

# 1

## Industrial Surfactant Syntheses

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### I. INTRODUCTION

For over 2000 years, humankind has used surfactants or surface-active ingredients in various aspects of daily life, for washing, laundry, cosmetics, and housecleaning. In the United States alone, over 10 billion pounds of detergents are used annually. Anionic surfactants represent 70–75% of the detergent market. Natural soaps are the oldest anionic surfactants and are used mainly in personal care and in the detergent industries. However, the development of more economical processes for the manufacture of surfactants has contributed to an increased consumption of synthetic detergents. Nonsoaps or synthetic detergents account for 84% of the total detergent market. In 1996, over 5 billion pounds of nonsoap surfactants were produced. In the Asia-Pacific region, the total surfactant consumption grows at an annual rate of 3.9% with a projection of 5.8 million tons in 2010. From a global perspective, the consumption and proportion of surfactants exhibit a different pattern for the North American and Western European regions compared with the Asia-Pacific region or Japan in particular. However, the major surfactants common (with respect to detergent) to all regions are linear alkylbenzene sulfonates (LASs), alcohol

ether sulfates (AESs), aliphatic alcohols (AEs), alcohol sulfates (ASs), and soap.

In the past decades, new surfactants have proliferated mainly as nonionic or nonsoap surfactants offering unique properties and features to both industrial and household markets. Nonsoap surfactants are widely used in diverse applications such as detergents, paints, and dyestuffs; as specialty surfactants in home and personal care; and in the cosmetics and pharmaceutical industries. Since the 1960s, biodegradability and a growing environmental awareness have been the driving forces for the introduction of new surfactants. These forces continue to grow and influence the surfactant market and production. A new class of surfactants, carbohydrate-based surfactants, has gained significant interest and increased market share. Consequently, sugar-based surfactants, such as alkyl polyglycoside (APG\*), are used as a replacement for polyoxyethylene alkylphenols (APEs) where biodegradability is a concern. They represent a new concept in compatibility and care.

\*APG is a registered trademark of Cognis Deutschland GmbH.

Nonetheless, over 35 different types of surfactants are produced and used commercially in the formulation of home care, personal care, and industrial products. Contrary to many textbooks that elaborate on surfactant physical properties or formulation guidelines, this chapter approaches the surfactant topic from both synthesis and manufacturing perspectives. It offers a comprehensive overview of the most commonly used industrial surfactants with respect to their synthesis and manufacturing processes; their reactions and applications; and their physical, ecological, and toxicological properties. A concise and thorough description of the most pertinent synthesis routes is presented for the major types of surfactants predominantly used in the home and personal care industry. These surfactants are primarily anionic, nonionic, cationic, and amphoteric.

Also reviewed is the synthesis of surfactants derived from carboxylation, sulfation, and condensation of fatty acid and phosphoric acid derivatives. The most commonly used anionic surfactants are LASs, ASs, and AESs.

Nonionic surfactants are produced mainly by alkoxylation technology, although amine oxides under alkaline conditions are also classified as nonionic. Section III discusses the synthesis, production, and applications of the most commonly used ethoxylated surfactants such as alcohol ethoxylates, nonyl phenol ethoxylates and fatty acid ethoxylates, fatty amine oxides (FAOs), and fatty alkanolamides (FAAs).

Section IV is concerned with a class of biodegradable and highly compatible carbohydrate- or sugar-based surfactants such as sorbitan esters, sucrose esters, and glucose-derived esters. Their syntheses encompass a significant list of renewable raw materials, including sucrose from sugar beet or cane, glucose from starch, and sorbitol as the hydrogenated glucose derivative. The most commonly used sugar-based surfactants, such as APG and fatty acid glucamides (FAGs), are reviewed in depth.

The syntheses of cationic and amphoteric surfactants are reviewed in Sections V and VI, respectively. Cationic surfactants contain exclusively a quaternary tetra-coordinated nitrogen atom (quaternary ammonium compounds). They are widely used as textile softeners in laundry formulations and in flotation. Amphoteric surfactants (including betaines) exhibit a zwitterionic character, i.e., they possess both anionic and cationic structures in one molecule.

Recent progress in the surfactant field focuses on polymeric, splittable, gemini, multifunctional, and biosurfactants.

## II. ANIONIC SURFACTANTS

### A. Carboxylates

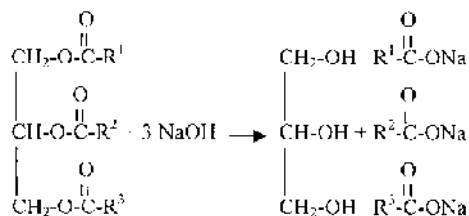
#### 1. Soaps

Soaps represent the oldest known class of surfactants. They have been known for at least 2300 years. In the period of the Roman Empire, the Celts produced soap from animal fats and plant ashes, which served as alkali. They gave this product the name “saipo” from which the word “soap” is derived [1]. The chemical nature of soaps, as alkali salts of long-chain fatty acids, was recognized many centuries later by Chevreul. He showed in 1823 that the process of saponification is a chemical process of splitting fat into the alkali salt of fatty acid and glycerine.

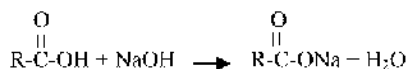
The term soap is mainly applied to the water-soluble alkali metal salts of fatty acids, although ammonia or triethanol amine salts are also used as technical soaps. Salts of fatty acids with heavy metals or with alkaline earth metals are water insoluble and are termed “metallic soaps.” They possess no detergent or soaplike properties.

Generally, three different processes are suitable for the large-scale production of soaps:

#### 1. The saponification of neutral oils (triglycerides)



#### 2. The saponification of the fatty acids obtained from fats and oils



#### 3. The saponification of the fatty acid methyl esters derived from fats and oils



The most important industrial process is the saponification of the neutral oils and of the fatty acids. Both processes may be run in either batch or continuous mode. All types of fats and oils can be used in this process. The most important ones are tallow and coconut oil.

The main application of soap is in the personal care industry, followed by the detergent industry.

For the preparation of high-grade soaps, the basic soap must be very pure and free of unpleasant odors. The color quality and the odor of the basic soap are determined by the content of by-products. These impurities are of different origins:

1. Natural constituents of fats and oils (waxes, phosphatides, cerebrosides, sterols, fat-soluble vitamins, diol lipids, carotenoids, etc.)
2. Substances generated by oxidation processes during storage of the raw materials
3. Substances generated in the manufacturing process

By using special purification steps during the production process, these by-products are eliminated.

## 2. Ether Carboxylic Acids

The sensitivity of soaps to water hardness is a big disadvantage for many applications. In contrast, the alkyl polyoxyethylene carboxylic or alkyl (poly-1-oxapropen) oxaalkene carboxylic acids, or short ether carboxylic acids, exhibit an extreme water hardness resistance combined with good water solubility.

The starting material for ether carboxylic acids is fatty alcohol ethoxylates. Conversion to the ether carboxylic acid can be carried out by three different routes (Fig. 1).

The fatty alcohol ethoxylates can be carboxymethylated by reaction with monochloroacetic acid in the presence of sodium hydroxide [2] or through terminal oxidation of the fatty alcohol ethoxylate [3–5]. The ether carboxylic acid can also be synthesized by the addition of a vinylic system, i.e., acrylonitrile, to an oxyethylated fatty alcohol and subsequent hydrolysis. Ether carboxylic acids are temperature stable and re-

sistant to alkali and hydrolysis, even under strong acidic or alkaline conditions.

Because of their advantageous ecological, toxicological, and physicochemical properties and good compatibility with representatives of all surfactant classes, ether carboxylic acids can be applied effectively in many fields. They are used in washing and cleaning agents as well as cosmetics. They are utilized as emulsifying and auxiliary agents in the textile, printing, paper, plastics, metalworking, and pharmaceutical industries [6].

The salts of ether carboxylic acids with a high degree of ethoxylation are considered to be very mild and skin-compatible surfactants. Therefore, they are particularly suitable for applications in cosmetics [7].

Ether carboxylic acids are also used for manual dish-washing detergents, carpet cleaners, and other household products [8].

In the plastics industry, ether carboxylic acids are employed as auxiliary agents for emulsion polymerization and as antistatic agents (or antistats).

They also exert a good corrosion-inhibiting effect and, therefore, ether carboxylic acids are also used as emulsifiers in drilling, rolling, and cutting oil emulsions and cooling lubricants [9].

## B. Sulfonation Technology

The technology of sulfonation (C—S coupling reaction) and sulfation (C—O—S coupling reaction) can be realized by various processes. Only industrial processes that are of significant importance are discussed here. Those are sulfonation and sulfation or sulfoxidation and sulfochlorination (see Alkane Sulfonates).

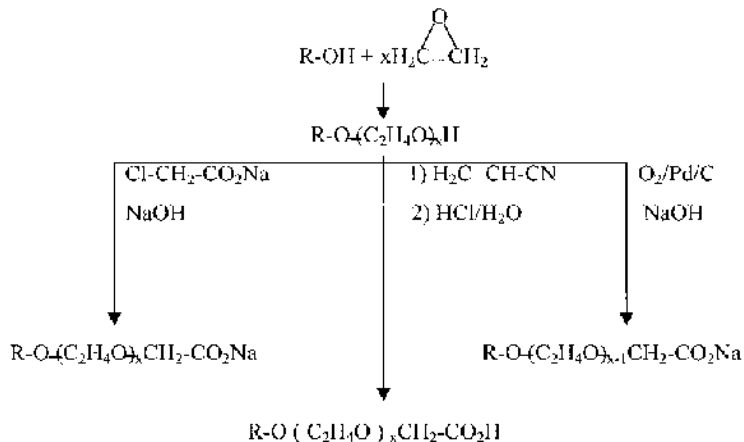


FIG. 1 Synthesis of ether carboxylic acids.

(a) *Sulfonation with Sulfur Trioxide.* Sulfonation with SO<sub>3</sub>/air raised from sulfur has become the predominant technology for manufacturing sulfonation products [10–12]. The diluted SO<sub>3</sub> gas is generated by burning sulfur, followed by catalytic oxidation of SO<sub>2</sub> at a vanadium pentoxide contact (conversion). Alternative sources for gaseous SO<sub>3</sub> are liquid SO<sub>3</sub> and oleum (65%), which is not only hazardous in transport, handling, and storage but also more expensive.

The sulfonation is done mostly in falling-film reactor with 3–5% SO<sub>3</sub> in dry air (dew point < –60°C). A falling-film reactor, such as the Ballestra SULFUREX F system (Fig. 2), is a bundle of about 6-m-long reaction tubes in a shell in which heat exchange takes place with cooling water.

The organic raw material is fed to the top of the reactor and is distributed on the inner walls of the reaction tubes by identical annular slots. The contact time with SO<sub>3</sub> is relatively short to prevent undesired color-developing side reactions. After removal of the exhaust gas with a gas-liquid separator, the sulfonic acid is generally transferred to a neutralization loop. In some cases in which aging of the raw sulfonic acid is necessary to achieve a high degree of sulfonation (LAS, estersulfonates), a residence time is achieved by using an aging vessel or loop. Falling-film reactors of different designs are now available on the market.

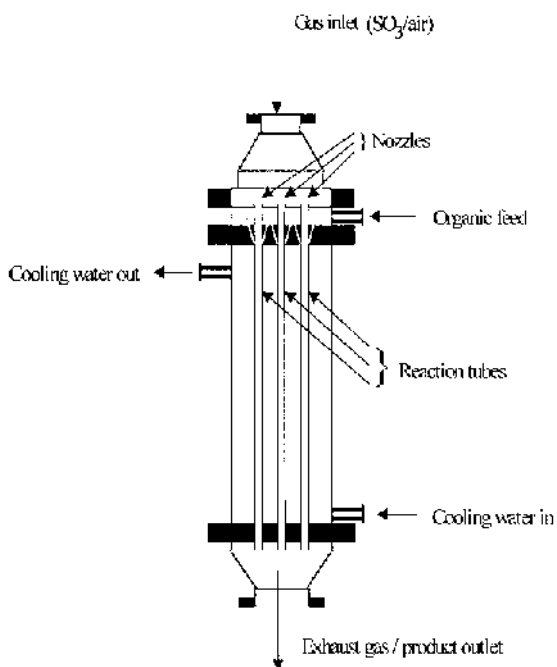
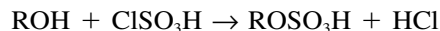


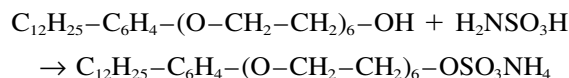
FIG. 2 Multitube sulfonation reactor.

(b) *Sulfonation with Chlorosulfonic Acid* [13]. Chlorosulfonic acid (CSA) is used in batch or continuous processes for the production of sulfates or ether sulfates on a relatively small scale:



The HCl must be removed by degassing and absorbing; the sulfonic acid ester can be neutralized with the desired bases. This chemistry requires glass-lined steel or glass equipment. In contrast to falling-film reactors, the sulfation equipment takes less space and investment. The costs and handling of CSA are disadvantageous compared with those of sulfur trioxide.

(c) *Sulfonation with Amidosulfonic Acid* (“Sulfamic Acid”). Amidosulfonic acid is a relatively seldom used sulfation agent. It is used, for example, to sulfate alkylphenol derivatives to avoid ring sulfonation by-products:



Another example is the production of aliphatic ether sulfates [14].

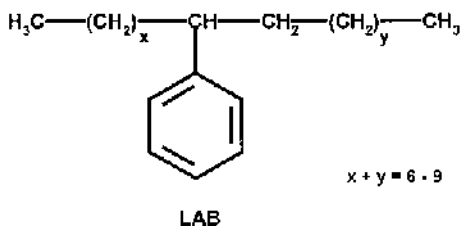
### 1. Alkylarylsulfonates [10–12,15,16]

Linear alkylbenzene sulfonates (LABSs, LASs) or general alkylbenzene sulfonates (ABSs) have a long history, going back to the 1930s.

Using a Friedel-Crafts reaction of olefins with benzene in the presence of either aluminum chloride or hydrogen fluoride made alkylbenzene an economically attractive raw material for the synthesis of this class of anionic surfactant, which developed into the “work-horse” of detergents.

The first market product was tetrapropylenebenzene-sulfonate (TPS) derived from  $\alpha$ -dodecylene synthesized by tetramerization of propylene, giving a branched alkyl chain. Because of the insufficient biological degradability of the highly branched alkyl chain, which led to contamination of surface waters, TPS was replaced by the biologically more degradable LAS.

The linear alkylbenzene is structurally a nonuniform product. The most common product has a carbon number range of the alkyl chain from C<sub>10</sub> to C<sub>13</sub> (Scheme 1). The phenyl isomer distribution occurring therein is determined by the choice of catalyst. With use of AlCl<sub>3</sub>, the content of 2-phenyl isomers is approximately 30% in mixture with 3-, 4-, 5-, and other phenyl isomers. In products of HF-catalyzed reaction, the content of 2-phenyl isomers is significantly lower at about 20%.



**SCHEME 1**

The sulfonation of alkylbenzenes [17–21] can be handled with oleum, sulfuric acid, or gaseous sulfur trioxide. The sulfonate group is introduced into the benzene ring primarily in the *p*-position. The process may be operated as either a batch or continuous process. The industrial sulfonation of LAB is accomplished today frequently with  $\text{SO}_3$  in multitube falling-film reactors on a highly economical scale. The continuous sulfonation of alkylbenzene sulfonates is carried out at 40–50°C with a molar excess of 1–3% sulfur trioxide, diluted to 5–7 vol% in dry air.

During the sulfonation step, the desired sulfonic acids are not the only products. Anhydrides, called pyrosulfonic acids, are also formed as by-products (Scheme 2).

The content of alkylbenzenesulfonic acid can be increased with a postreaction (aging) step, which is necessary for a sufficient degree of sulfonation (Scheme 3). During aging, the pyrosulfonic acids can react with further alkylbenzene, sulfuric acid, or traces of water, increasing the content of alkylbenzenesulfonic acid.

Another undesirable side reaction is the formation of sulfones, which are part of the “free oil” content of

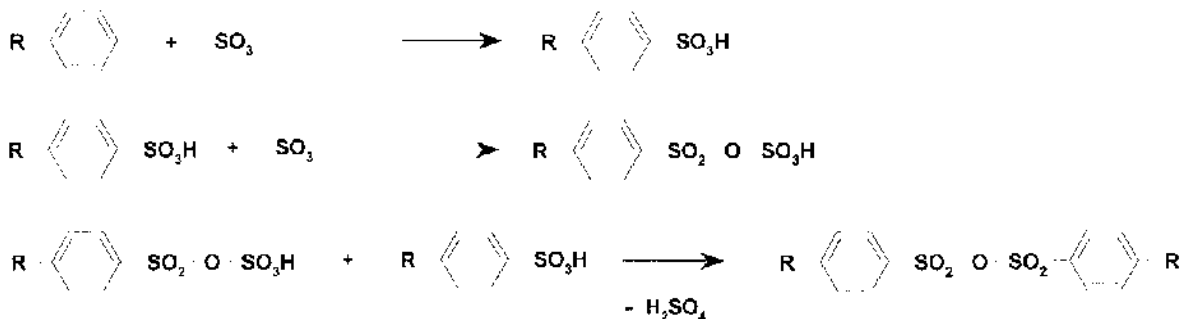
LAS (Scheme 4). The reaction mixture is neutralized with sodium hydroxide solution. Aqueous pastes with up to 60% active substance content can be produced (Scheme 5). Other side reactions, for example, oxidation, whose chemistry is hard to state more precisely, give dark-colored by-products that can require bleaching of the aqueous LAS paste.

Unlike other sulfonation or sulfation products, the crude alkylbenzenesulfonic acid, although very corrosive, can be stored in the acid form. The anhydrides are converted to alkylbenzenesulfonic acid by addition of 1–2% water at 80°C in order to stabilize the product.

LAS is a good soluble anionic surfactant mainly for use in detergents [22]. It is moderately sensitive to water hardness. Most formulations contain surfactant mixtures in order to decrease sensitivity to water hardness and to enhance foam stability. The combinations are, for example, LAS with alkyl(ether) sulfates and/or nonionics.

LAS is completely biodegradable under aerobic conditions, resulting in high environmental safety. Degradation under anaerobic conditions (the relevance of which has been controversial [23–31]) is, as for sulfonate structures, poor. As LAS is and will continue to be the major component of detergent systems because of its good price/efficiency ratio, more environmental data are available for it than for any other surfactant (European Center for Ecotoxicology and Toxicology of Chemicals, ECETOC Technical Report No. 51, Brussels, 1992).

