Surfactants

KURT KOSSWIG, Hüls AG, Marl, Federal Republic of Germany

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

1. Interfacial Phenomena [9–11]

Forces holding the particles of a condensed phase together (cohesive forces) become anisotropic in the phase boundary region, and their normal component becomes smaller compared to the parallel component. To simplify the description and facilitate theoretical treatment, the properties of the boundary region of a condensed phase are projected onto a two-dimensional surface (Gibbs "dividing surface"). The tensile stress resulting from the anisotropic forces in the boundary region is then termed the interfacial tension. This quantity corresponds to the reversible work required to bring particles from the volume phase to the interface during enlargement of the former, and thus corresponds to the increase in free enthalpy of the system per unit surface area:

$$\left(\frac{\mathrm{d}G}{\mathrm{d}F}\right)_{P,T} = \gamma$$

where G is the free enthalpy, F the surface area, and γ the interfacial tension.

The unit of interfacial tension is accordingly $N \cdot m/m^2$, i.e., N/m, and is normally expressed as mN/m. The interfacial tension in most cases decreases with increasing temperature and with increasing pressure.

Interfaces exist between all contacting but immiscible phases; in current usage the term interface is understood to mean the contact region of two condensed phases, whereas the term surface refers to the boundary region between a condensed phase and a gas. Surface tensions of liquids and interfacial tensions between two liquid phases can easily be measured. The capillary rise of a liquid in a capillary tube can be used to calculate the surface tension of a liquid if the walls of the capillary tube are completely wetted by the liquid (capillary attraction).

The value of γ can be obtained directly by measurement of the force required to enlarge the surface or interface between two liquids over a specific length. A small wettable measuring plate (Wilhelmy plate) or a ring slowly withdrawn from the liquid (Lecomte du Noüy tensiometer) is used for this purpose. In the droplet-volume method the volume of a droplet released from a capillary tube, which is directly proportional to the interfacial tension, is measured. The surface tension of a liquid can also be determined by measuring the maximum pressure in air bubbles forced through a capillary tube into a liquid, this pressure being directly proportional to the surface tension. Extremely low interfacial tensions in the range from 10^{-1} to 10^{-5} mN/m can be measured with a spinning drop tensiometer, in which a droplet of the lighter phase is suspended in the heavier liquid contained in a rotating capillary [12], [13]. Also, capillary wave spectroscopy is used to measure the interfacial tension between two liquids [14].

In the equilibrium state only very small energy interactions occur between the particles at the surface of a condensed phase and those of the gaseous phase. The surface tension can therefore be regarded simply as an expression of the interactions between the particles in the surface of the condensed phase. However, at the interface between two condensed phases interactions between the particles of the two phases occur through the interface, resulting in a reduction of the interfacial tension. When examining the interactions between the particles of condensed phases a distinction has to be made between London dispersion forces and polar forces. Accordingly, the surface tension comprises components that may be attributed to pure dispersion forces (γ_d) and to polar interaction (γ_p):

$$\gamma = \gamma_d + \gamma_p$$

For example, water has a surface tension of 72.8 mN/m, composed of 21.8 mN/m for γ_d and 51.0 mN/m for γ_p.

In contrast, alkanes and also polyethylene have no surface tension attributable to polar forces, and in this case $\gamma = \gamma_d$. If one of the phases at an interface is completely nonpolar, then the interaction through the interface is restricted to dispersion forces and the interfacial tension between two condensed phases is given by Fowkes equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_{d1}\gamma_{d2}}$$

The equation includes the polar component of the surface tension if polar interactions also act through the interface:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\sqrt{\gamma_{d1}\gamma_{d2}} + \sqrt{\gamma_{p1}\gamma_{p2}})$$

If a droplet of a liquid is brought into contact with the surface of a first liquid – the two liquids being immiscible – two phenomena can occur, depending on the magnitude of γ_{12}. If γ_{12} is smaller than ($\gamma_1 - \gamma_2$), the second liquid spreads over the surface of the first liquid in the form of a thin (in the limiting case monomolecular) film. The liquid that has spread exerts a surface pressure π in the opposite direction to the surface tension γ_1 of the underlying phase, resulting in a reduced surface tension γ'_1 of this phase:

$$\gamma_1 - \pi = \gamma'_1$$

The surface tension γ'_1 can be measured by the aforementioned methods, and the surface pressure π by a Langmuir surface balance, which measures the force acting on a barrier that restricts the spreading film. If the particles of the spread liquid are sufficiently far apart, the liquid film behaves as a two-dimensional gas described by the equation of state:

$$\gamma F = RT$$

where F is the available surface, R the gas constant, and T the temperature. Such a surface film is elastic. If the film is compressed, a region characterized by a sharp increase in surface pressure is reached since the forces of repulsion between the particles then come into play. This region corresponds to the state of a condensed liquid. On compressing the surface film further the latter may finally break up due to furrow formation, layer stacking, etc., whereupon the surface pressure decreases.

If the interfacial tension γ_{12} between a first liquid having a surface tension γ_1 and a second liquid having a surface tension γ_2 applied as a droplet to the surface of the first liquid is greater than ($\gamma_1 - \gamma_2$), the applied droplet remains in the form of a lens in the surface of the underlying liquid (Fig. 1). The forces resulting from the two surface tensions γ_1 and γ_2, as well as from the interfacial tension γ_{12}, act at the point of contact of the two liquid phases with the gas phase. If the resultant angles α, β, and ϕ are measured and two of the tensions are known, the third can be calculated (Neumann triangle). If the underlying phase 1 is a solid and its surface is not deformed, then γ_1 and γ_2 act in opposite directions along a straight line, and the contact or wetting angle ϕ between the applied liquid and the surface of the solid is formed at the point of contact of the three phases (Fig. 2). The contact angle ϕ is given by Young's equation:

$$\cos\phi = \frac{\gamma_1 - \gamma_{12}}{\gamma_2}$$

The contact angle can be measured by direct observation of a droplet on a horizontally mounted plate of the solid. If the liquid is advancing the contact angle generally becomes larger than in the stationary state on account of the restricted elasticity of the liquid and the roughness of the solid surface, and if the liquid

Figure 2. Formation of a contact (wetting) angle ϕ between a liquid 2 and a solid surface 1 (schematic)

is receding the contact angle becomes smaller (Fig. 3).

The determination of the contact angle is important for evaluating the wetting of solids and for indirect determination of the surface tension γ_1 of a solid. The nonpolar and polar components of the surface tension of the solid must be determined separately by measuring the contact angles with nonpolar and polar liquids which are then added to obtain the total surface tension. The surface tension γ_1 of the solid employed in Young's equation accordingly corresponds only to the force resulting from the effective interactions (γ_{12}) between liquid and solid on the one hand, and the surface tension of the liquid (γ_2) on the other. This surface tension γ_1 therefore generally does not correspond to the true surface tension of the solid, but only to a part thereof.

The reversible work per unit area that is exchanged with the surroundings in the formation of a liquid – solid interface is the adhesion or wetting tension γ_j, which expresses the adhesion forces between liquid and solid surface:

$$\gamma_j = -\gamma_2\cos\phi = \gamma_{12} - \gamma_1$$

If the solid is wetted by the liquid the adhesion tension is negative ($\phi < 90°$), whereas if it is not

**Figure 1.** Lens formed by a nonspreading liquid 2 on another liquid 1 (schematic)
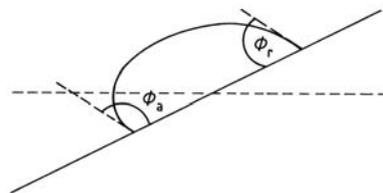
Figure 3. Contact angle ϕ of a liquid on a solid surface in the advancing state (a) and receding state (r) (diagrammatic)

wetted the tension is positive ($\phi > 90°$). For example, the adhesion tension between water and glass is negative, i.e., energy is released to the surroundings on formation of the interface, and the contact angle is $< 90°$. Thus water wets glass and rises in a glass capillary. In contrast, the adhesion tension between water and polyethylene is positive, i.e., work must be expended to produce a water – polyethylene interface, and the contact angle is $> 90°$. Hence water does not wet polyethylene completely and is displaced from a polyethylene capillary.

The wetting of a solid surface by a liquid is analogous to the spreading of a substance on a liquid surface.

The afore-described phenomena are observed for phases of a pure substance and for multicomponent phases. In the latter case, as a result of anisotropic interactions in the boundary region of a condensed phase, accumulation or depletion of components in this region may occur (positive or negative adsorption at the interface). Substances that accumulate from a liquid phase at the interface (or surface) are referred to as interface-active, usually as surface-active or, more loosely, capillary-active; substances that accumulate in the volume phase, rather than at the interface, are accordingly termed inactive.

Interfacial activity leads to a decrease of the interfacial tension compared to that of the pure substance, whereas interfacial inactivity increases the interfacial tension. Most water-soluble organic substances lower the interfacial and surface tensions of water, whereas inorganic salts increase them. For example, 20 wt % of butyric acid reduces the surface tension of water from 73 to 27 mN/m, whereas the addition of 20 wt % of water to pure butyric acid does not reduce the surface tension of butyric acid of 27 mN/m. Thus butyric acid is surface-active in water, but water is not surface-active in butyric acid. A 10 % sodium chloride solution has a surface tension that is 3 mN/m higher than that of pure water; the strongly hydrated sodium chloride ions in the volume phase are surface-inactive.

Strong accumulation of substances at the interface is termed adsorption. The adsorption of substances from a liquid phase at its interface is described by the Gibbs equation:

$$-\frac{d\gamma}{d \ln c} = \frac{\Gamma RT}{x}$$

where γ denotes the surface tension, c the concentration of a substance in the volume phase in mol/cm^3, γ the excess concentration of this substance in the interface over the concentration in the volume phase in mol/cm^2, R the gas constant, T the temperature, and x is a correction factor between 1 and 2 that depends on the degree of dissociation of the adsorbed substance. For non-dissociated substances $x = 1$, and for completely dissociated substances $x = 2$.

If γ is negative, i.e., if the concentration of a dissolved substance in the interface is lower than in the volume phase, the interfacial and surface tensions increase, whereas if γ is positive, which means a higher concentration of the dissolved substance in the interface than in the volume phase, the interfacial and surface tensions of the condensed phase decrease with increasing concentration of the dissolved substance in the volume phase. The greater the excess concentration γ of a substance at the interface, the more strongly surface-active it is. Surfactants, also referred to as tensides, are active substances whose molecules or ions have the property that when a characteristic concentration in aqueous solution is exceeded, they associate by reversible aggregation to form larger particles, known as micelles, which impart colloidal behavior to the solution.

The reason for the large adsorption at the interface lies in the chemical structure of the adsorbed substance. Surfactants are amphiphilic substances: their molecules contain endophilic and exophilic groups. Endophilic groups are those that interact strongly with the condensed phase, whereas exophilic groups are those that interact more strongly with one another than with the volume phase, and are therefore expelled from the latter. With amphiphilic substances the exophilic group is forced out of the volume phase and the endophilic group is drawn in, an accumulation in the form of an oriented adsorption occurrs at the interface. In aqueous systems the endophilic groups are termed hydrophilic, and the exophilic groups are termed hydrophobic.

In addition to the interfacial phenomena, which can be described with the aid of thermodynamics, electrical potentials are generally produced between condensed phases in ionizable systems. By dissociation, adsorption, desorption, and exchange of ions in the interface, an electrical double layer is formed consisting of

two components: a relatively rigid adsorption layer and a diffuse component that extends to a greater or lesser extent into the volume phase, depending on the ionic strength. The electrical potential of the rigid adsorption layer (Stern potential) can be determined approximately by electrophoresis or flow potential measurements (zeta potential [15]).

2. Overview of Surfactants

The highly diagrammatic tail – head model is widely used in the graphical representation of simple surfactants; the tail symbolizes the hydrophobic group, and the head the hydrophilic group.

The hydrophobic groups are mainly alkyl or alkylaryl hydrocarbon groups, but fluoroalkyl, silaalkyl, thiaalkyl, oxaalkyl groups, etc., are also possible. Some important hydrophobic and hydrophilic groups are listed below:

Since surfactants mainly act in aqueous systems, it is expedient to classify surfactants according to the chemical structure of their hydrophilic groups. The hydrophilic groups may be ionic or nonionic, and their chemical structure can vary widely.

The following classification of surfactants has proved convenient (arranged in order of industrial importance).

Anionic Surfactants, anionics, anion-active compounds, are amphiphilic compounds in which the hydrophobic residues carry anionic groups with small counterions such as sodium, potassium, or ammonium ions which only slightly influence the surface-active properties of the substance. Examples include soaps, alkylbenzenesulfonates, alkyl sulfates, and alkyl phosphates.

Nonionic Surfactants, niosurfactants, are amphiphilic compounds that are unable to dissociate into ions in aqueous solution, for example, alkyl and alkylphenyl polyethylene glycol ethers, fatty acid alkylolamides, sucrose fatty acid esters, alkyl polyglucosides, or trialkylamine oxides.

Cationic Surfactants, cationics, cation-active compounds, are amphiphilic compounds in which the hydrophobic residues exist as cations with counterions such as chloride, sulfate, or acetate that only slightly influence the active properties of the compound. Examples include tetraalkyl ammonium chloride or *N*-alkylpyridinium chloride.

Amphoteric Surfactants, amphosurfactants, (i.e., ampholytes and betaines) have zwitterionic hydrophilic groups. Examples include aminocarboxylic acids, betaines, and sulfobetaines:
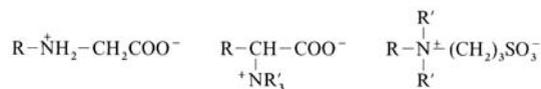
The electrical charge state of the amphosurfactants, which are often sparingly soluble at the isoelectric point, depends on the pH of the solution.

The subdivision of surfactants according to this classification is sometimes unambiguous.

Nonionic surfactants may assume a cationic character in acid solution due to protonation; amine oxides are an example of this:

$$R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} \to O + H^+ \longrightarrow R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}} \to OH$$
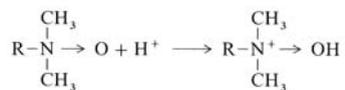
Anion – Cation Surfactants, in which anions and cations are amphiphilic and which are obtained by mixing anion and cation surfactants, are a special case. They are often sparingly soluble in water and in their properties resemble nonionic surfactants rather than ionic surfactants.

The structures of surfactants are not restricted to the simple tail – head model. Surfactants may contain several hydrophilic or hydrophobic groups. Examples include the sodium salts of the dialkyl sulfosuccinates:

$$\text{wwwOww} \qquad C_8H_{17}OCOCH_2\underset{\underset{SO_3Na}{|}}{CH}-COOC_8H_{17}$$
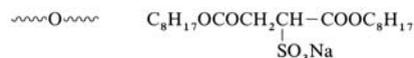
with a hydrophilic group flanked by two hydrophobic groups, or the disodium salt of 1,14-disulfatotetradecane with two hydrophilic groups at both ends of a long hydrophobic residue:

$$\text{O-www-O} \qquad NaO_3SO-[CH_2]_{14}-OSO_3Na$$
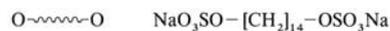
Surfactants of the latter type are also termed bola surfactants.

Industrial surfactants [8] are not pure defined substances, but mixtures of a large number of isomeric, homologous, and chemically similar substances. Low molecular mass products account for the bulk of the industrial products. Amphiphilic higher molecular mass compounds also have surface-active properties and are produced for numerous special applications. Examples include sulfated or ethoxylated condensation products of alkylphenols and formaldehyde, ethylene oxide – proylene oxide block copolymers, modified polysiloxanes, polyvinyl-*N*-alkylpyridinium salts, or copolymers of vinyl pyridine and methacrylic acid, the last-mentioned being an example of polymeric amphosurfactants. The "polysoaps" combine polymeric cations (e.g., the cation of polyvinylpyridine) with fatty acid anions.

In the theoretical treatment of surfactants the demarcation with respect to other amphiphiles that form higher ordered aggregates such as vesicles or membranes but not micelles is not always sharp [16], [17]. Substances such as polar lipids or water-soluble proteins play an extremely important role in the physiological processes of living organisms [18].

The vast majority of surfactants have hydrophobic groups derived from hydrocarbons. Only a few groups of surfactants bear hydrophobic residues containing heteroatoms. Hydrocarbon-derived surfactants are discussed here according to the nature of their hydrophilic groups (anionic, nonionic, cationic, amphoteric); the remaining surfactants are treated according to the structural features of their hydrophobic groups (polypropylene glycol derivatives, silicone-based surfactants, fluorosurfactants).

The so-called biosurfactants produced by microorganisms, are treated in [19]; for high polymer surfactants, see [20].

3. Properties of Aqueous Surfactant Solutions [21–23]

In highly dilute aqueous solutions surfactants exist in monodisperse form and are concentrated at the interfaces by hydrophilic – hydrophobic oriented adsorption. The surface concentration γ of a surfactant can be calculated from the Gibbs equation by measuring the surface tension as a function of the volume concentration (see Chap. 1). With a rise in volume concentration the surface concentration increases until the surface is completely covered by the surfactant molecules or ions. Further surfactant particles cannot be accommodated at the surface and Gibbs' equation is no longer valid. The area requirement of a surfactant molecule or ion in the adsorption layer can be calculated from the surface concentration at maximum occupancy. Such calculations show that the surfactant molecules are adsorbed with their longitudinal axis perpendicular to the surface. The projection of the largest surface-parallel cross section of the surfactant particle onto the surface gives its area requirement.

An entropy effect is extremely important for the interfacial activity. The hydrophobic groups of the surfactant molecules or ions are hydrophobically solvated in aqueous solution. Thus the water molecules are highly ordered in the

immediate vicinity of the hydrophobic species, which is associated with a decrease in entropy. If the hydrophobic group is displaced from the aqueous phase, the state of disorder of the water and thus the entropy of the system increases. This effect is also termed the hydrophobic effect. If, under total occupancy of the surface, the volume concentration of the surfactant in equilibrium with the surface concentration prevailing in this case is exceeded, the surfactant molecules or ions, which up to this concentration are mainly present in the volume phase in monodisperse form, congregate in an entropy-governed manner to form larger aggregates (micelles) in which they are oriented with the hydrophilic groups pointing towards the aqueous volume phase and the hydrophobic groups towards the interior of the micelles.

The aggregation of surfactant molecules or ions into micelles takes place in a strictly limited concentration range characteristic of each surfactant; if the surfactant concentration rises further, the number of micelles per unit volume increases, but not, however, the number of monodisperse – dissolved surfactant molecules or ions (more correctly, their activity). Since micelle formation occurs at the volume concentration of the surfactant at which the surface is largely, if not completely, covered so that the surface tension becomes independent of any increase in volume concentration, measurement of the surface tension as a function of the concentration represents a simple method of determining the so- called critical micelle concentration (CMC) at which micellization or micelle formation begins (Fig. 4).

The increase in the number of particles in a surfactant solution with concentration suddenly drops at the critical micelle concentration due to micelle formation, and consequently the concentration dependence of all colligative properties such as vapor pressure and osmotic pressure, and in the case of ionic surfactants also the equivalent conductance, changes at this concentration.

Micelles are dynamic structures that are in equilibrium with the surrounding monodisperse surfactant solution; their average aggregation number fluctuates in purely aqueous solutions at the critical micelle concentration around a mean value characteristic of each surfactant. This value is between 100 and 1000 in simple nonionic surfactants, and is generally below 100 in ionic
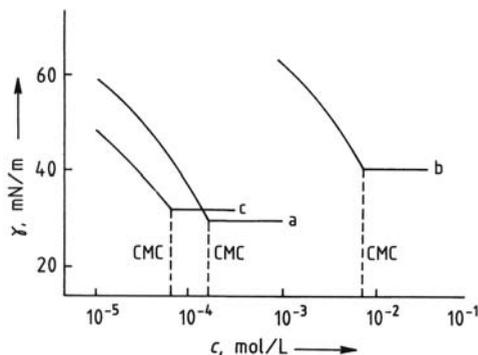
Figure 4. Surface tension γ as a function of concentration c, and critical micelle concentration (CMC)
a) Nonionic surfactant (dodecylheptaglycol ether) in water; b) Ionic surfactant (dodecyl sulfate) in water; c) Dodecyl sulfate in 0.1 N sodium chloride solution

surfactants; with the latter, the electrostatic repulsion acting between the ionic head groups opposes further aggregation.

Above the CMC surfactant solutions are colloidal solutions; the surfactants form "association colloids" and behave like sols, and at higher concentrations behave like gels. This behavior is connected with the shape of the micelles that form under particular conditions. A distinction is made between spherical, rod-shaped, and disk-shaped micelles [24].

The shape of the micelle is determined primarily by the ratio of the area requirement of the head group of the surfactant under the prevailing conditions to the volume of the hydrophobic tail group. If this ratio is large, for example in the case of ionic n-alkyl surfactants, spherical micelles are formed. For small ratios, such as in the case of nonionic alkyl polyglycol ethers, rod-shaped micelles are formed. However, simple ionic surfactants too can aggregate to form rod-shaped micelles if the electrostatic repulsion of the head groups is screened by adding an electrolyte and their spatial requirement on the surface of the micelle is reduced.

Surfactants with voluminous or several hydrophobic groups, as well as fluorosurfactants, form disk-shaped micelles. Some micelles as constituents of lyotropic mesophases are illustrated schematically in Figure 5.

Spherical micelles can transform at higher surfactant concentrations into rod-shaped or disk-shaped micelles. Such a transition may be
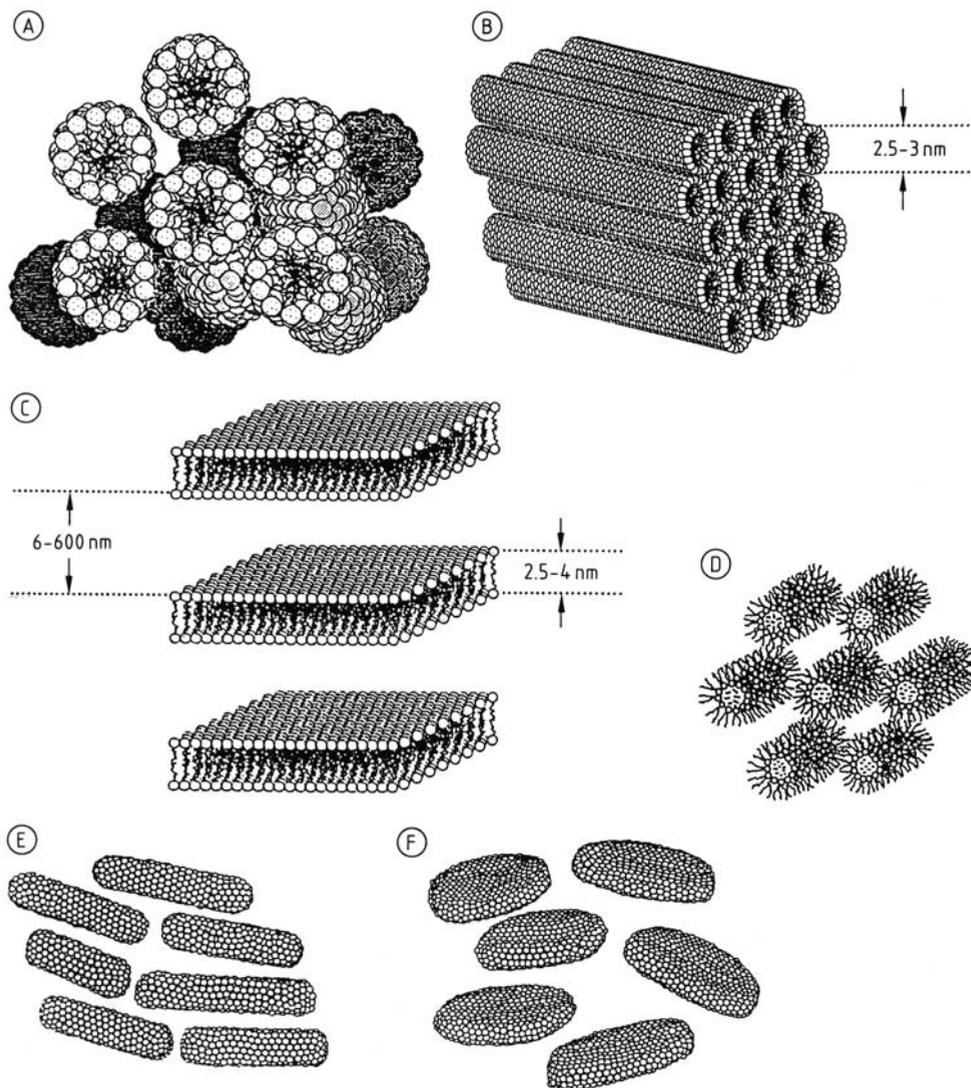
Figure 5. Structure of lyotropic mesophases formed from micellar aggregates [24] (reproduced from [6], with permission)
A) Cubic phase; B) Hexagonal phase; C) Lamellar phase; D) Inverse hexagonal phase; E) Nematic rod phase; F) Nematic disc phase

indicated by a second critical micelle concentration, at which the colligative properties of the solution once more change abruptly.

At higher surfactant concentrations spatially extensive, ordered structures, known as liquid crystal mesophases or lyotropic liquid crystals, are formed. In a number of nonionic surfactants of the poly(ethylene glycol) ether type such liquid crystal phases can be attributed to the formation of specific hydrates [25].

Provided they do not transform into rod-shaped or disk-shaped micelles, spherical micelles condense into cubic phases, rod-shaped micelles into hexagonal phases, and disk-shaped micelles into lamellar phases, whose basic structure resembles the bilayer lipid membranes (BLM) of living organisms. The bilayer structures present in lamellar phases transform under high shear forces (e.g., by ultrasound) into vesicles – namely spherical structures having an
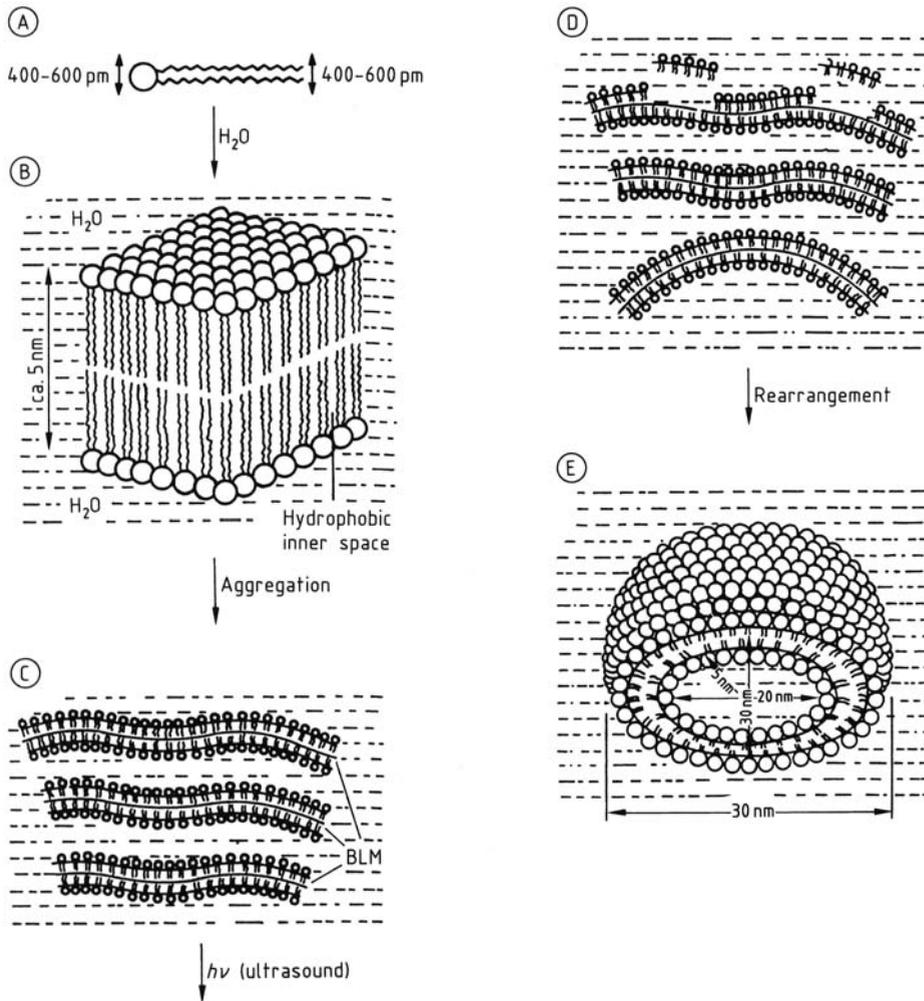
Figure 6. From bilayer lipid membranes (BLM) to vesicles
A) Amphiphilic molecule; B) BLM (section); C) Myelin structure; D) Partially broken myelin structure; E) Cross section through a vesicle (from [26], with permission)

outer bilayer membrane (Fig. 6) [26–28]. This structure was first observed in natural fat particles (liposomes), formed from lipids.

The ordered and oriented, monolayer and multilayer adsorption of surfactants or amphiphiles leads to the formation of Langmuir – Blodgett films [29], which are important in surface treatment and coating technology.

Solutions of spherical micelles and cubic phases formed therefrom are isotropic, whereas solutions of rod-shaped and disk-shaped micelles and their liquid crystal phases are anisotropic. Due to this anisotropy the flow of surfactant sols and gels deviates from Newtonian behavior. A

knowledge of this divergence from Newtonian flow is important in the preparation and formulation of surfactants, and in the design of pipelines and conveying and mixing equipment. A distinction is made between *pseudoplasticity* (shear thinning), namely decreasing in viscosity with increasing shear rate; and *dilatancy* (shear thickening), namely increasing viscosity with increasing shear.

When the mechanical stress is released pseudoplastic and dilatant liquids return to their original state.

Thixotropy is a decrease in viscosity as a result of sustained mechanical stress, and *rheopexy* an

increase in viscosity as a result of sustained mechanical stress. The terms thixotropy and rheopexy imply that the liquids return to their original state, even after a time delay, when the mechanical stress is released; in practice, however, both expressions are used even if this is not the case.

Gels can also exhibit plastic behavior, acting as elastic solids below a certain critical shear stress (the yield stress or yield point) and transforming into the liquid Newtonian or non-Newtonian state only when the yield stress is exceeded.

Pseudoplasticity, thixotropy, and plasticity are often observed in surfactant solutions, whereas dilatancy and rheopexy occur less often. The flow behavior of surfactant solutions depends largely on the temperature, concentration, and on the presence of other additives, especially electrolytes. Transitions from one flow behavior to another are often produced by slight changes in the conditions, which must be taken into account when diluting or mixing surfactant solutions. The "thickening" of surfactant solutions, e.g., of alkyl polyethylene glycol ether sulfate solutions with sodium chloride is utilized in the formulation of such solutions. Conversely, the addition of a number of compounds such as urea or short-chain alkylbenzene sulfonates leads to the dissociation of the gel structure and thus decreased viscosity. Such substances are termed hydrotropics, and the effect, hydrotropy.

In addition to being viscous, many surfactant solutions at relatively high concentrations, exhibit limited elastic deformation, which is mainfested *inter alia* in vibrational phenomena. The flow behavior of such liquids is termed viscoelastic [30].

The flow behavior of surfactant solutions is measured in rotational viscometers ($\rightarrow$ Rheometry). The solution is added to the gap between two concentric cylinders, one of which is at rest, while the other rotates. A shear rate gradient is generated due to the relative movement of the cylinders. The torque necessary for this movement is measured, from which the shear stress and viscosity of the solution are calculated. The cone-and-plate system is based on the same principle. A cone having an obtuse angle rotates over a plate and the liquid is subjected to shear forces in the gap between cone and plate.

Surfactant sols and gels often exhibit segregation phenomena. Coacervation is the separation of an initially uniform phase into two phases, one of which contains more of the colloidal component, and the other less. A further property of sols and gels is aging, known as deswelling or syneresis, i.e., the coagulation of gel particles and their dehydration, with the formation of a compacted gelatinous mass and a low-colloid liquid phase. To prevent such segregations, which can lead to difficulties in the storage and metering of surfactant solutions, mixing equipment must often be provided in storage vessels.

The fact that dissolved surfactants are adsorbed at interfaces and form micelles confers a number of properties on their solutions, which are described below.

Wetting. The formation of a liquid – solid interface inplace of a gas – solid interface is termed wetting. Young's equation describes the relevant relationships (see 1). A prerequisite, however, is that the surface-active substances are adsorbed at the interface so that their hydrophilic groups are directed towards the aqueous phase. If these hydrophilic groups are adsorbed on the solid surface and the hydrophobic groups project into the aqueous phase (inverse adsorption), the solid surface becomes hydrophobic, an effect that is exploited in water-repellent textiles, fabric softeners, and ore flotation, for example.

Rewetting. If a liquid, in particular a surfactant solution, displaces a liquid droplet or a solid particle insoluble in the latter from the surface of a solid, with emulsification or suspension of the displaced substrate, this is termed rewetting.

Solubilization is the apparent dissolution of substances that are insoluble or slightly soluble in water, in a surfactant solution by incorporation into the micelles. On the other hand, water can be solubilized in hydrophobic solvents by adding surfactants. Thereby, inverse micelles are formed, with the hydrophobic groups aligned outward and the hydrophilic groups inward (see Fig. 5D). Solubilization, like the decrease in surface tension and interfacial tension, is regarded as a characteristic property of surfactants in aqueous solutions.

Emulsion Stabilization (see also $\rightarrow$ Emulsions) is the stabilization of disperse systems of two liquids that are insoluble or only slightly

soluble in one another. This stabilization is based on covering the interfaces with surfactants that counteract coalescence of the droplets of the disperse phase. Such emulsions are metastable systems, and are also termed macroemulsions to distinguish them from the thermodynamically stable microemulsions [31–33].

Suspension Stabilization is the prevention of coagulation and delay of sedimentation of solids finely dispersed in a liquid. The surfactants are solid – liquid adsorbed at the phase interface and prevent the aggregation and coagulation of the dispersed solid particles by means of steric screening and, in the case of ionic surfactants, also by electrostatic repulsion. Furthermore, under certain conditions surfactants are also able to deflocculate, without mechanical action, suspensions that have coagulated.

Protective colloid action is the suspension stabilization of hydrophobic colloids, especially against the coagulating action of inorganic salts.

Lime Soap Dispersion. A number of surfactants having relatively large or several hydrophilic groups can disperse sparingly soluble calcium and magnesium salts of fatty acids (lime soaps) in water. Examples of such surfactants include:

$C_9H_{19} —C_6H_4 —(OCH_2CH_2)_{10} —OH$

$C_{17}H_{35}CONH(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$

$C_{10}H_{21} —C_6H_4 —SO_2NHCH_2CH_2SO_3Na$
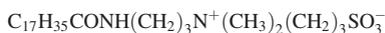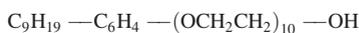
Foams (see also → Foams and Foam Control). Surfactants accumulate at the interface of a gas bubble in aqueous solution, with their hydrophobic residues directed to the interior of the bubble. When the ascending bubble bursts through the surface of the liquid phase the film of surfactants present there becomes attached to the surface of the bubble. A lamella consisting of two films of surface-active substance is obtained, with hydrophilic groups pointing into the interior of the lamella and hydrophobic groups pointing away from the lamella. Liquid entrained from the solution is found between the films. The combination of numerous such bubbles constitutes a foam. The properties of foams are connected with the mechanical properties of the lamellae and the dynamic processes in and on the lamellae (viscosities of the surface films and interlamellar liquid, elasticity of the surface films, diffusion and spreading rate of the surface-active substances, electrical repulsion, Van der Waals attraction between the two films of the lamella, and gas permeability, leading to drying and breaking of the lamella).

The properties of surfactant solutions are the result of adsorption and aggregation of the surfactant molecules and ions; the attainment of the equilibrium state is determined by the rate of diffusion, orientation, and organization of the surfactant molecules and ions. Many properties of surfactant solutions are therefore *time-dependent*. The attainment of the equilibrium value for the surface tension of a surfactant solution is an example. Another example is the restoration force that spontaneously occurs in the expansion of a surface of a surfactant solution, as the result of a depletion in surfactant per unit area of the surface, resulting in an increase in surface tension. This increased surface tension is restored to the original value by diffusion of surfactant from the volume phase to the surface, or, in the case of spatially limited regions of increased surface tension, also by expansion of the surfactant film of the neighboring regions. The Marangoni effect, i.e., the transportation of a liquid layer adhering to the surfactant film to the site of higher surface tension, is observed in the latter case.

For the sake of convenience, the properties of the boundary region between two phases are regarded as properties of a two-dimensional surface (see Chap. 1). Although this model representation satisfactorily explains many phenomena, it does not provide a detailed understanding of the conditions in boundary regions between two phases. For example, lamellae, membranes, or multimolecular surface films should no longer be regarded as two-dimensional; rather, they form three-dimensional structures between two phases (i.e., a third phase, known as the interphase).

