

## SURFACTANTS FROM FATS

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## INTRODUCTION

A typical surfactant molecule contains one or two (and occasionally more) long alkyl chains, 8 to 20 carbon atoms in length, and a polar group which may be anionic, cationic, amphoteric, or nonionic in nature. Except for wetting agents which usually contain two or three shorter alkyl chains in the C<sub>6</sub>-C<sub>10</sub> range, the bulk of the present day surfactants have alkyl chains in the C<sub>12</sub>-C<sub>18</sub> range. Natural fats and oils are thus obvious and in many ways ideal raw materials for the synthesis of surfactants, and indeed most of the surface-active agents developed up to about 1940 were based on fats and oils.

In the course of the tremendous development of petrochemical technology since about 1935 the fat- and oil-derived surfactants were gradually displaced by the newer petrochemical derivatives, particularly in the light and heavy duty detergent fields. At present fat-derived surfactants have survived and are the materials of choice in several areas of application. Soap, the world's oldest surfactant, is still the most widely used ingredient of toilet bars and even the so-called syndet toilet bars contain blends of soap and synthetic surfactants derived from fats and oils. Fat-derived surfactants are also used in alkanolamide foam stabilizers and alcohol sulfates for hair and rug shampoos, although petroleum-derived alcohols obtained via the Ziegler process are also used here. Certain specialty surfactants such as the so-called sulfonated oils, fatty acid amides of N-methyltaurine, or fatty acid esters of sodium isethionate and other specialty surfactants are made from fats and oils. Finally, virtually all commercial cationic and amphoteric surfactants are derived from lipid starting materials.

Lipid-derived surfactants have unique properties which

make them attractive, particularly in this era of environmental concern. The linearity of the fat-derived alkyl chains results in more rapid and complete biodegradation than can be attained with analogous petrochemical derivatives. Furthermore, since the fats and oils have linear alkyl chains to begin with, no sophisticated chemical processing is required to achieve linearity.

Petrochemical starting materials at present have lost some of the economic advantages they possessed ten years ago. While fats and oils still fluctuate in price, they have not shown the dramatic price increases of petrochemicals in recent years. Fats and oils are replenishable agricultural products or byproducts whereas petroleum is slowly depleted.

The following sections deal primarily with advances in the lipid-derived surfactant field during the past decade, since the earlier literature has been amply covered in various monographs on surfactants (1-5).

## ANIONIC SURFACTANTS

### *INTRODUCTION*

Of the various types of surface-active agents, anionic surfactants have the greatest importance from an economic viewpoint. These substances constituted about 73% of the total United States production of surfactants in 1976. The remaining 27% were furnished by nonionic, cationic, and amphoteric types.

Anionic surfactants contain negatively charged polar groups which confer hydrophilicity to a relatively hydrophobic molecule. These groups are usually carboxylate, sulfonate, sulfate, or phosphate. Soaps are often classified as anionic surfactants and are discussed in a separate portion of this section.

Anionic surfactants are synthesized from petroleum or from lipid and other nonpetrochemical raw materials. Non-petroleum-derived surfactants accounted for 2.0 billion pounds of the total of 3.4 billion pounds of anionic surfactants produced in 1976. These nonpetrochemical sources include 1) potassium and sodium salts of fatty, rosin, and tall oil acids; 2) calcium, ammonium, and sodium salts of lignosulfonates; 3) sulfated fatty and tall oil acids and their derivatives; 4) sulfated fatty and sperm oil alcohols; and 5) sulfated natural fats and oils. The anionic detergents obtained from these sources are usually biodegradable (6-8).

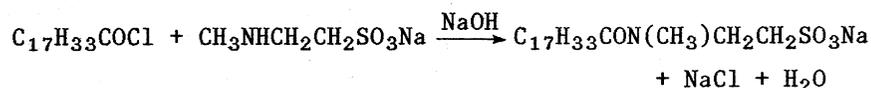
## SULFONATES

Sulfonates with a general structure  $\text{RSO}_3\text{Na}$ , where R represents a biodegradable hydrophobic moiety, are often effective anionic surfactants. A high percentage of these materials is prepared by sulfonation of petroleum-based substrates such as dodecylbenzene obtained by alkylation of aromatic nuclei, but sulfonation products of naturally-derived materials are also commercially important. For example, over one billion pounds of lignosulfonates were prepared in 1976. Also, sulfonated castor oil (Turkey red oil) is probably the oldest non-soap surfactant in use today. Although sulfuric acid has been traditionally employed to effect the sulfonation of castor oil, sulfur trioxide has recently been used to advantage (9). 2-Alkylbenzimidazoles prepared from fatty acids have been sulfonated to give surface-active agents.