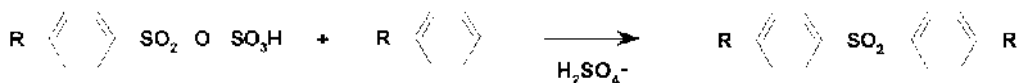
The processing of LAS toward compact detergent powders will have to be revised because of the sticky behavior of water-free products. Combinations of LAS



**SCHEME 2**



**SCHEME 3**



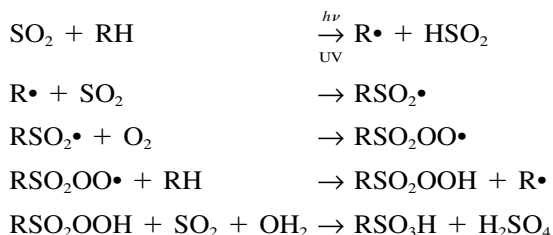
SCHEME 4

with alkyl sulfates are already employed because of the good crystallization of alkyl sulfates. Extension of the application of LAS to cosmetics was suggested by the use of the milder Mg salts [32].

## 2. Aliphatic Sulfonates

(a) *Alkane Sulfonates.* Sulfoxidation and sulfochlorination are the core technologies for the preparation of alkane sulfonates. Sulfoxidation, the older process, is more important than sulfochlorination.

**Sulfoxidation.** Sulfoxidation [33–37] is a photochemically induced process starting with sulfur dioxide, oxygen, and an *n*-alkane, normally in the range C<sub>12</sub>–C<sub>18</sub> or C<sub>14</sub>–C<sub>17</sub>. The radical chain reaction gives many isomers with mainly secondary sulfonate groups. The following sequence explains the reaction steps:

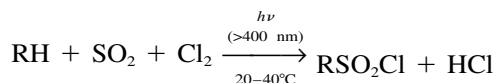


In practice, a paraffin-water mixture is contacted with SO<sub>2</sub> gas and oxygen at 30–40°C under irradiation with ultraviolet (UV) lamps. The process is run with an excess of paraffin in order to avoid the formation of multisubstituted products.

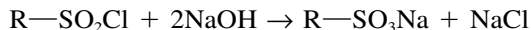
The excess of paraffin can be removed from the reaction mixture after cooling (with a separator) and can be recycled. Different work-up procedures have been established: the “Hoechst Light Water Technology” and the Hüls process. Both processes have in common separation and recirculation of the paraffin from the crude reaction product by extraction. Also, the sulfur dioxide can be removed by degassing and washing in order to be recycled. The sulfuric acid can be separated by phase separation or extraction.

The final product has to be bleached and neutralized, giving a yellowish paste with about 65% active matter.

**Sulfochlorination.** The sulfochlorination technology [37,38] is used for the conversion of paraffins or alkanes to alkane sulfonates. In a photochemically induced reaction, the paraffin is contacted by dry sulfur dioxide and chlorine:



The resulting sulfochloride is a mixture of approximately 94% mono- and 6% disulfochloride. In a subsequent hydrolysis step with NaOH solution at 80°C, the sulfonates are formed:

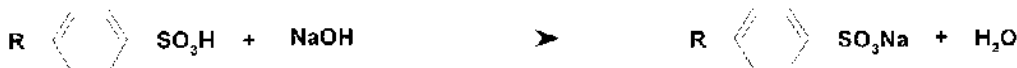


Alkane sulfonates are highly soluble surfactants and are preferably used in liquid products or concentrates. The trend to use renewable raw materials has reduced their use in household products to some extent. Typical applications are in detergents, personal care products, cleaners, and dishwashing detergents.

As is common to all sulfonates, alkane sulfonates are easily biodegradable under aerobic conditions [39] but fail under anaerobic conditions.

(b) *Olefin Sulfonates.* Alpha olefin sulfonates (AOSs) [40,41] are, in contrast to internal olefin sulfonates (IOSs), the most important products of this class. AOSs are mainly based on C<sub>12</sub>–C<sub>18</sub> alpha-olefins derived from ethylene oligomerization (Ziegler process). There is considerable interest in this class of surfactants today because they are derived from low-priced raw materials coupled with an inexpensive sulfonation process.

The most important sulfonation process works with SO<sub>3</sub> (Fig. 3), which adds in the primary step to the double bond of the olefin, giving a ring-structured sulfone intermediate. Through different reaction steps of sulfone formation, elimination, rearrangements, transi-



SCHEME 5



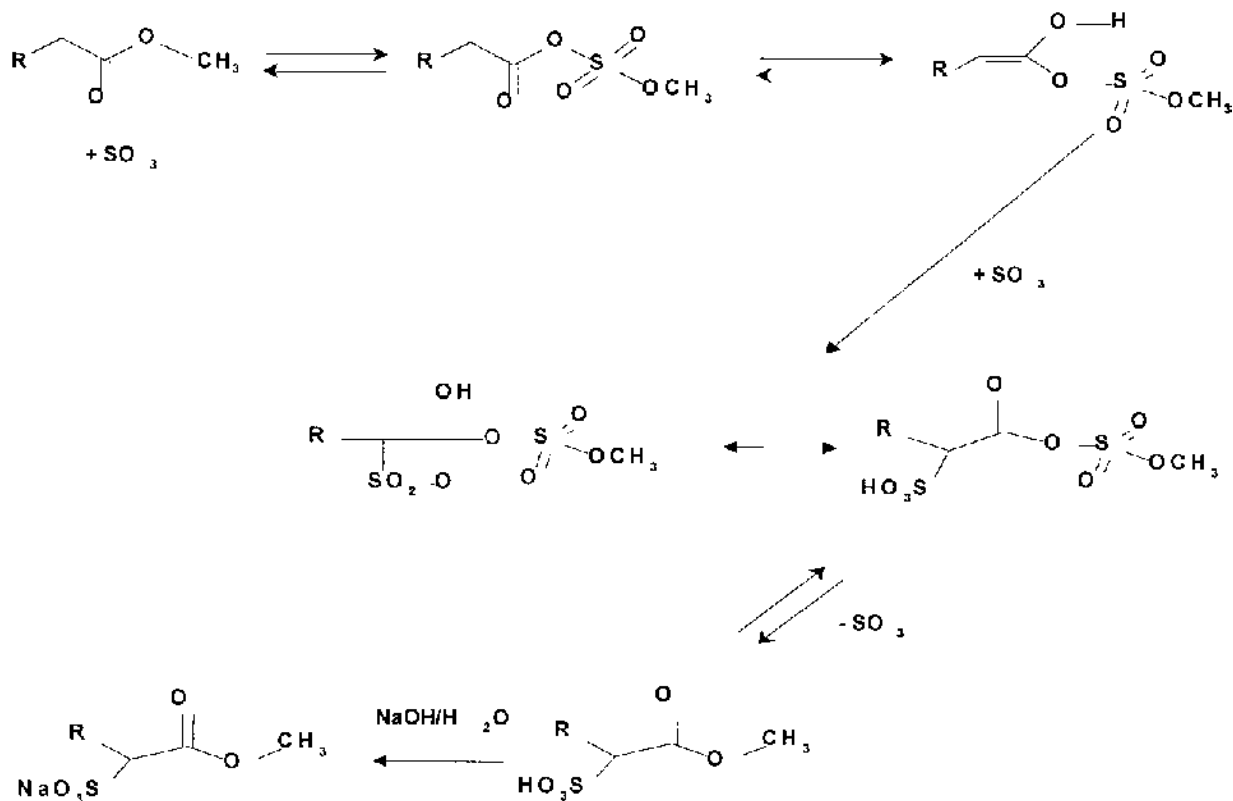


FIG. 4 Reaction mechanisms of the sulfonation of esters.

mediate anhydride of the  $\alpha$ -sulfo acid is hydrolyzed to the disodium salt. To avoid this, hydrolysis of the  $\alpha$ -sulfo acid anhydride with methanol is carried out. To achieve good color, bleaching of the sulfonic acid with hydrogen peroxide is necessary. The color of MES is dependent on the ester raw material. Raw materials with low iodine values (<0.1%) are suitable for the process.

The same reaction can be carried out with fatty acids, giving directly the disodium salt of the  $\alpha$ -sulfo acid, which is of no industrial importance.

**Sulfosuccinates.** Sulfosuccinates (sulfosuccinic acid esters) are anionic surfactants based on maleic acid anhydride. One distinguishes mono- and dialkyl esters of the sulfosuccinic acid (Fig. 5).

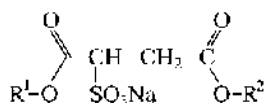


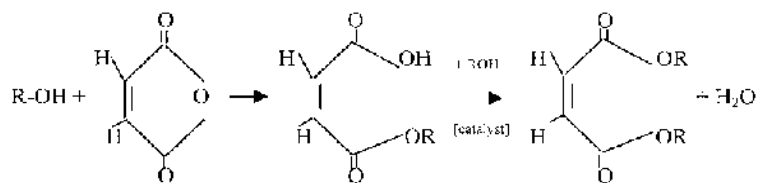
FIG. 5 Structure of sulfosuccinic acid esters.  $R^1, R^2 = H$ , alkyl, POE-alkyl.

Both mono- and diesters are obtained in a two-step process. In the first reaction step, maleic acid anhydride is esterified with compounds containing hydroxyl groups to the mono- or diester (Fig. 6). Diesters are mainly produced with alcohols. For monoesters, many different raw materials with hydroxyl groups are used, e.g., fatty alcohols and their ethoxylates and fatty acid alkanol amides and their ethoxylates [60]. Usual esterification catalysts such as *p*-toluenesulfonic acid are suitable as catalysts for diester production.

In the second reaction step, the maleic acid ester is sulfonated with an aqueous sodium hydrogen sulfite solution to obtain the corresponding sulfosuccinate (Fig. 7). In the case of the sulfosuccinic acid monoester, two regioisomeric sulfosuccinates are possible (Fig. 8). It was detected by  $^1H$  nuclear magnetic resonance (NMR) analysis that the  $\beta$  position is preferred during sulfonation. The  $\beta/\alpha$  ratio is approximately 4:1 (Henkel KGaA, unpublished results).

Sulfosuccinates are used in many different fields of application. Comprehensive overviews have been published [60,61–63]. Sulfosuccinic acid dialkyl esters are weakly foaming surfactants with good wetting power.





**FIG. 6** Reaction scheme for the synthesis of maleic acid mono- and dialkyl esters. R = alkyl, POE-alkyl.

In particular, products based on *n*-octanol or 2-ethyl hexanol are distinguished by their outstanding wetting properties. Therefore, they are applied as “rapid wetting agents” in the textile industries [64]. In fiber technology, these products are used in spinning oils for nylon production. Furthermore, they are used in agriculture for pesticides as well as in paint formulations and in the leather industry. With regard to household products, the application of sulfosuccinic acid dialkyl esters is restricted to specific glass cleaners, e.g., for spectacle lenses or glass panes, as well as carpet shampoos.

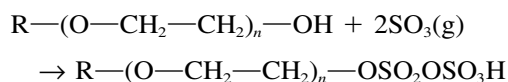
In contrast to sulfosuccinic acid dialkyl esters, sulfosuccinic acid monoalkyl esters are good-foaming surfactants, especially products based on ethoxylated fatty alcohols, e.g., lauryl or myristyl polyoxyethylene (3) alcohol, which exhibit outstanding skin compatibility [65]. Because of their mildness to skin, large quantities of sulfosuccinic acid monoalkyl esters are used in personal care products such as shower gels, shampoos, and skin-cleaning agents. In particular, they are utilized in mild products such as baby shampoos or shampoos for sensitive skin. Their compatibility is very good, not only on sensitive skin but also on diseased skin [66]. Sulfosuccinic acid monoalkyl esters are very soluble in water and have good hard-water resistance with a low tendency to form calcium soaps. They exhibit high detergency that is synergistically enhanced in combinations with other surfactants [67]. Because of the hydrolysis-sensitive ester bond, their application is limited to a pH range of 6 to 8. In the industrial sector, sulfo-

succinic acid monoalkyl esters are, for example, used as emulsifiers in emulsion polymerization. Both the mono- and dialkyl esters are readily biodegradable and have low toxicity [60].

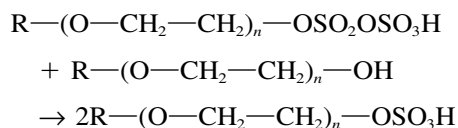
### 3. Alcohol Sulfates (ASs)/Alcohol Ether Sulfates (AESs)

Through conversion of alcohol ethoxylates with sulfation agents, alcohol ether sulfates [68] are obtained. On a large technical scale, ether sulfates are produced mainly in a continuous process through mild conversion with sulfur trioxide in a “multitube falling-film” reactor. The importance of sulfation with chlorosulfonic acid has diminished considerably.

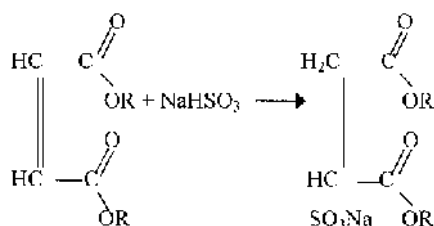
The reaction with  $\text{SO}_3$  leads primarily to a pyrosulfate:



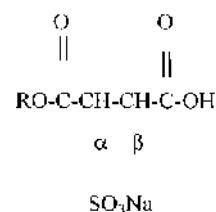
The pyrosulfate primarily obtained is metastable and decomposes very rapidly in the presence of further alcohol into the desired sulfuric acid half-ester:



The next step is neutralization with an aqueous solution of the respective base, e.g., NaOH, KOH, or  $\text{NH}_4\text{OH}$ ,

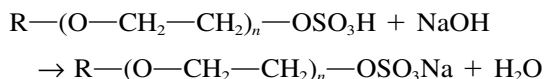


**FIG. 7** Reaction scheme to sulfosuccinates.  $\text{R}^1, \text{R}^2 = \text{H}$ , alkyl, POE = alkyl.



**FIG. 8** Regiometric isomers of sulfosuccinic acid monoalkyl ester. R = alkyl.

or, in the case of organic amines without solvent, into the desired salt:



Alcohol sulfates ( $n = 0$ ) are interesting raw materials for detergents. Modern high-density, heavy-duty detergents require solid surfactants with excellent powder properties [69,70]. Water-free alkyl sulfates crystallize quite well. The production volume is steadily rising, whereas the capacity for LAS is decreasing. ASs can be classified as environmentally compatible, with complete biodegradation [71,72].

Ether sulfates are usually obtained as aqueous pastes with concentrations of approximately 30 or 70%. The process is continuous, and the short residence time between formation of the sulfuric acid half-ester and neutralization contributes to the high conversion rate of up to 98%. Because sulfur trioxide is oxidative, under unfavorable conditions and with qualitatively inadequate raw materials, discoloration (yellow and brown) of the product may occur. This can be eliminated in a bleaching step (preferably with  $\text{H}_2\text{O}_2$ ) after neutralization. Ether sulfates are stable in the alkaline range but are easily hydrolyzed in an acid medium (autocatalytic reaction). The products are safe for the consumer and the environment. A by-product that has been discussed is dioxane. The dioxane quantity can be reduced to <10 ppm, referring to 100% achievement, by technical measures such as conscientious process optimization and aftertreatment. These residual concentrations do not involve any health risk for the consumer.

Because of their good foaming power, alcohol ether sulfates are preferably used in foam baths, shampoos, and manual dishwashing detergents; in combination with sulfosuccinates, amphoteric surfactants, and amine oxides, they have synergistic effects with regard to skin compatibility.

#### 4. Sulfated Oils and Glycerides

A sulfated oil is a reaction product of a sulfation agent, e.g., sulfuric acid, and a fatty oil. One can differentiate between natural fats and oil (triglycerides) and partially esterified glycerol (mono- or diglycerides) by the position of the sulfo group: an internal sulfo group exists in the case of sulfated fat or oil, and an external group at the end of the hydrophobic chain exists in the case of partially esterified glycerol.

Sulfated oils were the first nonsoap organic surfactants. In 1834, F. F. Runge prepared a "sulfuric acid oil" from a mixture of olive oil and sulfuric acid and

used it as a mordant. In 1875, sulfated castor oil, "Turkey-red oil," was introduced as the first commercial sulfated-type textile auxiliary [73].

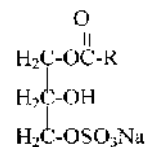
The composition of sulfated oils is a complex mixture of sulfo esters, soap, water, fatty acids, and neutral oil. Most of the products are tailor made for special applications and end uses. Self-emulsifiable oils represent the largest group of applications. In addition, they are used as cutting oils for metalworking compositions, as oil sprays for insecticides, as spinning oils for textile processing, and as a so-called fat liquor in the leather industry.

In the group of sulfated mono- and diglycerides, sulfated fatty acid monoglycerides (Fig. 9) are the most important. As early as 1935, Colgate-Palmolive Peet Co. launched a soap-free shampoo formulation under the brand name "Halo" making use of monoglyceride sulfates as a surfactant component. Accordingly, monoglyceride sulfates are among the first synthetic surfactants used in cosmetics.

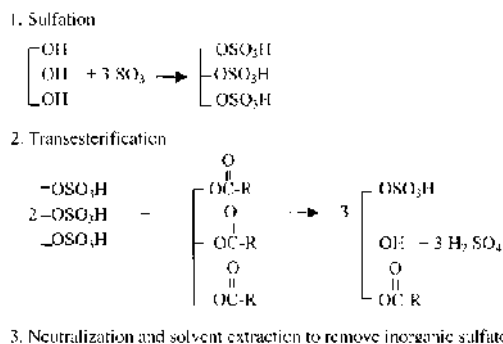
In 1954, Colgate-Palmolive claimed a continuous process for the preparation of monoglyceride sulfates [74]. In a first reaction step, glycerol is converted with oleum to the corresponding fatty acid glycerol sulfuric acid half-ester. This intermediate product is then transesterified with a triglyceride, usually coconut oil, thus leading to monoglyceride sulfate (the mechanism of this conversion is described in the following).

The resulting products were, for example, applied in the household cleaner "Vel," which was marketed by Colgate in the 1950s and 1960s. The industrial production process is a multistep process that uses 20% oleum as a sulfation agent. In the first reaction step, glycerol is reacted with oleum in such a way that all three hydroxyl groups of the glycerol are sulfated, thus forming a glycerol trisulfuric acid half-ester (Fig. 10). In a second reaction step, this glycerol trisulfuric acid half-ester is converted with a triglyceride, usually hardened coconut oil (molar ratio 2:1).

