1 INTRODUCTION TO SURFACTANTS

Surfactants Adsorb at Interfaces

Surfactant is an abbreviation for surface active agent, which literally means active at a surface. In other words, a surfactant is characterized by its tendency to absorb at surfaces and 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:

Solid–vapour	*surface*
Solid–liquid	
Solid–solid	
Liquid–vapour	*surface*
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 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, then the larger the reduction in surface tension.

Surfactants may adsorb at all of the five types of interfaces listed above. Here, the discussion will be restricted to interfaces involving a liquid phase. The liquid is usually, but not always water. Examples of the different interfaces and products in which these interfaces are important are given in Table 1.1.

In many formulated products several types of interfaces are present at the same time. Water-based paints and paper coating colours 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

Table 1.1 Examples of interfaces involving a liquid phase

Interface	Type of system	Product
Solid–liquid	Suspension	Solvent-borne paint
Liquid–liquid	Emulsion	Milk, cream
Liquid–vapour	Foam	Shaving cream

(but unwanted) phenomenon at the application stage. All of the interfaces are stabilized by surfactants. The total interfacial area of such a system is immense: the oil–water and solid–water interfaces of one litre of paint may cover several football fields.

As mentioned above, the tendency to accumulate at interfaces is a fundamental property of a surfactant. In principle, the stronger the tendency, then the better the surfactant. The degree of surfactant concentration 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. In the normal case that limit is reached when micelles start to form in bulk solution. Table 1.2 illustrates what effective surfactants can do in terms of lowering of 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 tensions, i.e. values in the range of 10^{-3} mN/m or below, can be obtained. An example of a system giving ultra-low interfacial tensions is a three-phase system comprising a microemulsion in equilibrium with excess water and oil phases. Such systems are of interest for enhanced oil recovery and are discussed in Chapter 22.

Table 1.2 Typical values of surface and interfacial tensions (mN/m)

Air–water	72–73
Air–10% aqueous NaOH	78
Air–aqueous surfactant solution	40–50
Aliphatic hydrocarbon–water	28–30
Aromatic hydrocarbon–water	20–30
Hydrocarbon–aqueous surfactant solution	1–10

Surfactants Aggregate in Solution

As discussed above, 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 we will use 'unimer' and the term 'monomer' will be restricted to the polymer building block.) Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups 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 as free unimers in solution. Only surfactant unimers contribute to 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 may be seen as a reservoir for surfactant unimers. The exchange rate of a surfactant molecule between micelle and bulk solution may vary by many orders of magnitude depending on the size and structure of the surfactant.

Micelles are already generated at very low surfactant concentrations in water. The concentration at which micelles start to form is called the critical micelle concentration, or CMC, and is an important characteristic of a surfactant. A CMC of 1 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 2.

Surfactants are Amphiphilic

The name amphiphile is sometimes used synonymously with surfactant. The word is derived from the Greek word *amphi*, meaning both, and the term relates to the fact that all surfactant molecules consist of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one which is insoluble (the lyophobic part). When the fluid is water one usually talks about the hydrophilic and hydrophobic parts, respectively. The hydrophilic part is referred to as the head group and the hydrophobic part as the tail (see Figure 1.1).

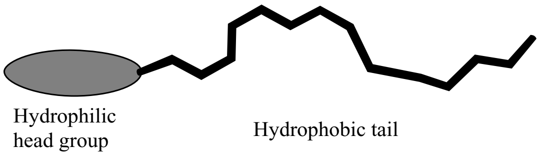


Figure 1.1 Schematic illustration of a surfactant

In a micelle the surfactant hydrophobic group is directed towards the interior of the cluster and the polar head group is directed towards the solvent. The micelle, therefore, is a polar aggregate of high water solubility and without much surface activity. When a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic group towards the surface and exposes its polar group to the water. The surface has 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 17.

The hydrophobic part of a surfactant may be branched or linear. The polar head group is usually, but not always, attached at one end of the alkyl chain. The length of the chain is in the range of 8–18 carbon atoms. The degree of chain branching, the position of the polar 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 non-ionic and the choice of polar group determines the properties to a large extent. For non-ionic 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 and polar groups, not the absolute size of either of the two, is decisive in determining the physicochemical behaviour of a surfactant in water.

A surfactant usually contains only one polar group. Recently, there has been considerable research interest in certain dimeric surfactants, containing two hydrophobic tails and two head groups linked together with a short spacer. These species, generally known under the name gemini 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 (16 mM) and that of the corresponding gemini surfactant, having a 2 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 discussed further in Chapter 11.

Weakly surface active compounds which accumulate at interfaces but which do not readily form micelles are of interest as additives in many surfactant formulations. They are referred to as hydrotropes and serve the purpose of destroying the ordered packing of ordinary surfactants. Thus, addition of a hydrotrope is a way to prevent the formation of highly viscous liquid crystalline phases which constitutes a well-known problem in surfactant formulations. Xylene sulfonate and cumene sulfonate are typical examples of hydrotropes

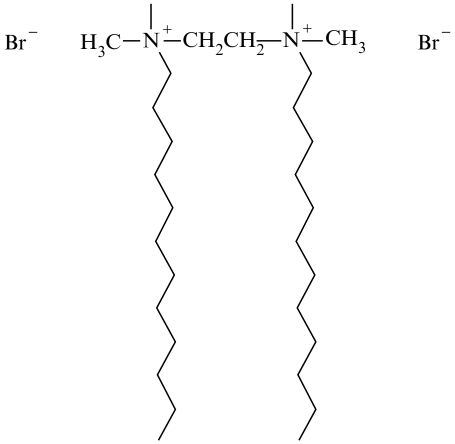


Figure 1.2 A gemini surfactant

used, for instance, in detergent formulations. Short-chain alkyl phosphates have found specific use as hydrotropes for longer-chain alcohol ethoxylates.

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, etc. 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 the surfactant liquid crystal type and such structures constitute the membranes of cells. Figure 1.3 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.

Micro-organisms are sometimes efficient producers of surface active agents. Both high molecular weight compounds, e.g. lipopolysaccharides, and low molecular weight polar lipids can be produced in good yields, particularly when the micro-organism is fermented on a water-insoluble substrate. Surface active polymers of this type are dealt with in Chapter 12. Figure 1.4 gives the structure of a low molecular weight acylated sugar, a trehalose lipid, which has

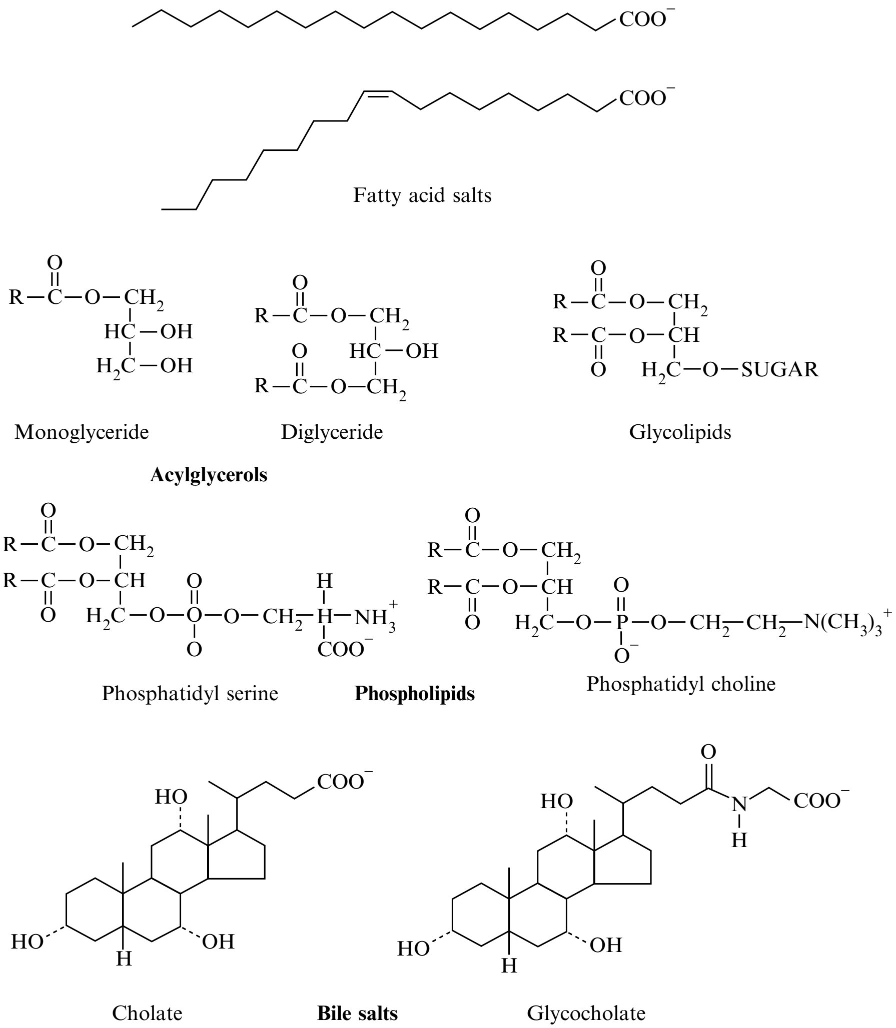


Figure 1.3 Examples of polar lipids

proved to be an effective surfactant. Trehalose lipids and several other 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 very limited due to their high price.