4. Relationship between Structure and Properties of Surfactants

The nature of the hydrophilic group of a surfactant exerts a decisive influence on the behavior of the surfactant in aqueous solution. The solubility of ionic surfactants depends on the electrolytic
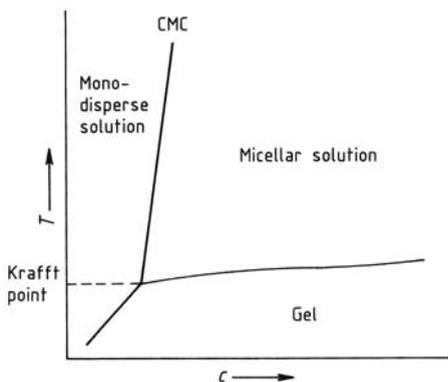
Figure 7. Phase diagram of an anionic surfactant of the sulfonate type in aqueous solution, as a function of concentration c and temperature T

dissociation and solvation of the hydrophilic group, whereas the solubility of nonionic surfactants depends essentially on the hydration of the polarized but undissociated hydrophilic group. The solubility of ionic surfactants generally increases with increasing temperature, whereas that of nonionic surfactants decreases because the extent of hydration via hydrogen bond formation decreases with increasing temperature (see Figs. 7 and 8). Aqueous anionic-surfactant gels (Fig. 7) dissolve in a monodisperse fashion at low concentration, and in a micellar manner at higher concentrations. The solution temperature rises only slightly with increasing concentration, and likewise the critical micelle concentration increases only slightly with temperature. The triple point monodisperse solution – gel – micellar solution is known as the Krafft point
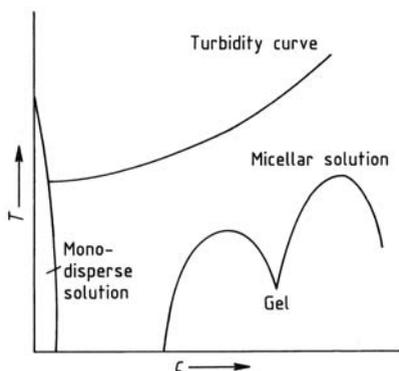

Figure 8. Phase diagram of a nonionic surfactant of the ethoxylate type in aqueous solution, as a function of concentration c and temperature T

(or temperature), and is characteristic for each ionic surfactant. It can be determined sufficiently accurately for most purposes as the point at which a surfactant solution above the critical micelle concentration becomes clear on heating. This is because above the critical micelle concentration the solution temperature (clear point) depends only slightly on the concentration.

The phase diagram of a nonionic alkyl polyethylene glycol ether is illustrated schematically in Figure 8. The critical micelle concentration decreases with increasing temperature. At elevated temperature micellar solutions separate into two phases; thus, initially clear solutions become turbid on heating. The temperature at which a solution of a nonionic surfactant becomes turbid is termed the turbidity or cloud point, and is a characteristic parameter of a nonionic surfactant.

Ionic surfactants aggregate into micelles at molar concentrations that are a factor of ten higher than in the case of nonionic surfactants. The reason for this is the electrostatic repulsion of the surfactant ions, which counteracts orientated association. In the presence of electrolytes the electrostatic repulsion of the surfactant ions is counteracted to some extent due to the increased concentration of the counterions; electrolytes thus greatly reduce the CMC of ionic surfactants and increase the aggregation number. The CMC of nonionic surfactants is only slightly influenced by electrolytes (see Fig. 4). Critical micelle concentrations of some well-defined chemical compounds are listed in Table 1, while those of some industrial products are listed in Table 2. The tables illustrate the influence of the chemical structure of the surfactants on the CMC and the surface tension:

1. With linear alkyl groups in the hydrophobic part, the amphiphilic substances require 7 – 9 carbon atoms or more in the hydrocarbon chain to exhibit surface activity and micelles formation. Only with the very highly surface-active fluorosurfactants, whose fluorocarbon residues are extremely hydrophobic, is interfacial activity observed for shorter chains, starting with perfluorobutanecarboxylic acid and perfluorobutanesulfonic acid.

2. In a series of homologues the CMC decreases with increasing size of the hydrophobic residue. For linear alkyl hydrophobic groups,

Table 1. CMCs of some surfactants of defined structure, and their surface tensions at the CMC

Surfactant	Temperature, °C	CMC		Surface tension, mN/m
		mmol/L	g/L	
Na 1-decyl sulfate	50	34.0	8.3	40
Na 1-dodecyl sulfate	50	8.1	2.2	38
Na 1-tetradecyl sulfate	50	2.0	0.60	37
Na 1-hexadecyl sulfate	50	0.66	0.22	38
Na 1-octadecyl sulfate	50	0.23	0.76	38
Na 2-hexadecyl sulfate	20	0.48	0.17	37
Na 4-hexadecyl sulfate	20	0.62	0.21	36
Na 6-hexadecyl sulfate	20	1.20	0.41	35
Na 8-hexadecyl sulfate	20	2.20	0.76	30
Na p-1-tetradecylbenzenesulfonate	75	0.67	0.25	38
Na p-2-tetradecylbenzenesulfonate	75	0.72	0.27	37
Na p-3-tetradecylbenzenesulfonate	75	0.77	0.29	36
Na p-5-tetradecylbenzenesulfonate	75	0.93	0.35	34
Na p-7-tetradecylbenzenesulfonate	75	1.73	0.65	34
Na 2-dodecene-1-sulfonate	30	13.0	3.51	36
Na 2-tetradecene-1-sulfonate	30	2.7	0.77	32
Na 2-hexadecene-1-sulfonate	30	0.61	0.81	33
Na 2-octadecene-1-sulfonate	50	0.18	0.06	31
Na 3-hydroxydodecane-1-sulfonate	30	24.8	7.15	42
Na 3-hydroxytetradecane-1-sulfonate	30	6.33	1.91	41
Na 3-hydroxyhexadecane-1-sulfonate	30	1.45	0.46	39
Na 3-hydroxyoctadecane-1-sulfonate	50	0.38	0.13	37
1-Dodecyl pentaglycol	20	0.06	0.024	31
1-Dodecyl heptaglycol	20	0.09	0.045	34
1-Dodecyl nonaglycol	20	0.12	0.070	37
1-Dodecyl dodecaglycol	20	0.17	0.121	41
Perfluoropentanecarboxylic acid	20	0.09	0.028	17
Perfluoroheptanecarboxylic acid	20	0.01	0.04	17
Perfluorononanecarboxylic acid	20	0.001	0.005	20

Table 2. CMCs of some industrial surfactants at 20 °C and their surface tensions at this concentration

Surfactant	CMC, g/L	Surface tension mN/m
Potassium oleate	0.35	25.5
Alkylbenzenesulfonate[a]	0.50	35.0
Alkanesulfonate[b]	0.44	34.5
Olefinsulfonate[c]	0.60	32.5
Fatty alcohol ether sulfate[d]	0.17	36.5
Fatty alcohol ethoxylate[e] (6 EO)[f]	0.008	30.5
Fatty alcohol ethoxylate (9 EO)	0.015	30.5
Fatty alcohol ethoxylate (12 EO)	0.020	31.5
Nonylphenol ethoxylate[g] (9 EO)	0.054	34.0
Nonylphenol ethoxylate (12 EO)	0.084	35.5
Nonylphenol ethoxylate (14 EO)	0.096	35.5
Distearyldimethylammonium chloride	2.5	35.5
Cetylpyridinium chloride	0.6	39.5

[a] Linear $C_{10} - C_{13}$ alkylbenzenesulfonate having a mean alkyl chain length of C_{12}, as sodium salt.
[b] Linear $C_{13} - C_{17}$ alkanesulfonate having a mean alkane chain length of C_{15}, as sodium salt.
[c] From linear C_{14}/C_{16} α-olefin, as sodium salt.
[d] From linear $C_{12} - C_{14}$ fatty alcohol with 3 mol EO/mol, as sodium salt.
[e] From linear $C_{12} - C_{14}$ fatty alcohol.
[f] Mol EO/mol.
[g] From alkylphenol with branched nonyl residue.

Stauff's rule applies:

$$\log(CMC) = A - B\,n$$

where A and B are constants and n is the number of carbon atoms in the alkyl residue. Traube's rule states that in a homologous series the interfacial activity increases with increasing size of the hydrophobic group and that the surfactant concentration at which a specific interfacial activity is achieved decreases with increasing size of the hydrophobic group. For simple linear hydrocarbon chains in the hydrophobic part

$$\log C_n = -n \log A + B$$

where C_n is the concentration of the homologue, n is the number of carbon atoms in the hydrocarbon chain, and A and B are constants. For aqueous solutions of sodium salts of fatty acids, for example, the concentration required to lower the surface tension by a specific amount is three times lower when the alkyl chain is extended by one methylene group.

3. In a series of isomers the CMC and interfacial activity increase with increasing internal position of the hydrophilic group.

4. Branching of the hydrophobic hydrocarbon has the same effect on the CMC and interfacial activity as a shortening of a linear hydrocarbon residue. A central rather than terminal substitution of the alkyl chain by a phenyl group bearing the hydrophilic group has the same effect (effective chain length – see Fig. 9).

5. For nonionic surfactants of the polyethylene glycol ether type the water solubility and CMC increase with increasing length of the polyethylene glycol chain.
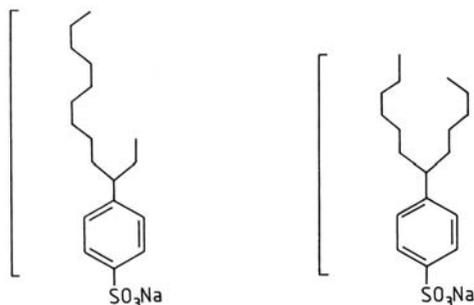

Figure 9. Effective chain length of alkylbenzenesulfonates

Micelle formation, interfacial activity, and absolute values of the interfacial tension are decisively influenced by the size and structure of the hydrophobic groups, which determine the cohesive forces between the surfactant molecules and ions as well as their spatial requirement at the interface. Cohesive forces that increase with increasing chain length exist between surfactants having unbranched alkyl residues, and are stronger than the forces between branched alkyl chains. Surfactants with linear alkyl groups accordingly associate at lower concentrations than those with branched chains, while surfactants with long chains associate at lower concentrations than those with short chains.

Fluoroalkyl groups are substantially more hydrophobic than the corresponding aliphatic alkyl groups. Fluorosurfactants therefore form micelles at much lower concentrations than their aliphatic analogues.

Surfactants with straight-chain aliphatic groups can form a tightly packed film at the interface, with parallel linear chains; their spatial requirement is small, and the strength (tension) of the film increases with increasing chain length. In contrast to branched-chain surfactants, such surfactants only reduce the surface tension slightly, though they do so already at low volume concentrations. Surfactants with branched-chain hydrophobic groups, which reach the CMC only at relatively high concentrations, lead to lower surface tensions because their surface films have a relatively low cohesion but relatively high spatial requirement. Surfactants with straight-chain aliphatic groups have been referred to as "efficient" surfactants since they are already active at low concentrations, and surfactants with branched hydrophobic residues as "effective" surfactants, since they produce a marked decrease in surface tension, albeit at higher concentrations [34] (Fig. 10).

The low cohesion between the perfluoroalkyl groups in perfluoroalkyl surfactants results in very low interfacial tensions in solution. Surfactants with methylpolysiloxanes as hydrophobic group lie between surfactants with alkyl groups, and perfluoroalkyl surfactants as regards interfacial tension, due to the moderate cohesive forces between the dimethylsiloxane groups.

On account of the marked decrease in the interfacial and surface tension, solutions of effective surfactants generally exhibit good
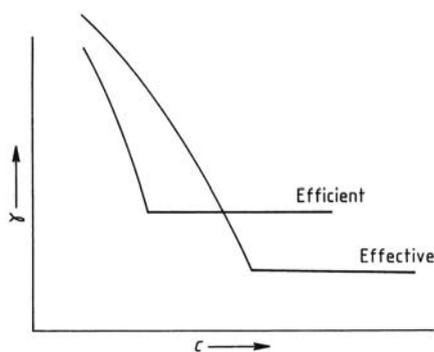
Figure 10. Surface tension γ of an efficient and an effective surfactant as a function of concentration *c*
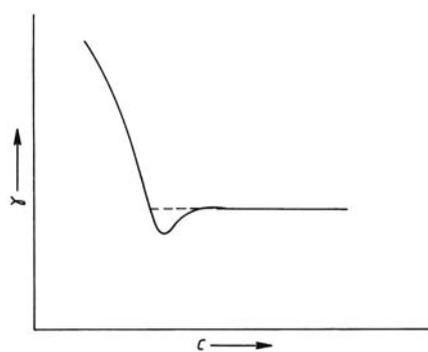
Figure 11. Surface tension γ of a contaminated surfactant as a function of concentration *c*

wetting and foaming abilities but have a low detergent power due to the high CMC; the opposite is true for efficient surfactants. This rule of thumb applies provided that the molecular masses of the surfactants are not so large that the adjustment of the equilibrium state is adversely affected by the reduced diffusion rate. Minima of the interfacial and surface tensions as a function of the length of the hydrophobic or hydrophilic (ethoxylate) residue given in the relevant literature refer to "dynamically" measured values, i.e., values that have been obtained without waiting for equilibrium to be established, which can take several hours in the case of slowly diffusing surfactants. For application technology, however, it is largely the dynamic interfacial tensions that are decisive, since in processes of wetting, washing, emulsification, etc., the instantaneous effects are of most importance.

Surfactants of varying structures form mixed films at interfaces. At low concentration surface-active substances with the higher surface activity preferentially accumulate in the interface. With increasing surfactant concentration the more strongly surface-active species may be expelled from the interface and absorbed by micelles in the volume phase, forming mixed micelles. As a result the interfacial tension, which drops with increasing surfactant concentration until the CMC is reached, may subsequently increase, reaching a constant end value (Fig. 11).

Such concentration-dependent interfacial tension behavior is often observed for industrial surfactants, which consist of mixtures of various chemical species. At fairly high concentrations of the second component permanent mixed films may form, whose properties deviate from the films of the individual components because of their different structure and, thus, stability. For example, lauryl alcohol in lauryl sulfate or lauric acid ethanolamide in alkylbenzene sulfonate stabilizes the foam on aqueous solutions of the corresponding surfactants because the nonionic substances are incorporated in the film and oriented in a hydrophilic – hydrophobic manner. Thus, the distance between the electrically charged hydrophilic groups of the surfactant is increased and their electrostatic repulsion is reduced.

Similar to mixed films at interfaces mixed micelles can form in solution, whose structure can be greatly altered by the mixing proportions up to the formation of "swollen" micelles, which are regarded as constituents of microemulsions.

5. Industrial Development

The industrial development of the wide range of surfactants now available received its initial and most important stimulus from the burgeoning textile industry of the mid-1800s. The various processes involved in the finishing and processing of raw cotton and wool into finished textiles required, besides the soap and natural saponins (→ Saponins) known from antiquity, special surface-active substances, dispersants, softeners, and sizing agents, with resistance to water hardness being one of the initial requirements. The first steps in this direction were taken by RUNGE in 1834 and by MERCER in 1846 with sulfated olive oil, followed in 1875 by turkey red oils, which were obtained by sulfating castor oil. These processes underwent many improvements, and are still of some importance.

Until 1930 industrial surfactant chemistry was almost exclusively an adjunct of the textile industry, and only in the 1930s did developments occur that opened up new markets for synthetic or semi-synthetic surfactants, including household detergents. Whereas oils and fats were formerly, with a few exceptions, the only raw materials for surfactants including soaps, during this period raw materials based on coal and petroleum also became increasingly important, although the natural materials based on oils and fats have never completely lost their importance.

In 1963 Püschel identified five periods in the development of surface-active substances [35]:

1. Up to 1925: Turkey-red oils
2. From 1925 to 1929: highly sulfonated oils
3. From 1929 to 1935: invention of the principal types of synthetic surfactants
4. From 1935 to 1945: coal and petroleum were exploited as raw material base
5. From 1945 to 1960: new, special types of surfactants were developed

This subdivision of surfactant development can be concluded by a sixth period beginning around 1960, characterized by increasing environmental awareness, which has considerable repercussions on research and technology in surfactant chemistry. Nowadays, particular attention is being paid to "mild" surfactants, i.e., those with a low irritation potential for the skin and mucous membranes.

Two developments in the 1930s in Germany have permanently affected the development of surfactant chemistry.

Schrauth et al. at the Deutsche Hydrierwerke in Rodleben accomplished the catalytic high pressure hydrogenation of fatty acids to fatty alcohols. Bertsch et al. at H. T. Böhme in Chemnitz, who had already developed sulfated fatty acid esters (Avirol) and fatty acid amides (Humectol), obtained primary alkyl sulfates by sulfating fatty alcohols, which already appeared on the market in 1932 as a constituent of the specialty detergent FEWA, the first soap-free detergent.

In 1930, Schöller and Wittwer at I.G. Farbenindustrie in Ludwigshafen invented ethoxylation, i.e., the reaction of compounds having a dissociating hydrogen atom with ethylene oxide. This reaction leads to derivatives of poly(ethyl-ene glycols) or also oligo(ethylene glycols), known as ethoxylates. This was the birth of a new class of surfactants, the nonionic surfactants. I.G. Farbenindustrie introduced in rapid succession the following nonionic surfactants to the market:

Fatty acid ethoxylates	Soromin SG
Fatty alcohol ethoxylates	Peregal O
Alkylphenol ethoxylates	Igepal C

Parallel to these developments, I.G. Farbenindustrie offered a range of new oleic and fatty acid derivatives:

O-acylisethionate	Igepon A
N-acyl-*N*-methyltaurine	Igepon T
N-acylsarcosine	Medialan
N-acylaminoethyl sulfate	Igepon C

The particularly dermatologically friendly condensation product formed from oleic acid and oligopeptides, Lamepon A, was developed at Chemische Fabrik Grünau.

The first cationic surfactants, *N*-acylaminoethyltrialkyl ammonium salts, Sapamines, were produced in 1927 by Ciba. In 1934 Domagk discovered the disinfectant action of cationic surfactants, the so-called invert soaps; I.G. Farbenindustrie developed alkyldimethylbenzyl ammonium salts under the name Zephirol. Betaines (Du Pont) and ampholytes (Th. Goldschmidt) came later, in 1937 and 1948.

In the mid-1940s Atlas Powder introduced, a new class of nonionic surfactants (Spans and Tweens) to the market with the fatty acid sorbitan esters and their ethoxylates.

The first surfactant to be based on a coal product was diisopropylnaphthalenesulfonate, which was synthesized in 1917 by Gunther at BASF. This compound and other short-chain dialkylnaphthalenesulfonates are still used as wetting agents under the generic name Nekal. Alkylbenzenesulfonates with longer chain alkyl groups were produced in 1933 by I.G. Farbenindustrie and, independently, in 1936 by National Aniline in the United States. The predominant position in terms of quantity that alkylbenzenesulfonates nowadays occupy was achieved, however, only after 1945. Up to then, besides soaps, alkyl sulfates and alkanesulfonates played an important role in detergents and cleansing

agents. Alkyl sulfates are obtained by sulfating primary (natural) alcohols or by addition of sulfuric acid to long-chain olefins. In the latter case secondary alkyl sulfates are obtained, which were marketed as Teepol (Shell, 1934). Secondary alkanesulfonates were produced on an industrial scale from 1941 onward at I.G. Farbenindustrie in Leuna by sulfochlorination followed by saponification; they are still important nowadays as emulsifiers under the name Mersolat.

Until the expansion of refinery capacities and the conversion of chemicals production to raw materials derived from petroleum, the mainly linear hydrocarbons obtained from Fischer – Tropsch synthesis plants were used in Germany as feedstocks for the industrial production of surfactants. $C_{10} - C_{14}$ alkenes were used for alkylating benzene to produce alkylbenzenesulfonates, while $C_{13} - C_{18}$ alkanes were used for the production of alkanesulfonates. The higher molecular mass hydrocarbons (Fischer – Tropsch slack wax) were oxidized to fatty acids, which were used among other things as synthetic soaps.

With the expansion of petroleum refining low molecular mass olefins became available as starting materials. Ethylene was particularly valuable as a starting material for ethylene oxide, the basic building block of nonionic surfactants, and propylene as the starting material for hydrophobic groups. Propylene trimer was used for producing isononylphenol, the starting material for nonionic surfactants, while propylene tetramer was used for producing branched-chain dodecylbenzene, the starting material for a new type of alkylbenzene sulfonates (tetrapropylbenzenesulfonate), which was primarily developed in the United States and was also widely used in Europe.

In the 1950s the alkylbenzenesulfonates, nonylphenol ethoxylates, and fatty alcohol ethoxylates were produced in such amounts that a very large proportion of surfactant demand could be met. Nevertheless, the development of special surfactants for particular purposes continued after 1950. During this period novel surfactants were synthesized, in particular by incorporating new hydrophobic groups into the surfactant molecules. Examples include the Pluronic and Tetronic types produced by Wyandotte, in which polypropylene glycol or polyoxypropylated ethylenediamine are used as hydrophobic building blocks, and also the fluorosurfactants intro-

duced from 1950 onward by 3 M containing (per)fluoroalkyl groups, and the silicone surfactants produced by Th. Goldschmidt, containing a large variety of polydialkylsiloxanes as hydrophobic groups.

Although for a long time surfactant chemistry obtained a basic stimulus from the textile industry, nowadays the development of industrial products is largely determined by the requirements of the detergent, cleansing agent, and cosmetics industries since the bulk of surfactants is nowadays used in these sectors.

From 1960 onward the demand for biodegradability of surfactants in detergents and cleansing agents led to major changes. The most important product, tetrapropylenebenzenesulfonate, was replaced with great technical effort and expenditure by linear alkylbenzenesulfonate; in addition to nonylphenol ethoxylate, fatty alcohol ethoxylates based not only on natural raw materials but also on synthetic products appeared. A further ecological factor – the demand for a reduction or elimination of phosphate in detergents – together with the demand for a more rapid biodegradability, stimulated new technical developments: alkanesulfonates, alkenesulfonates, and α-sulfo fatty acid esters were considered as potential industrial products. Alkanesulfonates, produced by sulfoxidation of paraffins in a process developed in the 1940s by Hoechst, have in the meantime secured a firm market in Europe. The alkenesulfonates have achieved some importance in the United States and Japan, whereas the α-sulfo fatty acid esters have still not found any major use. With the expansion of oil palm plantations (e.g., in Malaysia and the Philippines), fatty alcohol sulfates based on these renewable raw materials are becoming increasingly important.

With the demand for particularly mild surfactants, besides the fatty alcohol ether sulfates and sulfosuccinic acid esters of fatty alcohol oligoglycol esters, a number of surfactants that were already developed in the 1930s have attracted renewed interest, including fatty acylisethionates and fatty acyltaurates, amino acid derivatives, ampholytes and betaines, carboxymethylated fatty alcohol ethoxylates, and so-called sugar surfactants. In parallel to the demand for mild products, there has been a more emotionally motivated wish for "natural" products, raw materials and surfactants based on renewable,

preferably plant raw materials. There is thus a potential for substituting products from petrochemical raw materials by those from renewable raw materials, which will be reflected in the extent to which corresponding amounts of renewable raw materials, primarily coconut, palm, and palm kernel oils, are available at comparable prices for industrial purposes [36].

6. Anionic Surfactants

6.1. Carboxylates

Soaps, the salts of fatty acids, are still important among surfactants (→ Soaps). Soaps are obtained mainly by saponification of natural fats. The oxidation of paraffins, olefins, aldehydes, or alcohols (Stass reaction) is no longer of importance for the production of fatty acids. The salts of carboxylic acids occurring in petroleum (naphthenic acids), which are also surfactants, are treated in → Metallic Soaps.

6.1.1. Carboxymethylated Ethoxylates

The sensitivity of soaps to water hardness is a disadvantage for some applications (e.g., textile washing). In contrast, the so-called super soaps, the sodium salts of carboxymethylated ethoxylates exhibit an extreme hardness resistance combined with good water solubility.

The carboxymethylated ethoxylates or polyether carboxylates, as they have also been named, are known to be dermatologically friendly. Since they also have outstanding dispersion and emulsification properties, they are suitable for a wide range of uses, for example as surfactants in detergents and cosmetics [37], [38], and as industrial emulsifiers [39].

The carboxymethylated ethoxylates are prepared by reacting an alcohol ethoxylate or alkylphenol ethoxylate with chloroacetic acid and caustic soda:

$$R-O-[CH_2CH_2O]_n-H + ClCH_2COOH + 2\,NaOH$$
$$\downarrow$$
$$R-O-[CH_2CH_2O]_n-CH_2COONa + NaCl + 2\,H_2O$$
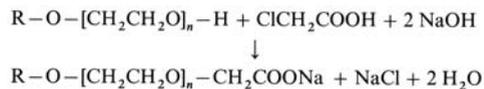
The sodium chloride byproduct is best removed by acidifying the reaction mixture, whereby the carboxylate separates as water-insoluble polyethercarboxylic acid and the sodium chloride remains in the aqueous phase. The polyether acids are clear, mobile liquids that can be transported in stainless steel or plastic containers, they are the most suitable form for handling this group of products. By neutralizing them with caustic soda colorless, highly viscous pastes are obtained that yield mobile solutions only at concentrations below 25 wt %. Typical data for some carboxymethylated products are listed in Table 3.

Manufacturers include Auschem, Chem-Y, and Hüls in Europe; Rhône-Poulenc Surfactant, Croda, Sandoz, Finetex, and Witco in the United States; and Nikko Chemicals in Japan.

Table 3. Data for some commercial carboxymethylated fatty alcohol ethoxylates, $R-[OCH_2CH_2]_n-OCH_2COOH$ and $-OCH_2COONa$, based on coconut oil alcohol ($R = C_{12}H_{25}/C_{14}H_{29}$)

Property	n = 4		n = 10	
	Acid	Na salt[*]	Acid	Na salt[*]
Appearance	clear to turbid pale yellow liquid	clear to turbid pale yellow liquid	clear to slightly turbid colorless liquid	clear colorless liquid
Active substance, %	88 – 90	21 – 23	85 – 90	21 – 23
Water content, %	ca. 10	ca. 78	10 – 15	ca. 78
Degree of carboxymethylation, %	ca. 95	ca. 95	ca. 95	ca. 95
Acid number, mg KOH/g	ca. 66	0	ca. 115	0
pH (1 %)	2.5 – 3	6 – 7	2.5 – 3	6 – 7
Setting point, °C	8			
Clear point, °C	ca. 18	max. 10	ca. 11	max. 10
Density, 20 °C, g/mL	1.01	1.03	1.05	1.03
Brookfield viscosity, 20 °C, mPa · s	ca. 200	ca. 30	ca. 300	ca. 100

[*]CAS numbers are [*33939-64-9*] and [*50546-32-2*].

6.1.2. Amino Acid Derivatives

Condensation products of fatty (oil) acids and amino acids are also less sensitive to hardness and hydrolysis than soaps. Sarcosides, for example, are obtained by reacting a fatty acid chloride with sodium sarcosinate according to the Schotten-Baumann reaction:

$$RCOCl + CH_3NHCH_2COONa + NaOH \rightarrow$$
$$RCON(CH_3)CH_2COONa + NaCl + H_2O$$
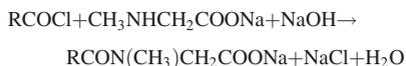
Sarcosides are good wetting agents and lime soap dispersants.

Industrially more important than the condensation products of amino acids are those with oligopeptides, which are obtained by partial hydrolysis of collagen, an animal skeletal protein that has no antigenic properties. The oligopeptides have molecular masses of 200 – 600. The condensation products are prepared similarly to the sarcosides, by condensation of a fatty acid derivative (chloride or anhydride) at the terminal amino group of the oligopeptide [40], [41].
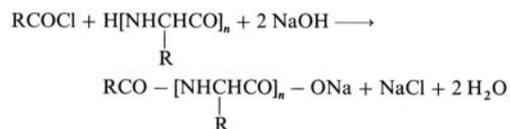
The products can be freed from byproducts by acidifying the reaction mixture; the pure condensation products separate as acids, which can be redissolved with a base.

As salts, fatty acid/protein condensation products are highly water soluble. They have a high lime soap dispersion power and foaming ability. Fatty acid/protein condensation products are preferentially used as highly skin-friendly surfactants in cosmetic preparations, bodycare agents, shampoos, and children's bathing products. They are stored and transported as 30 – 40 % solutions in steel or plastic vessels. If preserved against bacterial growth, they can be stored for prolonged periods at 20 °C and above. Typical data of two commercial products are listed in Table 4.

CAS Numbers. Sodium lauroyl sarcosinate [*137-16-6*], potassium cocoyl hydrolyzed collagen [*68920-65-0*], triethanolamine cocoyl hydrolyzed collagen [*68952-16-9*], potassium undecenoyl hydrolyzed collagen [*68951-92-8*], triethanolamine abietoyl hydrolyzed collagen [*68918-77-4*].

Producers. Sarcosides are produced by Croda, Hoechst, and ICI in Europe; Clough, Grace, and Stepan in the United States; Nikko Chemicals in Japan; and Zohar in Israel.

Fatty acid/protein condensation products are produced by Croda and Henkel in Europe; Ajinomoto, Croda, Henkel, and Inolex in the United States; and Ajinomoto and Nikko Chemicals in Japan.

6.2. Sulfonates

Sulfonates are the salts of sulfonic acids, in which a hydroxysulfonyl group is bonded via the sulfur atom directly to a carbon atom of the hydrophobic residue. This bond is thermally and chemically very stable. The strong affinity of the sulfonate group for water results in good water solubility, which decreases with increasing molecular mass. The alkaline-earth salts of sulfonic acids are less soluble in water than the alkali metal salts. The sensitivity of sulfonates to water hardness increases with increasing molecular mass. Being salts of strong acids, the alkali and alkaline-earth sulfonates give a neutral reaction in aqueous solution.

Sulfonates are nowadays the most important group among the synthetic surfactants. Besides the sulfonates discussed hereinafter, lignin sulfonates ($\rightarrow$ Lignin, Chap. 5.) and petroleum sulfonates are industrially important. Being outstanding dispersants, lignin sulfonates are used to

Table 4. Typical data for the potassium salt of a dipeptide/coconut oil acid condensate (A) and triethanolamine salt of a tetrapeptide/coconut oil acid condensation product (B)

Property	(A)	(B)
Molecular mass, g/mol	500 – 600	790 – 890
Dry content, wt %	31.5 – 32.5	39.5 – 40.5
Active substance, wt %	29.0 – 30.0	37.5 – 39.0
pH of a 10 % solution	6.2 – 7.0	6.5 – 7.0
Viscosity at 20 °C, mPa · s	1500 – 500	> 400
Density at 20 °C, g/mL	1.05 – 1.07	1.06 – 1.09
Gardner color index	max. 8	max. 10
Protein content, wt %	10 – 13	14 – 16
Ash, wt %	max. 8	max. 4

improve the viscosity of concrete mixtures and drilling muds, while petroleum sulfonates are used mainly as oil-soluble surfactants for producing water-in-oil emulsions. Both types of sulfonates could become important as surfactants in tertiary crude oil production.

6.2.1. Alkylbenzenesulfonates [42], [43]

p-Alkylbenzenesulfonates having (on average) 8 – 20 carbon atoms in the alkyl chain have a wide range of uses. *p*-Alkylbenzenesulfonates with less than 6 carbon atoms in the alkyl group are not surface-active.

$$R-\langle\!\!\!\bigcirc\!\!\!\rangle-SO_3^-$$
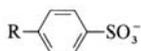
The alkylbenzenesulfonates are mainly used in the form of sodium salts, and occasionally also as potassium and ammonium salts and as salts with aliphatic amines. The octyl- to decylbenzenesulfonates have a good wetting action, but are unsuitable as emulsifiers and cleansing agents due to the shortness of the hydrophobic group. The most universally usable alkylbenzenesulfonates are those with an average of ca. 12 carbon atoms in the alkyl chain, comprising homologues with 10 – 14 carbon atoms (dodecylbenzenesulfonate). Because of their outstanding suitability as surfactants in detergents and cleansing agents (→ Laundry Detergents) and their low production costs compared to other surfactants, the dodecylbenzenesulfonates are nowadays the most important group of synthetic surfactants in terms of quantity. They are a constituent of powder and liquid heavy-duty household and industrial detergents. They are used less in fine detergents, shampoos, and cosmetic preparations.

Alkylbenzenesulfonates with ≥ 15 carbon atoms in the alkyl chain are sparingly soluble in water, but are readily soluble in organic media. Solutions in mineral oils play a role as drilling and cutting oils in the metal-processing industry, and as spinning, dust-binding, and batch oils in the textile industry.

Alkylbenzenesulfonates are produced by alkylation of benzene (Friedel – Crafts reaction), sulfonation of the alkylbenzene obtained, and neutralization. In the dodecylbenzenesulfo-

nates a distinction is made between those derived from highly branched tetrapropylene (TPS = tetrapropylenebenzenesulfonate) and those with linear alkyl groups (LAS = linear alkylbenzenesulfonate). Tetrapropylenebenzenesulfonate is less soluble in water than linear dodecylbenzenesulfonate (ca. 10 % and 20 % at 20 °C), is less toxic to fish, but is a stronger skin irritant than the latter. Sodium tetrapropylenebenzenesulfonate is less hygroscopic and less plastic than linear sodium dodecylbenzenesulfonate, and accordingly can be processed more easily into powder formulations. Tetrapropylenebenzenesulfonate is, however, becoming increasingly less important because of its unsatisfactory biodegradability.

In the first stage of the alkylbenzenesulfonate synthesis, benzene is alkylated with the corresponding alkyl chlorides or olefins. Linear alkyl chlorides are obtained by chlorination of alkanes, whereby conversion is limited to at most 30 % to minimize the proportions of polychlorinated hydrocarbons. Tetrapropylene, which can be obtained by oligomerization of propylene, is already present as an olefin. Linear olefins are nowadays obtained by oligomerization of ethylene or by catalytic dehydrogenation of linear paraffin cuts.

The oligomerization of ethylene using aluminum alkyls (Alfen process) or by transition metal complexes (Shell Higher Olefin Process, SHOP) affords mixtures of homologous, even-numbered, unbranched α-olefins with a broad Schulz – Flory molecular mass distribution [44], [45] (see also → Hydrocarbons, Section 2.1.2.2.). Such olefins are less suitable for producing commercial alkylbenzene mixtures, since narrow olefin cuts are required for this purpose. One possible way of narrowing the homologue distribution is to isomerize α-olefins to olefins with double bonds, as carried out in the SHOP process, followed by comproportionation or cometathesis of higher and lower olefins. Although mixtures of olefins with internal double bonds and a broad molecular mass distribution are again formed, the advantage of this process is that the desired olefin cut (e.g., $C_{10} - C_{13}$) can be distilled from the mixture, and the unrequired fractions can be returned to the cometathesis reaction, so that ultimately the mixture of α-olefins with a broad distribution that is obtained in the oligomerization is converted to

a mixture of linear olefins of narrow distribution having internal double bonds.

The process most widely employed nowadays for producing olefins for industrial alkylbenzene synthesis is the dehydrogenation of *n*-alkanes. In conjunction with the back-integrated process for obtaining linear starting alkane from corresponding petroleum fractions (kerosene) by means of molecular sieves and the forward-integrated benzene alkylation catalyzed by hydrogen fluoride, it is nowadays carried out worldwide in numerous plants and is known as the UOP process (Universal Oil Products) [46], [47].

Nowadays, exclusively aluminum chloride and hydrogen fluoride are used as alkylation catalysts in alkylbenzene synthesis, whereby hydrogen fluoride can only be used for alkylation with olefins but not with alkyl chlorides.

A fixed-bed catalyst was described for the first time in 1990, which has advantages compared to hydrogen fluoride- catalyzed alkylation and is to be marketed by UOP under the name "Detal" [47], [48].

Alkylation always gives mixtures of isomeric (and homologous) alkylbenzenes. The isomer distribution of the alkylbenzenes obtained with the two catalysts is different. Both processes are Friedel – Crafts reactions, in which only secondary or tertiary alkyl residues occur on the benzene ring. Regardless of whether primary or secondary linear alkyl chlorides or linear olefins having terminal or internal double bonds are used as starting materials, alkylbenzenes are always obtained in which the phenyl groups is bonded internally along the alkane, but not in the terminal position.

The isomer distribution depends on the catalyst used. With aluminum chloride and linear alkyl chlorides or olefins roughly the same isomer distribution is obtained, in which 2-phenylalkanes predominate and 3-, 4-, and 5-phenylalkanes, etc., are present in lesser amounts. If benzene is alkylated in the presence of hydrogen fluoride, then 2-phenylalkanes are present in the lowest concentration in the resultant isomer mixture, and the proportion of the more internal phenylalkanes increases the closer the position of the phenyl group to the middle of the alkane chain. These relations are illustrated in Table 5 for industrial alkylbenzenes. Various isomerization reactions are responsible for these isomer distributions. Lewis acids such as aluminum chloride isomerize the phenylalkanes already formed, whereas protic acids such as hydrogen fluoride isomerize the unreacted olefins but not the phenylalkanes [49]. If branched olefins such as tetrapropylene are used as starting material, the phenyl residue is always bonded to a tertiary carbon atom, e.g.:

$$CH_3-CH-CH_2-C-CH_2-CH-CH-CH_3$$
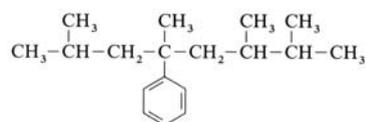
Table 5. Composition of industrial alkylbenzenes in wt % [50]

Component	From olefin with HF catalysis (molar mass 240)	From alkyl chloride with AlCl₃ catalysis (molar mass 241)	From olefin with AlCl₃ catalysis (molar mass 240)
Sum of *n*-alkylbenzenes	93	88	98
2-Phenylalkanes	18	29	29
Dialkyltetralins	0.5	9	0.5
Phenyldecane	14	13	14
Phenylundecane	34	30	29
Phenyldodecane	31	30	32
Phenyltridecane	20	25	24
Phenyltetradecane	1	2	1
Isomer distribution of phenyldodecanes			
1-Phenyldodecane	0	trace	0
2-Phenyldodecane	18	28	29
3-Phenyldodecane	16	19	19
4-Phenyldodecane	17	17	18
5-Phenyldodecane	24	18	18
6-Phenyldodecane	25	18	17

Processes for preparing linear industrial "dode-cylbenzene", a mixture of decylbenzene to tri-decylbenzene, from linear alkyl chlorides and from linear olefins are described hereinafter by way of example, the preparation of the alkyl chlorides or olefins being integrated components of the processes.