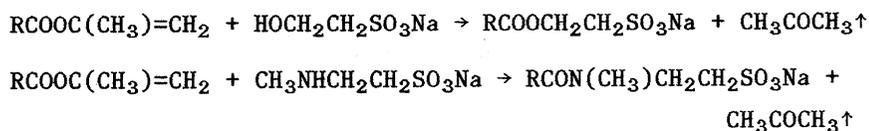
Indirect methods are useful in preparing fat-based surfactants containing sulfonate groups. For example,  $\beta$ -sulfesters of fatty acids have been prepared from sodium isethionate by reaction with fatty acyl halides as follows:



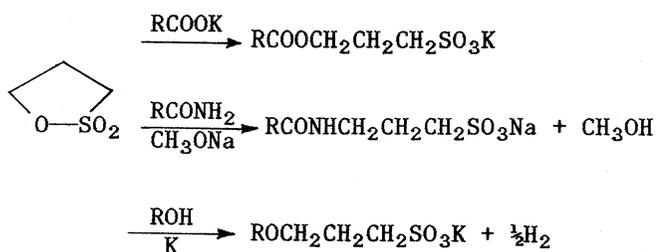
Also, anionic surfactants are prepared by acylation of N-methyltaurine:



Acylation of sodium isethionate and N-methyltaurine can be effected by use of isopropenyl esters of fatty acids (10). Acetone is the only byproduct formed as indicated below:



Fatty derivatives of 3-hydroxypropanesulfonic acid have been prepared from fatty acids, alcohols, and amides by reaction with 1,3-propanesultone (11). The surfactant properties of the derivatives were compared with those of analogous 2-sulfoethyl esters.

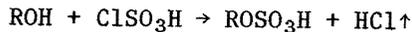


#### *α-SULFOCARBOXYLATES*

Alpha-sulfomonocarboxylic acids and their low molecular weight esters have been found to be surface-active. They are usually prepared by direct sulfonation which is discussed in another chapter of this book. Recent work (12) has investigated the preparation and properties of mannitol, sorbitol, and sucrose esters of  $\alpha$ -sulfo fatty acids. Benzyl, cyclohexyl, and phenyl esters of the acids have properties similar to the corresponding propyl, butyl, or amyl esters (13). A study of the manufacturing of  $\alpha$ -sulfonated fatty acids and esters as well as their properties and applications has been reported (14).

#### *SULFATES*

Sulfates contain a hydrophilic group,  $-\text{OSO}_3^-$ , directly attached to a carbon atom of a hydrophobic moiety. The resulting surfactants become more water soluble and are biodegradable when derived from fat-based substrates. Thus sulfated fatty alcohols with the general structure  $\text{CH}_3(\text{CH}_2)_n-\text{OSO}_3\text{Na}$  (with  $n$  varying from 8 to 18) are of considerable importance. Oleyl alcohol as well as other long chain alcohols obtained by reduction of natural fats and oils can be conveniently sulfated with agents such as chlorosulfonic acid.

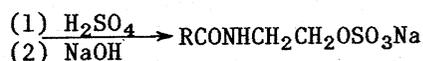
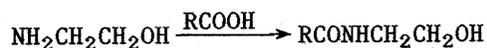


The hydrochloric acid liberated is absorbed by pyridine and the sulfate ester can be subsequently neutralized. A study has been made of the use of chlorosulfonic acid in sulfation of linear primary alcohols (15). 9,10-Dichlorostearyl alcohol, prepared by reduction of 9,10-dichlorostearic acid (16) or by chlorination of oleyl alcohol (17), was sulfated to obtain the detergent sodium 9,10-dichlorooctadecyl sulfate, which was as soluble as sodium oleyl sulfate and could be

prepared by ordinary sulfation techniques.

Sulfuric acid is often used as a sulfating agent of saturated alcohols. It is also employed for sulfation of unsaturated glycerides that may or may not contain hydroxyl groups. In this reaction, the unsaturated linkages are attacked. Natural fats and oils that have been sulfated include castor oil, cod oil, neatsfoot oil, soybean oil, sperm oil, and tallow.