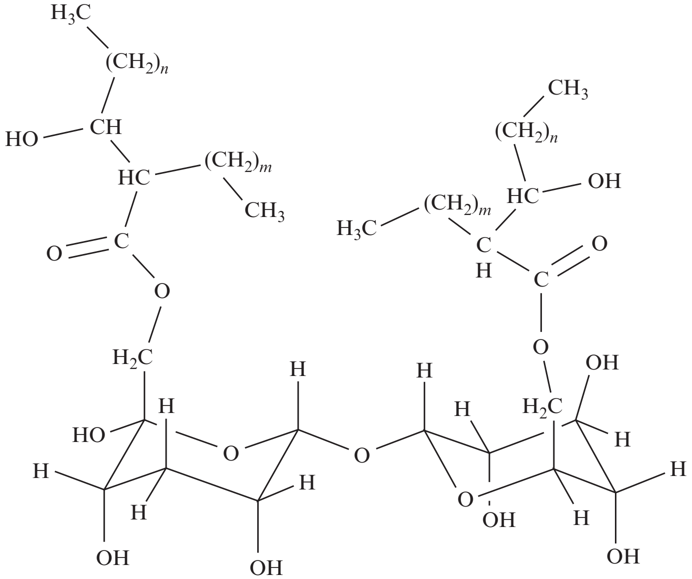


Figure 1.4 A surface active trehalose lipid produced by fermentation

Surfactant Raw Materials May be Based on Petrochemicals or Oleochemicals

For several 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 instance, 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 which 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. Surfactants based on oleochemicals are made from renewable raw materials, most commonly vegetable oils. Surfactants from petrochemicals are made from small building blocks, such as ethylene, produced by cracking of naptha. 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 instance, linear alcohols in the C10–C14 range, which are commonly used as hydrophobes for both non-ionics (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 aluminium as the 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 friendly surfactant than the petrochemical route. However, from the carbon dioxide cycle point of view chemical production based on renewable raw materials is always 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 to give an aldehyde, which is subsequently reduced to the alcohol by catalytic hydrogenation. 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 commercial 'oxo alcohols' are mixtures of linear and branched alcohols of specific alkyl chain length ranges. The different routes to higher molecular weight primary alcohols are illustrated in Figure 1.5.

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, non-ionics 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, depending on pH, can be either cationic, zwitterionic or anionic. Among normal organic substances, simple amino acids are well-known examples of amphoteric compounds. Many so-called zwitterionic surfactants are of this category. However, other zwitterionic surfactants retain one of the charges over the whole pH range. Compounds with a quaternary ammonium as the cationic group are examples of this. Consequently, a surfactant that contains a carboxylate group and a quaternary ammonium group, a not uncommon combination as we shall see later in this chapter, is zwitterionic unless the pH is very low, but is not an amphoteric surfactant.

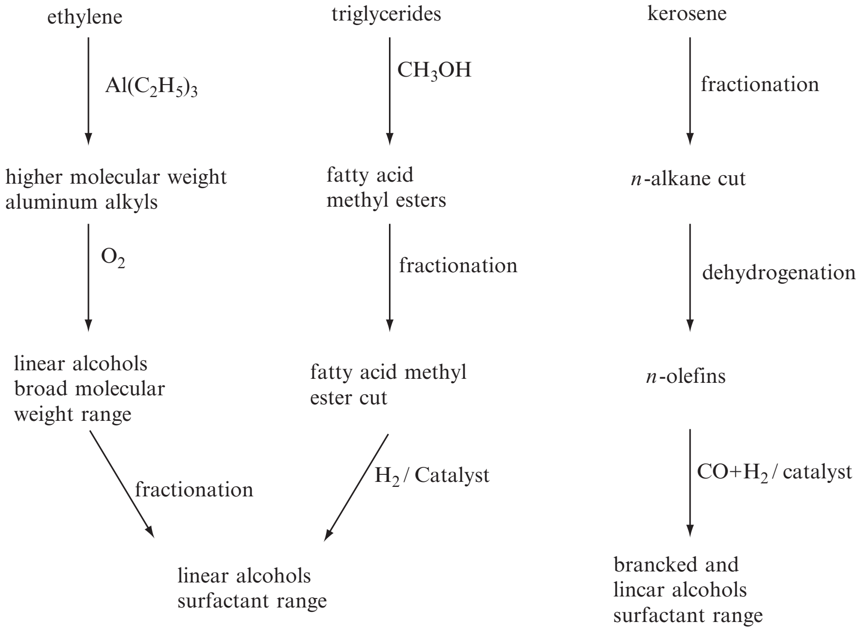


Figure 1.5 Different pathways for preparation of primary alcohols of interest as surfactant raw materials. From left to right: Ziegler–Natta polymerization of ethylene; reduction of fatty acid methyl esters; hydoformylation of higher olefins (the Oxo process)

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 the physicochemical properties. Most anionic surfactants have sodium as counterion but other cations, such as lithium, potassium, calcium and protonated amines, are used as surfactant counterions for speciality purposes. The counterion of cationic surfactants is usually a halide or methyl sulfate.

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 non-aqueous 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 non-ionics. 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 non-ionic compounds. Fatty amine ethoxylates which contain both an amino nitrogen atom (cationic polar group) and a polyoxyethylene chain (non-ionic polar group) may be included in either the cationics or the non-ionics class. The non-ionic 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, etc., invariably contain short polyoxyethylene chains, typically two or three oxyethylene units, and are therefore always 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 greater volume than any other surfactant class. A rough estimate of the worldwide surfactant production is 10 million tons per year, out of which approximately 60% are anionics. One main 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 alkylarye chains in the C12–C18 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.

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

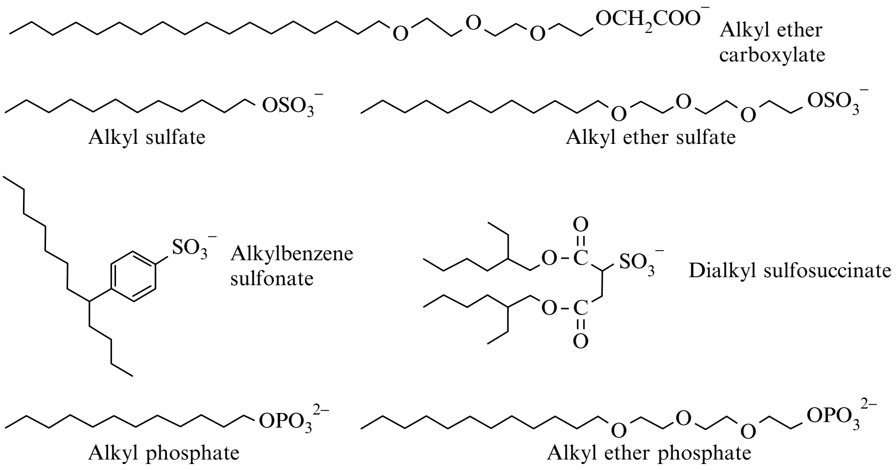
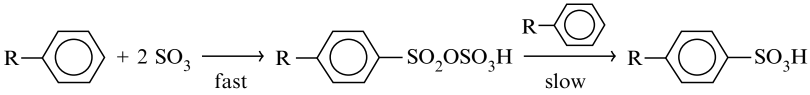


Figure 1.6 Structures of some representative anionic surfactants

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. A very specific use of the lithium salt of a fatty acid, i.e. lithium 12-hydroxystearic acid, is as the major constituent of greases.

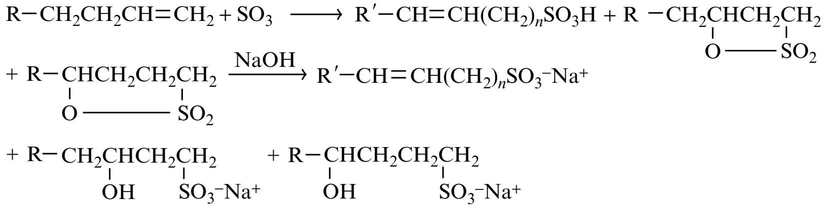
Alkylbenzene sulfonates have traditionally been the work-horse among synthetic surfactants. They are widely used in household detergents as well as in a variety of industrial applications. They are made by sulfonation of alkylbenzenes. In large-scale synthesis, sulfur trioxide is the sulfonating agent of choice but other reagents, such as sulfuric acid, oleum ($H_2SO_4nSO_3$), chlorosulfonic acid ($ClSO_3H$) or amidosulfonic acid (sulfamic acid, H_2NSO_3H), 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 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 $AlCl_3$ as catalyst. The reaction yields a mixture of isomers with the phenyl group attached to one of the non-terminal positions of the alkyl chain.

Other sulfonate surfactants that have found use in detergent formulations are paraffin sulfonates and α-olefin sulfonates, with 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 mainly produced in Europe. They 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 carbons give much more stable radicals than primary, the sulfonate group will be introduced more or less randomly on all non-terminal carbon atoms along the alkane chain. A C14–C17 hydrocarbon cut, sometimes called the ‘Euro cut’, is normally used as hydrophobe raw material. Thus, the product obtained will be a very complex mixture of both isomers and homologues.

