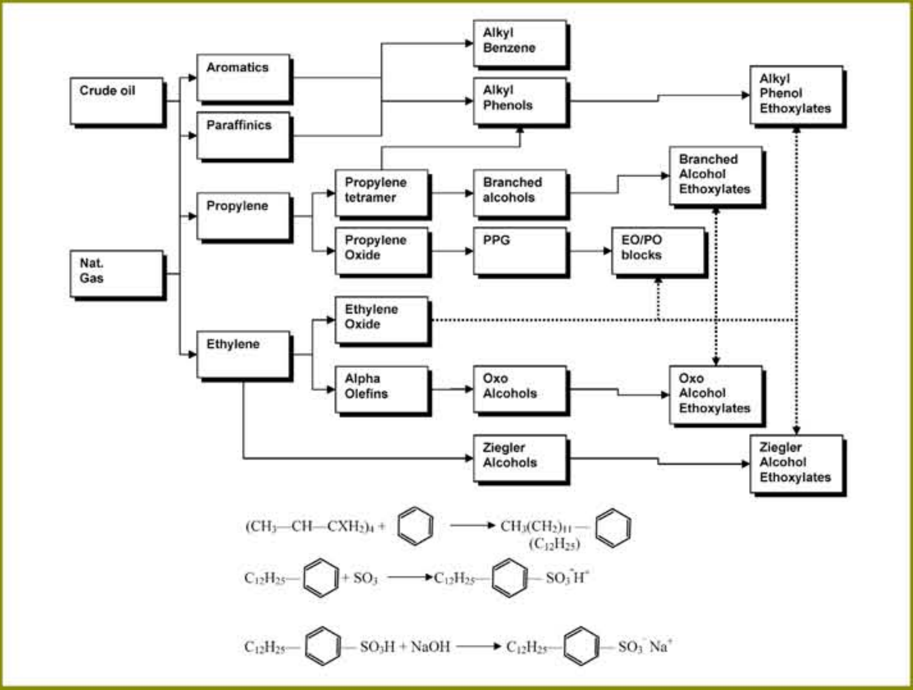
surfactant science series

volume **142**

HANDBOOK OF DETERGENTS

Part F: Production



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HANDBOOK OF DETERGENTS

Part F: Production

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HANDBOOK OF DETERGENTS

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Part F: Production

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Handbook Introduction

The battle cry for sustainable development in our globalized world is persistent in all circles, gaining acceptance as the guiding rationale for activities or processes in the science–technology–environment–economy–society–politics interfaces, targeting at improvement and growth. Such activities are expected to result in higher standards of living leading, eventually, to a better quality of life for our increasingly technology-dependent modern society. Models of sustainable development and exemplary systems of sustainable management and applications are continually being developed and adapted and creatively applied, considering, more than before, human needs, rather than "wants" on the one hand, and long- versus short-term benefits and trade-offs on the other.

"Detergents" constitute a classic case study within this context: this is a multidimensional systemic enterprise, operating within complex sociopolitical/technoeconomical realities, locally and globally, reflecting in its development and contemporary "state of affairs," the changing dynamic equilibria and interrelationships between demands/needs, cost/benefits, gains/trade-offs, and social preferences–related policies. It is not surprising, therefore, that despite the overall maturity of the consumer market, detergents continue to advance, in the modern world and developing societies, more rapidly than population growth.

The soap and detergent industry has seen great change in recent years, requiring it to respond to the shifts in consumer preferences, requests for sustainability, the availability and cost of raw materials and energy, demographic and social trends, as well as the overall economic and political situation worldwide. Currently, detergent product design is examined against the unifying focus of delivering performance and value to the consumer, given the constraints of the economy, technological advancements, and environmental imperatives. The annual 2–3% growth of the detergent industry and the faster growth in personal care products reflect impressive developments in formulation and application. The detergent industry is thus expected to continue its steady growth in the near future in response to the ever-increasing demands of consumers for products that are more efficient, act fast, and are easier to use. For the detergent industry, the last decade of the twentieth century was one of transformation, evolution, and consolidation. On both the supplier and consumer market sides (both remain intensely competitive), the detergent industry has undergone dramatic changes, with players expanding their offerings, restructuring divisions, or abandoning the markets altogether. This has resulted in changing hands and consolidation of the market, especially in the last several years. This trend appears to be gaining momentum. Yet, the key concepts have been and still are innovation, consumer preferences, needs, multipurpose products, cost/benefit, efficiency, emerging markets, partnership/cooperation/collaboration/merging (locally, regionally, and globally), and technological advancements. Although substantial gains and meaningful rapid changes with respect to the preceding concepts have been experienced by the surfactant/detergent markets, the same cannot be said for detergent/surfactant technology itself. The $9-billion-plus detergent ingredient market and the annual global consumption of ~13 million tons of "surfactants" in 2006 have many entrenched workhorse products. This may suggest that the supply of "solutions" to most cleaning "problems" confronted by consumers in view of the increasing global demand for formulations having high performance and relatively low cost and the need for compliance with environment-related regulation are based on modifications of existing technologies.

What does all this mean for the future of the "detergents" enterprise? How will advances in research and development affect future development in detergent production, formulation, applications, marketing, consumption, and relevant human behavior as well as the short- and long-term impacts on the quality of life and the environment? Since new developments and emerging technologies are generating new issues and questions, not everything that can be done should be done; that is, there should be more response to real *needs* rather than *wants*.

Are all these aforementioned questions reflected in the available professional literature for those who are directly involved or interested, for example, engineers, scientists, technicians, developers, producers, formulators, managers, marketing people, regulators, and policy makers? A thorough examination of the literature, in this and related areas, suggests that a comprehensive series is needed to deal with the practical aspects involved in and related to the detergent industry, thus providing a perspective beyond knowledge to all those involved and interested. The *Handbook of Detergents* is an up-to-date compilation of works written by experts, each of whom is heavily engaged in his/her area of expertise, emphasizing the practical and guided by the system approach.

The aim of this six-volume handbook project (properties, environmental impact, analysis, formulation, application, and production) is to provide readers who are interested in any aspect of or relationship to surfactants and detergents, a state-of-the-art comprehensive treatise written by expert practitioners (mainly from industry) in the field. Thus, various aspects involved—properties, environmental impact, analysis/test methods, formulation application and production of detergents, marketing, environmental, and related technological aspects, as well as research problems—are dealt with, emphasizing the practical. This constitutes a shift from the traditional, mostly theoretical focus, of most of the related literature currently available.

The philosophy and rationale of the *Handbook of Detergents* series are reflected in its title and plan and the order of volumes and flow of the chapters (in each volume). The various chapters are not intended to be and should not, therefore, be considered to be mutually exclusive or conclusive. Some overlapping segments focus on the same issue(s) or topic(s) from different points of view, thus enriching and complementing various perspectives.

There are several persons involved whose help, capability, professionality, and dedication made this project possible: the volume (parts) editors, contributors, and reviewers are in the front line in this respect. Others deserve special thanks: my colleagues and friends in (or associated with) the detergent industry, whose timely help and involvement facilitated in bringing this project home. I hope that the final result will justify the tremendous effort invested by all those who contributed; you, the reader, will be the ultimate judge.

Uri Zoller
Editor-in-Chief

Handbook of Detergents Series

Editor-in-Chief
Uri Zoller

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- *Handbook of Detergents Series Part F: Production*, edited by Uri Zoller and Paul Sosis

Preface

With the annual global consumption of surface-active agents reaching 13×10^6 metric tons and more than $9 billion worth of the detergent ingredients market, this industry embraces sustainability. Recently, the environmental impact of detergents has gone from being a fringe issue to a mainstream concern. Thus, regardless of the state of the art and affairs in the detergent industry worldwide, with respect to scientific-, technological-, economics-, safety-, and "greening"-related regulation of detergent production and formulation, the basic modes of the former will continue to be an issue of major concern. Yet, given our increasingly fast-moving world and skyrocketing oil prices, customers demand products that are more effective, energy saving, and can help to save *time* for the customers. This means demands for products that are cheaper, effective, faster acting, easier to use, more efficient, and environment friendly. This is so in view of the operating global free-market economy that is expected to ensure sustainable development, given the contemporary shifts in consumer preferences, availability and cost of basic raw materials, and energy, demographic, and social trends, as well as the overall economical/political situation worldwide.

This volume (Part F) of the six-volume series *Handbook of Detergents* deals with the production of various components of detergents—surfactants, builders, sequestering/chelating agents—as well as of other components of detergent formulations.

This volume is a comprehensive treatise on the multidimensional issues involved, and represents an international industry–academia collaborative effort of many experts and authorities, worldwide, mainly from industry. As such, *Part F—Production*, represents the state of the art concerning these multidimensional technological practices.

All of these are accompanied and supported by extensive relevant data, occasionally via specific "representative" case studies, the derived conclusions of which are transferable. Also, this resource contains several cited works and is, thus, aimed to serve as a useful and practical reference concerning the "production" aspect of surfactants—detergents—for engineers, technologists, scientists, technicians, regulators, and policy makers, associated with the detergent industry.

I thank all the contributors, reviewers, publisher's staff, and colleagues who made the realization of this and all the previous five volumes possible.

Editor

Uri Zoller is professor emeritus of chemistry and science education at Haifa University—Oranim, Kiryat Tivon, Israel. He has more than 220 published journal articles, 1 patent, and 9 books to his name, including the published five parts and the sixth part—Production, of the *Handbook of Detergents*, of which he is the editor-in-chief. He is an active member of several professional organizations, including the American Chemical Society and the Royal Society of Chemistry (United Kingdom), and is currently the chairman of the European Association for Chemical and Molecular Sciences (EuCHeMS) Committee on Education in Environmental Chemistry. His main areas of interest and research are synthetic organic chemistry, environmental chemistry, and science and environmental education and assessment. Following 10 years of research and development work in the detergent industry, Dr. Zoller received his BSc (summa cum laude) followed by an MSc in chemistry and industrial chemistry, respectively, from the Technion–Israel Institute of Technology, Haifa, Israel; an SM degree from the Massachusetts Institute of Technology in the United States; the DSc degree from the Technion–Israel Institute of Technology, Haifa, Israel; and the EdD in science education from Harvard University, Cambridge, Massachusetts. Currently, Dr. Zoller is the project coordinator of the Israeli Unified, National Infrastructural Research Project (UNIRP).

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1 Surfactant Production: Present Realities and Future Perspectives

Matthew I. Levinson

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1.1 INTRODUCTION

The annual global consumption of surface active agents or “surfactants” in 2006 was estimated to reach ~13 million metric tons,[1] with the break up of regional sales as depicted in Figure 1.1. There are arguably five major participants in the surfactant supply chain including (1) basic raw-material processors, (2) feedstock and diversified chemical producers, (3) surfactant converters, (4) product formulators, and (5) distributors/retailers,[2] some of which are listed in Figure 1.2.

Basic raw-material processors extract and refine crude oil into petrochemicals such as petroleum oil distillates including paraffins, benzene, and other basic aromatics and extract and convert natural gas into ethylene and propylene. Processors of oleochemicals extract and purify seed oils from palm, soybean, sunflower seed, palm kernel, and coconut, and render animal fats such as tallow to provide triglyceride oils with varying chain distributions.

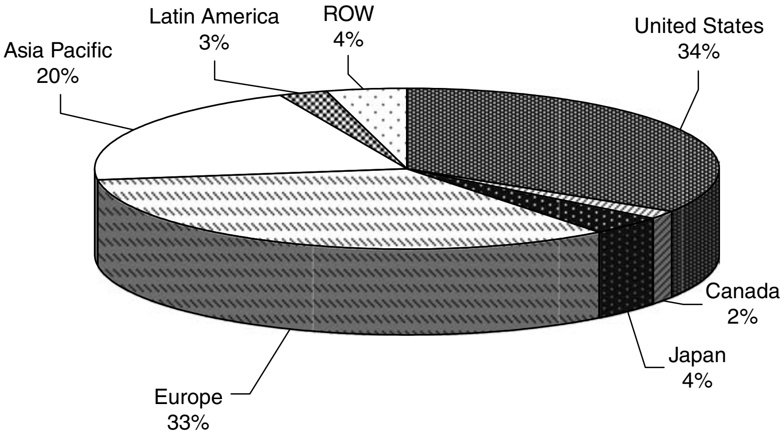


FIGURE 1.1 Estimated percentage of annual global volume sales of surface active agents for 2006 by region, based on a total of 13 million metric tons. (From Global Industry Analysts, Inc., *Surface Active Agents—A Global Strategic Business Report 08/06*, August, 2006. With permission.)

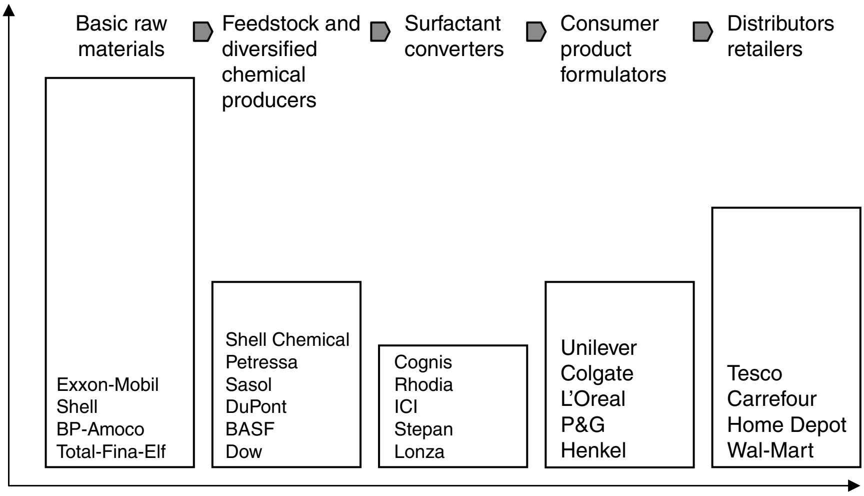


FIGURE 1.2 Consumer surfactant supply chain participants and their relative average market capitalizations.

Feedstock producers convert the aforementioned basic raw materials into numerous derivatives useful in a wide range of industries and applications, and particularly suitable for the manufacture of surfactants. These derivatives include the reaction products of paraffins with aromatics such as alkylbenzenes and alkylphenols, derivatives of ethylene and propylene such as polyalkylenes, primary alpha olefins, and their further oxidized or carbonylated derivatives such as Ziegler or oxo alcohols and their subsequent reaction products with ethylene oxide (EO) and propylene oxide (PO). Producers of petrochemical feedstocks are subsidiaries of basic raw-material processors in some cases, and so are integrated back into the key raw materials providing them economic and logistical advantages in producing their products. Examples include Shell, Sasol, ExxonMobil, Chevron, and Petressa.