Alkylation with Alkyl Chlorides (Fig. 12). The alkane, a homologous mixture of linear alkanes with average carbon number 12, is reacted with gaseous chlorine at 100 – 140 °C in a chlorination tower to a conversion of 30 mol %. To minimize backmixing and, thus, the proportion of higher chlorinated paraffins, the chlorination can also be carried out in a cascade of reactors. Suitable reactor materials are lead, silver, or enamel; iron is not suitable.

The hydrogen chloride released in the reaction $RH + Cl_2 \rightarrow RCl + HCl$ escapes from the head of the chlorination tower and is washed in countercurrent with fresh alkane to trap unreacted chlorine. The hydrogen chloride is of high purity and can be used for further chemical syntheses. The "chlorine oil", consisting of alkyl chlorides and unreacted paraffin, is passed to the alkylation stage. The alkyl chlorides consist of positional isomers, secondary alkyl chlorides predominating by far.

The active catalyst in the alkylation is a liquid complex compound formed in the reaction mixture and containing up to 35 wt % aluminum chloride. This complex is only slightly soluble in the reaction mixture and can, therefore, be separated as a heavier phase and recycled. Losses can be replenished by adding fresh aluminum chloride or aluminum, which reacts with hydrogen chloride to form aluminum chloride.

The alkylation is preferentially carried out in glass-lined reaction towers at 80 °C. To minimize multiple alkylation, benzene is added in a manyfold molar excess. The hydrogen chloride released in a stoichiometric amount according to the equation $RCl + C_6H_6 \rightarrow RC_6H_5 + HCl$ maintains the reaction mixture in a turbulent state and is removed at the upper end of the reactor. It is also washed with fresh paraffin, but still contains low boiling point hydrocarbons (e.g., isobutane) and accordingly cannot be reused directly.

The reaction mixture leaving the alkylation tower is passed to a separating vessel in which the catalyst complex separates out. The organic phase is freed from residual catalyst by washing with water and sodium hydroxide and is worked up in a distillation unit. First benzene, then unreacted paraffin, and finally alkylbenzene accounts for only ca. 10 % of the alkylation mixture are separated. More highly alkylated benzenes and diphenylalkanes formed by reaction with dichloroalkanes in the "chlorine oil" can be isolated as a tail fraction.
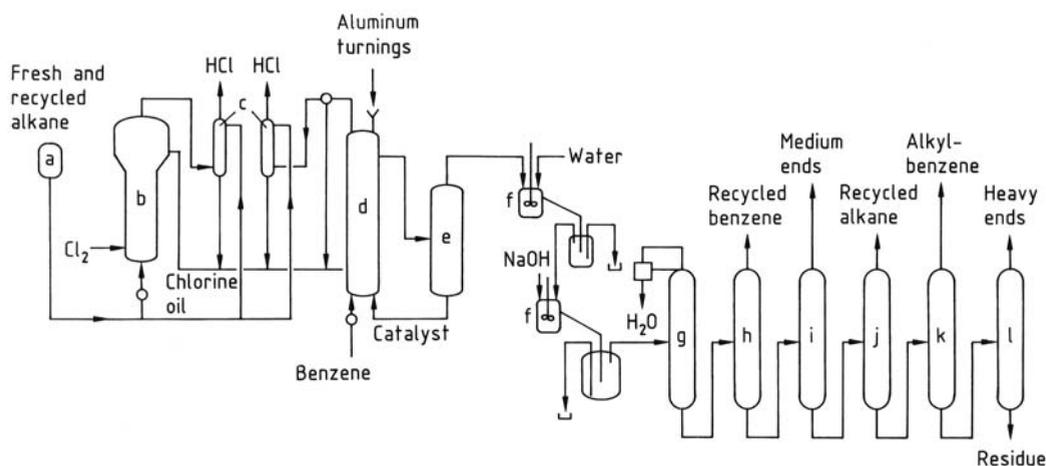
**Figure 12.** Preparation of a linear alkylbenzene by the aluminum chloride process
a) Storage vessel for fresh and recycled alkane; b) Chlorination tower; c) Wash towers for hydrogen chloride; d) Alkylation column; e) Separating vessel for catalyst removal; f) Water and sodium hydroxide wash; g) Dewatering column; h) Benzene column; i) Intermediate cut column; j) Paraffin column; k) Alkylbenzene column; l) Tails column

The dichloroalkanes react also form bicyclic compounds such as 1,3-dialkyltetralins, which during distillation remain in the alkylbenzene in amounts of 5 – 10 wt %

RCH₂—[tetralin structure]—CH₂R'
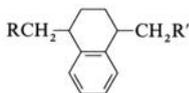
Alkylation with Olefins. The UOP process for producing alkylbenzenes, the most widely used process worldwide, is illustrated in Figure 13 [47]. The process consists of three stages: olefin production (Pacol = paraffin conversion to olefins), selective hydrogenation (DeFine), and alkylation.

The dehydrogenation of n-alkanes takes place at ca. 500 °C and with a slight hydrogen excess pressure of ca. 3 bar over a fixed-bed of modified platinum catalyst on aluminum oxide.

The alkane conversion is held at 10 – 15 % to minimize further dehydrogenation to diolefins and aromatics. The hydrogen released contains small amounts of lower alkanes; some of the hydrogen is recycled to the dehydrogenation reactor, while another part is used in a connected reactor for the selective hydrogenation of diolefins, formed in small amounts, to monoolefins (DeFine). The removal of diolefins is important to suppress the formation of byproducts, bicyclic hydrocarbons, and diphenylalkanes in the alkylation. The dehydrogenation product, containing 10 – 15 wt % monoolefins is passed to the alkylation reactor, in which it is intensively mixed with benzene and hydrofluoric acid, which is only slightly miscible with the hydrocarbons. The benzene is used in a manyfold molar excess to minimize multiple alkylation. The reaction is carried out at < 50 °C with intensive cooling. The acid catalyst is removed in a separating vessel connected to the reactor and is recycled to the alkylation reaction; a partial stream is passed through a distillation column (not shown in Fig. 13) in which the hydrofluoric acid (*bp* 19 °C) is freed from small amounts of dissolved, higher-boiling organic constituents, the so-called acid tar, a constant regeneration of the catalyst thereby being ensured. Since water is excluded from the whole alkylation section the latter can be manufactured from normal steel without risk of corrosion.

After stripping residual dissolved hydrogen fluoride in a distillation unit, the upper, organic phase from the separating vessel is fractionated into benzene, alkane, alkylbenzene, and higher-boiling compounds, the so-called heavy alkylate, which can be further fractionated. Benzene and alkane are returned to the process.

The distillation is simplified if paraffin-free olefins (e.g., tetrapropylene or linear alkenes from the SHOP process) are used for the alkylation. In the preparation of higher alkylbenzenes such as hexadecylbenzene, paraffin-free olefins are preferably used as starting materials since the distillation becomes more difficult as the boiling point rises.
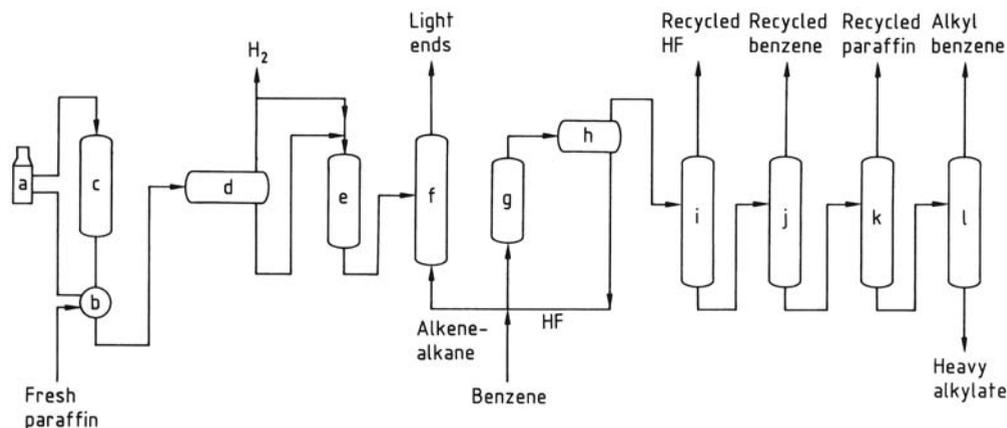

Figure 13. Preparation of a linear alkylbenzene by the UOP process
a) Heater; b) Heat exchanger; c) Dehydrogenation reactor; d) Gas – Liquid separator; e) Hydrogenation reactor; f) Stripper column; g) Alkylation reactor; h) Acid settler; i) HF stripper; j) Benzene column; k) Paraffin column; l) Rerun column

Formerly, hydrofluoric acid was the exclusive catalyst for the alkylation of benzene with olefins; however, more recently a plant came on stream in which aluminum chloride is also used for this reaction [50]. The linear alkylbenzene produced in this way is reported to be particularly pure.

Sulfonation. The sulfonation of alkylbenzenes, which at low temperature mainly occurs in the *p*-position, can be performed with concentrated sulfuric acid, oleum, or sulfur trioxide. Sulfonation with sulfur trioxide is now the predominant process. It has major advantages over sulfonation with sulfuric acid or oleum, including much faster reaction rate and higher space – time yield. Also, in sulfonation with sulfur trioxide no waste sulfuric acid is formed, and accordingly there are no workup or disposal problems.

The high reaction rate, combined with strong evolution of heat (ca. 170 kJ/mol, corresponding to ca. 700 kJ/kg of dodecylbenzene), necessitates intensive mixing and efficient cooling. The sulfur trioxide used is diluted to $4 - 8\%$ in air or nitrogen as carrier gas. This mixture is formed in sulfur combustion combined with the contact process; it can also be obtained by passing air or nitrogen over heated oleum or liquid sulfur trioxide.

Bubble-column reactors are suitable for discontinuous sulfonation with sulfur trioxide. The mechanical momentum of the inert gas produces a high turbulence, which can be enhanced by stirrers. The heat of reaction is dissipated through the jacket, through internal cooling tubes and, in the case of rapid product circulation, by external heat exchangers. The inert gas leaving the reactor must be freed of entrained sulfur trioxide and acid droplets by washing with alkylbenzene, for example. The course of the reaction is followed by acidimetric titration, and the addition of sulfur trioxide is discontinued when the desired "titer value" is reached.

The preferentially employed continuous sulfonation with sulfur trioxide is carried out in special reactors in which backmixing of the reaction material is largely avoided and in which the reaction takes place in intensively cooled thin layers. Many modifications of suitable reactors, namely falling film, multitube, or concentric tube reactors, are available [51], [52]. Such reactors are used particularly for the sulfonation of alkenes and for sulfation of ethoxylates, since with these substrates localized overheating and excessive concentrations of sulfur trioxide can have an even more disadvantageous effect on the product quality than in the case of alkylbenzenes.

The production of alkylbenzenesulfonate is illustrated in Figure 14. The sulfur trioxide/inert gas (air or nitrogen) mixture passes via a mist eliminator, in which entrained sulfuric acid is removed, to the continuous sulfonation reactor. The sulfur trioxide is used in a slight excess (up to 10 mol %).

The residence time of the liquid and gas in this reactor is a few minutes, and the reaction temperature is $40 - 50\ °C$. The reaction product passes to a separator, where the inert gas is removed. This waste gas is washed with liquid (e.g., alkylbenzene) to remove entrained acid droplets. The degassed sulfonation mixture passes through a digester where small amounts of pyrosulfonic acid present react with unreacted alkylbenzene:
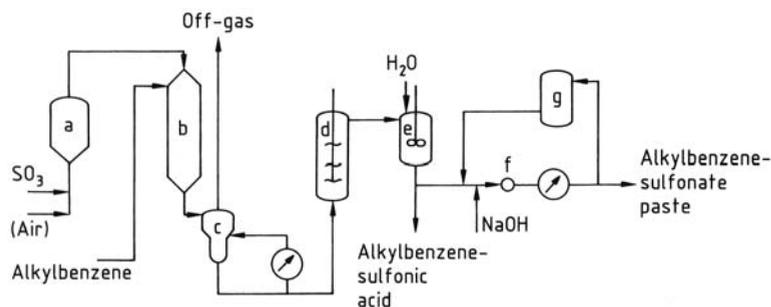

Figure 14. Continuous production of alkylbenzenesulfonate
a) Mist separator; b) Sulfonation reactor; c) Gas separator; d) Digestor; e) Hydrolyzer; f) Mixing pump; g) Intermediate vessel

$$C_{12}H_{25}\text{—}\langle\text{benzene}\rangle\text{—}SO_2OSO_3H + C_{12}H_{25}\text{—}\langle\text{benzene}\rangle$$

$$\longrightarrow 2\ C_{12}H_{25}\text{—}\langle\text{benzene}\rangle\text{—}SO_3H$$
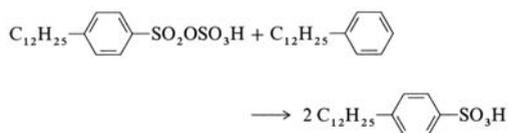
Acid anhydride, also present in small amounts, is hydrolyzed at 80 °C in a following hydrolyzer by adding 1 – 2 wt % of water:

$$C_{12}H_{25}\text{—}\langle\text{benzene}\rangle\text{—}SO_2\text{–}O\text{–}SO_2\text{—}\langle\text{benzene}\rangle\text{—}C_{12}H_{25} + H_2O$$

$$\longrightarrow 2\ C_{12}H_{25}\text{—}\langle\text{benzene}\rangle\text{—}SO_3H$$
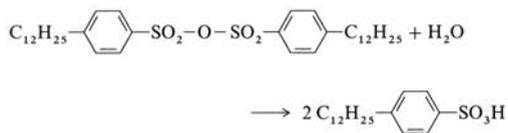
The sulfonic acid obtained in this way can then be neutralized directly, but as with sulfonic acid produced batchwise it can also be transported to the consumption site and neutralized there.

Anhydrous alkylbenzenesulfonic acids do not attack iron if water (and also atmospheric moisture) are excluded. Dodecylbenzenesulfonic acid can therefore be stored and dispatched in steel vessels. It can easily be poured, transferred, and metered as a liquid. Typical characteristic data of a high-quality dodecylbenzenesulfonic acid are given below:

Content of alkylbenzenesulfonic acid	97 – 98 %
Content of sulfuric acid	ca. 0.5 %
Content of water	0 %
Content of unsulfonated compounds	1.5 – 2 %
Titer value (mL 1 N NaOH/10 g acid)	31 – 32 mL
g Sodium salt/100 g acid	103 – 105 g
Density at 50 °C	ca. 1.03 g/mL
Viscosity at 50 °C	ca. 300 mPa · s
Color	yellow to brown

Neutralization. In the neutralization of the alkylbenzenesulfonic acid, in general only so much water is added as is necessary to form a flowable 50 % paste. The heat of neutralization is ca. 180 kJ/kg; a temperature of 60 °C is maintained by cooling. During neutralization the reaction mixture must be intensively mixed to avoid locally excessive sulfonic acid concentrations, since sulfonic acid containing 10 – 50 % water forms highly viscous gels. It has proved most convenient to add acid and sodium hydroxide continuously, while monitoring the pH, to an already neutralized mixture. In the continuous process illustrated in Figure 14 this is effected by circulating a large stream of already neutralized product and adding sulfonic acid as well as sodium hydroxide to this product stream, just in front of the mixing pump.

The brown to dark brown sulfonic acid becomes considerably lighter in color during neutralization. The light brown sulfonates obtained can be lightened by adding 1 – 3 wt % of sodium hypochlorite solution (containing 100 – 150 g of active chlorine per liter). The product then contains small amounts of chloride ions, which can cause stress corrosion cracking in steel, especially at high temperature. The apparatus for the bleaching stage must therefore be cladded with tantalum, silver, hastelloy, or earthenware.

Storage and Dispatch. Linear alkylbenzenesulfonates are water-soluble at 20 °C in an amount of up to 25 wt % to form clear solutions, and at higher concentrations pastes are formed that in the concentration range from 30 % to 60 % separate into two phases after a few hours. Such pastes must therefore be stirred during storage. The 75 % pastes do not decompose into two phases. The 65 – 75 % pastes can be dispatched only in the hot state on account of their high viscosity, and at room temperature they solidify to form rigid gels. The pastes, which can readily be pumped at 60 – 80 °C, can be stored and transported in stainless steel or glass fiber reinforced polyester vessels. They can be conveyed through heated stainless steel pipelines by using rotary piston pumps.

Anhydrous alkylbenzenesulfonates are hygroscopic and tend to agglomerate due to absorption of atmospheric moisture. Additives such as sodium sulfate or sodium toluenesulfonate counteract agglomeration; alkylbenzenesulfonates containing such additives can be worked up directly into pulverulent formulations. Anhydrous alkylbenzene sulfonate is obtained by drying hydrated pastes, e.g., on a drum dryer; it can be packed in plastic bags and palleted. Some typical data of an industrial sodium alkylbenzene sulfonate in various concentrations are shown in Table 6.

CAS Numbers. $C_{10} - C_{13}$ alkylbenzenesulfonic acid [*85536-14-7*], its sodium salt [*68411-30-3*], its diethanolamine salt [*84989-15-1*], its triethanolamine salt [*68411-31-4*]; $C_{10} - C_{16}$ alkylbenzenesulfonic acid [*68584-*

Table 6. Typical characteristic data of an industrial sodium alkylbenzenesulfonate

Property	Concentration			
	50 %	75 %	80 %	90 %
Appearance at 20 °C	yellowish, flowing, inhomogeneous paste	yellowish, viscous, homogeneous paste	white to yellowish powder	white to yellowish powder
Active substance, wt %	50	75	80	90
Sodium sulfate, wt %	0.5	0.7	5	6
Sodium chloride, max. wt %	0.3	0.3	0.5	0.5
Neutral oil, max. wt %	1	1	1	1
Iron, max. ppm	5.0	5.0		
Sodium toluenesulfonate, wt %			14	
Water, wt %	remainder	remainder	1	1.5
Iodine color value (10 % solution)	1	1.5		
pH (2 % in fully deionized water)	7.5 – 8.5	7.5 – 8.5	8	8 – 9
Density, g/mL	1.06	1.06		
Bulk density, g/L			470	550

22-5], its sodium salt [*68081-81-2*], its potassium salt [*68584-27-0*], its ammonium salt [*68910-31-6*], its calcium salt [*68584-23-6*], its magnesium salt [*68584-26-9*].

Producers. Major producers of alkylbenzenesulfonic acids and alkylbenzenesulfonates in Europe include Albright & Wilson, Berol-Nobel, Harcros-Chemicals, Hüls, ICI, Kao, Manro, Pulcra, Rhône-Poulenc, Stepan, Unger, Wibarco, Witco; in the United States, A. Harrison, Ardmore, Cromton & Knowles, Eastern Color & Chemical, Emkay Chemical, Exxon, Harcros, Henkel, ICI America, Pilot Chemicals, Rhône-Poulenc Surfactants, Stepan, Unger, Witco; in . Taiwan, Taiwan Surfactant; and in Israel, Zohar.

Whereas the sulfonation of alkylbenzene and the neutralization of the sulfonic acid takes place in relatively simple plants and is accordingly even carried out by many producers for captive use (e.g., for detergents), production of the alkylbenzene is more complex. The number of producers of alkylbenzene is therefore limited. Producers of linear alkylbenzenes by hydrogen fluoride catalysis include Hüls, Enichem, and Petresa in Europa; Vista and Monsanto in North America; YPF La Plata and Deten in South America; Al Astra in Saudi Arabia; Egyptian Generalpet in Egypt; Mitsubishi Petrochemical and Nippon Petroleum in Japan; Isu Chemical in South Korea; and Formosan Union in Taiwan. Enichem and Wibarco in Europe, Vista in the United States, and Nalken in Japan also produce alkylbenzene using aluminum chloride as catalyst.

Producers of tetrapropylenebenzene include Chevron in France, Monsanto in North America, Pemex in Mexico, Mitsubishi Petrochemical and Nippon Petroleum in Japan, and Formosan Union in Taiwan.

6.2.2. Alkylnaphthalenesulfonates

The first synthetic surfactants based on fossil raw materials were the alkylnaphthalenesulfonates such as dipropylnaphthalene- and dibutylnaphthalenesulfonates, which still play a role as wetting agents in the textile industry. These substances are obtained in a one-pot reaction by alkylating naphthalene with isopropanol, butanol, or other alcohols in the presence of concentrated sulfuric acid as catalyst and water binder, and immediately treating the reaction product with oleum to form (di)-alkylnaphthalenesulfonic acid, in a similar manner to the sulfonation of alkylbenzene, and then separating the "waste sulfuric acid", and finally neutralizing with sodium hydroxide.
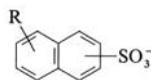
The salts of naphthalenesulfonic acid condensed with formaldehyde are chemically related to the alkylnaphthalenesulfonates, and can also be obtained in a one-pot reaction. For this purpose naphthalene is first of all sulfonated and the acid sulfonation mixture is then reacted with formaldehyde.

After the condensation the reaction product is neutralized. The molar ratio is chosen so that n is between 2 and 3. The salts of these condensation products are outstanding dispersants for finely divided solids, and are used as pigment dispersants and cement plasticizers.
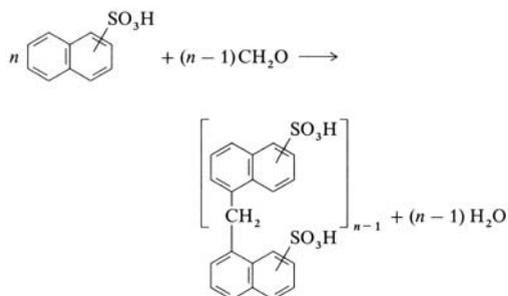
Producers. of both types of products include BASF, Hoechst, Auschem, Rhône-Poulenc, and ICI in Europe; American Cyanamid, Du Pont, Emkay, Henkel, and Witco in the United States; Takemoto Oil & Fat in Japan; and Taiwan Surfactant in Taiwan.

6.2.3. Alkanesulfonates [53–56]

Of the large number of possible ways of synthesizing alkanesulfonates ($\to$ Sulfonic Acids, Aliphatic), only sulfochlorination (the reaction of alkanes with sulfur dioxide and chlorine to form alkane sulfonyl chlorides and their saponification with sodium hydroxide) and sulfoxidation (the reaction of alkanes with sulfur dioxide and oxygen and neutralization of the sulfonic acids) are of industrial importance. The radical addition of sodium hydrogensulfite, which proceeds with satisfactory yields only in the case of terminal olefins, gives terminal alkanesulfonates, which are only slightly soluble in water and are therefore of no industrial importance [57].

In sulfochlorination and sulfoxidation, mixtures of straight-chain alkanes with 12 to 18, preferably 13 to 17 carbon atoms, are used as starting materials. Both reactions proceed appropriate by a radical-chain mechanism. In sulfoxidation a sulfoperoxy acid first of all being formed:

$$\begin{aligned}
R^{\cdot} + SO_2 &\longrightarrow RSO_2^{\cdot} \\
RSO_2^{\cdot} + Cl_2 &\longrightarrow RSO_2Cl + Cl^{\cdot} \\
Cl^{\cdot} + RH &\longrightarrow R^{\cdot} + HCl \\
\hline
RH + SO_2 + Cl_2 &\longrightarrow RSO_2Cl + HCl
\end{aligned}$$

$$\begin{aligned}
R^{\cdot} + SO_2 &\longrightarrow RSO_2^{\cdot} \\
RSO_2^{\cdot} + O_2 &\longrightarrow RSO_2O_2^{\cdot} \\
RSO_2O_2^{\cdot} + RH &\longrightarrow R^{\cdot} + RSO_2O_2H \\
\hline
RH + SO_2 + O_2 &\longrightarrow RSO_2O_2H
\end{aligned}$$
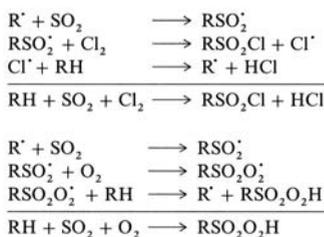
The reaction can be started by radical initiators (e.g., peroxides) or by irradiation. Ultraviolet radiation is used industrially. In sulfochlorination chlorine radicals are formed initially and react with an alkane:

$$RH + Cl^{\cdot} \to R^{\cdot} + HCl$$
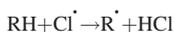
In sulfoxidation the mechanism of the UV initiation has not been fully clarified. It is assumed that activated sulfur dioxide is formed, which reacts with the alkane:

$$RH + SO_2^* \to R^{\cdot} + HSO_2^{\cdot}$$
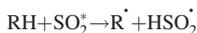
Aromatics, olefins, branched alkanes, and many other substances (e.g., amines) inhibit the radical-chain reaction; the paraffins must therefore be of high purity and linearity for both processes. With high-purity alkanes quantum yields of 10 000 Einstein are achieved in sulfochlorination; termination reactions necessitate constant re-initiation (irradiation). In sulfoxidation, alkanesulfoperoxyacids are formed initially but are unstable under the reaction conditions, and decompose with the formation of additional radicals:

$$RSO_2O_2H \to RSO_3^{\cdot} + {}^{\cdot}OH$$

$$RSO_3^{\cdot} + RH \to RSO_3H + R\cdot$$

$${}^{\cdot}OH + RH \to H_2O + R^{\cdot}$$
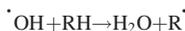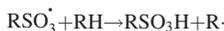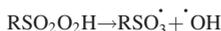
These radicals compensate the deficit of radicals due to chain termination; being a radical-chain reaction with degenerative branching, in pure alkanes sulfoxidation accordingly takes place after a single initiation, without further radical-producing measures. The decomposition products of the peroxyacid result in a number of byproducts (esters, alcohols, discoloring substances), which adversely affect the product quality. Sulfoxidation is therefore carried out

industrially with the addition of water, which together with the sulfur dioxide present in the reaction medium traps the sulfoperoxy acid before its radical-type decomposition begins:

$$RSO_2O_2H + SO_2 \rightarrow R\,SO_3H + H_2SO_4$$
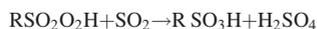
A radical donor is lacking if the decomposition of the peroxyacid occurs by an ionic mechanism, and sulfoxidation in the presence of water therefore requires constant initiation; in the case of pure alkanes the quantum yield is ca. 10 Einstein.

In both processes substitution mainly takes place at the internal, secondary carbon atoms of the alkane. The oxysulfonyl groups are distributed randomly over the molecule. The degree of polysubstitution increases with increasing conversion. Since the interfacial activity of the sulfonates obtained after saponification decreases with increasing proportions of polysulfonates, the paraffin conversion is restricted.

Alkanesulfonates below C_8 are not surface active. $C_{12} - C_{18}$ sodium alkanesulfonates are readily soluble in water; the solubility is increased still further by the disulfonate fraction that is always present in industrial products. On account of their proportion of species with central sulfonate groups ("effective surfactants") the alkane sulfonates are good wetting agents. They are preferably used in liquid formulations for detergents and cleansing agents, but can also be incorporated in washing powders. Alkanesulfonates are widely used as emulsifiers, for example, in the polymerization of vinyl chloride.

Sulfochlorination Processes. Alkanesulfonates obtained from sulfochlorination processes are known as Mersolates. They are obtained in two steps:

$$RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl$$

$$RSO_2Cl + 2\,NaOH \rightarrow RSO_3Na + NaCl$$
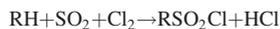
In the first stage the liquid paraffin is reacted at $20 - 40\,°C$ in chlorine- and acid-resistant reactors (earthenware, enamel, PVC) with an approximately equimolar mixture of sulfur dioxide and chlorine under irradiation from mercury vapor lamps. The waste gas consists of hydrogen chloride contaminated with sulfur dioxide; the former can be recovered as aqueous hydrochloric acid.

The paraffin conversion is adjusted to ca. 30 %; the sulfonyl chlorides then contained in the reaction mixture (Mersol 30) in amounts of ca. 30 % consist of 94 % monosulfochlorides and 6 % disulfochlorides. Mersol H, with 45 % sulfonyl chlorides in the reaction mixture already contains 16 % disulfonyl chlorides and polysulfonyl chlorides, while Mersol D, with 80 % sulfochlorides, contains ca. 40 % disulfonyl chlorides and polysulfonyl chlorides.

In the second step the degassed sulfochlorination mixture is saponified with 10 % sodium hydroxide. Elevated temperatures must be avoided since the alkane sulfonyl chloride is desulfonated to the alkyl chloride starting above ca. $80\,°C$, with elimination of sulfur dioxide. While hot, the neutralized product deposits part of the unreacted alkane as upper phase, and when cold deposits most of the sodium chloride derived from the saponification as an aqueous lower phase. The remaining sulfonate "glue" is freed from residual alkane in an evaporator, which together with the paraffin from the phase separation is returned to the sulfochlorination. The sulfonate is obtained as a melt flowing at $150 - 175\,°C$, which solidifies on cooling drums and can be removed as flakes. The flakes are hygroscopic and readily agglutinate – they can be dispersed in water and processed into pastes. The melt can, however, also be taken up directly under pressure in water. Table 7 summarizes typical data for industrial commercial products of different concentrations.

Half the chlorine used in the process is converted to low-grade hydrochloric acid, and half into valueless sodium chloride solution. Thus the process is economically inefficient. This disadvantage is offset by the advantage that the highly reactive alkanesulfonyl chloride intermediates can be used in the preparation of a large number of derivatives besides alkanesulfonates. For example, reaction of an alkanesulfonyl chloride with glycine yields and alkylsulfamidocarboxylic acid, which can be used to prepare effective emulsifiers and corrosion inhibitors. Esters, obtained with alcohols and phenols, are used as plasticizers for plastics.

Storage. Alkanesulfonate flakes are hygroscopic and should be processed in total. The pastes undergo segregation on standing and must

Table 7. Typical data of industrial sodium alkanesulfonates [*68037-49-01*] obtained by the sulfochlorination process

	Concentration		
	32 %	62 %	93 %
Appearance	solution	paste (pumpable)	colorless flakes
Active substance, wt %	32	62	93
Disulfonate and polysulfonate, wt %	5	10	14
Sodium chloride, max. wt %	2.0	3.5	4.2
Sodium sulfate	trace	trace	trace
Neutral oil, max. wt %	1.0	1.0	0.5
Iron, max. ppm	5	5	10

be homogenized before use. The products can be stored for an unlimited time.

Sulfoxidation Processes. Figure 15 illustrates a production process for alkanesulfonates using the following reactions

$$RH + 2\,SO_2 + O_2 + H_2O \rightarrow RSO_3H + H_2SO_4$$

$$RSO_3H + NaOH \rightarrow RSO_3Na + H_2O$$
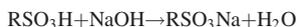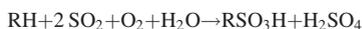
When carried out under UV irradiation with addition of water, this process is known as the light – water process.

The reactors must be resistant to acids and oxidation, and are of large volume in order to maximize the quantum yield. High-pressure 10 – 40 kW mercury vapor lamps are used. The protective tubes are made of quartz and are double-walled to absorb the thermal radiation from the lamp, with water cooling being provided between the lamp and reaction space. Since oxygen is substantially less soluble than sulfur dioxide in alkanes the reaction gas must be circulated at a high rate with a blower to maintain a sufficient supply of dissolved oxygen in the reaction mixture. This circulating gas also ensures intensive mixing of the reactor contents, which, however, can also be achieved by powerful stirrers. This is important because the aqueous and alkane phases must be constantly mixed so that the alkanesulfoperoxyacid formed initially comes into immediate contact with water and sulfur dioxide, whereby it is decomposed to the alkanesulfonic acid. Furthermore, the aqueous phase constantly extracts sulfonic acids and sulfuric acid from the alkane phase. The unusually high degree of polysubstitution – with a 1 % paraffin conversion the sulfonic acids formed already contain 10 % of disulfonic and polysulfonic acids – is due to the multiphase nature of the system. To avoid a higher proportion of disulfonic acids, the alkane conversion is limited to ca. 1 %. The mixture leaving the reactor, which consists of about 25 parts of alkane and one part of aqueous phase, passes to a separator in which
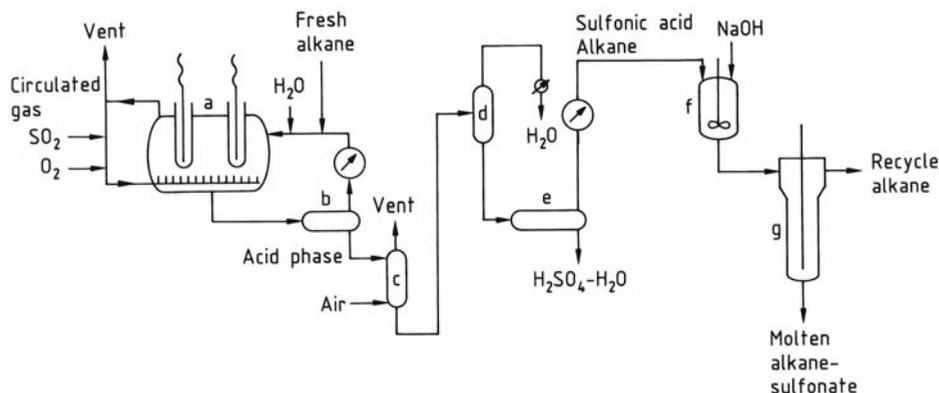

Figure 15. Production process flow sheet for alkanesulfonates using sulfoxidation
a) Photoreactor; b) Acid settler; c) Degassing column; d) Evaporation column; e) Separator for sulfuric acid; f) Neutralization vessel; g) Evaporator

the alkane forms the upper phase. The alkane is recycled through a cooler to the reactor, together with fresh alkane and process water. At 1 % conversion the amount of recycled alkane is very large, and can be used for external cooling of the reaction mixture. The reaction temperature is maintained at 20 – 40 °C.

The acid phase that separates out in the settler contains acids (sulfonic acids and sulfuric acid), water, and alkane in roughly equal amounts. This phase is freed from dissolved sulfur dioxide by degassing and is concentrated by distilling off part of the water under vacuum. The low-water-content bottom product from the evaporating column separates into two phases, the lower phase consisting of 50 to 65 % aqueous sulfuric acid, which is thereby largely removed from the sulfonic acid phase. Discolorations, which can occur in this stage due to heating (60 – 120 °C) of the sulfonic acids, can be counteracted by addition of hydrogen peroxide. The organic phase remaining after separating the sulfuric acid consists of roughly equal parts of sulfonic acids and alkane. It is neutralized with concentrated sodium hydroxide and freed from residual alkane, e.g., in a thin-layer evaporator at 200 °C in vacuo, which is recycled to the reaction. The sulfonate melt that is formed can be cooled on a rotating drum and converted to flakes, or processed with water into 60 – 65 % pastes.

As an alternative to the thermal separation of sulfuric acid, the sulfonic acids together with the alkane can be extracted from the mixture with weakly polar solvents such as alcohols, ketones, or ethers, leaving behind a 20 % aqueous sulfuric acid. The solvent must then be separated after the neutralization in an additional distillation column [58].

Some data for commercial products of various concentrations are listed in Table 8.

Storage and Dispatch. The flake product can be stored for an unlimited period without undergoing any change provided moisture is excluded. The 60 % paste tends to undergo phase separation, which is prevented by stirring or circulation with a pump at 65 °C. The 30 % solution remains homogeneous and is easily pumpable.

Stainless steel, aluminum, and glass fiber reinforced polyester resin are suitable materials for storage tanks and pipelines. Normal steel is unsuitable because even very small amounts of rust seriously affect the quality.

Producers. Alkanesulfonates are produced by the sulfochlorination process by Bayer, Leuna and at Volgograd (Russia), and by the sulfoxidation process by Hoechst and Hüls.

6.2.4. α-Olefinsulfonates [59–63]

Olefinsulfonates are obtained by hydrolysis and neutralization of the sulfonation products of olefins. Suitable sulfonating agents include sulfur trioxide and its complexes (e.g., with dioxan), and chlorosulfonic acid; gaseous sulfur trioxide is used exclusively in industry. The fact that only α-olefins are used for the production of sulfonates is due primarily to the availability of $C_{12} - C_{18}$ olefins of this type in the required degree of

Table 8. Typical characteristic data of industrial sodium alkanesulfonates [85711-69-9], [7757-82-6], and [7732-18-5] obtained by the sulfoxidation process

	Concentration		
	30 %	60 %	93 %
Appearance at 25 °C	clear, almost colorless liquid	yellowish, soft paste	yellowish, waxy flakes
Active substance, wt %	30	60	93
of which disulfonate and polysulfonate, wt %	4	7	11
Sodium sulfate, max. wt %	2	4	6.5
Alkane, max. wt %	0.3	0.5	0.7
APHA color (10 % active substance in water)	40	40	50
Bulk density, g/L			500

purity. Since the sulfonation takes place without double bond isomerization, α-sulfonates (α-olefinsulfonates = AOS) having good application properties are obtained from α-olefins. If olefins containing a centrally situated double bond are sulfonated, sulfonates with a centrally bonded sulfonate group are obtained, which have not yet achieved any industrial importance [64], [65].