Other sulfated derivatives include those prepared by fatty acid acylation of compounds such as monoethanolamine and subsequent sulfation. Thus:



The effect of structure on the surface-active properties of the sulfation products has been investigated (18). All of the sulfated alkanolamides of fatty acids had good calcium ion stability and were effective lime soap dispersants. The critical micelle concentrations were slightly higher than those of alcohol sulfates having the same hydrocarbon chain length.

#### SOAP

Soap, whose origins go back to ancient Egypt, was the most widely used anionic surfactant until the end of World War II. At present soap is used in Western countries primarily in toilet bars and has essentially disappeared as the major active ingredient of laundry detergents. Recent advances in the bar soap field have been largely in the areas of mechanical improvements and additives such as antibacterial agents and have been summarized by Jungermann and coworkers (19-21). Toilet soap bars have been fairly constant in composition, containing 75-95% tallow soap and 5-25% coconut oil soap. The latter contributes to flash lathering but also to the slushing of the bars (22). Toilet bars containing varying amounts of lime soap dispersants have attained popularity in the United States. Such bars may, for instance, contain alcohol sulfates (23) or a fatty acid ester of isethionic acid (24) as the major lime soap dispersant.

#### MODIFIED SOAP DETERGENTS

In an effort to develop phosphate free detergent formu-

lations based upon replenishable raw materials, research workers at the U.S. Department of Agriculture developed the concept of a soap based detergent modified by the addition of lime soap dispersants. Such formulations contain typically 63% tallow soap, 19% lime soap dispersant, and 15% sodium silicate builder (25) as the major ingredients.

For a surfactant molecule to function as a lime soap dispersing agent (LSDA), it must possess a bulky polar group. In general, bulk can be introduced into the LSDA surfactant molecule in the form of one or more ester or amido groups, ether linkages, or by inclusion of both an anionic and cationic group. Introduction of a second anionic group such as  $-\text{COO}^-$  or  $-\text{SO}_3^-$  into an anionic LSDA molecule does not enhance lime soap dispersing properties. The lime soap dispersing ability of a given compound is conveniently measured by a test developed by Borghetty and Bergman (26) that measures the minimum lime soap dispersant requirement (LSDR) in grams to keep 100 g of sodium oleate from precipitating in hard water (333 ppm as  $\text{CaCO}_3$ ). A more complex titrimetric method for the determination of lime soap dispersing ability of surfactants was developed by Schönfeldt (27). A large variety of surfactants has been examined for lime soap dispersing and other surface active properties (28). Many anionic and amphoteric surfactants are suitable LSDA but nonionics and cationics are not (29).

#### *ANIONIC LSDA*

Among the anionic LSDA types the best known one is probably the fatty acid amide of N-methyltaurine or Igepon T type. While it is a very good detergent by itself and an excellent lime soap dispersant with an LSDR of 5, the commercial product has the disadvantages of high cost and high sodium chloride content. Some sulfated alkanolamides provide a less expensive alternative and have the same good surface-active properties (30). The development of a practical sulfation method is quite recent. It is based on cosulfation of a mixture of the monoisopropanolamide and diglycolamide of tallow fatty acid and n-butanol (31).

Another type of LSDA that was thoroughly investigated was that of the  $\alpha$ -sulfo fatty esters. It is prepared from hydrogenated tallow by transesterification and subsequent continuous sulfonation with  $\text{SO}_3$ , followed by neutralization (32,33). The  $\alpha$ -sulfonated methyl esters are less stable to hydrolysis than sulfated fatty acid alkanolamides.

#### ZWITTERIONIC LSDA

Zwitterionic surfactants are the most efficient LSDA studied, and they offer better detergency than the anionics. Their synthesis is discussed in a later portion of this chapter. In general, superior LSDA are produced when the anionic group in the zwitterionic molecule is a sulfo ( $-\text{SO}_3^-$ ) or sulfato ( $-\text{OSO}_3^-$ ) group. These surfactants have an LSDR of 4-5, depending on the alkyl chain length, and exhibit good detergency (34). When an amido group is introduced into the molecule, the lime soap dispersing power is usually greatly enhanced, and the LSDR drops to 2. These types of compounds are the most potent lime soap dispersants encountered so far.