In a step similar to a transesterification reaction, sulfuric acid half-ester functions are now exchanged for a fatty acid residue, so that from two molecules of glycerol trisulfuric acid half-ester and one triglyceride mol-



**FIG. 9** Molecular formula of monoglyceride sulfate sodium salt. R = alkyl.



**FIG. 10** Reaction pathway to fatty acid monoglyceride sulfates.

ecule, three molecules of monoglyceride disulfuric acid half-esters are obtained. According to Colgate, the sulfuric acid half-ester function in the  $\beta$ -position with the fatty acid ester function is unstable. Therefore, after neutralization, e.g., with ammonia or caustic soda solution, a 1,3-fatty acid monoglyceride sulfate is obtained in a highly selective process. Because of the high oleum excess during sulfation of the glycerol, large quantities of sodium sulfate are formed in the neutralization step. The unwanted salts are removed from the monoglyceride sulfate by means of an extraction process as follows: By adding alcohol with a low boiling point, e.g., ethanol, to the aqueous, neutralized surfactant solution, two liquid phases are formed—a heavier aqueous phase that is saturated with sodium sulfate and an alcohol phase that contains the monoglyceride sulfate. The salt-containing aqueous phase is separated, and the surfactant is obtained by evaporation of the ethanol. The resulting product yields the desired monoglyceride sulfate in a purity of approximately 80%; by-products are partial glycerides and fatty acid.

Patent literature describes further manufacturing processes for monoglyceride sulfates [75–81]. In the early 1990s, Henkel KGaA developed a continuous process for the preparation of monoglyceride sulfates [82]. In this process, technical grade monoglycerides are converted to the corresponding monoglyceride sulfates with gaseous  $\text{SO}_3$  in a continuous falling-film reactor.

Monoglyceride sulfates, in particular those based on coconut oil, are soluble, high-foaming anionic surfactants. They are distinguished by excellent skin compatibility, which is comparable to that of mild anionic surfactants such as sulfosuccinate or ether sulfate [83]. Based on these properties, coconut monoglyceride sulfate was used in a hair shampoo as early as 1935, as mentioned earlier. In the 1950s and 1960s, the coconut-

based monoglyceride sulfates, which Colgate produced on an industrial scale for sale under the brand names Arctic Syntax L and M and Monad G, were applied in many household products, e.g., a household cleaner with abrasive additives [84] and the household cleaner “Vel.” In the United States, monoglyceride sulfates are still used as mild surfactants in syndet soaps [85]. In addition to lauryl sulfate, monoglyceride sulfates are described as surfactants for toothpastes and dental care products in combination with specific active substances [86–91]. The excellent skin compatibility of monoglyceride sulfates predestines these products for application in personal care products. A large variety of combinations of monoglyceride sulfates with other mild surfactants has been described for this field of application, e.g., combinations of monoglyceride sulfate with phosphoric acid esters [92], with succinic acid [93], with an aminophosphate surfactant [94] for skin-cleansing agents, and in combination with amino acids and amphoteric surfactants for hair shampoos [95].

Detergent mixtures of alkyl polyglycosides with monoglyceride sulfates show synergistic effects with regard to washing, rinsing, foaming, and cleansing power as well as its skin compatibility [96]. In this combination, high-performance and especially mild shaving preparations [97] or toothpastes [98] can be obtained.

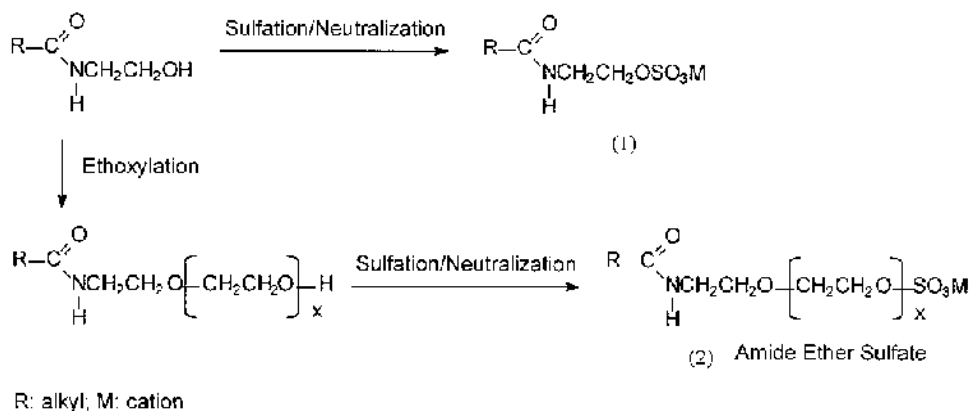
## 5. Sulfated Alkanol Amides

The synthesis of sulfated alkanol amides has been reviewed in a previous volume of this series [99] comprising literature up to the early 1970s. That reference to basic preparation steps for sulfated alkanol amides is still up to date [100], so that recent developments focus on the fields of application and new starting materials.

To produce amide ether sulfates, alkanol amides may be sulfated directly or first ethoxylated and then sulfated, yielding amide sulfates (1) or amide polyoxyethylene sulfates (2) after subsequent neutralization with a base as shown in Fig. 11.

The most common alkanol amine basis for sulfated alkanol amides is definitely monoethanol amine [101], although *N*-alkyl-substituted as well as branched alkanol amines such as isopropanol amine have also been used [102]. Apart from these monoalkanol amides, polyhydroxy alkanol amides such as diethanol amides or 2,3-hydroxy propyl amides have also been prepared [103].

The corresponding alkanol amides are derived from (saturated or unsaturated)  $\text{C}_2$ - to  $\text{C}_{22}$ -carboxylic acids or hydroxy carboxylic acids [104], mainly from coco-



**FIG. 11** Reaction paths to amide sulfates and amide polyoxyethylene sulfates.

nut or tallow-based feedstocks. A main drawback of the sulfation process for alkanol amides is the high viscosity of the sulfation mixture, which may be overcome by means of cosulfation with lower molecular weight alcohols [105], alkanol amines [106], fatty alcohols [107], or oxethylated fatty alcohols [108]. Because of a lower sulfation temperature, the products obtained by this route have an improved color. The choice of cations comprises ammonium (including alkyl and alkanol ammonium), alkali, and alkaline earth metals.

Sulfated alkanol amides are excellent foaming surfactants with good detergency [109]. Their hydrolytic stability as well as physicochemical data have been cited elsewhere [100]. Sulfated alkanol amides are used almost exclusively as cosurfactants together with anionic, nonionic, and sometimes cationic components.

Cosmetics (body, hair, and baby care) and manual dishwashing are the main fields of application because of the low skin irritancy of alkanol amide sulfates [110], which was observed during the late 1960s [111].

Alkanol amide sulfates are good lime soap dispersants and have thus been used in detergent compositions suitable for hard-water applications [112].

Technical applications concerning emulsion polymerization of ethylenically unsaturated monomers [113] or leather preparations [114] are related to the favorable emulsifying properties of sulfated alkanol amides. Sulfated alkanol amides have also been used as mold release [115] or antiadhesive reagents for rubber [116]. Together with cationic surfactants, alkanol amide sulfates may serve as dehydration promotion agents for the production of granular slag [117].

### C. Fatty Acid Condensation Products

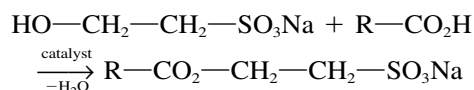
Fatty acid condensation products have a long history. Most of the products were developed during the early

1930s by the former IG-Farben and still have value as mild cosurfactants and as specialty primary surfactants.

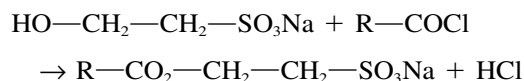
#### 1. Isethionates

Isethionates [118] are mild cosurfactants and are especially used in syndet bars. The largest market is the United States with about 20–30,000 tons per annum. The most common product has a C<sub>12</sub>–C<sub>18</sub> alkyl chain derived from coconut oil. The most recent development in isethionates was the ammonium cocoyl isethionate [119], which is an alternative to the poorly soluble sodium salt with regard to liquid formulations.

The condensation of fatty acid with sodium isethionate can be carried out in the presence of an esterification catalyst in a temperature range above 180–200°C.



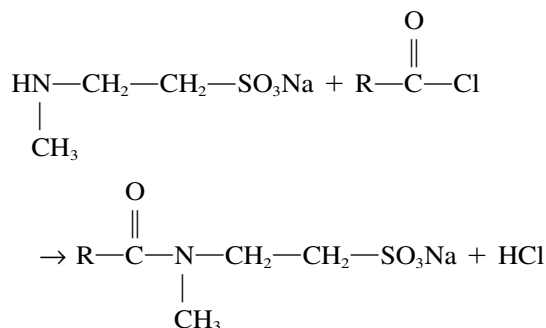
An alternative route is the reaction corresponding to Schotten-Baumann with an acid chloride and sodium isethionate:



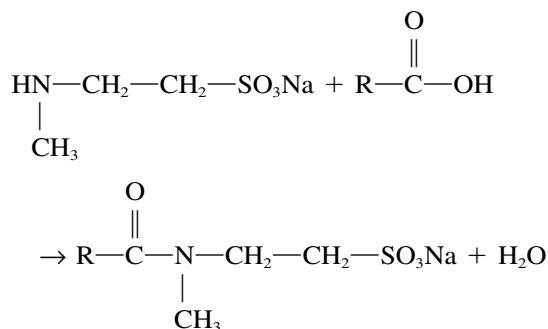
The direct esterification route is more economical than the acid chloride route, but it yields a larger amount of unreacted fatty acid.

#### 2. Taurates

Taurates [120,121] also belong to the class of fatty acid condensation products and can be prepared using the same reaction pathways as isethionates. The most common preparation starts with Na-*N*-methyltaurate:



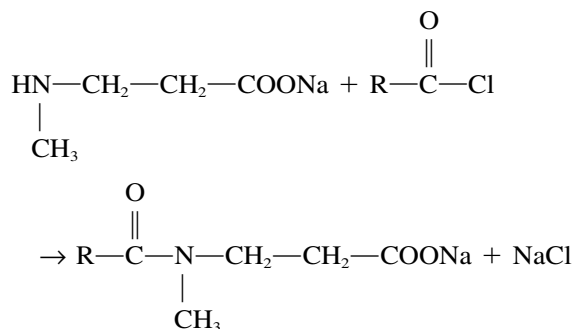
The alternative is the direct reaction of fatty acids with Na-*N*-methyltaurate at high temperatures:



Taurates are more soluble in water than isethionates and are also very mild [121]. Taurates find applications in shampoos, toothpastes, and shaving foam and in various technical applications.

### 3. Sarcosinates

*N*-Acyl sarcosinates [122–124] are mild anionic surfactants derived from the amino acid sarcosine (*N*-methylglycine) and fatty acids. The reaction proceeds via the Schotten-Baumann route with an acid chloride and sodium sarcosinate:



The *N*-acyl sarcosinic acid is insoluble in acid medium and can be isolated upon acidification. Aqueous solutions can be prepared with bases such as NaOH, KOH, NH<sub>4</sub>OH, or triethanol-amine (TEA). Commercial products are available as 30% solutions in water or as spray-dried solids with different C chains from C<sub>12</sub>, C<sub>14</sub> to

technical cocoyl sarcosinate (C<sub>8</sub>–C<sub>18</sub>) or oleyl sarcosinate.

Acyl sarcosinates are applied in numerous personal care products [125] such as shampoos, skin cleansers, bath additives, and toothpastes, where they show good foaming properties. Sarcosinates are, to some extent, compatible with cationic surfactants, which is an interesting point for formulations. Other applications are in corrosion inhibition, industrial emulsification, and detergents.

### 4. *N*-Acyl Amino Acids

The chemical preparation of *N*-acyl amino acids is basically the same as the manufacturing of sarcosinates. *N*-Acyl amino acids [126–130] are well known. With technical production capacities rising for the use of some products in nutrition, they have become attractive raw materials for the surfactant industry. Newer developments worth mentioning are *N*-acyl glutamate [131] or *N*-acyl aspartate. Sodium glutamate is used in food applications as a flavor enhancer, and L-aspartic acid is used as material for the popular artificial sweetener aspartame.

One example is the synthesis of *N*-lauroyl glutamate (Fig. 12). In contrast to the acylation of monocarboxylic amino acids, the reaction of sodium glutamate with acid chloride requires an additional water-miscible solvent such as acetone or isopropanol. The acylation product can be separated after acidification by filtration. It can be handled as dry powder in the acid form or neutralized with NaOH as a 25% solution.

Applications of *N*-acyl amino acid are mainly in the field of cosmetics because of its extreme mildness, good foaming, and cleaning properties.

### 5. Protein/Fatty Acid Condensates

Protein/fatty acid condensates [129,132–134] are produced on the basis of proteins as renewable raw materials. The hydrophilic part is a mixture of peptides, while the hydrophobic part is based on fatty acid. The peptide chain can vary in amino acid sequence and in molecular weight. Depending on the protein and the hydrolysis conditions, molecular weights of 600 to 5000 are achieved.

The acylation is carried out with a protein hydrolysate, a water-soluble peptide mixture obtained from the hydrolysis of an insoluble protein, and a fatty acid chloride (Fig. 13). The acyl group is normally formed by a C<sub>8</sub>–C<sub>18</sub> fatty acid. Proteins may come from collagen or vegetable sources such as soya or rice.

Protein/fatty acid condensates are processed as aqueous yellow to amber-colored solutions with 30–35% active matter or as powders.

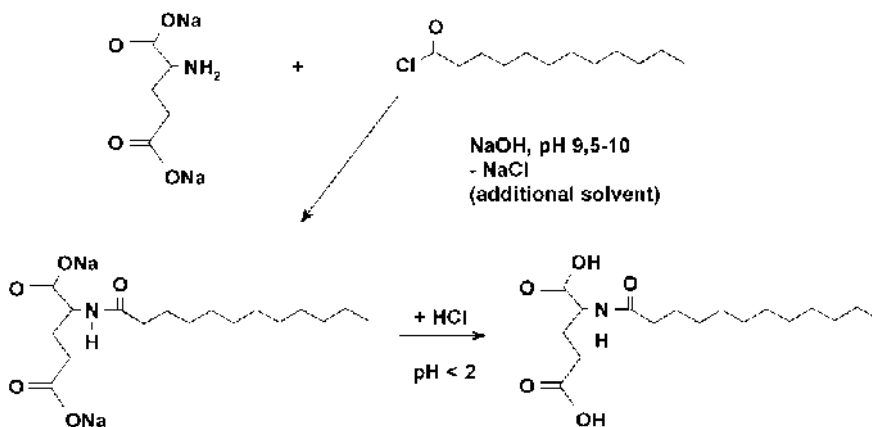


FIG. 12 Acylation of sodium glutamate.

Protein/fatty acid condensates are used mainly as mild surfactants in cosmetics, in the textile industry, and in laundry or dishwashing detergents.

#### D. Phosphoric Acid Derivatives

Another group of anionic surfactants with a significant market potential are phosphoric acid esters. They are based on fatty alcohols as well as on oxethylated alcohols [135] and may be used for special applications such as emulsifiers, wetting agents, antistats, lubricants, flotation auxiliaries, and corrosion inhibitors.

Regarding chemical properties, partial phosphoric acid esters show marked stability to hydrolysis except in strongly acidic conditions. The sensitivity to hard water is a real disadvantage for this surfactant class. Sometimes, compensation may be possible by application of phosphoric acid esters based on oxethylated alcohols.

Most of the practically used derivatives are mixtures of mono- and diesters; triesters are present only as minor components (Fig. 14).

Generally applied synthesis methods are “phosphations” by means of phosphorus pentoxide. The reaction is very complex and may occur as follows (Scheme 7).

The postulated molar ratio is obtained only if the phosphorus pentoxide used is of a highly pure grade. Because phosphorus pentoxide always contains polyphosphoric acid, at best a mole ratio of 1.2:1 mono- to diester is available. For the same reason, the final products often include pyrophosphates and *o*-phosphoric acid, which are formed in subsequent steps as follows, where polyphosphoric acid reacts with an alcohol (Scheme 8).

The pathway just described is also suitable for the preparation of monoalkyl phosphates, although they are always accompanied by *o*-phosphoric acid and, depending on the amount of alcohol, pyrophosphoric acid. The latter may be hydrolyzed by treatment with water at elevated temperatures.

Triesters based on oxethylated alcohols, which are used as cosmetic emulsifiers for ointments, creams, or lotions [136], can be produced by the reaction of al-

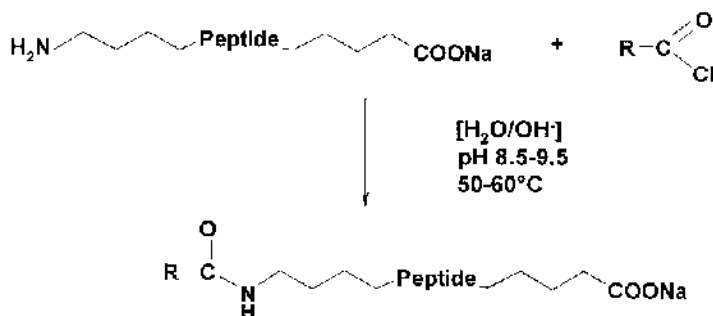
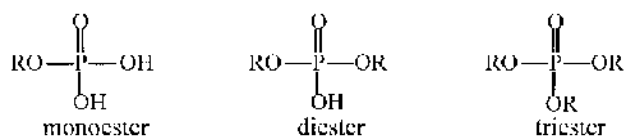


FIG. 13 Acylation of protein hydrolysate.



**FIG. 14** Structures of phosphoric acid esters.

cohols with phosphorus oxychloride in the presence of tertiary amines as absorbents for the hydrochloride gas generated. This prevents, for the most part, the formation of alkyl chlorides as by-products [137] (Scheme 9). The relatively large quantity of amine salt must be removed by filtration.

