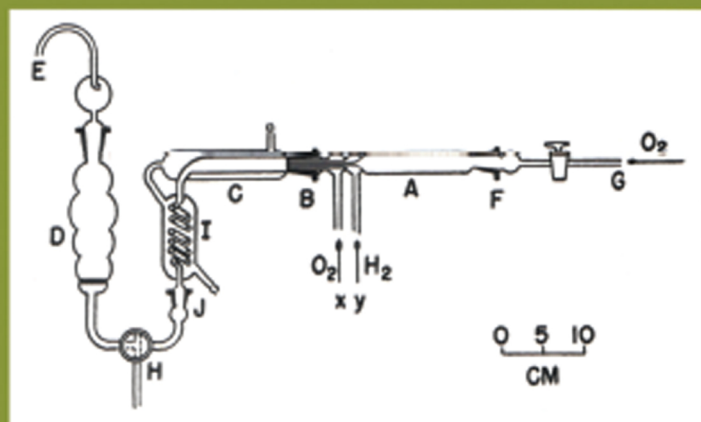


surfactant science series  
volume **73**

# ANIONIC SURFACTANTS

## Analytical Chemistry

Second Edition, Revised and Expanded



edited by  
John Cross

 **CRC Press**  
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# **ANIONIC SURFACTANTS**

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## **Analytical Chemistry**

### **Second Edition, Revised and Expanded**

edited by

John Cross

*University of Southern Queensland  
Toowoomba, Queensland, Australia*



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## Preface

Two decades have elapsed since the publication of the previous volume in the Surfactant Science Series that concentrated solely upon the analysis of anionic surfactants (Vol. 8, 1977). During that time a huge volume of water has passed beneath the proverbial bridge—much of which was more heavily laden with detergent residues than desirable.

World production of surfactants since that time has continued to grow steadily: the domestic and industrial markets have been expanding at annual rates of 2–3 and 4–5%, respectively, with the major growth being observed in eastern Europe, east Asia, and China. Despite inroads made by nonionic surfactants into the market, anionic surfactants have maintained their dominant position at the head of the total production of synthetic surfactants. The global capacity for the most popular class, the alkylbenzenesulfonates, is expected to reach between 2.7 and 3.0 Mt/y by the end of the century. This market position is not surprising given their excellent technical application behavior, favorable cost/performance characteristics, and well-researched biological properties.

During the past 20 years, new surfactants derived from new raw material feedstocks, improved process technology, and constantly changing consumer and environmental demands have kept formulations continually changing. Methyl ester sulfonates, for example, are making a significant assault on the market dominance of the linear alkylbenzenesulfonates, and liquid detergent concentrates are rapidly replacing the conventional powdered detergents on supermarket shelves.

Increasingly sophisticated techniques for the study of the behavior of surfactants both in solution and on surfaces such as skin, hair, and fabrics and the intensification of the scrutiny of the ecological and environmental impact of the



surfactants themselves and of their breakdown products have resulted in a corresponding increase in the degree of sophistication required in the analytical techniques applied to these materials. For example, the well-known determination of traces of anionic surfactants in wastewaters as “methylene blue active substances” has now been reduced virtually to the level of a screening test.

The enormous advances in instrumental techniques, typified by high-performance liquid chromatography, nuclear magnetic resonance, and hyphenated techniques such as gas chromatography–mass spectroscopy, have enabled the analyst to respond to these new challenges. However, many routine and nonroutine analyses still rely upon classical techniques such as titrimetry and even gravimetry: the standard methods adopted by such bodies as the International Organization for Standardisation and the American Society for Testing and Materials are heavily weighted in this direction.

Like other volumes in this series that I have compiled, this book is aimed at the chemist who has a firm grasp of the principles of analytical chemistry but is without any specialized knowledge of surfactants. Emphasis will be placed upon detailed examination of the methods used for the identification and determination of the surfactant itself, rather than attempting to present comprehensive schemes for the full analysis (i.e., every component) of formulated products such as shampoos or heavy-duty washing liquids. Sources that offer such a detailed examination are listed as recommended reading at the end of Chapter 1. Neither is it intended that this volume should function as a laboratory manual, although appropriate experimental procedures have been included in some instances. Again this function has been covered by some of the recommended readings. Rather, this volume is a critical appraisal of the literature and methodology currently available—a tour through the techniques, from which the analyst can select those necessary to tackle the problem at hand.

Following a brief introduction, the book falls naturally into three segments. Early chapters deal with colorimetry, titrimetry, and potentiometry—techniques that permit quantification without defining the structure of the surfactant to any precise degree. A chapter on tensammetry could have been included at this point, but the chapter written by M. Bos for Vol. 53 (*Cationic Surfactants: Analytical and Biological Evaluation*) of this series was sufficiently broad in its approach and content to serve as a reference for this book without further amendment. Subsequent chapters concentrate on the major instrumental techniques used for the separation and more specific identification of the separated components: quantification is also possible in most cases. The final chapter deals with fluorinated surfactants: in these compounds, the fully fluorinated alkyl chain is both hydrophobic and oleophobic, giving rise to some unique properties beyond those of their hydrocarbon-based counterparts.

The authors in this volume comprise an international collection of experienced practitioners, all of whom have industrial backgrounds. They have neither

been required to adhere to any preconceived format or guidelines in producing their chapters nor been asked to cover a predetermined set of surfactants: rather, they have been encouraged to present their material as they saw fit.

My sincere thanks go to these authors for providing their contributions on schedule (well, almost!) and to their employers for supporting their efforts: to the Series Editor, Dr. Martin Schick, for his ever-readiness to help; to the team at Marcel Dekker, Inc., for steering me through the production process in such a stress-free manner; to Dr. Norbett Buschmann for his help and interest; and to my dear wife for patiently excusing me from “other duties” while compiling this volume. The final dedication, however, must go to the many researchers, both past and present, whose published works have provided the raw material for this project.