Feedstocks derived from triglyceride oils include fatty acids, methyl esters, and natural alcohols through splitting, transesterification, hydrogenation, and hydrogenolysis. In several cases, the natural feedstock producers are or were part of highly integrated supply strategies of consumer product companies that converted triglycerides to fatty acids for soap production, and later converted them to fatty alcohols for alcohol sulfates production, which was formulated into fabric and dish detergents, and personal wash products. Companies such as Uniqema and Cognis were originally a part of Unilever and Henkel, respectively, and the Procter & Gamble (P&G) chemicals division still supplies the consumer products division with key raw materials for internal conversion.

Diversified chemical producers are a part of the second group within the supply chain, and provide the highly reactive materials that are used by surfactant converters to affix or create a hydrophilic head group on the hydrophobic materials discussed earlier. The highly reactive reagents include sulfur trioxide (SO_3), phosphorous pentoxide (P_2O_5), EO, PO, dimethyl sulfate, hydrogen peroxide, epichlorohydrin, monochloroacetic acid, and methyl chloride. There are many materials in this category, such as alkanolamines and short chain alkyl amines, sulfur dioxide, ammonium hydroxide, sodium hydroxide, polyphosphoric acid, and volatile alcohols that are less reactive, but pose handling and safety challenges. These are provided by large, very well-known members of the chemical industry that have had some historical and continuing participation as surfactant converters in their own right, and include DuPont, Dow-Union Carbide, BASF, Bayer, Rhodia, Monsanto, FMC, and Huntsman.

Surfactant converters rely on approximately eight core chemical processes that are broadly practiced in the global manufacture of surfactants, including sulfonation, sulfation, amidation, alkoxylation, esterification, amination, phosphation, and quaternization. These process steps are used to affix or create a highly water-soluble functional group (hydrophilic head group) on a water-insoluble feedstock (hydrophobic tail group). The surfactants derived from the permutations of head groups and tail groups fall into one of the four broad categories of anionic, cationic, nonionic, and amphoteric surfactant, based on the nature of the charge that is carried by the head group. The dynamics of the surfactant market place are impacted at a fundamental level by the cost, variety, and availability of hydrophobes, and the cost and complexity of attaching or creating hydrophilic head groups.

Surfactants are consumed globally in a broad range of consumer and industrial product compositions,[3] and are formulated at active levels ranging from nearly 100% in some cleaning products down to mere parts per million levels in high-performance applications such as pharmaceutical delivery systems, precision optics coatings, and electronics manufacturing. Broad categories of applications and uses include

Laundry detergents, fabric softeners, dish washing, and household cleaning products
Personal cleansing and conditioning products, and skin creams and cosmetics
Industrial and institutional cleaning products
Emulsion polymers used in paints, coatings, and adhesives
Agricultural product formulations containing insecticides, herbicides, and fungicides
Food-grade emulsifiers
Metal-working lubrication products and metal cleaners
Pulp and paper washing, deinking, and emulsifying
Oil field and natural gas drilling, completion, and production chemicals
Plastic mold release agents, lubricants, and processing chemicals
Textile and fiber lubricants, dying aides, and scouring and finishing chemicals
Mining chemicals

The ratio between surfactants used in consumer products and commercial and industrial application is approximately 65:35 as depicted in Figure 1.3. The markets for industrial and commercial surfactants in the United States are highly segmented and range between 10 and 20% of the entire application area as shown in Figure 1.4.

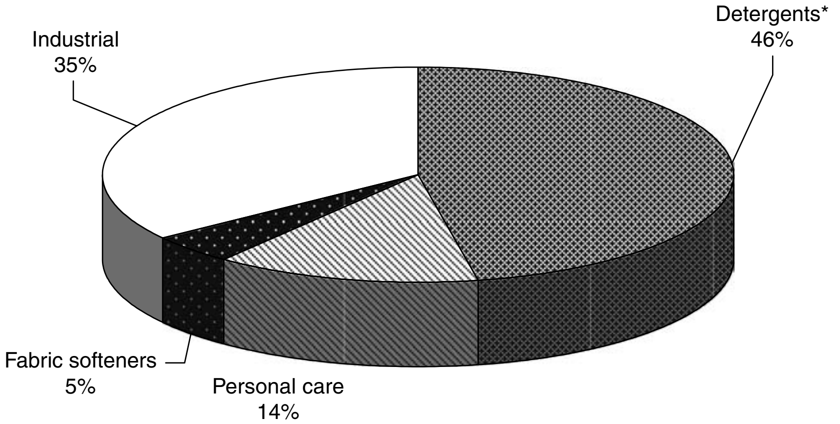


FIGURE 1.3 Percentage of global surfactant consumption by major application area for 2006 based on total sales of 13 million metric tons. (Note: * – approximately half is produced for captive use by integrated consumer companies.)

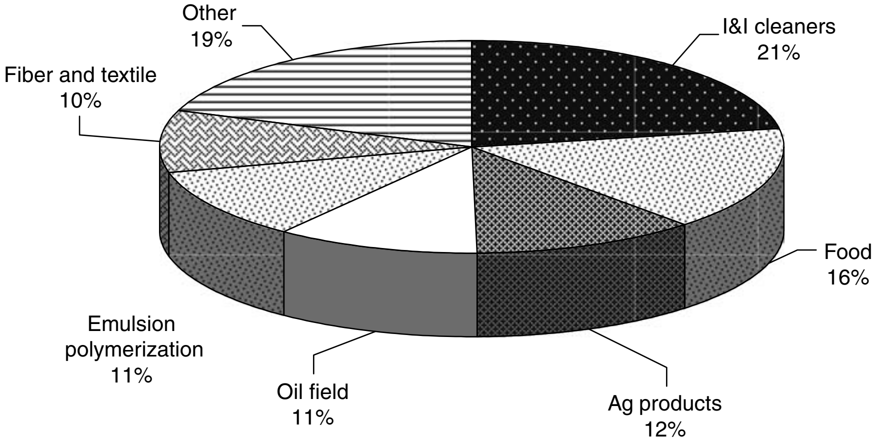


FIGURE 1.4 Industrial and commercial surfactant production, 2004 in the United States (total = 1100 t). (From Modler, R.F., Muller, S., and Ishikawa, Y., *Surfactants*, SRI Consulting; Specialty Chemical Update Program, July, 2004. With permission.)

1.2 COMPETITIVE FORCES AFFECTING THE PRODUCTION OF SURFACTANTS

There are varied and changing forces impacting the manufacture of surfactants in the world today, and the challenges producers of surfactant ingredients face are many.

1. Globalization and consolidation of surfactant users have accelerated over the past 20 years, and have affected all of the major end markets. This has driven standardization of surfactant product composition and specifications turning them into “commodity” products that command lower margins.
2. Globalization and consolidation within the retail channel, through which the preponderance of consumer products are sold, are allowing superretailers to dictate shelf space and packaging size that narrows formulation options, and to position their own house-label versions effectively even against global brands, reducing their profit margins and applying further downward pressure on surfactant margins.

3. Slowing demand and overcapacity in mature markets of North America and Europe have driven consolidation among surfactant producers attempting to achieve economies of scale, resulting in asset rationalization and product-line integration, and an ongoing need to drive out costs.
4. Medium and rapidly growing markets in Asia Pacific, India, Eastern Europe, and Latin America is creating the need for local manufacturing capacity for large volume, low-margin commodity surfactants to provide a cost-effective supply chain in the face of rising transportation costs.
5. Fluctuating and increasing raw material prices for feedstocks derived from oleochemicals and petrochemicals, respectively, as well as reagent chemicals and fuels used for manufacture and transport of intermediates and products have demanded significant price increases by surfactant converters, which until very recently were suppressed by surfactant formulators in part due to pressure by megaretailers.
6. More swings are anticipated in cost and availability of both petrochemical and oleochemical feedstocks, driving surfactant producers and formulators to develop flexible feedstock and formulation strategies.
7. Labor costs as a proportion of the total cost to produce surfactants continue to rise in mature markets, further motivating production of commodity and dilute surfactants within local markets where labor costs are low.
8. Low margin and dilute surfactants will continue to be made locally in mature markets and will not be effectively challenged by imports from developing regions due to transportation cost and service barriers such as surety of supply.
9. The cost of materials of construction and engineering services are very high in mature markets today, but are rising quickly in emerging markets as fast-paced growth in all sectors, which challenges local resources and infrastructure.
10. Ongoing concerns over the safety, health, and environmental fate of surfactants have propelled regulatory agencies in mature markets to demand extensive testing on new products, and data-gap backfilling for existing products, adding cost and slowing development of new surfactants.
11. Rapid adoption by emerging economies of regulatory standards developed in Europe or North America will drive out the use of some long-standing ingredients creating opportunities for competitive challenges.

1.3 HISTORICAL PERSPECTIVE ON PRODUCTION AND FEEDSTOCKS

The evolution of the sophisticated products and chemical-process technologies that are used today trace their origins back to the nineteenth century and the nascent chemical industry that relied on renewable oleochemical feedstocks. Synthetic surfactants prepared by the reaction of olive oil with sulfuric acid, performed by Fremy in 1831, was among the first.[4]

Some of the largest users of surfactants today originated as vertically integrated retailers of soap and candles, utilizing tallow and other animal fats obtained from the meat-processing industry, and later, vegetable oils such as palm, palm kernel, and coconut. Companies such as P&G, Lever Brothers, Colgate-Palmolive, Henkel, and others gained expertise in processing fats and oils into sodium carboxylate soaps in a variety of forms such as bars, flakes, and prills.[5]

The first “synthetic” detergents/surfactants were developed by the Germans during World War I followed by a burst of development in the late 1920s and early 1930s. Natural fats were in high demand for more important uses than soap, and this drove the search for alternatives capable of equivalent cleaning performance. The availability of coal tar as a basic raw material provided naphthalene and other polynuclear aromatics, which were alkylated using short-chain and fatty alcohols to yield feedstock alkylaromatics that were subsequently converted into surfactants by sulfonation with chlorosulfonic or sulfuric acid.[6] Although this class of surfactants delivers only moderate detergency, they were found to be good wetting agents and are still used in large quantities today as textile auxiliaries.[7]

The competitive drive for consumer products with enhanced performance and convenience, coupled with the rapid development of the chemicals industry in the 1930s, gave rise to innovations such as glyceryl ester sulfates[8] by Colgate-Palmolive-Peet Company and alcohol sulfates[9] made from fatty alcohols. Fatty alcohols were newly available feedstocks produced through catalytic hydrogenation of coconut and palm kernel oil derivatives developed in parallel by Deutsche Hydrierwerke in Germany, and E.I. DuPont in the United States in the early 1930s. P&G and Hydrierwerke pooled their U.S. interests to form American Hyalsol Corporation, which held U.S. patents for the production of alcohol sulfates. P&G was able to market and develop alcohol sulfates as synthetic detergents in household and laundry markets, and Dreft, the first household synthetic laundry detergent was launched in 1933. Finding the right builder, sodium tripolyphosphate, and formulation to maximize cleaning took another 13 years and resulted in the launch of Tide detergent in 1946.[10]

Refining of petroleum led to the separation of paraffinic alkanes, alkenes, benzene, and other aromatics that provided the feedstocks used in alkylation processes to yield alkylbenzenes. The petrochemical industry that emerged following World War II created a wide range of synthetic materials that became the alternatives to oleochemical feedstocks of the nineteenth century and the building blocks of the modern surfactant manufacturing industry of today. In the late 1940s, UOP developed a process to economically produce commercial quantities of branched alkylbenzene sulfonate (BABS), which became one of the surfactants most widely used in synthetic detergents at that time.

Even as early as 1939, the soap industry began to create laundry detergents using surfactants that were supplied to the soap manufacturers by the petrochemical industry. Because the cleaning formulations produced from these synthetic detergents were a substantial improvement over soap products in use at the time, they soon gave rise to a global surfactant industry based on branched alkyl benzene (BAB) derived from branched paraffins.

The hydrocracking of paraffins or reforming of methane gas provided the highly useful intermediates ethylene and propylene, which were used in the production of alpha olefins and polypropylenes (PP), which were used to alkylate benzene, or further converted to synthetic alcohols through Ziegler and oxo catalyst chemistry. Oxidation processes were developed to convert ethylene and propylene to their respective epoxides, EO and PO, which became building blocks for the preparation of alkoxylated alcohols and glycols, useful as nonionic surfactants and hydrophobes for further derivatization. During the 1950s and 1960s, advances in petrochemical technology provided feedstock molecules such as alkylphenol, linear and branched alpha olefins and fatty alcohols, and alkyl amines, which were suitable for derivatization and the basis for development of broad classes of synthetic surfactants as shown in Figure 1.5.

In the late 1950s, it was found that BABS had a slow rate of biodegradation that resulted in generation of large amounts of foam in surface waters such as rivers and streams.[11] Process technology was developed in the 1960s to produce linear alkylbenzene (LAB) from linear alpha olefins, as shown in Figure 1.6, or chloroparaffins. This new surfactant raw material was used to make linear alkylbenzene sulfonate (LAS), deemed to be a much more biodegradable surfactant, and grew to be the largest synthetic surfactant in use worldwide. Although it has been supplanted in some markets by alcohol ether sulfate (AES), it is still used globally in the manufacture of detergents today. The increasing use of synthetic surfactants and decline of soap sales following World War II are highlighted in Table 1.1.