α-Olefin sulfonates are prepared by reacting linear α-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 α-olefin fractions used as starting material are C12–C16 and C16–C18. The ratio of alkene sulfonate to hydroxyalkane sulfonate is to some degree governed by the ratio of SO_3 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:



$$R{-}CH_2CH_2CH{=}CH_2 + SO_3 \longrightarrow R'{-}CH{=}CH(CH_2)_nSO_3H + R{-}CH_2\underset{O\text{———}}{CH}CH_2\underset{SO_2}{CH_2}$$

$$+\ R{-}\underset{O\text{————}}{CH}CH_2CH_2\underset{SO_2}{CH_2} \xrightarrow{NaOH} R'{-}CH{=}CH(CH_2)_nSO_3^-Na^+$$

$$+\ R{-}CH_2\underset{OH}{CH}CH_2\underset{SO_3^-Na^+}{CH_2} \quad +\ R{-}\underset{OH}{CH}CH_2CH_2\underset{SO_3^-Na^+}{CH_2}$$

An alkyl sulfonate surfactant widely used in surface chemistry research 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 (see Figure 1.6), is particularly useful for preparation of water/oil (w/o) microemulsions, as is discussed in Chapter 6.

Isethionate surfactants, with the general formula $R-COOCH_2CH_2SO_3^-Na^+$, 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, etc.

Sulfated alcohols and alcohol ethoxylates constitute another important group of anionics, widely used in detergent formulations. These are monoesters of sulfuric acid and the ester bond is a labile linkage which splits with particular ease at low pH where hydrolysis is autocatalytic. Both linear or branched alcohols, typically with eight to sixteen carbon atoms, are used as raw materials. 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 process is similar to the sulfonation discussed above. Sulfur trioxide is the reagent used for large-scale production and, in analogy to sulfonation, the reaction proceeds via an intermediate pyrosulfate:

$$\mathrm{R{-}OH} + 2\ \mathrm{SO_3} \xrightarrow[\text{fast}]{} \mathrm{R{-}O{-}SO_2OSO_3H} \xrightarrow[\text{slow}]{\mathrm{R{-}OH}} \mathrm{R{-}O{-}SO_3H}$$

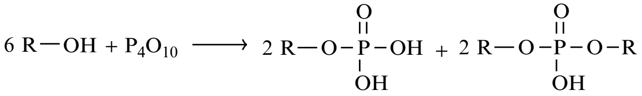
Synthesis of sulfate esters of ethoxylated alcohols proceeds similarly. In this reaction 1,4-dioxane is usually formed in non-negligible amounts. Since dioxane is toxic, its removal by evaporation is essential. These surfactants are usually referred to as ether sulfates. Such surfactants are good at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

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

$$\mathrm{R{-}(OCH_2CH_2)}_n\mathrm{{-}\,OH} + \mathrm{ClCH_2COO^{-}Na^{+}} \longrightarrow \mathrm{R{-}(OCH_2CH_2)}_n\mathrm{{-}\,O{-}\,CH_2COOH} + \mathrm{NaCl}$$

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 consurfactant 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 $\mathrm{CaCO_3}$.

Phosphate-containing anionic surfactants, both alkyl phosphates and alkyl ether phosphates, are made by treating the fatty alcohol or alcohol ethoxylate with a phosphorylating agent, usually phosphorus pentoxide, $\mathrm{P_4O_{10}}$. 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:



$$6\,R{-}OH + P_4O_{10} \longrightarrow 2\,R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH + 2\,R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}R$$

All commercial phosphate surfactants contain both mono-and diesters of phosphoric acid, but the relative amounts vary from one producer to another. Since the physico-chemical 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, $POCl_3$, can also be used as a phosphorylating agent to produce alkyl phosphate surfactants. Also with $POCl_3$ 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. Some important facts about anionic surfactants are given in Table 1.3.

Non-Ionics

Non-ionic surfactants have either a polyether or a polyhydroxyl unit as the polar group. In the vast majority of non-ionics, the polar group is a polyether consisting of oxyethylene units, made by the polymerization of ethylene oxide. Strictly speaking, the prefix ‘poly’ is a misnomer. The typical number of oxyethylene units in the polar chain is five to ten, although some surfactants, e.g. 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, e.g. 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

Table 1.3 Important facts about anionic surfactants

1. They are by far the largest surfactant class.
2. They are generally not compatible with cationics (although there are important exceptions).
3. They are generally sensitive to hard water. Sensitivity decreases in the order carboxylate $>$ phosphate $>$ sulfate $\simeq$ sulfonate.
4. A short polyoxyethylene chain between the anionic group and the hydrocarbon improves salt tolerance considerably.
5. A short polyoxypropylene chain between the anionic group and the hydrocarbon improves solubility in organic solvents (but may reduce the rate of biodegradation).
6. Sulfates are rapidly hydrolysed by acids in an autocatalytic process. The other types are stable unless extreme conditions are used.

alcohol formed and subsequent partial condensation of the ethoxylated species. Castor oil ethoxylates, used for animal feed applications, constitute an interesting example of triglyceride-based surfactants.

Examples of polyhydroxyl (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 Atlas 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, which have found use as antifoam agents, particularly in coatings applications.

Figure 1.7 gives structures of the more common non-ionic surfactants. As mentioned 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 poly(ethylene glycol) and fatty acid as by-products. The single most important type of non-ionic surfactant is fatty alcohol ethoxylates. They are used in liquid and powder detergents as well as in a variety of industrial applications. They are particularly useful to stabilize oil-in-water emulsions and their use as an emulsifier is discussed in some detail in Chapter 21. 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, e.g. aldehydes and hydroperoxides, are more irritating to the skin than the intact surfactant. Throughout this text fatty alcohol ethoxylates are referred to as C_mE_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 non-ionic surfactants are given in Table 1.4.

Table 1.4 Important facts about non-ionic surfactants

1. They are the second largest surfactant class.
2. They are normally compatible with all other types of surfactants.
3. They are not sensitive to hard water.
4. Contrary to ionic surfactants, their physicochemical properties are not markedly affected by electrolytes.
5. The physicochemical properties of ethoxylated compounds are very temperature dependent. Contrary to ionic compounds they become less water soluble—more hydrophobic—at higher temperatures. Sugar-based non-ionics exhibit the normal temperature dependence, i.e. their solubility in water increases with temperature.

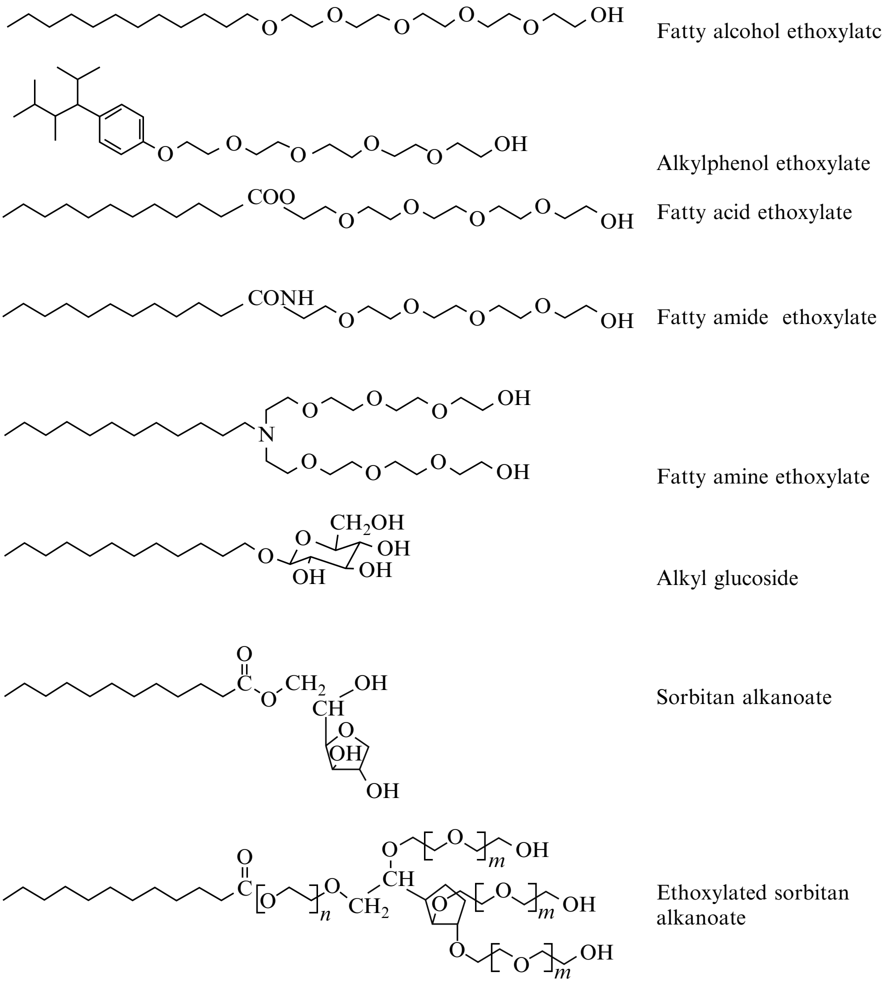
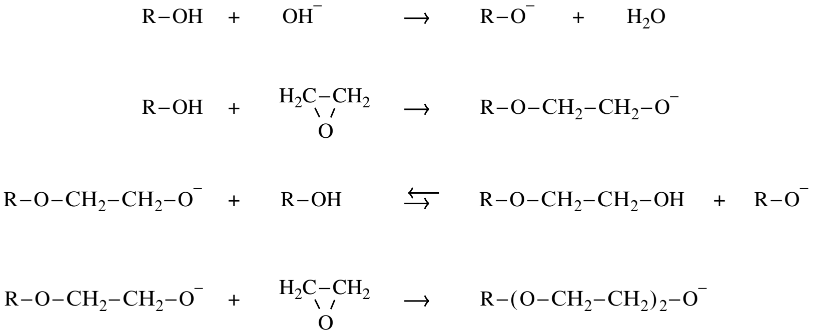


