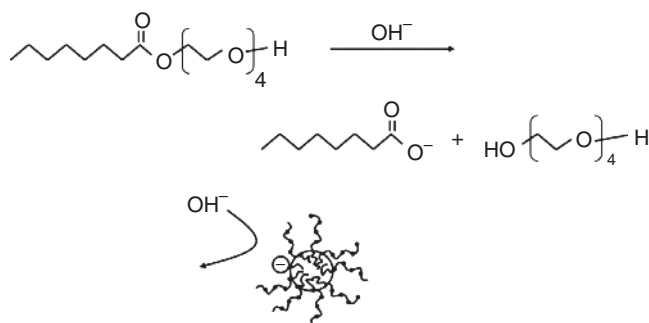
the locally elevated pH in the micellar pseudophase. The reaction rate will thus be substantially higher when the surfactant is present at a concentration above the CMC compared to the rate observed for a unimeric surfactant or a betaine ester that is not surface active under the same conditions. The decrease in reaction rate observed at higher concentrations for the  $C_{12}$ – $C_{18:1}$  compounds is a consequence of competition between the reactive hydroxyl ions and the inert surfactant counterions at the micellar surface. The chloride ions are more polarizable than hydroxyl ions and, thus, show a stronger affinity to the charged micellar surface. The decrease in rate at higher concentration will be even stronger if bromide is the counterion. Addition of extra salt may completely eliminate the micellar catalysis. The hydroxyl ions may then not be able to compete with the other anions for a place in the micellar pseudophase.

### Decreased Hydrolysis Rate—Micellar Inhibition

Figure 1.26 illustrates alkaline hydrolysis of a noncharged ester surfactant above and below the CMC. As can be seen, the half-life of the surfactant is constant at concentrations below the CMC, while above the CMC there is a linear increase of the half-life. This means that below the CMC the values are in accordance with pseudo-first-order kinetics and above the CMC they express zero-order kinetics, that is, the rate is independent of the concentration of the reacting species. This implies that only surfactant molecules present as unimers are cleaved. Those residing in micelles are protected from hydrolysis. (Above the CMC the unimer concentration will, under the assumption that the micellar dissociation is faster than



**Figure 1.26** Half-life of a non-charged ester surfactant, tetra(ethylene glycol) monoester of octanoic acid ( $C_7H_{15}CO-(OCH_2CH_2)_4-OH$ ) as a function of initial surfactant concentration. The surfactant has a CMC of 50 mM. (With permission from Stjern Dahl, M. and Holmberg, K. (2003) *Synthesis and chemical hydrolysis of surface-active esters*. *Journal of Surfactants and Detergents*, **6**, 311–318. Copyright © 2003, Springer.)



**Figure 1.27** Hydrolysis of the ester surfactant present as unimers generates an anionic surfactant, which will enter the micelle and render it a negative charge. Hydroxyl ions are repelled by the negatively charged micelle in analogy with the attraction of hydroxyl ions to positively charged micelles, as illustrated in Figure 1.24

the hydrolysis reaction, be practically constant.) Evidently, aggregation into micelles protects these nonionic ester surfactants from undergoing alkaline ester hydrolysis, that is, the opposite to what happens to the cationic ester-containing surfactants discussed above. It is likely that the effect is due to the fact that hydrolysis of the unimers in bulk generates a fatty acid soap, that is an anionic surfactant. Anionic and nonionic surfactants readily combine into mixed micelles, as is discussed in Chapter 13; thus, the micelles will gradually build up a negative charge. Hydroxyl ions will be repelled by such negatively charged aggregates, as is illustrated in Figure 1.27.