Esterification directly with *o*-phosphoric acid is impossible. The reaction requires a temperature above 180°C, at which the ester formed will be destroyed, generating olefins [138]. In the presence of small

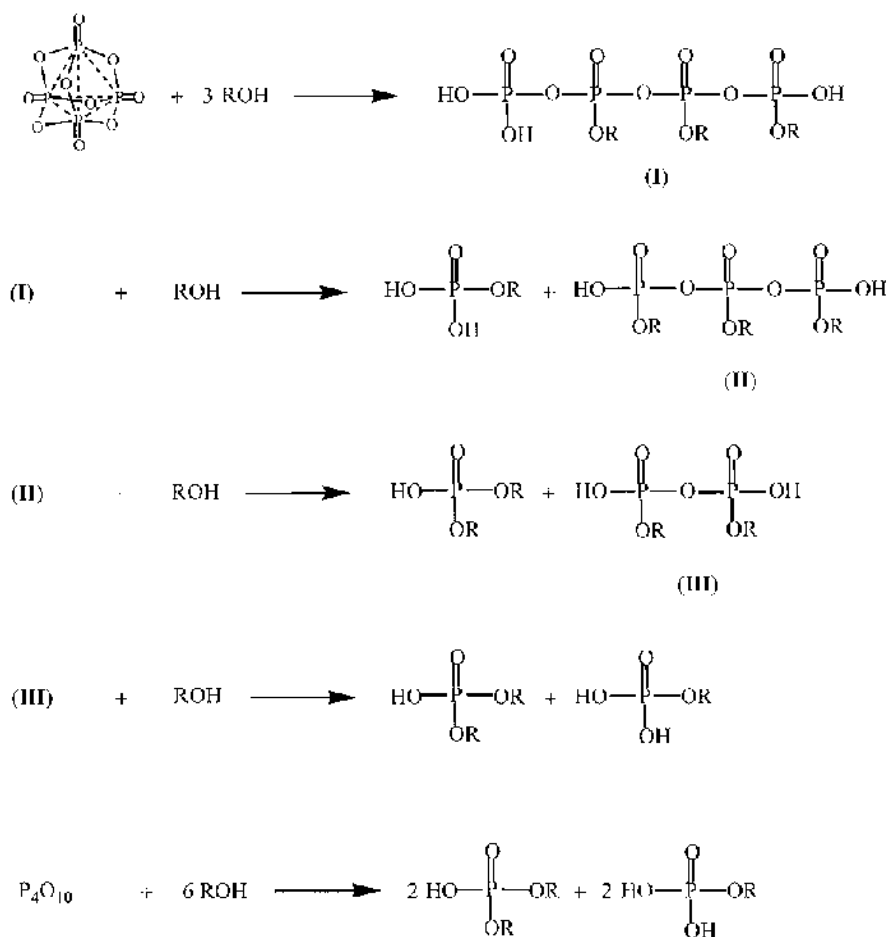
amounts of basic components, however, the cleavage will be avoided [139]. But this technology has not found practical interest.

Mostly, the partial esters are sold in a neutralized form, usually as potassium or alkanolamine salts.

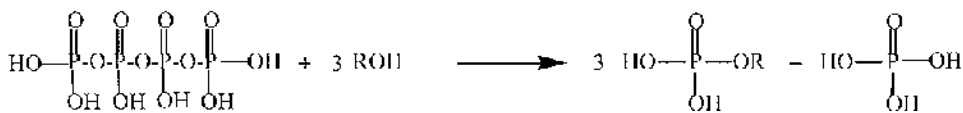
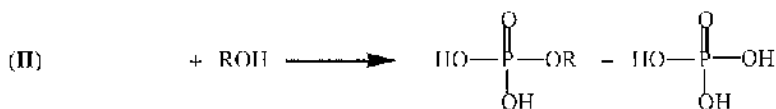
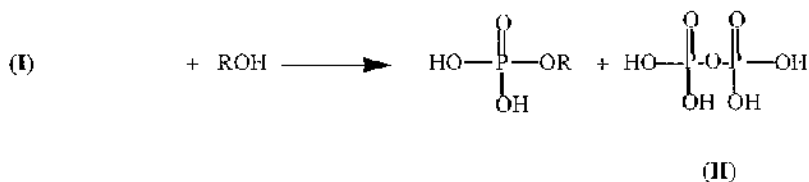
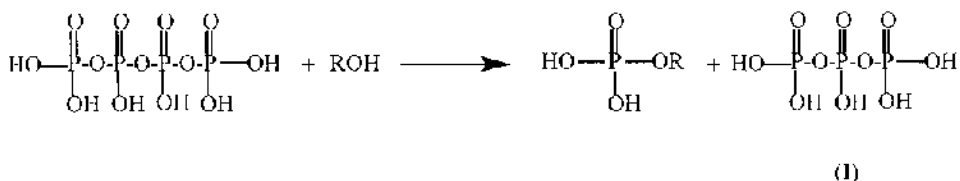
### III. NONIONIC SURFACTANTS

#### A. Alkoxylation Technology

The most important technology in synthesizing nonionic surfactants is the reaction of alcohols, or other active hydrogen compounds, with alkylene oxides such as ethylene oxide (EO) and propylene oxide (PO) [140]. The reaction with ethylene oxide is used most frequently in order to increase hydrophilicity and thus the water solubility of alcohols and is commonly known as “ethoxylation” or, chemically more precisely, “oxethylation.”

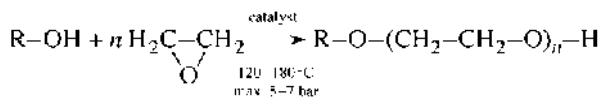


**SCHEME 7**



**SCHEME 8**

The reaction scheme is



The ethoxylation reactions are normally carried out batchwise in a stainless steel reactor (Fig. 15) with a sparger of EO in the bottom, mixing of EO in an external circulation loop, or dosing with nozzles to the vapor phase. Temperatures range from 120 to 180°C at a pressure of 5–7 bar. The risk of spontaneous polymerization of EO with a high temperature jump has to be minimized by applying expensive computer control systems combining all safety features. The control system measures temperatures and pressure and automatically shuts the system down if critical limits are exceeded. There is also a safety lock to prevent catalyst mixtures from being back-mixed with ethylene oxide. Important criteria for safety are quick reaction with

consistently low stationary concentrations of ethylene oxide and dilution with nitrogen.

Raw materials have to be dried before ethoxylation in order to reduce the undesired side reaction yielding polyethylene glycol. Traces of oxygen or air have to be removed before dosing EO to avoid the formation of explosive mixtures and to reduce discoloration. After the reaction, a posttreatment, applying vacuum to reduce traces of EO and sometimes 1,4-dioxane (stripping with steam), is necessary. The catalyst is normally neutralized with acetic acid, phosphoric acid, propionic acid, or lactic acid, resulting in soluble salts or salts that can be removed by filtration.

The reaction with propylene oxide gives the molecule a more hydrophobic character. Propylene oxide can be copolymerized with ethylene oxide in a random manner or blockwise in order to obtain certain product characteristics such as reduction of foaming, improvement of wetting, liquefaction, and others.



**SCHEME 9**



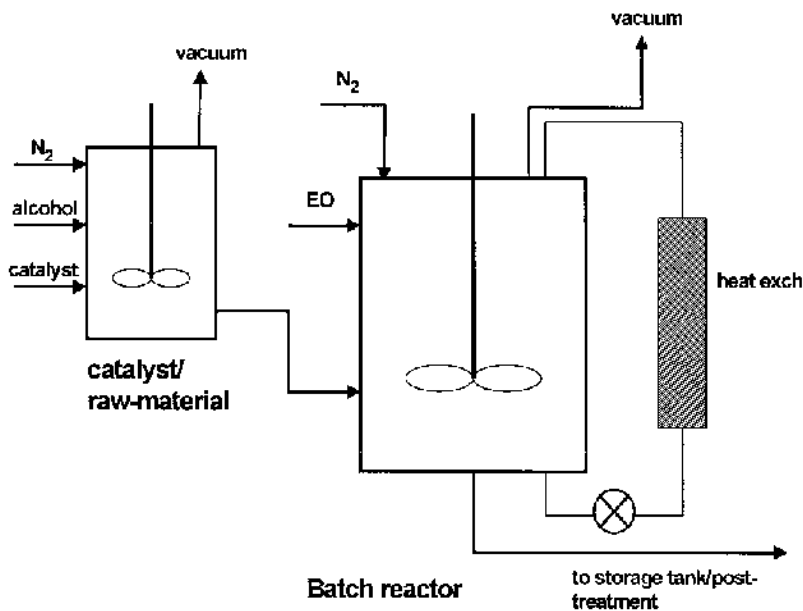


FIG. 15 Ethoxylation reactor.

Technical alkylene oxide derivatives always have a distribution of oligomers or polymers with a mean degree of polymerization, reflecting the mole ratio of the reaction of alcohol and EO. The product is not uniform in composition but has a distribution of homologues that strongly depends on the type of catalyst used [141]. Conventional alkaline catalysts such as KOH [142] or NaOMe give a relatively broad distribution

(BRE = broad range ethoxylates, Fig. 16). However, it should be noted that special catalysts can be applied resulting in a narrow distribution (NRE = narrow range ethoxylates, Fig. 17).

The difference between BRE and NRE products from an application point of view is not as great as one might have predicted. The problem with NRE is the higher manufacturing expenditure and costs, making

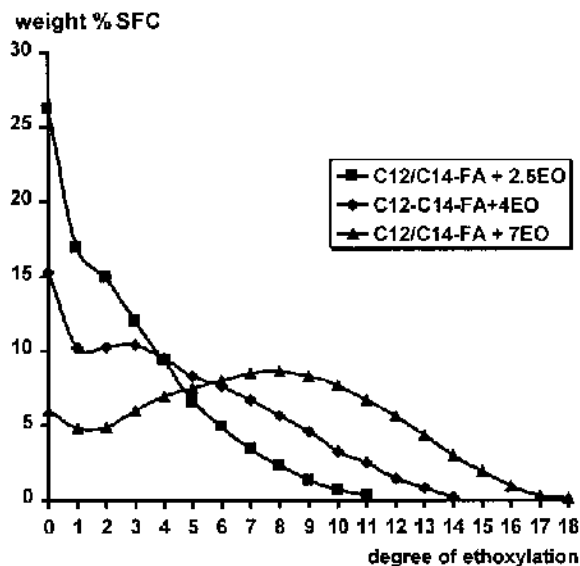


FIG. 16 Homologue distribution of broad-range ethoxylates.

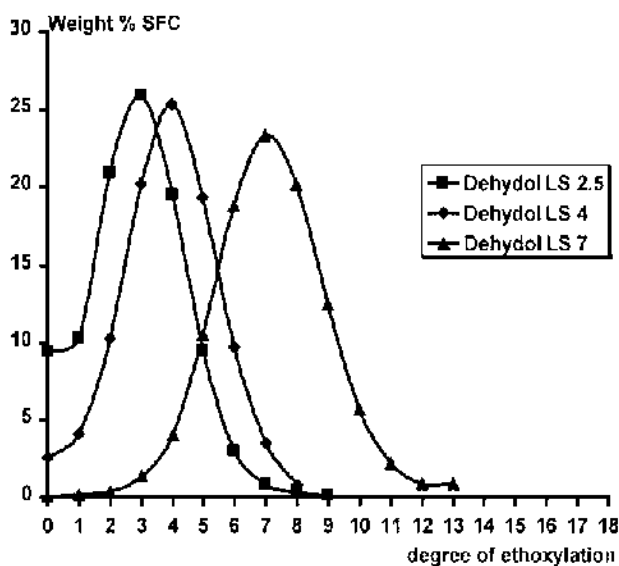


FIG. 17 Homologue distribution of narrow-range ethoxylates.

them unattractive for use as commodities. Areas of application can be found, however, where the improved physicochemical behavior gives enough benefits. Examples are thickeners for surfactant systems, cloud point extractions, lower odor, better solubility, etc.

## 1. Polyoxyethylene Alkyl Phenols (APEs) [143]

APEs have played an important role in the nonionic surfactant market. Most commonly these products are based on nonyl phenol or octyl phenol. Their application is almost universal because of their good performance characteristics. The alkyl phenols are normally *para*-substituted phenols with highly branched alkyl groups derived from the alkylation of phenol with olefins at an acidic catalytic contract such as boron trifluoride, acid montmorillonite-clay, or others. In contrast to nonyl phenol (nonyl is derived from propylene trimer), octyl phenol has a more defined structure with the alkyl chain coming from diisobutylene.

The process for the production of APEs is very similar to the ethoxylation of aliphatic alcohols. The homologue distribution is narrower than for alcohol ethoxylates because the first mole of EO reacts nearly quantitatively with the relative acidic alkyl phenol, giving a nearly statistical (Poisson) distribution for the rest of the chain.

APEs have a very broad application range, for example, in agriculture, detergents, cleaners, textile, paints, paper, and leather. The importance of APEs in European countries is decreasing because of environmental considerations [144,145]. There are environmentally persistent degradation products with possible estrogenic effects. The European detergent industry has agreed on self-limitation of the use of APEs. Numerous discussions and environmental risk assessments of APE are continuing.

## 2. Aliphatic Polyoxyethylene Alcohols (AEs)

Aliphatic alcohols are the most important source for nonionic surfactants made by ethoxylation or propoxylation [140]. The alcohols are derived either from natural fats and oils or from petrochemical raw materials.

Transesterification with methanol or esterification of fatty acids, resulting from the hydrolysis of natural triglycerides, followed by hydrogenation of the methyl ester results in straight-chain saturated or unsaturated alcohols in the alkyl range from C<sub>8</sub> to C<sub>18</sub>.

Synthetic alcohols can be prepared from Ziegler or oxo processes [146–148]. The former results in even carbon numbers [149,150], which can compete with natural fatty alcohol; the latter results in branched-

chain alcohols (hydroformylation of olefins). The oxo derivatives are more interesting for cold-water applications.

Polyethylene alcohols are mostly classified by their hydrophile-lipophile balance (HLB) [151–153], which is a measure of the balance between the hydrophilic EO headgroup and the lipophilic hydrocarbon tail.

The simplest way to calculate the HLB number is from the following equation:

$$\text{HLB} = E/5$$

where E is the amount of EO calculated in wt% of the molecule. Knowledge of the HLB value gives a rough guide to the application areas of AE:

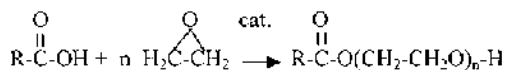
HLB	Application
4–6	w/o—emulsifier
7–15	wetting agents
8–18	o/w—emulsifier
10–15	typical detergent
10–18	solubilizers

An important physical chemical property of AEs is the cloud point (ASTM D2024 test method). Whereas the solubility of ionic surfactants increases with temperature, polyoxyethylene alcohols become insoluble at high temperatures. The temperature at which the aqueous surfactant solution becomes cloudy is called the cloud point and is also a characteristic of the relation of the hydrophilic EO chain to the hydrophobic alkyl chain. This phenomenon can be explained by the breaking of hydrogen bonds that cause insolubility at high temperatures and is used as an important specification of AEs.

Interestingly, the detergency of AEs reaches its optimum near the cloud point, so the cloud point can be useful in the choice of the right surfactant for a specific application. Alternatively, the hydrophile of AE can be measured by clouding phenomena in mixed systems such as isopropanol/water or butyldiglycol/water.

Another systematic approach in choosing the right AE for application as an emulsifier is the phase inversion temperature (PIT) concept [154,155]. This refers to the phase inversion from oil/water (o/w) to w/o in a ternary system of oil, water, and surfactant.

The applications of AEs are widespread: detergents and cleansers, emulsifiers, textile, agriculture, intermediates for sulfonation, paper industry, and emulsion polymerization, to name a few. With regard to their importance, AEs have been studied very intensively



**SCHEME 10**

concerning their ecotoxicity and can be regarded as environmentally safe [156].

### 3. Ethoxylated Fatty Acids and Esters

(a) *Fatty Acid Ethoxylates.* Ethoxylated fatty acids can generally be obtained by two different methods: (1) esterification of fatty acids with polyethylene glycol and (2) Ethoxylation of fatty acids. In the esterification [157] mixtures of mono- and diacids, esters are formed because of the two hydroxyl groups in the polyethylene glycol that exhibit the same reactivity. By using an excess of fatty acid, the formation of diesters is favored [158]. Pure monoesters can be obtained by reaction of polyethylene glycol with basic acid, esterification of the borate obtained with fatty acid, and then selective splitting of the boric acid ester [159].

The ethoxylation of fatty acids is carried out in the presence of alkaline catalysts at temperatures between 120 and 200°C and a pressure of 1–5 bars (Scheme 10). Because monoesters of polyoxyethylene transesterify easily, polyoxyethylene diesters and free polyoxyethylene are also formed during the ethoxylation of fatty acids (Scheme 11). The molar ratios of monoesters to diesters to free polyoxyethylene (polyethylene glycol) are found to be approximately 2:1:1. For example, a 7 mole EO adduct of pentadecanoic acid contains monoester (48%), diester (40%) and polyethylene glycol (12%) [160]. A comprehensive overview of the chemistry and the properties of ethoxylated fatty acids has been published [161,162]. Their main areas of application are emulsifiers in metalworking, mold lubricants, textiles, and because of their toxicologic and dermatologic harmlessness, cosmetic and pharmaceutical formulations.

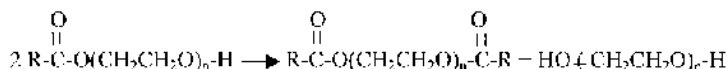
(b) *Ethoxylates of Fatty Acid Methyl Esters.* Raw materials that contain an active hydrogen atom in the molecule, e.g., fatty alcohol, fatty acids, anions, or partially esterified polyol esters, can easily be converted with ethylene oxide to the corresponding ethoxylates by using standard alkaline catalysts (e.g., NaOCH<sub>3</sub>, KOH). Therefore, direct conversion of methyl esters is

not possible if these conventional catalysts are used. However, new catalysts based on Ca/Al or Mg/Al compounds were developed that enable insertion of ethylene oxide into the ester bond and yield a monomethyl ether of an ethoxylated monoester or a fatty acid methyl ester ethoxylate (FMEO or MEE) [163–167] (Scheme 12).

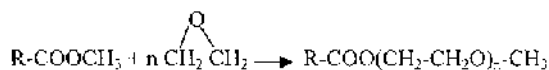
It is assumed that the reaction takes place on the surface of the catalyst, where the bifunctional effect of acid-base active sites, caused by the different cations, results in a dissociative chemisorption of fatty acid methyl ester. This leads to a direct insertion of ethylene oxide, which involves coordinated anionic polymerization [164,168]. The products are obtained in high yields with a normal or narrow range homologue distribution. Because the product composition is very similar to that of alcohol ethoxylates, the general surfactant properties are comparable [163,165,167,169]. FMEOs can be used in dishwashing agents, household hard surface and all-purpose cleaning, as well as in industrial and institutional applications. Mid- to high-mole lauryl and tallow range FMEO exhibit high detergency. Compared with alcohol ethoxylates, FMEOs are less foaming and dissolve in water much faster without going through a gel phase [166]. FMEOs are readily biodegradable, exhibit low aquatic toxicity [166], and have outstanding dermatological compatibility [170,171]. Because of the ester bond, FMEOs are susceptible to hydrolysis. They are stable in aqueous formulations in a pH range from 3 to 9.

### 4. Ethoxylated Oils and Glycerides

Partially esterified glycerol with fatty acids, monoesters (“monoglycerides”), and diesters (“diglycerides”) can be ethoxylated by using standard alkaline catalysts (e.g., NaOCH<sub>3</sub>, NaOH, KOH) and standard reaction conditions. Purified triesters (“triglycerides”) do not possess an active hydrogen atom in the molecule to offer ethylene oxide a reaction site (an exception is castor oil, which contains a secondary hydroxyl group). In this case the addition of water or glycerol, which causes the formation of partial glycerides, enables the reaction. In both cases using partial glycerides or triglycerides, a complex mixture of different products is obtained: free glycerol and glycerides (mono-, di-, tri-) and ethoxylated glycerol and glycerides as well as fatty acid ethoxylates and free polyethylene glycol. In



**SCHEME 11**



**SCHEME 12**

the case of castor oil ethoxylated with 40 moles of ethylene oxide, the product composition has been analyzed [172].