Table 1.1, compiled from figures submitted by the American Soap and Detergent Association and the German firm of Henkel & Cie, shows both soap and detergent sales in the United States for various years from 1940 to 1972.[12]

In parallel with the evolving supply of petroleum raw materials, natural oil production from seed crops has increased worldwide to the volumes depicted in Figure 1.7. Palm oil has grown globally to become the single largest oil crop, comprising >35 million metric tons/year of the global production

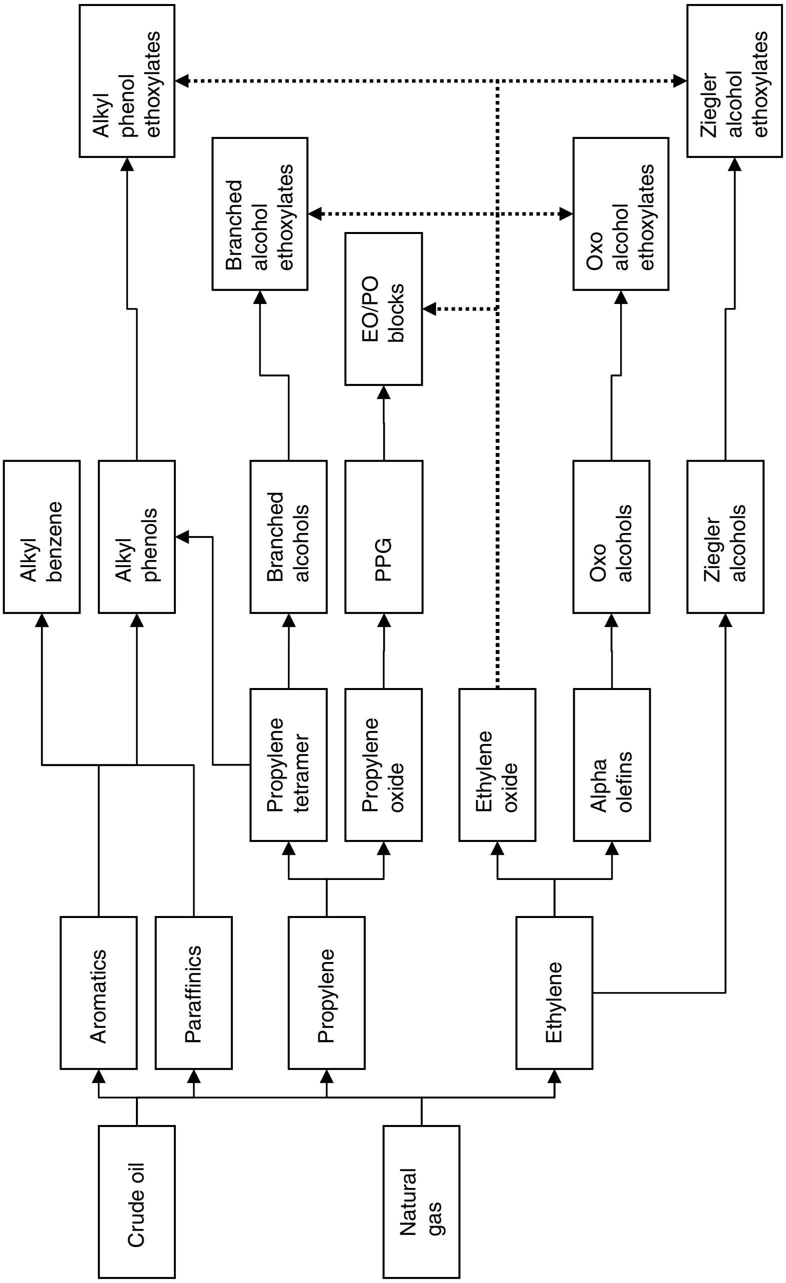


FIGURE 1.5 Intermediates and feedstocks for the production of anionic and nonionic surfactants derived from crude oil and natural gas.

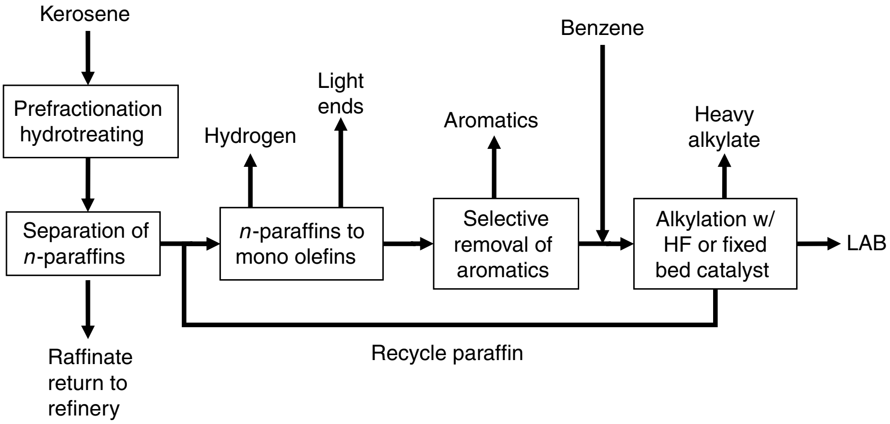


FIGURE 1.6 Integrated complex for production of alkylbenzene from normal paraffins based on UOP process technologies. (From UOP LLC, at http://www.uop.com. With permission.)

TABLE 1.1
Soap and Detergent Sales in the United States for Various Years from 1940 to 1972

Year	Soap Sales (1000 t)	Synthetic Sales (1000 t)
1940	1410	4.5
1950	1340	655
1960	583	1645
1972	587	4448

Note: Compiled from figures submitted by the American Soap and Detergent Association and the German firm of Henkel & Cie.

Source: Information available from About.com, accessible at http://www.chemistry.co.nz/deterghistory.htm.

of >110 million metric tons/year, and is used predominantly for food, and in substantially lesser quantities for derivatives and feedstocks for the chemical industry. For thousands of years, the production of soap for personal and clothes washing relied on natural triglyceride oils for preparation of fatty acids and their respective neutral sodium salts. Today palm oil, palm kernel oil, coconut oil, and tallow are converted, in significant volumes, into fatty acids, methyl esters, and alcohols, which are extensively used in the surfactant industry.[13]

However, tallow is composed of ~30% C16 and 70% C18 chains with substantial unsaturation. The choices of carbon numbers available are limited by the type of oil used as a feed material. Coconut oil is ~50% C_{12} with up to 20% C_{14} and ~15% each of C_{8-10} and C_{16-18}. Palm kernel oil has a similar distribution. However, tallow is mostly C_{16}–C_{18}. The shorter chain C12–C14 fatty acids and methyl esters derived from coconut and palm kernel oil are key starting materials for a host of surfactant derivatives in each of the major categories (anionics, cationics, nonionics, and amphoterics).

The commercial manufacture of fatty alcohols started in the late 1920s. The very first natural fatty alcohol was obtained by a simple ester cleavage of oil originating in the skull of the sperm whale. But a mere 4 years later, the first industrial-scale process had already been developed for producing a fatty alcohol from coconut fatty acid by high-pressure hydrogenation. In 1958, a route was developed from fatty acid methyl ester, which still remains the most economic method of producing

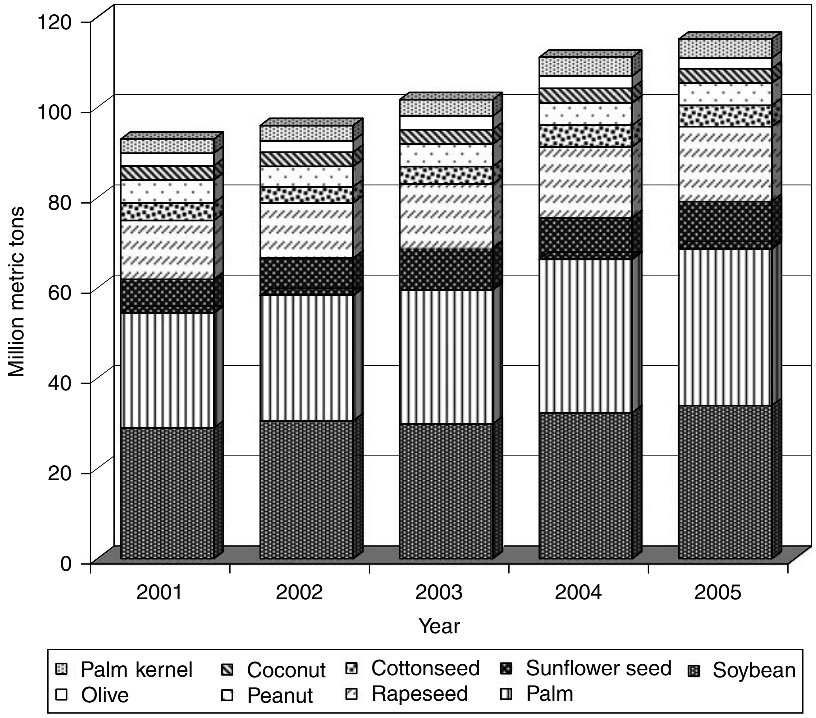


FIGURE 1.7 World vegetable oil supply and distribution between 2001–2005 showing volumes now exceed 110 million metric tons. (From Brackmann, B. and Hager, C.-D., *CESIO 6th World Surfactants Congress*, Berlin, June 20–23, 2004. With permission.)

natural fatty alcohols, and opened the door to the broad range of derivatives available from the flow depicted in Figure 1.8. Three years later, a more selective hydrogenation process allowed the preservation of the unsaturation found predominantly in the C16 and C18 chain fractions. The first unsaturated fatty alcohols became commercially available in the early 1960s, and since then, no more whales were harvested for the sake of oil.[14]

Today, natural detergent alcohols are produced using processes such as that developed by Davy Process Technology, depicted in Figure 1.9, which convert fatty acids into nonacidic intermediate methyl esters and hydrogenates these to alcohols, then separates C12–C14 and C16–C18 product streams.[15] This vapor phase process has been licensed around the world in ten ester hydrogenation plants with a total installed capacity of 350,000 t/year of alcohols. These plants have virtually no effluents; small by-product streams are recycled and consumed within the process, thus they have minimal environmental impact.

In 1963, the first petroleum-based fatty alcohols were produced based on ethylene and utilizing Ziegler's trialkylaluminum catalyst technology. This technology produces highly linear, even-numbered higher alcohols with little or no branching. The development of the oxo and modified oxo process that relies on hydroformylation of alpha olefins made mixtures of odd- and even-numbered alcohols containing around 20% methyl branching available; an example of this is depicted in Figure 1.10. Experience with slow biodegradation of BABS caused practitioners to assume that only linear alcohols would demonstrate superior biodegradability. However, over the past few years, studies sponsored by a number of groups have confirmed that if branching is properly controlled, the biodegradability of the resulting surfactant is retained and the surfactant properties are actually improved. Branched alcohols derived from Sasol's Fischer–Tropsch (FT) paraffins and alpha olefin isomerization technology developed by Shell have achieved commercial success and meet current biodegradability standards.[16]

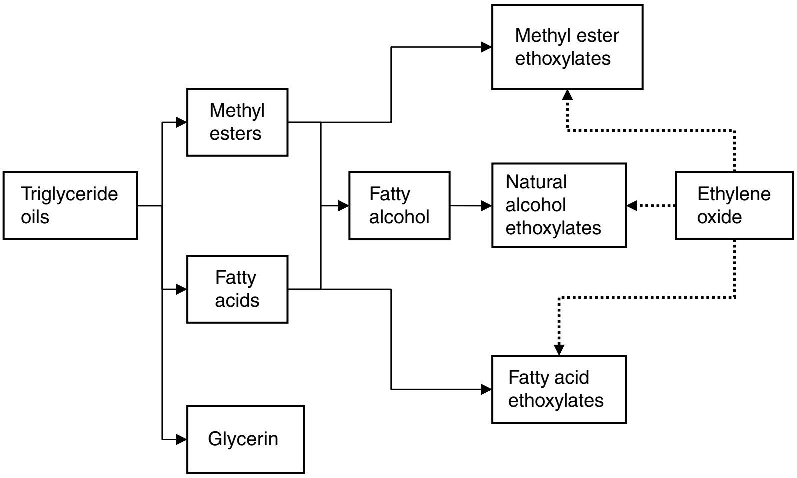


FIGURE 1.8 Intermediates and feedstocks for the production of anionic and nonionic surfactants derived from natural triglyceride oils.

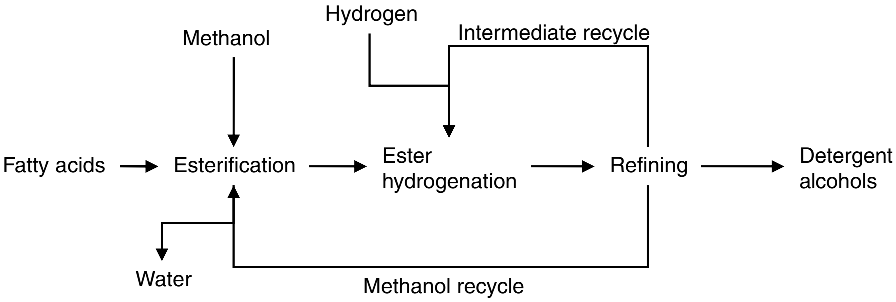


FIGURE 1.9 Process flow for the conversion of fatty acids to detergent alcohols via the Davy Process Technology Natural Detergent Alcohol process. (From Renaud, P., *CESIO 6th World Surfactants Congress*, Berlin, June 20–23, 2004. With permission.)

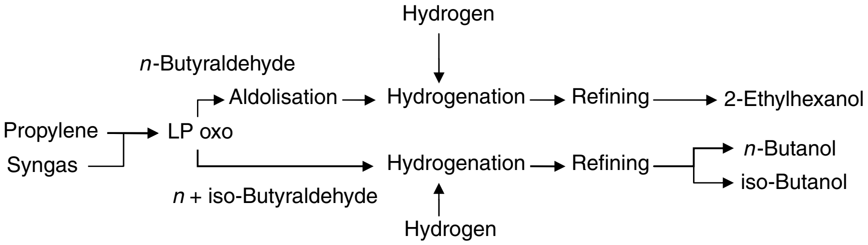


FIGURE 1.10 Davy Process Technology low-pressure hydroformylation technology was developed in collaboration with The Dow Chemical Company. The LP Oxo™ process has been applied commercially to produce detergent-grade alcohols from higher olefin cuts from FT synthesis. (From Renaud, P., *CESIO 6th World Surfactants Congress*, Berlin, June 20–23, 2004. With permission.)

The ultimate impact of FT technology is yet to be determined. Coal-to-liquid (CTL) processes are based on a technology that was developed in the early 1920s by German scientists Franz Fischer and Hans Tropsch. The FT process has been used since 1955 for CTL in South Africa where a government-sponsored plant was built by the South African Synthetic Oil Ltd corporation, now known as Sasol.[17] Currently, the U.S. Department of Energy through the National Energy

Technology Laboratory is supporting demonstration projects in the United States for CTL and GTL processes.[18] However, the cost to construct CTL plants is high, and the add-on capital cost to convert the branched paraffins generated from FT processes into alcohols is not likely to compete effectively with ethylene-based or natural alcohol processes.

1.4 SPECIALTY FEEDSTOCKS AND SURFACTANTS

Although the hydrophilic "head" groups of surfactants usually fit into one of the four categories described earlier, there are a number of exotic hydrophobic "tail" groups, both synthetic and natural, that populate the niches of specialty surfactants. Hydrophobes based on telomers of tetrafluoroethylene[19] or polydimethylsiloxane[20] bring unique surface-active properties to all classes of surfactants, reach extraordinarily low air/water and interfacial tensions, and enhance consumer and industrial product performance at amazingly low levels of use.[21]

Similarly, naturally derived surfactants extracted from fermentation broths or prepared by partial hydrolysis of natural extracts can contain polysaccharides, proteins, and phospholipids.[22,23] For example, rhamnolipids and sophorolipids have unique structural features that cause them to deposit on chemically similar surfaces and modify surface energy even at very low concentrations. Clearly, the emergence of biotechnology in the twenty-first century will drive the development of new surfactants from microbial fermentation, and improve the commercial viability of known surfactants from such processes.