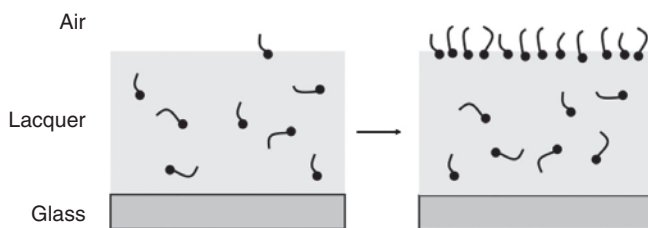
## Use of Polymerizable Surfactants is a Way to Immobilize the Surfactant

Polymerizable surfactants are examples of what is sometimes referred to as *functional surfactants*, that is surfactants that possess one characteristic property besides that of pronounced surface activity. The interest in polymerizable surfactants originates from the fact that surfactant action may be needed at some stage of an operation but unnecessary, or even unwanted, at some later stage. The problems with residual surfactants may be environmentally related, such as with slowly biodegradable surfactants in sewage plants. The problems may also be of a technical nature because the presence of surface active agents in the final product may affect the product performance in a negative way.

The paint area is a good example where surfactants are needed at one stage but unwanted at a later stage. Surfactants are used in paints as emulsifier for the binders, as dispersant for the pigments, and to improve wetting of the substrates. In the dried paint film, the presence of surfactant frequently causes problems, however, since the surfactant acts as an external plasticizer in the film, imparting softness and flexibility. This could be taken advantage of had the plasticizer been evenly distributed in the coating. However, due to its surface activity, the surfactant will migrate out of the bulk phase and concentrate at the interfaces. It has been shown that surfactant molecules go to the film–air interface, where they align with their hydrophobic tails pointing towards the air (Figure 1.28). (The surfactant may also align at the film–substrate interface, but the extent at which this happens will depend on the nature of the substrate.) As an example, calculations from Electron Spectroscopy for Chemical Analysis (ESCA) (or X-ray Photoelectron Spectroscopy (XPS)) spectra show that the dried film from a lacquer containing 1% surfactant may have an average surface surfactant concentration of 50%. The overall bulk concentration of surfactant is still approximately 1%, since the modified surface region is a very thin layer when compared to the thickness of the whole film. The surfactant surface layer constitutes a so-called weak boundary layer when a second coating is applied, sometimes leading to poor adhesion of a second lacquer layer or to poor quality when the surface is printed.

It is also known that during the drying of emulsion paints the surfactant may undergo phase separation, forming lumps, tenths of microns wide, distributed throughout the film. Atomic force microscopy studies have revealed that these surfactant lumps can extend far down into the film. On exposure to water the surfactant is washed out of the film, with the result being that deep cavities appear where the lumps had been. Such film defects can severely reduce the protective action of a coating on wood.

A way to overcome the problems associated with the presence of surfactant in the final product is to have the surfactant chemically bound to the latex particle or, alternatively, to



**Figure 1.28** Migration of surfactant in a lacquer film leads to enrichment at the surface



make the surfactant polymerize during the setting or curing stage. In principle, the surfactant may either undergo homopolymerization or copolymerize with some other component of the system. In paints and lacquers, the obvious other component is the binder.

A completely different way to avoid the problem of residual surfactant in the end product is to use cleavable surfactants, that is, surfactants that spontaneously break down at some stage. This concept was discussed in a previous section of this chapter.

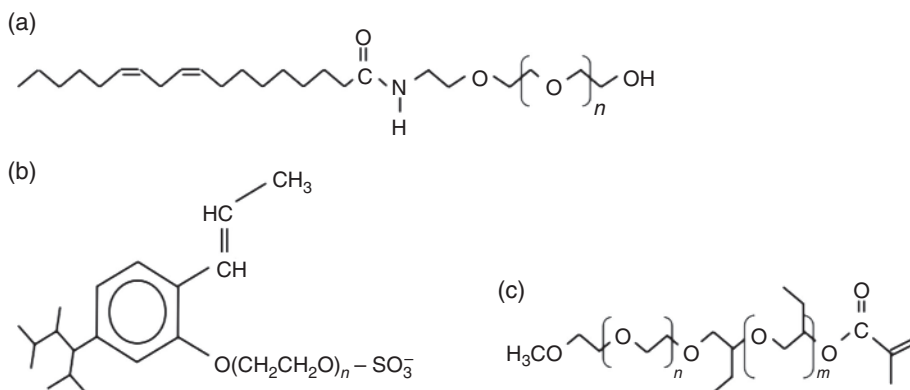
## Mode of Surfactant Polymerization

### *Homopolymerization versus Copolymerization*

In a formulation containing reactive surfactant, homopolymerization of the amphiphile may take place if the concentration is high enough. However, in most technical formulations the surfactant concentration is too low to allow substantial homopolymerization in the bulk phase. The reactive surfactant will instead copolymerize with another component in the bulk. A monolayer of surfactant, on the other hand, may homopolymerize when adsorbed at an interface, as is shown below. The palisade layer may either form by adsorption from an aqueous solution or by migration through a film, as discussed above.