Figure 1.7 Structures of some representative non-ionic surfactants

Ethoxylated surfactants can be tailor-made with high precision with regard to the average number of oxyethylene units added to a specific hydrophobe, e.g. a fatty alcohol. However, the ethoxylation invariably gives a broad distribution of chain lengths. If all hydroxyl groups, i.e. those of the starting alcohol and 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 disfavoured, leading to a lower probability for reaction with ethylene oxide. The reaction scheme is given in Figure 1.8.



$$\text{R-OH} + \text{OH}^- \longrightarrow \text{R-O}^- + \text{H}_2\text{O}$$

$$\text{R-OH} + \underset{\text{O}}{\text{H}_2\text{C-CH}_2} \longrightarrow \text{R-O-CH}_2\text{-CH}_2\text{-O}^-$$

$$\text{R-O-CH}_2\text{-CH}_2\text{-O}^- + \text{R-OH} \leftrightarrows \text{R-O-CH}_2\text{-CH}_2\text{-OH} + \text{R-O}^-$$

$$\text{R-O-CH}_2\text{-CH}_2\text{-O}^- + \underset{\text{O}}{\text{H}_2\text{C-CH}_2} \longrightarrow \text{R-(O-CH}_2\text{-CH}_2)_2\text{-O}^-$$

Figure 1.8 Base catalysed 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 more narrow homologue distribution. The distribution can be affected by the choice of ethoxylation catalyst and it has been found that alkaline earth hydroxides, such as $Ba(OH)_2$ and $Sr(OH)_2$, give a much more narrow distribution than KOH, probably due to some coordination mechanism. Also Lewis acids, e.g. $SnCl_4$ and BF_3, give narrow distributions. Acid catalysed ethoxylation suffers 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.

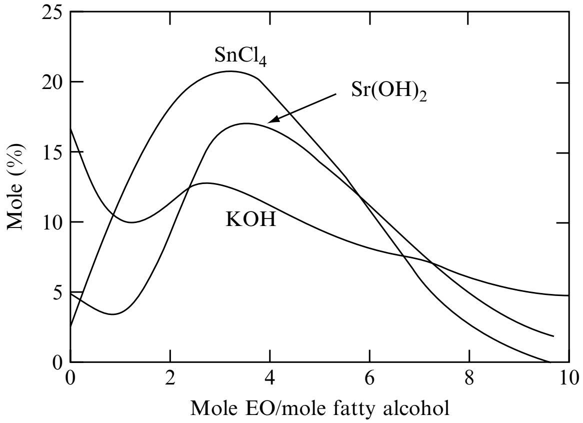


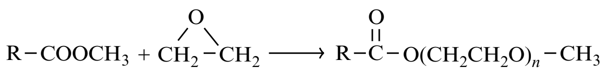
Figure 1.9 Typical homologue distribution of a fatty alcohol reacted with 4 moles of ethylene oxide (EO) using different ethoxylation catalysts

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.

As mentioned in Table 1.4, non-ionic surfactants containing polyoxyethylene chains exhibit reverse solubility versus temperature behaviour 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, and it can be determined with great accuracy. In the manufacture of polyoxethylene-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 non-ionic surfactants is discussed in detail in Chapter 4.

Ethoxylated triglycerides, e.g. castor oil ethoxylates, have an established position on the market and are often regarded as 'semi-natural' surfactants. In recent years there has been a growing interest in fatty acid methyl ester ethoxylates, made from the methyl ester by ethoxylation using a special type of catalyst, e.g. hydrotalcite, a magnesium-aluminium hydroxycarbonate. The methyl ester ethoxylate has the advantage over alcohol ethoxylate in being much more soluble in aqueous solution. Surfactants which 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 a category of niche products. Such 'end-capped' non-ionics 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 characterized by unusually low foaming.

Cationics

The vast majority of cationic surfactants are based on the nitrogen atom carrying the cationic 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 as high pH. Quaternary ammonium compounds, 'quats', on the other hand, are not pH sensitive. Non-quaternary cationics are also much more sensitive to polyvalent anions. As discussed previously, ethoxylated amines (see Figure 1.7) possess properties characteristic of both cationics and non-ionics. The longer the polyoxyethylene chain, than the more non-ionic the character of this surfactant type.

Figure 1.10 shows the structures of some typical cationic surfactants. The ester 'quat' represents a new, environmentally friendly type which to a large extent has replaced dialkyl 'quats' as textile softening agents.

The main synthesis procedure for non-ester quaternary ammonium surfactants is the nitrile route. A fatty acid is reacted with ammonia at high temperature

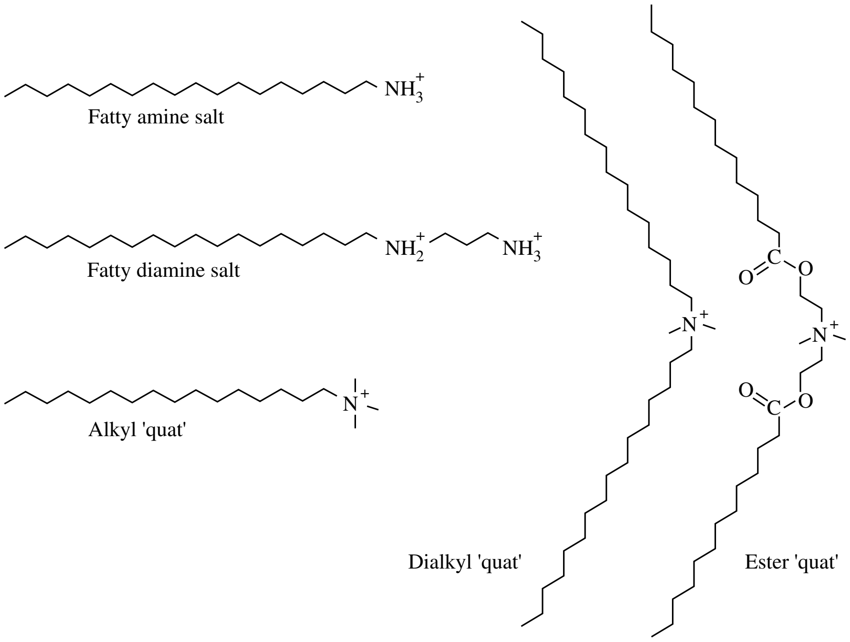


Figure 1.10 Structures of some representative cationic surfactants

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:

$$\mathrm{R{-}COOH + NH_3 \xrightarrow{-H_2O} R{-}C{\equiv}N \xrightarrow{H_2} R{-}CH_2NH_2}$$

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:

$$\mathrm{R{-}C{\equiv}N + R{-}CH_2NH_2 + 2H_2 \longrightarrow (R{-}CH_2)_2NH + NH_3}$$

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

$$\mathrm{R{-}CH_2NH_2 + CH_2{=}CHCN \longrightarrow R{-}CH_2NH(CH_2)_2CN \xrightarrow{H_2} R{-}CH_2NH(CH_2)_3NH_2}$$

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

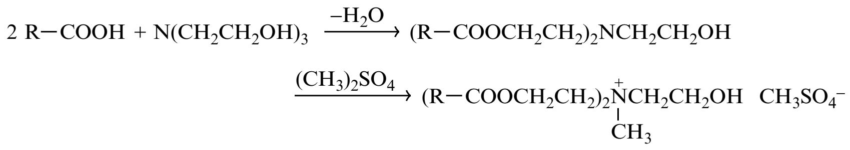
$$\mathrm{(R{-}CH_2)_2NH + HCHO + H_2 \longrightarrow (R{-}CH_2)_2NCH_3}$$

Ethylene oxide can also be used as an alkylating agent to convert primary or secondary amines to tertiary amines with the general structures $\mathrm{R{-}CH_2N(CH_2CH_2OH)_2}$ and $\mathrm{(R{-}CH_2)_2NCH_2CH_2OH}$.

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:

$$\mathrm{(R{-}CH_2)_2NCH_3 + CH_3Cl \longrightarrow (R{-}CH_2)_2N + (CH_3)_2\ Cl^-}$$

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 for triethanol amine as the amine alcohol and dimethyl sulfate as the methylating agent:



$$\mathrm{2\,R{-}COOH + N(CH_2CH_2OH)_3 \xrightarrow{-H_2O} (R{-}COOCH_2CH_2)_2NCH_2CH_2OH}$$

$$\mathrm{\xrightarrow{(CH_3)_2SO_4} (R{-}COOCH_2CH_2)_2\underset{\displaystyle CH_3}{\overset{+}{N}}CH_2CH_2OH\ \ CH_3SO_4^-}$$

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 trialkyl phosphine or dialkyl sulfide, respectively, with alkyl chloride, as is shown for phosphonium surfactant synthesis:

$$R_3P + R'X \longrightarrow R_3P^+{-}R'\ X^-$$

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. Surface active phosphonium surfactants carrying one long-chain alkyl and three methyl group have found use as biocides.