*John Cross*



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# 1

## Anionic Surfactants—An Introduction

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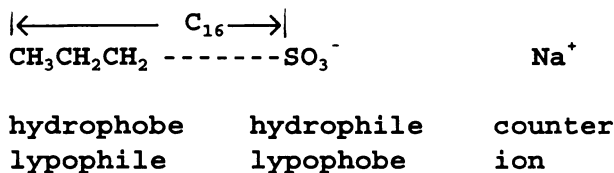
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## I. AN INTRODUCTION

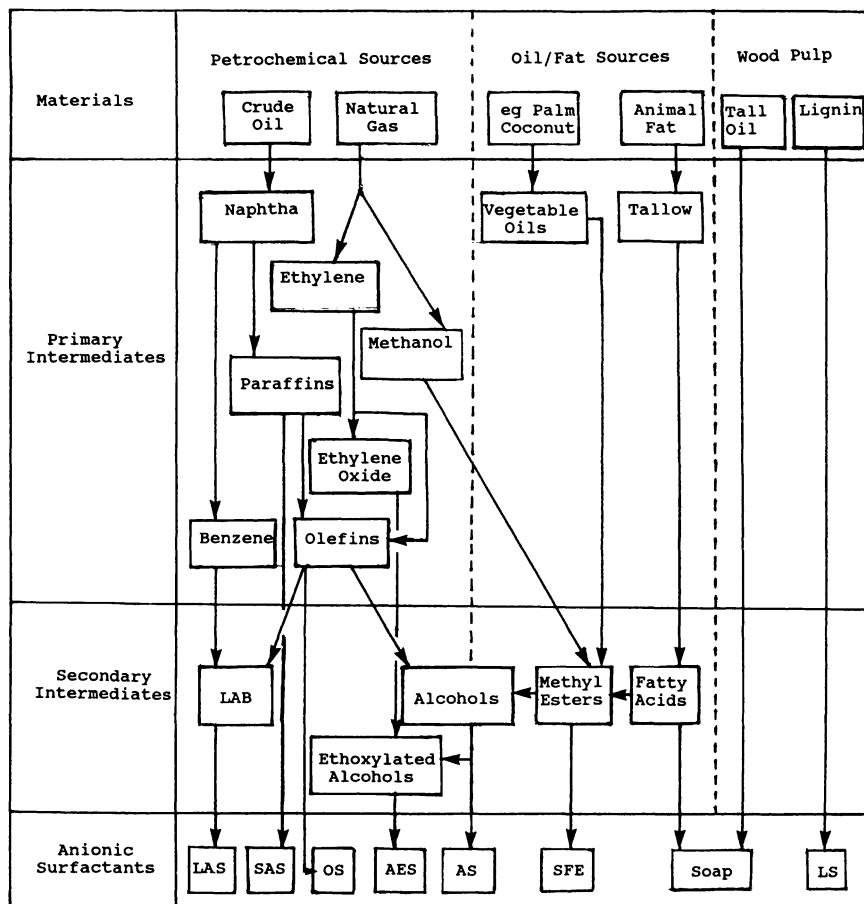
This chapter is intended to introduce the class of chemical compounds collectively known as anionic surfactants, the members of that class that have achieved major importance, and, as far as it affects the analyst, the raw materials, processes, and by-products that may be found. Some of the principal routes from the raw materials to surfactant are shown in Fig. 1. At this very early stage of this book, the author recommends to all readers interested in more detail that they consult the companion volume in the Surfactant Science Series, which concentrates on the preparation and properties of a wide range of anionic surfactants [1].

Surfactants are by necessity large molecules with molar masses usually in excess of 300. In the simplest case they consist of a nonpolar (usually hydrocarbon) chain attached to a highly polar or ionic group. These sections are known as the hydrophobe/oleophile/lipophile and the hydrophile/oleophobe/lipophobe, respectively, depending on the attraction—or lack thereof—to water or hydrocarbon oil.



It is essential that the ends of the hydrophobe and the hydrophile are sufficiently remote from each other to react with surfaces and solvent molecules independently. The relative weightings of these groups was quantified by Griffin [2] in the form of the hydrophile-lipophile balance (HLB), a parameter that indicates the field of application to which the surfactant is most suited [3]. For example, cetyl alcohol (HLB = 1.0) relies upon a single -OH group to provide any hydrophilic character; it is virtually insoluble in water but will spread over the surface of water in a dam to provide a surface film that significantly reduces evaporation. Glyceryl monostearate possesses two -OH groups plus a less polar ester group and consequently has a higher HLB (3.8): such compounds are excellent water-in-oil emulsifiers. As the hydrophilic factor grows, the surfactant becomes more suited for use as a wetting agent (e.g., sorbitan monolaurate, HLB = 8.6) and an oil-in-water emulsifier (e.g., polyoxyethylene monostearate, HLB = 11–15). Anionic surfactants (anionics) have high HLBs due to the presence of ionic hydrophiles such as  $-\text{COO}^-$  and  $-\text{SO}_3^-$ . HLBs range upwards from about 13 (e.g., sodium dodecanesulfonate, 13; sodium oleate, 18.5; and sodium dodecyl sulfate, 40): the major applications are to be found in the fields of detergency and solubilization.

Many treatises draw a distinction between “synthetic” and “natural” surfac-



**FIG. 1** Some principle routes for the production of anionic surfactants. LAB: linear alkylbenzene; LAS: linear alkylbenzenesulfonate; SAS: secondary alkanesulfonate; OS: olefinsulfonate; AES: alkyl ether sulfate; AS: alkyl sulfate; SFE: sulfonated fatty esters; LS: ligninsulfonate. (From Ref. 40.)

tants, the latter class being principally the soaps. Exactly what is natural about being boiled with sodium hydroxide is not made clear. As the public in general continues to strengthen its embrace of the concepts of “green” and “environmental capacity,” surfactant products have tended to become regarded as being “of natural origin” if they contain hydrophobes derived from fats and oils of recent animal or vegetable origin, despite the intensive chemical processing that follows. On the other hand, surfactants derived from fossil fuels are regarded as

“synthetic” despite the fact that their ultimate origin was, in fact, vegetable/natural [4].

It is appropriate that the next section should examine the major sources of the hydrophobes, their treatment, and the likely structures that may arise as a consequence.

## II. SOURCES OF THE HYDROPHOBE

The total global consumption of soaps is estimated to be some 8.5 million tons per annum (Mtpa). The fatty acids come almost exclusively from natural sources, i.e., animal fats and vegetable oils. Those derived from the oxidation of paraffin waxes tend to contain by-products and are of inferior quality. For the production of all other hydrophobes (except for the lignosulfonates), the fossil-based hydrophobes outweigh those from fats/oils sources 10-fold [5].

### A. Animal Fats and Vegetable Oils

The major fatty acid content of some of the common oils and fats are listed in Table 1. The distribution of the various homologs and ratio of saturated-to-unsaturated acids was once believed to be a fingerprint of the parent oil, but in practice there is too much variation in composition arising from the particular strain of seedstock used and environmental factors such as soil type, nutrient availability, etc. In addition, a certain degree of fractionation, intended or otherwise, is likely to occur during processing.