### *Autoxidative versus Nonautoxidative Polymerization*

Autoxidation, that is, oxygen-induced curing, may take place both during copolymerization in the bulk phase and during homopolymerization of a surface monolayer. A surfactant capable of undergoing autoxidation is shown in Figure 1.29. The surfactant is a monoethanolamide ethoxylate of an unsaturated fatty acid. The fatty acid originates from an unsaturated triglyceride, such as linseed oil or tall oil. Such surfactants belong to the class fatty acid ethoxylates that was discussed under the section Nonionics earlier in this chapter and illustrated in Figure 1.7. Surfactants that can undergo autoxidation are of



**Figure 1.29** Examples of polymerizable surfactants: (a) a monoethanolamide ethoxylate of an unsaturated fatty acid capable of undergoing autoxidative polymerization; (b) a sulfated nonylphenol ethoxylate derivative capable of undergoing free-radical polymerization; and (c) a copolymer based on polyoxyethylene and polyoxybutylene segments with a methacrylate group at the hydrophobic end, also capable of undergoing free radical polymerization

particular interest in combination with alkyd resins, which also contain unsaturated fatty acid residues. The autoxidation, that is, the curing of the alkyd-based film containing reactive surfactant, is normally catalyzed by cobalt or manganese salts.

Nonautoxidative polymerization includes UV curing or thermally induced curing with the use of free radical initiators, such as benzoyl peroxide or potassium persulfate. Similar to autoxidation, both bulk and surface curing may occur. Surfactants based on activated vinyl groups, such as acrylate and methacrylate esters, are typical examples of this class. Examples of surfactants capable of rapid free radical curing are also shown in Figure 1.29.

### **Position of the Polymerizable Group**

In principle, the reactive group may be present either in the polar, hydrophilic or in the apolar, hydrophobic part of the surfactant molecule.

In emulsion systems the solubility characteristics of the initiator are important. The distribution of the initiator between the oil and the water phases should be such that it is predominantly present in the phase where the polymerizable function is located. Thus, surfactants with a polymerizable bond in the polar head group are best served with a water-soluble initiator whereas an oil-soluble initiator is preferred when the polymerizable bond is situated in the hydrocarbon part.

In general, polymerization at the polar end of nonionic surfactants requires relatively severe conditions and often gives poor yield. When the same functional group is present in the hydrophobic tail, the reactivity in a two-phase system is much higher. Cross-linking of the polar groups should also be avoided if the surfactant after polymerization is supposed to provide steric stabilization, for example, in the stabilization of dispersed systems. The entropy term, which is the main driving force behind steric stabilization, will be reduced if the freedom of motion of the polar head groups is restricted.