The majority of surfaces, metals, minerals, plastics, fibres, cell membranes, etc., are negatively charged. The prime uses of cationics relate to their tendency to adsorb at these surfaces. In doing so they impart special characteristics to the surface. Some examples are given in Table 1.5, while some important facts about cationic surfactants are given in Table 1.6.

Table 1.5 Applications of cationic surfactants related to their adsorption at surfaces

Surface	Application
Steel	Anticorrosion agent
Mineral ores	Flotation collector
Inorganic pigments	Dispersant
Plastics	Antistatic agent
Fibres	Antistatic agent, fabric softener
Hair	Conditioner
Fertilizers	Anticaking agent
Bacterial cell walls	Bactericide

Table 1.6 Important facts about cationic surfactants

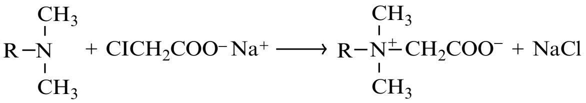
1. They are the third largest surfactant class.
2. They are generally not compatible with anionics (although there are important exceptions).
3. Hydrolytically stable cationics show higher aquatic toxicity than most other classes of surfactants.
4. They adsorb strongly to most surfaces and their main uses are related to *in situ* surface modification.

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 p. 0, the terms are not identical. An amphoteric surfactant is one that changes from net cationic via zwitterionics to net anionic on going from low to high pH. Neither the acid nor the base site is permanently charged, i.e. the compound is only zwitterionic over a certain pH range.

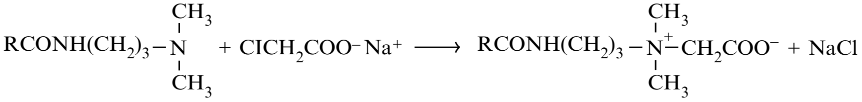
The change in charge with pH of the truly amphoteric surfactants naturally affects properties such as foaming, wetting, detergency, etc. These will all depend strongly on solution pH. At the isoelectric point the physicochemical behaviour often resembles that of non-ionic surfactants. Below and above the isoelectric point there is a gradual shift towards the cationic and anionic character, respectively. Surfactants based on sulfate or sulfonate to give a negative charge remain zwitterionic down to very low pH values due to the very low pK_a values of monoalkyl sulfuric acid and alkyl sulfonic acid, respectively.

Common types of zwitterionic surfactants are *N*-alkyl derivatives of simple amino acids, such as glycine (NH_2CH_2COOH), betaine ($(CH_2)_2NCH_2COOH$) and amino propionic acid ($NH_2CH_2CH_2COOH$). 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 alkyldimethyl amine with sodium monochloroacetate:



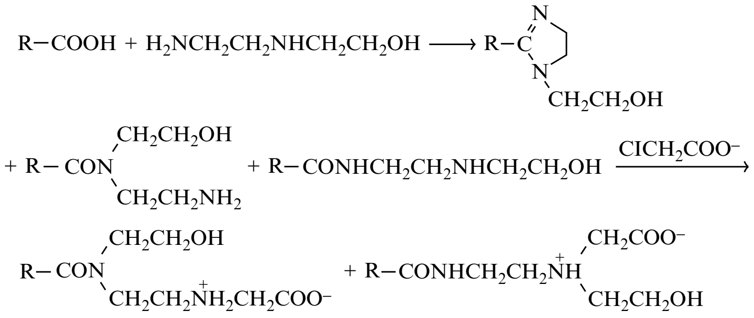
$$R-\overset{CH_3}{\underset{CH_3}{N}} + ClCH_2COO^-Na^+ \longrightarrow R-\overset{CH_3}{\underset{CH_3}{N^{\pm}}}-CH_2COO^- + NaCl$$

Amidobetaines are synthesized analogously from an amidoamine:



$$RCONH(CH_2)_3-\overset{CH_3}{\underset{CH_3}{N}} + ClCH_2COO^-Na^+ \longrightarrow RCONH(CH_2)_3-\overset{CH_3}{\underset{CH_3}{N^{+}}}-CH_2COO^- + NaCl$$

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



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 non-ionics, 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 Table 1.7 summarizes some general information about this surfactant class. As mentioned previously, amine oxide surfactants, or more correctly *N*-oxides of tertiary amines, are sometimes categorized as zwitterionics, sometimes as non-ionics and sometimes as cationics. They have a formal charge separation on the nitrogen and oxygen atoms. They basically behave as non-electrolytes, but at low pH or in the presence of anionic surfactants they will pick up a proton to form the cationic conjugate acid. 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.

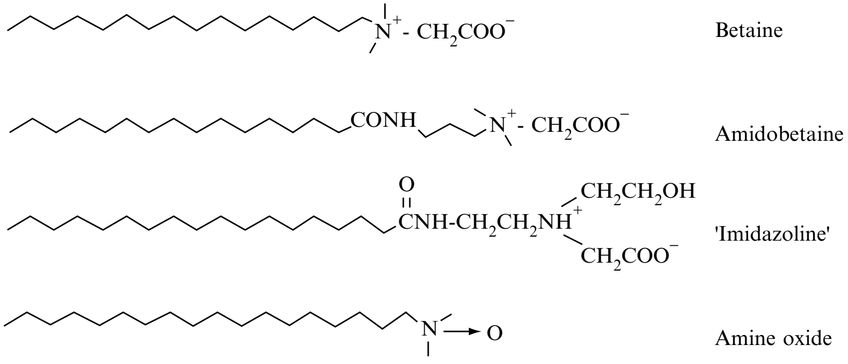


Figure 1.11 Structures of some representative zwitterionic surfactants

Table 1.7 Important facts about zwitterionic surfactants

1. They are the smallest surfactant class (partly due to high price).
2. They are compatible with all other classes of surfactants.
3. They are not sensitive to hard water.
4. They are generally stable in acids and bases. In particular, the betaines retain their surfactant properties in strong alkali.
5. Most types show very low eye and skin irritation. They are therefore well suited for use in shampoos and other personal care products.

Dermatological Aspects of Surfactants are Vital Issues

The dermatological effects of surfactants are important issues which are subject to much current concern. A large fraction of dermatological problems in normal working life can be related to exposure of unprotected skin to surfactant solutions. These solutions are often cleaning formulations of different kinds but may also be cutting fluids, rolling oil emulsions, etc. Skin irritation of various degrees of seriousness are common, and in rare cases allergic reactions may also appear. Whereas skin irritation is normally induced by the surfactant itself, the sensitization causing the allergic reaction is usually caused by a by-product. A well-known example of a severe allergic reaction is the so-called 'Margarine disease' which struck The Netherlands in the 1960s and which was subsequently traced to a by-product of a new surfactant which had been added to a margarine brand as an anti-spattering agent, i.e. a surfactant that keeps the water droplets finely dispersed during frying. Sensitizing agents are electrophiles which react with the nucleophilic groups of proteins, creating unnatural protein derivatives which the body then detects as foreign. The margarine surfactant contained an appreciable amount of an unreacted intermediate, a maleic anhydride derivative, which could be ring-opened in the body by protein amino or thiol groups.

The physiological effects of surfactants on the skin are investigated by various dermatological and biophysical methods, starting with the surface of the skin and progressing via the horny layer and its barrier function to the deeper layer of the basal cells. At the same time, subjective sensations, such as the 'feeling' of the skin, are recorded by verbalization of tactile sense and experience. Surfactant classes that are generally known to be mild to the skin are polyol surfactants, e.g. alkyl glucosides, zwitterionic surfactants, e.g. betaines and amidobetaines, and isethionates. Such surfactants are frequently used in cosmetics formulations.

For homologous series of surfactants there is usually a maximum in skin irritation at a specific chain length of the hydrophobic tail. For instance, in a comparative study of alkyl glucosides in which the C8, C10, C12, C14 and C16 derivatives were evaluated, a maximum irritation effect was obtained with the C12 derivative. Such a maximum is normally also obtained when it comes to the biocidal effects of surfactants. This probably reflects the fact that the biological effect, caused by surfactant action on the mucous membrane or the bacterial surface, respectively, is favoured by high surface activity and high unimer concentration. Since an increasing chain length of the hydrocarbon tail of the surfactant leads to an increased surface activity and to a reduced CMC, i.e. a reduced unimer concentration, there will somewhere be an optimum in hydrocarbon chain length (assuming the same polar head group for all surfactants).

Alcohol ethoxylates are relatively mild surfactants but not as mild as polyol-based non-ionics, such as, for instance, alkyl glucosides. Recent investigations have revealed that the dermatological effect seen with alcohol ethoxylates may not be caused by the intact surfactant but by oxidation products formed during storage. All ethoxylated products have been found to undergo autoxidation to give hydroperoxides on the methylene groups adjacent to the ether oxygen. Hydroperoxides formed at methylene groups in the polyoxyethylene chain seem to be too unstable to be easily isolated. The hydroperoxide with the OOH group at carbon number 2 of the hydrophobic tail is relatively stable, however, and has been isolated in an amount of around 1% after storage of a normal fatty alcohol ethoxylate for one year. This hydroperoxide exhibited considerable skin irritation. Another oxidation product of some dermatological concern that has been isolated is the surfactant aldehyde shown below. This aldehyde is not very stable, however, and further oxidation leads to a break-down of the polyoxyethylene chain with formaldehyde formed as one of many degradation products. Both the surfactant aldehyde and formaldehyde are irritating to the skin and eye:

$$\begin{aligned}&C_nH_{2n+1}(OCH_2CH_2)_{m+1} \longrightarrow C_nH_{2n+1}(OCH_2CH_2)_m - CH_2CHO\\&\longrightarrow HCHO + \text{ other degradation products}\end{aligned}$$

An indirect way to monitor the autoxidation of alcohol ethoxylates is to measure the change in cloud point with time. Figure 1.12 shows an example of such a storage test. As can be seen from this figure, both of the surfactants investigated show a considerable drop in cloud point on storage at 40°C.