Sulfobetaines can be obtained via the addition of a tertiary fatty amine to 1,3-propanesultone. Because of the carcinogenic nature and high cost of the latter, two alternative synthetic routes were developed which led to closely related compounds with similar surface-active properties (35). Introduction of an amido group into the sulfobetaine molecule usually improves its water solubility. Introduction of a second amido group does not cause further improvement in the LSDR but increases solubility in water, i.e., lowers the Krafft point (36,37).

The relative positions of the anionic and cationic sites in the molecule are very important. When the quaternary ammonium group is placed at the terminal position of the molecule and the sulfo group is placed away from the end position as in  $\text{RCH}(\text{SO}_3^-)\text{COOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$ , for example, the surface-active properties show remarkable decline (38).

#### NATURE OF SOAP-LSDA BLENDS

An interesting phenomenon observed with soap-LSDA blends is that soap and LSDA solubilize each other. For example, a blend of an insoluble LSDA and sodium palmitate, a high Krafft point soap, is more water soluble than either component (39). Since poor solubility of soap, and hence poor detergency in cold water, has been a serious drawback to the use of soap as a detergent, this difficulty can now be overcome by the addition of an LSDA to the soap. Fabric washed repeatedly with soap-LSDA formulations in hard water showed no buildup whatsoever of foreign matter when viewed under a scanning electron microscope. The same results were obtained with a high phosphate built commercial detergent, whereas a heavy buildup of soap scum occurred with soap alone (40).

It has been frequently assumed that the soap component in soap-LSDA blends acts as a scavenger for hard water ions, whereas the LSDA is solely responsible for detergency. This

view does not agree with the experimental findings. All evidence obtained indicates that soap, LSDA, and calcium and magnesium ions are tightly bound together in a suspended particle. Convincing evidence for this was obtained when a soap-LSDA dispersion in hard water was filtered on a small porosity polymer membrane and analyzed. The filter residue contained all of the soap, all of the LSDA, all of the  $\text{Ca}^{++}$ , most of the  $\text{Mg}^{++}$ , but no  $\text{Na}^+$ . The filtered material could be redispersed in water, and the resulting dispersion exhibited high surface activity including detergency, whereas the filtrate was essentially devoid of surface activity (41). The surface tension behavior of soap-LSDA mixtures likewise indicated a mixed micelle, and the mixture gave surface tension vs. log concentration curves that are typical of single surfactants rather than of mixtures (42).

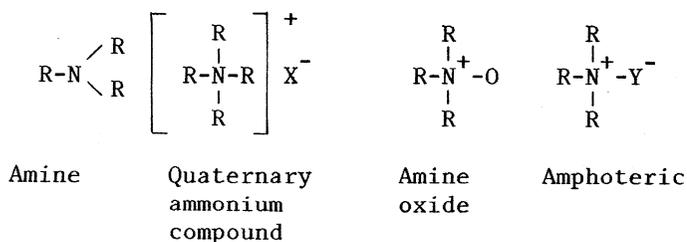
## CATIONIC SURFACTANTS

### INTRODUCTION

Cationic surfactants continue to grow in importance. United States Tariff Commission reports show that production of these materials reached 252 million pounds in 1976, an increase of almost 56% over the 162 million pounds reported in 1966. Cationic surface-active agents have found extensive use as bacteriostats, softeners for textiles, chelating agents, antistatic agents, and foam depressants.

These surfactants often contain a hydrophobic alkyl chain attached directly or indirectly to a positively charged nitrogen atom. The long chain groups are usually fat or petroleum based, but we shall restrict ourselves to those derived from fats. An excellent discussion of cationic surfactants was published in 1970 (4), and many shorter reviews of this field have appeared.

Several classes of surfactants are based on derivatives of fatty amines. They include: amines and their salts, quaternary ammonium compounds, amine oxides, and amphoteric. Their structures are given below. In all of the compounds

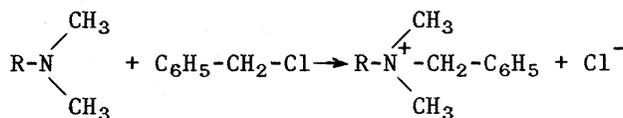


at least one of the R groups consists of a long alkyl chain. In addition, the agents may have more than one cationic nitrogen atom, as in long chain derivatives of diamines.