Yet another class of niche surface-active agents includes higher molecular weight polymers based on acrylate or maleate esters, vinyl pyrolidone, and other vinyl monomers that contain, or can be modified with hydrophilic head groups. There are numerous chapters dedicated to polymeric surfactants and polymer surfactant interactions that enhance surfactant efficiency.[24,25] The use of surface-active polymers across all categories is increasing as these materials are customized and optimized to deliver enhanced product performance at very low levels.

Because of the cost, complexity to produce, and specificity of the surfactants, the development of new surfactants in these categories are conducted by highly specialized research organizations with strong technical depth in the core chemistries, often pursuing broad strategies with the same technology platform well beyond surfactants. Much of the fermentation-based surfactant development has originated from academia or federal research programs, and has been driven to commercial implementation through government seed money or private investment funds. As the large volume of surfactants described in this chapter are increasingly pushed toward commodity status, the continued development of new specialty surfactants will help to expand the limits of product performance and create value for technology-driven organizations.

1.5 BASIC RAW MATERIALS

In 2004, there were approximately 73.5 million bbl of crude oil produced per day, totaling annual production of 3600 million metric tons of oil worldwide, of which 90% was used for energy, and only 8% for chemical production.[26] The quantity of gas produced, converted into the equivalent quantity of oil, amounted to ~2400 million metric tons. A much larger portion of natural gas is consumed by the chemical industry, both for energy and as raw material feedstocks. Out of the refining, cracking, and reforming processes of these two key raw materials, ~90 million metric tons of ethylene and higher olefins were produced, and ~3 million metric tons of paraffins, of which <5% of these raw materials were consumed in the production of detergent alcohols.[13]

In the same year, a total of 5500 million metric tons of coal was produced, but only a small fraction was consumed in the production of surfactants.[27] Thus, the demand for basic petrochemicals to produce surfactant feedstocks represents a very small portion of total production, and feedstock producers find their raw material cost and supply position dictated by world energy demand and other larger chemical uses such as poly(ethylene terephthalate) (PET), polyethylene (PE), and PP plastic manufacturing.

Counterbalancing the fossil-based raw materials, in 2005, the world produced 180,000 million metric tons of biomass, of which only 67 million metric tons was used as a commercial source of energy. In the same year, the world harvested ~115 million metric tons of vegetable oils, of which ~80, 15, and 5% was consumed for food, chemical products, and animal feed, respectively.[28] A significant portion of the 15% for chemical use included 7.5 million metric tons of high-lauric content coconut and palm kernel oil, approximately half of which is converted into fatty acids for bar soaps, and the other half consumed in the manufacture of detergent grade alcohols used in surfactant production.[13]

Food and chemical uses for oils may soon be challenged by energy consumption as biodiesel production cuts into the available supplies. The 2005 global demand of 3 million metric tons of biodiesel is less than half of the 2006 demand of 6.9 million metric tons, and supply–demand is expected to increase at 133% through 2010 and projected to reach 45 million metric tons, with production capacity projected to greatly exceed supply–demand by as much as 100%.[29] Although the chain length of soybean and palm oil used for biodiesel is much longer than the optimal surfactant chain length of C12–14 found in coconut and palm kernel oils, high demand for the longer chain oils will raise their price, and drive substitution with shorter chain oils when necessary. It is not clear how global agricultural production of fats and oils can keep pace with these projections, suggesting an imminent conflict of interest between the basic need for food in the developing world and government incentives and mandates for renewable fuel use in the developed world.

Both oleo and petroleum-based surfactant feedstocks have come under supply pressure in the first decade of the twenty-first century due to rapid growth in many regional economies especially throughout Asia, and due to political factors in the Middle East, as well as poor reinvestment economics in the developed markets. Demand for petroleum, natural gas, vegetable oils, their derivatives, and other chemical intermediates used in the manufacture of surfactants is expected to continue to grow due to expanding economies in several regions of the world. At the same time, consolidations in the retail supply chain in Europe and the United States have concentrated purchasing power and allowed retailers to suppress price increases up and down the supply chain from the CPCs to the chemical manufacturers for several years.

The impact has been to force chemical manufacturers and converters to reduce their cost structure, delay or abandon capacity expansions, delay equipment upgrades, and minimize their investment in infrastructure. As a result, the chemical industry in the United States and Europe has operated in recent years near their maximum capacity, such that the occurrence of mechanical failure results in a major disruption to the supply chain. The years 2004 and 2005 saw record numbers of *force majeures* due to unplanned outages and the lack of capacity in the chemical supply chain to compensate for major supply disruptions.[30]

The future perspective for surfactant production is to expect swings in the cost and availability of feedstocks influenced by all of the factors mentioned earlier. Where possible, consumer product formulators will work toward flexible feedstock strategies, allowing them to switch between natural and synthetically based surfactants as forced by the market, or to take advantage of abundant raw materials with favorable economics.

1.6 THE FOUR MAIN SURFACTANT CLASSES AND THEIR PRODUCTION TODAY

The four main surfactant classes include anionics, cationics, nonionics, and amphoterics or zwitterionics. Within each of the general classes of surfactants, there are a broad range of variants, which are summarized in the following sections.

Anionic and nonionic surfactants represent almost equally large segments with global sales approaching 6 million metric tons in 2006 as depicted in Figure 1.11. Although cationic and

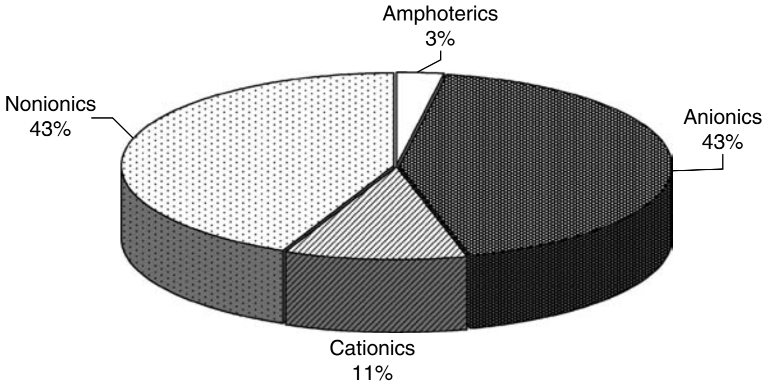


FIGURE 1.11 Percentage of global surfactant consumption by major application area for 2006 based on total sales of 13 million metric tons. (From Modler, R.F., Muller, S., and Ishikawa, Y., *Surfactants*, SRI Consulting; Specialty Chemical Update Program, July, 2004. With permission.)

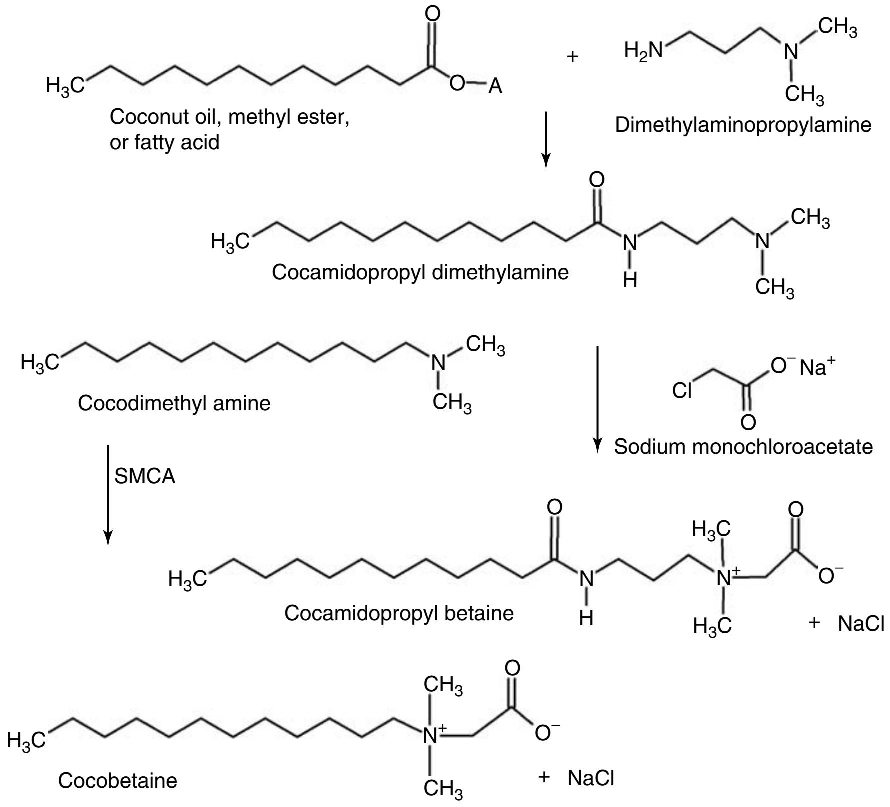
amphoteric surfactants represent much smaller segments of the market, they are projected to be the fastest-growing segments in dollar terms, with compound annual growth rate (CAGR) of 5.5 and 4%, respectively.[1]

1.6.1 AMPHOTERIC SURFACTANTS

The amphoteric surfactants, which represent the smallest of the four categories, are identified as molecules that have the potential for a positive and negative ionic group to be present in the head group, and where the net charge may be changed by varying the pH of the system. Amphoterics, which typically have the highest raw material and production costs, are usually produced as dilute, low-active products that sell at a premium and command higher margins. Several classes of products based on chloroacetic acid or epichlorohydrin contain substantial levels of sodium chloride salt as a by-product and present long-term corrosion issues throughout manufacturing, transfer, and storage systems. Even in light of some of the barriers to producing amphoteric surfactants, their unique properties make them valuable surfactants with growing demand. They allow coupling of otherwise incompatible anionic and cationic surfactants, which greatly reduces the irritancy of primary anionic surfactants, build foam volume, increase foam stability, and reduce the total surfactant load to achieve target performance in a range of applications. Several texts are dedicated to the broad range of amphoteric surfactant chemistry.[31,32]

There are at least five main subcategories within amphoterics, the largest in use being betaines followed by amine oxides. There is a further subdivision within these two product categories based on the type of amine: Alkyl dimethyl amines (ADMAs) are used to produce alkyl betaines and amine oxides, which find substantial use in Europe. The second subdivision is derived from amides of dimethylaminopropylamine (DMAPA) where these are used to produce the alkylamidobetaines and alkylamidoamineoxides that are ubiquitous in most markets around the world. Lesser quantities of specialty amphoterics are widely used across several market segments, and these include the general product classes of amphoacetates, amphopropionates, sulfobetaines, and phosphobetaines.

The workhorse amphoteric surfactants are the alkyl- and alkylamidopropyl betaines, containing C8–C18 linear chain distributions that are derived from coconut or palm kernel oil, or ethylene-based alpha olefins. The alkyl betaines are prepared from ADMA feedstocks that are typically derived from alpha olefins and dimethyl amine through hydrohalogenation and alkylation reaction steps. The alkylamidopropyl betaines are based on tertiary amines derived from whole triglycerides or their fractionated derivative fatty acids or methyl esters reacted with DMAPA.



SCHEME 1.1 Preparation of alkyldimethyl betaines and alkylamidopropyl betaines.

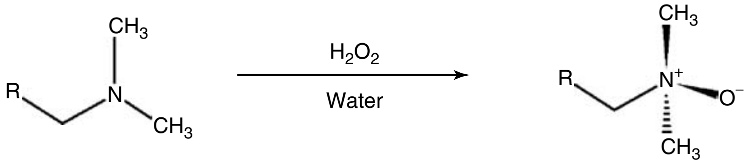
Cocamidopropyldimethyl amine can be prepared from whole coconut oil, coconut fatty acid, or methyl esters either whole cut or stripped of the C6–C10 chain fractions. The aforementioned tertiary amines are converted to betaines by reaction with sodium monochloroacetate (SMCA) in a relatively dilute aqueous system (Scheme 1.1).

The alkylation step is conducted at temperatures between 50 and 100°C, is modestly exothermic, and requires some induction period during which a small portion of the betaine surfactant is formed and helps to emulsify the insoluble amine in the continuous aqueous phase making it available for reaction with the SMCA and accelerating the rate of conversion. Typical with two-phase surfactant forming reactions, a gel phase can be observed to develop under lower temperature conditions as conversion approaches 50%, and persists through >70% conversion at which point the viscosity drops and returns to a classic Newtonian state. Rapid conversion can occur at elevated reaction temperatures reducing the duration or virtually eliminating the appearance of a gel phase. However, the combination of a two-phase latent reaction coupled with the exothermic alkylation reaction and changing viscosity can lead to temperature excursions over 100°C and kettle foam out when operating at atmospheric pressure. The higher reaction temperatures coupled with sodium chloride levels approaching 5% constitute a corrosive environment for low-grade steel, recommending glass-lined vessels or construction from corrosion-resistant alloys.

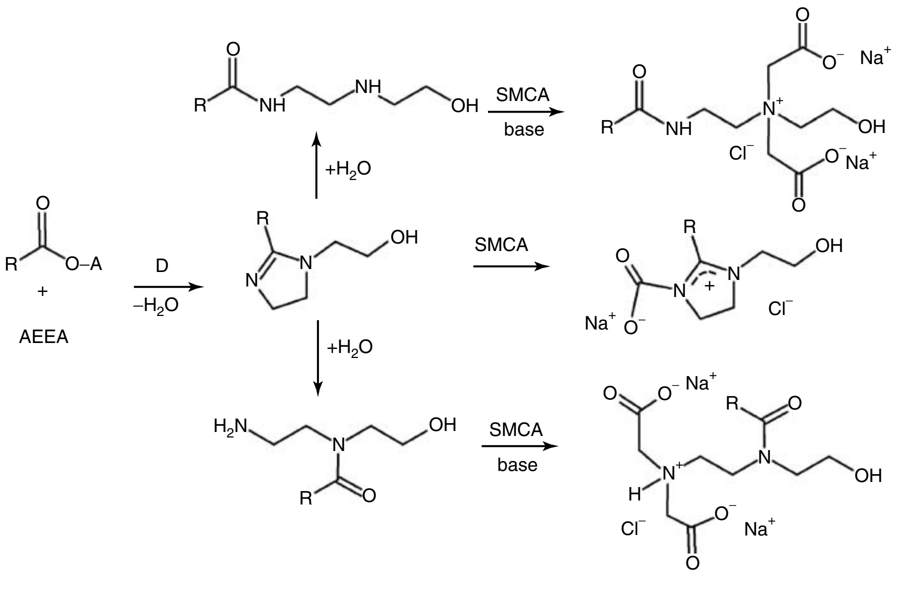
Betaines are formulated into a wide range of personal cleansing products used on hair and skin. The inclusion of higher levels of the C16–C18 chains improves product mildness, whereas the C12–C14 chains effectively boost viscosity in the presence of additional sodium chloride, enhance foam volume, stability, and quality. Betaines demonstrate excellent thermal stability and caustic and hypochlorite compatibility, and are used in aggressive formulations developed for drain cleaning and hard-surface cleaning, as well as foaming applications in oil field and other industrial products.