Whether a particular triglyceride is a solid or liquid at ambient temperatures depends largely upon the length of the hydrocarbon chains (higher intermolecular forces) and the degree of unsaturation. The enforced planar arrangement around the ethylenic linkages causes a kink in what otherwise could become a regular conformation of the chains: this, in turn, prevents the chains from packing into a neat crystalline array. The unsaturated compounds, therefore, have a lower melting range than their saturated counterparts. Soft soaps, for these reasons, may be derived from oils with a high unsaturated fatty acid content, such as cottonseed oils: alternatively, the counterion used may be potassium instead of the more usual sodium.

Tallow-sourced acids are frequently hydrogenated (i.e., hardened) and typically contain C14, C16, and C18 saturated acids with a ratio of 5:30:65 [7]. This process is so common that many marketing companies feel that it is unnecessary to declare that this has been carried out. Consequently, the term “tallow” attached to a product could refer to either the natural or the hydrogenated version.

The production of fats and oils is growing steadily and is expected to reach 100 Mtpa by the year 2000. Some 85% of oils are consumed as food, and the remainder, usually of poorer quality, is directed towards the oleochemicals indus-

**TABLE 1** Typical Percent Fatty Acid Distribution Among Some Common Oils and Fats

Name	Fatty acid			Source							
	Carbon no.	Unsaturated groups		Coconut	Palm kernel	Olive	Groundnut	Cottonseed	Sunflower	Mutton tallow	Beef tallow
Caprylic	8	—		8	3						
Caproic	10	—		7	5						
Lauric	12	—		46	47						
Myristic	14	—		15	15	0.4				2	5
Palmitic	16	—		9	7	18	6	20	6	25	28
Stearic	18	—		2	2		3	2	2	27	21
Arachidic	20	—					6				
Oleic	18	1		6	14	68	60	24	25	41	40
Linoleic	18	2		1	1	12	25	50	66	4	3

Source: Ref. 6.

try. Fatty acids are liberated from the triglycerides by saponification, by direct high pressure hydrolysis with water, or by transesterification with methanol. The crude acids may be contaminated with mono- or diglycerides and various other components, which may induce color and odor. Fractionation by vacuum distillation of the free acids or distillation of the methyl esters will produce cuts from the homologous series according to variations in volatility: such processing will have little effect upon the ratio of saturated to unsaturated components.

For conversion to alcohol sulfates or alcohol ether sulfates, the methyl esters are catalytically hydrogenated to the intermediate fatty alcohols and methanol. In contrast to fatty alcohols produced from mineral sources, those from vegetable oils and animal fats will reliably be primary alcohols with linear chains. The most useful fatty alcohols from these sources are coconut alcohol (and different cuts thereof), tallow alcohol, cetyl/stearyl alcohol, oleyl alcohol, and oleyl/cetyl alcohol [8]. Another unique feature of hydrophobes derived from natural sources is the presence of only chains with even carbon numbers, e.g., C12, C14, C16, C18, etc.

Apart from natural fats and oils, the other major natural contributor to surfactant raw materials is the wood-pulping industry. By-products include (a) tall oil, a dark, oily mixture of fatty acids and rosin acids (basically polycyclic terpene carboxylic acids), which can be treated either by acid-washing or fractional distillation to yield fatty acids containing approximately 40% and 5% rosin acids, respectively, and (b) lignin, a polymeric material as complex as wood itself, which is separated from cellulose and other compounds. During the bisulfite bleaching process a significant amount of addition occurs to produce lignosulfonic acids with molecular masses of 100,000 or more [9].

## B. Petrochemical Sources

The petrochemical industry provides the largest contribution to the hydrophobes of the nonsoapy anionic surfactants. The principal primary intermediates are benzene and linear paraffins, olefins, and alcohols. Hydrocarbon chains of suitable length must, in general, be generated either by polymerization of low molecular mass alkenes or by cracking of much larger molecules. Ethylene oxide and maleic anhydride (for sulfosuccinate synthesis) also arise from petroleum sources. In contrast to the products of fats/oils processing, petrochemically derived hydrocarbons contain both odd- and even-numbered carbon chains (unless produced by polymerization of ethylene).

### 1. Linear Paraffins

Linear paraffins in the molecular range C10–C18 are important as hydrophobes and are found in the kerosene and gas oil fractions. They are separated from other components of similar volatility by preferential adsorption onto synthetic

zeolites, which function as molecular sieves: the small cross-sectional area of *n*-alkanes allows them to enter the cavities of the adsorbent, whereas the much bulkier branched-chain, cyclic and aromatic species are too large to do so. Paraffins in this range are used to produce alkanesulfates or are dehydrogenated to alkenes.

Higher molecular mass alkanes in the C20–C30 range are components of the lubricating oils fraction. They are not amenable to isolation by molecular sieving, but can be separated from other components of the fraction by a process known as urea dewaxing (via formation of a clathrate type compound between urea and the paraffins). The principal use of these materials to the surfactant industry is as a feedstock for the production of lower molecular mass alkenes by steam cracking.

These processes, and most others outlined in this section, are discussed in some detail by Fell [5] and Hons [10].

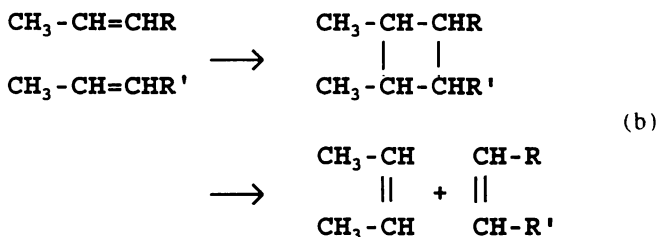
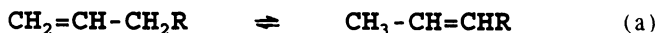
## 2. Linear Olefins

Linear olefins in the range C10–C18 are important intermediates in the synthesis of alkylbenzenes, olefinsulfonates, and fatty alcohols. The ethylenic link can be at the end of the chain ( $\alpha$ -olefins) or within the chain ( $\psi$ -olefins), depending upon the source of the hydrocarbon feedstock and the process to which it is subjected.

(a) *Wax Cracking.* The C20–C30 wax fraction of paraffins can be cracked to produce smaller alkenes and hydrogen. The fission occurs randomly along the length of the chain, but typically yields 40–45% of *n*- $\alpha$ -olefins in the desired C10–C18 range. However, also present will be significant amounts of  $\psi$ -olefins (5–10%), alkanes (1–5%), and dienes (2–4%), which serve to reduce the quality of the product. In addition, the supply of the required quantities of wax is often not reliable. For these reasons, this process is seldom used in heavily industrialised countries.