*ACYCLIC QUATERNARY AMMONIUM COMPOUNDS*

The general industrial chemical methods of preparation of amines from fatty acids have been reviewed as well as the surfactant applications of these compounds and their quaternary ammonium compounds (43). The relationship of the structures of the amine derivatives to their performance as flotation agents, corrosion inhibitors, emulsifiers, bactericides, and fabric softeners have also been described (43).

Although quaternary ammonium compounds may have up to four fatty alkyl chains, only those with one or two chains have achieved industrial significance. Quaternary ammonium compounds are prepared by (A) alkylation of a primary, secondary, or tertiary amine, (B) alkylation of a low molecular weight tertiary amine such as diethyl or dimethyl amine with a fatty alkyl halide, or (C) reaction of a tertiary amine or its salt with an epoxide. Large tonnages of quaternary ammonium compounds are obtained by exhaustive methylation of primary or secondary amines. Fatty quaternary type compounds are used as antimicrobial agents and for modifying textile surfaces. Those compounds prepared from ditallow amine have found application as textile softeners. Benzalkonium chlorides with useful bacteriostatic properties are obtained by reaction of a fatty tertiary amine with benzyl chloride. Thus:



The following are a few examples of some recent preparations of quaternary ammonium surfactants. Lanolin acids obtained by saponification of lanolin esters have been reacted with amines such as N,N-diethyl-1,3-diaminopropane to form an amidoamine intermediate such as Lan-CO-NH-(CH<sub>2</sub>)<sub>3</sub>-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. The intermediate was then quaternized with benzyl chloride. The resulting quaternary ammonium compound is used in hair treatment preparations (44). Similar structures have been used in compositions for souring and softening textiles (45).

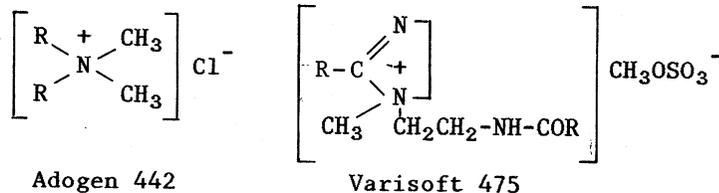
A series of fatty amidoamine derivatives and their salts have been shown to have excellent antistatic properties and to be substantive to hair and skin (46). Fatty amidoamines

prepared from diethylenetriamine and soya or coconut oil acids have been ethoxylated with ethylene oxide and quaternized with methyl chloride. The product is used in forming stable oil and water emulsions (47).

Tertiary amines have been quaternized with 1-chloro-2-hydroxy-3-alkoxypropane to form salts used as emulsifiers and germicides (48). Acylation of L-arginine with fatty acid chlorides followed by esterification with ethyl alcohol containing dry hydrogen chloride yields salts of acylated arginine esters useful as antimicrobial surfactants (49).

#### CYCLIC QUATERNARY AMMONIUM COMPOUNDS

Another major class of cationic surfactants consists of quaternary ammonium compounds in which the nitrogen atom carrying the positive charge is part of a heterocyclic ring such as pyridine or isoquinoline. Many of these materials are prepared by methods analogous to those used for straight chain derivatives. Their properties parallel those of their acyclic counterparts. They find applications as wetting and dispersing agents, detergents, sanitizing compounds, and fabric softeners. A study of interactions of cationic softeners with detergent components has been carried out (50). The commercial fabric softeners used were Adogen 442, a hydrogenated tallow dimethylammonium halide, and Varisoft 475, an imidazolinium type of quaternized ammonium compound. The latter is formed by reaction of a fatty acid with



diethylenetriamine and subsequent quaternization of the resulting imidazoline (51).

#### MISCELLANEOUS

In a novel approach, chelate surfactants, such as N-lauroyl ethylenediamine which has been treated with ferric sulfate, have been prepared (52). The resulting cationic charge is on the transition metal, unlike the examples cited previously in this section. The chelates have shown good surface activity.

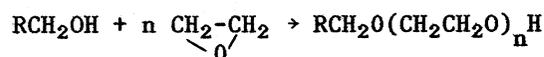
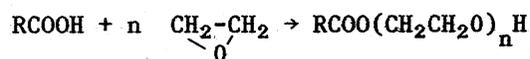
Cationic surfactants may be synthesized from any element capable of forming "onium" structures  $\text{R} \overset{+}{\text{N}} \text{Y}^-$  where X can be

sulfur, phosphorus, or iodine as well as nitrogen (53). Although such compounds are at present not commercially prominent, interest in their formation still exists. Fatty phosphonium compounds have been useful as textile softeners, emulsifiers and antibacterial agents (54).