In the sulfonation of α-olefins 1,2-sultones are probably formed initially, which then isomerize rapidly to 1,3-sultones, and more slowly to 1,4-sultones:

$$RCH_2CH_2CH=CH_2 + SO_3 \longrightarrow RCH_2CH_2CH-CH_2$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O\text{---}SO_2$$

$$\longrightarrow RCH_2CHCH_2CH_2 \longrightarrow RCHCH_2CH_2CH_2$$
$$\quad\quad\quad\quad\quad O\text{---}SO_2 \quad\quad\quad\quad O\text{---------}SO_2$$
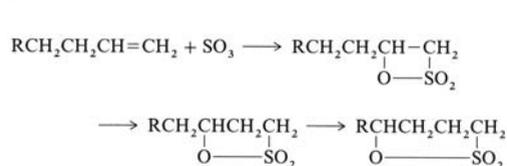
In the reaction with sulfur trioxide diluted with inert gas, at temperatures up to 40 °C, almost exclusively sultones are formed at up to 60 % olefin conversion, and at higher conversions the sultones isomerize to some extent to alkenesulfonic acids:

$$RCH_2CHCH_2CH_2 \longrightarrow$$
$$\quad\quad O\text{---------}SO_2$$

$$RCH_2CH=CHCH_2SO_3H + RCH=CHCH_2CH_2SO_3H$$
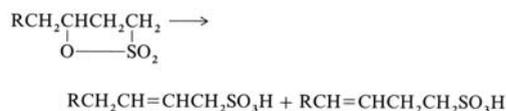
With increasing conversion side reactions such as disulfonation and oxidation also increase, leading to discoloration of the product. To convert the sultones completely to sulfonic acids or sulfonates, the sulfonation mixture must be hydrolyzed. Hydrolysis can be performed under acid or alkaline conditions. Acid hydrolysis gives predominantly alkenesulfonic acids with double bonds in the 2- and 3-positions, though compounds with more internal double bonds are also obtained; in alkaline hydrolysis about two-thirds of the reaction product consists of salts of hydroxyalkanesulfonic acids, and the remainder, salts of alkenesulfonic acids, as isomer mixtures:

$$RCH_2CHCH_2CH_2 \xrightarrow{\text{NaOH}}$$
$$\quad\quad O\text{---------}SO_2$$

$$RCH_2CH=CHCH_2SO_3Na + RCH_2CH-CH_2CH_2SO_3Na$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad OH$$
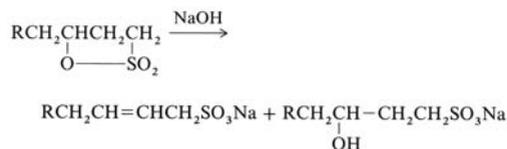
Industrial hydrolysis is carried out exclusively under alkaline conditions, mixtures of 60 to 65 % of alkenesulfonates and 40 – 35 % of hydroxyalkanesulfonates being obtained, which for the sake of simplicity are termed α-olefinsulfonates.

β-Branched α-olefins, formed by dimerizing short-chain α-olefins, are sulfonated either as such, but generally mixed with linear α-olefins. Due to the presence of a tertiary carbon atom, exclusively β-branched isomeric alkenesulfonic acids are obtained, e.g.,

$$\overset{R'}{\underset{|}{RCH_2C}}=CH_2 + SO_3 \longrightarrow \overset{R'}{\underset{|}{RCH}}=C-CH_2SO_3H$$

Since they have a long-chain hydrophobic residue and a terminal hydrophilic group, α-olefinsulfonates derived from linear α-olefins are efficient surfactants, with low CMCs, high detergent power, and good foaming ability in water. On account of their good water solubility sulfonates obtained from 1-dodecene to 1-hexadecene are widely used in liquid detergents and cleansing agents, in cosmetic preparations, and shampoos. Sulfonates obtained from α-hexadecene to α-octadecene can be used in powder formulations. Sulfonates obtained from β-branched α-olefins are only slightly watersoluble; they are good wetting agents, but are less suitable for detergents and cleansing agents. In industrial products they are used as a blend with linear α-olefin sulfonates in a maximum proportion of 30 %.

Production. The reaction of sulfur trioxide with olefins is rapid and strongly exothermic (ca. 180 kJ/mole; i.e., for example, 860 kJ/kg hexadecene). Local overheating, which leads to carbonization and thus brown to black products, cannot be avoided in conventional sulfonation reactors, even with intensive cooling and thorough mixing, especially if high olefin conversions are used for economic reasons.

The sulfonation of α-olefins is nowadays carried out industrially in continuous, short-time sulfonation reactors, like those used for sulfonation of alkylbenzene (see 6.2.1), and for sulfating ethoxylates [51], [52]. The principle of these reactors, supplied by Allied, Ballestra, Chemithon, Lion, or Mazzoni, is to bring the substrate in the form of thin, fast-flowing and strongly cooled films or layers into contact with sulfur trioxide
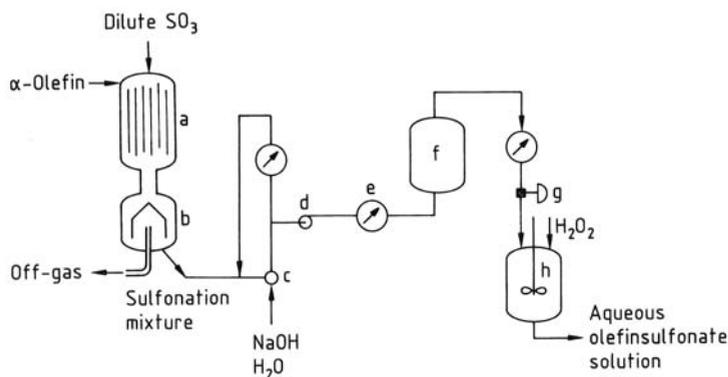
Figure 16. Continuous preparation of sodium α-olefinsulfonate
a) Sulfonation reactor; b) Gas separator; c) Mixing pump; d) Booster pump; e) Heater; f) Hydrolysis reactor; g) Pressure maintenance valve; h) Reactor for bleaching

gas diluted with inert gas. Air or residual air from the combustion of sulfur dioxide to sulfur trioxide serves as inert gas; the concentration of sulfur trioxide is adjusted to 4 – 6 vol %.

Figure 16 illustrates the continuous production of a sodium α-olefinsulfonate. The olefin is reacted with a 10 – 20 % excess of sulfur trioxide in the reactor at as low a temperature as possible (40 °C; at lower temperature the high viscosity can cause problems). The reaction product flows into a separator, in which liquid and gas separate. The waste gas, which contains traces of sulfur trioxide and small amounts of sulfur dioxide is washed with caustic soda before being discharged to the atmosphere. The sulfonation mixture is introduced into the circulating stream of neutralized sulfonic acid and mixed with caustic soda in a pump. A partial stream is charged via a booster pump and a heater to a hydrolysis reactor where residual sultones are saponified. Hydrolysis is carried out at 150° to 250 °C with a residence time of < 1 h. If the solution still contains fairly large amounts of unsulfonated hydrocarbon, this separates as upper phase and can be removed. The hydrolysate is cooled and the pressure is released. The amount of water added in the neutralization is measured so that 30 to 40 % solutions are formed, which are bleached with hydrogen peroxide.

The olefinsulfonates produced in this way contain, relative to total sulfonate, 10 – 15 % of disulfonates and small amounts of neutral oil (olefins, sulfones, oxidation products) and sodium sulfate.

Typical data of two industrial products based on C_{14}/C_{16} and C_{16}/C_{18} α-olefins are summarized in Table 9.

Table 9. Typical data of industrial sodium α-olefinsulfonates

Olefin	C_{14}/C_{16}	C_{16}/C_{18}
CAS no.	[68439-57-6]	[977067-81-4] (RD)
Appearance at 25 °C	clear, pale yellow liquid	slightly turbid, pale yellow liquid
Active substance, wt %	37	33
of which disulfonate, wt %	4	3
Sodium sulfate, wt %	1	1
Sodium chloride	trace	trace
Unsulfonated substance, wt %	1.5	1.5
Klett color index (5 % in 5 % butyl diglycol)	60	100
Viscosity, mPa · s	ca. 1000	ca. 1000

Storage and Dispatch. Olefinsulfonate solutions can be stored and dispatched in stainless steel or plastic vessels. The solutions are pumpable. Olefinsulfonates are not sensitive to heat, though overheating should be avoided. Reversible precipitation can occur below 0 °C.

Producers. α-Olefinsulfonates are produced by Akzo, Albright & Wilson, Hoechst, Rhône-Poulenc, and Witco in Europe; by Pilot Chemicals, Rhône-Poulenc Surfactant, Stepan, and Witco in the United States; and by Lion in Japan. Important producers of α-olefins, which are produced on a large scale for various purposes such as sulfonation, hydroformylation, or alkylation, are Chevron in the United States, Ethyl in Belgium and the United States, Nizhnekamsk in Russia, Shell in England and the United States, Spolana in Czechoslovakia, and Idimitsu Petrochemical in Japan.

6.2.5. α-Sulfo Fatty Acid Esters [63], [66–70]

The sodium salts of α-sulfo fatty acid methyl esters based on coconut, palm kernel, or tallow fatty acids are far more soluble in water than the disodium salts of α-sulfo fatty acids:

$$\underset{\underset{SO_3Na}{|}}{R-CH-COOCH_3} \qquad \underset{\underset{SO_3Na}{|}}{R-CH-COONa}$$
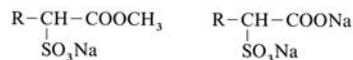
For this reason the esters are preferred. The α-sulfo fatty acid esters are stable to hydrolysis in the pH range 4 – 9 and are relatively insensitive to water hardness. They have good emulsifying and lime soap dispersing properties, and their aqueous solutions foam well and have a good cleaning ability with respect to textiles. They are accordingly used as components of soap bars and detergents.

The α-sulfo fatty acid esters are prepared by sulfonation of fatty acid methyl esters. The reaction proceeds in two stages [71]. Sulfur trioxide is rapidly absorbed by the ester at < 50 °C to give a 2 : 1 addition compound that rearranges to the α-sulfo fatty acid methyl ester at 70 – 90 °C. Sulfonation with 5 vol % of sulfur trioxide in an inert gas can be carried out in a stirred vessel cascade, in which the temperature increases from vessel to vessel. With sulfonation in a continuous short-time sulfonation reactor, a further reactor must be connected that ensures complete rearrangement at elevated temperature. Sulfonation is carried out with a 10 – 20 % excess of sulfur trioxide. The sulfonation mixtures are dark colored, and are bleached with hydrogen peroxide at 60 to 80 °C and then neutralized with sodium hydroxide. The sodium salts of the α-sulfo fatty acid esters are handled as ca. 40 % pastes or slurries.

Producers. α-Sulfo fatty acid esters are produced by Henkel and Lion.

6.2.6. Sulfosuccinates [72], [73]

The sodium salts of sulfosuccinate esters are obtained by reacting dialkyl maleates or salts of monoalkyl maleates with sodium hydrogensulfite in aqueous-alcoholic solution. Esterification components for dialkyl esters are mainly $C_5 – C_8$ alcohols and fatty acid ethanolamines, and for monoalkyl esters, fatty alcohols, fatty acid etha-

nolamides, and fatty acid ethoxylates. The sulfosuccinates thus offer a wide variety of molecular structure, which can be adapted to numerous applications. The pure sulfo esters are also termed sulfosuccinates, while the amide-group- containing products are known as sulfosuccinamates:

$$NaO_3S-\underset{\underset{COOR}{|}}{CH}-\overset{\overset{CH_2-COOR}{|}}{}$$

$$NaO_3S-\underset{\underset{COOCH_2CH_2NHCOR}{|}}{CH}-\overset{\overset{CH_2-COOCH_2CH_2NHCOR}{|}}{}$$

$$NaO_3S-\underset{\underset{COONa}{|}}{CH}-\overset{\overset{CH_2-CO[OCH_2CH_2]_nOR}{|}}{}$$

$$NaO_3S-\underset{\underset{COONa}{|}}{CH}-\overset{\overset{CH_2-CO[OCH_2CH_2]_nNHCOR}{|}}{}$$
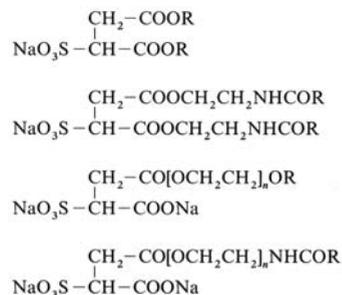
The dialkyl sulfosuccinates with short- chain alkyl groups R such as butyl, hexyl, or ethylhexyl are readily soluble in water and have outstanding wetting power (fast wetters) and dispersing properties, and are therefore used in textile processing and dyeing. They crystallize readily, like the sulfosuccinamates, and are therefore ideally suited as components of dry cleaning agents. With increasing alkyl chain length the solubility and wetting ability of sulfosuccinates decrease, while their detergent power and emulsifying power increase. The disodium salts of monosulfosuccinates are becoming increasingly important as hardness-insensitive and dermatologically compatible surfactants [74]. They are used in detergents and cleansing agents, especially for body-care products, and as emulsifiers in cosmetics. They are also used as polymerization emulsifiers and in ore flotation. Suitable alkyl residues in these sulfosuccinates are fatty alkyl or nonylphenyl residues; the degree of ethoxylation n is between 3 and 12. Natural fatty acids are used as starting products for sulfosuccinamates.

A common feature of all sulfosuccinates is that they are readily saponified at the ester group. They can therefore be used only in approximately neutral media (pH 6 – 8).

Storage and Dispatch. The sodium salts of the diesterified sulfosuccinic acids can be obtained as powders by evaporating their solutions. They are generally transported as concentrated solutions in plastic drums or stainless steel

Table 10. Typical data of some industrial sulfosuccinates

	Sodium diethylhexyl sulfosuccinate	Disodium lauryltriglycol sulfosuccinate	Disodium lauroylaminoethyl sulfosuccinate
CAS no.	[577-11-7]	[58450-52-5]	[25882-44-4], [55101-78-5]
Apperance	clear liquid	clear liquid	clear liquid
Active substance, wt %	68 – 70	34	35
Clear point, °C	< 0	12	−2
pH (1 % active substance)	6 – 7	6 – 7	6 – 7
Klett color index (5 % active substance)	40	150	150
Density, g/cm^3	1.0	1.1	1.1
Viscosity, mPa · s	300	50	25
Flash point, °C		45	>100

vessels. Table 10 gives some typical data for three industrial products, which may contain a few percent of a solvent (isopropanol) in order to render them clear.

Producers include Albright & Wilson, Auschem, BASF, Cyanamid, Harcros, Henkel, Hüls, Manro, Rewo, Rhône-Poulenc, Stepan, Union Carbide, Witco, and Zschimmer & Schwarz in Europe; American Cyanamide, Croda, Enkay, Harcros, Hart, Henkel, The McIntyre Group, Mona Industries, Rhône-Poulenc, Sherex, Stepan, and Union Carbide in North America; Zohar in Israel; Toho and Sanyo in Japan; and Taiwan Surfactant in Taiwan.

6.2.7. Alkoxyalkane-, Acyloxyalkane-, and Acylaminoalkanesulfonates

Methods of preparation of alkoxyalkanesulfonic acid salts, which would be useful for synthesizing alkylpolyglycol ether sulfonates, which in contrast to ether sulfates are resistant to hydrolysis, have not yet been carried out on an industrial scale.

$$ROH + ClCH_2CH_2SO_3Na + NaOH \longrightarrow$$
$$ROCH_2CH_2SO_3Na + NaCl + H_2O$$

$$ROH + HOCH_2CH_2SO_3Na \xrightarrow{\Delta}$$
$$ROCH_2CH_2SO_3Na + H_2O$$

$$ROH + CH_2-CH_2 + NaOH \longrightarrow$$
$$ROCH_2CH_2CH_2SO_3Na + H_2O$$
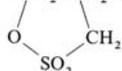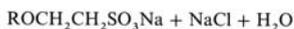
The reaction of alcohols with epichlorohydrin to form alkoxyhydroxychloropropane, which reacts with sodium sulfite to give an alkoxyhydroxypropanesulfonate, has achieved some importance:

$$ROH + CH_2-CHCH_2Cl \longrightarrow ROCH_2CHOHCH_2Cl$$

$$ROCH_2CHOHCH_2Cl + Na_2SO_3 \longrightarrow$$
$$ROCH_2CHOHCH_2SO_3Na + NaCl$$
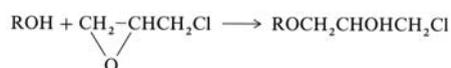
Such sulfonates are stable to water hardness and have good wetting and dispersing properties. They are dermatologically compatible and are used occasionally in the United States in body cleansing agents. Their water solubility, however, is low. Products containing $C_{16} - C_{18}$ alkyl groups are only sparingly soluble.

Due to their insensitivity to water hardness, good foaming power, soil suspending power, and dermatological compatibility, the fatty acid-derived salts of acyloxyethanesulfonic and acylaminoethanesulfonic acids are industrially fairly important (e.g., in the textile industry and in bodycare and cleansing agents). They are prepared by reacting the corresponding acid chlorides with sodium isethionate or *N*-methyltaurine.

$$RCOCl + HOCH_2CH_2SO_3Na \longrightarrow$$
$$RCOOCH_2CH_2SO_3Na + HCl$$

$$RCOCl + CH_3NHCH_2CH_2SO_3Na + NaOH \longrightarrow$$
$$RCON(CH_3)CH_2CH_2SO_3Na + NaCl + H_2O$$

Whereas the reaction of the isethionate with the acid chloride takes place at 100 – 120 °C without solvent and the reaction product occurs in a friable solid form after the hydrogen chloride,

N-methyltaurine is reacted with the fatty acid chloride in aqueous solution at 20 – 30 °C. The *N*-acyl-*N*-methyltauride is obtained as a 30 – 40 % solution, which can be converted into an anhydrous powder by drying.

Since the fatty acid chlorides must be synthesized from the fatty acids by reaction with phosphorus trichloride or thionyl chloride, attempts have been made to react the free acids directly with isethionate or *N*-methyltaurine at elevated temperature. Although the desired derivatives of ethanesulfonic acid are formed in 80 – 90 % yield, they are less pure than those obtained from acid chlorides.

Producers. Isethionates are produced in Europe by Hoechst, in the United States by Henkel-Emery, Hoechst-Celanese, and Rhône-Poulenc Surfactant; taurates are produced in Europe by Croda, in the United States by Finitex, Hart, Henkel-Emery, Hoechst-Celanese, Sherex, and Union Carbide, in Israel by Zohar, and in Japan by Nikko Chemicals and Nippon Oil & Fats.

6.3. Sulfates

In surfactant chemistry the term "sulfates" refers to the salts of acidic sulfuric acid esters, $R-OSO_3M$. In this class of compounds the sulfur atom of the hydrophilic sulfate group is bonded via an oxygen atom to the hydrophobic residue. This ester group is susceptible to hydrolysis, more strongly in acid media than in alkaline media, and is less thermally stable than the analogous sulfonates. Sulfates are prepared by sulfation of hydroxyl- containing substrates with sulfuric acid, oleum, chlorosulfonic acid, sulfuryl chloride, amidosulfonic acid, complexes of sulfur trioxide, or sulfur trioxide itself, or by addition of sulfuric acid to double bonds ($\rightarrow$ Sulfonic Acids, Aliphatic). A large variety of surfaceactive sulfates is thus available, including the sulfated unsaturated fatty acids and oils that formed the starting point of surfactant chemistry and which still play a role in the textile industry [75], to the sulfates of fatty acid ethanolamides and their ethoxylates, which on account of their dermatological safety are used in cosmetics [76], and to the highly surface-active sulfated monoglycerides of fatty acids [76].

6.3.1. Alkyl Sulfates [67], [77–79]

The primary alkyl sulfates developed in the 1930s, based on natural alcohols obtained by hydrogenating fatty acid esters, were the first synthetic surfactants to be produced on an industrial scale. They give a neutral reaction in aqueous solution. Their physicochemical and applicational properties have been investigated intensively, especially the influence of the structure of the hydrophobic group on the above-mentioned properties has been described in detail, since individual defined substances can readily be prepared [79].

The sodium salts of alkyl sulfates prepared from primary, linear alcohols up to C_8 are scarcely surface-active. Industrially important sulfates are derived from dodecyl and tetradecyl alcohols (coconut oil and palm kernel alcohol); these sulfates are water-soluble and resistant to water hardness, and form good detergents, foaming agents, and emulsifiers. Their good dispersant properties are offset by a poor soil-suspending power. The sodium salts of the sulfates of hexadecyl and octadecyl alcohols (tallow fat alcohol) are fairly insoluble in water, especially in hard water; however, because the solubility increases markedly with increasing temperature, these sulfates are very active at elevated temperature (e.g., in textile washing).

In acidic aqueous solution (pH 3 – 4) alkyl sulfates are stable in the cold but hydrolyze on heating. They are stable in hot neutral and alkaline solution.

The primary, linear alkyl sulfates have high thermal stability, and can be spray dried at high temperature without decomposition. In contrast, the sulfates obtained from α-branched, primary and from secondary alcohols are thermally less stable, and readily decompose into sodium hydrogensulfate and alkene.

Due to the more central position of their hydrophilic groups the sulfates of highly branched alcohols obtained by the oxo or Guerbet processes or of secondary alcohols are less suitable as detergents and emulsifiers; however, in aqueous solution they have higher wetting power than the sulfates of linear primary alcohols. Secondary alkyl sulfates are no longer in use.

Production of Alkyl Sulfates. Since esterification of alcohols with sulfuric acid, followed

by neutralization

$$ROH+H_2SO_4 \rightleftharpoons ROSO_3H+H_2O$$
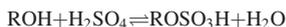
is an equilibrium reaction the sulfuric acid must be used in excess to maximize alcohol conversion. Apart from corrosion problems caused by the water formed in the reaction, the separation of the excess sulfuric acid from the reaction mixture is a problem. This can be avoided if a slight excess of chlorosulfonic acid is used as sulfating agent:

$$ROH+ClSO_3H \rightarrow ROSO_3H+HCl$$
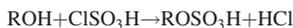
The gaseous hydrogen chloride formed is absorbed in water or sodium hydroxide. The reaction with chlorosulfonic acid must be carried out at the lowest possible temperature to avoid side reactions. Residual hydrogen chloride can be removed from the reaction mixture almost completely by air sparging.

Although sulfation with chlorosulfonic acid is still carried out in small production units, sulfation with sulfur trioxide diluted with inert gas is the method of choice for large-scale plants. In the same way as in the already discussed preparation of α-olefinsulfonates (see Section 6.2.4), this reaction can be carried out in a continuously operating short-time sulfonation reactor [51], [52]. Sulfation is performed with equimolar amounts of sulfur trioxide; an excess promotes side reactions and discoloration of the product. Since elevated temperatures have the same effect, the reaction temperature should be below 50 °C. The reaction product leaving the reactor is degassed and neutralized as quickly as possible, preferably with sodium hydroxide:

$$ROH+SO_3 \rightarrow ROSO_3H$$

$$ROSO_3H+NaOH \rightarrow ROSO_3Na+H_2O$$
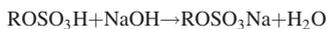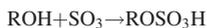
Often, the product is bleached with hydrogen peroxide.

The fatty alkyl sulfates are generally commercially available as 30 % pastes; above this concentration highly viscous pastes form, which are difficult to handle. The linear, primary alkyl sulfates crystallize well and are therefore also handled as powders that have been dried on rollers or in the spray process. Characteristic data of some industrial alkyl sulfates are listed in Table 11.

Table 11. Typical data of some industrial fatty alkyl sulfates (sodium salts)

CAS no.	[97375-27-4]	[68140-10-3]	[68955-19-1]
Appearance	paste	paste	powder
Active substance, %	30	32	93
Na_2SO_4, % max.	1.0	4.0	3.0
Nonsulfated proportion, % max.	0.5	1.8	1.0
pH	7 – 8	9 – 10	7 – 9
Color, APHA, max.	50	100	
Density, g/cm^3	1.03	0.98	0.33[*]

[*] Bulk density.

Storage and Dispatch conditions correspond to those of the alkylbenzenesulfonates (see Storage and Dispatch) or alkanesulfonates. The products must not be heated too strongly since they may be acidified further due to hydrolysis.

Producers of fatty alkyl sulfates include Akzo, Albright & Wilson, Auschem, Berol Nobel, Chem-Y, Harcros, Henkel, Hüls, Manro, Rewo, Stepan, Unger, Witco, and Zschimmer & Schwarz in Europe; Du Pont, Emkay, Henkel, Lonza, Rhône-Poulenc Surfactant, Stepan, Unger, and Witco in the United States; Daiichi, Kao, Nippon Oil & Fats in Japan; and Zohar in Israel.

Leading producers of the fatty alcohol starting materials by fatty ester hydrogenation are: Henkel, Hüls, Marchon, Oleofina, Rodleben, RWE-DEA in Europe; Procter & Gamble and Sherex in the United States; Kao and New Japan in Japan, and joint ventures of local and Western companies in the Philippines and Malaysia. Ethylene-base Ziegler alcohols are produced by RWE-DEA in Germany and by Ethyl in the United States. Important producers of oxo alcohols by hydroformylation of olefins are BASF, Enichem, Exxon, ICI, Shell in Europe, and Shell and Vista in the United States.

6.3.2. Ether Sulfates [67], [77], [80–83]

Ether sulfates is the short name for salts of sulfuric acid hemi-esters of alkyl or alkylaryl oligoglycol ethers of general formula

$$RO[CH_2CH_2O]_nSO_3Na$$

The oligoglycol ethers, namely ethers of oligooxyethylenes or ethoxylates, on which the ether sulfates are based are homologous mixtures where $n = 0, 1, 2 \ldots$, etc.; the number n in the above formula specifying the mean degree of ethoxylation. Industrial ether sulfates are accordingly also homologous mixtures; with increasing degree of ethoxylation the content of alkyl sulfate ($n = 0$) decreases.

The oligoglycol group of the ether sulfates results in better water solubility and higher stability to water hardness, compared to sulfates containing the same alkyl or alkylaryl group. The most important surfactants of this group are the alkyl ether sulfates derived from ethoxylates of dodecanol and tetradecanol (coconut and palm kernel fatty alcohols) with a mean degree of ethoxylation of 2 – 4. Instead of natural alcohols, synthetic fatty alcohols are also used in the corresponding C- cut range. These ether sulfates have achieved considerable importance due to their good stability to hard water, dermatological compatibility, foaming and detergent power, their good emulsifying and lime soap dispersing power, their rheological behavior, and also on account of synergistic effects that they exhibit in conjunction with some other anionic surfactants (sulfonates). They are used in cosmetic preparations, foam baths, shampoos, liquid detergents, cleansing agents, especially fine detergents and rinsing agents, generally in combination with other surfactants. Being sulfuric acid hemi-esters, ether sulfates can be saponified only with difficulty in alkaline media, but are readily saponified under acid conditions. Slow saponification also occurs in neutral media, but since sodium hydrogensulfate is produced the solution becomes increasingly acidic and the saponification is thereby accelerated autocatalytically:

$$RO[CH_2CH_2O]_n SO_3Na + H_2O \rightarrow RO[CH_2CH_2O]_n H + HOSO_3Na$$
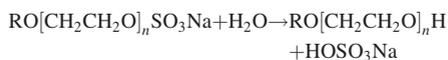
Solutions of ether sulfates are protected against this autocatalytic decomposition by adding citrate, lactate, or phosphate buffers.

A well known property of ether sulfates is the thickening effect, i.e., the increase in viscosity by several orders of magnitude of even dilute solutions on adding electrolytes. The increase in viscosity passes through a maximum, depending on the electrolyte concentration in the solution;
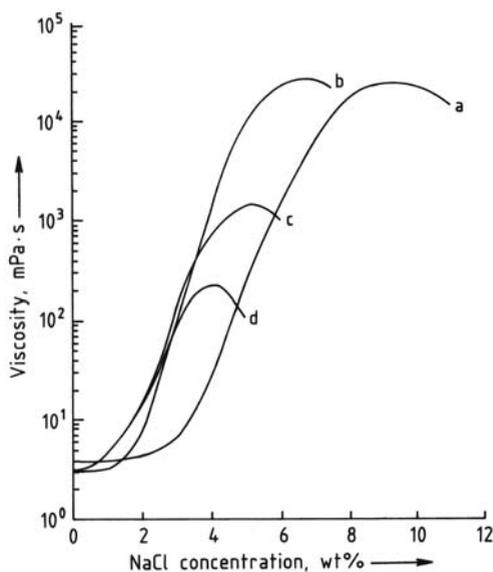
Figure 17. Thickening of 10 % aqueous solutions of fatty alcohol ether sulfates containing 3 mol EO/mol, as a function of the structure of the fatty alcohol residue
a) C_{12}/C_{14} 100 % linear; b) C_{12}/C_{15} 90 % linear; c) C_{12}/C_{15} 50 % linear; d) C_{12}/C_{15} 10 % linear

the effect also depends on the concentration and structure of the ether sulfate (Fig. 17).

Production.   Ether sulfates are obtained by sulfation of the corresponding ethoxylates and neutralization of the resulting sulfuric acid hemi-esters. Sulfuric acid is no longer used for sulfation, because it must be added in excess and remains in the product as sodium sulfate after neutralization. In smaller production units sulfation is performed with chlorosulfonic acid, as described for the preparation of primary alkyl sulfates (see Production of Alkyl Sulfates), and the neutralized product then contains a few percent of sodium chloride. Amidosulfonic acid is occasionally used as sulfating agent, with the advantage that no byproducts or waste products are formed. In this case, however, ammonium ether sulfates are obtained:

$$RO[CH_2CH_2O]_n H + HSO_3NH_2 \rightarrow RO[CH_2CH_2O]_n SO_3NH_4$$

Amidosulfonic acid is preferably used in the sulfation of alkylphenyl ethoxylates, since in this way sulfonation of the aromatic nucleus is largely avoided.

Ether sulfates are now mainly produced by continuous sulfation of ethoxylates in short-time sulfonation reactors using gaseous sulfur trioxide, and continuous neutralization (see preparation of alkylbenzenesulfonates and olefinsulfonates, Sulfonation). The sulfation mixture should be neutralized as quickly as possible since decomposition and disproportionation reactions occurring in the acidic reaction mixture lead to accumulation of byproducts, reduction of the content of active substance, and darkening of the color.

One of the decomposition products is 1,4-dioxane, a suspected carcinogen ($\rightarrow$ Dioxane). The dioxane content can be kept below 50 ppm by precise control of the sulfation reaction (maintenance of low temperature, avoidance of excess sulfur trioxide, dilution of the sulfur trioxide gas, maintaining uniform throughput with optimum mixing and minimum residence time) as well as rapid degassing and neutralization [84], [85].

Even when the reaction is carefully controlled, the ether sulfates are not colorless. They exhibit a self-bleaching effect for several days when allowed to stand in air, presumably due to autooxidation processes. The products are normally rebleached with hydrogen peroxide or sodium hypochlorite.

Typical data of industrial sodium salts of ether sulfates are listed in Table 12.

Storage and Dispatch.   Up to 30 % aqueous ether sulfate solutions are stored and transported in plastic containers or in plastic-lined vessels.

Figure 18. Viscosity of an alkyl ether sulfate as a function of its concentration [80]

Aluminum vessels are also suitable for short-term transportation. Phase separation may occur during storage in the cold, which can be prevented by stirring.

Alkyl ether sulfates in aqueous solutions of between 25 and 30 % concentration exhibit a sharp rise in viscosity from ca. 100 mPa $\cdot$ s to $\geq$ 100 000 mPa $\cdot$ s. This viscosity reaches a maximum value between 40 and 50 %, then decreases to 10 000 mPa $\cdot$ s at 60 – 70 % concentration (Fig. 18). Since pastes of this viscosity are still pumpable, 60 – 70 % products are also marketed.

The concentration-dependent viscosity behavior makes precautionary measures necessary when diluting concentrated pastes with water, so as to avoid the high-viscosity gel state at 40 – 50 % concentration. Dilute solutions are best prepared by adding the concentrated paste to water.

Producers. include Akzo, Albright & Wilson, Auschem, Berol Nobel, Chem-Y, Harcros, Henkel, Hüls, Manro, Pulcra, Rewo, Rhône-Poulenc, Shell, Unger, Witco, and Zschimmer & Schwarz in Europe; Clough Chemical, Henkel, Niacet, Pilot Chemicals, Rhône-Poulenc Surfactant, Sandoz, Stepan, and Witco in North America; Kao, Lion, Marubishi Oil Chemical, Nikko Chemicals, Nippon Nyu Kazai, Nippon Oil & Fats, and Sanyo in Japan; and Zohar in Israel.

Table 12. Typical characteristic data of some industrial ether sulfates (sodium salts)

| Fatty alcohol	C_{12}/C_{14}		C_{13}/C_{15}	
Degree of ethoxylation	2		3	
CAS no.	[9004-82-4]		[25446-78-0]	
Active substance, %	28	70	28	70
NaCl, % max.	0.3	1.2	2.0	1.2
Na$_2$SO$_4$, % max.	1.0	1.5	1.5	1.5
pH	6 – 8	6 – 8	6 – 8	6 – 8
Color, APHA, max.	75	250	200	250
Viscosity, mPa $\cdot$ s	300	thixotropic	4000	thixotropic
Density, g/cm^3	1.05	1.1	1.05	1.1

6.4. Alkyl Phosphates [86–88]

Acid phosphate esters and their salts are prepared by reacting alcohols or ethoxylates with phosphorus pentoxide:

$$3\ ROH + P_2O_5 \rightarrow ROPO_3H_2 + (RO)_2PO_2H$$

followed by neutralization, if required.

Alkyl phosphates thus generally consist of mixtures of monoalkyl and dialkyl esters of phosphoric acid. Monoalkyl, dialkyl, and trialkyl esters can specifically be prepared by stepwise reaction of a hydroxyl compound with phosphoryl chloride, followed by saponification of the resulting phosphoric ester chlorides.

Phosphoric partial esters with short-chain alkyl groups (e.g., butyl phosphoric acids) are strong acids, which have corrosion-inhibiting and bactericidal action. They are readily soluble in hard water and act as wetting and dispersing agents, and are therefore used in acid-adjusted cleansing agents, e.g., for vehicles or swimming baths.

The water solubility and acid strength of phosphoric partial esters decrease with increasing length of the alkyl chain. The sodium salts of long-chain alkyl phosphoric acids readily dissolve in water, have low sensitivity to water hardness, and are resistant to saponification, especially in alkaline media. They are good wetting agents and emulsifiers; the salts of monoalkyl phosphoric acids inhibit foam formation by other anionic or nonionic surfactants. Since the phosphates also have high dermatological compatibility, they are used both in highly alkaline cleansing agents, and in general cleansing agents, including body cleansing agents (the latter especially in Japan).

Producers. of alkyl phosphates include Albright & Wilson, Auschem, BASF, Berol Nobel, Croda, Finetex, Harcros, Henkel, Hoechst, Hüls, Pulcra, Rewo, Rhône-Poulenc, Witco, and Zschimmer & Schwarz in Europe; Climax Performance, Croda, Dexter, Graden Chemical, Harcros, Hart, Henkel, Intex, Lonza, Mona Industries, Norman & Fox, Olin, PPG/Mazer, Reilly Whiteman, and Rhône-Poulenc Surfactant in North America; Kao, Nikko Chemicals, Takemoto Oil & Fat, and Yoshimura Oil Chemicals in Japan; and Taiwan Surfactant in Taiwan.

7. Nonionic Surfactants [89–91]

The polarity of covalently bonded oxygen atoms in oligoethylene glycol ethers (also termed polyglycol ethers) and oligohydroxy compounds or of oxygen atoms bonded in a semipolar manner to a heteroatom imparts water solubility and interfacial activity to hydrophobic parent structures to which such oxygen-containing hydrophilic groups are bonded. The most important nonionic surfactants are the ethoxylates, which are formally condensation products of hydrophobic alcohols, phenols, mercaptans, amines, carboxylic acids, carbonamides, etc., with oligoglycol ethers, the fatty acid esters of glycerol, diglycerol, sugars, hydrogenated sugars such as sorbitol, and alkyl(poly)glucosides. Nonionic surfactants with semipolar bonded oxygen as hydrophilic group include fatty amine oxides such as lauryldimethylamine oxide, which is used to a limited extent in liquid cleansing agents, as well as the industrially unimportant sulfoxides and phosphine oxides.

7.1. General Properties

Nonionic surfactants are colorless substances, but may be colored pale yellow to brown depending on the production process. Low molecular mass products are liquid, and with increasing molecular mass the products have a pasty to waxy consistency. In the anhydrous state, especially in the case of ethoxylates, the oligoglycol ether chains of short-chain ethoxylates are present in a stretched zig-zag form, while those of long-chain ethoxylates have a meandering structure, which is also formed in the micelles in aqueous solution.

Nonionic surfactants are less sensitive to water hardness than anionic surfactants. Their aqueous solutions foam less strongly than those of many anionic surfactants. The possible applications of nonionic surfactants are universal, given the large variability of their structure and thus of their properties. The differences between the individual types of nonionic surfactants are slight, and the choice is primarily governed having regard to the costs of special properties, e.g., effectiveness and efficiency, toxicity, dermatological compatibility and biodegradability, or permission for use in foodstuffs. The solubility of nonionic surfactants

in water results from hydration of the oxygen groups by hydrogen bonding. The degree of hydration decreases with increasing temperature, and the water solubility of nonionic surfactants therefore decreases with increasing temperature. In the case of surfactants that dissolve in water to give a clear solution, i.e., ethoxylates with a fairly high degree of ethoxylation, turbidity and separation of a surfactant phase that is immiscible with water occur at a specific temperature characteristic of the surfactant (cloud point).

The cloud point can be determined for water-insoluble ethoxylates by dissolving the surfactant in aqueous butyl diglycol. For highly water soluble ethoxylates whose solutions do not become turbid even on boiling, the cloud point can be determined in aqueous sodium chloride solution. Figure 19 shows the cloud point of industrial fatty alcohol ethoxylates as a function of the degree of ethoxylation in 25 % butyl diglycol solution, in fully deionized water, and in 10 % sodium chloride solution.

Correlations exist between the cloud points and the hydrophilic – lipophilic balance (HLB) values or phase inversion temperatures of emulsions with the corresponding surfactants as emulsifiers [92].

The concept of an HLB is of practical value [93].

The HLB system enables nonionic surfactants to be arranged on a value scale from 0 to 20. In the ideal case the HLB value of a surfactant is defined

as the ratio of the molecular mass of the hydrophilic fraction in the molecule M_h to the total molecular mass M of the surfactant, multiplied by 20:

$$HLB = 20 \cdot \frac{M_h}{M}$$

The HLB scale allows rough classification of nonionic surfactants according to their solubility in water and their possible areas of application. Table 13 provides a summary.