(b) *Dehydration of Primary Alcohols.* Primary alcohols dehydrated via a carbenium ion intermediate yield a mixture of  $\psi$ -olefins with only about 1%  $\alpha$ -olefin. Pure  $\alpha$ -olefin can be produced by the pyrolysis of simple esters of the alcohols, but this route involves an extra step. Recently, an aluminum oxide catalyst has been developed that results in the formation of about 93% *n*- $\alpha$ -olefins and 6% *n*- $\beta$ -olefins.

(c) *Dehydrogenation of Paraffins.* Paraffins may be dehydrogenated to a mixture of  $\psi$ -alkenes by numerous processes, which usually involve a platinum-based catalyst. Unfortunately, dienes, aromatics, and products from cracking and isomerization reactions are also formed. By careful selection of catalyst and conditions and accepting a low degree of conversion, the side reactions can be largely avoided and the alkane/alkene mixture can be used for the alkylation of



**FIG. 2** Oligomerization of olefins: (a) internal isomerization; (b) disproportionation.

benzene: the unreacted alkane can be separated by fractionation and recycled through the dehydrogenation process.

(d) *Oligomerization of Ethylene.* The polymerization of ethylene produces  $n$ - $\alpha$ -olefins of high purity, especially with regard to the absence of dienes, and with even numbers of carbon atoms in the chains. The two major processes, the Ziegler using triethyl aluminium or catalysis with a transition metal complex, both result in a wide range of molecular sizes for the  $n$ - $\alpha$ -olefin plus small amounts of  $\beta$ -alkyl-1-olefin and linear  $\psi$ -olefins. After fractionation to isolate the desired cut (C10–C18), the remaining olefins in the C4–C8 and C18+ range may be reprocessed by isomerization to internal olefins (Fig. 2a) followed by disproportionation (Fig. 2b).

A substantial portion of the  $\psi$ -olefins produced falls within the desired molecular range [10].

### 3. Branched Olefins

Propene, usually in admixture with propane, can be polymerized using a phosphoric acid catalyst at 200° and at high pressure to produce alkenes suitable for conversion to alkylbenzene and subsequently to alkylbenzenesulfonate. Fractional distillation of the product yields first unconverted propane, followed by tripropylene, which can be returned to the reactor or removed for use as motor fuel. The next fraction is an extremely complex mixture known as tetrapropylene and consists of many structural and double bond isomers of dodecene that are so closely related in physical properties that even capillary gas chromatography cannot fully resolve them [11].

Isobutene polymerization by the above process results in a simpler fraction of C12 alkenes, but they tend to depolymerize under the conditions needed for the

subsequent Friedel-Craft conversion to alkylbenzene. An alternative reaction route results in a product with much less chain branching that is suitable. Since surfactants manufactured from alkylbenzenes with substantial branching in the alkyl chain are resistant to biodegradation, they are not to be found extensively in most industrialised countries. By way of comparison, the global capacity for production of linear alkylbenzenesulfonates in the early 1990s was about 2 Mtpa, whereas for the branched-chain equivalents it was less than 500 kt. Principal producers are France, Latin America, and Japan [12].

### III. COMMON TYPES OF ANIONIC SURFACTANTS

The majority of surfactants to be discussed here are either sulfonates or sulfate esters. In the latter case, the hydrophobe is attached to the hydrophile by a labile C-O-S linkage; this is relatively easily hydrolyzed to the corresponding alcohol and (bi)sulfate ion by dilute aqueous acids. Sulfonates, on the other hand, contain a robust C-S linkage that is much more stable; it is broken only by drastic treatment such as refluxing with concentrated phosphoric acid. The sulfonates, therefore, find application in a variety of pH conditions that are too drastic for sulfate esters. The sulfonates will be considered first.

#### A. Alkylbenzenesulfonates

The behavior of alkylbenzenesulfonates, both in the washing machine and in the environment, must surely be ranked as the most intensively studied of all the surfactants. Second only to soap in its production volume, it was first reported in 1923, but large-scale production in the Western world did not commence on a significant basis until after the end of World War II. Propene was being produced in large quantities as a by-product of the oil-processing industry; it could be simply and inexpensively polymerized using a phosphoric acid catalyst. The C12 distillation cut of the mixture, tetrapropylene, could be used to produce first tetrapropylbenzene and then tetrapropylbenzenesulfonates (TPBS). These surfactants could be formulated into a detergent with an excellent price : performance ratio and in the late 1950s represented two thirds of the Western world's synthetic anionic SA production [13]. However, at this time, huge quantities of foam, albeit usually stabilized by wastes from other sources, were all too frequently to be seen on inland waters of Western Europe and the United States. This precipitated a detailed study (beyond the scope of this book, but admirably covered by Swisher [14]), from which it was ascertained that the root of the problem lay in the resistance of the highly branched alkyl chain to biodegradation. Regulations were introduced into most regions requiring that the surfactants used in detergents be degraded to



an extent of at least 80% after a specified period in a wastewater treatment plant. Alkylbenzenesulfonates made from linear olefins (LAS) met this requirement easily.

The ecological suitability of LAS was the subject of a major conference in 1989, reported in detail in an issue of *Tenside, Surfactants, Detergents* [16]. A quality objective of 12–25  $\mu\text{g/L}$  had been deduced from NOEC (no observable effect concentration). Occasional concentrations of 20–30  $\mu\text{g/L}$  were reported in the Ruhr River at that time, and the need for continued vigilance and search for even more ecologically acceptable surfactants was stressed [17].

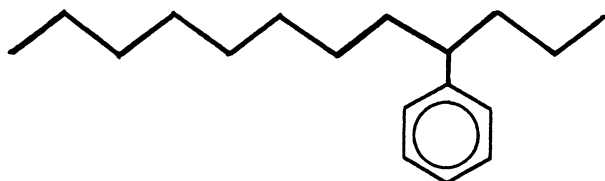
In addition to being the mainstay of laundry and general household products, LAS finds application in cosmetics, plastics, petroleum production, agriculture, the food and textile/dyeing industries, and metal treatment. With markets for LAS increasing in Latin America, the Near East, the Far East and Southeast Asia, the global capacity for production could reach 3 Mtpa going into the next century [15]. Alkylbenzenesulfonates with branched chains, however, have not entirely disappeared from the global scene: Fell listed the annual production as approximately 0.5 Mtpa [18,19].