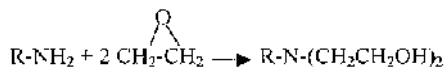
Besides the preceding ethoxylation products, higher esters were identified in which the secondary hydroxyl group is esterified with ricinoleic acid. Surprisingly, the degree of ethoxylation of the secondary hydroxyl group was rather low. Ethoxylated glycerol esters are used widely in the cosmetic industry, e.g., for emulsification, solubilization, refatting, thickening, improvement of the dermatological properties of basic surfactants, and improvement of skin feel [173]. Castor oil or hydrogenated castor oil ethoxylates play an important role in body care applications and as solubilizers or emulsifiers in pharmaceutical formulations.

### 5. Ethoxylated Amines and Alkanol Amides

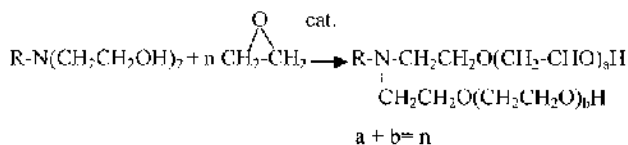
The synthesis of ethoxylated amines can be separated into two reactions [174,175]. In the first step an amine is reacted with ethylene oxide to an amino alcohol in such a way that every H atom of the amine reacts with one ethylene oxide molecule (Scheme 13). The second step is the growth of the polyoxyethylene chain through reaction of more ethylene oxide with the hydroxyl groups of the amino alcohol (Scheme 14). Whereas in the first reaction step no catalyst is necessary, the second step requires a catalyst such a sodium or potassium hydroxide.

The most commercially available surfactants prepared by this method are the fatty amine ethoxylates. Another class of ethoxylated amines are the "Jeff-amines" and the "Tetronics." Jeffamines are prepared by first ethoxylating a short-chain alcohol or glycol. This alcohol ethoxylate is then aminated to generate an amine [176,177]. Tetronics are made by ethoxylation of low-molecular-weight diamines, e.g., ethylenediamine. These products are tertiary amines and often consist of mixtures of ethylene oxide and propylene oxide adducts.

Ethoxylated amines have a wide range of applications [178]. They are used, for example, as emulsifiers,



**SCHEME 13**



**SCHEME 14**

solubilizers, and antistat additives. This application range varies from cleaning and detergent formulations to additives in gasoline and drilling fluids.

### B. Amine Oxides

A special class of surface-active substances are amine oxides, which belong in the class of nonionic components. This classification is true, however, only under alkaline and neutral conditions. In acid solutions they react weakly to form cationics.

The synthesis of amine oxides happens relatively simply by the reaction of tertiary amines with hydrogen peroxide in an aqueous medium according to Scheme 15. Because of the oxidizing environment, amine oxides sometimes contain nitroso amines, which are suspected of being carcinogenic. References [178–182] describe manufacturing methods to avoid these undesirable by-products.

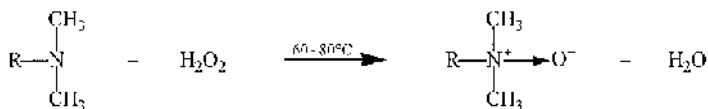
The foaming, wetting, and cleaning properties as well as the ecotoxicological aspects of C<sub>12</sub>–C<sub>18</sub> alkyl dimethylamine oxides have been discussed previously [183]. Also, good thickening performance is mentioned.

Amine oxides are very important emulsifiers for many applications in which the reemulsification of absorbed components must be prevented. Such an application is possible because of the decomposition of amine oxides at temperatures above 100°C to yield olefins and derivatives of hydroxylamine (Scheme 16). This reaction is taken advantage of, for example, in the application of waterproofing agents to textiles.

An interesting variety is the thermal decomposition of amine oxides that are based on ethers of dimethyl ethanolamine [184]. The vinyl ethers formed are known as reactive olefins [185]. Produced from a base of dimethyl ethanolamine esters, the preparation of vinyl esters becomes possible (Scheme 17).

## IV. CARBOHYDRATE BASED SURFACTANTS

Carbohydrate-based surfactants are the final result of a product concept that is based on the greatest possible



**SCHEME 15**

use of renewable resources. Whereas the derivatization of fats and oils to produce a variety of different surfactants for a broad range of applications has a long tradition and is well established [186], the production of surfactants based on fats, oils, and carbohydrates on a larger industrial scale is relatively new. The following will discuss the most important carbohydrate-based surfactants, such as sorbitan esters, sucrose esters, alkyl polyglucosides, and fatty acid glucamides, with primary focus on the glucose-derived products.

Considering the amphiphilic structure of a typical surfactant with a hydrophilic headgroup and a hydrophobic tail, it has always been a challenge to attach a carbohydrate molecule as the perfect hydrophilic group, due to the numerous hydroxyl groups, to a fat and oil derivative such as a fatty acid or a fatty alcohol [187]. Although scientists have reported numerous ways of making such linkages and have also described a large number of different carbohydrates used in such reactions, it is clear from an industrial perspective that only a few carbohydrates fulfill the criteria of price, quality, and availability to be an interesting raw material

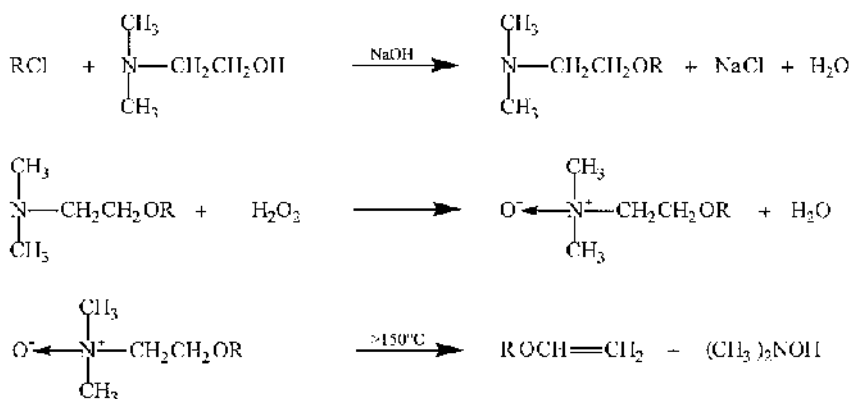
source. These include sucrose from sugar beet or sugar-cane, glucose derived from starches, and sorbitol as the hydrogenated glucose derivative (Table 1). Most industrial developments in the field of sugar-based surfactants have concentrated, and still concentrate, on these carbohydrate feedstocks.

### A. Sorbitan Esters

Sorbitan esters have been known for decades since the first industrial processes were established for their manufacture. One differentiates between a one-stage and a two-stage process (Fig. 18). In the first process, water is eliminated from sorbitol as a first step to form sorbitan, which is subsequently derivatized with fatty acid as a second step. In the second process, both reactions are carried out simultaneously [188]. Both methods have been developed for industrial scale production. Depending on the type and amount of fatty acid used, different types of sorbitan esters (e.g., laurates, oleates, or stearates) are produced with hydrophilic-lipophilic balance (HLB) values in a range of 1 to 8. To modify



**SCHEME 16**



**SCHEME 17**

**TABLE 1** Availability of Carbohydrate Raw Materials

Material	Production volume (t/a) <sup>a</sup>	Average price (\$/kg) <sup>b</sup>
Sucrose	130,000,000	0.70–0.80
Glucose	16,000,000	0.55–1.12
Sorbitol	8,000,000	0.53–1.70

<sup>a</sup>Private communication (Cerestar, Henkel).

<sup>b</sup>According to Chem. Market. Rep. 3/97 and 7/97.

these relatively hydrophobic materials, it is common technology to derivatize the sorbitan esters further by reaction with ethylene oxide to produce sorbitan ester ethoxylates—or polysorbates for short—with HLB values of 10–17, depending on the number of ethylene oxide units attached (Fig. 19) [188a].

The main manufacturers for sorbitan ester products today are listed in Table 2. The total market size for sorbitan esters (including the ethoxylated products) is estimated to be approximately 25,000 tons per year. Mainly used as emulsifiers in pharmaceuticals, foods, cosmetic products, for emulsion polymerization and explosives, and for other technical applications, sorbitan ester products seem to have a relatively stable market size and there is obviously no attempt, and no need, for further development of this mature technology.

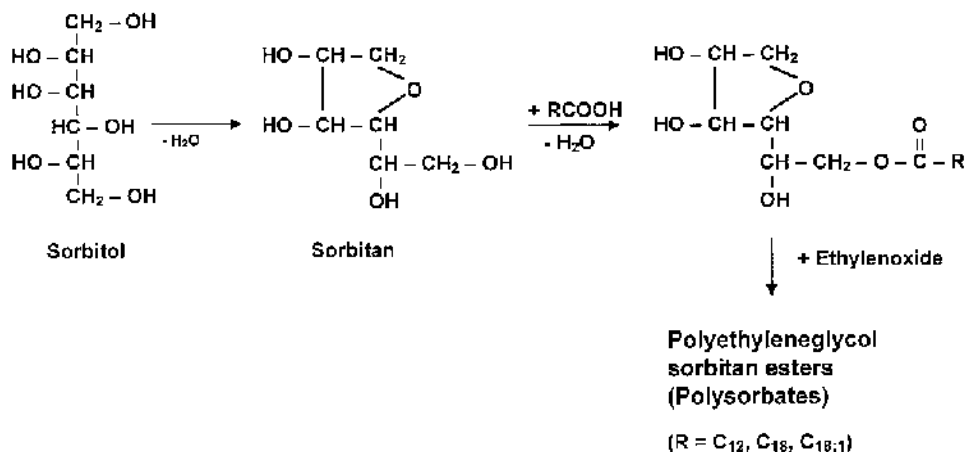
## B. Sucrose Esters

The situation is different in the field of sucrose esters. Described as very mild with regard to their dermatological properties and approved as food additives in

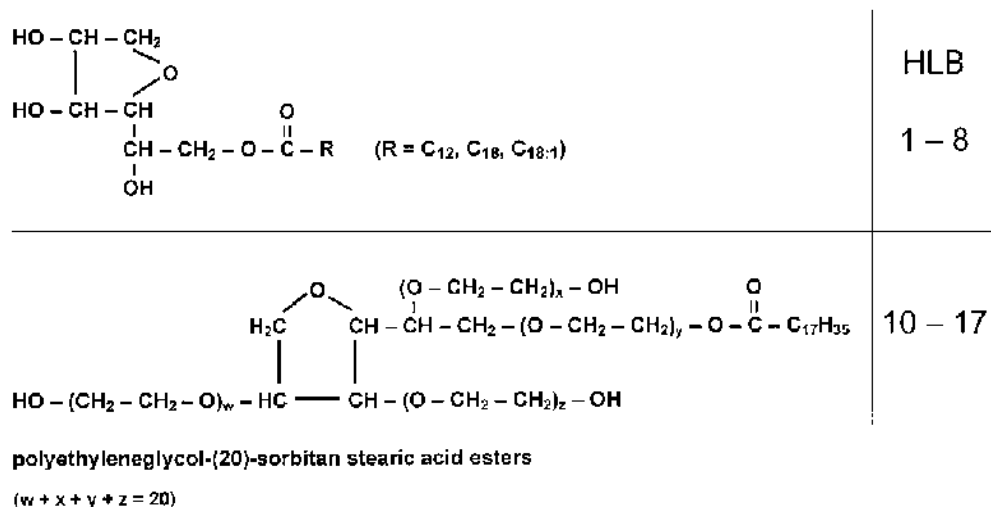
many countries, these products are perfect raw materials for personal care products, cosmetic applications, and food emulsifiers [189]. In Asia, one can find sucrose esters in special detergent products as well.

The problem in manufacturing sucrose esters is related to the high functionality of the sucrose molecule with eight hydroxyl groups, which compete during the derivatization step (Fig. 20). In a typical esterification reaction of sucrose with fatty acid methyl ester, a complex product mixture consisting of mono-, di-, tri-, tetra-, and pentaesters is formed (Fig. 21). These products are very hydrophobic and of limited application potential. Therefore, several methods have been developed to achieve higher selectivity in the reaction or provide economical purification procedures and, as a result, a high quantity of monoester. These include the use of solvents and fatty acid chlorides, special extraction and crystallization techniques, enzymatic catalyses, and equilibrium reactions. Figure 22 shows the increase of the monoester content in a sucrose laurate product achieved by alcoholysis with methanol [189c]. However, most of the methods remain limited to laboratory scale because of the process economics. Standard technology (conventional method, Fig. 23) is still transesterification combined with purification. Here, an optimized solvent-free process has been described (Fig. 23) [189b].

Today, the major producers of sucrose esters are Dia-Ichi Kogyo Seiyaku and Mitsubishi in Japan, Croda in the United States, Sisterna (a joint venture of Dai-Ichi with Suiker Unie from The Netherlands), and Goldschmidt in Germany (Table 2). It seems that the production capacities that exist today are much higher



**FIG. 18** Synthesis of sorbitan esters by intramolecular dehydration of sorbitol in the presence of acid (e.g.,  $\text{NaH}_2\text{PO}_3$ ) at about 150–200°C and subsequent base-catalyzed (e.g.,  $\text{Na}_2\text{CO}_3$ ) esterification with fatty acids ( $\text{RCOOH}$ ) at 200–250°C.

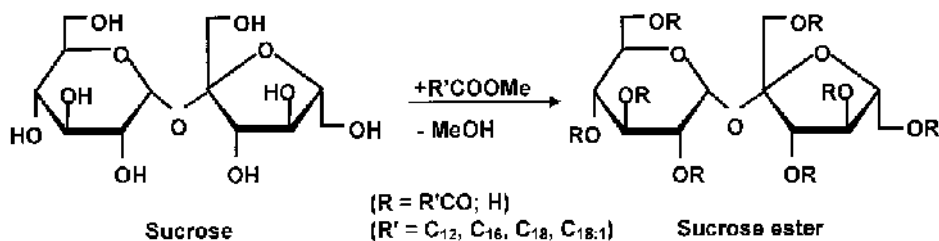


**FIG. 19** Hydrophilicity of sorbitan esters.

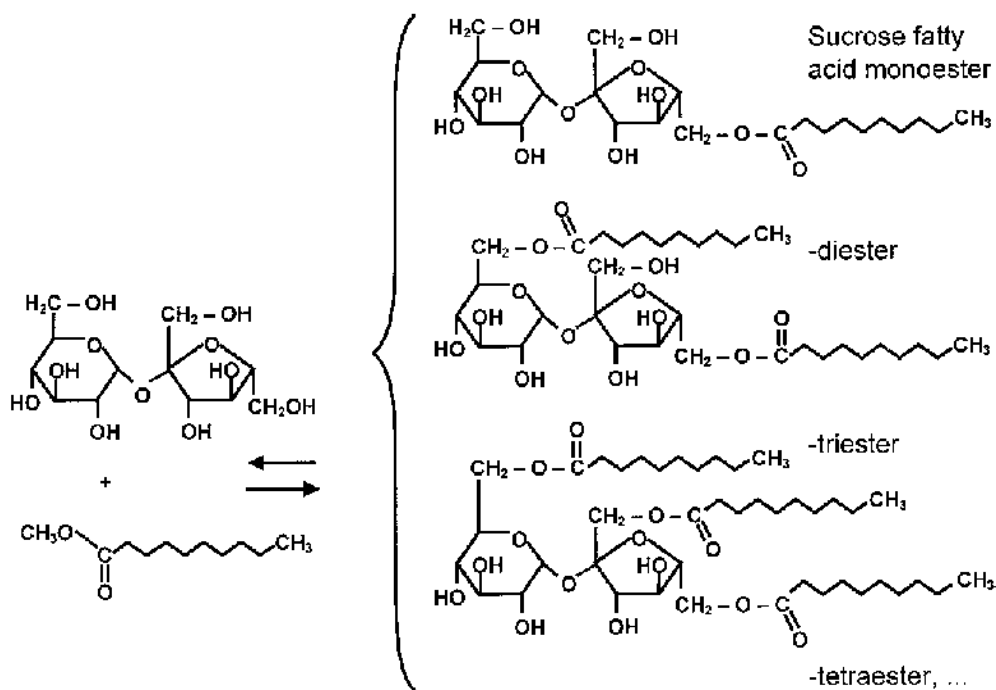
**TABLE 2** Fields of Application and Production Capacities for Sugar-Based Surfactants

Surfactants	Manufacturers	Fields of application	Production capacity, world (t/a) <sup>a</sup>
Sorbitan esters	Akros, Dai-ichi Kogyo Seiyaku, Cognis, Kao, ICI, Montedison, PPG, Riken Vitamin, SEPPIC, Witco	Pharmaceuticals, personal care, food, fiber, agrochemicals, coatings, explosives	20,000
Sucrose esters	Croda, Dai-ichi Kogyo Seiyaku, Goldschmidt, Mitsubishi, Sisterna, Weixi Spark	Food, personal care, pharmaceuticals	<4,000
Alkyl polyglycosides	Akzo Nobel, BASF, Cognis, ICI, Kao, Nihon Seika, SEPPIC, Union Carbide	Personal care, detergents, agrochemicals, I + I	80,000
Fatty acid <i>N</i> -methyl glucamides	Pfizer/Hatco, Clariant	Detergents	40,000
Methylglucoside esters	Amerchol, Goldschmidt	Personal care, pharmaceuticals	10,000
Anionic alkyl polyglycoside derivatives	Pilot Chemical Co., Lamberti Spa.	Personal care	

<sup>a</sup>Estimated figures based on private communications and literature data, references given in the text.



**FIG. 20** Synthesis of sucrose esters by base-catalyzed ( $\text{K}_2\text{CO}_3$ ) transesterification with fatty acid methyl esters ( $\text{R}'\text{COOMe}$ ), usually carried out in solvents (e.g., dimethyl formamide at  $\sim 90^\circ\text{C}$ ) or microemulsions.



**FIG. 21** Product composition and equilibrium in the synthesis of sucrose esters by transesterification with fatty acid methyl ester.

than the actual market potential, which is estimated to be less than 4000 tons per annum. However, demand and market volume could increase substantially if reaction processes, especially for the synthesis of high-mono products, can be further optimized.

### C. Glucose-Derived Surfactants

The first step in overcoming the problem of nonselective derivatization of carbohydrates was achieved when Emil Fischer discovered the reaction of glucose with alcohol to form alkyl glucosides [190]. The glucosidation reaction is highly selective because of the hemiacetal function in the glucose molecule and the resulting high reactivity of the hydroxyl group at C-1. The same is true for the synthesis of fatty acid glucamides. Here the glucose molecule reacts initially with methylamine, which, after hydrogenation, selectively yields the glucamine as an intermediate [191]. Further derivatization with fatty acid methyl ester leads to the desired product.