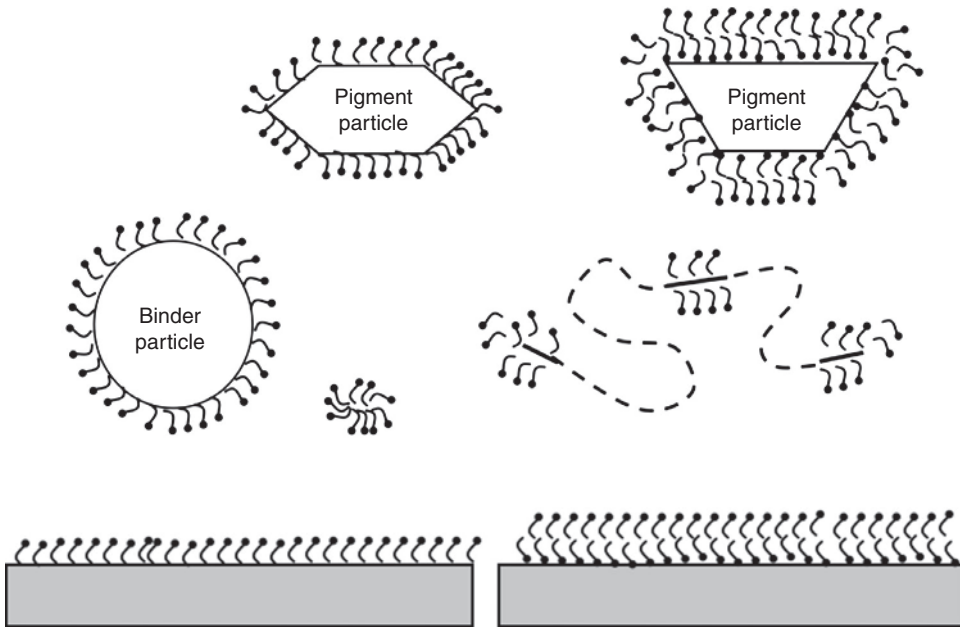
Cross-linking of the hydrophobic tails is also the best choice in those cases where the surfactant polymerizes when adsorbed at a hydrophobic surface. Adsorption at such surfaces occurs with the surfactant hydrophobic chains close together, an orientation that should facilitate formation of inter-chain bonds.

## **Applications of Polymerizable Surfactants**

### **Emulsion Polymerization**

Polymerizable surfactants are of interest in emulsion polymerization, for example, in the conversion of vinyl chloride to poly(vinyl chloride) and of acrylates and vinyl acetate to latices for coatings. Use of a reactive surfactant in vinyl chloride polymerization leads to poly(vinyl chloride) with improved shear stability. In latices, polymerizable surfactants can bring about several advantages such as:

- improved stability against shear, freezing, and dilution;
- reduced foaming;
- reduced problems with competitive adsorption (see below);
- improved adhesion properties of the film;
- improved water and chemical resistance of the film.