## 1. Production of Alkylbenzenes

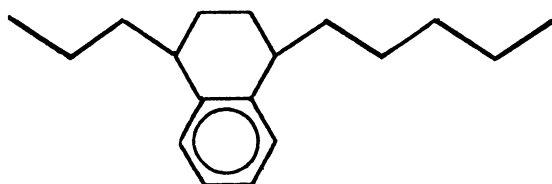
The alkylation of benzene with an *n*-olefin is a Friedel-Craft reaction, catalyzed by hydrogen fluoride, aluminum chloride, or aluminosilicates: a fourth process using chloroparaffins as intermediates is no longer of commercial importance. Since the ease of carbonium ion production is in the order of tertiary carbon > secondary carbon > primary carbon, there is virtually no 1-phenylalkane in the product. The result of such a reaction is a complex mixture: a C9–C14 cut of *n*-olefin, for example, can produce 30 structural isomers and homologs (Fig. 3a) in addition to dialkyltetralins (Fig. 3b). The spread of these isomers is very much dictated by the catalyst. The aluminosilicate and aluminum chloride routes result in some 25% 2-phenylalkanes, whereas hydrogen fluoride causes the proportion of these isomers to fall to around 15%. As another example, a nominal C12 olefin yields approximately 28 and 19% of 5-phenylalkanes with hydrogen fluoride and aluminum chloride respectively. (Further details are to be found in Ref. 1.)

For alkylation with tetrapropylene (Fig. 3c) (already a complex mixture), both the hydrogen fluoride and aluminum chloride catalysts promote side reactions such as polymerization, isomerization, and also fragmentation. In the latter process a C12 isomer might fragment into, say, C4 and C8 fragments, which result in the formation of *t*-butyl- and *t*-octylbenzene, respectively. Such low molecular mass alkylbenzenes are largely removed by fractionation prior to sulfation.

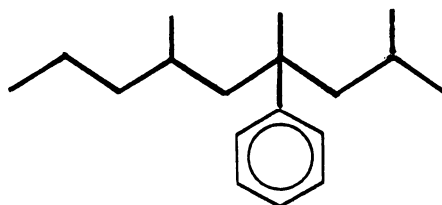
In summary, the alkylbenzenes used for commercial surfactant production are complex mixtures.



(a)



(b)



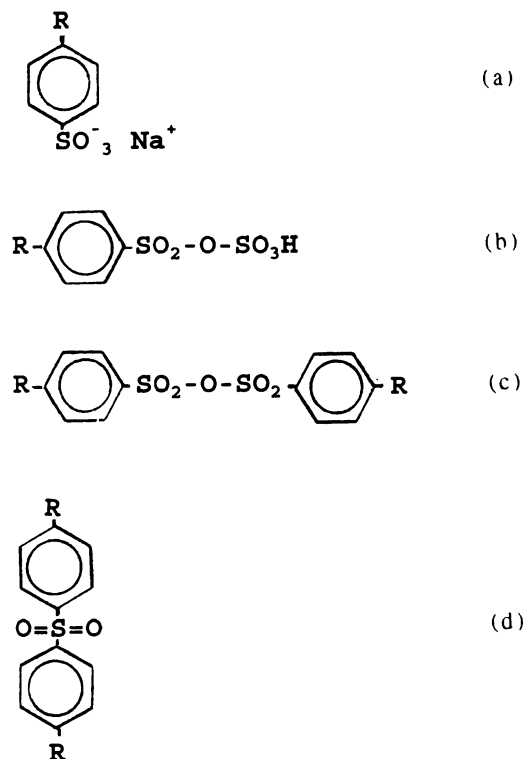
(c)

**FIG. 3** Alkylbenzene structures: (a) a linear alkylbenzene; (b) a dialkyltetralin; (c) a highly branched alkylbenzene.

## 2. Sulfonation of Alkylbenzenes

The sulfonation can be achieved with concentrated sulfuric acid, oleum, or sulfur trioxide, the latter being preferred. Substitution occurs almost exclusively in the *para* position (Fig. 4a), since the large hydrophobic chain effectively hinders approach to the *ortho* positions. Conversion efficiency varies between 92 and 98%: attempts to increase the yield result in the formation of highly sulfonated by-products.

The actual route is quite complex. Pyrosulfonic acid (Fig. 4b) and the sulfonic anhydride (Fig. 4c) are formed as intermediates: these later react with more



**FIG. 4** Alkylbenzenesulfonate production: (a) an alkylbenzene sulfonate; (b) a pyrosulfonic acid (intermediate); (c) a sulfonic acid anhydride (intermediate); (d) a dialkyldiarylsulfone (by-product).

alkylbenzene or added water to yield the desired sulfonic acid. A good-quality product typically contains:

Alkylbenzenesulfonic acid: 97–98%

Sulfuric acid: ~0.5%

Neutral oil: 1.5–2.5%

Any dialkytetralins present are also sulfonated and in the final product will function as hydrotropes. The neutral oil consists mainly of the by-product dialkylarylsulfones (Fig. 4d) and unreacted alkylbenzenes.

## B. Secondary Alkanesulfonates

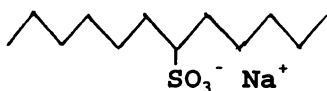
Secondary alkanesulfonates are produced in the order of 160,000 tons a year, mainly in Europe and Japan [20]. They occupy a position in a class between the

“workhorse” alkylbenzenesulfonates and the speciality surfactants to be found in later pages [21]. Although excellent performers in the laundry, they cannot compete economically with LAS in powdered products but come into their own in concentrated liquid formulations (due to their high solubility in water), in which they are frequently to be found together with alkylether sulfates: these two types of surfactants form a particularly effective synergistic system. Major domestic applications are in (liquid) laundry detergents, dishwashing liquids, shampoos, and other personal care products. Industrial applications include cleaners, emulsifiers for PVC polymerization and products for the textile industries (washing of fibers, desizing, mercerizing, carbonization, and fatting of leather).

There are two major routes for synthesis, both photochemically induced free radical reactions. In the sulfoxidation process, the paraffin is reacted with a mixture of sulfur dioxide and oxygen. In the sulfochlorination process a mixture of chlorine and sulfur dioxide is used to produce an alkanesulfonyl chloride intermediate, which is saponified with sodium hydroxide to yield the sodium alkane-sulfonate. Traces of organic chlorine compounds (approximately 0.15%) in the final product indicate this route for preparation.

Being the product of free radical attack upon the alkane, the position of substitution depends largely upon the homolytic fission energy of the C-H bonds. In practice this results in the sulfonate group group being distributed fairly evenly between the internal carbon atoms of the chain and only about 1% of the 1-isomer. Consequently, this class of surfactant is frequently termed secondary sulfonate (Fig. 5a). A C13–C18 paraffin cut, for example, has over 40 such isomeric/homologous positions to offer. In addition, about 10% of poly (mainly di-)sulfonates are formed. The biodegradability of this class of surfactants is excellent. Primary degradation occurs to the extent of 90% in 2 days and more than 99% in 4 days [21].