Amine oxides are produced by the reaction of the earlier-mentioned alkyl or alkylamidoamines with hydrogen peroxide in a two-phase system containing a large volume of water yielding dilute products typically containing <35% active (Scheme 1.2). Amine oxides have the same excellent secondary surfactant characteristics as betaines, and provide arguably better mildness and ability to mitigate skin irritation in formulations containing LAS or alcohol sulfates. They avoid corrosion problems associated with sodium chloride, and have inherent stability in the presence of hydrogen peroxide making them useful in oxygen bleaching and cleansing products. They find use in a broad range of formulations including personal cleansing products, LDLs (Light Duty Liquids–dish detergent), drain cleaners, hard surface, and fabric cleaning compositions.

The amphoacetates (also known as amphocarboxyglycinates) and amphopropionates comprise a third significant class, and are predominantly based on a mixture of amides and imidazolines derived from aminoethylethanolamine (AEEA) reacted with fatty acids or derivatives. The forcing reaction conditions and use of excess AEEA favor the imidazoline component, but when the amine mixture is reacted with aqueous SMCA solution, it undergoes partial hydrolysis to a mixture of alkylated and quaternized amidoamines and imidazolium quaternaries, yielding the product



SCHEME 1.2 Oxidation of tertiary amines with hydrogen peroxide to produce amine oxides.



SCHEME 1.3 Preparation of amphoacetates, or amphocarboxyglycinates, through the reaction of fatty derivatives with AEEA to produce the imidazoline intermediate, then partial hydrolysis and reaction with SMCA.

mixture generically labeled amphoacetate (Scheme 1.3). The coco and lauryl amphoacetates and amphodiacetates (two moles of SMCA) find use in personal cleansing applications due to mildness and foam-building characteristics with additional sodium chloride.

Amphopropionates are prepared by the reaction of an AEEA imidazoline/amide mixture with methyl acrylate through the Michael reaction followed by mild hydrolysis of the resulting B-amino-ester giving rise to a complex mixture of components. The lauryl and cocoamphopropionates and amphodipropionates do not contain sodium chloride, but typically contain residual methanol from hydrolysis of the ester, and so are more suitable for use in hard surface cleaning formulations where chlorides may be undesirable and traces of methanol can be acceptable. The amphopropionates are stable in formulations containing high levels of inorganic salts and high levels of alkalinity.

Epichlorohydrin (ECH) is an effective linking group between tertiary amines and acid salts and is used to produce sulfonated amphoterics known as *sulfobetaines*. Sodium sulfite is reacted with epichlorohydrin in water to produce a solution of 1-chloro-2-hydroxypropane sulfonate, which is further reacted with a tertiary amine to yield a quaternary ammonium group linked to the hydroxypropane sulfonate, with sodium chloride as the primary by-product. Reaction of ECH with partially neutralized phosphorous or phosphoric acid produces an intermediate, which when reacted with tertiary amines yields the respective phosphitobetaines or phosphatobetaines.

Key issues include corrosivity of the reaction conditions to steel and proper handling of volatile alkylating agents such as epichlorohydrin. The resulting products are very stable to high temperature and aggressive pH conditions, and find use in a number of household and industrial applications.

The demand for amphoteric surfactants is expected to increase in step with the global growth of personal cleansing and home cleaning products. They provide mildness to formulations used in household applications, as well as foam stability and thickening properties. The challenges that will face amphoteric surfactant producers will include

- Cost inefficiencies associated with producing and shipping low-active materials, giving local/regional producers a competitive advantage.
- Corrosivity to ferrous reactors, piping, and storage vessels when producing amphoterics containing high levels of sodium chloride.
- Amidoamine-based amphoterics made with excess volatile amine require stripping, recovery, recycling or disposal of impure distillate streams, and process control to ensure very low levels of residual volatile amine in the intermediate.
- Use of alkylating agents including monochloroacetic acid or SMCA, ECH, and methyl acrylate require special precautions for safe use, and products must be certified to contain exceedingly low levels before shipment.
- The imidazoline-based products are very complex mixtures whose compositions are highly dependent on the precise composition of the intermediates and the reaction conditions of the quaternization, making them “products by process” requiring tight process control and often difficult to match against performance of competitive products.
- Customers look for multiple suppliers to keep pricing competitive, and usually solicit products that meet well-defined, narrow specifications.
- A number of granted patents exist that cover preferred processes for manufacture of several classes of amphoterics, and cover advantageous surfactant blends.
- Safety testing and registration costs stand as tall barriers to new amphoteric products limiting opportunities for differentiation through innovation.

1.6.2 ANIONIC SURFACTANTS

Anionic surfactants are the largest category of surfactants produced on a volume- and value basis, the bulk of which are accounted for by a relatively small number of products that are produced by sulfonation or sulfation, are used extensively in household laundry detergents and cleaning products, and also in personal cleansing products. At least two other categories of anionic surfactants are produced in substantially smaller volumes, including phosphate and polyphosphate esters, and carboxylate salts (excluding simple fatty acid soaps), and the general category is covered in several volumes.[33,34] Bar and flaked forms of traditional carboxylate soaps are still ubiquitous, and are still used globally for hand and body cleansing, and for laundering of soiled clothes in markets outside of North America and western Europe.[35]

1.6.2.1 Sulfonates and Sulfates

The broad class of products described as sulfonates results from reactions that create a carbon–sulfur bond and utilizes sulfur VI reagent SO_3 and its derivatives and adducts such as sulfuric acid. A smaller number of sulfonate products are prepared using sulfur IV reagent SO_2 as well as its derivatives and adducts such as sodium bisulfite. The preparation of sulfate esters involves the creation of carbon–oxygen–sulfur bonds, and can utilize SO_3, sulfuric acid, or chlorosulfonic acid to form alcohol sulfates that are labile and susceptible to hydrolysis in the presence of water as well as elimination reactions at elevated temperatures, and must be handled under milder conditions than sulfonates during formation and neutralization. Numerous older reviews and recent publications exist covering sulfonation and sulfation processes to produce surfactant products.[36–38]

Historically, sulfonation of alkylated aromatics for detergent was practiced with concentrated sulfuric acid, and later with fuming sulfuric acid or oleum, a mixture of SO_3 in sulfuric acid. The batch sulfonation or continuous sulfation processes utilizing these reagents are corrosive to steel, have poor productivity, and produce products with inferior color containing large amounts of sulfuric acid, which demand excess of caustic on neutralization. Resulting products are laden with sodium sulfate, and are suitable for use in low-density powdered detergents, and low concentration liquid detergents.

Chlorosulfonic acid (CSA) sulfation of alcohols or alcohol ethoxylates is usually conducted in batch reaction mode, typically in glass-lined vessels, but requires little or no excess reagent to drive the reaction to completion and can be conducted in a continuous liquid–liquid contacting process. The reaction evolves a stoichiometric quantity of HCl gas, which can be captured either as an HCl solution or with caustic to yield sodium chloride. Product color, yield, and quality can be very high, but throughput efficiency is modest in batch mode.

Liquid sulfur trioxide is the most reactive reagent used for sulfonation and sulfation, and is either obtained as a low boiling liquid or prepared at a point of use by combustion of sulfur in air and oxidation over catalyst at high temperature as depicted in Figure 1.12. The vaporized SO_3 steam

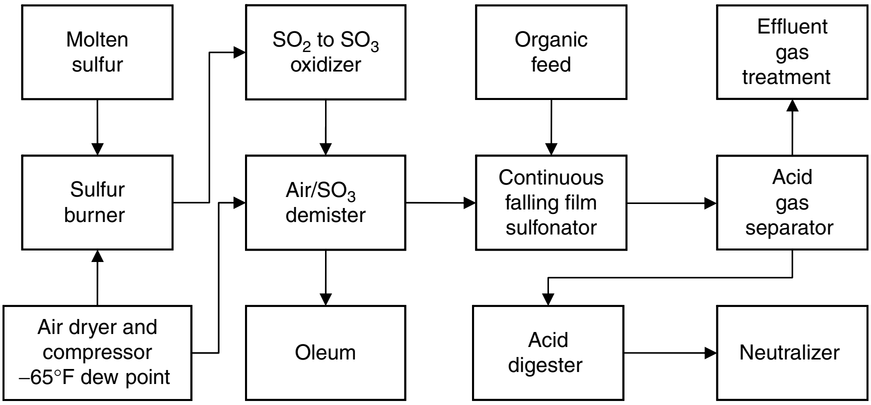


FIGURE 1.12 Continuous SO_3 falling film sulfonation process flow.

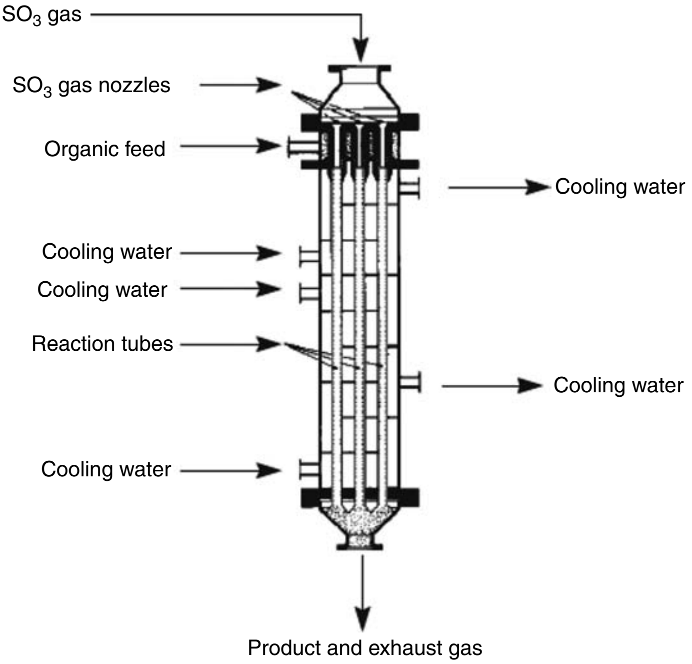
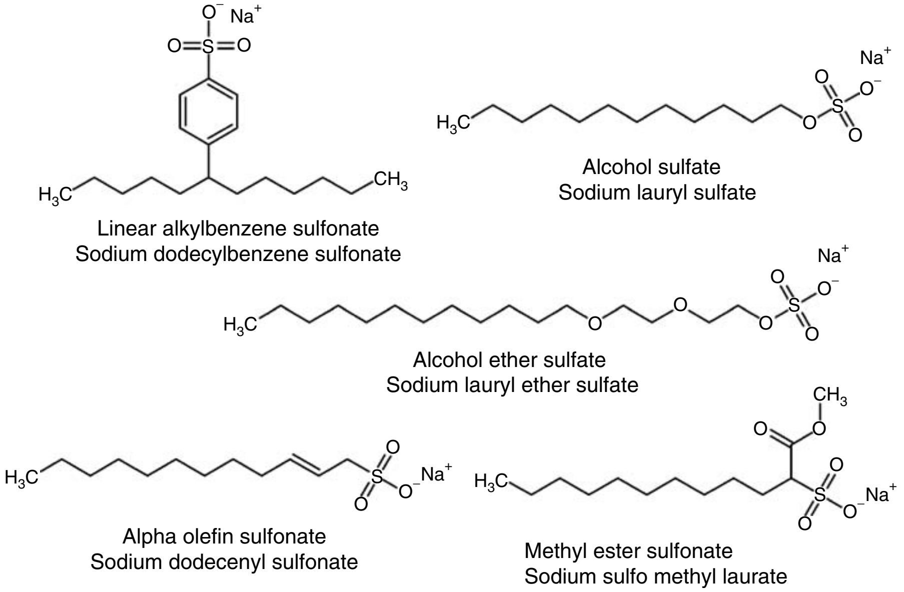


FIGURE 1.13 Ballestra multitube film sulfonation reactor. (From Ballestra, S.P.A., 2005. With permission.)



SCHEME 1.4 Anionic surfactants based on SO_3 with non-IUPAC generic and industry-specific nomenclature.

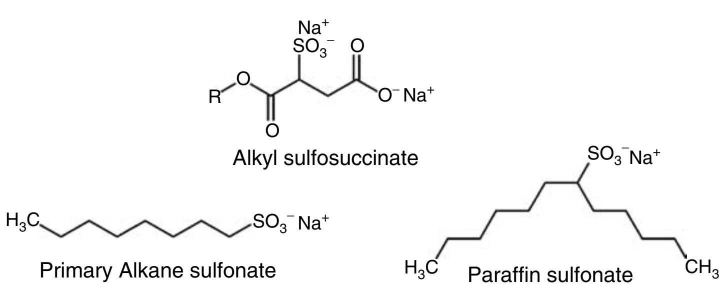
is diluted down to 2–6% in dry air and contacted with a broad variety of feedstocks in a continuous thin film reactor (Figure 1.13)[39] to produce an acid product, which is either stabilized for storage and later neutralization in the case of alkylates, or subjected to immediate neutralization in water with a variety of inorganic or organic bases as is done with fatty alcohols and fatty alcohol ethoxylates to give the range of products depicted in Scheme 1.4. In many locations around the world, LAB is sulfonated, digested, stabilized, and stored in the acid form, then later neutralized and dried along with a variety of nonionic surfactants and inorganic salts to make heavy-duty powdered detergent products.

Alpha olefin sulfonates are prepared through the falling-film sulfonation of alpha olefins, which involves the formation of a complex mixture of unsaturated sulfonic acids and cyclic sultones. The intermediate mixture is neutralized with excess base and then subjected to a rigorous high-temperature hydrolysis step during which all cyclic intermediates are converted to sodium sulfonate derivatives. The low molecular weight of alpha olefins compared to other feedstocks results in a relatively high heat of reaction per unit mass, requiring slower treatment rates to maintain product color and minimize volatilization and fouling of the reactor, separator, and emission-control equipment surfaces, and avoid subsequent volatile organic compound (VOC) emissions.