The HLB values can be determined by emulsification tests and comparison with emulsifiers of known HLB values (see also → Emulsions).

7.2. Ethoxylates

Ethoxylates are generally obtained by addition of ethylene oxide to compounds containing dissociating protons.

Substrates used for ethoxylation are primarily linear and branched, primary and secondary $C_{12} – C_{18}$ alcohols, i.e., natural and synthetic fatty alcohols, alkylphenols with branched octyl (butene dimer), nonly(propylene trimer) or dodecyl(propylene tetramer) groups, fatty acids, fatty acid ethanolamides, fatty amines, and fatty acid esters of polyhydroxyl compounds. The degree of ethoxylation, i.e., the molar ratio of ethylene oxide added per mole of substrate, varies within wide ranges, in general between 3 and 40, and is chosen according to the intended use (HLB value, Table 13).

The addition of ethylene oxide to a substrate containing acidic hydrogen is catalyzed by bases or (Lewis) acids.

Amphoteric catalysts, prepared in situ and probably existing as finely dispersed solids having a large surface area [94], as well as heterogeneous catalysts [95], have also been described.

The reaction mechanisms of base- catalyzed and acid- catalyzed ethoxylation differ, which affects the composition of the reaction products. In base- catalyzed ethoxylation an alcoholate anion formed initially by reaction with the catalyst (alkali metal, alkali-metal oxide, carbonate, hydroxide, or alkoxide), nucleophilically attacks ethylene oxide. The resulting anion of the ethylene oxide addition product can undergo an equilibrium reaction with the alcohol starting
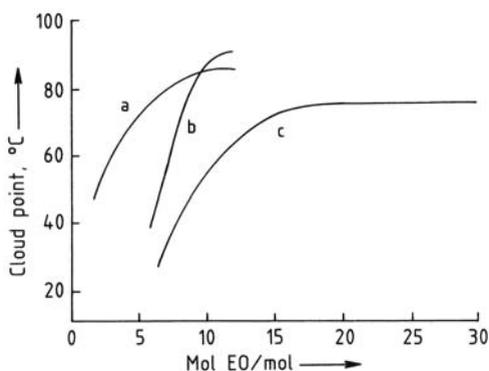

Figure 19. Cloud point of ethoxylates of a C_{12}/C_{14} fatty alcohol (linear) as a function of the degree of ethoxylation (mol EO/mol)
a) 10 % solution in 25 % butyl diglycol; b) 2 % solution in demineralized water; c) 2 % solution in 10 % NaCl

Table 13. HLB values of nonionic compounds

HLB range	Behavior in water	Example of use	Example	HLB value
0 – 3	Insoluble	defoaming agent, dispersant for solids in oil, co-emulsifier, refatting agent	Glycerol trioleate Glycerol dioleate Glycerol monooleate	0.8 1.5 2.7
3 – 6	Insoluble, dispersible	water-in-oil emulsions, co-emulsifier	Glycerol monostearate	3.8
			Propylene glycol monolaurate	4.5
			Diethylene glycol monolaurate	6.0
6 – 9	Dispersible, giving milky solution	wetting agent, water-in-oil emulsions	Sorbitan monopalmitate	6.7
			Sorbitan monomyristate	7.6
			Sorbitan monolaurate	8.6
8 – 10	Soluble, giving milky turbid to translucent solutions	wetting agent	Isotridecanol ethoxylate with 3 EO[*]	8.3
			Isotridecanol ethoxylate with 4 EO	10.0
			Isotridecanol ethoxylate with 5 EO	11.2
10 – 13	Soluble giving translucent to clear solutions	oil-in-water emulsions, detergents and cleansing agents	Isononylphenol ethoxylate with 5 EO	10.7
			Isononylphenol ethoxylate with 6 EO	11.5
			Isononylphenol ethoxylate with 7 EO	12.3
13 – 15	Soluble, giving clear solution	oil-in-water emulsions, detergents and cleansing agents	Octadecanol ethoxylate with 10 EO	13
			Octadecanol ethoxylate with 12 EO	14
			Octadecanol ethoxylate with 16 EO	15
> 15	Soluble, giving clear solutions	solubilizer, cleansing agent	Dodecanol/tetradecanol ethoxylate with 13 EO	15
			Dodecanol/tetradecanol ethoxylate with 17 EO	16
			Dodecanol/tetradecanol ethoxylate with 25 EO	17
			Dodecanol/tetradecanol ethoxylate with 38 EO	18

[*] Moles ethylene oxide per mole.

material or ethoxylate product, or can react further with ethylene oxide:
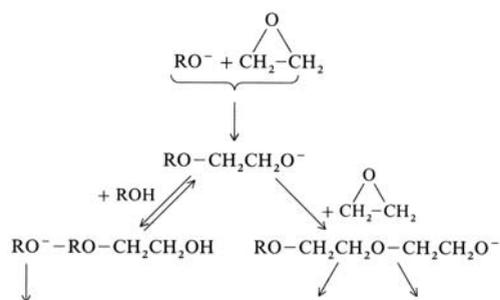
As this simplified reaction scheme illustrates, in alkaline-catalyzed ethoxylation several reactions proceed in parallel, the addition of ethylene oxide to an anion with the formation of an ether bond being irreversible.

Proton exchange between various anions, occurring as an ionic reaction, is fast; the addition reaction of ethylene oxide to an existing anion is the rate-determining step. Thus in a reaction mixture, the more acidic species preferentially react with ethylene oxide. If carboxylic acids or phenols are ethoxylated, the reaction proceeds exclusively via the left-hand path in the above scheme, and the initially formed monoethylene glycol ester or ether only reacts further when all the starting material in the reaction mixture is consumed. The fast equilibrium proton exchange reaction which precedes the addition of the ethylene oxide to the anionic species leads to a peculiarity of the reaction rate in the case of strongly acidic substrates such as carboxylic acids or phenols. On account of the lower nucleophilicity of their conjugate bases corresponding to the acidic parent substances, these bases react relatively slowly with ethylene oxide; thus, the reaction proceeds slowly until the starting material is consumed. Thereafter the reaction rate increases sharply with further supply of

ethylene oxide since the ethoxylate anions now present react substantially more quickly with ethylene oxide than do the anions of the carboxylic acids or phenols [96].

The situation is different in the ethoxylation of alcohols. The ether oxygen atoms in alkyl (oligo) glycol ethers increase the acidity of the terminal primary hydroxyl group compared to the initial alcohol; glycol ethers once formed thus react preferentially with ethylene oxide and lead to the formation of a mixture of homologous oligoglycol ethers, and unreacted starting alcohol remains in the reaction mixture up to high degrees of ethoxylation. This is particularly true for the ethoxylation of secondary alcohols.

Assuming the same acidity of the starting alcohol and all (oligo)glycol ethers present in the mixture, a Poisson distribution of the individual species must be expected in the ethoxylation, with a maximum corresponding to that oligoglycol ether in which the number of added ethylene oxide units corresponds to the molar ratio of ethylene oxide to starting alcohol. However, on account of the aforementioned different acidities of the individual species in the reaction mixture the homologue distribution that is actually observed in an ethoxylation mixture differs from the Poisson distribution (Fig. 20).

This is true for all alkaline catalysts, although the deviations in the case of alkaline-earth compounds are less strongly pronounced than in the case of sodium hydroxide or sodium methoxide [97]. The distribution pattern of the homologous polyethylene glycol ethers in an ethoxylate obtained by alkaline catalysis is independent of
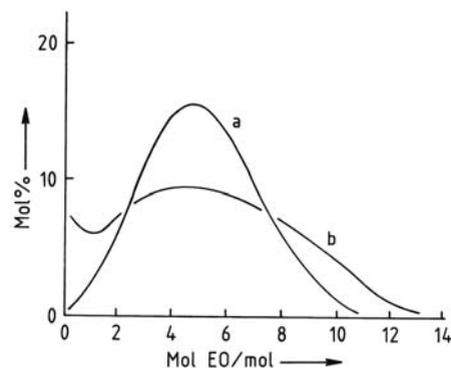
the temperature, pressure, and catalyst concentration [98], [99]. The occasionally observed dependence of the homologue distribution on the stirring rate can be attributed to an insufficiently complete mixing of the reactor contents.

When Lewis acids such boron trifluoride, tin tetrachloride, or antimony pentachloride are used as catalysts, homologue distributions approximating to the Poisson distribution are obtained (Fig. 20), because here it is not the proton activity but the nucleophilicity of the substrate that determines the reaction pathway. Lewis acids activate ethylene oxide and not the alcohol:

$$R \atop H \Big\rangle O \cdots CH_2 \overset{\overset{\displaystyle H_2}{C}}{\underset{BF_3}{}} O \longrightarrow \left[R - \overset{\overset{\displaystyle +}{O}}{\underset{H}{}} - CH_2CH_2O - \bar{B}F_3 \right]$$

$$\longrightarrow R - O - CH_2CH_2OH + BF_3$$
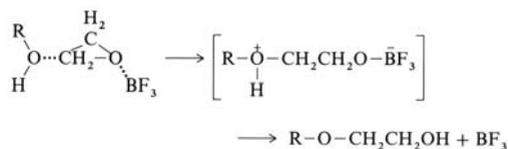
Lewis acids have not become established as catalysts since they must be laboriously removed from the reaction product and because they lead to the formation of polyethylene glycol [the so-called polydiol, $HO(CH_2CH_2O)_nH$], methyldioxolane and dioxane, due to side reactions and decomposition reactions.

Since ethoxylates with a narrow, Poisson-like homologue distribution, so-called narrow range ethoxylates (NRE), have advantages in some applications, amphoteric catalysts have been developed that give distributions similar to those produced by Lewis acids [94].

Among these catalysts a calcined hydrotalcite of idealized empirical formula $Mg_6Al_2O_5(OH)_2$ is of interest since it can readily be handled as a pneumatically conveyable powder and can easily be separated as an insoluble solid from the reaction medium [95].

Advantages of narrow range ethoxylates, which also have a substantially lower content of starting alcohol, include: less odor, better solubility, lower volatility (reduced pluming on spray drying) and better thickening properties of both the ethoxylates and the ether sulfates derived therefrom [100–102]. However, broad distributions may also be advantageous, for example, in emulsification processes [103].

The large variability of the hydrophobic group – straight-chain and branched fatty alcohols, alkylphenols, fatty amines, fatty acids and

Figure 20. Homologue distribution of a lauryl ethoxylate containing 6 mol EO/mol [97]
a) Acid catalysis; b) Base catalysis

fatty acid (alkanol)amides – as well as the option to achieve any desired degree of ethoxylation, make the ethoxylates an extremely versatile class of surfactants. The ethoxylates of fatty alcohols and alkylphenols as such or in combination with anionic, occasionally also cationic surfactants, play a major role in detergents and cleansing agents. Objections have been raised against the use of alkylphenol ethoxylates on the basis of ecotoxicological findings, which has led to their discrimination in some European countries [104]. When adjusted to the necessary HLB value by means of the degree of ethoxylation, fatty alcohol ethoxylates are used as emulsifiers in cosmetics formulations, dry cleaning, crop protection agents, metal working and processing, and textile auxiliaries, paints and coating compositions. Like the alkylphenol ethoxylates, they are also used as dispersants in petroleum production and in ores flotation. Fatty acid polyglycol esters have numerous uses as emulsifiers in bodycare products and in textile treatment. The same is also true of fatty acid alkanolamides and their ethoxylates, which moreover are used as antistatics in plastics processing and as emulsifiers and corrosion inhibitors in metal working and processing. Finally, fatty amine ethoxylates are used as finishing agents and antistatics in textile treatment and leather processing, and as emulsifiers in the petroleum industry and bitumen production.

General Production Processes. Molecularly uniform ethoxylates can be prepared by the Williamson ether synthesis. Industrial ethoxylates, obtained by ethylene oxide addition are mixtures of homologues. These mixtures generally have superior application properties to molecularly uniform substances.

Special safety precautions must be adopted in industrial ethoxylation. Ethylene oxide, *bp* 10.7 °C, is stored, transported, and metered as a liquid under pressure. The flash point is -57 °C, the ignition temperature in air is 429 °C, and the decomposition temperature of pure ethylene oxide vapor is 571 °C. The heat of polymerization of ethylene oxide, which is released during ethoxylation, is 2090 kJ/kg; 1900 kJ/kg is released in the decomposition of ethylene oxide vapor. In ethoxylation processes the reaction can run out of control if there is overheating and a consequent rise in pressure; ethylene oxide tends to ignite or undergo self-decomposition (e.g., on overheated stirrer or pump shafts). Ethoxylation must therefore be carried out under strict pressure and temperature control. The reactors must be safe-guarded against excessive pressure by means of safety valves or rupture disks. The excess of ethylene oxide in the reaction mixture must be kept low. On account of the limited solubility of ethylene oxide in the reaction medium the presence of a second, liquid ethylene oxide phase in the reaction vessel must be avoided. The storage vessel from which the ethylene oxide is metered into the reaction vessel must be protected against backflow of reactants containing polymerization-initiating catalyst, e.g., by nonreturn valves and intermediate vessels.

Industrial ethoxylations are carried out mainly in a batchwise manner. Stainless steel pressure vessels are used as reactors. The substrate together with the catalyst, generally sodium hydroxide, is first placed in the vessel. The water introduced with the sodium hydroxide solution and the water formed in the reaction

$$ROH + NaOH \rightleftharpoons RONa + H_2O$$
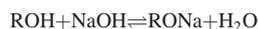
is removed by heating and applying a vacuum or by passing nitrogen through the reaction mixture, to avoid formation of polyglycols ("polydiols"). Polydiols do not, in general, affect the properties of ethoxylates provided their concentration does not exceed a few percent, but not being surface-active they result in a wastage of ethylene oxide. The catalyst content is usually 0.1 – 1.0 %. The ethoxylation is carried out between 130° and 180 °C, and the substrate first must be heated up to this temperature. The reactor contents must be cooled during the addition of ethylene oxide. Heating and cooling can be performed by external jackets, internal tubes or by heat exchangers through which the reactor contents are constantly pumped.

The gaseous phase is inertized by diluting it with nitrogen. The reaction is carried out at 1 – 5 bar gauge pressure. The liquefied ethylene oxide is metered into the reaction medium with intensive mixing. The temperature and pressure are monitored so that the ethylene oxide supply can be adjusted if the reaction becomes quiescent or goes out of control. The desired degree of ethoxylation is adjusted via the amounts of substrate and ethylene oxide.

The product specifications can quickly be checked by determining the cloud point.

The reaction time depends on the effectiveness of cooling and amount of ethylene oxide to be added; the production of an ethoxylate having a medium degree of ethoxylation takes a few hours in conventional stirred vessels provided with internal cooling.

The catalyst is neutralized with carbon dioxide, acetic acid, or citric acid. Phosphoric acid gives a precipitate that can be filtered off, but in most cases the neutralized catalyst remains dissolved in the product. Any slight discoloration of the products can be removed by bleaching with hydrogen peroxide.

The products are discharged hot into stainless steel storage tanks or vats, or are cooled in the reactor and discharged into plastics vessels.

Discoloration and polydiol concentration increase with increasing reaction temperature. The formation of polydiols is due to increasing elimination of water from ethoxylates as the temperature rises:

$$RO-[CH_2CH_2O]_n-OCH_2CH_2OH \longrightarrow$$

$$RO-[CH_2CH_2O]_n-OCH=CH_2 + H_2O$$

$$H_2O + nCH_2\overset{O}{-}CH_2 \longrightarrow HO-[CH_2CH_2O]_n-H$$
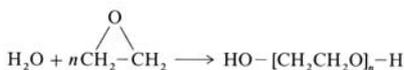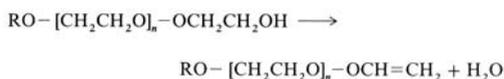
Further impurities can be formed by reactions of other compounds introduced with the ethylene oxide (e.g., formaldehyde and acetaldehyde).

Although continuous ethoxylation processes are also described in the literature [105], industrial ethoxylations, like other alkoxylations, are mainly carried out as batch operations.

The Pressindustria alkoxylation process for addition of ethylene oxide and/or propylene oxide operates according to a different principle than the stirred vessel method (Fig. 21). The liquid reaction mixture, circulated at high speed, is dispersed by a special device in a gas phase consisting of ethylene oxide (possibly also propylene oxide), ensuring rapid absorption of ethylene oxide [106], [107]. Catalyst and substrate are mixed in a heated receiving vessel and freed from water by heating under vacuum. This mixture is passed to the reactor and circulated by means of a pump through the special mixing unit (c) and the reactor. The mixture is heated to reaction temperature in the heat exchanger (e); residual moisture is removed by applying a vacuum or passing nitrogen through the mixture. The addition of ethylene oxide then starts, the ethylene oxide being flashed into the gas phase of the mixer (c). Here the liquid reaction mixture introduced in finely dispersed form adsorbs the ethylene oxide. The reaction proceeds in the liquid phase in the mixer and reactor, into which the liquid phase flows from the mixer. The heat of reaction is dissipated by the cooler (f). When the desired degree of ethoxylation is reached the product is passed to the neutralization vessel. The reaction is carried out at 180 – 190 °C, and a maximum pressure of 5 bar.

The process has a high reaction rate and uniform product quality. The safety risks involved with gaseous ethylene oxide are minimized by keeping the gas phase as small as possible. Since this part of the reactor contains no moving parts, ignition of the gas phase by shafts, for example, overheating, is ruled out. This process can also be operated continuously.
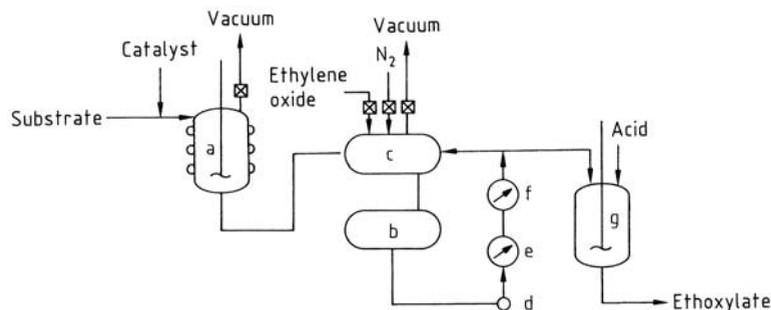

Figure 21. Pressindustria alkoxylation apparatus [106]
a) Receiving vessel; b) Reactor; c) Mixer for gas and liquid; d) Circulating pump; e) Heater; f) Cooler; g) Neutralization vessel

High reaction rates and low formation of byproducts can also be achieved in a jet nozzle reactor or jet suction reaction mixer [108].

Production of Ethoxylates of Fatty Acids, Fatty Acid Amides, and Fatty Amides. All industrial products based on primary alcohols or alkylphenols can be ethoxylated by the above processes.

In the ethoxylation of fatty acids the transesterification of the initially formed oligoglycol esters that is unavoidable with alkaline catalysis leads to the formation of diesters and free oligoglycols, which in the further course of the ethoxylation lead to undesirably high polydiol contents in the end product:

$$2\ RCOO-[CH_2CH_2O]_n-H \longrightarrow$$

$$R-COO-[CH_2CH_2]_n-COR + HO-[CH_2CH_2O]_n-H$$
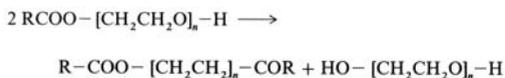
As carboxylic esters, fatty acid ethoxylates are sensitive to hydrolysis.

Ethoxylates of fatty acid amides are obtained not by ethoxylation of amides but by alkaline-catalyzed ethoxylation of fatty acid monoethanolamides or diethanolamides, which are obtained from the reaction of fatty acids or their methyl esters with ethanolamine or diethanolamine, which themselves are valuable products:

$$RCO-NH-CH_2CH_2OH$$

$$RCO-N(CH_2CH_2OH)_2$$
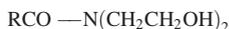
In the ethoxylation of primary amines, in the presence of basic catalysts, only one hydrogen atom bonded to nitrogen reacts, and the initially formed *N*-alkylethanolamine reacts further with ethylene oxide at the hydroxyl group, with the retention of the secondary amino group. Amines doubly ethoxylated on the nitrogen atom are obtained if the amines are first converted to the *N*-alkyldiethanolamine under proton catalysis, for which purpose small amounts of water are generally sufficient, and this diethanolamine is then ethoxylated further with alkaline catalysis.

Properties. Ethoxylates are described according to the state of aggregation (liquid, pasty, waxy, solid) and color (iodine no. < 2), and the density (ca. 1 g/cm^3), refractive index, and viscosity are specified as physical data. Characteristic data also include the cloud point

(according to DIN 53 917) and the hydroxyl value. The content of active substance is generally given as 100 %, despite the fact that ethoxylates contain amounts of polydiols that increase with increasing degree of ethoxylation. An industrial lauryl alcohol ethoxylate containing 5 mol of EO/mol contains, e.g., ca. 0.5 %, an ethoxylate with 15 mol EO/mol contains 1.0 %, and one with 30 mol EO/mol contains 3.0 % of polydiol.

Storage and Dispatch. Ethoxylates are stored and transported in stainless steel or plastic vessels. Tank wagons and storage tanks for higher ethoxylated products that are solid at ambient temperature must be thermally insulated and heatable.

When ethoxylates are dissolved or diluted with water the possibility of gel formation in specific concentration ranges must be borne in mind.

CAS Numbers. of some important ethoxylates are listed below. Irrespective of the degree of ethoxylation, ethoxylates with identical hydrophobic groups have the same CAS numbers.

Hydrophobic starting material	CAS number
100 % linear C_{10}-prim. alcohol	[26183-52-8]
100 % linear C_{10}/C_{12}-prim. alcohol	[66455-15-0]
100 % linear C_{12}-prim. alcohol	[9002-92-0]
100 % linear C_{12}/C_{14}-prim. alcohol	[68439-50-9]
100 % linear C_{12}/C_{14}/C_{16}/C_{18}-alcohol	[68213-23-0]
100 % linear C_{16}/C_{18}-prim. alcohol	[68439-49-6]
100 % linear oleyl alcohol	[9004-98-2]
	[68920-66-1]
80 % linear C_9– C_{11} prim. alcohol, monobranched	[68439-45-2]
80 % linear C_{12} – C_{13} prim. alcohol, monobranched	[66455-14-9]
80 % linear C_{12} – C_{15} prim. alcohol, monobranched	[68131-39-5]
80 % linear C_{14} – C_{15} prim. alcohol, monobranched	[68002-97-1]
60 % linear C_{13} – C_{15} prim. alcohol, monobranched	[64425-86-1]
50 % linear C_{12} – C_{13} prim. alcohol, monobranched	[66455-14-9]
50 % linear C_{12} – C_{15} prim. alcohol, monobranched	[68131-39-5]
50 % linear C_{13} – C_{15} prim. alcohol, monobranched	[68002-97-1]
Branched C_{10}-alcohol	[61827-42-7]
Branched C_{13}-alcohol	[69011-36-5]
p-Isooctylphenol	[9004-87-9]
p-Isononylphenol	[37205-87-1]
	[68412-54-4]
Lauric acid	[9004-81-3]
Coco fatty acid	[61791-29-5]
Oleic acid	[112-80-1]
Stearic acid	[57-11-4]
Ricinoleic acid	[61791-12-6]
Tallow fatty amine	[61791-26-2]

Oleylamine	[112-90-3]
Stearylamine	[124-30-1]
Alkanolamides	
Coco fatty acid monoethanolamide	[68140-00-1]
Coco fatty acid diethanolamide	[61790-63-4]
Tallow fatty acid monoethanolamide	[68153-63-9]

Producers. Fatty alcohol ethoxylates are produced in Europe, e. g., by Akzo, Albright & Wilson, Amerchol Europe, Auschem, BASF, Berol Nobel, Chem-Y, Croda, Harcros, Henkel, Hoechst, Hüls, ICI, Kolb, Pulcra, Rewo, Rhône-Poulenc, Seppic, Shell, Stepan, Witco, and Zschimmer & Schwarz; in North America, e. g., by Amerchol, BASF, Chemax, Croda, Exxon, Hart, Henkel/Emery, Hoechst Celanese, ICI Americas, Lonza, Olin, Procter & Gamble, Rhône-Poulenc Surfactant, Sandoz, Shell, Sherex, Stepan, Texaco, Union Carbide, Vista, and Witco; in Japan by Dai-Ichi, Nikko Chemicals, Nippon Nyukazai, Nippon Oil & Fat, Sanyo Chemical, and Takemoto Oil & Fat; in Australia by ICI; and in Taiwan by Sino-Japan Chemical and Taiwan Surfactant.

Alkylphenol ethoxylates are produced in Europe by Akzo, Auschem, BASF, Berol Nobel, Chem-Y, Dow, Harcros, Hefti, Hoechst, Hüls, ICI, Kolb, Pulcra, Stepan, Witco, and Union Carbide; in North America by Chemax, Clough Chemical, Exxon, Hart, Henkel/Emery, Hoechst Celanese, Norman/Fox, Rhône-Poulenc Surfactant, Sandoz, Stepan, Texaco, Union Carbide, and Witco; in Japan by Dai-Ichi, Kao, Lion, Marubeni Oil, Nippon Nyukazai, Nippon Oil & Fat, Sanyo Chemical, and Toho Chemical Industry; in Australia by ICI; and in Taiwan by Sino-Japan Chemical and Taiwan Surfactant.

Fatty acid ethoxylates are produced in Europe by BASF, Croda, Fina Oleochemicals, Harcros, Hefti, Henkel, Hüls, ICI, Stepan, Witco, and Zschimmer & Schwarz; in North America by Chemax, Emkay, Hart, Henkel, Hodag Chemical, ICI Americas, Lipo Chemicals, Lonza, PPG/Mazer, Rhône-Poulenc Surfactant, and Reilly-Whiteman; in Japan by Dai-Ichi, Kao, Nikko Chemicals, Nippon Nyukazai, Nippon Oil & Fat, and Toho Chemical Industry; in Australia by ICI; in Taiwan by Sino-Japan Chemical and Taiwan Surfactant; and in Israel by Zohar.

Special ethoxylated fatty esters and oils are also produced by companies such as Auschem, Croda, ICI, Th. Goldschmidt and Westbrook Lanolin in Europe, and Heterene Chemical, ICI Americas, Lonza, Rhône-Poulenc Surfactants, and Sherex in the United States.

Ethoxylated amines and/or fatty acid amides are produced in Europe by Albright & Wilson, Akzo, BASF, Berol Nobel, Harcros, Henkel, Hoechst, Hüls, Rewo, Rhône-Poulenc, and Zschimmer & Schwarz; in the United States by Akzo, Chemax, Ethox Chemicals, Hart, Henkel, Heterene Chemical, Karlshanns, PPG/Mazer, Rhône-Poulenc Surfactant, Sandoz, Sherex, Union Carbide and Witco; in Japan by Dai-Ichi, Kao, Nippon Nyukazai, Nippon Oil & Fats, and Sanyo; in Australia by ICI; and in Taiwan by Taiwan Surfactant and Sino-Japan Chemical.

7.3. Terminally Blocked Ethoxylates
[109], [110]

By substituting the hydrogen atom of the terminal hydroxyl group of an ethoxylate by hydrophobic residues such as benzyl, butyl, or methyl groups, terminally blocked ethoxylates are obtained that are chemically more resistant, especially in alkaline media, than the corresponding ethoxylates with a free hydroxyl group. Since blocked ethoxylates also foam less in aqueous solution than their starting ethoxylates, they have a certain value in (alkaline) cleaning processes involving strong mechanical action.

The addition of higher alkylene oxides, in particular propylene oxide, may also be regarded as a terminal blocking:

$$RO-[CH_2CH_2O]_m-H + n\, CH_2\overset{O}{\overbrace{-}}CH-CH_3 \longrightarrow$$
$$RO-[CH_2CH_2O]_m-[CH_2\underset{CH_3}{C}-O]_n-H$$
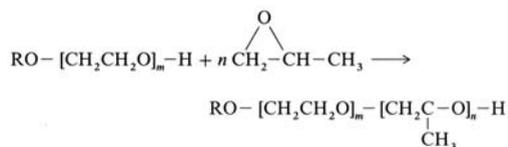
However, since such products also contain free hydroxyl groups they are no more stable than their starting ethoxylates against alkalis, but in aqueous solution foam less than the pure ethoxylates. Due to the blocking of the terminal hydroxyl groups by hydrophobic residues such ethoxylates to some extent lose their surfactant character, and become less water-soluble and

less amphiphilic. This is already noticeable in propoxylated products, the propoxy group itself being hydrophobic. This property can be utilized to enlarge a hydrophobic residue before ethoxylation by addition of propylene oxide. Finally, alkoxylation can be performed with mixtures of ethylene oxide and propylene oxide and various effects can be achieved by appropriately choosing the ratio of the two epoxides, by alternating the order of addition, etc.

7.4. Fatty Acid Esters of Polyhydroxy Compounds

Polyhydroxy compounds such as glycerol, diglycerol, polyglycerol, erythritol, pentaerythritol, xylitol, sorbitol, mannitol, sucrose, and other glucosides that are partially esterified with fatty acids have surface-active properties. The hydrophilicity (HLB value) of such esters can be increased and matched to the desired application by ethoxylating the unesterified hydroxyl groups. Esters of glycerol, sorbitol, and sucrose are discussed hereinafter by way of example, as are the so-called alkyl polyglucosides, which have recently attracted increased attention.

Fatty Acid Esters of Glycerol [111]. Disproportionating transesterification of fats and oils, the fatty acid triesters of glycerol (triglycerides), with glycerol in the presence of acid, but preferably alkaline catalysts, yields, depending on the glycerol excess, equilibrium reaction mixtures containing 35 – 60 % of monoglycerides, 35 –50 % of diglycerides, 1 – 20 % of triglycerides, 1 – 10 % of fatty acids and their alkali metal salts, and 1 – 10 % of glycerol after ca. 1 h at 200 –250 °C. Such so-called mono-diglycerides, which can also be obtained by direct reaction of free fatty acids with glycerol under acid catalysis, are marketed as mixtures. They are insoluble in water, and when they contain alkali metal salts of fatty acids, they are self-emulsifying. The fatty acids that are used are predominantly from the tallow fat range (palmitic and stearic acids). The above-mentioned mixtures are generally marketed under the name "monoglycerides", e.g., "glycerol monostearates" (GMS).

High-concentration monoglycerides are obtained from the mixtures by molecular distillation. They consist mainly of α-glycerides, and contain less than 10 % of β-glycerides:

$$
\begin{array}{ll}
CH_2OCOR & CH_2OH \\
| & | \\
CHOH & CHOCOR \\
| & | \\
CH_2OH & CH_2OH
\end{array}
$$
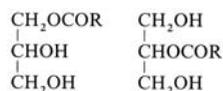
Since they crystallize in fine platelets, they impart a pearl gloss to pasty liquid detergents and cleansing agents.

Glycerides are widely used as emulsifiers in foods and cosmetics, as they are physiologically harmless. Characteristic data of some commercial products are listed in Table 14.

The enzymatically catalyzed synthesis of glycerides has not yet become industrially important [112].

Anionic surfactants having properties similar to those of the ether sulfates are obtained by sulfating monoglycerides and diglycerides [113].

Producers of glycerides include Akzo, Croda, Fina Oleochemicals, Gatte-Fosse, Hefti, Henkel, Hüls, ICI, Quest, Rewo, and

Table 14. Typical data of some industrial glycerides

	Glycerol monostearate	Glycerol mono/ distearate	Glycerol mono/ distearate, self-emulsifying	Glycerol monolaurate
CAS no.	[61789-09-1]	[68308-54-3]	[68308-54-3] [593-29-3]	[27215-38-9]
Color, consistency	white powder	white powder or flakes	whitish flakes	white, crystalline
Melting point, °C	66 – 71	56 – 61	56 – 61	56 – 60
Monoglyceride content, %	90	50	35	95
Diglyceride content, %	5	40	45	2
Glycerol content, %	1	1	3	1
Sodium stearate content, %	0	0	3	0
Acid number, mg KOH/g	< 3	< 3	< 6	< 3
Saponification number, mg KOH/g	155 – 170	160 – 175	150 – 175	195 – 205
Iodine color number, mg I$_2$/100 mL	< 3	< 3	< 6	< 3

Th. Goldschmidt in Europe; Goldschmidt Chemical, Henkel, Hodag, Hoechst-Celanese, Humko, Inolex, Karlshamns, Lonza, PPG/Mazer, and Witco in North America; Kao, Nikko Chemicals, Nippon Oil & Fats, and Toho in Japan; Taiwan Surfactant and Sino-Japan Chemical in Taiwan; and Zohar in Israel.

Fatty Acid Esters of Sorbitol. [114]. Sorbitol can be converted to monoesters or polyesters by reaction with fatty acid chlorides under mild conditions in the presence of pyridine. The esterification is performed industrially with the free fatty acids or their methyl esters at elevated temperature; sorbitol readily undergoes dehydration to sorbitan, which can lose a further molecule of water to give isosorbitol, especially in the presence of acid catalysts:
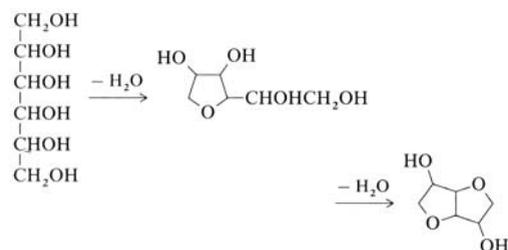
Esterification is generally carried out at 200 – 250 °C after the addition of small amounts of alkali, e.g., 0.1 % sodium hydroxide; depending on the molar ratio of the starting materials, fatty acid monoesters, diesters, or triesters of sorbitan are obtained. First marketed by Atlas Powder, these are known as "Span" types. They are water-insoluble products having low HLB values that are liquid at ambient temperature or melt below 100 °C. Ethoxylation of the Span types yields products having better water solubility and higher HLB values, namely the "Tweens", which are waxy to solid products.

Spans and Tweens are dispatched in plastic containers, plastic-coated cardboard containers, or bags.

Producers of sorbitan esters include Akzo, Auschem, Croda, Hefti, Henkel, and ICI in Europe; Chemax, Croda, Henkel/Emery, Hodag, ICI Americas, Karlshamns, Lipo Chemical, Lonza, Norman/Fox, PPG/Mazer, Stepan, and Witco in North America; Kao, Nikko Chemicals, Nippon Nyukazai, Nippon Oil & Fats, Sanyo, and Toho

in Japan; and Sino-Japan Chemical and Taiwan Surfactant in Taiwan.

Fatty Acid Esters of Sucrose. [115], [116]. As a plentifully available natural raw material, sucrose is a suitable parent substance for the hydrophilic group of surfactants. Surfactants based on sucrose, especially their fatty acid esters, are nontoxic, do not irritate the skin, and are fully biodegradable. However, they have not hitherto gained wide acceptance industrially due to a certain instability of the sucrose glycoside bond, and the insolubility of sucrose in conventional organic solvents, which makes reactions involving sucrose more difficult. Fatty acid esters of sucrose are prepared by alkaline-catalyzed reaction with 1 – 2 mol of fatty acid methyl ester per mole of sucrose, the methanol being distilled off under vacuum. The temperature should not exceed 100 °C. Dimethylformamide or dimethyl sulfoxide, both highly toxic substances, are used as solvents and must be removed completely from the reaction product, which is laborious since sucrose esters are temperature sensitive and must not be heated too strongly.

Producers of sucrose esters include Croda, Gattefosse, and ICI in Europe; Amerchol, Croda, and Union Carbide in the United States; and Dai-Ichi in Japan.

Alkyl Polyglucosides. [117–120]. Acetal-bonded glucosides mixed with oligoglucosides are obtained as a randomly distributed mixture of homologues by acetalation of glucose with fatty alcohols; the average number of glucose units per molecule being between 1 and 3, depending on the reaction parameters. Strictly speaking the products should be called alkyl oligoglucosides, though the incorrect term alkyl polyglucosides (APG) has persisted.
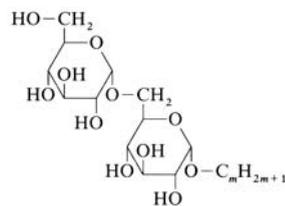
Alkyl polyglucosides are waxy, soft to glassy-solid, and colored yellow due to impurities.

They are generally extremely soluble in water and are handled as 50 % aqueous solutions. The HLB values lie above 10, and can be varied in the range 11 – 15 by changing the length of the hydrophobic group and the degree of glucosidation. The surface tension of aqueous solutions is ca. 30 mN/m and the interfacial tension toward hydrocarbons 1 mN/m. Alkyl polyglucosides are moderate foaming agents and outstanding emulsifiers. They are suitable for washing textiles and hard surfaces, particularly in combination with other anionic and nonionic surfactants, with which they give synergistic effects. Alkyl polyglucosides decompose on heating; their aqueous solutions are stable in the pH range 3 –13. They are nontoxic, only slightly irritating to the skin, and biodegrade rapidly.

Alkyl polyglucosides can be prepared by direct reaction of anhydrous glucose with fatty alcohols. In another method, in which also aqueous glucose solution can be used, the latter is first reacted with butanol to form butyl glucoside, which is then reacted in a second stage with fatty alcohol to form the fatty alkyl oligoglucoside. Butanol and excess fatty alcohol are distilled off. Strong acids such as sulfuric acid are used as catalysts in both methods.

The alkyl polyglucoside thus obtained as a melt is dissolved in water and bleached with hydrogen peroxide.

CAS Numbers C_8/C_{10}-Fatty alkyl polyglucoside [*128664-36-8*], C_{12}/C_{14}-fatty alkyl polyglucoside [*136797-44-9*].

Producers include Henkel in the United States, Kao in Japan, Seppic in France, and BASF, Henkel, and Hüls in Germany.