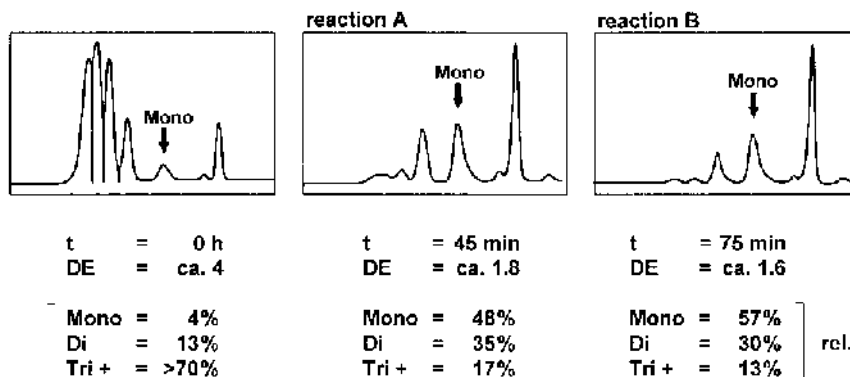
#### 1. Synthesis of Alkyl Polyglycosides

The first syntheses of alkyl polyglycosides were carried out more than 100 years ago. In the course of further developments, the reaction of glucose with alcohols was applied to long-chain alcohols with alkyl chains

from  $C_8$  to  $C_{16}$ . The result of the reaction is a complex mixture of alkyl mono-, di-, tri-, and oligoglycosides as a mixture of  $\alpha$ - and  $\beta$ -anomers (Fig. 24). Therefore, the industrial products are called alkyl polyglycosides. The products are characterized by the length of the alkyl chain and the average number of glucose units linked to it—the degree of polymerization (DP) [192].

The crucial point with regard to the development of an industrial process was to establish reaction conditions that allowed the manufacturing of high-quality products under safe and economically acceptable conditions. This was achieved by optimizing the reaction parameters temperature, pressure, reaction time, and ratio of glucose to fatty alcohol. Of equal importance was the design of a special distillation technology to remove the excess fatty alcohol as smoothly as possible, as well as appropriate bleaching and stabilization in the final treatment step (Fig. 25). This so-called direct synthesis of alkyl polyglycosides is the currently preferred manufacturing mode. However, two-stage processes have been developed as well and are used, for example, by Hüls AG on a pilot plant scale. The breakthrough in the production of long-chain ( $C_{12/14}$ ) alkyl polyglycoside occurred in 1992 with the inauguration of an approximately 25,000 tons per annum production plant for APG surfactants by Henkel Corporation in the





**FIG. 22** High mono sucrose esters by transesterification of sucrose in excess fatty acid methyl ester (without additional solvent) at about 140°C (~20 h) and simultaneous removal of methanol to form sucrose esters with a high degree of esterification (DE = ~4), subsequent alcoholysis of the sucrose ester by addition of methanol at 75°C (reaction A: 45 min, reaction B: 75 min) to form sucrose monoester and fatty acid methyl ester, and removal of residual methanol and fatty acid methyl ester using a thin-film evaporator (160°C, 0.2–0.3 mbar). Product analysis by high-performance liquid chromatography shows the increase of the sucrose monoester (Mono) content to 48% (DE = ~1.8, reaction A) and 57% (DE = ~1.6, reaction B) relative to sucrose diester (Di) and sucrose oligoesters (Tri+).

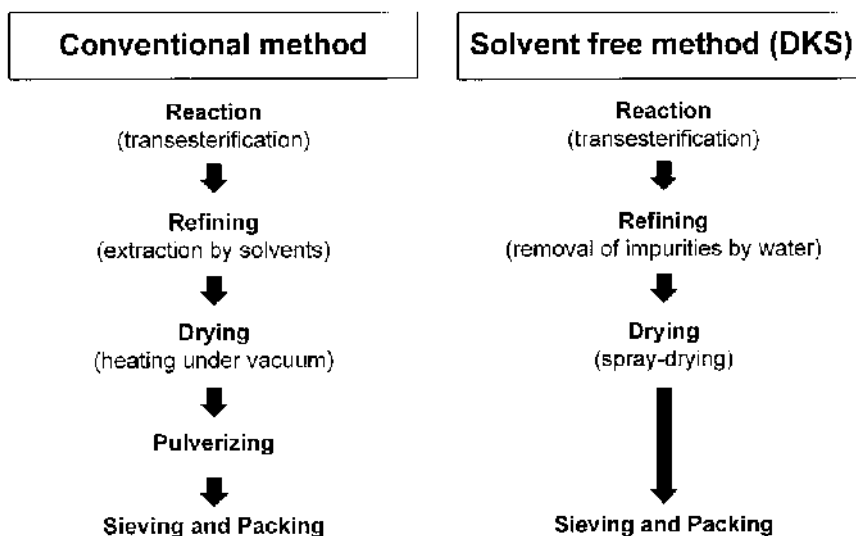
United States and in 1995 with the opening of a second plant of equal capacity by Henkel in Germany.

Today, the main producers of alkyl polyglycosides are Cognis, Seppic, ICI, Kao, Union Carbide, and BASF with an estimated total production capacity of approximately 80,000 tons per annum. The main applications for the C<sub>12/14</sub> alkyl polyglycosides are liquid dishwashing agents and detergents and personal care products. For the C<sub>8/10</sub> (or branched C<sub>8</sub>) alkyl polyglycosides, there are hard surface cleaners, agrochemicals,

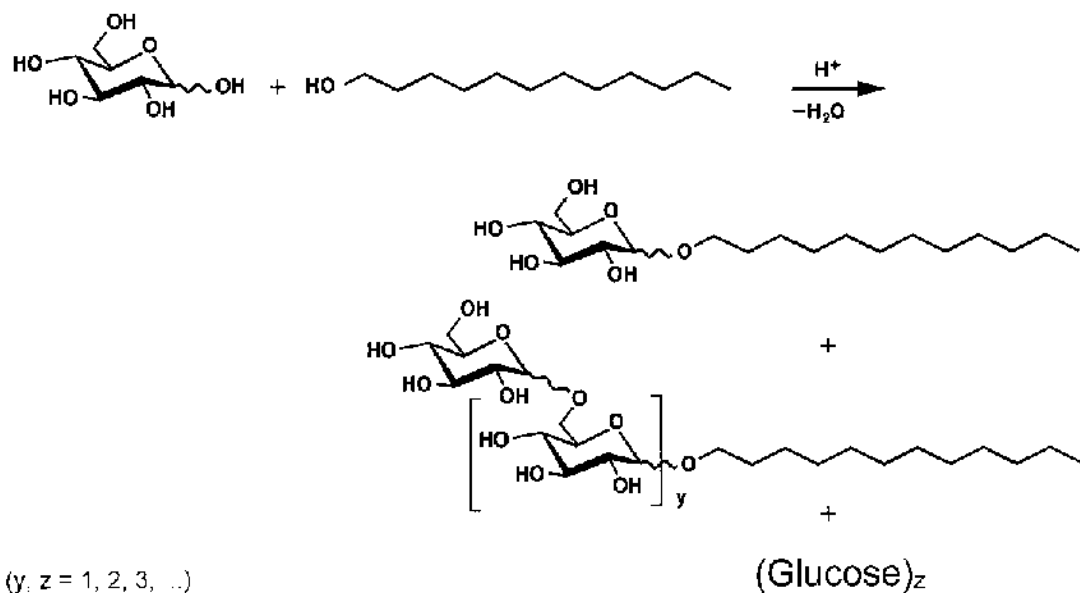
and products for industrial, institutional, and personal care cleansing (Table 2).

## 2. Fatty Acid Glucamides

The synthesis to produce fatty acid glucamides involves the reaction of glucose with methylamine, under reductive conditions, to form the corresponding *N*-methylglucamine. In a subsequent reaction step, this intermediate is converted with fatty acid methyl ester to the corresponding fatty acid amide. Compared with



**FIG. 23** Process schemes for the production of sucrose esters.

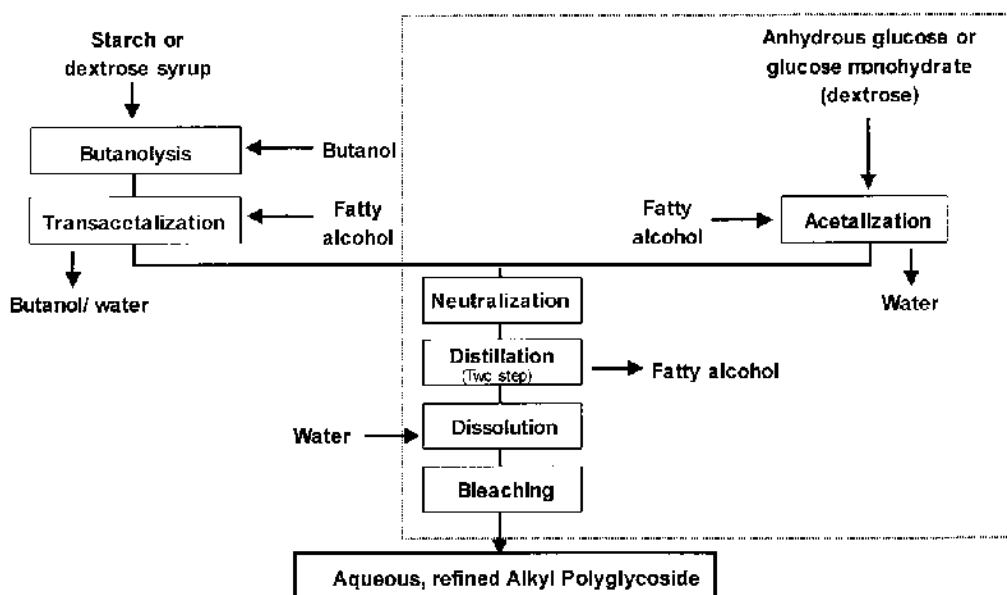


**FIG. 24** Synthesis of alkyl polyglycosides by acid-catalyzed (*para*-toluenesulfonic acid) acetalization of glucose in molar excess of fatty alcohol (2- to 6-fold) and removal of water under vacuum at 100–120°C.

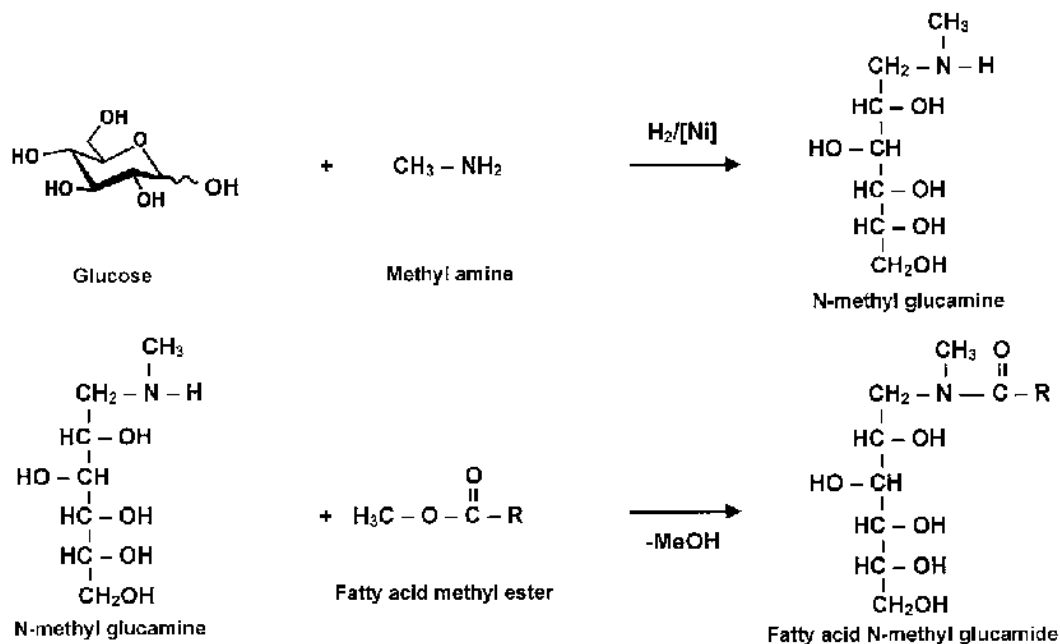
the alkyl polyglycosides, fatty acid glucamides are composed of only a single carbohydrate molecule attached to the fatty acid chain (Fig. 26). This is one reason why fatty acid glucamides are less soluble and tend to crystallize more easily from aqueous solutions.

Figure 26 shows the manufacturing scheme for the production of fatty acid glucamides. To avoid signifi-

cant amounts of unreacted *N*-methylglucamine, which could be considered as potential precursors for nitrosamines, Procter & Gamble has developed an optional reaction with acetic anhydride in the finished product. Free secondary amines can be acetylated in this step, and the resulting acetates can remain in the final product [193].



**FIG. 25** Scheme for the production of alkyl polyglycosides.



**FIG. 26** Two-step synthesis of fatty acid glucamides by reductive alkylation of methylamine with glucose using Raney nickel as the hydrogenation catalyst to obtain *N*-methyl glucamine, which is acylated by base-catalyzed reaction with fatty acid methyl ester in a second step.

The existing production capacity is estimated to be 30,000 to 50,000 tons per annum active substance according to a study by Colin A. Houston & Associates [194]. Producers are Pfizer, Hatco in the United States, and Clariant (formerly Hoechst) in Germany (Table 2).

### 3. Properties of Alkyl Polyglycosides and Fatty Acid Glucamides

With regard to their basic physicochemical properties, such as surface and interfacial tension and critical micelle concentration, alkyl polyglycosides and fatty acid glucamides ( $C_{12/14}$ ) are very comparable. There are slight differences in the basic foam behavior for the pure sugar-based surfactants as well as binary combinations. With regard to their ecological, toxicological, and dermatological properties, alkyl polyglycosides as well as fatty acid glucamides can be considered as surfactants with extraordinary product safety characteristics. This has been proved for both products in a series of detailed investigations. The results are published in several papers, mainly by Henkel and Procter & Gamble but also by independent research institutes [195].

Although it can be concluded that alkyl polyglycosides and fatty acid glucamides are more or less comparable with regard to their basic performance in detergents and dishwashing agents, there might be dif-

ferences in specific product formulations. If, for example, the stability of concentrated manual dishwashing detergents is investigated, as in the case of a paste based on alkyl ether sulfate and alkyl polyethylene glycol ether, it is found that best results are obtained when alkyl polyglycosides are used as cosurfactants (Table 3) [196]. In general, glucose-derived surfactants have shown to be very efficient components in manual dishwashing detergents and liquid and powder detergents [196]. In contrast to alkyl polyglycosides, fatty acid glucamides are thus far not known in applications other than detergents.

In personal care products, alkyl polyglycosides represent a new concept in compatibility and care. They may be combined with conventional components and can even replace them in new types of formulations, leading to a broad spectrum of supplementary effects. With regard to foam, they are comparable to betaines and sulfosuccinates but do not match the foam volume of alkyl ether sulfates. On the other hand, alkyl polyglycosides can stabilize the foam of anionics in hard water and in the presence of sebum. The alkyl polyglycoside foam consists of finer bubbles and is more creamy than in the case of SLES (Fig. 27) [197a].

To demonstrate the large performance spectrum of alkyl polyglycosides, one more application should

**TABLE 3** Stability of Concentrated Manual Dishwashing Detergents (Pastes)

Ingredients	Product 1 (wt%)	Product 2 (wt%)	Product 3 (wt%)	Product 4 (wt%)
Alkyl ether sulfate	10	10	10	10
Alkyl polyethylene glycol ether	15	15	15	15
Fatty acid alkanolamide	18	—	—	—
Alkylamidobetaine	—	18	—	—
Fatty acid glucamide	—	—	18	—
Alkyl polyglycoside	—	—	—	18
Appearance at 68°F (20°C)	Cloudy	Gel	Clear	Clear
Pour point	—	—	54°F (12°C)	32°F (0°C)
Storage test 3 weeks, 41°F (5°C)	Solid	Solid	Solid	Clear-liquid

be mentioned briefly. Alkyl polyglycosides ( $C_{8/10}$  and  $C_{12/14}$ ) have been shown to be substitutes for alkyl phenol ethoxylates in agrochemical formulations. They lead to higher salt tolerances and show good results as adjuvants in several post applied herbicides, such as control of giant foxtail in soybeans with Assure II (DuPont) and control of common lambsquarters in soybean with Pursuit (American Cyanamid). Currently, the short-chain products ( $C_{8/10}$  and  $C_{9-11}$ ) are approved as inert ingredients by the U.S. Environmental Protection Agency (USEPA) [198].

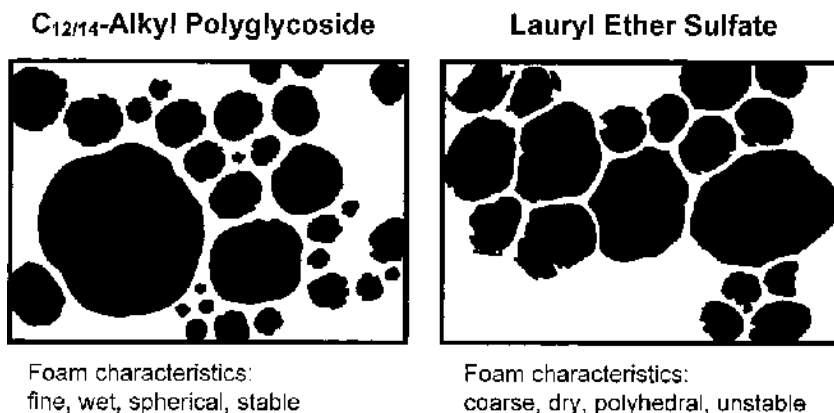
#### D. Derivatives of Alkyl Polyglycosides

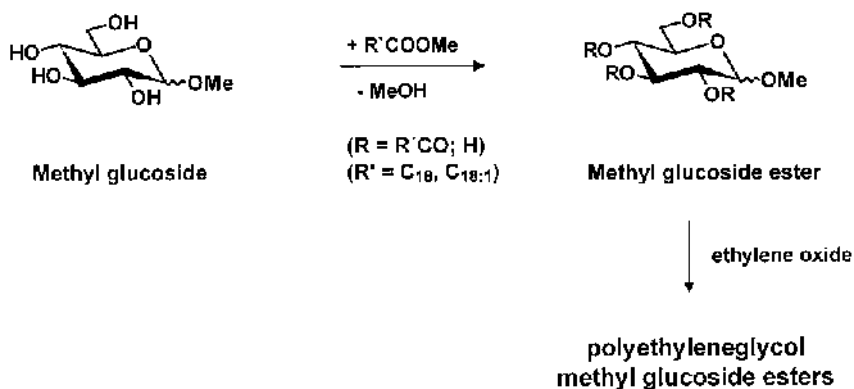
In principle, two different approaches exist to combine a hydrophobic alkyl chain with the hydrophilic glucose molecule. These are glycosylation, the reaction of glucose with an alcohol as described earlier, and acylation, the esterification or amidation of a suitable glucose derivative, such as the alkyl polyglycosides.