Sulfonated methyl esters are prepared through falling-film sulfonation of highly saturated methyl esters. The complex mechanism of sulfonation is discussed in several reviews and patents, but is thought to involve two molecules of SO_3 per molecule of ester, where SO_3 must first be inserted into the ester linkage. The scrambled mixture of inserted and uninserted sulfonation products requires a reesterification step before neutralization to maximize methyl ester sulfonate content. Bleaching steps and neutralization may be practiced in forward or reverse order, and can produce a low- or high-active neutralized aqueous product containing moderately low levels of impurities such as sulfonated carboxylate disalt, unreacted ester, sodium methylsulfate, and methanol. Commercially, this type of product is sold in liquid form, or can be dried, ground, and classified into uniform particles suitable for incorporation in powdered detergent products or for dissolution into liquid products.

Sulfur in oxidation state IV can be used to produce a variety of anionic sulfonates, as depicted in Scheme 1.5. Sodium bisulfite can be used to prepare sulfonates of a,b-unsaturated acids and esters, such as those prepared from maleic anhydride. The mechanism involves Michael addition to the activated double bond by the more nucleophilic sulfur atom, and is conducted in an aqueous two-phase system where, for example, a maleate half acid ester or diester is dispersed and heated under narrowly controlled pH conditions to minimize ester hydrolysis and avoid competitive hydroxide addition to the double bond. The resulting classes of surfactants include sulfosuccinates (which are in fact carboxylate sulfonate disalt surfactants) prepared from the maleic half acid esters of fatty alcohols or alcohol ethoxylates. Diesters of maleic are sulfonated by the same type of process to produce surfactants such as the ubiquitous dioctyl sulfosuccinate (DOSS) from the diester of 2-ethylhexyl alcohol and maleic anhydride.

Bisulfite or SO_2 can be reacted through free radical mechanisms with alpha olefins or with paraffins to give sulfonated alkanes. The former reaction with alpha olefins is conducted in water, usually in the presence of a cosolubilizing alcohol and a free radical initiator, and excluding all oxygen. By balancing the concentration of sulfite and bisulfite and utilizing techniques developed in the emulsion polymerization process industry, good conversion to primary alkane sulfonates can



SCHEME 1.5 Examples of anionic surfactants prepared from sulfur dioxide, sodium bisulfite, or sodium sulfite.

be achieved with minimal formation of disulfonated by-products. The short-chain primary alkane sulfonates have utility as hydrotroping agents and low-foaming surfactants for use in extreme pH or strongly oxidizing formulations.

The reaction of SO_2 with paraffins is conducted in water in the presence of oxygen or chlorine, and is photoinitiated to generate oxygen or chlorine radicals that abstract hydrogen from the paraffinic backbone, creating alkane free radicals that react with gaseous SO_2 and further interact with oxygen to reach the S VI oxidation state and perpetuate the free-radical reaction. Excess SO_2 is consumed and by-products include hydrogen peroxide in the oxygen process, and hydrochloric acid in the chlorine-initiated process, as well as sulfuric acid, which must be separated at low temperatures from the alkane sulfonic acid before neutralization. The oxygen process is still practiced in several locations in Europe today, whereas the chlorine process was developed and practiced in the former German Democratic Republic, and is no longer in use due to the formation of undesirable chlorinated paraffinic by-products.

Continuous SO_3 sulfonation process equipment is available in well-designed modular packages, and involves numerous unit operations including air compressing and drying, sulfur burning, sulfur dioxide oxidation, thin-film sulfonation, gas/liquid separation, electrostatic precipitation, and final scrubbing as partially depicted in Figure 1.12. For production of alcohol and ether sulfates, immediate neutralization and deaeration are practiced to avoid degradation of color and generation of undesirable by-products such as 1,4-dioxane. A very large number of relatively small volume sulfonation units (1–5 metric tons/h) have been installed around the world, most of them relying on molten sulfur burning, several still using liquid SO_3 delivered from central production facilities.

The resulting sulfation/sulfonation overcapacity in many regions has driven down the profitability of operation, and made smaller sulfation/sulfonation units very uncompetitive. Increasingly tighter restrictions on air emissions and higher costs for disposal of scrubber wastes will present challenges for older, smaller units in mature regions, and will shape the strategy for installation of larger units in emerging countries. Since sulfation/sulfonation does not represent a significant value-added conversion for many feedstocks, it is not a highly attractive forward integration strategy for feedstock producers. Because of recent dramatic price fluctuations in petroleum and oleo feedstocks, surfactant consumers find themselves needing a flexible feedstock strategy that exceeds the simple single-flavor plant designs for making LAS or AES. Increasingly, consumer product companies are redefining themselves as marketing and technology implementation companies, and as such are abandoning backward integration strategies, divesting existing sulfation/sulfonation assets, and avoiding the construction of new facilities.

The demand for sulfated and sulfonated anionic surfactants is expected to increase in step with the global growth of consumption of laundering, personal cleansing, and home-cleaning products.[1,3] They are almost always the primary or secondary component in cleansing formulations; are responsible for reducing surface tension, forming micellar structures, which solubilize oily soil; and help suspend particulate soil by generating a significant negative zeta potential that prevents coalescence and redeposition through charge repulsion. They provide foaming and allow for thickening by manipulation of electrolyte concentration in formulations.[40] The challenges that will face anionic surfactant producers include

- Ongoing oscillations in the price and supply of both petroleum and naturally derived feedstocks due to a variety of socioeconomic forces, including significant growth in demand in east and west Asia, eastern Europe, and Latin America driven by increasing surfactant consumption as well as competing uses for fuel, food, and nonsurfactant applications
- Continued overproduction capacity in developed markets and emergence of multiple competitors in developing markets
- The need to manage a flexible feedstock strategy that supports the demand for LAS for powdered detergents as well as actives for liquid product forms based on alcohols, alcohol ethoxylates, alpha olefins, and methyl esters

- Continuous process control that produces products within narrow specifications, with low color, and with minimal formation of impurities such as 1,4-dioxane in alcohol ether sulfates and sultones in AOS
- Rigorous emission controls that minimize the release of SO_2 and SO_3 gas, as well as VOCs
- Ability to produce highly active neutralized products that are rheologically difficult to handle, require sophisticated storage, dispensing, shipping, and dilution infrastructure.
- Specialized assets with no general utility beyond production of sulfated or sulfonated surfactants

1.6.2.2 Phosphated Surfactants

A substantially smaller subset of anionic surfactants includes the reaction products of alcohols and alcohol ethoxylates with P_2O_5, polyphosphoric acid, or phosphoric acid, which is covered in detail in several review chapters.[33,34] The resulting products include varying mixtures of mono and diesters of phosphoric acid, which are neutralized with a variety of inorganic or organic amine bases. Phosphate esters have outstanding mildness properties and impart excellent skin feel when used in personal cleansing formulations. Depending on the ester ratio and chain length, they can have excellent emulsification properties, tolerance to electrolytes, thickening properties, and hydrolytic stability across a wide pH range making them suitable for use in acidic or basic hard surface and drain-cleaning formulations. However, the abundance of local city-, county-, and state-level legislation practically banning the use of phosphates since the 1980s in the United States in consumer and industrial cleaning products has limited this class of products to specialty applications such as agricultural emulsifiers, and plastic and fiber additives.

1.6.2.3 Carboxylated Synthetic Surfactants

In a separate category from soap are the carboxylated synthetic surfactants, which typically comprise an alcohol ethoxylate capped with a carboxymethyl group. Generally, two processes are practiced, one involving the reaction of sodium monochloroacetate and a base to form a carboxymethyl ether, with sodium chloride as a by-product. The second process involves oxidation of the terminal hydroxyl ethyl group of an alcohol ethoxylate using nitric acid or other strong oxidizing systems. These products are mild, foaming surfactants that find use in liquid and solid-form personal care products. The cost, corrosivity, and salt-removal issues of the SMCA process make it less competitive than the oxidation process.[38]

1.6.3 CATIONIC SURFACTANTS

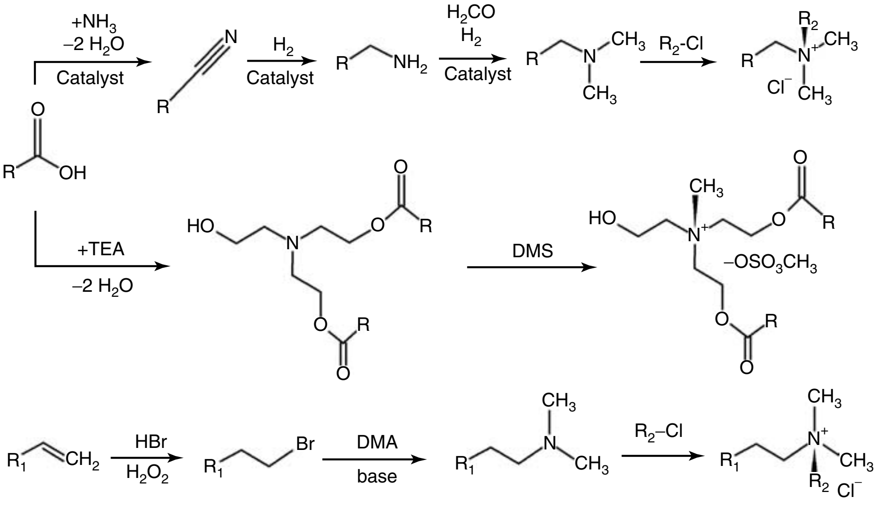
Cationics represent the third-largest group of surfactants by volume. By virtue of a positively charged head connected to a hydrophobic tail, cationics are attracted to negatively charged molecules and surfaces, and their physical properties have been reviewed extensively.[41,42] Ion pairing and deposition can change the net surface charge and impart benefits related to dimensions of the hydrophobic chains: linear saturated hydrocarbons containing >16 carbons impart a high degree of lubricity and water repellency. Unsaturated carbon chains provide less lubrication, but can attract and hold water molecules, improving wicking properties of textiles. When used on fabrics, long-chain cationics deposit well beyond the formation of a Langmuir monolayer, creating a lubricating layer that results in fiber smoothing and fabric softening. In the dying process, cationic surfactants form highly insoluble complexes with anionic-charged dye molecules, affixing the dyes and inhibiting their loss through subsequent washings. The ability of cationic surfactants to associate with metal surfaces provides corrosion inhibition and lubricity. Biocidal properties are attributable to interaction with anionically charged surfaces of simple biological systems building sufficient local concentrations to disrupt cell wall structures of single-celled organisms and to inactivate viruses.

Cationic surfactants are produced by three general process routes that attach a nitrogen atom or nitrogen-containing fragment to a hydrophobic group. The three routes include (1) conversion of a carboxylic acid–containing group into a nitrile intermediate, followed by hydrogenation to the amine; (2) condensation products based on fatty acids and their derivatives, but without nitrile intermediates; and (3) from alpha olefins or fatty alcohols. These process routes can yield a range of product types, and some individual products may be derived through several routes.[43]

The nitrile route is exemplified by the process to manufacture one of the earliest commercial fabric softener materials, dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC), developed by Armour & Company in the 1950s as a means to utilize tallow and lard by-products of their meat-packing business. The product is prepared by the process detailed in Scheme 1.6: Tallow is steam-split by the Colgate–Emery process and the glycerin is recovered as a dilute aqueous “sweet water” stream. The fatty acids are distilled, then reacted at high temperature with ammonia over a bauxite catalyst with elimination of two equivalents of water to generate fatty nitriles, which are subsequently reduced by batch hydrogenation over Rainey nickel catalyst to yield a mixture of fatty primary amines. As originally practiced, the catalyst and reaction conditions reduced the olefins in the tallow chain yielding a mixture of saturated C16 and C18 alkyl amines. New catalysts allowed selective reduction of the nitrile while preserving unsaturation in the chain. Two equivalents of fatty amine are disproportionated over the same catalyst with elimination of ammonia to yield a mixture of mono-, di-, and tritallowamines, which are purified by distillation. The di(hydrogenated)tallow amines are subjected to reductive alkylation with formaldehyde and hydrogen over nickel catalyst to yield the dialkylmethyl amine, which is quaternized with methyl chloride or other alkylating agents.

The saturated and unsaturated primary amines from this process are converted through a series of derivatization steps into tertiary amines utilizing reagents such as EO, PO, a,b-unsaturated esters, formaldehyde, or acrylolnitrile followed by reduction to the respective alkyldimethyl- and alkylaminopropylamines, all suitable for quaternization with aliphatic and aromatic alkylating agents. Alternatively, the tertiary amines may be neutralized with acids to form the respective trialkylammonium salts, which have many of the attributes of the quaternary ammonium salts when maintained at acidic pH.

The sequence of multiple processing steps including operating conditions at high temperatures and pressures is both capital- and energy-intensive.



SCHEME 1.6 Three routes to cationic derivatives including fatty acid to nitrile to alkyl amine (*top*), fatty acid to alkanolamine ester (*center*), and olefin to alkyl bromide to alkyl dimethyl amine (*bottom*).

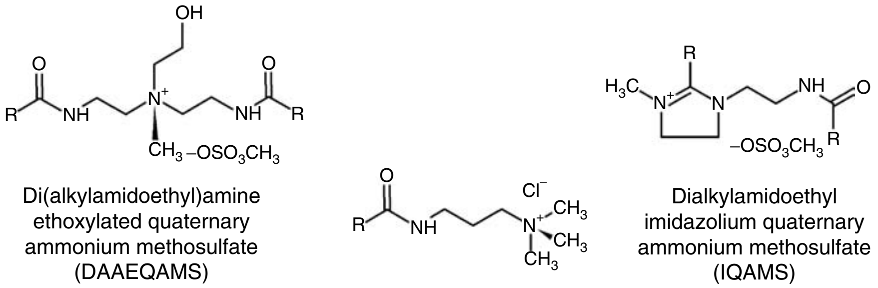
Condensation products based on fatty acids and derivatives include reaction products with alkanolamines such as triethanolamine (TEA) as in Scheme 1.6 and methyl diethanolamine (MDEA) and dimethylmonoethanolamine (DMMEA) to give estersamines, which are quaternized with methyl chloride or dimethyl sulfate (DMS). Hoechst and BASF filed patent applications, in 1970 and 1971, respectively, disclosing diester-based quaternaries of MDEA with methyl chloride, DMS, or benzyl chloride (BC) for use as fabric-softening agents.[44,45] Esterquats based on TEA were first patented for use as fabric softeners in 1974 by Stepan Company,[46] and comprise a thermodynamically controlled statistical distribution of mono-, di-, and triesters prepared from fatty acid or methyl esters that are commercially quaternzied with DMS. Various versions of esterquat products are now used globally in fabric softener formulations and have displaced DHTDMAC in many regions of the world by virtue of their biodegradability and lower capital cost to produce.[47] Cationics based on coconut fatty acid esters of DMMEA quaternized with DMS or methyl chloride are used as additives in laundry detergents and claimed to enhance the cleaning performance of LAS in numerous patents.[48]

A wide range of derivatives are prepared from alkyleneamines and poly(ethyleneamines) such as diethylene triamine (DETA), triethylenetetramine (TETA), imidazolines, amidoamines, and their ethoxylated and propoxylated derivatives as depicted in Scheme 1.7.[49] Reaction products of fatty acids and their derivatives with DMAPA (see Section 1.6.1) can be quaternized with various alkylating agents to produce amidopropyl ammonium quaternaries, many of which have been patented and commercialized in a variety of applications, including personal care, fabric softening, and industrial/oil-field applications.