## NONIONIC SURFACTANTS

### INTRODUCTION

Nonionic surfactants have no charge when dissolved in water and are completely compatible with anionic, cationic, and amphoteric surfactants. Many of these surfactants are formed by reaction of fatty substrates with alkylene oxides, including ethylene or propylene oxide. Fatty acids and alcohols react as follows with ethylene oxide:



Amines, amides, and other compounds with active hydrogen behave in analogous fashion. Alkaline catalysts are most often used, although  $\text{BF}_3$  and acid clays have been employed. Moderate (100-200°C) temperatures and pressures (up to 200 psi) are required. A continuous process for the alkoxylation of long chain carboxylic acids, alcohols, and amines in the presence of alkaline catalysts has been reported to give good yields and is especially suitable for the manufacture of products with a low degree of alkoxylation (55). Mechanisms for the reaction of oxides with fatty acids (56) and alcohols (57) were proposed in 1957 and have recently been confirmed (58). With fatty acids, the alkali catalyzed addition of ethylene oxide proceeds in two stages. A slow reaction of the acid with ethylene oxide forms ethylene glycol monoester. The reaction rate then increases and transesterification occurs, leading to formation of polyethylene glycol monoester and diester as well as free polyethylene glycol.

With alcohols, reactivity towards ethylene oxide decreases in the order primary > secondary > tertiary (59). In general, viscosity increases as the amount of alkylene oxide added is increased and products vary from liquids to waxy solids. The oxyalkylated derivatives of fatty alcohols have found extensive use as emulsifiers and as fiber lubricants. Natural fats and oils such as castor oil react with varying amounts of ethylene oxide to form water-soluble surfactants

useful as emulsifiers, dispersants, and lubricants and in numerous additional applications. Fatty lanolin alcohols from wool can also be treated with ethylene oxide to form nonionic emulsifying agents.

#### *ESTERS*

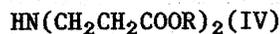
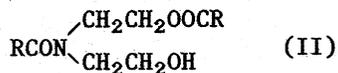
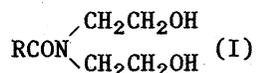
Fatty acid esters of various types of polyhydroxy compounds are useful as surfactants before and after addition of ethylene oxide. Mono- and diglycerides of saturated and unsaturated fatty acids have found use as surfactants even though their water solubility is limited. They have had extensive application as emulsifiers in baked goods, candies, and other foods and cosmetics as well as in metal lubrication. Partial esters of polyhydric alcohols such as sorbitans have been ethoxylated with varying amounts of ethylene oxide to form emulsifiers with particular properties and applications depending on their HLB (hydrophile-lipophile balance) values. Fatty esters of polyethylene glycol show useful properties as emulsifiers, textile softeners, and in cosmetics. Similar properties are given by fatty acid monoesters of polyoxyethylene glycol (60).

#### *SUGAR ESTERS*

Fatty esters of sugars have been found to have good surfactant properties and can be prepared by transesterification of sucrose with methyl esters of fatty acids (61). Alkaline catalysts and polar solvents such as dimethyl sulfoxide and dimethylformamide are required. A microemulsion technique in which propylene glycol is used as solvent has been developed (62) as well as a solventless procedure in which sucrose is interesterified with fatty acids in the presence of alkali metal soaps (63,64). The water solubility of sucrose esters can be increased by addition of ethylene oxide. Polyol glycosides obtained from starch have been polyalkoxylated by treatment with ethylene and propylene oxide prior to transesterification with fatty methyl esters (65). More recently, surfactants have been prepared from fatty esters of lactose and its reduction product, lactitol (66-68). Polyols derived from lactose have been prepared by glycosylation of the latter with glycerol or propylene glycol. The resulting polyol was alkoxylated with ethylene oxide and transesterified with methyl palmitate to form food emulsifiers, cosmetic surfactants, and biodegradable industrial surfactants (69).