7.5. Amine Oxides [121], [122]

Reaction of tertiary amines such as fatty alkyldimethylamine or fatty amines doubly ethoxylated at the nitrogen atom with hydrogen peroxide yields amine oxides:

$$R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} + H_2O_2 \longrightarrow R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} \longrightarrow O + H_2O$$
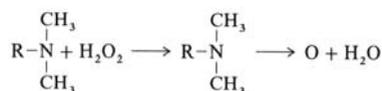
Surfactant amine oxides such as lauryldimethylamine oxide are insensitive to water hardness.

They disperse lime soaps, foam satisfactorily and are mild to the skin. They are therefore widely used as constituents of dishwasher detergents, shampoos, and soaps. Amine oxides in neutral aqueous solution should be regarded as nonionic surfactants. They are protonated in acid solution and thus represent the transition to cationic surfactants.

CAS Numbers Lauryldimethylamine oxide [*1643-20-5*]; Stearyldimethylamine oxide [*2571-88-2*]; Coco fatty alkyldimethylamine oxide [*61788-90-7*].

Producers of amine oxides include Akzo, Albright & Wilson, Ceca, Croda, Pulcra, Rewo, and Th. Goldschmidt in Europe; Clough, Ethyl, Goldschmidt Chemical, Henkel, McIntyre, PPG/ Mazer, Rhône-Poulenc Surfactant, Sherex, Sher Chemicals, Stepan, and Witco in the United States; Nippon Oil & Fats in Japan; and Taiwan Surfactant in Taiwan.

8. Cationic Surfactants [123–125]

Surfactants whose hydrophilic group is a cation are termed cationic surfactants. The cationic structure may already be present in the surfactant molecule, as in the case of quaternary ammonium or phosphonium salts, or may be formed only in aqueous solution, as, for example, in ethoxylated fatty amines. In acidic solution, nonionic surfactants can adopt a cationic character due to protonation at a heteroatom; examples are fatty amine oxides and even ethoxylates, whose ether groups can form oxonium structures. However, strictly speaking only those surfactants that do not require protonation to become cationic are regarded as cationic surfactants.

The most important cationic surfactants are the quaternary nitrogen compounds: tetraalkylammonium salts, *N*,*N*-dialkylimidazolinium compounds, and *N*-alkylpyridinium salts. The positive electrical charge of the hydrophilic moiety confers on cationic surfactants properties that open up areas of application for which anionic and nonionic surfactants are unsuitable or less suitable. Important uses of these cationic surfactants are as microbicides, herbicides, corrosion inhibitors, oxidation inhibitors, adhesives, finishing and sizing agents, water repellents, fabric

softeners, flotation aids, dispersants, levelling agents, etc.

Other cationic surfactants, e.g., the quaternary phosphonium salts or tertiary sulfonium salts are less important industrially, although they are very useful as phase-transfer catalysts in synthesis [126].

8.1. Quaternary Ammonium Compounds

Quaternary ammonium compounds are obtained by alkylating tertiary amines. At least one of the alkyl residues must be a relatively long alkyl group. In general, tertiary amines having one or two long alkyl residues are used as starting compounds ($\rightarrow$ Amines, Aliphatic), to which are added shorter alkyl groups in the form of methyl chloride, ethyl chloride or bromide, or dimethyl sulfate. The corresponding ammonium chlorides, ammonium bromides, or ammonium methyl sulfates are then obtained. The addition requires a polar solvent (e.g., alcohol); in the case of alkyl chlorides, which are mainly used for the alkylation, temperatures of 50 – 100 °C and reaction times of several hours are required. The process can be simplified by carrying out the reaction under pressure in excess alkylating agent (e.g., methyl chloride as solvent). The product is isolated by releasing the pressure and evaporating unreacted alkyl chloride [127].

Benzyl chloride reacts very readily as alkylating agent; the disinfectant Zephirol is obtained by addition to dimethyldodecylamine:

$$C_{12}H_{25}N\begin{matrix}CH_3\\\\CH_3\end{matrix} + ClCH_2C_6H_5 \longrightarrow \left[C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N}}-CH_2C_6H_5\right]^+ Cl^-$$
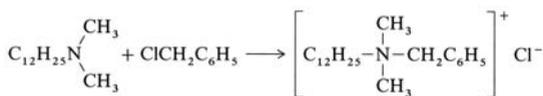
Another method of quaternizing tertiary amines, as well as ethoxylated fatty amines, is the reaction with ethylene oxide and water in the absence of a catalyst:

$$C_{12}H_{25}N\begin{matrix}CH_3\\\\CH_3\end{matrix} + CH_2\overset{O}{-}CH_2 + H_2O$$

$$\longrightarrow \left[C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N}}-CH_2CH_2OH\right]^+ OH^-$$
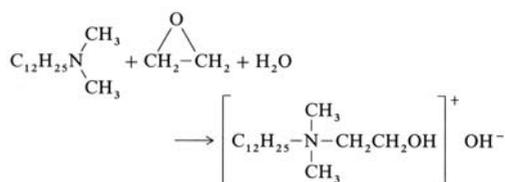
For special applications quaternary compounds can also be obtained from fatty acid derivatives such as the amides of diamines or esters of triethanolamine:

$RCONHCH_2CH_2N(CH_3)_2$
$RCOOCH_2CH_2N(CH_2CH_2OH)_2$
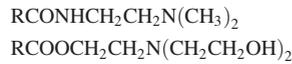
A further group of amines that is suitable for quaternization is obtained by hydrogenating substituted propionitriles, which are obtained by addition of fatty alcohols or fatty amines to acrylonitrile:

$ROCH_2CH_2CH_2NH_2$ and $RNHCH_2CH_2CH_2NH_2$
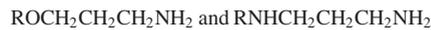
Distearyldimethylammonium chloride (DSDMAC) or, more correctly, since the long alkyl residues are tallow fat alkyl residues, di-tallow alkyl dimethyl ammonium chloride (DTDMAC), was for a long time the most important component in fabric softeners. Since it proved to be relatively toxic to water-borne organisms [128], it has been replaced by less toxic ammonium compounds, which contain ester group as cleavage sites which lead to rapid breakdown of the compounds in water. These are the so-called esterquats obtained from fatty acid, triethanolamine or N-methyldiethanolamine, and dimethyl sulfate [129], [130]:

$$\left[RCOOCH_2CH_2-\overset{CH_2CH_2OH}{\underset{CH_3}{N^+}}-CH_2CH_2OCOR\right]^+ CH_3O-SO_3^-$$
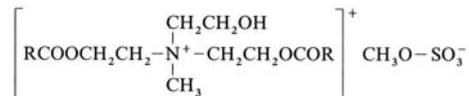
and the diesterquats obtainable from epoxypropyltrimethylammonium chloride and fatty acids [131]:

$$RCOOCH_2\underset{RCOO}{\overset{|}{CH}}CH_2-\overset{+}{N}(CH_3)_3 \; Cl^-$$
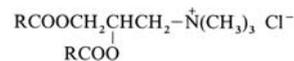
Typical data of some simple quaternary ammonium chlorides that are stored and transported in the form of aqueous or aqueous-alcoholic solution in stainless steel or plastic drums are listed in Table 15.

Producers of quaternary ammonium compounds include Akzo, BASF, Bayer, Berol, Ceca, Croda, Fina Oleochemicals, Hoechst, Hüls, ICI, Pulcra, Rewo, Rhône-Poulenc, Stepan, and Witco in Europe; Akzo, Emkay, Henkel, Hoechst, Humko, ICI, Karlshamns, Rhône-Poulenc,

Table 15. Typical data of some industrial quaternary ammonium compounds

	Stearyltrimethyl-ammonium chloride	Stearylbenzyldimethyl-ammonium chloride	Ditallowalkyl-dimethylammonium chloride	Ditallowacyloxyethyl hydroxyethylmethyl ammonium methyl sulfate ("Ester quat")
CAS no.	[112-03-8]	[122-19-0]	[61789-80-8]	[93334-15-7] [91995-81-2]
Consistency	liquid	liquid	liquid – solid	liquid – solid
Flow point, °C			ca. 35	ca. 35
Active substance content, %	50 – 52	50 – 52	74 – 76	ca. 90
Content of free amine and hydrochloride, %	1	1	2	
Isopropanol content, %	30	0	16	10
Density, g/mL	0.89	0.95	0.90	0.96
Color index (Gardner)	< 7	< 7	4	3
pH (1 % aqueous solution)	5 – 7	6 – 8		
Ash, %	< 0.8	1.0	< 0.35	< 0.1
Flash point, °C	15		ca. 20	26 – 32

Sherex, and Witco in North America; Kao, Marubishi Oil, Sanyo Chemical, Takemoto Oil, Tokai Seiyu, and Yoshimura Oil in Japan; and Taiwan Surfactant in Taiwan.

8.2. Imidazoline Derivatives

Condensation of fatty acids with ethylenediamine or substituted ethylenediamine yields substituted imidazolines, e.g.:

$$RCOOH + H_2NCH_2CH_2NHCH_2CH_2OH$$

Such compounds are strongly cationic in acidic solution, but undergo slow hydrolysis [132]:
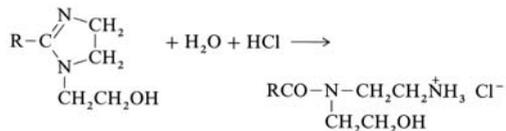
True cationic surfactants are obtained by alkylating imidazoline derivatives, mainly with chloromethane:

Such surfactants have properties similar to those of acyclic quaternary ammonium salts; they are dermatologically extremely compatible, are antiseptic, and are used as wetting agents, dispersants and cleansing agents, including bodycare products.

An imidazoline derivative obtained by reacting 1 mol of *N*-aminoethylethylenediamine with 2 mol of fatty acid, and quaternized with dimethyl sulfate, is an important fabric softener [86088-85-9] [133]:

9. Amphoteric Surfactants [134–136]

Amphoteric surfactants can be classified as ampholytes and betaines. Ampholytes are compounds having at least one active proton, the best-known example being aminocarboxylic acids, which at the isoelectric point exist as inner salts, at low pH values as cationic species, and at higher pH values as anionic species:
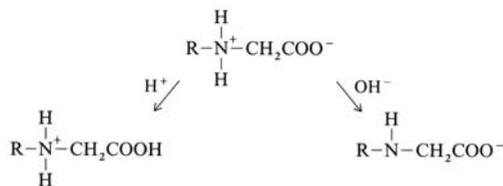
Betaines have no mobile protons and are true amphoteric ions which assume a cationic nature in strongly acid media:

$$R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}}-CH_2COO^- \xrightarrow{H^+} R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^+}}-CH_2COOH$$
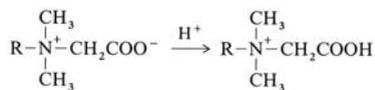
Ampholytes are of minor industrial importance, largely on account of the marked dependence of their properties on pH. Ampholytes are prepared by reacting fatty amines with chloroacetic acid and sodium hydroxide, or by alkaline-catalyzed addition of acrylic acid to fatty amines:

$$RNH_2 + ClCH_2COOH \xrightarrow{NaOH} RNHCH_2COOH$$
$$RNH_2 + CH_2=CHCOOH \longrightarrow RNHCH_2CH_2COOH$$
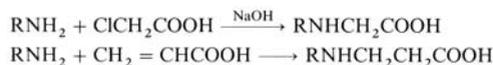
Betaines are prepared by reacting a tertiary amine with chloroacetic acid and sodium hydroxide:

$$RN(CH_3)_2 + ClCH_2COOH \xrightarrow{NaOH} RN^+\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{}}CH_2COO^-$$

or

$$RCONH(CH_2)_3N(CH_3)_2 + ClCH_2COOH$$

$$\xrightarrow{NaOH} RCONH(CH_2)_3N^+\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{}}CH_2COO^-$$
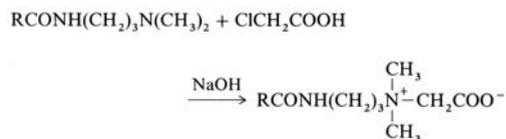
The sulfobetaines are now of only minor importance. Of the various ways of preparing sulfobetaines, the elegant synthesis from amines, alkyl chloride, and sodium hydrogensulfite is mentioned here [137]:

$$RN(CH_3)_2 + CH_2=CH_2CH_2Cl \longrightarrow$$
$$[RN(CH_3)_2CH_2CH=CH_2]^+ \ Cl^-$$
$$[RN(CH_3)_2CH_2CH=CH_2]^+ \ Cl^- + NaHSO_3$$
$$\xrightarrow{-NaCl} RN(CH_3)_2CH_2CH_2CH_2SO_3^-$$
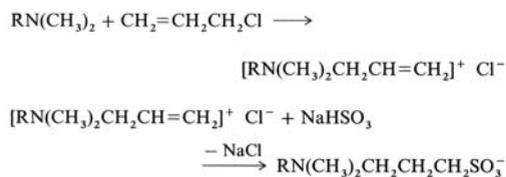
Nowadays only true betaines are of economic importance, especially acid amide betaines and the betaines derived from imidazolines:

$$R-C\underset{\underset{CH_2CH_2OH}{\underset{|}{N}}}{\overset{\overset{N-CH_2}{\underset{|}{}}}{\diagdown}}\underset{CH_2}{\overset{}{}} + ClCH_2COOH \xrightarrow{NaOH} R-C\underset{\underset{CH_2CH_2OH}{\underset{|}{N}}}{\overset{\overset{CH_2COO^-}{\overset{|}{N^+}-CH_2}}{\diagdown}}\underset{CH_2}{\overset{}{}}$$
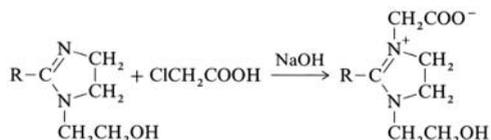
The latter, which are prepared in aqueous solution, probably exist in the open-chain form [138].

Betaines are insensitive to the water hardness and pH value of industrial water, are only slightly toxic, are compatible with the skin and mucous membranes, and have antimicrobial properties. They have good washing and foaming performance and are highly compatible with other classes of surfactants, and are therefore ideally suited for use in bodycare products.

Lecithin or phosphatidylcholine, a naturally occurring phospholipid also belongs to the class of betaines [139], [140]:

$$\begin{aligned} &C_{17}H_{35}CO-O-CH_2 \\ &C_{17}H_{33}CO-O-CH_2 \qquad O \\ &\qquad\qquad\quad CH_2-O-\overset{\overset{\displaystyle \parallel}{}}{\underset{\underset{O^-}{|}}{P}}-CH_2CH_2-\overset{+}{N}(CH_3)_3 \end{aligned}$$
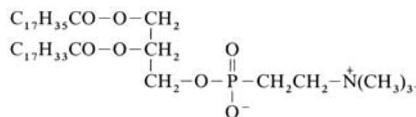
Producers of ampholytes and betaines include Akzo, Albright & Wilson, Auschem, Croda, Harcros, Henkel, Hüls, Manro, Pulcra, Rewo, Rhône-Poulenc, Seppic, Stepan, Th. Goldschmidt, Union Carbide, and Zschimmer & Schwarz in Europe; Clough, Goldschmidt Chemicals, Henkel, Inolex, McIntyre, Mona, PPG/Mazer, Rhône-Poulenc Surfactant, Sher Chemicals, Sherex, Stepan, and Witco in the United States; Lion, Nippon Oil & Fats, Sanyo, and Toho in Japan; Taiwan Surfactant in Taiwan; and Zohar in Israel.

10. Surfactants with Heteroatoms in the Hydrophobic Group

10.1. Block Copolymers of Propylene Oxide and Ethylene Oxide [141], [142]

The incorporation of propoxy groups in a surfactant increases its hydrophobicity. Hydrophobic parent substances of any desired molecular mass can be prepared by addition of propylene oxide to a low molecular mass starter molecule. Propoxylation is performed analogously to ethoxylation, with alkaline catalysts at 120–180 °C under a slight excess pressure:

$$ROH + n\,CH_3CH-CH_2 \longrightarrow RO-[CHCH_2O]_n-H$$
$$\underset{CH_3}{}$$
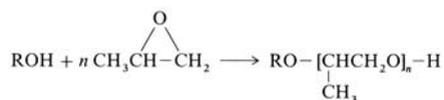
Suitable starter molecules are monofunctional or polyfunctional protic substances, for example, methanol, ethanol, propanol, or higher alcohols; diols such as butanediol; and triols such as gylcerol. Propylene glycol itself is also a suitable diol, and ethylenediamine is a suitable tetrafunctional starter molecule. Subsequent ethoxylation of hydrophobic parent substances obtained in this way yields nonionic surfactants, which can be described as block copolymers of propylene oxide and ethylene oxide. When using polyfunctional starters, branching occurs at the starter molecule. Derivatives of propylene glycol and ethylenediamine, first introduced by Wyandotte under the trade names of Pluronics and Tetronics, are now the most important surfactants of this type:

$$H-[OCH_2CH_2]_m-[OCHCH_2O]_n-[CH_2CH_2O]_m-H$$
$$\underset{CH_3}{}$$

$$H-[OCH_2CH_2]_m-[OCH_2CH]_n \diagdown$$
$$\underset{CH_3}{} NCH_2CH_2N \quad [CHCH_2O]_n-[CH_2CH_2O]_m-H$$
$$H-[OCH_2CH_2]_m-[OCH_2CH]_n \diagup \qquad [CHCH_2O]_n-[CH_2CH_2O]_m-H$$
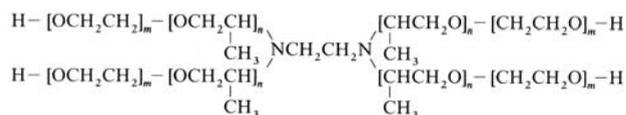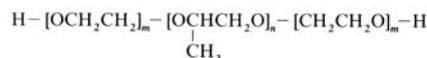
As the structural formulas indicate, a wide range of block copolymers can be synthesized. The products are not uniform, and a homologue distribution range exists for each propoxylate chain and for each ethoxylate chain. Mean molecular masses of 1000 – 5000 are preferred in the case of hydrophobic propoxylate parent substances. Ethoxylation can also be varied over a wide range; depending on the desired application, HLB value and cloud point, between 10 and 80 wt % of ethylene oxide is added.

The products are liquids, pastes, or waxy solids, depending on the molecular mass. They are water-soluble above a content of about 25 wt % of bound ethylene oxide. They are also relatively stable to alkalis and acids.

Their outstanding property is the lack of foaming ability of their aqueous solutions; the propylene oxide – ethylene oxide addition products also suppress the foam of strongly foaming solutions. The block copolymers are therefore preferably used as wetting and cleaning agents in processes involving high mechanical stress and

in high-speed cleaning machines. They are also used as demulsifiers and dispersants. However, their unsatisfactory biodegradability prevents their widespread use.

Producers include BASF, Berol, Nobel, Dow, Harcros, Hoechst, Hüls, ICI, and Rhône-Poulenc in Europe; BASF, Hart, Henkel, ICI Americas, Norman/Fox, Olin, and PPG/Mazer in North America; Dai-Ichi and Nippon Oil & Fats in Japan; ICI in Australia; and Sino-Japan Chemical in Taiwan.

10.2. Silicone-Based Surfactants
[143–148]

Silicone-based surfactants are mainly derived from methylsilicones (polydimethylsiloxanes, → Silicones, Section 2.2.→ Silicones→ Silicones). They lower the surface tension of water to a greater degree than hydrocarbon-based surfactants, and in this respect are inferior only to fluorosurfactants. In their molecular structure silicone-based surfac-tants resemble surfactants containing polypropylene glycol as hydrophobic parent substance, since the hydrophobic silicone group also has a random molecular mass distribution. The following basic structures (linear, comb, and branched) occur, where A denotes hydrophilic groups:

$$A-\begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{bmatrix}_n \begin{matrix} CH_3 \\ | \\ Si-A \\ | \\ CH_3 \end{matrix}$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ A \end{bmatrix}\begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{bmatrix}_n \begin{matrix} CH_3 \\ | \\ Si-CH_3 \\ | \\ CH_3 \end{matrix}$$

$$A-\begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{bmatrix}_n \begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ O \\ | \\ (CH_3-Si-CH_3)_n \\ | \\ A \end{bmatrix} \begin{bmatrix} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{bmatrix}_n \begin{matrix} CH_3 \\ | \\ Si-A \\ | \\ CH_3 \end{matrix}_m$$
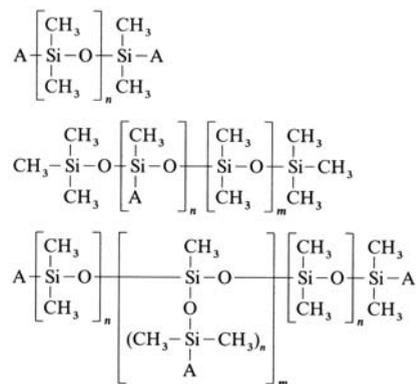
Polydimethylsiloxanes are prepared by selective hydrolysis of dimethyldichlorosilane:

$$n\,Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl + (n-1)\,H_2O \longrightarrow$$

$$Cl\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_{n-1}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl + (2\,n-2)\,HCl$$
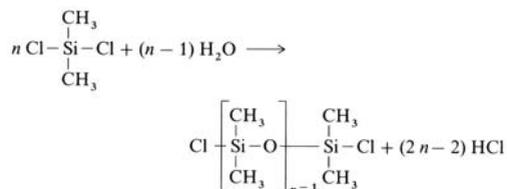
The terminal chlorine atoms may be substituted in the presence of bases by polyethylene glycol residues, resulting in nonionic surfactants of the ethoxylate type.

A special feature of silicone chemistry is the "equilibration" of the polymers, in which molecular mass distribution and distribution of the individual siloxane building blocks can be brought into a reproducible equilibrium by redistribution of the siloxane bonds under acid catalysis. The linear, comb, and branched silicones are formed in this way.

Equilibration enables substituents to be incorporated in the silicone molecule. The silicon – hydrogen bonds of silanes can add to an aliphatic double bond in the presence of hexachloroplatinic acid:

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-H + CH_2{=}CHR \longrightarrow CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-CH_2CH_2R$$

The group R can carry functional groups. By addition of allyl alcohol, for example, hydroxyl-containing dichlorosilanes can be produced, which are converted by selective hydrolysis to poly(methylhydroxypropyl)siloxane, which can be equilibrated with a polydimethylsiloxane. The hydroxyl groups introduced in this way can be reacted further, for example by sulfation to give sulfuric hemi-esters, which yield anionic surfactants.

The choice of the siloxane building blocks, selective hydrolysis, and equilibration enable a wide variety of silicone surfactants to be synthesized. The polysiloxane residues of most silicone surfactants have a polymeric character, in contrast to the previously discussed hydrocarbon-based surfactants. Polar and nonpolar groups alternate in the polymer chain, similar to the polypropylene glycol derivatives or the polypeptides. In the polysiloxanes discussed here, the alternating groups are oxygen bridges and dimethylsilyl groups. The oxygen bridges can interact weakly with water, with the result that a polydimethylsiloxane residue forms a layer on the water surface, with oxygen atoms oriented towards the aqueous phase. The same is true of pure, nonfunctionalized polydimethylsiloxanes, which have a surfactant character because they have a lower surface tension due to the weak mutual cohesive forces of the siloxane residues.

The layer structure of the polysiloxane boundary films, on the other hand, renders these films a certain strength. Polysiloxanes modified with polyethers are therefore important as integrated constituents of polyurethane foams, in which they act as foam stabilizers. The stability of films of silicone surfactants in aqueous foams makes them useful as additives to aqueous fire-extinguishing agents. Although silicone surfactants form stable foams, they are able to destroy foams of hydrocarbon-based surfactants, which they displace from the surface because of their higher surface activity.

The polysiloxane skeleton is biologically persistent, and is broken down only slowly in the environment by hydrolysis. However, polydimethylsiloxanes are physiologically harmless. Silicone-based surfactants are used in a wide range of special applications, for example, in skincare and haircare preparations [145]; in the production of fibers and textiles [146]; as wetting agents, dispersants, and flow-control agents in the production of paints and coatings [147]; as mold release agents in plastics processing; and as defoaming agents, emulsifiers, demulsifiers, and water repellents.

Producers. Silicone-based surfactants are produced in Europe by Hoechst and Th. Goldschmidt; in the United States by Dow Corning, Goldschmidt Chemical, Rhône-Poulenc Surfactant, Troy Chemical, and Union Carbide; and in Japan by Tosho and Yoshimura Oil Chemical.

10.3. Fluorosurfactants [149–151]

The fluorosurfactants used nowadays can be regarded as analogues of surfactants containing

aliphatic hydrocarbon groups, in which the hydrogen atoms have been wholly or partly replaced by fluorine atoms. The extreme hydrophobicity of fluorinated hydrocarbons means, however, that amphiphilic fluorine compounds with substantially shorter hydrophobic residues than their aliphatic analogs are already surface-active. Whereas a marked interfacial activity in salts of aliphatic carboxylic acids is observed starting with 8 – 9 carbon atoms in the hydrophobic group, perfluorobutyric acid and its salts are already considerably surface-active. The very low cohesive forces between the fluorinated alkyl groups result in extremely low surface tensions of fluorosurfactants. Surface tensions $\leq$ 20 mN/m can be achieved only with fluorosurfactants. Fluorosurfactants have very low CMCs and are hence already active at very low concentrations, which to some extent compensates for their high cost. Fluorosurfactants have high chemical and thermal stability, and accordingly are used for special applications (high-temperature processes, electroplating techniques). They diffuse rapidly in aqueous solution, and are therefore also suitable for high-speed industrial processes.

Perfluoroalkane carboxylic or perfluoroalkanesulfonic acids are prepared by electrochemical fluorination of the corresponding carboxylic acids or sulfonic acids. Telomerization of perfluoroethylene with, for example, pentafluoroiodoethane as starter molecule yields homologous perfluoro-1-iodoalkanes, which can be converted to carboxylic acids, sulfonic acids, phosphonic acids, or amines. Perfluoroalkenes, possibly branched, are obtained by anionically catalyzed oligomerization of tetrafluoroethylene; a fluorine atom located at the double bond can be electrophilically replaced, in the presence of a base, by alcohol, phenol, ethylene glycol, or olgioethylene glycol to give nonionic surfactants of the ethoxylate type.

Fluorosurfactants are used as wetting, emulsifying, and flow- control agents; as absorption agents for imparting water-repellent and soil-repellent properties to textiles, leather, and paper; in coating photocopying paper; as mold release agents for plastics; and as additives in fire-extinguishing agents.

Producers of fluorosurfactants include Hoechst in Europe and 3 M and Du Pont in the United States.

11. Analysis [152–157]

Surface-active substances are identified qualitatively by the fact that their solutions foam and wet fibers or solid surfaces more quickly than pure water, and also by the reduction in surface tension of water, which is recognized by the rapid sinking of a small thin metal or PVC plate carefully laid on the surface of the water, which would otherwise be held on the surface in the absence of surfactants. These test methods are not unambiguous, however, not all surface-active substances should be regarded as surfactants.

11.1. Identification of Surfactants

A number of group-specific detection reactions are known for identifying different types of surfactants, which, however, have become less important with improvements in instrumental analysis. The property of anionic and cationic surfactants of forming sparingly soluble salts in water can be used as a quick aid; an anionic surfactant, for example a sulfonate, can be precipitated with a cationic surfactant, for example a quaternary ammonium salt, and vice versa. Anionic surfactants produce a precipitate on addition of aluminum acetate, and soaps are converted to water-insoluble fatty acids on acidification. Nonionic surfactants of the ethoxylate type and cationic surfactants form precipitates sparingly soluble in water with phosphotungstic and phosphomolybdic acids, potassium hexacyanoferrate, and Dragendorff's reagent (barium bismuth iodide). Amphoteric surfactants also form precipitates with phosphotungstic and phosphomolybdic acids; generally, they are sparingly soluble at their isoelectric point.

The modern method of choice for identifying surfactants is IR spectroscopy, for which many reference spectra exist. This technique has been refined to such an extent that amounts of less than 1 µg can be measured. UV spectroscopy allows identification of surfactants containing aromatic groups.

Mass spectroscopy, which is generally employed in combination with gas chromatography and high-pressure liquid chromatography, has also become a valuable aid in surfactant analysis, especially after the introduction of soft ionization methods such as direct chemical ionization (DCI),

field desorption (FD), and fast atom bombardment, which can also be applied to nonvaporizable substances. Although mass spectroscopy is complex and therefore unsuitable for routine investigations, NMR spectroscopy, especially ^{1}H NMR, has become an extremely useful tool in surfactant analysis, for example, in identifying hydrophobic hydrocarbon parent substances and in determining the number of added ethylene oxide or propylene oxide molecules in alkoxylates.

Gas chromatography is now an important method in surfactant analysis. Substances of low volatility are often modified chemically for GC analysis. Ethoxylates, for example, are determined as trimethylsilyl ethers; homologues containing up to seven ethylene oxide units per mole can be determined in this way. Fatty acids and sulfonic acids are subjected to GC in the form of their methyl esters. Gas chromatography and mass spectroscopy are suitable for identifying hydrophobic residues of surfactants after specific pyrolytic decomposition. With concentrated phosphoric acid at 215 °C the structurally unchanged alkylbenzene is obtained from the corresponding alkylbenzenesulfonate, while alkanes shortened by the hydrophilic group are obtained from alkyl sulfates, fatty acid esters, and fatty acid amides. Alkanesulfonates and α-sulfocarboxylic esters produce nonuniform fragments in this type of pyrolysis. In the pyrolysis of alkylbenzenesulfonate or alkanesulfonate in a KOH − NaOH melt at 290 °C, the parent hydrocarbons are obtained as alkylphenols or alkenes. Quaternary ammonium compounds are subjected to Hofmann degradation with potassium hydroxide or sodium hydroxide, in which alkene and tertiary amines are formed. Decomposition and GC separation can be coupled on-line (pyrolysis – gas chromatography). Decomposition is often performed as Curie point pyrolysis to ensure reproducible fragmentation under controlled conditions.

Iodoalkane, ethylene, and iodine are formed when ethoxylates are reacted with boiling 58 % hydroiodic acid:

$$RO-[CH_2CH_2O]_n-H+(2n+1)HI \rightarrow$$
$$RI+n\,CH_2=CH_2+n\,I_2+(n+1)H_2O$$
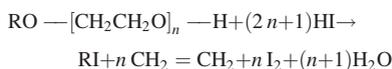
The parent substances and their simple derivatives obtained from the reaction can also be identified by gas chromatography or mass spectrometry.

The decomposition of ethoxylates with hydroiodic acid is also utilized in the wet chemical determination of the degree of ethoxylation n of an ethoxylate; the iodine released is titrated with thiosulfate solution.

A modification of this Zeisel cleavage converts the ethoxy groups to ethyliodide and propoxy groups to propyliodide which again can be determined by GC.

11.2. Isolation and Separation

Surfactants often exist as a mixture of different types of surfactant or mixed with nonsurfactant components. A number of methods are available for separating and specifically isolating individual surfactants and for removing byproducts.

Extraction. Nonpolar constituents (neutral oil) can be extracted with petroleum ether from neutral or alkaline-adjusted aqueous or aqueous-alcoholic solutions of anionic surfactants. If the solution is acidified, fatty acids also pass into the petroleum ether phase.

Surfactant sulfonic acids are extracted from aqueous hydrochloric acid sulutions with diethyl ether. Short-chain alkylbenzenesulfonic acids, disulfonic acids, etc., remain in the aqueous phase, from which they can be extracted with butanol.

Polyglycols (polydiols) can be extracted from solutions of ethoxylates in ethyl acetate by using aqueous sodium chloride solution. Ethoxylates are extracted from aqueous solution by chloroform after saturating the solution with sodium chloride.

Blowing Out. Blowing out is a nonspecific method for isolating traces of all surface-active substances from aqueous solutions. A stream of nitrogen loaded with ethyl acetate vapor is passed through a frit into the solution. Surfactants are adsorbed on the surfaces of the nitrogen bubbles and transported upwardly, where they are absorbed in an ethyl acetate phase covering the aqueous solution. This method is used in trace analysis of surfactants, especially in effluents and wastewaters.

Adsorption. Surfactants can be separated by adsorption on aluminum oxide, activated charcoal, polymer resins, or silica gel. Using solvents

of increasing polarity it is possible, by column chromatography, to separate nonionic surfactants from anionic surfactants, and nonionic surfactants of different HLB value from one another. Reverse-phase cartridges have been used to recover traces of surfactant from aqueous solution.

Ion exchangers. are being used increasingly in surfactant separation and analysis, and a quantitative analysis procedure has been proposed [152]. Three ion-exchange columns are connected in series: a strongly acidic cation exchanger in the H^+ form, in which quaternary ammonium compounds, betaines, and imidazoline derivatives are retained from ethanolic solution; a strongly basic anion exchanger in the Cl^- form, which retains sulfonates and sulfates; and a strongly basic anion exchanger in the OH^- form, where fatty acids and aminocarboxylic acids are retained. The nonionic surfactants appear in the eluate. The surfactants retained in the columns are eluted with aqueous ethanolic hydrochloric acid or 2 % aqueous isopropanolic sodium hydroxide and then separated further.

A procedure for separating surfactants from heavy-duty detergents that do not contain any cationic surfactants is as follows [158]: the ethanol-soluble material is redissolved in a mixture of isopropanol and water and subjected to a double ion exchange (cation exchanger and macroporous anion exchanger). The eluate contains the nonionic surfactant. The anion exchanger is then charged with ethanol saturated with carbon dioxide, whereby the soaps are eluted. The hydrotropic compounds (e.g., cumenesulfonate) are then isolated with a solution of 1 N ammonium bicarbonate in 80 parts of water and 20 parts of isopropanol, and finally the sulfonates and sulfates are isolated with 0.3 N ammonium bicarbonate solution in 60 parts of water and 40 parts of isopropanol.

The two separation processes described above demonstrate the numerous possibilities provided by ion exchangers in surfactant analysis.

Chromatographic Methods. Besides gas chromatography (GC), thin-layer chromatography (TLC) is an important method [159], which has the advantage of being able to identify directly individual surfactants even in mixtures.

High-performance liquid chromatography (HPLC) and gradient gel-permeation chromatography (GPC) are being increasingly used. Not only can homologous and analogous compounds be separated in this way, but trace constituents can be also detected.

Supercritical fluid chromatography (SCF) has recently become important especially for higher ethoxylates [160], and capillary electrophoresis, which is suitable for separating ionic compounds, is also occasionally used.

11.3. Quantitative Determination

The afore-described methods of identifying and isolating surfactants are often also suitable for their quantitative determination. HCLP has become a powerful tool for quantitative analysis in the last few years. In chromatographic methods, quantiative determination is performed by calibration with reference substances. For extracts or eluates available in larger amounts, this is performed gravimetrically after evaporation or after precipitation with a specific reagent. Also, direct or indirect photometric determination in solution using calibration curves is often employed. The term indirect photometric determination refers to the photometric determination of a substance containing a chromophor that forms a salt, an addition compound or a complex of defined composition with the surfactant and which is quantitatively determined after reaction with the surfactant.

Anionic and cationic surfactants can also be determined by volumetric analysis if the molecular mass is known or assumed. A solution of a surfactant having an opposite electrical charge to that of the surfactant ion is used for titration. Anionic and cationic surfactants generally form sparingly soluble salts in water; the titration can be performed turbidimetrically as a precipitation titration. The determination of the endpoint can also be achieved potentiometrically with tenside-selective electrodes, e. g., by means of a graphite electrode coated with poly(vinyl chloride) [161].

Two-phase Epton titration is universally employed, especially for the volumetric determination of sulfonates and sulfates. The titration of the anionic surfactant is performed in two mutually immiscible solvents (water and trichloromethane) with a cationic surfactant such as n- cetylpyridinium chloride or Hyamine 1622.

The water-insoluble cation and anion surfactant salt formed in the titration dissolves in the chloroform phase. The end point is indicated by dyes or dye mixtures which form salts with the surfactants and pass from one phase to the other at the end point.

Modified Epton Titration (CIA Method). The anionic surfactant is titrated in the two-phase system water–trichloromethane with Hyamine 1622, a cationic surfactant. The indicator is a mixture of the cationic dye dimidium bromide and the anionic dye Disulfin Blue VN. The anionic surfactant forms a salt with the cationic dye, which dissolves in trichloromethane to give a pinkish-red color. At the end point the Hyamine cation displaces the dimidium cation from the salt and thus from the trichloromethane, the red coloration migrating to the aqueous phase. Excess Hyamine forms a salt with the dye Disulfin Blue, which dissolves in trichloromethane to give a blue color. At the end point the color of the trichloromethane phase thus changes from red through colorless to blue.

Longwell – Maniece Methylene Blue Method. Sulfonate and sulfate surfactants form salts with the cationic dye methylene blue that are insoluble in water but soluble in trichloromethane. Since methylene blue, which is added as its hydrochloride, is practically insoluble in trichloromethane, when the aqueous and trichloromethane phases are mixed the dye passes into the trichloromethane phase only in an amount equivalent to the quantity of anionic species. The surfactant concentration in the trichloromethane extract can then be determined accurately by photometric determination at 650 nm.

The Longwell – Maniece methylene blue method can be combined with the blowing out process for trace analysis of residual surfactants in biodegradation experiments and of surfactants in effluents and wastewaters. As little as 20 µg of alkylbenzenesulfonate can be determined.

The anionic surfactant determined with this method is termed methylene blue active substance (MBAS).

Determination of Cationic Surfactants with Disulfin Blue (Kunkel Method). This method is based on the formation of a trichloromethane soluble salt of a cationic surfactant with the anionic dye Disulfin Blue. A solution of the cationic surfactant in trichloromethane is thoroughly mixed with the aqueous ethanolic solution of the dye. After separating the phases the trichloromethane phase is evaporated, and the residue dissolved in methanol. This solution is determined photometrically at 628 nm. Substance-specific calibration curves are used for evaluation. This method can be used in combination with the blowing out process for trace analysis; 10 µg of cationic surfactant can be determined. The cationic surfactant determined using this method is termed Disulfin Blue substance (DSBS).