Another class of surfactant, the alkylethoxysulfonates (Fig. 5b), is strictly included in this group. These are produced from alkyl or alkylphenol ethoxylates



(a)



(b)

**FIG. 5** Sulfonates: (a) an alkanesulfonate; (b) an alkylethoxysulfonate.

by conversion of the terminal -OH group initially to a chloro derivative (with thionyl chloride) and thence to a sulfonate (with sodium or potassium sulfite). The products are too expensive for widescale use but have a high tolerance to salinity and find application in enhanced oil-recovery operations [22].

### C. Olefinsulfonates

As has already been pointed out, olefins for surfactant manufacture are conveniently divided into  $\alpha$ - and  $\psi$ -olefins according to the position of the ethylenic link (terminal or internal, respectively). Both types may be sulfonated to yield the products known as  $\alpha$ -olefinsulfonates (AOS) and internal olefinsulfonates (IOS), respectively.

The production and application of AOS is well established, whereas that of IOS is embryonic. The composition of both types is quite complex and varies not only with the choice of olefin feedstock but also with the sulfonation method used and the reaction conditions employed [23].

#### 1. Sulfonation of $\alpha$ -Olefins

(a) *Sulfonation.* The  $\alpha$ -olefin/sulfur trioxide reaction mixture (Fig. 6a) results initially in the formation of a reactive intermediate 1,2-sultone (Fig. 6b). During a follow-up aging process, this either (1) rearranges to a 1,3-sultone (rapid) or a 1,4-sultone (slow) (Figs. 6c and 6d) or (2) reacts to yield alkenesulfonic acids (Fig. 6e). The ratio of these products varies according to the initial ratio of sulfur trioxide to olefin. If this ratio is less than 1.0, the 1,3-sultone predominates; if it is in the region of 1.0–1.2, a larger proportion of the sulfonic acid will be formed. Excessive amounts of sulfur encourage the formation of disulfonic- and sultonesulfonic acids. As the aging time increases, the 1,3-sultone concentration decreases as it rearranges to the 1,4-sultone [24]. Prolonged aging leads to the formation of dimers and higher polymers.

(b) *Neutralization and Hydrolysis.* Heating with sodium hydroxide not only neutralizes the alkenesulfonic acid, but also causes the 1,3- and 1,4-sultones to become hydrolyzed into 3- and 4-hydroxyalkanesulfonates (Figs. 6f and 6g). The sultones remain in trace quantities only after this treatment. A typical commercial sample might be composed as follows:

Sodium alkenesulfonates: 65%

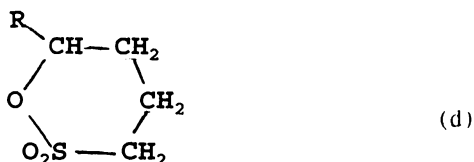
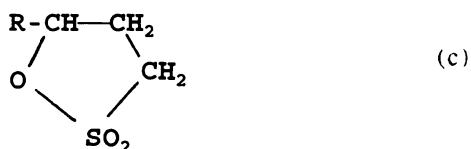
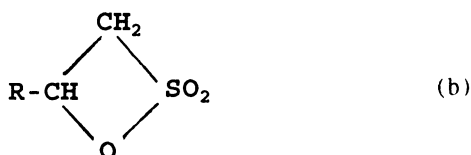
Sodium 3- and 4-hydroxyalkane sulfonates: 28%

Disulfonates\*: 5%

Sodium 2-hydroxyalkanesulfonates: <1%

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\*The term "disulfonate" is strictly a misnomer. The correct description is sulfatosulfonate (Fig. 6h) [25].



**FIG. 6** Sulfonation of  $\alpha$ -olefins: (a)  $\alpha$ -olefin/sulfur trioxide reaction mixture; (b) a 1,2 sultone (intermediate); (c) a 1,3 sultone (intermediate); (d) a 1,4 sultone (intermediate); (e) alkenesulfonic acids; (f) a sodium 3-hydroxyalkane sulfonate; (g) a sodium 4-hydroxyalkane sulfonate; (h) a disodium sulfatoalkanesulfonate.

## 2. Sulfonation of Internal Olefins

One of the main purposes of aging of the  $\alpha$ -olefin sulfonation product is to minimize the 1,2-sultone content, because this intermediate will otherwise hydrolyze to the 2-hydroxyalkanesulfonate, a compound of poor solubility. The  $\beta$ -hydroxy-sulfonates formed from internal olefins, however, have a higher solubility and consequently the aging process can be omitted. The product of such an approach is typically:

Sodium  $\beta$ -hydroxyalkanesulfonates: 83%

Sodium alkanesulfonates: 10%

Sodium  $\alpha$ -hydroxyalkanesulfonates: 5%

Unulfonated oils: 2%

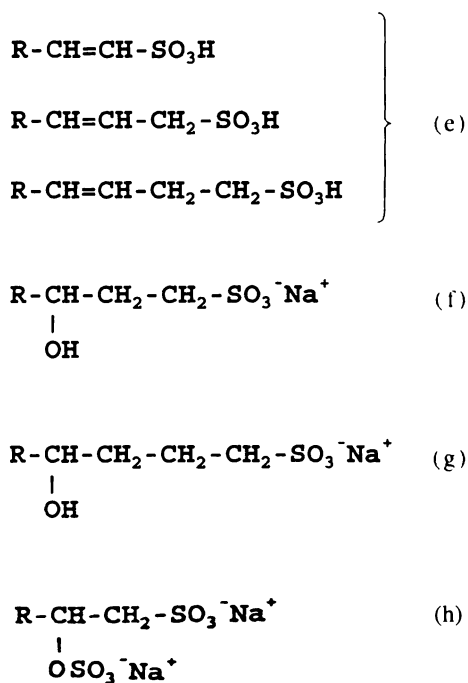


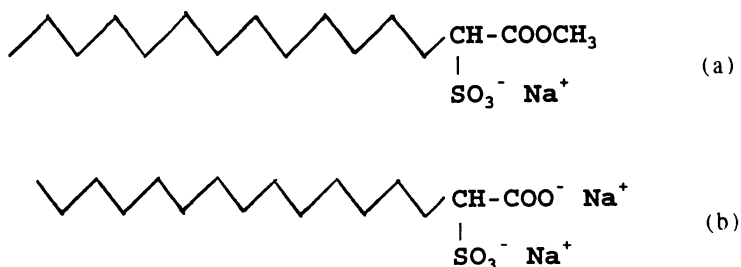
FIG. 6 Continued

If an aging step is introduced, the  $\beta$ -hydroxyalkanesulfonate content falls and that of the other two surfactants rises accordingly. A comprehensive account of the factors affecting the composition of the mixture was recently presented by Radici et al. [26].