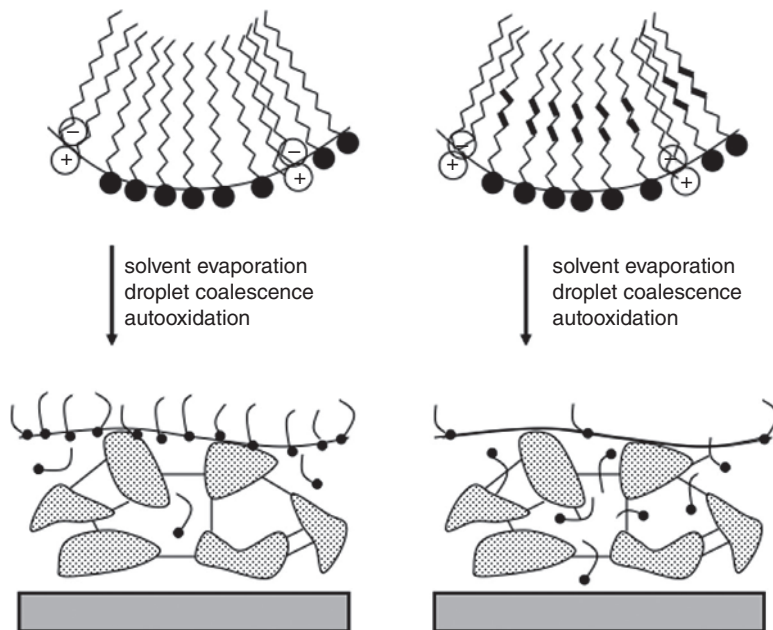


**Figure 1.30** The surfactant may adsorb at many different surfaces in a paint formulation

Competitive adsorption is a serious problem in many paint systems, as well as in many other surfactant-containing formulations. A pigmented latex coating contains a variety of interfaces at which surfactants may adsorb, such as binder–water, pigment–water, substrate–water, and air–water. In addition, the surfactant molecules may assemble in micelles or form aggregates together with hydrophobic segments of the associative thickener, which is normally present in today’s latex paints. The situation is illustrated in Figure 1.30. Since different surfactants are normally introduced into the system together with the individual components, for example, emulsifier (often a mixture of an anionic and a nonionic surfactant) with the binder, pigment dispersant with the pigment, wetting agent added directly to the formulation, and so on, the situation becomes very complex and competitive adsorption is a potential problem in all pigmented emulsion paints and in many related systems. The surface active agent used as the emulsifier for the binder may desorb from the emulsion droplet and adsorb at the pigment surface. The pigment dispersing agent may go the other way. Such an exchange is known to occur and to cause problems in terms of instability and unwanted rheological behavior. Competitive adsorption in general is discussed in Chapter 13.

### Alkyd Emulsions

Alkyd resins are traditionally used in formulations based on organic solvents, such as white spirit or xylene, in which the alkyd is molecularly dissolved. Emulsions of alkyds came later and can be seen as the response by the alkyd industry to environmental demands. Stable emulsions can be made from most alkyds, provided the resin viscosity is not too



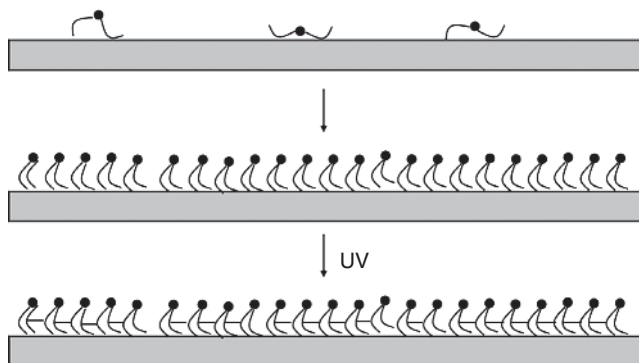
**Figure 1.31** Curing of an alkyd emulsion based on (left) a conventional surfactant and (right) a reactive surfactant containing homoconjugated double bonds in the hydrophobic tail. Whereas the conventional, unreactive surfactant migrates to the surface, most of the reactive surfactant molecules become chemically bound to the resin network. (With permission from Holmberg, K. (1992) *Polymerizable surfactants*. Progress in Organic Coatings, **20**, 325–337. Copyright Elsevier Limited.)

high and sufficient shear forces are applied in the emulsification. It has been found that by using emulsifiers capable of participating in the autoxidative drying of the binder, the film properties can be considerably improved. Surfactant (a) of Figure 1.29 is an example of a surfactant that can copolymerize with the alkyd binder during autoxidative curing of the film. Such copolymerization is a way to reduce the above-mentioned problems with free surfactant molecules in the film. Figure 1.31 depicts schematic representations of the curing process with a conventional emulsifier and with a surfactant capable of copolymerizing with unsaturated fatty acid chains of the binder.

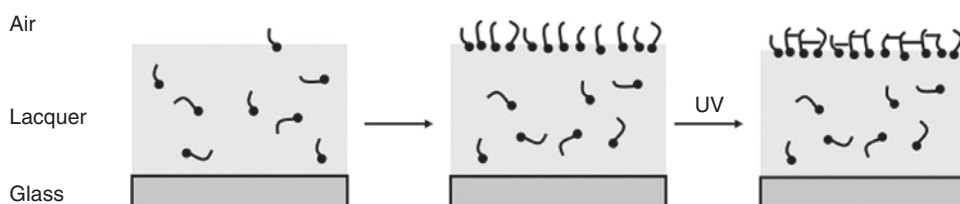
### Surface Modification

Modification of solid surfaces can be achieved by an adsorbed layer of reactive surfactant on the surface, as illustrated in Figure 1.32. Provided that the surfactant molecules are extensively cross-linked, such a thin surface film will be attached irreversibly. In this way, hydrophobic surfaces can be made hydrophilic or a specific functionality can be introduced.