Alpha olefins are reacted with HBr or HCl in the presence of peroxides to give the antimarkovnikov addition product primary alkyl halides, which are further reacted with alkylamines such as dimethylamine to give the respective alkyldimethylamines. Addition of inorganic bases such as sodium hydroxide to break the resulting amine salts generate highly purified NaBr which has significant market value in electronic and other specialty chemical applications.

Fatty alcohols are less commonly converted into intermediate alkyl halides through a reaction with $POCl_3$, PCl_3, or $SOCl_2$, and then reacted with dimethylamine to form the tertiary amine. The resulting by-products include mixtures of phosphorous and phosphoric acids and their partially chlorinated forms that present handling and disposal challenges.

Alternatively, aliphatic alcohols may be converted directly to the respective dimethyl alkylamines by catalytic amination in the presence of dimethylamine and low-pressure hydrogen over copper catalyst. The mechanism is believed to involve catalytic dehydrogenation of the alcohol to an aldehyde, addition of DMA with concomitant water elimination to form the enamine, and then subsequent reduction to the alkyldimethylamine. This route is particularly favored with longer-chain alcohols, which are derived through hydrogenation of tallow, or palm fatty acids, or methyl esters



Di(alkylamidoethyl)amine ethoxylated quaternary ammonium methosulfate (DAAEQAMS)

Alkyl amidopropyl trimmonium chloride

Dialkylamidoethyl imidazolium quaternary ammonium methosulfate (IQAMS)

SCHEME 1.7 Examples of quaternary ammonium surfactants based on DETA and DMAPA.

and are more plentiful than alpha olefins in the C16–C18 chain range. The hydrogenation of imines derived from the condensation of aliphatic aldehydes and primary amines is also used to produce secondary amines, which may be exhaustively alkylated to produce quaternary surfactants.

The global demand for cationic surfactants will be driven primarily by consumer fabric-softening applications, and to a lesser degree by personal care-product applications. The proliferation of washing machines coupled with increasing disposable income in developing regions and relatively low-current market penetration will create opportunities for significant growth even where hand washing still predominates. Cationic surfactants are uniquely functional in a broad range of consumer and industrial applications, and will continue to grow in use across the diverse range of application areas, from biocides to agricultural products, to oil-field chemicals. Challenges facing manufacturers of cationic surfactants include

- Increasing price and tightening supply of both petroleum and naturally derived fatty amines, PE amines, and alkanolamines due to increasing demand across the broad range of application areas, and the high capital cost of building new capacity
- Limitations on feedstock substitution options for fatty amines due to the unique performance features associated with amines produced from olefins versus fatty alcohols
- Cost of building and operating batch-processing facilities to produce customized and made-to-order (MTO) products to support consumer product differentiation strategies, as well as the diversity of small volume specialty products used in nonconsumer applications
- Ability to safely operate pressurized reactions with methyl chloride, a flammable gas reactant, or work with highly hazardous liquid alkylating agents such as dimethyl sulfate, diethylsulfate, or BC
- Rigorous emission controls that minimize the release of MeCl gas as well as VOCs

1.6.4 NONIONIC SURFACTANTS

Nonionic surfactants have found strong utility as compliments or alternatives to anionic surfactants in household cleaning and industrial applications due to their tolerance of hard water, lesser foaming characteristics, and efficiency at removing greasy and oily soils.[50–52] They can act synergistically with anionic surfactants and improve packing in mixed micelles, providing charge separation and mitigating the effects of repulsion between head groups of anionic surfactants, as well as maintaining micelle stability in the presence of polyvalent cations found in hard water. Nonionic surfactants have been tailored to produce little or no foam, and can act as defoaming agents in optimized formulations. When treated to remove trace levels of metal salts used as manufacturing catalysts, nonionic surfactants can be used effectively in high-performance cleaning applications where electrolyte residues are unacceptable, such as metalworking and electronics and optics manufacturing. Several classes of nonionic surfactants are used as foam boosting and skin-feel enhancing agents in personal cleansing products, and as emulsifying and conditioning agents in leave-on products such as creams and lotions.

The three broad classes of nonionic surfactants consist of esters, amides, and ethers, where the class name characterizes the essential bond-making process involved in linking the hydrophobic tail to the hydrophilic head. Some of the earliest nonionic surfactants were derived through esterification, typically by reaction of triglycerides or fatty acids and glycerin to yield mixtures of mono-, di-, and triesters. Esters, as a class, represent a small but significant volume of nonionic surfactants in commercial use today. Alkanolamide nonionic surfactants evolved based on the availability of alkanolamines, from which Kritchevsky developed diethanolamine (DEA) and monoethanolamine (MEA) amides of coconut fatty acid and triglycerides,[53] and these products found their way into synthetic liquid dish detergents and personal care products in the 1940s and 1950s. Ethers derived from the reaction of active hydroxyl groups with ethylene, propylene, or butylene oxide constitute the largest general class of nonionics by volume, and accounting for at least half of the 2 million metric tons of nonionics produced annually. Ethers based on polyhydroxy compounds such as glycerin, sorbitol, and glucose or dextrose, have achieved some significant commercial volumes in consumer applications involving skin contact where product mildness justifies their higher cost of manufacture.

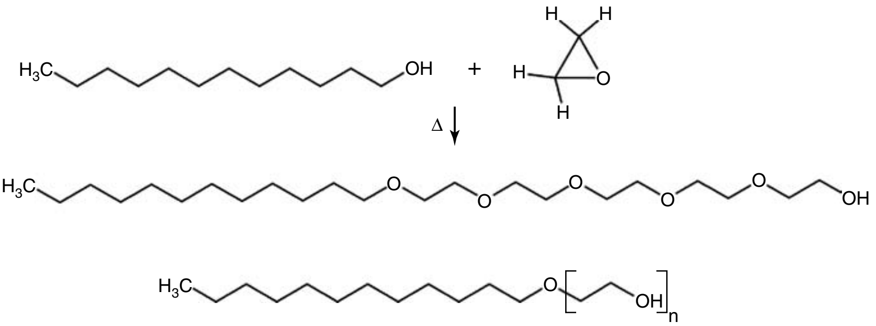
1.6.4.1 Alkanolamide Nonionic Surfactants

Alkanolamides are the reaction products of mono- or dialkanolamines with fatty acids or their esters to form the respective secondary or tertiary amides, examples of which are depicted in Scheme 1.8.[54] Monoalkanolamides can be prepared by the reaction of monoalkanolamines with triglycerides such as coconut or palm kernel oil as well as from fatty acids or their methyl esters. The reaction of MEA with triglyceride at temperatures of 140–160°C liberates glycerin as a by-product, and because of the stability of the secondary amide formed, the reaction can be driven to a very low ester content with only a slightly super-stoichiometric amount of MEA.

Alkanolamides based on DEA are tertiary amides and are not as stable as MEA amides such that a significant amount of esters can remain in equilibrium with the amide. The ester amines and esteramides of DEA have undesirable performance properties, but these components can be reduced by utilizing an excess of DEA to drive equilibrium toward the amide form. The most common version is prepared by the reaction of 2 moles of DEA with 1 mole of coconut fatty acid or ester to give the Kritchevsky or Ninol-type DEA amide, which is liquid at room temperature. Products made with slightly more than a 1:1 molar ratio of DEA to fatty acid or ester are referred to as *superamides*; and at reaction temperatures of 140–160°C, the mixture contains high level of ester components and free amine. However, with sufficient time at storage temperatures <50°C, the composition will increase in amide and decrease in ester and free-amine components and thus can be "aged" into specification for free DEA and ester content.

Solid amides from MEA and DEA can be chill flaked, but during formulation the mixture must be heated to 50–70°C for effective incorporation, whereas liquid DEA amides are stored and transported at <50°C, and are easier to incorporate at lower formulation temperatures. A variety of blends have been developed where high-melting amides are incorporated into aqueous anionic surfactant products such as the typical mixture of neutral alcohol sulfate and alcohol ether sulfates used in shampoo products, providing improved ease of transport, storage, and dilution, even at near-ambient temperature.

Alkanolamides that are liquid at room temperature have been commercialized based on increased content of unsaturated C18 acids, use of branched alkanolamines such as monoisopropanolamine (MIPA), or propoxylation of MEA amides, as well as blends of all these with PEG esters to improve thickening performance of the products. The higher cost of the earlier-mentioned feedstocks



SCHEME 1.8 Reaction of dodecyl alcohol with EO to prepare the nominal 5-mole ethoxylate, also referred to as Dodeceth-5. The product is a mixture containing the Gaussian distribution of dodecyl polyoxyethylene ethers units from $n = 0$ to > 10.

or multiple processing steps to prepare and blend translate into a higher price to the customer in exchange for ease of storage, handling, and formulating.

1.6.4.2 Alkoxylated Nonionic Surfactants

The production and properties of alkoxylated nonionic surfactants have been reviewed extensively.[55,56] They are produced by the reaction of hydrophobic feedstocks containing hydroxyl or amine groups with alkylene oxides under pressures of 30–90 psia and at temperatures of 100–140°C in the presence of catalytic quantities of basic or transition metal elements. The degree and type of alkylene oxide appended and the blocking or random copolymerization that is allowed to occur drastically affects the physical and performance properties of the resulting nonionic surfactant.

Because of the competing reactions of water or short-chain alcohols with target functional groups, the stepwise process involves pretreatment of the hydrophobe with a catalytic quantity of base, typically NaOH or KOH, applying heat and vacuum to eliminate water and drive the composition to the respective metal alkoxylate or carboxylate salt of the substrate, optionally releasing the vacuum with nitrogen to provide an inert diluent for operation with EO, then introducing EO or PO as a gas or liquid into the catalyzed substrate. Although alkoxylated amines are often exploited for their cationic character when formulated under basic conditions, this class of surfactants functions comparably with alkoxylated alcohols with some potential advantages due to the presence of two independent PEG chains in the case of alkoxylated primary amines.

The process of alkoxylation is exothermic and involves a balance of working reactor pressure with batch temperature to achieve acceptable product color and reasonable cycle times. For reactions involving EO, there is a well-defined partial pressure of EO that should be controlled by the use of nitrogen dilution gas, batch temperature, and headspace volume to exclude the accidental inclusion of oxygen and avoid conditions that could result in a spontaneous vapor-phase reaction such as decomposition, isomerization, or polymerization, any of which generates between 2000 and 3000 kJ/kg heat of reaction and associated pressure spike. Batch alkoxylation processes have been conducted safely and efficiently at numerous plant locations since the 1950s with only a small number of serious safety issues. A consortium of EO producers actively promotes safe handling, process design, and operation and provides supporting information to this end.[57]

The rate of reaction of EO in typical ethoxylation reactions is mass transfer and often heat-transfer limited, where the low vapor pressure of EO coupled with reaction temperatures from 70 to 140°C allows a large quantity to remain in the gaseous phase occupying the headspace of a traditional batch reactor. Several reactor designs have been introduced over the past 25 years that specifically enhance gas–liquid mixing to the extent that very low partial pressures of EO exist during the course of the reaction, and the time to complete the addition is dramatically reduced. Designs such as the buss loop reactor[58] educt the headspace gas into the reaction mixture through recirculation loops comprising passive or active gas–liquid mixing devices. The rate of ethoxylation is accelerated to the extent that production of large volume commodity ethoxylates can be conducted in a semibatch mode. A supply of catalyzed feed thoroughly stripped of water and low molecular weight alcohols is prepared in the first pretreatment stage, whereas the second stage loop reactor completes the alkoxylation step, and the third finishing stage reacts or strips away trace levels of EO, where the catalyst can be neutralized, or removed by treatment through an ion-exchange bed (Figure 1.14). This arrangement is particularly suitable for production of low-mole ethoxylated alcohols used as feedstocks for sulfonation to produce ether sulfates.

Ethoxylation involves a random reaction that results in a Poisson distribution of products with varying amounts of alkylene oxide groups appended to the substrate. For conventional catalysis with sodium or potassium alkoxylates, the distribution is particularly broad and consistent. When applying <6 moles of EO, the amount of unethoxylated substrate can be significant. A large body of development work over the course of the past 20 years has identified a range of alternative catalysts

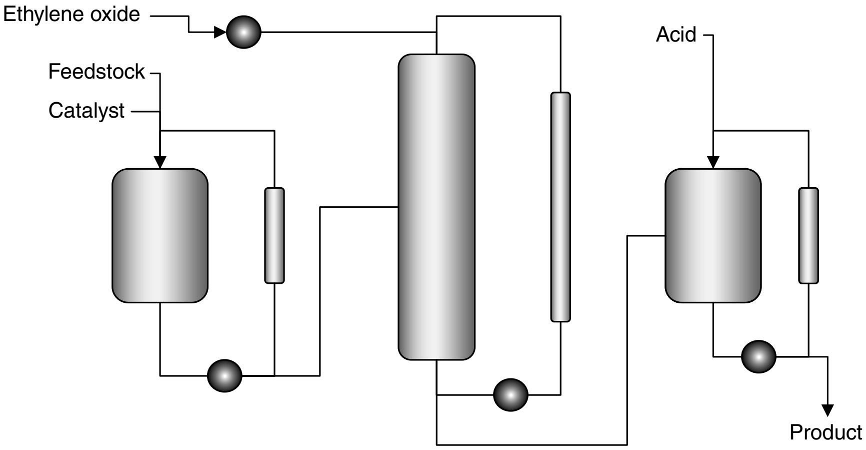


FIGURE 1.14 Commercial process for alkoxylation with precatalysis reactor, alkoxylator, and posttreatment reactor. (From Buss Process Technology, U.S. Patent 3,915,867, 1975; U.S. Patent 6,017,874, 2000. With permission.)

that can reduce the amount of unreacted substrate and narrow the distribution of alkoxylated products for reactions where <10 moles of EO or PO are added. The catalysts typically have a lower "basicity" and comprise simple or complex salts of calcium, magnesium, or a host of transition or rare earth metals that are added as powders, and usually require a longer induction or reaction period to conduct the alkoxylation reaction. Many of these same catalysts have functionality for catalyzing insertion alkoxylation reactions of methyl esters, yielding methyl-PEG or methyl-PPG esters.