The olefin sulfonates possess both good wetting and detergency properties plus high tolerance to calcium and magnesium ions, i.e., hard water. They are used mainly in light duty liquids (C12–C16) and heavy duty powders (C16–C18). Japan is the major consumer, followed by North America, Europe, South Korea, and India; the latter country represents a major future market for AOS.

#### D. Ester Sulfonates

This class of surfactants goes under a variety of names, namely,  $\alpha$ -sulfomono-carboxylic esters,  $\alpha$ -sulfo fatty acid esters (SFE), fatty acid  $\alpha$ -sulfonates, or alkyl (usually methyl) ester sulfonates (MES) (Fig. 7a). They are of increasing interest, particularly in Japan [4], by virtue of being derived from a renewable (natural) source coupled with good wetting and washing performance, rapid



**FIG. 7** Ester sulfonates: (a) a sodium alkyl (methyl ester) sulfonate; (b) disodium salt of  $\alpha$ -sulfofatty acid (by-product).

biodegradability and excellent performance in hard water, even to the extent of improving the behavior of soaps in such a solvent (lime soap dispersion) [27,28]. This latter property makes the ester sulfonates logical inclusions in phosphate-free formulations. A mixture of linear alkylbenzenesulfonate (which performs well in soft water but not in hard) and MES (which performs better in hard water than in soft) provides a combination that works well as a heavy duty detergent in both hard and soft waters, especially if an alcohol ethoxylate is present [27].

In the initial step of the manufacturing process, fatty acid triglycerides are trans-esterified with a low molecular mass alcohol (usually methanol, but could be up to a C4 alcohol). The monoesters can be fractionated at this stage (low C numbers for liquid detergents, high C numbers for powder detergents) and hydrogenated (high unsaturation results in a bad color upon sulfonation). Since the surfactants perform better when the hydrophilic group is at the end of the chain rather than in the middle, the use of the methyl ester ensures that the second alkyl chain is as short as possible.

The mechanism of the sulfonation reaction is complex [27] and involves formation of a mixed carboxylic-sulfonic acid anhydride as an intermediate. Substitution into the  $\alpha$ -position on the fatty chain is favored not only by the activation of that position by the adjacent carbonyl group but also by its proximity to the cyclic structure of the intermediate.

This reaction provides an example of the perpetual conflict between the speed of the transformation and product quality. The reaction mixture is one that requires aging for optimum results. If the mixture is neutralized too soon, an unacceptable quantity of the di-salt of the  $\alpha$ -sulfo fatty acid is formed (Fig. 7b), which reduces the performance of the final surfactant mixture. This by-product is also enhanced if the concentration of sulfur trioxide is raised to speed up the reaction.



Cullum [25] cites soaps, unsulfonated ester, and sodium methosulfate as additional by-products.

## E. Other Sulfonated Surfactants

A large number of additional sulfonated surfactants has found application: the more commercially important ones are listed here. Largely they are regarded as being in the low-volume/high-cost bracket. One property that they all have in common is a good tolerance to hard water.

### 1. Fatty Acid Isethionates

Acyl isethionates have been known for over 60 years. Sodium isethionate (Fig. 8a) is first produced by the reaction of ethylene oxide and sodium hydrogen sulfite; this, in turn, is reacted with a fatty acid using a mineral acid catalyst to give the surfactant ester (Fig. 8b). Due to the susceptibility of the ester group to hydrolysis, especially under alkaline conditions, these surfactants are generally to be found in products of moderate pH such as cosmetics and soap/syndet combinations [28]. The only likely impurities are sodium isethionate and free fatty acid or soap [25] and sodium chloride if the preparation involved a fatty acid chloride as an intermediate.

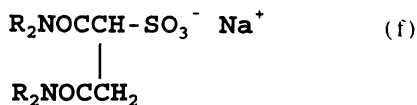
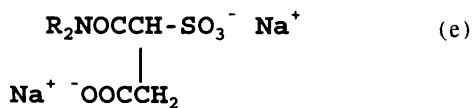
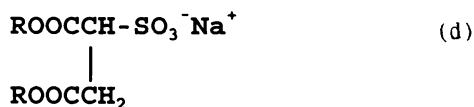
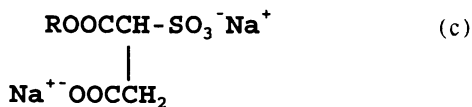
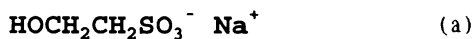
### 2. Sulfosuccinate Esters

Since succinic acid is a diprotic acid, it can give rise to either mono- or diesters. Both types can be sulfonated to give two distinct series of surfactants.

The first step is the reaction between maleic anhydride and the hydrophobe, which is commonly a C12–C18 fatty alcohol or a fatty acid alkanolamide (either of which could be ethoxylated). When equimolar amounts of reactants have been consumed, the synthesis of the maleic monoester is deemed to be complete and a slight excess of sodium sulfite is added. Since neither of these reactions goes to completion, the overall product is a complex mixture comprising about 80% sulfonated monoester (Fig. 8c) plus some diester (Fig. 8d), the trisodium (nonester) salt, and unreacted raw materials [29].

To produce the diester, a higher temperature and a catalyst are employed and the water produced is continuously removed to shift the reaction equilibrium towards completion. The sulfonation step is also carried out more efficiently, so that the final product contains only minor amounts of impurities. The alcohols used for the initial diester formation are shorter, typically in the C6–C8 range. The di(2-ethylhexyl) derivative, for example, is a popular wetting agent for the textile industry.

Cullum [25] points out that ammonium bisulfite is sometimes used as the sulfonating agent, in which case small amounts of mono- and dialkyl aspartates are also formed. Typical fields of application as wetting agents include personal care products (these surfactants are particularly mild to the skin), emulsion polymerization, textile industry, paints, and agricultural sprays.



**FIG. 8** Production of miscellaneous sulfonated surfactants: (a) sodium isethionate; (b) a sodium acyl isethionate; (c) disodium salt of a sulfonated monoalkyl succinate; (d) sodium salt of a sulfonated dialkyl succinate; (e) disodium salt of a sulfosuccinamate; (f) sodium salt of a sulfosuccindiamide; (g) sodium of an acyl methyl taurate.