Ethoxylates are determined not in a two-phase titration, but indirectly via a precipitation reaction.

Determination of Ethoxylates with Dragendorff's Reagent (Wickbold Method). With modified Dragendorff's reagent (barium chloride/potassium tetraiodobismuthate (III) in glacial acetic acid) ethoxylates containing ≥ 6 mol of ethylene oxide per mole form sparingly soluble precipitates in water. The precipitate is filtered, washed with glacial acetic acid, dissolved in ammonium tartrate solution, and acidified with sulfuric acid. The bismuth present in solution is titrated with ethylenediamine tetraacetate solution with xylenol orange as indicator. To calculate the amount of ethoxylate, substance-specific calibration factors are required, which can also be calculated if the mean molecular mass of the surfactant is known sufficiently accurately.

In another type of titration, especially suitable for trace analysis, the precipitate is dissolved in ammonium tartrate and titrated with pyrrolidine dithiocarbamate solution; the end point is determined potentiographically. Using this method allows as little as 50 µg of nonylphenol ethoxylate (10 mol EO/mol) to be detected.

The nonionic surfactants determined by this method are termed bismuth-active substances (BiAS).

The four methods of quantitative surfactant determination outlined above presuppose a knowledge of the mean molecular mass of the investigated surfactant. As calibration or reference substance tetrapropylenebenzenesulfonate is used for anionic surfactants, nonylphenol ethoxylate containing 10 mol of ethylene oxide per mole for nonionic surfactants, and dodecyldimethylbenzylammonium chloride for cationic surfactants.

11.4. Unspecific Additive Parameters

The titrimetric methods discussed above for the analytical, in particular quantitative determination of surfactants are group-specific and are associated with the amphiphilic nature of the surfactants. The methods fail as soon as polar, hydrophilic groups are introduced into the hydrophobic residue, for example, by enzymatic attack. However, especially in investigations on the biodegradation of surfactants, not only is the loss of surface-active properties of interest but also their further degradation, i.e., enzymatic oxidation to water, carbon dioxide, sulfate, nitrate, etc. It is thus important to determine the intermediate products, the metabolites. However, due to the large number of possible metabolites, which in many cases occur only in very small amounts, the effort and cost involved in their individual determination is disproportionately large. To obtain some information about the overall biodegradability of surfactants, attempts were already made early on to determine substance-unspecific additive parameters that are generally employable for characterizing the pollution of rivers and waters by organic substances (BOD and COD values) and, more recently, the TOC and DOC values.

BOD Value. In the measurement of the biological oxygen demand (BOD) the biological decomposition (biodegradation) of a surfactant is simulated by adding it to a mineral nutrient salt solution that has been inocculated with a broad-spectrum bacterial culture. The solutions are incubated at 20 °C in closed flasks; the oxygen content in the initially air-saturated solution is determined after 5, 15, and 30 d. The oxygen consumption calculated from these values is expressed as a percentage BOD 5, BOD 15, or BOD 30 value, relative to the amount of oxygen required for total oxidation of the test substance.

COD Value. In the determination of the chemical oxygen demand (COD) the organic water-borne constituents are characterized by chemical oxidation with potassium dichromate in sulfuric acid solution in the presence of silver ions. The COD values depend largely on the chemical structure. For example, the readily biodegradable compound acetic acid is scarcely attacked by chromic acid. However, in the case of more complex compounds such as surfactants, correlations exist between COD and BOD values for groups of similar surfactants. Thus the quickly and easily performed COD determination can be used to give an indication of the BOD value. The COD is expressed as a percentage of the amount of oxygen calculated for total oxidation.

TOC Value. The total organic carbon (TOC) in an aqueous solution is the most suitable quantity for expressing the extent of mineralization of a substance in aqueous, bacterially infected solution. The TOC value is determined by combustion of the organic substances to carbon dioxide in a hot reactor through which a stream of air is passed and into which a measured water sample is injected. The amount carbon dioxide in the off-gas from the reactor is determined quantitatively by IR spectroscopy and is used to calculate the carbon content in the sample. With the development of analytical equipment that determines carbon automatically in the mg/L range, the TOC method has become an important analytical tool. The degree of biodegradation of a substance can be specified simply as a percentage by determining the TOC value before and after the degradation experiment if the investigated substance is the sole source of carbon for the microorganisms. Since inorganic carbon in the form of dissolved carbon dioxide or carbonate may also be present in the investigated solutions, the sample is acidified before combustion and the inorganic carbon is expelled as carbon dioxide. The TOC analysis can however also be carried out in two parallel determinations, one of which, performed at a high temperature, determines the total dissolved carbon, while the other, performed at a low temperature, determines only the inorganically bound carbon by acidification and sparging with air. The TOC value is then the difference between the total carbon and inorganically bound carbon.

DOC Value. If the carbon determination is carried out by the TOC method after filtering the sample, then the DOC value (dissolved organic carbon) is obtained.

12. Utility Evaluation of Surfactants

Besides the purely analytical methods a large number of utility evaluation methods, in some

cases standardized, have been introduced for the characterization and quality control of surfactants. A list of the relevant ISO and DIN regulations is given below:

ISO 304:   Surface Active Agents – Determination of Surface Tension by Drawing Up Liquid Films

ISO 607:   Surface Active Agents and Detergents – Methods of Sample Division

ISO 696:   Surface Active Agents – Measurements of Foaming Power – Modified Ross – Miles Method

ISO 697:   Surface Active Agents – Washing Powders – Determination of Apparent Density – Method by Measuring the Mass of a Given Volume

ISO 1063:   Surface Active Agents – Determination of Stability in Hard Water

ISO 1064:   Surface Active Agents – Determination of Apparent Density of Pastes on Filling

ISO 1065:   Non-Ionic Surface active agents obtained from Ethylene Oxide – Determination of Cloud Temperature (cloud point)

ISO 2131:   Surface Active Agents – Simplified Classification

ISO 2174:   Surface Active Agents – Preparation of Water with Known Calcium Hardness

ISO 2267:   Surface Active Agents – Evaluation of Certain Effects of Laundering – Methods of Preparation and Use of Unsoiled Cotton Control Cloth

ISO 2456:   Surface Active Agents – Water Used as a Solvent for Tests – Specification and Test Methods

ISO 4198:   Surface Active Agents – Detergents for Hand Dishwashing – Guide for Comparative Testing of Performance

ISO 4311:   Anionic and Non-Ionic Surface Active Agents – Determination of the Critical Micellization Concentration – Method by Measuring Surface Tension with a Plate, Stirrup or Ring

ISO 4312:   Surface Active Agents – Evaluation of Certain Effects of Laundering – Methods of Analysis and Test for Unsoiled Cotton Control Cloth

ISO 4316:   Surface Active Agents – Determination of pH of Aqueous Solutions – Potentiometric Method

ISO 4317:   Surface Active Agents – Determination of Water Content – Karl Fischer Method

ISO 4319:   Surface Active Agents – Detergents for Washing Fabrics – Guide for Comparative Testing of Performance

ISO 4320:   Non-Ionic Surface Active Agents – Determination of Cloud Point Index – Volumetric Method

ISO 4324:   Surface Active Agents – Powder and Granules – Measurement of the Angle of Repose

ISO 6387:   Surface Active Agents – Determination of the Power to Disperse Calcium Soap – Acidimetric Method (Modified Schoenfeldt Method)

ISO 6388:   Surface Active Agents – Determination of Flow Properties Using a Rotational Viscometer

ISO 6836:   Surface Active Agents – Mercerizing Agents – Evaluation of the Activity of Wetting Products for Mercerization by Determination of the Shrinkage Rate of Cotton

ISO 6837:   Surface Active Agents – Water Dispersing Power in Dry Cleaning Solvents

ISO 6839:   Anionic Surface Active Agents – Determination of Solubility in Water

ISO 6840:   Cationic Surface Agents (Hydrochlorides and Hydrobromides) – Determination of Critical Micellization Concentration – Method by Measurement of Counter Ion Activity

ISO 6889:   Surface Active Agents – Determination of Interfacial Tension by Drawing Up Liquid Film

ISO 7535:   Surface Active Agents – Detergents for Domestic Machine Dishwashing – Guide for Comparative Testing of Performance

ISO 8022:   Surface Active Agents – Determination of Wetting Power by Immersion

ISO 8212:   Soaps and Detergents – Techniques of Sampling During Manufacture

ISO 9101:   Surface Active Agents – Determination of Interfacial Tension – Drop Volume Method

DIN 59 900: Terms and Definitions

DIN 53 901: Determination of the Wetting Ability of Surfactant Solutions by Measuring the Time required for a Small Piece of Cotton Cloth Added to the Solution to Sink

DIN 53 902: Determinations of the Foaming Power of Surfactant Solutions by the Perforated Disk impact Method or the Ross – Miles Method

DIN 53 903: Determination of the Power to Disperse Calcium Soaps for Pure Calcium Water Hardness

DIN 53 904: Determination of the Ability to Wash Out Lubricants from Textiles

DIN 53 905: Determination of the Hard Water Resistance of Surfactants

DIN 53 908: Determination of the Dispersive Power of Surfactants with Respect to Dyes

DIN 53 910: Preparation of Hard Water having Adjusted Calcium Hardness

DIN 53 911: Sampling of Powders and Preparation of Size-Reduced Average Samples

DIN 53 912: Determination of the Bulk Density of Powders and Granules

DIN 53 913: Determination of the Filling Density of Pastes, Ointments, and Gelatinous Materials

DIN 53 914: Determination of the Surface Tension

DIN 53 916: Determination of the Flowability of Powders and Granules

DIN 53 917: Determination of the Cloud Point of Ethoxylates

DIN 53 918: Determination of the Krafft Point and Solubility of Ionic Surfactants

DIN 53 921: Measurement of the Flow Properties by means of a Rotational Viscometer

DIN 53 988: Examination of the Action of Levelling Agents in Vat Dyes

DIN 53 989: Determination of the Turbidity Titration Number

DIN 53 990: Principles of the Comparative Examination of Utility Properties of Detergents for Washing Textiles

DIN 53 993: Determination of Interfacial Tension by the Stirrup or Ring Method.

Many methods used for testing the detergency and cleansing power of surfactants and surfactant formulations in their solutions have not hitherto been standardized. To evaluate the detergent power in textiles reproducibly soiled test fabrics are washed in the presence of the test substance in washing machines or washing simulators. After the test fabric has been dried and ironed its degree

of whiteness is measured as remission of white light (e.g., in a Zeiss Elrepho apparatus), and compared with the remission values of the unwashed soiled test fabric, and of the unsoiled clean test fabric.

To test the cleaning effect on hard surfaces the latter are dirtied with colored greases and treated with solutions of the test substances. The degree of removal of the colorant from the surface is a measure of the cleaning effect. In the plate-rinsing test greasy plates are washed in succession in the solution of the product to be tested. The detergent power is determined on the basis of the number of plates that can be cleaned until the detergent solution no longer contains any foam and the dirt that has been washed off collects visibly on the surface of the rinsing water.

An important property of surfactants and their formulations, mainly for aesthetic reasons, is their color. Slightly colored or even colorless surfactants are preferred. Among the various methods for determining the color, those predominate in which the yellow and brown shades that mainly occur in surfactants as also in other organic substances are determined. In the iodine color value (DIN 6162, standard method C IV 4a of the Deutsche Gesellschaft für Fettwissenschaft, DGF) the color of a solution of the test substance is compared optically with the color of solutions of iodine of various concentrations in aqueous potassium iodide solution and specified as mg iodine/100 mL. In the Hazen color index (APHA, ASTM D-1209–69; A.O.C.S. Td 1b-64) solutions of platinum and cobalt salts of different concentrations are used as reference solution. In the Klett color index the extinction ($E = \log I_0/I$) of blue light of wavelength 420 –430 nm passing through a solution of the test substance is directly measured photometrically and multiplied by the factor 1000; turbidities are also expressed as color indices in this method.

The Lovibond and Gardner color indices provide a differentiated expression of the color of a solution. In the Lovibond color index (standard method C IV 4b of the DGF) the color of a beam of light passing through the solution is compared in the optical field of a colorimeter with a second beam of light passed through yellow, red, and blue filters of adjustable thickness. The color index is specified by three figures, corresponding to the thicknesses of the three filters. The measurement of the Gardner color index (DIN – ISO 4630; A.O.C.S. Td 1a-64), standard method C IV c of the DGF) is based on the same principle, though the reference colors are already standardized as mixed colors and are specified by means of progressively numbered colored glasses.

The above methods have proved their worth in practice even though they have the disadvantage that they are based on a subjective and comparative perception or, as in the case of the Klett index, are restricted to measurements within a narrow spectral range.

Although an objective determination of the color shade in the CIE color triangle is possible by measuring the overall visible spectrum and conversion to tristimulus values, this method is laborious. A simplified method based on the latter for the colorimetric characterization of transparent liquids is proposed in [162].

13. Uses [1–3], [6]

The largest proportion of surfactants is used in *detergents* and *cleansing agents* for domestic and industrial use (→ Dry Cleaning, → Cleansing Agents, → Laundry Detergents, → Soaps) [4], [163–166]. In universal laundry detergents mainly combinations of alkylbenzenesulfonate, fatty alcohol ethoxylate, and soaps, in addition to other components, are used. In modern washing machines the soap serves primarily not as a surfactant and cleansing agent, but as a foam regulator. Nowadays it is increasingly being replaced by, for example, the more effective silicone oils. Occasionally, tallow fat alkyl sulfate is used to partly or completely replace alkylbenzenesulfonate. Specialty detergents are similar in surfactant composition as regards the components; instead of tallow fat alkyl sulfates, coconut oil alkyl sulfates and coconut oil ether sulfates, which dissolve better in the cold are preferred.

In fabric softeners, cationic surfactants are employed. On account of their good crystallizability sulfosuccinates and olefinsulfonates are employed besides alkylbenzenesulfonate and ethoxylates in foam cleaning agents and dry cleaning agents. Besides dodecylbenzenesulfonates, alkylbenzenes with shorter alkyl chains, $C_{14} - C_{17}$ alkanesulfonates, $C_{12} - C_{14}$ olefinsulfonates, and fatty alcohol ether sulfates are

preferably added to liquid rinsing agents and cleansing agents since they produce highly concentrated, clear solutions. Due to their better dermatological compatibility betaines are added to domestic washing up liquids. Alternatively a proportion of the anionic surfactants is replaced by nonionic surfactants such as fatty alcohol ethoxylates or alkyl polyglucosides.

In the industrial cleansing sector particular importance is placed on the degreasing and emulsifying ability, foam behavior, electrolyte compatibility, and chemical stability of the products. Besides alkylbenzenesulfonates, alkanesulfonates, fatty alcohol ethoxylates, alkylphenol ethoxylates, and fatty amine ethoxylates, phosphate esters and low-foam nonionic surfactants such as propylene oxide/ethylene oxide adducts or terminally blocked ethoxylates are also important here.

Mild surfactants that are gentle to the skin play an important role in bodycare products, and especially in cosmetic cleansing agents (→ Skin Cosmetics, Section 7.1.1.) [167–169]. Such surfactants include ether sulfates and ether carboxylates, sulfosuccinic esters of fatty alcohol polyglycol ethers, protein – fatty acid condensates and the related sarcosinates and taurides, isethionates, as well as ampholytes and betaines, amine oxides, fatty acid polyglycol and sorbitan esters, and alkyl polyglucosides.

A broad field of application of surfactants is the *textile industry*, historically the oldest sector, with its numerous processes such as washing, cleaning, lubricating, sizing, fulling, bleaching, mercerizing, carbonizing, and finishing (→ Textile Auxiliaries) [170], [171]. Almost exclusively nonionic surfactants are used for washing wool. Cotton is washed alkaline, for which purpose nonionic and anionic surfactants are suitable (alkylbenzenesulfonates, alkyl sulfates and sulfosuccinates). In lubricating, a process in which the slip of the fibers is improved, mainly fatty acid and fatty alcohol ethoxylates are used. Sulfonates, sulfates, or ethoxylates are used for desizing, in which the mutual adhesion of the fibers is overcome. Soaps or ethoxylates are used in fulling. Bleaching auxiliaries include alkyl sulfates, alkylbenzenesulfonates, and alkylphenol ethoxylates. Mercerization, the treatment of cotton with a concentrated lye, requires wetting agents such as alkanesulfonates, alkyl sulfates, or alkyl phosphates. Alkanesulfonates or alkyl sulfates are also used in carbonizing, i.e., treatment with sulfuric acid. Softening, which improves the handle of textiles, is largely carried out with cationic surfactants.

Surfactants are also required as emulsifiers, dispersants, levelling agents, and swelling agents in textile dyeing (→ Textile Dyeing; → Disperse Systems and Dispersants, Chap. 1.).

The *leather industry* uses nonionic and cationic surfactants as wetting and cleansing agents. Leather oils, which are used to grease leather, contain alkane sulfonates or alkyl sulfates. Cationic surfactants are used in the aftertreatment of leather to make it supple and water-repellent.

Surfactants have a wide range of application as *emulsifiers* (→ Emulsions) [172–175] and *dispersants* (→ Disperse Systems and Dispersants). The foods industry uses mainly natural substances such as fatty acid salts, glycerides, and fatty acid esters of lactic acid, tartaric acid, and sorbitol (→ Foods, 3. Food Additives, Section 3.5.→ Foods, 3. Food Additives, Section 3.6.).

Mainly fatty alcohol ethoxylates and fatty alcohol sulfates, fatty acid ethoxylates, and fatty acid esters of glycerol and sorbitol are used in *pharmacy*, where attention must be paid to pharmacological and toxicological innocuousness (→ Pharmaceutical Dosage Forms, Chap. 5.) [176].

Emulsifiers are added to *crop-protection* and pest-control agents since the active substances are often only sparingly soluble in water. Emulsifiers widely used here include the sodium, calcium, and diethanolammonium salts of alkylbenzenesulfonic acids, ethoxylates of alkylphenols and condensed phenols, and fatty acid esters of polyglycols, glycerol, and sorbitol. Short-chain alkylbenzene sulfonates and alkylnaphthalene sulfonates are used as wetting agents.

Emulsifiers are required in numerous operations involved in *petroleum production.* The drilling muds used in large amounts for cooling and rinsing in drilling technology contain, for example, alkylbenzenesulfonate or lignin sulfonate to suspend the solids. Lignin sulfonate and naphthalenesulfonate are used as a cement additive in the construction of boreholes. Demulsifiers, e.g., condensation products of propylene oxide and ethylene oxide, ethoxylates of alcohols, fatty acids, alkylphenols, and

condensed phenols, are indispensable in working up the oil, which is initially obtained as a water – oil emul-sion.

Emulsions of water and mineral oil are widely used in *metalworking* and machining. They act as lubricants and coolants in drilling, cutting, rolling, and drawing. Preferred emulsifiers include the heavy metal salts of fatty acids and naphtenic acids, as well as salts of phosphoric esters or carboxymethylated ethoxylates.

Quenching oils for steel hardening contain ethoxylates of fatty alcohols or alkylphenols. Emulsions prepared with ethoxylates or sulfonates are suitable as mold release agents in casting and founding. Alkaline-adjusted mineral oil emulsions, prepared using ethoxylates based on alkylphenols or fatty amines, are used as cleansing agents. Emulsions prepared with phosphates, quaternary ammonium salts or ethoxylated fatty acid ethanolamides are used as anti-corrosion agents.

In the *mineral oil industry* emulsifiers play a significant role as additives for cleaning carburetors and as flow enhancers and corrosion inhibitors.

Emulsifiers used in petroleum exploration, production and processing [177], and for oil slick control are mainly nonionic dispersants or demulsifiers [178]. A potential use of ethoxylates or modified ethoxylates is for transporting heavy oils and bitumen as low-water emulsions [179], or coal as concentrated coal – water slurries[180].

Almost exclusively cationic surfactants, more specifically amine oxides, fatty amine salts and imidazoline salts, are used for bitumen application in *road construction* work.

In the *cement industry* alkylnaphthalenesulfonates are used as wetting agents, phenol – formaldehyde – sodium bisulfite adducts or lignin sulfonates are used as flow enhancers, and ethoxylates are used to form air pores.

The production of numerous plastics by *emulsion polymerization* is only possible by using emulsifiers (soaps, alkylbenzenesulfonates, alkanesulfonates, alkyl sulfates, primary and quaternary ammonium salts, pyridinium salts, fatty alcohol ethoxylates and alkylphenol ethoxylates, glycerides, sorbitol esters, etc.). Other uses of surfactants in the plastics industry include stabilization of polymer dispersions, production of foamed plastics, mold release agents, and production of microcapsules.

In the production of *paints and coatings* a broad range of emulsifiers is required to disperse pigments and emulsify oils and resins, and to act as flow- control and thickening agents. Suitable dispersants include ethoxylates of alkylphenols, fatty alcohols and fatty acids, sulfated oils and naphthenates; ethoxylates and sulfonates are used as emulsifiers.

Adhesives contain mainly nonionic surfactants, which emulsify constituents of the adhesive, and ensure rapid wetting of the surfaces to be bonded.

In *pulp and paper* production, ethoxylates, alkanesulfonates, alkylnaphthalenesulfonates are used as wetting agents to remove resinous constituents. Various ethoxylates and sulfonates as well as cationic surfactants are used in paper sizing and finishing.

Surfactants are used in *electroplating* to clean metal surfaces and also to accelerate hydrogen evolution at the cathode. Fatty alcohol ethoxylates and sulfates are often used, and in some cases also alkylbenzenesulfonates. Fluorosurfactants are particularly advantageous in electroplating due to their chemical stability.

Fire-Extinguishing Foams are produced by adding alkyl or alkyl ether sulfates and fatty acid esters to water. Rapid wetting of the material to be extinguished can be achieved by using fluoro surfactants.

Alkylphenol ethoxylates, sorbitol esters, glycerides, alkylbenzenesulfonates, and sulfosuccinic esters are used in the *photographic industry* to produce light-sensitive emulsions.

An increasingly important use of surfactants is *ore flotation* (→ Flotation) [181–183].

The applications listed above by no means exhaust the possible uses of surfactants. Further applications are described in [183–186]. A few applications of minor industrial importance are: the catalysis of chemical reactions in micelles and vesicles [17], [187]; phase-transfer catalysis [188]; extractions in multiple emulsions on liquid membranes [189]; ion-pair extraction [190] and coacervate extraction [191], which is preferably used in the separation of biological materials from aqueous solutions; and admicellar chromatography [192], in which micelles adsorbed on a solid surface act as carrier phase.

Finally, the detailed study of microemulsions has opened up a broad application potential for the latter [193–195].

14. Economic Aspects

World production of surfactants is ca. 15×10^6 t/a. Of this, soaps account for ca. 8×10^6 t/a; in many countries they are still the most important surfactant for everyday use. After soaps, the alkylbenzenesulfonates are quantitatively the most important class of surfactants, accounting for ca. 2×10^6 t/a.

Surfactants are mainly marketed as constituents of finished products, together with nonsurfactant components. In many cases their specific consumption cannot be determined exactly on account of lack of knowledge of their content in commercial products, even when consumption data exist for products themselves. Also, most market estimates are limited to specific application sectors. There are therefore no accurate data on the total consumption. Estimated production figures in 10^3 t/a for some surfactants in 1990 were as follows:

Linear alkylbenzenesulfonates	1700
Branched alkylbenzenesulfonates	300
Lignin sulfonates	600
Fatty alcohol ether sulfates	400
Fatty alcohol sulfates	300
Petroleum sulfonates	200
Alkanesulfonates	100
Fatty alcohol ethoxylates	700
Alkylphenol ethoxylates	500
Fatty acid esters	300
Fatty acid alkanolamides	100
Quaternary ammonium compounds	300
Other amine derivatives	100

Surfactant consumption (in 10^3 t/a) according to fields of application in the United States, Japan, and Western Europe in 1982 broke down as follows [196]:

Washing and cleaning	1900
Cosmetics and pharmacy	300
Textiles and fibers	200
Leather and furs	50
Colorants, coatings, and plastics	200
Cellulose and paper	100
Mining, flotation, and oil production	300
Metalworking	130
Building and construction	50
Crop protection and pest control	100
Foods	200
Miscellaneous	400

15. Toxicology and Environmental Aspects

15.1. Introduction

Surfactants are used in many areas of human activity, in the home and in commerce, in agriculture, and in industry. Their effects on living organisms are therefore particularly important, even in cases where products, when used according to the instructions, do not come into direct contact with higher life forms. A large number of surfactants come into direct contact with human skin, as constituents of detergents and cleansing agents; their accidental oral ingestion, even if only as residues on washed dishes, therefore cannot be ruled out. Surfactants used as auxiliaries in foods and beverages are therefore subject to legal provisions that require them to be absolutely harmless. The special attention that is nowadays paid to the possible harmful effects of chemicals has meant that some surfactants intended for use in the foods sector are not permitted for use as such in all countries. A characteristic feature or surfactants permitted for use in the foodstuffs sector is that they are overwhelmingly natural products or are obtained from natural products by slight chemical modification. They are mainly derived from glycerides, fatty acids, lactic, tartaric, and citric acids, sugar, and sorbitol.

Irrespective of their intended use, product safety – including environmental protection – is of major importance for all surfactants. The fate and effect of surfactants in rivers and waters are of particular importance in environmental risk assessment, since a large proportion of surfactants is discharged after use into effluent and sewage and ultimately flows into rivers, lakes, and oceans. Here, the degradation of surfactants by microorganisms in natural waters and in sewage plants, which ultimately leads to their complete mineralization is particularly important.

15.2. Toxicology [197–199]

The majority of surfactants now in use – alkylbenzenesulfonates, alkyl ether sulfates, alkyl sulfates, alkanesulfonates, olefinsulfonates, alkyl polyglycol ethers, and nonylphenol polyglycol ethers – are nontoxic or have only a slight acute or chronic toxicity. Also, no toxic effects of the metabolites of these surfactants have been detected in mammals.

The oral LD_{50} values of both anionic and nonionic surfactants is generally in the range from several hundred to several thousand milligrams per kilogram of body weight (comparable to sodium chloride). Betaines, which are used in particular in body cleansing preparations, are nontoxic. The quaternary ammonium compounds, which are known to be bactericidal and fungicidal, exhibit a range of behavior. Whereas dialkyldimethylammonium chlorides used as fabric softeners have LD_{50} values of ca. 5 g/kg body weight and are nontoxic, alkylbenzyldimethylammonium chloride used as a disinfectant has a fairly low LD_{50} value of 0.35 g/kg.

There are few data on the toxicity of surfactants derived from polysiloxanes or fluoroalkanes. Methylpolysiloxanes are physiologically inert, but this is not necessarily the case for phenyl-substituted polysiloxanes.

Nothing is known of the carcinogenic, mutagenic, or teratogenic effects of surfactants.

There is no danger of acute lethal toxicity by resorption of surfactants through the skin or by inhalation. Surfactants can cause skin irritation and skin damage on prolonged action, since they destroy the water-lipid membrane that serves as the external protective layer of the skin, by dissolving individual constituents. The immediate results are swelling, drying, and chapping of the skin; prolonged action of surfactants can lead to eczematous changes in the skin, which recede when the source of irritation is removed.

There are a large number of standardized methods for testing irritation of the skin and mucous membranes. It is important to differentiate between tests under practically relevant conditions at realistic concentrations, and tests used to determine the potential hazard of pure substances, as required, for example, by the German Chemikaliengesetz (Chemicals Act). According to the latter most surfactants should be characterized as "irritant", a few as "moderately toxic", while strongly acidic or basic products, including a number of amine derivatives and ammonium salts, as "corrosive" [200]. Such effects detected at high concentration hardly ever occur if surfactants are used according to the instructions, either because such concentrations are not employed, or because the time the surfactant is in contact with the skin is too short to produce an irritant or indeed a corrosive effect.

Skin irritation generally increases in the sequence nonionic, amphoteric, anionic, cationic surfactants. Aromatic rings in the hydrophobic group increase the irritant action. Good wetting agents have a higher irritant potential than poor wetting agents. With anionic surfactants containing a linear alkyl group such as soaps, alkyl sulfates, and olefinsulfates, maximum skin irritation is found for an alkyl chain length of 12 carbon atoms. The incorporation of oligoglycol residues between hydrophobic and hydrophilic groups, as in fatty alcohol ether sulfates, fatty alcohol sulfosuccinates, or fatty alcohol carboxylates, reduces the irritant action of such anionic surfactants.

Nitrogen-containing surfactants irritate the skin less, and the action of sulfonates or sulfates is reduced by using their ammonium salts (e.g., triethanolammonium salts).

The above comments regarding skin irritation also apply to irritation of the mucous membranes, but the mucous membranes are much more sensitive than the skin.

Betaines and amine oxides are extremely weakly irritating to the skin; they reduce the irritant action of anionic surfactants.

On account of their compatibility with the skin and mucous membranes, betaines, fatty acid amidoalkylaminobetaines, amphoteric N-alkylamino acids, and fatty acid alkylolamidoether sulfates are playing an increasing role as constituents of body cleansing agents. Condensation products of fatty acids and protein degradation products (oligopeptides) have long been known to be particularly gentle to the skin and mucous membranes.

Allergies and sensitizations due to surfactants are uncommon. If they do occur, it should be checked whether they are caused by accompanying substances or impurities in the surfactants.

15.3. Biological Degradation [201–203]

Organic substances can be degraded aerobically and anaerobically by microorganisms in the presence of water. Since surfactants are discharged after use mainly into effluent and sewage and thus eventually into rivers and seas, their aerobic biodegradation is of primary interest, which is already reflected in Europe in a number of legislative measures (→ Laundry Detergents, Section 10.4.). In the determination of the biodegradability a distinction is made between the primary attack on the surfactant molecule and total degradation. Primary attack is the loss of interfacial activity due to a structural change in the surfactant molecule. Total degradation is the complete conversion of the surfactant into inorganic substances (e.g., sodium sulfate, carbon dioxide, water) and the incorporation of its constituents into the cellular material of microorganisms.

Primary attack, which has been shown to lead to total degradation, albeit after a long time, is easy to determine (in contrast to total degradation) by measuring analytically the residual surfactant in a degradation test. Intact anionic surfactants are detected as methylene blue-active substances (MBAS), nonionic surfactants as bismuth-active substance (BiAS), and cationic surfactants as DSBAS (see Section 11.3).

The investigation of the degradation pathways of a surfactant to total degradation is laborious and time- consuming, and up to now has been performed only on a few, industrially particularly important surfactants (e.g., linear alkylbenzene sulfonate; see below). To quickly obtain information on total degradation, additive parameters are nowadays preferably employed (see Section 11.4), which can readily be determined in degradation experiments.

15.3.1. Methods for Determining Biological Degradation

The test specifications recommended by the OECD have been adopted by the EC states as well as by some other countries. These are the static OECD screening test, which simulates the conditions of surface waters, and the continuous OECD confirmatory test in which the processes occurring in a sewage plant are approximated using activated sludge (→ Laundry Detergents,

Section 10.4.2., → Laundry Detergents, Section 10.4.3.) [204].

Whereas surfactant-specific analysis only provides information on primary attack, the introduction of the DOC method (dissolved organic carbon) provides further, but however only summary information, on the degradation of a surfactant. If the surfactant is the sole source of carbon in the test solution, then the determination of the organically bound carbon in the solution at the start and end of the experiment provides a direct measure of the degradation of the surfactant. The DOC method can be extended to the OECD confirmatory test if two units instead of one are operated, surfactant being added to the inflow of one unit but not to the other. A homogeneous composition of the bioceonosis in both batches is ensured by daily exchange of sludge between the parallel units. Entrainment of surfactant, which could influence the DOC values, is taken into account computationally in the evaluation of the results. Reliable balances and thus information on the degree of degradation of the surfactants can be obtained by this method by employing suitable technical and statistical measures [205].

Although it is complicated and costly, this so-called coupled units test has nowadays become a standard method (→ Laundry Detergents, Section 10.4.2.2.). If the overflowing effluent in this continuously operated test is recycled up to fifty times and replenished with fresh surfactant, additional information is obtained on difficultly degradable catabolites or byproducts in the surfactant used (catabolites test) [206].

In addition to these methods a large number of other test methods are used, some of which have been adopted and numbered in the OECD Guidelines as ready, inherent, and simulation tests:

Ready Tests

Die Away Test	301 A
Modified Sturm Test	301 B
Modified MITI (I) Test	301 C
Modified Closed Bottle Test	301 D
Modified OECD Screening Test	301 E

Inherent Tests

Modified SCAS Test (SCAS = Semicontinuous activated sludge)	302 A
Modified Zahn – Wellens Test	302 B
Modified MITI (II) Test	302 C

Simulation Test

Coupled Units Test	303 A
Inherent Biodegradability in Soil	304 A

Table 16. Test methods for determining total degradation (mineralization)

Test method	Characteristics of the test	Analysis	Test duration, d	Degree of degradation to be regarded as degradable
Modified OECD screening test	static test (small amount of organisms)	DOC	28	> 70 %
Closed bottle test	static test (small amount of organisms)	O_2	28	> 60 %
Sturm test	static test (small amount of organisms)	CO_2	28	> 60 %
Zahn – Wellens test	static test (activated sludge)	DOC	28	> 70 %
Coupled units test	continuous test (simulation of a communal clarification plant)	DOC	≥ 30	> 70 %
Catabolites test	continuous test with recycling and replenishment of the purified effuent	DOC	≥ 30	the necessary degree of degradation depends on the carbon content of the test substance
ECETOC test	static test (digested sludge); anaerobic conditions	CH_4 and CO_2	≥ 30	not specified

Whereas most of the aforementioned methods determine the biodegradation via DOC analysis, in the closed bottle test the oxygen consumption is measured, while in the MITI and STURM tests the carbon dioxide evolution is measured. Information on widely used test methods is given in Table 16 [207]. In the ready tests such as the closed bottle or Sturm tests, besides information on the biodegradability of the substance information can also be obtained on the ready biodegradability, which applies if a degree of degradation of at least 70 % is achieved after a degree of degradation of 10 % is exceeded within 10 d (Fig. 22).

All the methods mentioned here refer to the aerobic biodegradation of surfactants. Since the surfactants used nowadays in consumer products undergo rapid aerobic degradation, their anaerobic degradation plays only a minor role in ecological considerations. Accordingly, at present there are still no validated methods for determining anaerobic degradation. Occasionally, the ECETOC test is used.

A further, very informative but complex and expensive method is the use of radioactively labelled (generally ^{14}C) material in a degradation experiment and identification of the radioactive end products.

A specialist report has summarized a large amount of data on biogradation and other ecologically relevant data concerning surfactants [208]; this information is reproduced in abbreviated and supplemented form in Table 17.

15.3.2. Biodegradation Mechanisms

Surfactants whose hydrophobic group are derived from hydrocarbons can be oxidized enzymatically under aerobic conditions and thus biodegraded. Surfactants derived from hydrophobic parent substances such as perfluoroalkanes, poly(propylene glycols), or polydimethylsiloxanes are not biodegradable.

The enzymatic attack leading to biodegradation occurs in most surfactants at the hydrophobic group. For ionic surfactants the nature of the hydrophilic group has only a minor influence on the rate of degradation. High biodegradation rates have been found even for bactericidal quaternary ammonium compounds such as cetyltrimethylammonium bromide, benzyldodecyldimethylammonium chloride, and distearyldi-

Figure 22. Curves illustrating the DOC decrease of two readily biodegradable substances [207]

Table 17. Biodegradability and ecotoxicity of important surfactants [208], supplemented

Surfactant	Confirmatory test [a], %	Coupled units test [b], %	Mod. OECD screening test [b], %	Closed bottle test[c], %	Sturm test [d], %	Fish toxicity LC50, mg/L	Daphnia toxicity EC50, mg/L	Algae toxicity mg/L
Linear C_{10} – C_{13} alkylbenzenesulfonate	93 – 97	92	94	55 – 65	45 – 76	3 – 9	9 – 14	50[e]
C_{14} – C_{17} alkanesulfonate	97 – 98	99	88 – 96	63 – 95	56 – 91	3 – 24	9 – 13	96
C_{12} – C_{18} fatty alcohol sulfate	98 – 99	97	88 – 96	63 – 95	64 – 96	3 – 20	5 – 70	60
Dioctyl sulfosuccinate	96	49	96	50		39	33	
C_{14} – C_{18} α-olefinsulfonate	98	70 – 78	85	85	65 – 80	2 – 20	5 – 50	10 – 100
Soap				85 – 100	80 – 99		strongly dependant on water hardness	
C_{12} – C_{18} fatty alcohol + 10 EO	93 – 98	95 – 96	94	69 – 86		5	4	3
C_{16} – C_{18} fatty alcohol + 5 EO	95	>80			65 – 75	30	2	
C_{16} – C_{18} fatty alcohol + 30 EO	98	93		27	16	>1000		
C_{13} – C_{15} oxo alcohol + 10 EO	95	>80	75		3			
Isononylphenol + 9 EO	87 – 97	77 – 90	8 – 17	5 – 10	40	5 – 11	4 – 50	20 – 50
C_{16} – C_{18} fatty amine + 10 EO	97 – 98	6 – 33						
C_{12} – C_{18} fatty acid polyglycol ester + 5/29 EO	92 – 96	71 – 92	100	60 – 80		35 – >100		
Dimethyldistearylammonium chloride	94	108	0	5		1 – 6	0.1 – 1	
1-Methyl-1-octadecylamidoethyl-2-heptadecylimidazolinium methyl sulfate		97	75 – 100	84		1.5	1	3
Ditallowacyloxyethyl hydroxyethylmethyl ammonium methyl sulfate		>90	93	>73		3.3 [f]	87[f]	3[f]

[a] MBAS, BiAS, or DSB.
[b] DOC.
[c] BOD.
[d] CO_2 evolution.
[e] EC_{10}
[f] EC_0.

methylammonium chloride. With nonionic surfactants of the ethoxylate type the degradation rate is influenced by the length of the poly(ethylene glycol) chain (i.e., by the degree of ethoxylation); with the same hydrophobic residue, the degradation rate decreases with increasing length of the poly(ethylene glycol) chain.