## AMIDES

Amides prepared from fatty acids and hydroxyl-bearing amines such as mono- and diethanolamine have excellent foam stabilizing and soil suspension properties. The reaction is complex and can lead to a mixture of products. For example, with 1 mole of fatty acid and 2 moles of diethanolamine, the following compounds (70-72) are formed:



Analysis of the mixture is difficult, but compound I predominates (63%). Pure diethanolamides can be obtained via use of the acid chloride and the diethanolamine. A detailed description of the preparation and characterization of monoethanolamides is available (73). Diethanolamides of palmitic, stearic, and tallow fatty acids become water soluble on addition of 4 moles of ethylene oxide and can be used in soap-based detergent formulations with good lime soap dispersing properties (74).

## MISCELLANEOUS

The reaction of polyoxyethylene glycol with epoxidized fatty esters has been studied. Results indicate that potentially useful nonionic wetting agents can be produced, for example, from methyl epoxystearate and polyoxyethylene glycol (75). The reaction is catalyzed at ambient temperatures by the presence of 0.25% boron trifluoride.

## AMPHOTERIC SURFACTANTS

### INTRODUCTION

Unlike the other surfactant categories, the commercial amphoteric surfactants are largely derived from natural fats and oils. Amphoteric surfactants appear to be growing in importance both economically and scientifically. However, of the four major classes of surfactants, amphoteric surfactants are produced in the smallest volume, and because of their inherently greater chemical complexity they are more expensive than the others.

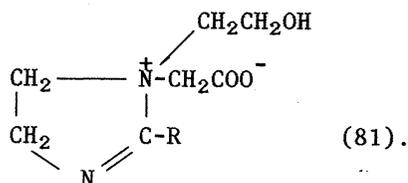
Because of the zwitterionic nature of these surfactants, they are endowed with unique physical properties such as high surface activity and excellent compatibility with both anion-

ic and cationic substances. Four types of amphoteric substances are discussed here: 1) amphoteric substances whose anionic site is a carboxy group, 2) those having either a sulfo or sulfato group as the anionic site, 3) the amine oxides, and 4) the aminimides.

#### CARBOXYLATES

Addition of fatty primary amines across the double bond of methyl acrylate and subsequent hydrolysis yields an amphoteric of the type  $\text{RNH}_2\text{CH}_2\text{CH}_2\text{COO}^-$  (76). Analogously a primary amine adds to crotonic acid to give  $\text{RNH}_2(\text{CH}_3)\text{CH}-\text{CH}_2\text{COO}^-$  (77). Reaction of mixed N-alkyl-ethylenediamine with acrylic or crotonic acid gives rise to analogous amphoteric surfactants (78).

Quaternization of a long chain alkyl dimethylamine with sodium chloroacetate yields a betaine  $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$  (79). Reaction of a fat, fatty acid, or fatty acid methyl ester with N,N-dimethyl-1,3-diaminopropane yields the intermediate  $\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  (46) which, in turn, can be quaternized with sodium chloroacetate to yield a betaine  $\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$  (80). The patent literature refers to imidazoline type betaines of the structure



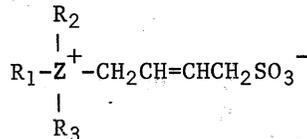
Since the unquaternized imidazolines hydrolyze readily (82), the product obtained may be only partially cyclized. Reaction of a bis-oxyethylated fatty amine with sodium chloroacetate gives  $\text{RN}^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{CH}_2\text{COO}^-$  (83).

#### SULFO- AND SULFATO-COMPOUNDS

The availability of 1,3-propanesultone led to the development of various sulfobetaines. Reaction of fatty tertiary amines with this sultone produced amphoteric surfactants whose detergency and fabric softening properties depended on the number and size of the long fat-derived alkyl chain attached to the molecule (84). Sulfobetaines whose structures may be exemplified by  $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  and  $\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-$  have been patented (85). Such sulfobetaines possess excellent lime soap dispersing and detergent properties useful in soap-based detergent formula-

tions (12). The water solubility of the sulfobetaines increases as the spacing between anionic and cationic sites is increased from two to three carbon atoms (86). Substitution of the sulfo group by a sulfato group does not alter the surface activity of the compounds but reduces water solubility. An alternate synthetic route towards sulfobetaines involves the quaternization of fatty alkyldimethylamine with allyl chloride, followed by addition of bisulfite in the presence of a free radical initiator. Yet another route consists of the reaction of epichlorohydrin with a blend of sodium sulfite and bisulfite followed by quaternization of the product with a tertiary amine to yield  $Z\overset{\oplus}{N}(CH_3)_2CH_2CHOHCH_2SO_3^-$ , where Z may be a long chain alkyl group or  $RCONHCH_2CH_2CH_2-$  (35,87).