For example, low-density polyethylene films can be hydrophilized with surfactants having one or two polymerizable groups, such as methacrylate or diacetylene. Adsorption can be made from buffer solution and the subsequent polymerization of the adsorbed monolayer achieved by UV irradiation. Particularly good results are often obtained with surfactants of



**Figure 1.32** Surface modification with a UV-curable surfactant



**Figure 1.33** Surface modification of a lacquer film through migration of the surfactant to the film-air interface, followed by UV curing

the twin-tail type, that is, having a hydrophobic part consisting of two hydrocarbon chains. This structure gives optimal packing on planar surfaces since the surfactants have a value of the critical packing parameter close to one (Chapter 6). Proper alignment of the surfactants at the surface is believed to be vital for effective cross-linking to occur. There is experimental evidence that surfactants that contain two polymerizable functions give better result in terms of permanent hydrophilization than surfactants containing only one reactive group. Most likely, surfactants with more than one polymerizable group give a cross-linked network of higher molecular weight.

Paint and lacquer films can also be surface-modified by migration of a dissolved surfactant to the film-air interface during the drying or curing stage followed by crosslinking. The principle is shown in Figure 1.33 for a UV-polymerizable surfactant. As an example, a fluorocarbon surface layer can be obtained by dissolving a small amount, less than 1%, of a polymerizable fluorosurfactant in a lacquer and cross-linking the surfactant monolayer formed at the surface. Such a surface becomes extremely water repellent with a minimal use of the costly and not so environmentally benign fluorinated surfactant.

### Surfactant Self-Assemblies

The homopolymerization of reactive surfactants in the form of assemblies, such as micelles or liquid crystals, has been attempted as a way to freeze the structure and prepare various types of nano-sized materials. Polymerization of micelles has not been entirely successful,

however. With both spherical and rod-like micelles the polymerized aggregates were of much larger size than the original structures. With liquid crystals and, in particular, with vesicles, the results are more promising. Stable vesicles, of interest for drug administration, have been prepared by free radical polymerization of preformed vesicles. Such vesicles need not to be based entirely on polymerizable surfactants. Incorporation of smaller amounts, 10–30%, of reactive species into a phospholipid-based vesicle formulation leads to vesicles with much improved stability.

### Special Surfactants Give Extreme Surface Tension Reduction

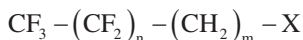
The vast majority of surfactants have the hydrophobic part of the molecule made up of a hydrocarbon chain, either aliphatic or alkylaryl. With a suitable choice of polar head group, the minimum surface tension that can be achieved with such surfactants is in the order of 26–28 mN/m. Such surface activity is sufficient for most uses of surface active agents. However, there are some applications where a lower surface tension of aqueous solutions is required. The spreading of aqueous foams on top of burning oil and the spreading of water-based formulations on surfaces of polyolefins are two relevant examples.

Two types of specialty surfactants are used to achieve extreme reduction of surface tension: silicone surfactants and fluorinated surfactants. The former type is based on polydimethylsiloxane as the apolar group, while the latter contains a fluorocarbon or a combination of fluorocarbon and hydrocarbon as the hydrophobic tail. Silicone surfactants are either low molecular weight or high molecular weight compounds. The low molecular weight silicone surfactants are excellent wetting agents and are discussed in Chapter 20. The high molecular weight compounds are treated together with other surface active polymers in Chapter 10.

Fluorinated surfactants are normally of low molecular weight and have the general structure:



or



where X can be any polar group, charged or uncharged. The fluorocarbon chain is usually rather short, with  $n$  typically being 5–9. Fluorinated carboxylates are common. Due to the inductive effect exerted by the electronegative fluorine atoms, these compounds are strong acids and, hence, relatively insensitive to low pH or hard water. There are also perfluorinated block copolymers, analogous to EO–PO block copolymers (Chapters 7 and 10), on the market.

Fluorinated surfactants are used for various applications where wetting and spreading of aqueous solutions are difficult. Another use of fluorinated surfactants is to render surfaces, for example, paper or textiles, both hydrophobic and lipophobic. Fluorinated surfactants, like silicone surfactants but unlike hydrocarbon-based surfactants, are also surface active in organic solvents and are, therefore, used as surfactants in paints and other nonaqueous formulations. The main disadvantage with fluorinated surfactants, besides their high price, is their poor biodegradability.

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