The constitution of the hydrophobic hydrocarbon group of a surfactant has a decisive influence on the degradation rate.

Branchings in an aliphatic group strongly decelerates degradation. Phenylidene groups between the aliphatic and hydrophilic groups can make degradation slower. Linear alkylbenzenesulfonates are degraded more slowly than alkanesulfonates and olefinsulfonates, and the latter more slowly than linear alkyl sulfates.

Natural fatty acids and their salts as well as some of their esters with glycerol, sorbitol or sugars are readily biodegradable, although in the case of the esters a decrease in the degradation rate is already observed, which can be explained by the need for a preceding hydrolysis. The enzymatic oxidative degradation of linear fatty acids takes place mainly by β-oxidation, in which the hydrocarbon chain is shortened each time by two carbon atoms.

Aerobic biodegradation of secondary alkanesulfonates probably begins with oxidative desulfonation; the resulting oxoalkanes are readily degraded.

In the case of internal sulfonates, alkylbenzenesulfonates, and alcohol ethoxylates, microbial degradation can be initiated by ω-oxidation, i.e., by oxidative attack on both terminal methyl groups. After introduction of the terminal carboxylate groups further degradation then proceeds as β-oxidation. In the degradation of alkylbenzenesulfonates sulfophenylalkanecarboxylic acids are formed as intermediates, while in the degradation of fatty alcohol ethoxylates polyglycol ethers of ω-hydroxyalkanecarboxylic acids are formed as intermediates.

The biodegradation of the industrially most important surfactant, alkylbenzenesulfonate (also named dodecylbenzenesulfonate since the mean number of carbon atoms in the alkyl group is 12) has been largely elucidated. The degradative pathway proceeds by ω-oxidation and subsequent β-oxidation, followed by ring opening. The sulfonate group remains bound to the carbon atom after opening of the aromatic ring. The homologous and isomeric species contained in the alkylbenzenesulfonate are attacked at various rates. According to the "distance principle", the degradation rate increases with increasing distance of the terminal methyl group from the coupling site of the sulfophenyl group, or the length of the available unsubstituted alkyl chain. For example, 2-dodecylbenzenesulfonate is degraded more rapidly than 6-dodecylbenzenesulfonate, which in turn is degraded more quickly than 6-undecylbenzenesulfonate.

That ca. 70 % of the benzene nuclei in industrial alkylbenzenesulfonate are already degraded under the conditions of the OECD confirmatory test has been confirmed by examining the degradation of an alkylbenzenesulfonate labeled in the benzene nucleus with ^{14}C [209].

Tetrapropylenebenzenesulfonate is difficultly biodegradable on account of its highly branched alkyl group.

Nonionic surfactants of the ethoxylate type are also preferentially degraded starting from the hydrophobic group by enzymatic attack on a terminal methyl group. The degradation rate decreases sharply with increasing branching of the hydrophobic alkyl group. With simple branching, which occurs for example in the case of isomeric oxoalcohols, the distance principle applies to the degradation of ethoxylates as it does for linear alkylbenzene sulfonates, whereby the surfactant is degraded more quickly the longer a linear alkyl residue starting from a branching site is:
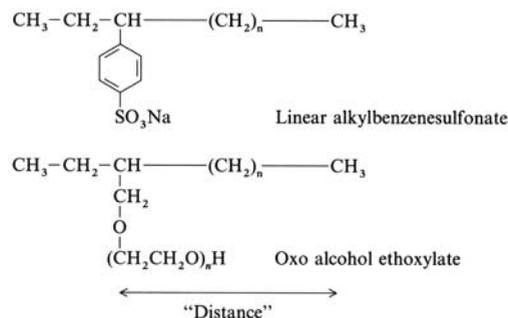
The biodegradation of linear ethoxylates proceeds by two different mechanisms that seems occur simultaneously:

1. The molecule is cleaved at the ether bridge between the alkyl group and the polyethylene glycol ether group, following which both fragments are degraded independently of one another
2. Microbial attack occurs simultaneously at both ends of the molecule, i.e., at the terminal methyl group of the alkyl chain and at the hydroxyl group of the poly(ethylene glycol) unit

The alkyl group of industrial alkylphenol ethoxylates are attacked microbially with difficulty on account of their high degree of branching. In this case the degradation proceeds from the polyglycol chain: The chain is shortened starting from the end of the free hydroxyl group, stepwise in each case by one ethylene glycol unit, glycolic acid presumably being formed as an intermediate:
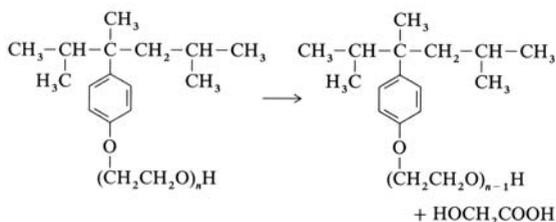
Degradation becomes slower with decreasing length of the polyglycol chain. Since the hydrocarbon skeleton is also degraded with difficulty, the total mineralization of alkylphenol ethoxylates proceeds more slowly than the fast primary degradation.

15.3.3. Toxicity of Surfactants and their Metabolites to Aquatic Organisms [210]

The toxicity of surfactants to aquatic organisms can only be evaluated if the rate and completeness of their biodegradation is taken into account. Thus substances with high toxicity will generally not have any harmful effect on aquatic organisms if they are degraded sufficiently quickly.

The toxicity is tested on green algae (Chlorella), water fleas (Daphnia), fish (trout, orfe, goldfish), and mixed bacterial cultures. These trout and young orfe are particularly sensitive to surfactants; therefore, lethal and nonlethal concen-

trations for these fish are measured to provide preliminary information (screening). In Germany orfe are used for testing; the test method, in which the fish are exposed for 48 h to graduated concentrations of the surfactant in the ambient water, has been standardized. Nonlethal concentrations (48-h LC_0 in mg/L) of some common surfactants for orfe are listed below:

Sodium tetrapropylenebenzenesulfonate	8.0
Sodium dodecylbenzenesulfonate (linear)	2.3
Sodium alkanesulfonate ($C_{14} - C_{17}$)	3.0
Sodium olefinsulfonate ($C_{14} - C_{16}$)	2.0
Sodium tallow fat alcohol sulfate	6.0
Sodium tallow fat alkyl ether sulfate containing 3 EO	10.0
Nonylphenol polyglycol ether with 9 EO	5 – 6
Fatty alcohol polyglycol ether with 5 EO	1 – 2
Fatty alcohol polyglycol ether with 10 EO	2 – 3
Fatty alcohol polyglycol ether with 14 EO	3 – 4

Fish toxicity is strongly dependent on the structure of the surfactant, as exemplified by the structural isomers tetrapropylenebenzenesulfonate (branched side chain) and dodecylbenzenesulfonate (linear side chain). In general, fish toxicity increases with the effective length of the hydrophobic group; in anionic surfactants, branching and an internally located hydrophilic group reduce the toxicity. This is exemplified by the fish toxicity (LC_{50}) of alkylbenzenesulfonate isomers (for *Carassius auratus* [210]):

5-decylbenzenesulfonate	76
2-decylbenzenesulfonate	36
6-undecylbenzenesulfonate	46.5
2-undecylbenzenesulfonate	14.5
6-dodecylbenzenesulfonate	20.5
2-dodecylbenzenesulfonate	4.5
7-tridecylbenzenesulfonate	8.5
2-tridecylbenzenesulfonate	2.0

These toxicity data demonstrate clearly that the toxicity of surfactants cannot be considered separately from their biodegradation in natural waters, since the toxic isomers are degraded most rapidly, (distance principle) and accordingly reach the waters in far lower concentration, if at all, than the less toxic internal isomers.

Except for one striking exception, up to now nothing is known about the aquatic toxicity of catabolites produced in the biodegradation of surfactants. The exception are the isononylphe-

nol ethoxylates, which, because of their marked degree of branching are degraded not from the alkyl residue but from the terminal hydroxyl group of the poly(ethylene glycol) chain, whereby the degradation rate decreases with decreasing number of ethylene oxide units in the poly(ethylene glycol) chain. The diethylene glycol and monoethylene glycol ethers that are formed as intermediates and degrade only slowly and exhibit, like the parent substance isononyl(or isooctyl)phenol, a pronounced toxicity to aquatic organisms, which is much higher than that of alkylphenol ethoxylate surfactants with degrees of ethoxylation of 5 and above [104].

Anionic and nonionic surfactants are generally nontoxic to bacteria. However, reference is made here to a remarkable connection between chemical structure and bacterial toxicity in the case of nonionic surfactants, which in particular cases may result in an inhibition of the biodegradation of some nonionic surfactants. The toxicity of ethoxylates increases sharply with decreasing length of the poly(ethylene glycol) chain (see Table 17). Some toxicity threshold values (TLV in mg/L) for *Pseudomonas* are given below:

Coconut oil fatty alcohol polyglycol ether with 10 EO	1000
Coconut oil fatty alcohol polyglycol ether with 2 EO	10
Stearyl alcohol polyglycol ether with 25 EO	10 000
Stearyl alcohol polyglycol ether with 10 EO	100
Stearyl alcohol polyglycol ether with 2 EO	10
Nonylphenol polyglycol ether with 10 EO	1 000
Nonylphenol polyglycol ether with 6 EO	500
Nonylphenol polyglycol ether with 4 EO	50

A number of quaternary ammonium compounds and betaines have a substantial bactericidal activity. However, if sufficiently diluted these compounds, too, are biodegraded if the chemical structure of the hydrophobic group allows enzymatic attack to occur.

15.4. Preservation of Surfactants
[211], [212]

The biodegradation of surfactants occurs not only at high dilution in waters and rivers, but in the presence of water can already start in the production process, in storage and transportation vessels, and in formulations. Bacteria cannot thrive on anhydrous surfactants or in highly concentrated solutions and pastes; however,

bacterial infection must already be expected in 20 to 30 % solutions of anionic or nonionic surfactants. Also, more highly concentrated solutions or pastes that tend to coacervate with the formation of low concentration phases can act as nutrient media for bacteria and exhibit signs of putrefaction. Bacterial infection must also be expected if highly concentrated surfactant formulations are handled incorrectly; small residues of surfactants in open vessels can be diluted by absorption of atmospheric moisture, and dilute surfactant solutions can accumulate on the floor or in dead spaces of vessels that have not been thoroughly cleaned with water. Cationic surfactants and amphoteric surfactants have a bactericidal action at and below the isoelectric point; except in highly diluted solutions (ppm range), a biodegradation of these surfactants can be ruled out.

Sterile conditions must be maintained to prevent premature biodegradation of surfactants during production. A sterile environment is generally ensured by mantaing high concentrations, high temperatures, and by using chemical bleaches. Transportation vessels can be filled in the hot state and thus under sterile conditions; the vessels must then be sealed in an air-tight and germ-proof manner. To protect surfactants against putrefaction during processing and in the dilute aqueous state (e.g., washing up liquids or shampoos), preservatives are added. Formaldehyde (0.1 – 0.3 %) is an excellent preservative, but has been discredited in some countries on account of its alleged carcinogenicity. Formaldehyde-releasing substances can also be used, for example, 2-Nitro-2-bromopropane-1,3-diol. 2-Methyl-3-isothiazolone, 5- chloro-2-methyl-3-isothiazolone, and 1,3-dicyano-1,2-dibromobutane are used in ppm amounts. 2-Phenoxyethanol, methyl and ethyl *p*-hydroxybenzoates and sorbic acid are effective at higher concentrations (ca. 0.5 %).

References

General References
1 K. Lindner: *Tenside-Textilhilfsmittel-Waschrohstoffe*, Wissenschaftl. Verlagsges., vols. 1 and 2, Stuttgart 1964; vol. 3, 1971.
2 G. Gawalek: *Tenside*, Akademie-Verlag, Berlin 1975.
3 H. Stache (ed.): *Tensid-Taschenbuch*, 2nd ed., Hanser Verlag, München 1981.

4 J. Falbe (ed.): *Surfactants in Consumer Products, Theory, Technology and Application*, Springer Verlag, Heidelberg 1987.

5 M. J. Rosen: *Surfactants and Interfacial Phenomena*, 2nd ed., J. Wiley & Sons, New York 1989.

6 K. Kosswig, H. Stache (eds.): *Die Tenside, Physik, Chemie, Anwendungstechnik*, Hanser Verlag, München 1993.

7 CESIO, Proceedings, World Surfactant Congress, Munich 1984, Paris 1988, London 1992.

8 *Mc Cutcheons Detergent and Emulsifiers*, 1992, International, published annually, with index of producers and trade names.

Specific References

9 R. D. Vold, M. J. Vold: *Colloid and Interface Chemistry*, Addison-Wesley Publ. Co., London 1983.

10 P. C. Hiemenz: *Principles of Colloid and Surface Chemistry*, 2nd ed., Marcel Dekker, New York 1987.

11 S. Ross, I. D. Morrison: *Colloidal Systems and Interfaces*, J. Wiley & Sons, New York 1988.

12 J. L. Cayias, R. S. Schechter, W. H. Wade, *ACS Symp. Ser.* **8** (1975) 234.

13 J. K. Borchardt, C. W. Yates, *JAOCS J. Am. Oil Chem. Soc.* **70** (1993) 47.

14 J. A. Mann, E. Matijevic (eds.): *Dynamic Surface Tension and Capillary Waves, Surface and Colloid Science*, vol. 13, Plenum Press, New York 1984, pp. 202 ff.

15 R. J. Hunter: *Zeta Potential in Colloid Science*, Academic Press, London 1981.

16 C. Tanford: *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed., J. Wiley & Sons, New York 1980.

17 J. H. Fendler: *Membrane Mimetic Chemistry, Characterizations and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host-Guest Systems and Polyions*, J. Wiley & Sons, New York 1982.

18 A. L. Lehninger: *Principles of Biochemistry*, Worth Publishers, New York 1982.

19 N. Kosaric, W. L. Cairns, N. C. C. Gray (eds.): *Biosurfactants and Biotechnology*, Marcel Dekker, New York 1987.

20 I. Piirma: *Polymeric Surfactants*, Marcel Dekker, New York 1992.

21 D. Atwood, A. T. Florence: *Surfactant Systems, Their Chemistry, Pharmacy and Biology*, Chapman and Hall, London 1983/1985.

22 S. E. Friberg, B. Lindmann (eds.): *Organized Solutions, Surfactants in Science and Technology*, Marcel Dekker, New York 1992.

23 J. H. Clint: *Surfactant Aggregation*, Blackie & Sons Ltd., Glasgow 1992.

24 H. Hoffmann, W. Ulbricht *Seifen Öle Fette Wachse* **111** (1985) 200 – 202, 467 – 471, 581 – 585; [6], pp. 1 ff.

25 R. Heusch, *Tenside Surf. Deterg.* **28** (1991) 1; *Naturwissenschaften* **79** (1992) 450.

26 J.-H. Fuhrhop, J. Mathieu, *Angew. Chem.* **96** (1984) 124; J.-H. Fuhrhop, *Nachr. Chem. Techn. Lab.* **28** (1980) 124.

27 D. Arndt, I. Fischer: *Liposomen, Darstellung-Eigenschaften-Anwendung*, Akademie Verlag, Berlin 1986.

28 H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **100** (1988) 117.

29 J. H. Clint in [23] , pp. 59 – 81.

30 H. Hoffmann *et al.*, *Tenside Deterg.* **22** (1985) 290.

31 M. Kahlweit, R. Strey, *Angew. Chem.* **97** (1985) 655; *Tenside Surf. Deterg.* **30** (1993) 83.

32 S. E. Friberg, P. Bothorel: *Microemulsions: Structure and Dynamics*, CRC Press, Boca Raton, 1987.

33 J. H. Clint in [23] , pp. 222 – 249.

34 M. J. Rosen, *JAOCS J. Am. Oil Chem. Soc.* **51** (1974) 461.

35 F. Püschel, *Z. Chem.* **3** (1963) 338.

36 C. A. Schirber, *INFORM* **2** (1991) 1062.

37 K. Schulze, *Seifen Öle Fette Wachse* **101** (1975) 37.

38 N. A. I. van Paassen, *Seifen Öle Fette Wachse* **114** (1988) 159.

39 W. Friedrich, H. Riemer, *Chem. Ind. III* **40** (1988) no. 4, 49.

40 O. J. Muscio *et al.*, *JAOCS J. Am. Oil Chem. Soc.* **59** (1982) 217.

41 D. B. Braun, *Cosmet. Toiletries* **104** (1989) Sept., 87.

42 K. Lindner in [1], vol. 1, pp. 768 ff.

43 F. Asinger: *Die petrolchemische Industrie*, vol. **2**, Akademie Verlag, Berlin 1975, pp. 1249 ff.

44 B. Fell, *Tenside Deterg.* **12** (1975) 3.

45 S. Warwell, *Tenside Deterg.* **19** (1982) 321.

46 B. V. Vora et al. in [7], vol. 1 (1988) pp. 177 – 189.

47 B. V. Vora *et al.*, *Tenside Surf. Deterg.* **28** (1991) 287.

48 *Eur. Chem. News* **54** (1990) no. 1420, 20.

49 F. Asinger *et al.*, *Erdöl Kohle Erdgas Petrochem.* **20** (1967) 786, 852.

50 L. Cavalli et al. in [7], vol. 1 (1992) pp. 105 – 114.

51 *Kirk-Othmer*, **22**, 1 – 45.

52 W. H. de Groot: *Sulfonation Technology in Detergent Industry*, Kluwer Academic Publ., Dordrecht 1991.

53 F. Asinger: *Chemie und Technologie der Paraffinkohlenwasserstoffe*, Akademie Verlag, Berlin 1956, pp. 395 ff., 534 ff.

54 H. Ramloch, G. Täuber, *Chem. Unserer Zeit* **13** (1979) 157.

55 J. M. Quack, M. Trautmann, *Tenside Deterg.* **22** (1985) 281.

56 H. G. Hauthal: *Alkansulfonate*, Deutscher Verlag für Grundstoffindustrie, Leipzig 1985.

57 R. Herke, K. Rasheed, *JAOCS J. Am. Oil Chem. Soc.* **69** (1992) 47.

58 A. Boy, R. Brard, H. Passedroit, *Chem. Eng. (N.Y.)* **82** (1975) , no. 22, 84.

59 F. Püschel, *Tenside* **4** (1967) 286, 320.

60 H. Baumann, W. Stein, M. Voss, *Fette Seifen Anstrichm.* **72** (1970) 247.

61 A. Mori, M. Nagayama, *Tenside Deterg.* **10** (1973) 64.

62 A. Mori, O. Okumura in [7], vol. 2 (1984) pp. 93 – 104.

63 I. Yamane in [7], vol. 1 (1992) pp. 15 – 38.

64 H. Yoshimura, Y. Endo, S. Hashimoto, *JAOCS J. Am. Oil Chem. Soc.* **68** (1991) 623.

65 J. Stapersma, H. H. Deuling, R. van Ginkel, *JAOCS J. Am. Oil Chem. Soc.* **69** (1992) 39.

66 W. Stein, H. Baumann, *JAOCS, J. Am. Oil Chem. Soc.* **52** (1975) 323.

67 H. Andree, G. Jakobi, M. Schwuger in [7], vol. 4 (1984) pp. 5 – 23.

68 F. Schambil, M. Schwuger *Tenside Surf. Deterg.* **27** (1990) 380; [7], vol. 2 (1988) pp. 505 –524

69 K. Umehara et al. in [7], vol. 3 (1992) pp. 234 – 242

70 T. Satsuki, K. Umehara, Y. Yoneyama, *JAOCS J. Am. Oil Chem. Soc.* **69** (1992) 672.

71 K. Schmid et al. in [7], vol. 2 (1984) pp. 105 – 115.

72 W. M. Linfield in W. M. Linfield (ed.): *Anionic Surfactants,* part II, Marcel Dekker, New York 1976, pp.405 – 443.

73 J. A. Milne in D. R. Karsa (ed.): *Industrial Applications of Surfactants II*, The Royal Society of Chemistry, Cambridge 1990, pp. 76 – 100.

74 T. Schoenberg, *Cosmet. Toiletries* **104** (1989) Nov., 105.

75 B. A. Dombrow in W. M. Linfield (ed.): *Anionic Surfactants*, "part I", Marcel Dekker, New York 1976, pp. 233 – 251.

76 J. K. Weil, A. J. Stirton in W. M. Linfield (ed.): *Anionic Surfactants*, "part I", Marcel Dekker, New York 1976, pp. 219 – 232.

77 S. Shore, D. R. Berger in W. M. Linfield: *Anionic Surfactants*, "part I", Marcel Dekker, New York 1976, pp. 135 – 217.

78 J. Steber, P. Gode, W. Guhl, *Fat. Sci. Technol.* **90** (1988) 32; *Soap Cosmet. Chem. Spec.* **64** (1988) Nov., 44.

79 H. Kölbel, P. Kurzendörfer, *Fortschr. Chem. Forsch.* **12** (1969) 252.

80 W. E. Adam, K. Neumann, *Fette Seifen Anstrichm.* **80** (1978) 392.

81 G. Czichocki, A. Greiner, B. Koch, *Tenside Deterg.* **21** (1984) 62.

82 M. F. Cox, *JAOCS J. Am. Oil Chem. Soc.* **66** (1989) 1637.

83 H. Hensen, H.-C. Raths, W. Seipel, *Seifen Öle Fette Wachse* **117** (1991) 592.

84 G. F. Moretti, I. Adami in [7], vol. 1 (1988) pp. 236 – 261.

85 K. L. Matheson, P. A. Schwab in [7], vol. 2 (1992) pp. 211 – 220.

86 S. G. Imokawa *et al.*, *J. Am. Oil Chem. Soc.* **55** (1978) 839.

87 H. Nielen, G. Sorbe, *Tenside Deterg.* **16** (1979) 199.

88 S. L. Paul in D. R. Karsa (ed.): *Industrial Application of Surfactants II*, The Royal Society of Chemistry, Cambridge 1990, pp. 114 – 131.

89 M. Hellsten, *Tenside Deterg.* **23** (1986) 337.

90 M. J. Schick (ed.): *Nonionic Surfactants – Physical Properties*, Marcel Dekker, New York 1987.

91 N. Schönfeldt: *Grenzflächenaktive äthylenoxid-Addukte*, Wissenschaftl. Verlagsges., Stuttgart 1976.

92 K. Shinoda, S. Friberg: *Emulsions and Solubilisation*, J. Wiley & Sons, New York 1986.

93 P. Becher (ed.): "Applications", *Encyclopedia of Emulsion Technology*, vol. **2**, Marcel Dekker, New York 1985.

94 Vista, EP 289 159, 1987 (B. E. Leach *et al.*); Shell International, EP 344 835, 1988 (C. L. Edwards); Union Carbide, EP 361 616, 1988 (S. W. King).

95 H. C. Raths et al. in [7], vol. 2 (1992) pp. 291 –300.

96 E. Santacesaria et al. in [7], vol. 2 (1992) pp. 281 –290.

97 A. Behler, U. Ploog, *Fat. Sci. Technol.* **92** (1990) 109.

98 R. R. Geissler, A. E. Johnson, *JAOCS J. Am. Oil Chem. Soc.* **67** (1990) 541.

99 R. R. Geissler, A. E. Johnson, L. D. Talley, *JAOCS J. Am. Oil Chem. Soc.* **68** (1991) 544.

100 M. F. Cox, *JAOCS J. Am. Oil Chem. Soc.* **67** (1990) 599.

101 D. L. Smith, *JAOCS J. Am. Oil Chem. Soc.* **68** (1991) 629.

102 G. Crass, *Seifen Öle Fette Wachse* **118** (1992) 921.

103 Y. Saito, T. Sato, I. Anazawa, *JAOCS J. Am. Oil Chem. Soc.* **67** (1990) 145.

104 C. G. Naylor *et al.*, *JAOCS J. Am. Oil Chem. Soc.* **69** (1992) 695.

105 W. Umbach, W. Stein, *JAOCS J. Am. Oil Chem. Soc.* **48** (1971) 394.

106 P. Straneo in [7], vol. 1 (1988) pp. 59 – 77.

107 P. Fanelli, S. Ditali, S. Senni in [7], vol. 1 (1992) pp. 86 – 96.

108 G. M. Leuteritz, *Fat. Sci. Technol.* **93** (1991) 383.

109 R. Piorr *et al.*, *Fat. Sci. Technol.* **89** (1987) 106.

110 K. H. Schmid et al. in [7], vol. 3 (1988) pp. 633 –645.

111 K. Hoffmann, *Seifen Öle Fette Wachse* **104** (1978) 3.

112 A. Weiss, *Fat. Sci. Technol.* **92** (1990) 392.

113 T. N. Kumar *et al.*, *JAOCS J. Am. Oil Chem. Soc.* **66** (1989) 153.

114 F. R. Benson in M. J. Schick (ed.): *Nonionic Surfactants*, Marcel Dekker, New York 1967, pp. 262 ff.

115 H. Bertsch, F. Püschel, E. Ulsperger, *Tenside* **2** (1965) 397.

116 F. R. Benson in M. J. Schick (ed.): *Nonionic Surfactants*, Marcel Dekker, New York 1967, pp. 266 ff.

117 K. Hill, W. von Rybinski, G. Stoll (eds.): *Alkyl Polyglycosides*, VCH Verlagsgesellschaft, Weinheim, Germany 1997.

118 S. Matsumura *et al.*, *JAOCS J. Am. Oil Chem. Soc.* **67** (1990) 996.

119 D. Balzer, *Tenside Surf. Deterg.* **28** (1991) 419.

120 D. Balzer, N. Ripke, *Seifen Öle Fette Wachse* **118** (1992) 894.

121 H. Rörig, R. Stephan in D. R. Karsa (ed.): *Industrial Applications of Surfactants II*, The Royal Society of Chemistry, Cambridge 1990, pp. 211 – 234.

122 K. R. Smith *et al.*, *JAOCS J. Am. Oil Chem. Soc.* **68** (1991) 619.

123 E. Jungermann (ed.): *Cationic Surfactants*, Marcel Dekker, New York 1970. J. M. Richmond (ed.): *Cationic Surfactants – Organic Chemistry*, Marcel Dekker, New York 1990. D. N. Rubingh, P. M. Holland (eds.): *Cationic Surfactants – Physical Chemistry*, Marcel Dekker, New York 1991.

124 G. Täuber, A. May, *Tenside Deterg.* **19** (1982) 151.

125 S. Billenstein, G. Blaschke, *JAOCS J. Am. Oil Chem. Soc.* **61** (1984) 353.

126 E. V. Dehmlow, S. S. Dehmlow: *Phase Transfer Catalysis*, Verlag Chemie, Weinheim, Germany 1980.

127 Henkel, GE 2 853 241, 1978 (W. Giede, H. Rützen).

128 D. J. Versteeg *et al.*, *Chemosphere* **24** (1992) 641.

129 L. Godefroy in [7], vol. 3 (1988) pp. 415 – 429.

130 R. Puchta, P. Krings, P. Sandkühler *Tenside Surf. Deterg.* **30** (1993) 186; [7], vol. 3 (1992) pp. 122 – 130.

131 J. Waters *et al.*, *Tenside Surf. Deterg.* **28** (1991) 377.

132 M. M. Watts, *JAOCS J. Am. Oil Chem. Soc.* **67** (1990) 993.

133 H. Hitz *et al.*, *Seifen Öle Fette Wachse* **109** (1983) 20, 43.

134 B. R. Bluestein, C. L. Hilton (eds.): *Amphoteric Surfactants*, Marcel Dekker, New York 1982.

135 U. Ploog, *Seifen Öle Fette Wachse* **108** (1982) 373.

136 R. E. Bilbo, R. A. Swenson, *Soap Cosmet. Chem. Spec.* **66** (1990) April, 46.

137 R. Ohme, D. Ballschuh, H. Seibt, *Tenside Surf. Deterg.* **28** (1991) 180, 235, 337.

138 Li Zongshi, Zhang Zhúangyú, *Tenside Surf. Deterg.* **31** (1994) 128.

139 H. Pardun, *Fat. Sci. Technol.* **91** (1989) 45.

140 D. E. Billek, *Seifen Öle Fette Wachse* **117** (1991) 617.

141 I. R. Schmolka, *JAOCS J. Am. Oil Chem. Soc.* **54** (1977) 110.

142 M. A. Plant in R. D. Karsa (ed.): *Industrial Applications of Surfactants*, The Royal Society of Chemistry, London 1986, pp. 318 – 332.

143 G. L. F. Schmidt in D. R. Karsa (ed.): *Applications of Surfactants*, The Royal Society of Chemistry, London 1986, pp. 24 – 32.

144 B. Grüning, G. Koerner, *Tenside Surf. Deterg.* **26** (1989) 312. I. Yilgör, E. Yilgör, B. Grüning, *Tenside Surf. Deterg.* **30** (1993) 158.

145 D. Schaefer, *Tenside Surf. Deterg.* **27** (1990) 154.

146 G. Schmidt, *Tenside Surf. Deterg.* **27** (1990) 324.

147 H. F. Fink, *Tenside Surf. Deterg.* **27** (1990) 306.

148 M. Gradzielski *et al.*, *Tenside Surf. Deterg.* **27** (1990) 366.

149 E. Kissa: *Fluorinated Surfactants, Synthesis, Properties, Applications*, Marcel Dekker, New York 1994.

150 H. C. Fielding in R. E. Banks (ed.): *Organofluorine Chemicals and their Industrial Applications*, Ellis Horwood Ltd., Chichester 1979, pp. 214 – 234.

151 J. N. Meussdoerffer, H. Niederprüm, *Chem. Ztg.* **104** (1980) 45.

152 H. König: *Neuere Methoden zur Analyse von Tensiden*, Springer Verlag, Berlin 1971.

153 E. Jungermann (ed.): *Cationic Surfactants*, Marcel Dekker, New York 1970.

154 J. Cross (ed.): *Anionic Surfactants, Chemical Analysis*, Marcel Dekker, New York 1977.

155 J. Cross (ed.): *Nonionic Surfactants, Chemical Analysis*, Marcel Dekker, New York 1987.

156 T. M. Schmitt: *Analysis of Surfactants*, Marcel Dekker, New York 1992.

157 G. Krusche in [6], pp. 251 – 279.

158 R. Wickbold, *Tenside Deterg.* **13** (1976) 177.

159 H. Jork et al.: *Dünnschichtchromatographie,* vol. 1 a, VCH, Weinheim 1989.

160 H. J. Kalinoski, A. Jensen, *JAOCS J. Am. Oil Chem. Soc.* **66** (1989) 1171.

161 W. Selig, *J. Chem. Educ.* **62** (1984) 80.

162 F. J. Gohlke, *Tenside Deterg.* **23** (1986) 213.

163 W. G. Cutler, R. C. Davis (eds.): *Detergency, Theory and Test Methods*, parts I (1972), II (1975), and III (1981), Marcel Dekker, New York.

164 W. G. Cutler, E. Kissa: *Detergency*, Marcel Dekker, New York 1987.

165 I. Geke et al. in [6], pp. 281 – 337.

166 G. Jakobi, A. Löhr: *Detergents and Textile Washing, Principles and Practice*, VCH Verlagsgesellschaft, Weinheim, Germany 1987.

167 G. A. Nowak: *Die kosmetischen Präparate,* vol. 2, Verlag für chem. Industrie H. Ziolkowsky AG, Augsburg 1984.

168 M. M. Rieger (ed.): *Surfactants in Cosmetics*, Marcel Dekker, New York 1985.

169 A. Reng in [6], pp. 339 – 356.

170 A. Chwala, V. Anger, C. Chwala: *Handbuch der Textilhilfsmittel*, Verlag Chemie, Weinheim, Germany 1977.

171 A. Datyner: *Surfactants in Textile Processing*, Marcel Dekker, New York 1983.

172 K. J. Lissant: *Emulsions and Emulsion Technology*, parts I and II (1974), part III (1984), Marcel Dekker, New York.

173 P. Becher (ed.): *Encyclopedia of Emulsion Technology*, vol. 1, "Basic Theory," 1983; vol. 2, "Applications," 1985; vol. 3, "Basic Theory/Measurements/Applications," 1988, Marcel Dekker, New York.

174 K. J. Lissant: *Demulsification*, Marcel Dekker, New York – Basel 1983.

175 R. Heusch in K. Kosswig, H. Stache (eds.): *Die Tenside, Physik, Chemie, Anwendungstechnik*, Hanser Verlag, München 1993, pp. 203 – 249; W. Adam, R. Heusch in K. Kosswig, H. Stache (eds.): *Die Tenside, Physik, Chemie, Anwendungstechnik*, Hanser Verlag, München 1993, pp. 357 – 408.

176 P. N. P. Chow (ed.): *Adjuvants and Agrochemicals*, CRC Press, Boca Raton, Florida 1989.

177 P. H. Ogden (ed.): *Chemicals in the Oil Industry, Developments and Applications*, The Royal Society of Chemistry, Cambridge 1991.

178 R. Leo, R. H. Lilie: *Ölwehrhandbuch, Bekämpfung von Ölunfällen im Inland und auf See*, K. O. Storck Verlag, Hamburg 1987.

179 Petroleos de Venezuela Europe S. A.: *Imulsion, the Technology for Handling Extra Heavy Crudes and Bitumens; Orimulsion, Characteristics and Combustibility*, The Orinoco Project, London 1987.

180 H. Riemer in [7], vol. 4 (1988) p. 15.

181 J. Leja: *Surface Chemistry of Froth Flotation*, Plenum Press, New York 1982.

182 A. N. Clarke, D. J. Wilson: *Foam Flotation, Theory and Application*, Marcel Dekker, New York 1983.

183 P. Somasundaran, B. M. Moudgil (eds.): *Reagents in Mineral Technology*, Marcel Dekker, New York 1988.

184 M. J. Rosen (ed.): *Surfactants in Emerging Technologies*, Marcel Dekker, New York 1987.

185 D. T. Wasan, M. E. Ginn, D. O. Shah (eds.): *Surfactants in Chemical/Process Engineering*, Marcel Dekker, New York 1988.

186 J. F. Scamehorn, J. H. Harwell (eds.): *Surfactant Based Separation Processes*, Marcel Dekker, New York 1989.

187 M. Grätzel, K. Kalyanasundaram (eds.): *Kinetics and Catalysis in Microheterogeneous Systems*, Marcel Dekker, New York 1991.

188 E. V. Dehmlow, S. S. Dehmlow: *Phase Transfer Catalysis*, 2nd ed., Verlag Chemie, Weinheim, Germany 1983.

189 R. D. Noble, J. D. Way: *Liquid Membranes, Theory and Application*, American Chemical Society, Washington, D.C., 1987.

190 M. Cox: *Chem. Ind. (London)* 1981, 355.

191 N. D. Gullickson, J. F. Scamehorn, J. H. Harwell in [186], pp. 139 – 152.

192 J. H. Harwell, E. A. O'Rear in [186], pp. 155 – 171.

193 D. O. Shah (ed.): "Macro- and Microemulsions, Theory and Applications," *ACS Symp. Ser.* **272** (1985).

194 G. Gillberg in [172], part III, pp. 1 – 43.

195 R. Leung, M. J. Hou, D. O. Shah in [185], pp. 315 –367.

196 B. W. Werdelmann in [7] vol. 1 (1984) pp. 3 – 21.

197 F. Bartnik, K. Künstler in [4], pp. 475 ff.

198 C. Gloxhuber, K. Künstler: *Anionic Surfactants, Biochemistry, Toxicology, Dermatology*, Marcel Dekker, New York 1992.

199 K. Künstler in [6], pp. 483 – 500.

200 Comité Européen des Agents de Surface et leurs Intermédiaires Organiques, CESIO: *Classification and Labelling of Surfactants*, Bruxelles 1990.

201 R. D. Swisher: *Surfactant Biodegradation*, 2nd ed., Marcel Dekker, New York 1987.

202 N. Nyholm, *Environ. Toxicol. Chem.* **10** (1991) 1237.

203 P. Schöberl in [6], pp. 409 – 464.

204 P. Schöberl, *Tenside Surf. Deterg.* **28** (1991) 1.

205 W. K. Fischer, P. Gerike, W. Holtmann, *Water Res.* **9** (1975) 1131.

206 P. Gerike, W. Holtmann, W. Jasiak, *Chemosphere* **13** (1984) 121; *Tenside Deterg.* **22** (1985) 305.

207 P. Schöberl, Jahrestagung SEPAWA 1991, pp. 33 – 39.

208 K. J. Bock, L. Huber, P. Schöberl, *Tenside Surf. Deterg.* **25** (1988) 86.

209 J. Steber, *Tenside Deterg.* **16** (1979) 140.

210 P. Schöberl, N. Scholz in [6], pp. 465 – 482.

211 H.-G. Schmidt, *Parfüm. Kosmet.* **68** (1987) 5.

212 S. B. Singh-Verman, *Parfüm. Kosmet.* **68** (1987) 752.

Further Reading

R. J. Farn: *Chemistry and Technology of Surfactants*, Wiley, Hoboken 2006

J. W. Goodwin: *Colloids and Interfaces with Surfactants and Polymers*, 2nd ed., Wiley, Chichester 2009.

M. Kjellin, I. Johansson: *Surfactants from Renewable Resources*, Wiley, Chichester 2010.

D. Myers: *Surfactant Science and Technology*, Wiley, Hoboken 2005

V. M. Starov: *Nanoscience*, CRC; Taylor & Francis, London 2009.

T. F. Tadros: *Applied Surfactants*, Wiley-VCH, Weinheim 2008.

T. F. Tadros: *Topics in Colloid and Interface Science*, vol. 1, Wiley-VCH, Weinheim 2008.

T. Tadros: *Surfactants, Kirk Othmer Encyclopedia of Chemical Technology*, 5th edition, John Wiley & Sons, Hoboken, NJ, online DOI: 10.1002/0471238961.1921180612251414.a01.pub2