Anionic surfactants are, in general, more skin irritating than non-ionics. For instance, sodium dodecyl sulfate (SDS), although used in some personal care products such as tooth pastes, has relatively high skin toxicity. Sodium alkyl ether sulfates are much milder than sodium alkyl sulfates which is one of the reasons why the ether sulfates are the most commonly used anionic surfactant in hand dishwashing formulations. (Their good foaming ability is another reason for their widespread use in such products.) The better dermatological characteristics of alkyl ether sulfates when compared to alkyl sulfates is one of the main reasons for the interest in ethoxylates with narrow homologue

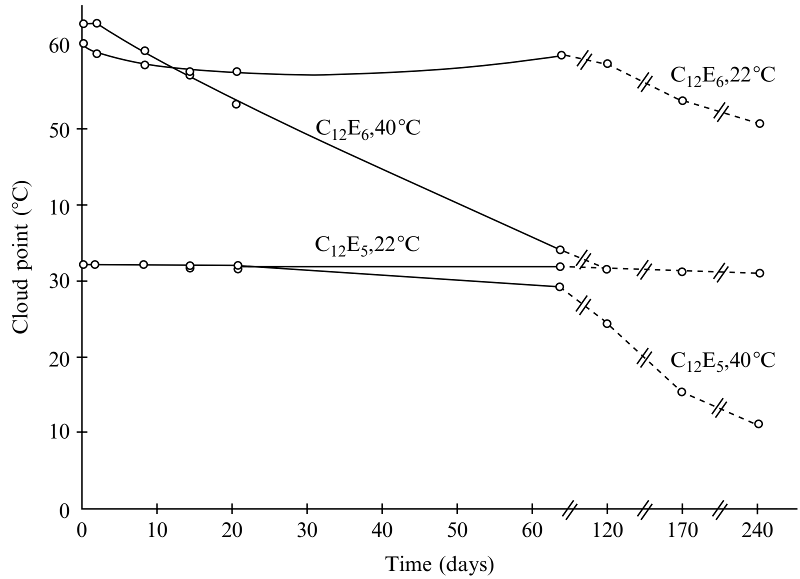


Figure 1.12 Cloud point versus time curves for the storage of 1% solutions of the surfactants $C_{12}E_5$ and $C_{12}E_6$, both 'homologue pure', measured at two different temperatures

distributions, i.e. 'peaked ethoxylates', as discussed above. With a peaked ethoxylate as the intermediate to be sulfated, the content of the more aggressive alkyl sulfate will be considerably lower than when a standard ethoxylate with a broad homologue distribution is used.

The effect of surfactants on the skin is often evaluated in the so-called modified Duhring chamber test. Figure 1.13 shows some typical results obtained for a sodium alkyl ether sulfate (sodium laureth sulfate), an alkyl glucoside (decyl glucoside) and combinations of the two. As can be seen, the skin irritation decreases relatively linearly with increasing amount of polyol surfactant. In other cases, already small additions of a mild surfactant may cause very large improvements in the dermatological properties. Such a 'synergistic effect' is probably related to a strong reduction in the CMC of the formulation due to mixed micelle formation. Some amphoteric surfactants, such as betaines, are known to give a very pronounced reduction of the skin irritation of anionics such as alkyl ether sulfates. This is probably due to a protonation of the carboxyl group of the betaine surfactant, transforming it into a cationic surfactant, and subsequent packing into mixed micelles together with the anionic surfactant. Thus, the energy gain in the mixed micelle formation (see Chapter 5) induces protonation of the carboxylate group of the betaine surfactant already at a pH level far above the pK_a value.

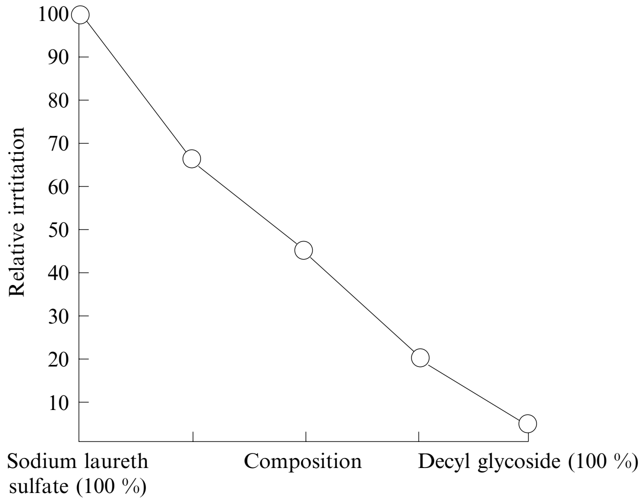


Figure 1.13 Modified Duhring chamber test with relative irritation scores for erythema formation. Reproduced by permission of Wiley-VCH from Hill, K., von Rybinski, W. and Stoll, G., *Alkyl Polyglycosides: Technology, Properties and Applications*, Wiley-VCH, Weinheim, 1997

The Ecological Impact of Surfactants is of Growing Importance

Although concern about the ecological impact of surfactants has been enshrined in legislation for more than 20 years, it is only recently that the issue has become a major factor in all formulation work involving surfactants. Most of the surfactants used in households and in industry go into the sewers. The rate of biodegradation in the sewage plant will determine the volume of surfactant that reaches the environment. The rate of biodegradation, in combination with the degree of aquatic toxicity, will determine the environmental impact. The OECD has issued guidelines and directives regarding:

Aquatic toxicity
Biodegradability
Bioaccumulation

Aquatic Toxicity

Aquatic toxicity may be measured on fish, daphnia or algae. Toxicity is given as LC_{50} (for fish) or EC_{50} (for daphnia or algae), where LC and EC stand for lethal and effective concentrations, respectively. Values below 1 mg/1 after 96 h testing on fish and algae and 48 h on daphnia are considered toxic. Environmently benign surfactants should preferably be above 10 mg/1.

Biodegradability

Biodegradation is a process carried out by bacteria in nature. By a series of enzymatic reactions, a surfactant molecule is ultimately converted into carbon dioxide, water and oxides of the other elements. If a product does not undergo natural biodegradation then it is stable and persists in the environment. For surfactants the rate of biodegradation varies from 1–2 h for fatty acids, via 1–2 days for linear alkylbenzene sulfonates, to months for branched alkylbenzene sulfonates.

In all testing of biodegradation it is important to realize that the rate of degradation depends on factors such as concentration, pH and temperature. The temperature effect is particularly important. The rate at which chemicals are broken down in sewage plants may vary by as much as a factor of five between summer and winter in Northern Europe.

Two criteria are of importance with respect to testing for biodegradation: primary degradation and ultimate degradation. Primary degradation of surface active agents relates to the loss of surfactants properties. For instance, an ester surfactant may rapidly break down into alcohol and acid, neither of which is very surface active. This type of test is of interest for specific purposes, e.g. to be able to predict whether or not a product persists in giving foams on rivers.

More important from an ecological point of view is the test for ultimate biodegradation. A plethora of test methods exists for so-called ready biodegradability. In most of these, such as the popular modified Sturm test (OECD Test 301 B for ultimate biodegradation), conversion into carbon dioxide is measured as a function of time. The test is performed in closed bottles to which samples of sludge from a sewage plant have been added. The surfactant is added to one set of bottles, while another set of bottles without added surfactant is used as the reference. The gas produced is monitored with time and the difference obtained between the two sets of bottles is related to the degradation of the surfactant. With most surfactants there is an induction period followed by a steep rise of the curve and then an abrupt levelling off. A typical test result, together with the criteria that must be fulfilled to pass the test, are given in Figure 1.14.

Bioaccumulation

Hydrophobic organic compounds are persistent in nature since all biodegradation requires some kind of aqueous environment. Bioaccumulation can be measured directly in fish but is more often calculated from a model experiment. Partitioning of the compound between two phases, octanol and water, is measured and the logarithm of the value obtained, log P, is used. (This is a common procedure for assigning hydrophobicity value to organic substances and tables of log P values are available in the literature.) A surfactant is considered to bioaccumulate if:

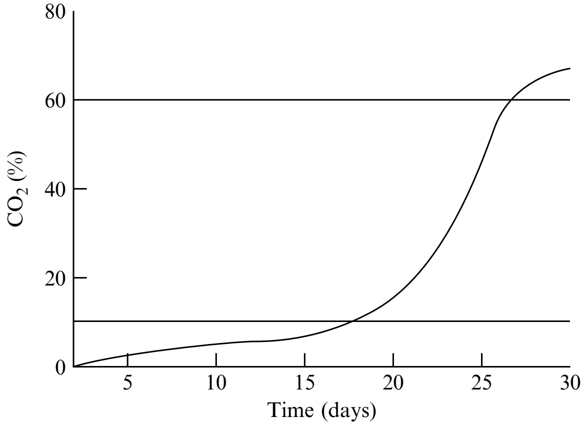


Figure 1.14 Criteria needed to pass the test for ready biodegradability and a typical example of a degradation curve. Note the long induction period before the degradation 'takes off'

$$\log P_{\text{oct/w}} > 3$$

The vast majority of surfactants have log *P* values below 3. Bioaccumulation, therefore, is not considered to be a crucial issue.