Because alkyl polyglycosides are available in sufficient quantities and at competitive costs at present, their use as a raw material for the development of specialty surfactants has generated considerable interest. The derivatization of alkyl polyglycosides is currently being pursued with a goal to modify the surfactant properties of alkyl polyglycosides [192b,199]. A broad range of alkyl polyglycoside derivatives can be obtained by using relatively simple methods, for example, nucleophilic substitution. In addition to the reaction to esters or ethoxylates, ionic alkyl polyglycoside derivatives, such as sulfates and phosphates, can be synthesized. However, only a few products are established in the market: methylglucoside esters and a series of special esters based on alkyl polyglycosides.

##### 1. Methyl Glucoside Esters

Esterification of methyl glucoside with methyl esters of stearic or oleic acid enhances the lipophilic character (Fig. 28). Methyl glucoside esters are, in contrast to

**FIG. 27** Foam structure of surfactant solutions.



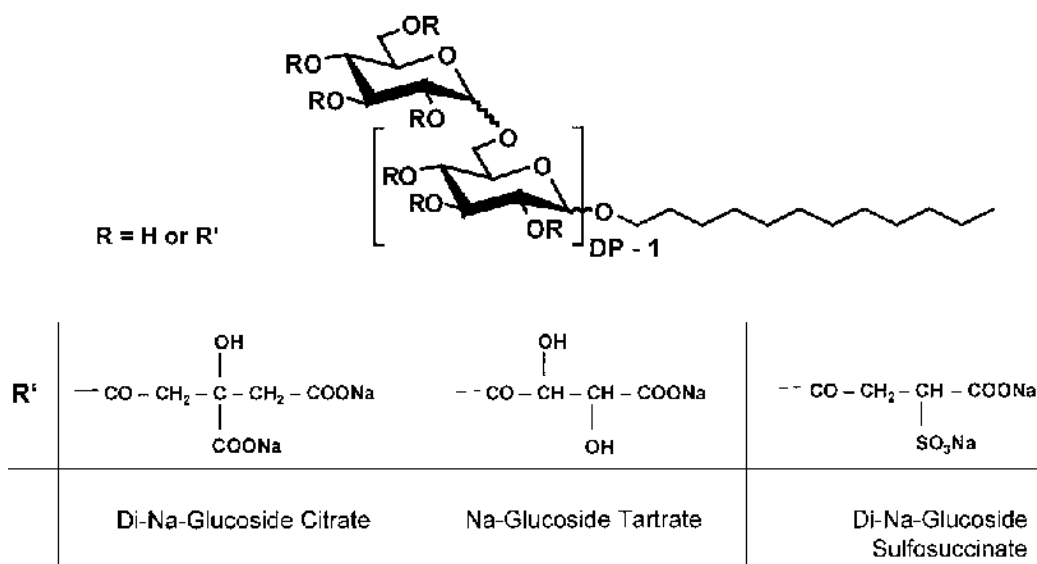
**FIG. 28** Synthesis of methyl glucoside ester by base-catalyzed ( $\text{K}_2\text{CO}_3$ ) transesterification of methyl glucoside with fatty acid methyl ester ( $\text{R}'\text{COOMe}$ ) at 120–160°C.

alkyl polyglycosides with the same hydrophobic chain length, hardly soluble in water, but they exhibit excellent emulsification properties [189b,200]. They have found application as emollients, moisturizing and emulsifying agents, and thickeners for cosmetics. The hydrocarbon length and degree of substitution can be varied to obtain specific w/o emulsification behavior. These surfactants can be further ethoxylated to give rise to polyethylene glycol methyl glucoside esters.

Major manufacturers for methyl glucoside esters are Amerchol and Goldschmidt. The total market size, including the ethoxylated products, is estimated to be 10,000 tons per annum (Table 2).

## 2. Anionic Derivatives of Alkyl Polyglycosides

Cesalpina Chemicals, a subsidiary of Lamberti Spa., Italy, has introduced three nonionic alkyl polyglycoside esters (AGEs), namely citrates, sulfosuccinates, and tartrates, that can be used in personal care applications [201a]. The syntheses start with an alkyl polyglycoside, which is esterified with citric acid, maleic anhydride and subsequent sulfonation, and tartaric acid, respectively. Structures are shown in Fig. 29. The products will be marketed in the United States by Pilot Chemical Co. (Table 2) [201b].



**FIG. 29** Examples of anionic alkyl polyglycoside derivatives.



FIG. 30 Structures of tetra-coordinated ammonium salts.

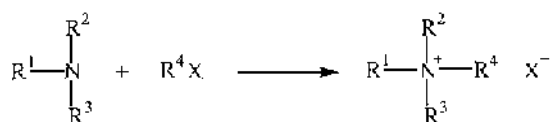
## V. CATIONIC SURFACTANTS

### A. Syntheses of Cationic Surfactants

Commonly used cationic surfactants all contain a quaternary respective tetracoordinated nitrogen atom. To possess a cationic character, these tetraalkyl ammonium salts need at least one longer alkyl chain. The simple salts of long-chain amines are often erroneously described as quaternaries as well. However, contrary to true cationic surfactants, these so-called pseudocationics are formed by neutralization with acids and thus represent protonated amines (Fig. 30). The substantial difference between both types exists in the fact that the pseudocationics show surfactant (cationic) properties only at pH values significantly lower than 7. However, this section is devoted exclusively to true quaternary surfactants.

The product class of surfactants consists of a variety of types and preparation methods. Therefore, only some basic knowledge can be considered in the scope of this review. Quaternary ammonium compounds based on nonionic surfactants are described as a specialty in Ref. 202.

Quantitatively, the most important cationics are obtained by the reaction of tertiary amines with classical alkylating reagents such as methyl chloride, dimethyl sulfate, benzyl chloride, and, infrequently, trimethyl phosphate or methyl tosylate according to Scheme 18. The residues  $\text{R}^1$ – $\text{R}^3$  represent at least one longer alkyl chain, another longer alkyl chain, or a short alkyl group such as methyl. The  $\text{R}_4$  stands for the alkyl or aryl part of the alkylating reagent, mostly methyl or benzyl, very rarely for a longer alkyl chain. Basically, the quaternization reaction is more quantitative if only one longer alkyl chain is present and the other chains are methyl groups. The quaternization reaction is carried out, nor-



SCHEME 18

mally, at a temperature between 80 and 100°C in substance or, depending on the viscosity and/or consistency, in a solvent.

Sometimes, primary or secondary amines may also serve as raw materials. First, however, they must be converted to tertiary amines by means of several alkylating methods, ultimately followed by the quaternization reaction (Scheme 19). The last reaction, Eq. (3), is of special interest because of the manufacturing of cationics on the basis of Guerbet alcohols [203].

Because of their easy biodegradability, so-called ester quats have become more important [204–206]. In principle, the synthesis is made by an esterification reaction of tertiary alkanolamines with 1.5–2 moles of fatty acids and the following quaternization (Scheme 20). Naturally, in practice, statistical mixtures of mono-, di-, and triester derivatives will be found.

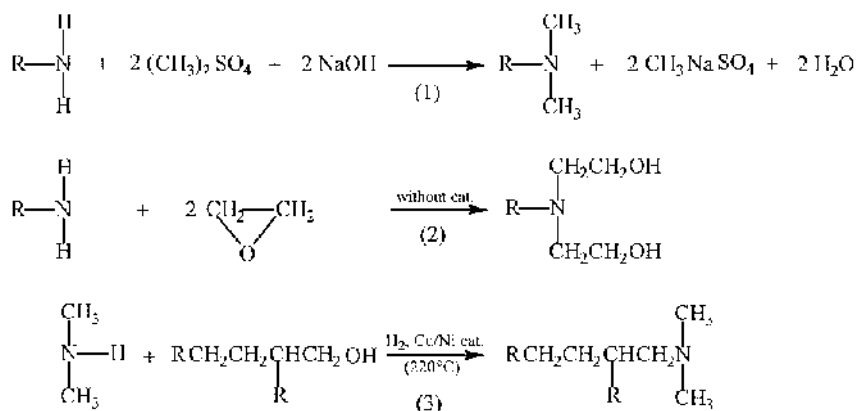
Another type of ester quat is derived from the natural substance choline and can be understood as an ester thereof. The synthesis of such cholinesters is based on dimethyl ethanolamine as a raw material (Scheme 21).

Also remarkable are cationic protein derivatives (Fig. 31) that are used for cosmetic purposes. For preparation, a partially hydrolyzed protein is reacted with epichlorohydrin and then added to a tertiary amine [207].

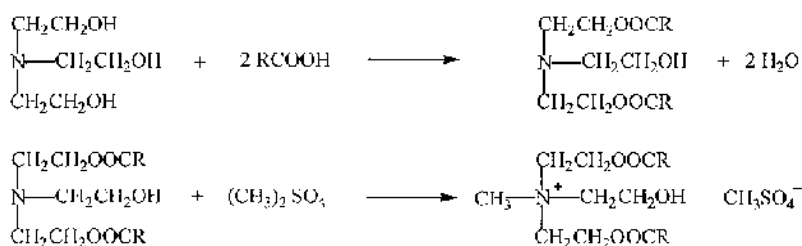
Furthermore, polymeric cationics play an important role, not with regard to the quantity but with a view to the application. There are numerous possibilities for their synthesis. For example, acrylic or methacrylic esters of dimethyl ethanolamine are used as one part in copolymers. Afterward, they can be quaternized (Scheme 22). Special reasons can make desirable an exchange of the anion, which is normally prescribed by the alkylating agents. Reference 208 presents a solution for such demands (Scheme 23).

A completely different route for the synthesis of cationic surfactants is a quaternization reaction with alkylene oxide in the presence of water [209,210] as follows (Scheme 24). The free quaternary ammonium base produced may be neutralized with any acid. Primary and secondary amines can be used advantageously in this reaction. They form quaternary derivatives with hydroxyethyl or polyoxyalkyl ether groups if the amount of epoxide is appropriate [211].

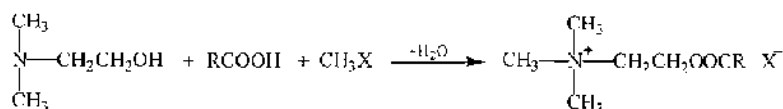
During the reaction, the thermal instability of the free quaternary ammonium bases obtained in the aqueous environment is an unpleasant disadvantage of the procedure and results in a minor yield. But fortunately, if the amine is neutralized before the addition of alkylene oxide, high yields of cationics are available



SCHEME 19



SCHEME 20



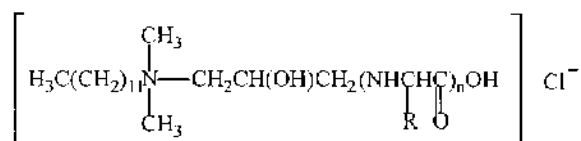
SCHEME 21

[212]. Inorganic as well as organic acids with a weak or strong character and even partial esters of polyvalent acids are suitable. The optimal reaction temperature is approximately 80°C. It should be mentioned that no strong acids force the formation of dioxane as a by-product if ethylene oxide was applied. Also, alkylene glycols are always present. Because of hydrolysis reactions, ester amines are unsuitable for this preparation method.

As per the following, a further interesting route for the preparation of polyquaternary compounds should be mentioned. Oxethylated fatty amines are polycondensed with dicarboxylic acids, i.e., adipic acid [213], and afterward quaternized with ethylene oxide [214] (Scheme 25).

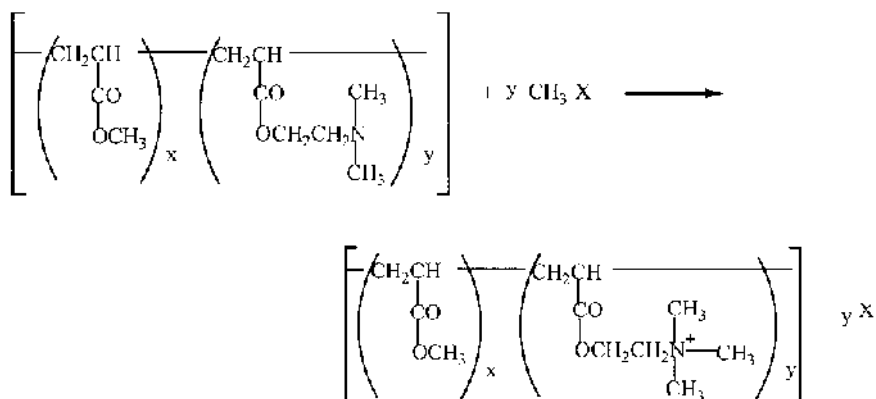
Most of the quaternization reactions here are performed with ethylene oxide or propylene oxide as well. Analogous works with long-chain epoxides normally failed because of the heterogeneity of the aqueous mixtures with the tertiary amine salts. This problem, however, has been solved [215] by the use of a phase transfer catalyst (PTC) such as dimethyl distearyl ammonium chloride. Because of its versatility, many other reaction systems are conceivable (Scheme 26).

Another class with minor technological importance are the so-called betaine esters. The somewhat misleading name can be traced back to the property that

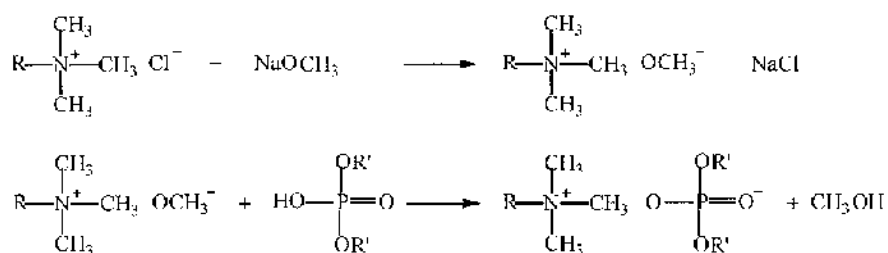


R = Side chains of amino acids in collagen

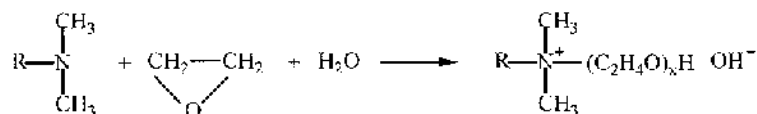
FIG. 31 Cationic protein derivative.



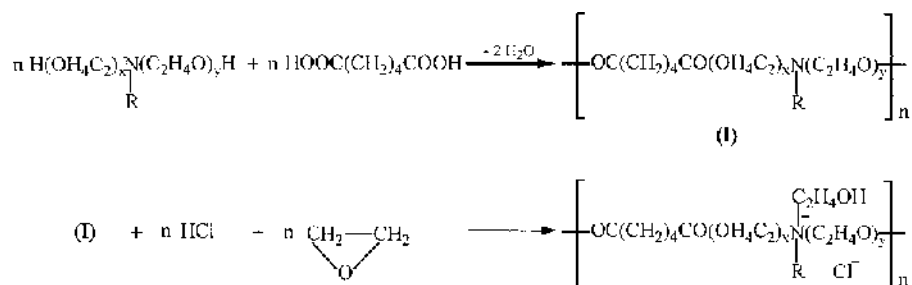
**SCHEME 22**



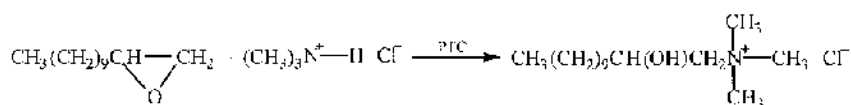
**SCHEME 23**



**SCHEME 24**



**SCHEME 25**

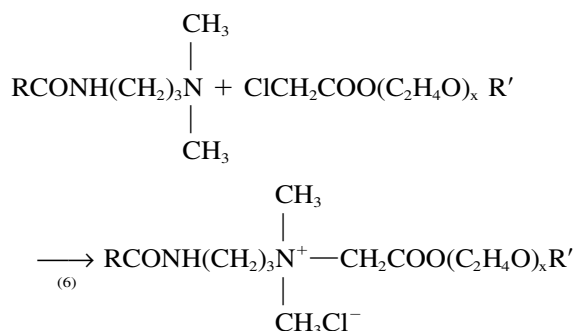
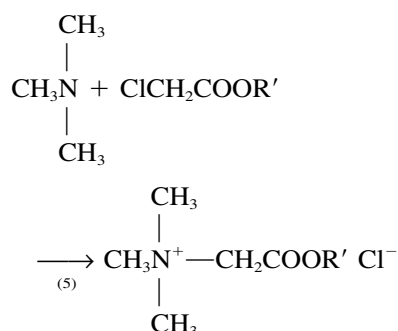
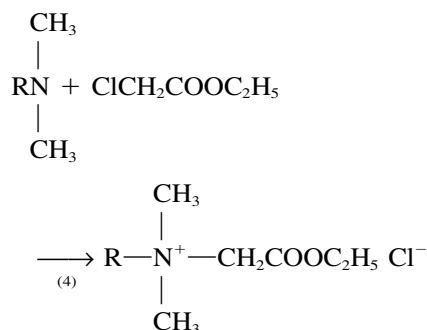


**SCHEME 26**



after hydrolysis of the ester group, a betaine results. The synthesis itself takes place by a quaternization of tertiary amines with, usually, chloroacetic acid esters. Basically, there are several possibilities:

1. The longer alkyl chain is part of the amine [216] [Eq. (4)].
2. The longer alkyl chain is part of the chloroacetic acid ester [217] [Eq. (5)].
3. Both reagents contain a longer alkyl chain [218] [Eq. (6)].



Using the same principle, multiple betaine esters based

on multifunctional tertiary amines or alcohols can be produced.

Also remarkable are cationic surfactants that are prepared by the addition of reactive substances, usually with an alcoholic group, with a preformed quaternary ammonium group. Specifically, glycidyl trimethylammonium chloride and 3-chloro-2-hydroxypropyl trimethylammonium chloride are suggested for such reactions (Scheme 27).