Somewhat more complex sulfobetaines of the structure  $RNHCO(CH_2)_nCONHCH_2CH_2CH_2\overset{\oplus}{N}(CH_3)_2CH_2CH_2CH_2SO_3^-$ , where n is an integer from 2 to 4, have been prepared from fatty amines (36,37). Such materials are excellent lime soap dispersants, and the presence of two amido groups impart high water solubility to the compounds. When the cationic site of the surfactant is at a terminal position and the anionic site a distance away as in the amino esters of  $\alpha$ -sulfo fatty acids, the detergency and lime soap dispersing ability are greatly diminished (38). Reaction of a tertiary amine or phosphine with 1,4-butenesultone yields an unsaturated sulfobetaine of the structure



where  $R_1$  represents a long alkyl chain,  $R_2$  and  $R_3$  short alkyl chains of one to six carbon atoms, and Z is a quaternary nitrogen or phosphorus atom (88). Another route to amphoteric akin to a sulfobetaine involves sulfonation of a benzalkonium chloride or of an amido analog of the benzalkonium chloride to give the following sulfobenzyl derivatives (89):



#### AMINE OXIDES

Amine oxides are widely used as foam stabilizers in liquid detergent formulations and some shampoos and can be considered to be zwitterionic in character. Amine oxides of the structures



are produced commercially by treatment of the appropriate tertiary amine or amidoamine with hydrogen peroxide (90). The amine oxides possess lime soap dispersing properties and give good detergency in tallow soap-based detergent formulations (91).

#### AMINIMIDES

Fatty acid derived acylaminimides function as amphoteric surfactants and have been produced commercially. They possess the general structure  $\text{R}_1\text{CONNR}_2\text{R}_3\text{R}_4$ , where  $\text{R}_1$  is a fatty acid derived long alkyl chain, and  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are usually  $\text{CH}_3$ ,  $\text{CH}_2\text{CH}_2\text{OH}$ , or  $\text{CH}_2\text{CHOHCH}_3$  groups. Such compounds are obtained from the reaction between an ester, 1,1,1-trialkylhydrazinium chloride and a sodium alkoxide (92). Another synthetic route involves the reaction of an ester with 1,1-dimethylhydrazine and an epoxide, such as propylene oxide to give  $\text{RCONN}^{\oplus}(\text{CH}_3)_2\text{CH}_2\text{CHOHCH}_3$  (93).

Yet another synthetic route involves reaction between a fatty acid methyl ester, hydrazine hydrate, and ethylene oxide to give  $\text{RCONN}^{\oplus}(\text{CH}_2\text{CH}_2\text{OH})_3$  (94). The acylaminimides exhibit the cloud point behavior of nonionic surfactants (95) and the Krafft point characteristics of ionic surfactants. Antimicrobial activity of the acylaminimides against a variety of microorganisms has been reported (96-98). Chain lengths of  $\text{C}_{14}$  or  $\text{C}_{16}$  in aminimides give maximum activity. Studies to date indicate that aminimides have wide spectrum biocidal properties and are promising antifungal agents.

#### CONCLUSIONS

Natural fats and oils are versatile starting materials for the synthesis of a great variety of all major classes of surface-active agents. In spite of competition from petrochemical derivatives, fat-derived surfactants predominate in the cationic and amphoteric areas. In specialized applications, particularly in the fields of food emulsification and cosmetic preparations, fat-derived surfactants appear to be preferred, while in laundry and hard surface cleaning applications petroleum-derived surfactants have displaced fat derivatives because of lower costs.

Since fats and oils represent renewable resources, it is conceivable that fat-derived surfactants will eventually experience a resurgence as petroleum becomes increasingly

expensive. The inherent low toxicity and ready biodegradability of most fat-derived surfactants is another favorable aspect of their growing importance as public awareness of environmental safety increases.

An interesting observation made in the course of compiling this chapter is that no novel surfactants of importance, either of petrochemical or fat origin, have been developed during the past twenty years. On the other hand, there was intensive activity in this field from 1935 to 1955. Apparently, the surfactant research field has reached a saturation point, and emphasis has shifted to processing research and investigations of physical and biological properties.

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NOTE

Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.