Log *P* values for many surfactants have been collected. It has been found that these values can be used as an indication of the surfactant hydrophilicity; the lower the log *P* value, then the higher the hydrophilicity. Values of surfactant hydrophilicity are often helpful in formulation work. A more well-known standard for the same purpose is the hydrophilic – lipophilic balance (HLB) concept which is widely used in the selection of emulsifiers. The HLBs of surfactants are discussed in some detail in Chapter 21. There is a reverse relationship between log *P* and the HLB, i.e. the higher the HLB value, then the lower the log *P* value. The critical packing parameter (CPP) concept (see Chapter 2) is yet another way to assign a number to the surfactant hydrophilicity.

Labelling

In the OECD guidelines for the labelling of surfactants, values of aquatic toxicity and ready biodegradation are taken into account. Figure 1.15 illustrates the procedure. Many of the commonly used surfactants today are borderline cases. There is a clear trend to replace these by compounds positioned 'upwards and right' in the diagram.

Tests for aquatic toxicity, ready biodegradation and bioaccumulation by no means give the complete picture of the environmental impact of a surfactant. A number of other relevant parameters are listed in Table 1.8. In addition, the

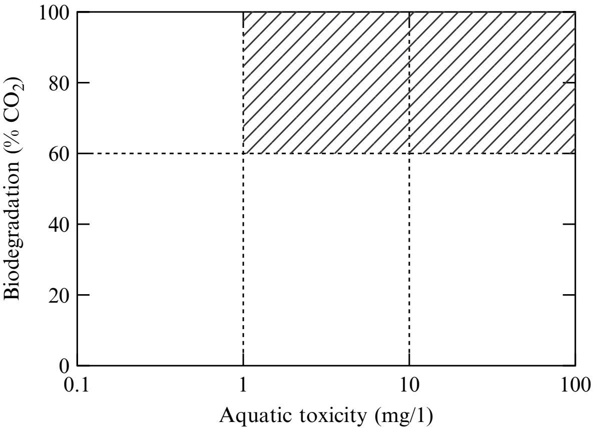


Figure 1.15 Environmental ranking of surfactants is based on the values of ready biodegradation and aquatic toxicity. The shaded areas of the diagram are 'approved areas'

Table 1.8 Relevant factors besides aquatic toxicity, ready biodegradability and bioaccumulation for assessment of surfactant ecotoxicity

1. Anaerobic biodegradation (alkylbenzene sulfonates, alkylphenol ethoxylates and EO–PO block copolymers are examples of surfactants with very slow anaerobic biodegradation).
2. Chronic toxicity.
3. Effect on function of sewage plants.
4. Toxicity in the production of surfactants.
5. Life cycle aspects.
6. Technical effect, i.e. the more effective the surfactant, then the smaller the amount needed; therefore, biotoxicity per effect unit is the relevant measure (this is particularly relevant for the formulated end-product).

formulated end-product often contains mixtures of surfactants or a blend of surfactant and polymer. Since it is well-known that the physicochemical behaviour of a surfactant may be very different in such mixtures than alone in solution, it is reasonable to believe that the biological effects may also be different. In order to obtain the full picture, ecological tests should be carried out on each individual end-product.

The Rate of Biodegradation Depends on Surfactant Structure

Several parameters are of importance for the rate of biodegradation of a surfactant. First of all, the surfactant needs to have a reasonable solubility in water. Very lipophilic amphiphiles such as fluorinated surfactants accumulate in lipid compartments in organisms and break down very slowly. As discussed above, most surfactants have a high enough water solubility that bioaccumulation of the intact molecule is not a problem. However, the initial degradation may lead to intermediates with very limited water solubility. A well-known example of this is the class of alkylphenol ethoxylates which degrade by oxidative cleavage from the hydroxyl end of the polyoxyethylene chain. This means that alkylphenol ethoxylates with polar head groups of just a few oxyethylene units will form. These are very lipophilic and biodegrade at a very slow rate. Analysis of fish in waters exposed to nonylphenol ethoxylates have shown high levels of nonylphenol with two and three oxyethylene units in lipid tissues. Such findings were one of the reasons for the strong concern about the environmental effects of this surfactant class. Fatty alcohol ethoxylates probably break down via many different pathways (oxidation at the terminal end of the polyoxyethylene chain, oxidation of the terminal end of the alkyl chain, and central cleavage to give fatty alcohol and poly(ethylene glycol)), with the result being that lipophilic metabolites are not formed in large amounts.

Besides water solubility, it is essential that the surfactant contains bonds that can be easily broken down by enzymatic catalysis. Most, if not all, chemical bonds will ultimately break down in nature but it is important that the rate is high enough so that unacceptable concentrations of a surfactant or its metabolites are not generated in the environment. In order to speed up the rate of biodegradation it has now become common practice to build a weak bond into the surfactant structure. Such easily cleavable bonds may be placed randomly in a surfactant but for synthesis reasons they are usually inserted between the hydrophobic tail and the polar head group. Typical examples of such bonds are esters and amides, the breakdown of which are catalysed by esterases/lipases and peptidases/acylases, respectively. The concept of surfactants with easily cleavable bonds is discussed in some detail in Chapter 11. One may have anticipated the ether bond of non-ionic surfactants to be a problem since ether-splitting enzymes are not common in nature. This is evidently not the case, however. Under aerobic conditions, hydroperoxides are generated in the α-position to the ether bond and the breakdown proceeds from there via aldehydes and acids.

A third factor to take into account in addition to water solubility and the presence of cleavable bonds is the degree of branching of the non-polar part of the surfactant molecule. Extensive branching of the hydrocarbon tail often leads to a reduced rate of biodegradation. This is probably due to the side chains causing steric hindrance in the approach of the surfactant into the active site of the enzyme. However, the picture is far from clear. Some branching patterns seem to be more troublesome than others and the effect is probably specific to the enzyme in question. It seems that methyl branching is less of a problem than branching involving longer alkyl chains, but if many methyl branchings appear in a row, such as in poly(propylene glycol) derivatives, they are still problematic. A very good example of the importance of linearity of alkyl chains is the difference in the rates of biodegradation between alkylbenzene sulfonates with linear or branched alkyl chains. As mentioned briefly above, branched alkylbenzene sulfonates, which are based on tetra-1,2-propylene as the alkyl chain, were once the bulk surfactant in household detergents—cheap, efficient and chemically stable—but too stable in the environment. When environmental aspects became an issue in the 1960s and 1970s, these surfactants were rapidly replaced by their counterparts with linear alkyl chains. The linear alkylbenzene sulfonates break down satisfactorily under aerobic conditions. Their rate of unaerobic biodegradation is relatively slow, however, a fact which is currently subject to some concern. In addition, the position of the branching along a hydrocarbon chain seems to be critical. Branching on a carbon two atoms away from a cleavable bond (such as in 2-ethylhexyl ethers, carboxylic esters, acetals and sulfates) is less harmful than branching on the carbon one atom away. This is of importance because the oxo alcohols, which are widely used as surfactant raw materials, contain a large proportion of 2-alkyl branching. It has also been found that the length of the 2-alkyl side chain has a negligible effect on the rate of biodegradation. However, considerably more work is needed before one is able to predict the biodegradation characteristics from inspection of the chemical formula of a surfactant alone.

Environmental Concern is a Strong Driving Force for Surfactant Development

All major types of surfactants, i.e. alkylbenzene sulfonates, alkyl sulfates, alcohol ethoxylates, etc., have been around for decades. Their routes of preparation have been carefully optimized and their physicochemical behaviour is relatively well understood. Besides the constant challenge of finding ways to minimize the manufacturing cost for existing surfactants, the market pull for ‘greener’ products has been the overriding driving force for surfactant development in later years. Clear trends in current developments are (i) to synthesize the surfactant from natural building blocks, and (ii) to make cleavable surfactants. Cleavable surfactants are covered in Chapter 11. Below is a brief account of current developments in the area of surfactants produced from natural building blocks.

The Polar Head Group

Two main types of natural products have been investigated as surfactant polar head groups, namely sugars and amino acids. Surfactants can be made from both by either organic synthesis or enzymatic synthesis, or by a combination of the two. The most interest has been directed towards sugar-based surfactants and this area will be presented below.

In recent years there has been a focus on three classes of surfactants with sugar or a polyol derived from sugar as the polar head group: alkyl polyglucosides (APGs), alkyl glucamides and sugar esters. Representative structures of the three surfactant types are shown in Figure 1.16.

There is currently a very strong interest in exploring alkyl polyglucosides (APGs) as surfactants for several types of applications. APGs are synthesized by the direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Alternatively, they are made by transacetalization of a short-chain alkyl glucoside, such as ethyl or butyl glucoside, with a long-chain alcohol. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction is used as the starting material. Figure 1.17 illustrates the synthesis. Alkyl glucosides can also be made by enzymatic synthesis, using β-glucosidase as the catalyst, which yields only the β-anomer (and gives low yield). The corresponding α-anomer can more readily be obtained by β-glucosidase catalysed hydrolysis of the racemate. There are considerable differences between the α, β mixture obtained by organic synthesis and the pure enantiomers obtained by the bio-organic route.