## B. Properties of Cationic Surfactants

### 1. Physicochemical Behavior

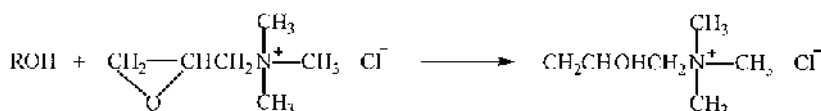
Depending on the alkyl chain, the number of longer alkyl chains, the fundamental chemistry, and, sometimes, the kind of anion, the properties of cationic surfactants are altogether highly varied. The main feature for all quaternary ammonium compounds is the substantivity to almost any surfaces that are negatively charged. By choosing a suitable product, the characteristics of many substrates may be influenced. Examples are the softness of textiles, performance of laundry detergents, antistatic behavior, corrosion inhibition, flotation processes, hydrophobic finishes, microbial treatment of hard surfaces, fixing of dyes, etc. The field of applications is almost infinitely extensive.

Regarding ambient conditions, quaternary ammonium salts are considerably stable. Only at temperatures above 100°C do they decompose through a dealkylation reaction. The incompatibility with anionic surfactants is also disadvantageous. However, the incorporation of polyoxyethylene ether chains [202] prevents this "malfunction."

Ester quats as well as betaine esters are sensitive to hydrolysis, which makes them easily decomposable into the sometimes desired non-surface-active compounds. For special information, hydrolysis studies of betaine esters can be found in Ref. 219.

### 2. Ecological and Toxicological Behavior

Both properties depend, to a high degree, on the kind of molecule and the chain length of the alkyl group(s). The quaternary ammonium salts that contain ester functions are easily biodegradable, whereas the other types of cationic surfactants are not eliminated even after a longer adaptation time. A study of the biodegradation



**SCHEME 27**

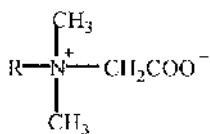


FIG. 32 Structure of betaines.

of the latter types [220] describes a pathway in which amine oxides are formed as intermediates.

Because of the variety of cationic surfactant types, it is impossible to make generally binding statements about toxicity within the scope of a short review. Only a few aspects should be highlighted.

Sometimes, the alkyl chain length may be responsible for toxicological effects. A comparison between behenyl and stearyl derivatives regarding eye and skin irritation showed that the behenyl chain dramatically lowers irritation potential [221].

Because of their excellent biodegradability, ester quats show moderate aquatotoxicity (Biological Laboratories of Henkel KGaA, private communications, 1988). Also, human toxicity with regard to skin and mucous membrane irritation, acute toxicity (oral/dermal), mutagenicity, and sensitization has been evaluated as very low for ester quats with long alkyl chains. Medium-chain ( $C_8$ – $C_{12}$ ) ester quats, however, may act as biocides, as may other quaternary ammonium salts with a comparable alkyl chain length range.

## VI. AMPHOTERIC SURFACTANTS

### A. Betaines

It was approximately 1969 when betaines were proposed as cosurfactants for shampoo formulations [222]. The mildness to skin and eyes has been the decisive reason.

Regarding the chemistry, betaines are homologues of trimethyl glycinate, which was discovered more than a century ago in sugar beet (*Beta vulgaris*) juice. The general structure is depicted in Fig. 32. The residue R normally represents an alkyl or an alkylamido popyl group based on coconut or palm kernel oil. The main carbon chain distribution includes the  $C_8$ – $C_{18}$  range. Sometimes products with a narrower chain distribution,

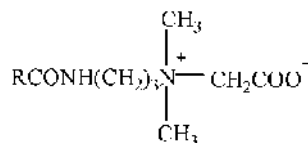


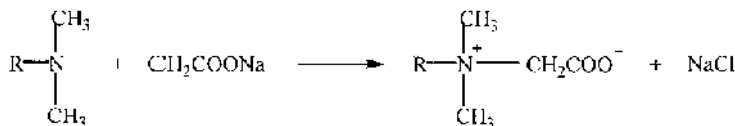
FIG. 33 Structure of an alkylamidopropyl betaine.

i.e.,  $C_{12}$ – $C_{18}$ , or pure  $C_{12}$  are prominent. Because of difficult handling, long-chain betaines play only a subordinate role.

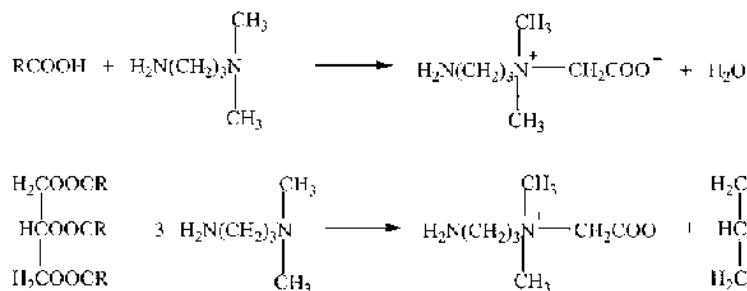
The synthesis proceeds relatively simply according to the following reaction (Scheme 28). In principle, the reaction must be understood as a quaternization reaction of a tertiary amine with monochloroacetate as an alkylating reagent. A high degree of conversion occurs only under the assumption that during the alkylation process, the salt form of chloroacetic acid is present because the free acid would block the amine function. Therefore, weakly alkaline conditions, analogous to the dissociation degree of chloroacetic acid, are recommended. Also, a slight excess of chloroacetate, usually the sodium salt, increases the yield. Depending on the type of tertiary amine used, a reaction temperature of 70–95°C is required. Normally, the reaction is carried out in an aqueous solution resulting in a final concentration of 30% betaine. Because of a tendency to gelatinize, slightly higher betaine concentrations may be possible only by adding special hydrotropes, such as polyols or fatty acids [223,224].

Besides the alkyl betaines already shown, alkylamidopropyl betaines (Fig. 33) are the predominant commercialized types. The preparation is a two-step process. First, fatty acids or their esters (glycerides or methyl esters) are condensed with, usually, dimethylaminopropyl amine, followed by reaction with sodium chloroacetate [225] (Scheme 29). For a quantitative yield of intermediate, a redistillable excess of amine should be applied. The reaction temperature is limited by the amine boiling point of approximately 140°C. The following betainization reaction takes place under conditions similar to those described before.

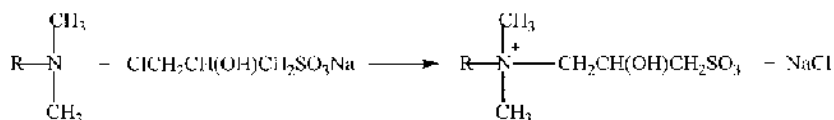
Usually, the sodium chloride generated remains in the betaine solution. Sometimes, however, special applications require salt-free products. For this reason, the



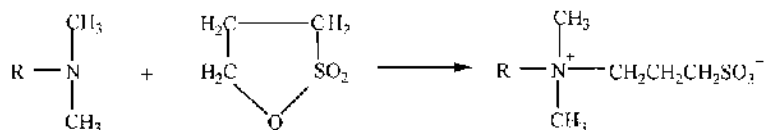
SCHEME 28



**SCHEME 29**



**SCHEME 30**



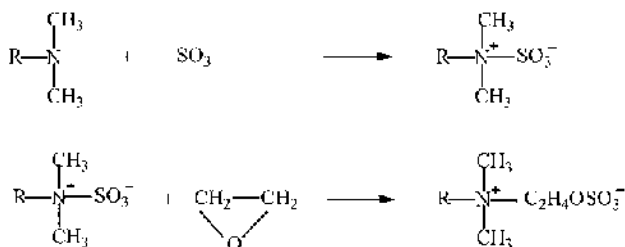
**SCHEME 31**

reaction is carried out in an alcoholic solution with subsequent filtration of the precipitated salt [226,227] or by means of ultrafiltration methods [228] (N. Kühne and G. Uphues, unpublished results, Henkel KGaA, 1991).

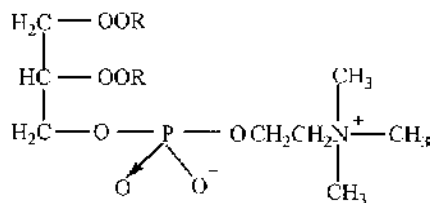
With regard to other by-products and trace impurities, environmental and product safety is becoming more and more relevant. A partial hydrolysis of monochloroacetate is responsible for a small content of harmless glycolic acid. Careful control of reaction conditions limits the amount. Concerning the removal of critical impurities, i.e., free amines and monochloro- and dichloroacetic acid, some hints are given in Ref. 229.

Another commercial betaine type is the sulfobetaines, also called sultaines. They are prepared similarly to the common types with chlorosulfonates instead of chloroacetate, usually 1-chloro-2-hydroxypropane sulfonate [230], as alkylating reagents (Scheme 30). In earlier times, propane sultone was the agent used for the manufacture of sulfobetaines. The high carcinogenic potential of sultones, however, prohibited the use of such substances more than 20 years ago (Scheme 31).

Of somewhat academic interest may be a synthesis route described for the preparation of sulfato betaines [231]. According to this method, a tertiary amine is reacted with sulfur trioxide followed by an insertion reaction of ethylene oxide. Ethylene or propylene carbonate is used as an inert solvent (Scheme 32).

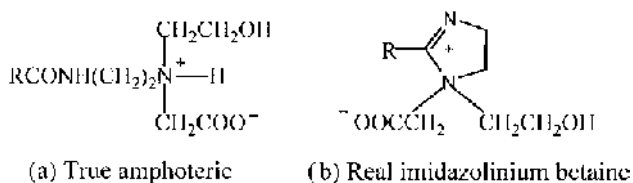


**SCHEME 32**



**FIG. 34** Structure of  $\alpha$ -lecithin.



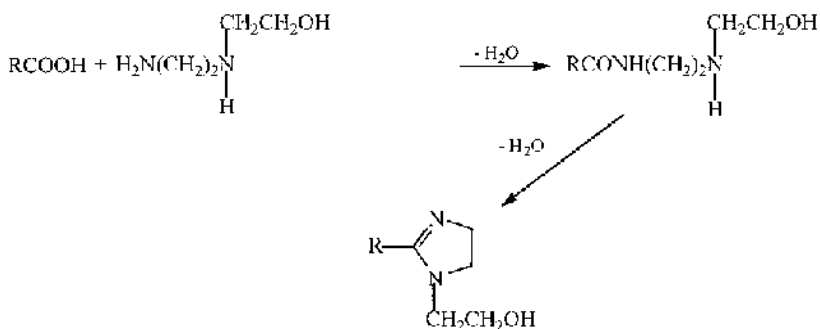


**FIG. 35** Structures of imidazoline-based ampherics.

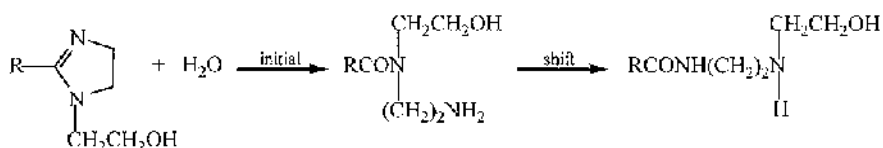
chloroacetate serves as the alkylating reagent. In practice, however, the chemistry is rather complicated. In relevant compendiums, monoacetates (Fig. 35a) as well as diacetates are mentioned. These differences have been traced back to the special chemistry of imidazolines.

The preparation itself takes place in a two-step reaction, at first forming an amino amide at a reaction temperature in the range of 150–180°C and ambient pressure, followed by the ring closure under additional vacuum conditions [236] (Scheme 35).

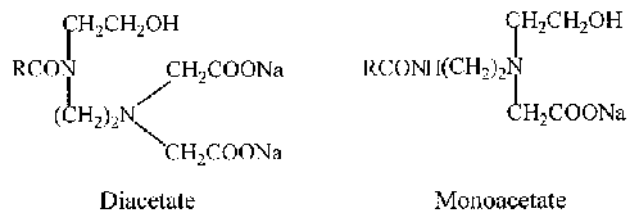
The most important property of imidazolines is instability in the presence of water at a pH value above 7. Even minor amounts of alkalinity suffice to open the ring system. Our own investigations (G. Uphues, unpublished results, Henkel KGaA, 1995) support the theory that the 2,3-double bond will be attacked, but depending on temperature, pH value, or amount of water present, the acyl group shifts more or less rapidly to the other nitrogen atom in the molecule, simulating a



**SCHEME 35**



**SCHEME 36**

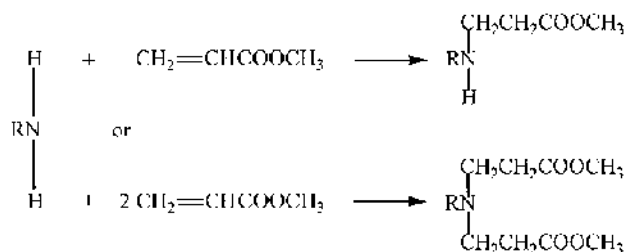


**FIG. 36** Structures of imidazoline-based true ampherics.

ring opening at the 1,2-position (Scheme 36). Both ring-opened substances are able to react with sodium monochloroacetate. Because of the primary amine function, the initial amido amine can add 2 moles of chloroacetate, whereas the other structure reacts with only 1 mole (Fig. 36).

Basically, the amount of alkali is equivalent to the amount of chloroacetate used. The “monoacetate/diacetate” ratio is influenced by the alkaline pH value during the reaction. The higher the pH value, the more monoacetate is formed. Because of the competitive situation with regard to the acyl shift and the alkylation reaction, in diacetates there are always monoacetates present.

For special applications, true ampherics based on fatty amines are necessary. Preferably, they are synthesized by a *Michael* addition of methyl acrylate to fatty amines [237,239]. Depending on the amount of acrylate, mono and bis adducts are possible (Scheme 37).



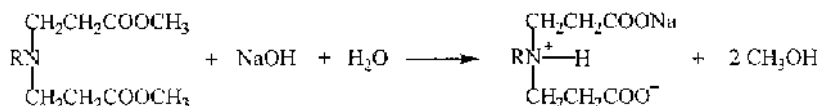
**SCHEME 37**

The methyl ester groups are hydrolyzed under pressure with various quantities of caustic in an autoclave, producing only sodium salts or mixtures of both salt and acid groups (Scheme 38).

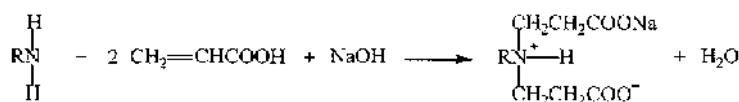
Unfortunately, the methanol generated cannot be removed completely by less expensive methods. As modern cosmetic products require methanol-free ingredients, the so-called propionates are prepared by the addition of acrylic acid. This alternative procedure is restricted by the fact that only diadducts can be obtained. Usually, the reaction is carried out in a neutral aqueous solution forming the monosodium salt (Scheme 39).

Another route for the manufacture of salt-free true amphoteric is the addition of acrylic acid to ring-opened imidazolines. As the addition reaction runs slower than the shift of the acyl group just mentioned, essentially mono adducts are obtained (Scheme 40).

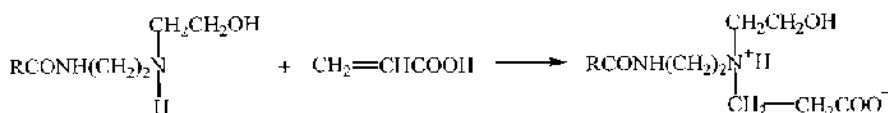
The specialized literature shows numerous other types and synthesis methods for amphoteric, but they have found only small or no commercial interest.



**SCHEME 38**



**SCHEME 39**



**SCHEME 40**

## C. Properties of Amphoteric Surfactants

### 1. Physicochemical Behavior

The particular properties of amphoteric surfactants are related to their zwitterionic character. That means that both anionic and cationic structures are found in one molecule. Differences between betaines and true amphoteric are caused by changing behavior at several pH values.

Regardless of the pH value, betaines permanently represent a four-bonded nitrogen atom. Only at a very low pH value can the anionic group be protonated to take on a cationic character.

Unlike betaines, true amphoteric form salts at pH values higher than the isoelectric point. At lower pH values, the basic nitrogen is protonated and the molecule behaves like a cationic surfactant. So it is understandable that true amphoteric show the best application results outside the isoelectric range.

The amphoteric are mainly used as cosurfactants for cosmetic shampoo or dishwashing formulations, where they provide mildness to skin and hair, especially in blends with alkyl and alkyl ether sulfates. Another advantage is compatibility with most ionic surfactants. In addition, the general surfactant properties, i.e., wetting power, cleansing ability, foaming power, hard-water tolerance, and lime soap dispersibility, are excellent.

### 2. Ecological and Toxicological Behavior

A coco betaine, a cocoamidopropyl betaine, and a cocoamphoacetate were extensively tested with regard to

**TABLE 4** Toxicological Behavior of Amphoteric Surfactants

Type of amphoteric surfactant	Acute toxicity (rat)	Irritation to skin <sup>a</sup> (rabbit)	Irritation to eye <sup>a</sup> (rabbit)	Sensitization (Magnusson-Kligman test)	Gene mutation (Ames test)	NOAEL <sup>b</sup> (mg/kg)
Coco betaine [35]	None	Yes	Yes	None	None	>250
Cocoamidopropyl betaine [36]	None	None	Yes	None	None	1000
Cocoamphoacetate [37]	None	Moderately	Slightly	None	None	>1000

<sup>a</sup>Concentration: 25% and 20%, respectively.

<sup>b</sup>Oral toxicity; NOAEL = no observed adverse effect level is the maximum dose tolerated in cumulative toxicity studies.

their environmental compatibility (Biological Laboratories of Henkel KGaA, private communications, 1996). They proved to be readily biodegradable in the stringent OECD (Organization for Economic Cooperation and Development) tests on ultimate biodegradation. As shown in the metabolite test, their degradation to CO<sub>2</sub>, H<sub>2</sub>O, inorganic salts, and biomass occurs quantitatively; i.e., no recalcitrant metabolites were formed. Using sewage treatment plant simulation tests, it was confirmed that they will be easily eliminated from wastewater.

The aquatic toxicity (toward algae, daphnia, and fish) of these substances is of the same order of magnitude as for other surface-active substances, ranging from toxic to moderately toxic (ratio of median effective concentration to median lethal concentration, EC<sub>50</sub>/LC<sub>50</sub>, >1–100 mg/L). For wastewater bacteria, these substances are minimally toxic.

According to their commercial importance, some toxicological data are presented for coco betaines, cocoamidopropyl betaines, and cocoamphoacetates [240–242]. The results are summarized in Table 4. More detailed toxicological information for cocoamidopropyl betaine is published in Ref. 243.

Whereas the ecological data indicate good environmental tolerance, the toxicological findings seem to reveal deficits with regard to skin and eye irritation values. These disadvantages, however, arise only at higher concentrations that do not conform to the practice. More important for a toxicological evaluation is the fact that amphoteric surfactants are usually combined with anionic surfactants, i.e., alkyl or alkyl ether sulfates. Besides other synergies, such blends have been found to be very mild to skin and mucous membranes [244–246].

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