### 3. Sulfonated Amides

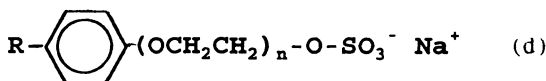
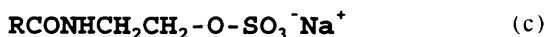
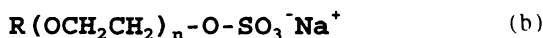
If fatty amines are used instead of alcohols to make the malate intermediates, the final product will be a sulfosuccinamate (Fig. 8e) or a sulfosuccinamide (Fig. 8f). These compounds do not have the wetting capabilities of the sulfosuccinate esters, but are used as detergents, solubilizers, and dispersants.

Acyl taurates and acyl methyl taurates (Fig. 8g), frequently oleic acid derivatives, are probably the only other members of this large group of surfactants of any general interest [25]. They are used in shampoos and syndet bars, etc.

## F. Sulfate Esters

As mentioned at the beginning of this section, sulfates differ from the various sulfonate species listed above in that they are esters (mono esters of the diprotic sulfuric acid) in which the hydrophobe is joined by a C-O-S linkage rather than a direct C-S bond. The hydrophobe containing the reactive -OH group needed to form the ester is normally a fatty alcohol, but could also be a fatty alcohol ethoxylate, an alkanolamide (ethoxylate), an alkylphenol ethoxylate or a mono/diglyceride. The surfactants resulting from sulfation of these species are shown in Fig. 9.

The fatty alcohols may be derived from natural fats and oils or may be synthesised via the Ziegler or OXO processes [30]. The alcohol sulfates are the classic members of this class, having been used extensively since the 1930s. It is estimated that about 40% of the global production of fatty alcohols is converted to the sulfate ester. The product is commonly marketed as the sodium salt, but



**FIG. 9** Sulfate esters: examples of sodium salts derived from (a) fatty alcohol; (b) fatty alcohol ethoxylate; (c) fatty acid alkanolamide; (d) alkylphenol ethoxylate; (e) fatty acid monoglyceride.

the triethanolamine salt is often used in preparations such as shampoo on account of its combination of higher solubility, good foaming properties, and lower irritance to the human eye.

The application varies with the alkyl chain length. The shorter chains, C8–C10, provide excellent wetting agents and hydrotropes (viscosity modifiers), sodium 2-ethylhexyl sulfate being a particularly common example. The longer chains give rise to products with better deterative, emulsifying, and dispersing properties: the C12–C15 members perform well at low temperatures and the C16–C18 members at higher temperatures. Tallow alcohol sulfates are popular ingredients of heavy duty detergents.

Sulfate esters prepared from fully-saturated alcohols tend to contain little by way of impurities other than unsulfated matter and sodium sulfate. Sodium dodecyl sulfate, prepared from carefully fractionated dodecanol, can be recrystallized and dried to produce a surfactant approaching 100% purity, which is used as *the* primary standard anionic surfactant in analytical and basic studies alike.

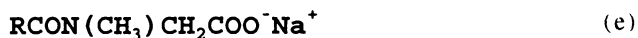
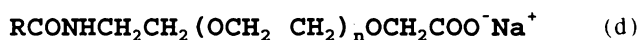
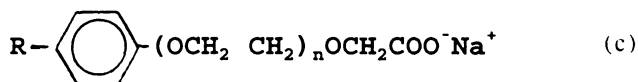
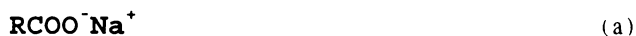
The fatty alcohols may be lightly ethoxylated prior to sulfation. The average ethylene oxide chain length is usually about two, seldom more than four. The inclusion of this additional hydrophile has the surprising effect of reducing the critical micelle concentration. These derivatives are more skin compatible than their unethoxylated counterparts and are popular as ingredients in high foam preparations. The use of ethylene oxide normally results in the inclusion of some 1,4-dioxane in the final product, but this is normally only of the order of a few parts per million and well below the concentration regarded as a health hazard.

Although the sulfate ester link is regarded as labile, it is only under acidic conditions ( $\text{pH} < 4$ ) that this becomes a problem. Domingo [30] sums up the alkyl sulfates thus:

It is difficult to find an industrial sector that does not use alcohol- or alcohol ether sulfates. These surfactants are rendered so versatile in their chemical structure through variations in alkyl chain distribution, the number of moles of ethylene oxide or the cation, that it is possible to find the adequate sulfate achieving the highest mark in every surfactant property. This and the relative low cost are the two main reasons for their vast industrial use.

## G. Carboxylates

The carboxylate anion has already been encountered in this introduction as it occurs conjointly with a sulfonate group (e.g., in sulfosuccinates), but it does, of course, stand as a hydrophile in its own right. The sodium salts of long-chain fatty acids, better known as soaps, are, of course, *the* classic surfactants, having been used for many centuries (Fig. 10a). Many treatises on surfactants treat soaps as a class of their own, not to be included under the heading of anionic



**FIG. 10** Carboxylate surfactants: (a) a carboxylate soap; (b) a polyether carboxylate derived from a fatty alcohol; (c) a polyether carboxylate derived from an alkylphenol; (d) a polyether carboxylate derived from a fatty acid monoethanolamide; (e) an acyl sarcosinate.

surfactants: the latter term is reserved for the synthetic members, the so-called *syndets*.

As indicated earlier, soaps may be derived from:

1. Animal fats, e.g., tallow soaps. Major constituents are palmitic acid (C16 saturated, 25–30%), stearic acid (C18 saturated, 15–20%) and oleic acid (C18 monounsaturated, or C18:1, 40–45%).
2. Vegetable oils, e.g., coconut oil. Major constituents are C12, 47%; C14, 17–20%; C16, 8–10%; C16:1, 5–6%.
3. Tall oil, a mixture of fatty acids, mainly unsaturated (70–75%), and rosin acids (25–30%) from the wood-processing industry.

The associated cation is normally sodium, but others are common. The alkanolamine (mono-, di-, and tri-) salts are more soluble than the corresponding sodium soaps, have better foaming characteristics, and are milder to the skin. Potassium salts are traditionally used as liquid soaps, but most modern “liquid soaps” are formulations of mild synthetic anionic surfactants and lather boosters, etc., and contain no soap at all [9].

Alkyl polyether carboxylates (Fig. 10b) are substantially different from soaps. Although known since the 1930s, their general application, apart from minor use in toilet preparations and the textile trade, did not flourish until the 1980s. At this time, increased attention to environmental issues and to skin compatibil-