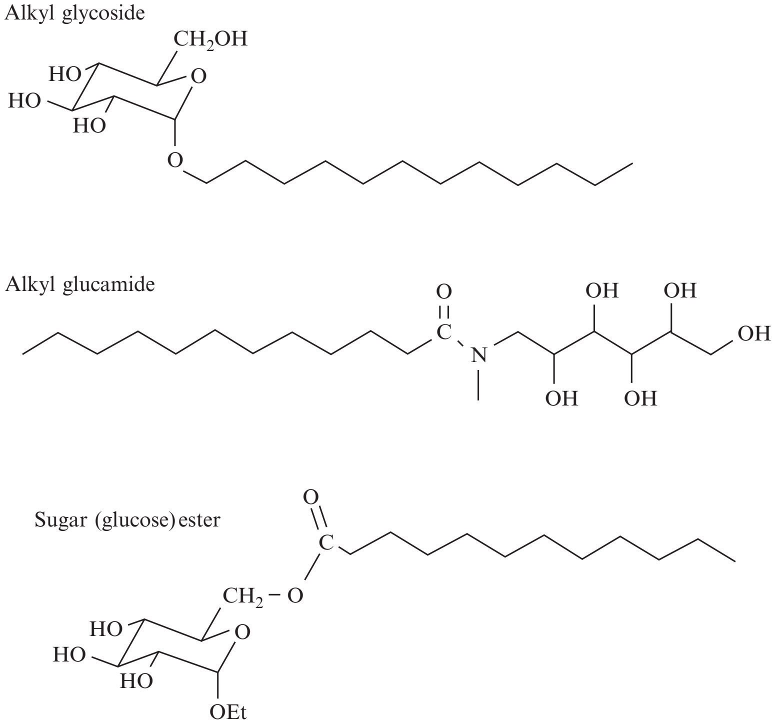


Figure 1.16 Structures of some representative polyol surfactants

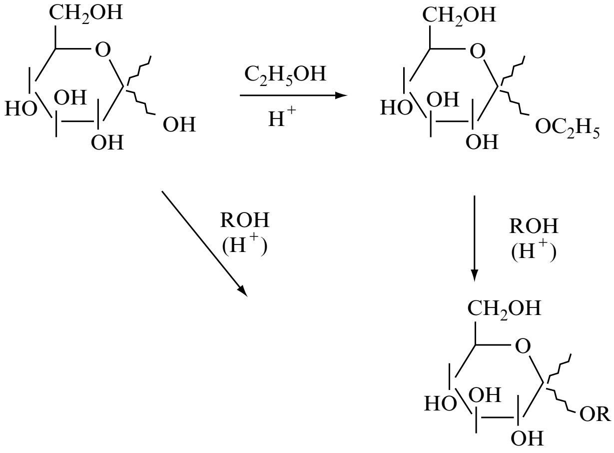


Figure 1.17 Routes of preparation of alkyl glucoside surfactants

The β-anomer of *n*-octyl glucoside has found use as a surfactant in biochemical work.

Alkyl glucosides are stable at high pH and sensitive to low pH where they hydrolyse to sugar and fatty alcohol. A sugar unit is more water-soluble and less soluble in hydrocarbons than the corresponding polyoxyethylene unit; hence, APGs and other polyol-based surfactants are more lipophobic than their polyoxyethylene-based surfactant counterparts. This makes the physicochemical behaviour of APG surfactants in oil–water systems distinctly different from that of conventional non-ionics. Furthermore, APGs do not show the pronounced inverse solubility vs. temperature relationship that normal non-ionics do. This makes an important difference in solution behaviour between APGs and polyoxyethylene-based surfactants. The main attractiveness of APGs lies in their favourable environmental profile: the rate of biodegradation is usually high and the aquatic toxicity is low. In addition, APGs exhibit favourable dermatological properties, being very mild to the skin and eye. This mildness makes this surfactant class attractive for personal care products, although APGs have also found a wide range of technical applications.

Alkyl glucamides (see Figure 1.16), more strictly named as *N*-alkanoyl-*N*-methylglucamines, are commercially important products. The product sold in large quantities for the detergent sector is *N*-dodecanoyl-*N*-methylglucamine, i.e. the C12-derivative. This product is prepared from glucose, methyl amine, hydrogen and methyl laurate by a two-step reaction. The physicochemical properties and many other characteristics of this surfactant class are similar to those of APGs. However, whereas alkyl glucosides are very stable to alkali and labile to acids, alkyl glucamides are stable to alkali and also relatively stable to acids.

Esters of glucose (see Figure 1.16) can be made either by enzymatic synthesis, using a lipase catalyst, or by an organic chemical route. Using the right enzyme the bio-organic route can give esterification almost exclusively at the 6-position of the sugar moiety. The organic synthesis requires extensive use of protecting groups to obtain high selectivity. The selective enzymatic synthesis of sugar esters other than glucose has been difficult to achieve without the use of protective groups. Starting from sugar acetals and fatty acids, monoesters of sugars can be obtained in good yield, after a deprotection step, from several starting materials, both mono-and disaccharides. All sugar esters are very labile on the alkaline side and fairly stable to acid. Their degradation products, i.e. sugar and fatty acids, are both very natural products; thus, sugar esters are ideal candidates as food surfactants. Sugar esters seem to undergo rapid biodegradation regardless of the sugar head group size or the acyl chain length. Sulfonated sugar esters have also been prepared. These anionic surfactants were found to undergo less rapid biodegradation.

Polyol surfactants have many attractive propeties: they are mild to the skin, they exhibit a low aquatic toxicity and a high rate of biodegradation, and they are easy to work with in that they show good tolerance to high electrolyte concentrations. Some characteristic properties of polyol surfactants in general are summarized in Table 1.9.

The Hydrocarbon Tail

Fatty acids are the first choice of a natural hydrophobe for surfactants. Fatty acids have been used for a long time, e.g. in fatty acid ethoxylates and in sorbitan esters of fatty acids. In recent years there has been increased interest in fatty acid monoethanolamide ethoxylates, or fatty amide ethoxylates. These surfactants are easily prepared by ethoxylation of the fatty acid monoethanolamide. The ethanolamide, in turn, is prepared by aminolysis of the fatty acid methyl ester by ethanolamine. The fatty amide ethoxylates are of interest as an alternative to fatty alcohol ethoxylates for several reasons: (i) they biodegrade readily to fatty acids and amino-terminated poly(ethylene glycols), (ii) the

Table 1.9 Characteristics of polyol surfactants

1. Aerobic and anaerobic biodegradation is fast.
2. Aquatic toxicity is low.
3. Hydroxyl groups are strongly lipophobic. At the same time, surfactants with long enough hydrocarbon chains are strongly hydrophobic. Polyol surfactants therefore have a high tendency to remain at the oil–water interface.
4. The effect of temperature on solution behaviour is small and opposite to that of ethoxylates. Mixtures of polyol surfactants (larger fraction) and ethoxylates (smaller fraction) can be formulated so that a non-ionic surfactant with phase behaviour unaffected by temperature is obtained.

amide bond in the structure may improve surfactant packing due to hydrogen bond formation, and (iii) double bonds in the fatty acid chain can be preserved in the product (although during the ethoxylation step 1,3-*cis*, *cis*-double bonds undergo migration to conjugated *trans*, *cis* structures).

Double bonds in the hydrocarbon tail have been found to increase the CMC. This may partly be due to the surfactants becoming more hydrophilic and partly to the increased bulkiness of the chains, thus rendering packing into closed aggregates and formation of hydrogen bonds between the amide groups more difficult. The presence of one double bond, *cis* (oleyl) or *trans* (elaidyl), does not greatly affect the molecular cross-sectional area at the surface. Two double bonds give much larger areas, however. Fatty amide ethoxylates with double bonds in the hydrocarbon tail are of interest as polymerizable surfactants, as is discussed further in Chapter 11.

Sterols are another class of natural hydrophobes of potential interest as surfactant building blocks. The special feature of sterol-based surfactants is the large hydrophobic group of fully natural origin which, due to its rather planar four-ring structure, may induce good packing at interfaces. Phytosterol is the common name for sterols of plant origin and they are already today used as surfactant raw materials. Their structure is similar to that of cholesterol, the prime example of sterols from animal sources. The sterols contain a secondary hydroxyl group that can be ethoxylated. The alcohol is sterically hindered, however, and the reaction with ethylene oxide is not straightforward. The best procedure seems to be to start the ethoxylation with a Lewis acid catalyst, cease the reaction after 3–5 moles of ethylene oxide have been added, and continue with KOH as initiator.

Sterol ethoxylates are large, stiff molecules. They need a long time to reach an equilibrium position at an interface. The decay of surface tension can take hours. Most likely, the long equilibrium time is due to exchange reactions of sterol ethoxylates with varying polyoxyethylene chain lengths at the air–water interface and to slow conformational changes of individual molecules at the surface. The multi-ring structure of sterols is rigid and the time required to adapt a favourable conformation at an interface may be long. Sterol surfactants are of interest as solubilizers and emulsifiers in drug and cosmetics applications.

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