Propoxylation is typically a slower reaction due to the steric hindrance between the propagating secondary hydroxide ion and the approaching PO. Attack of the hydroxide occurs essentially completely at the primary carbon of PO, regenerating a secondary hydroxide ion that is more basic than a primary hydroxide ion. In the presence of a primary alcohol substrate, complete capping with 1 mole of PO will occur before substantial polypropoxylation begins due to both steric constraints and the equilibrium concentration of alkoxide favoring the primary alcohol. This phenomenon allows for controlled capping of primary alcohols or block ethoxylates with a small amount of PO. Conversely, this effect makes it difficult to "cap" a secondary alcohol with a small amount of EO. Addition of EO first occurs on a small portion of the substrate and creates primary alcohols that are preferential sites for subsequent EO addition, driving the formation of a low mole fraction of a product with long EO blocks, and leaving a high mole fraction of the substrate unethoxylated. The production of "random" EO/PO block alkoxylate products by premixing EO and PO in a feed tank and pumping into the reactor thus tends to result in products containing blocks of EO separated by very short sectors of PO, and terminating in a large block of PO as the excess is consumed at the end of the reaction. Similarly, before adding an EO block to a propoxylate block, it is necessary to react away or strip off residual PO to a very low level to avoid random insertion of PO into the EO block, or PO capping at the end of the ethoxylation reaction that can dramatically change the performance characteristics of the product.

Longer reaction times are usually required for propoxylation reactions due to the preference for lower reaction temperatures necessary to maintain product color and avoid troublesome side reactions such as elimination of a terminal alcohol to generate allyl ethers. Propoxylation reactions can be selectively accelerated at lower temperatures with the use of a double metal cyanide catalyst. The catalyst is extremely sensitive and easily deactivated by moisture and conventional groups I and II catalysts, and will not effectively catalyze ethoxylation reactions.

The most common substrates for alkoxylated nonionics are listed as follows:

Natural C12–C16 fatty alcohols or C10–C15 synthetic fatty alcohols with 1–4 moles of EO. These nonionics are typically used as feedstocks for sulfonation to produce a wide range of ether sulfates used in household, personal care, and industrial applications (see Section 1.6.2.1).

Natural C12–C16 fatty alcohols or C10–C15 synthetic fatty alcohols with >4 moles of EO. Alcohol ethoxylates with 5–11 moles of EO are used in liquid and powdered laundry detergents as coactives with LAS and fatty alcohol ethers sulfate (FAES) in hard surface–cleaning formulations and in a host of industrial applications. Alcohol ethoxylates with 12–50 moles of EO and their respective sulfated and phosphated derivatives find use in emulsion polymerization and other select applications.

Alkylated phenol. The most commonly used alkylated phenol ethoxylates (APE) have included octyl phenol ethoxylate and nonylphenol ethoxylates with 3–11 moles of EO, which were produced by alkylation of butylene dimer or propylene trimer onto phenol and subsequent ethoxylation. They had been used extensively in laundry and hard surface–cleaning applications in the nonionic form, and as the sulfated and phosphated derivatives of the low-mole ethoxylates in a variety of industrial applications. Concerns over the environmental impact of the partial metabolites generated during the waste treatment of these surfactants has prompted their elimination from European consumer product formulations, and their deformulation from most consumer products in North America and elsewhere in the world.

Block propylene oxide. Several broad subfamilies of these surfactants were originally developed by Wyandotte Corp, later proliferated by BASF and are today produced through a process where PPG of varying molecular weight (MW) is used as the substrate for ethoxylation, or where PEG or alkyl PEG ethers of varying MW are block propoxylated. Concerns in the European Union (EU) over the anaerobic biodegradability of the block PO/EO surfactants will affect their ongoing breadth of use in consumer applications.

Secondary alcohols. Secondary alcohols derived from oxidation of primary alfa olefins are first selectively monoethoxylated under acid-catalyzed conditions before being polyethoxylated under basic conditions to avoid the EO blocking phenomenon described in the propoxylation discussed earlier. They offer the advantages of a highly branched surfactant such as low bulk-handling temperature and cloud point in formulations without the disadvantages of reduced biodegradability. The two-step process to ethoxylate represents a cost and efficiency penalty, and when ethoxylated even once, they are less stable substrates for sulfation, more susceptible to elimination reactions as a pathway to decomposition.

Glyceryl esters. Glyceryl esters such as glyceryl monostearate (GMS), including triglycerides such as castor oil are ethoxylated with classic group I catalysts and undergo insertion ethoxylation as well as ester interchange leading to highly complex mixtures of esters of ethoxylated glycerin where PEG ether chains are capped with fatty acid groups. As the degree of ethoxylation increases, the amount of remaining glyceryl esters decreases proportionately.

Polyhydric alcohol esters. Reactions of fatty acids with polyhydric alcohols derived from reduction of sugars such as sorbitol results in a mixture of esters of both the sorbitol and its dehydrated ethers sorbide and isosorbide. Ethoxylation of this complex mixture of esters involves insertion of ethoxylation and transesterification ethoxylation as described earlier, resulting in a highly complex composition with performance properties that are dependent on the precise conditions for both the esterification and the ethoxylation steps. This is described classically as a product-by-process, which is difficult to reproduce due to the affect of the commercial-scale manufacturing kit on the precise conditions of each step of the reaction.

Fatty acids. Fatty acids can be ethoxylated in what amounts to a two-step process where the first mole of EO adds slowly to the dry, precatalyzed acid to yield the hydroxyethyl ester. Because of the presence of carboxylic acid, the reaction runs slowly under general acid catalysis and does not produce substantial quantities of polyethoxylated product. Once the free carboxylic acids are completely capped, the pH of the system becomes alkaline and the reaction proceeds in a comparable manner to any primary alcohol ethoxylation. Some competing transesterification occurs at temperatures above 120°C, leading to a product distribution of PEG monoesters, diesters, and free PEG.

Amide ethoxylates. Mono- or dialkanolamides are alkoxylated to produce amide ethoxylates, which are noted to have some cationic character. At temperatures of alkoxylation, even monoalkanolamides will undergo ethoxylation on the amide nitrogen at a low rate, creating a low level of dialkanolamides. Dialkanolamides at temperatures of alkoxylation undergo an equilibrium 1,4 shift to form the respective ester amine, which is immediately alkoxylated to form an ester of a trialkanolamine. Thus, the concentration of esters of trialkanolamines increases during the course of and proportionately with the degree of alkoxylation.

1.6.4.3 Esterified Nonionic Surfactants

Fatty acids or their derivatives are connected to a variety of hydrophilic head groups through esterification of fatty acids or transesterification using fatty acid methyl esters or triglycerides[52] as depicted in Scheme 1.8. Hydrophilic head groups that are used to prepare nonionic ester surfactants fall into several of the following subcategories.

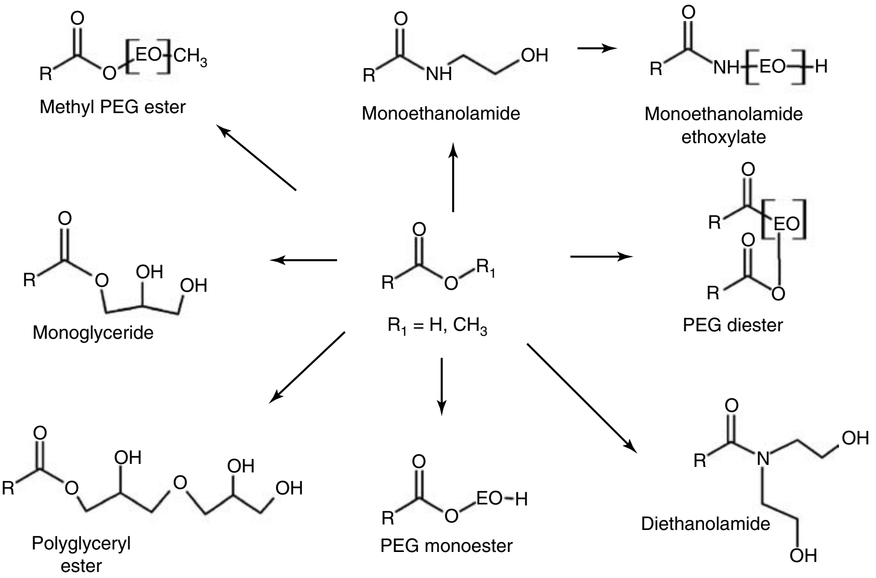
Nonether containing polyhydric alcohols derived from petroleum feedstocks include ethylene glycol, propylene glycol, butylene glycol, trimethylol propane, pentaerythritol, and several other feedstocks derived from epoxidation of olefins or condensation reactions based on formaldehyde. The exhaustively esterified derivatives are not surface active, but are used as emollients and lubricants. The partially esterified derivatives are typically used as emulsifying agents, and contain the distribution of mono- to polyesterified components. The monoester version can be produced at >70% yield by using more than three equivalent excess of hydroxyl to fatty acid residue where practical, and for the simple glycols the excess can be removed *in vacuo* using a wiped film distillation unit.

Nonether containing polyhydric alcohols derived from oleochemical sources include glycerin and reduced sugars consisting of erythritol, sorbitol, and manitol. The reactions and derivatives of glycerin are long known and well described,[59] and recent work on monoesters and polyesters of erythritol show them to be useful in several food-related applications. Esterification of polyhydric alcohols of more than four carbons involves competing ring-closing etherification reactions that generate anhydrides such as sorbides and isosorbides from sorbitol at reaction temperatures between 170 and 240°C with a basic catalyst. The esterification reaction rate exceeds the etherification rate, and open-chain polyol derivatives predominate as 60–80% of the product mixture depending on reaction time, temperature, and catalyst level.

Esterified nonionic surfactants are prepared from ether-containing polyhydric alcohols that include derivatives of EO and PO such as polyethylene glycol (PEG), polypropylene glycol (PPG), EO/PO block copolymers, polyglycerin that is prepared by thermal dehydration with basic catalyst, and ethoxylated glycerin (Scheme 1.9).

1.6.4.4 Etherified Nonionic Surfactants

The etherification of monosacharides with linear alcohols to produce alkyl polyglucosides has been known since Fischer developed this chemistry in 1893, but has only been practiced commercially since the early 1990s.[60] Variations and improvements on the process have been laid open in patents



SCHEME 1.9 Nonionic surfactants derived from fatty acids or esters.

issued to Henkel, Union Carbide, Akzo, Huls, and BASF, but fundamentally it involves a continuous plug-flow etherification reaction between a heterogeneous mixture of dextrose and a 3–10 molar excess of linear alcohol in the presence of an acid catalyst at elevated temperature. The excess amount of alcohol and reaction conditions affect the degree of polymerization (DP) of glucose, with the most useful products having a DP of <2, preferably between 1.1 and 1.3 and based on C10, C12, or coconut alcohol distributions. The excess alcohol must be stripped off for performance reasons and recycled for cost control. The alcohol stripping is best performed by subjecting the neutralized product to thin film distillation *in vacuo*.

The challenges facing producers of nonionic surfactants are multiple, and vary based on the type of surfactants they seek to produce.

- Alkoxylated surfactants will require construction of manufacturing facilities adjacent to EO production facilities to receive EO “over the fence” to achieve competitive economics and guarantee surety of supply.
- The cost of capital to construct alkoxylation facilities requires a large volume base load such as detergent-grade midrange alcohol ethoxylates and sulfonation grade low-mole ethoxylates, and the scale of such equipment is not effective at servicing small volume, specialty ethoxylate products.
- The operation of alkoxylation processes involves handling of volatile, flammable, highly reactive ingredients at elevated pressures and temperatures requiring a very high degree of attention to mechanical integrity and human safety.
- Nonalkoxylated nonionics based on amide or ester chemistry are easily prepared in small-volume batch-manufacturing facilities, making them low barrier-to-entry products, inviting competition and driving down margins and profits.
- Products that involve both esterification and alkoxylation steps comprise extremely complex mixtures that are best described as *products by process* and are often difficult to replicate.

1.7 CONSTRUCTION AND OPERATIONAL ISSUES

The history of surfactant manufacturing is related to its position in the value chain. Some of the largest original practitioners of surfactant manufacturing were, and still are the end-formulators, consumer product companies who sought control over the cost, quality, and availability of the key anionic surfactant ingredients for powdered laundry detergents. Their goal was to build and operate the most capital-efficient operation that produced essentially one type of product on a continuous or semicontinuous basis year round. Continuous sulfonation processing, as a key example, is usually designed and implemented with efficient logistics in mind: raw materials are received in bulk, transferred through hard piping to dedicated storage, and pumped into highly automated processes requiring minimal operator intervention, with finished product piped to dedicated tanks.

The second tier of surfactant manufacturers consists of nonintegrated toll or merchant producers who started their participation in the business by making one or two families of secondary surfactants such as amides, nonionics, or amphoterics. In most cases, the original product specifications were broad, their customers' formulated performance was very forgiving, and there was a lot of latitude in manufacturing procedures that would produce an acceptable product. Batch production operations were, and can still be run today in a highly manual mode, with operators receiving and handling many or all raw materials in drum quantities, transferring feeds, intermediates, and finished products through hoses and other temporary equipment, and operating through manual control of valves and pumps located on or near the reactors.

In locations where labor costs are modest, this can be the most cost efficient and flexible means of producing a wide range of customized products that are capable of meeting demanding performance specifications. In developed countries where labor costs are the highest, there is a natural drive toward increased efficiency through automation. Automation achieves its greatest cost benefit when it allows operators to multitask efficiently and operates multiple production units simultaneously, and without needing to make constant adjustments to process variables such as heating, cooling vacuum, mixing, or level control. When designed with appropriate raw material and finished-product storage infrastructure, a single person can operate several production batches in different reactors simultaneously, and help manage the receipt of inbound raw materials and the loading and certification of outbound products.

The cost and complexity of designing, building, and maintaining facilities with this high level of automation are most easily justified when producing a single version of a product that requires efficient production while operating within tight specifications, and especially when handling hazardous raw materials. The capital cost begins to increase significantly when trying to serve a family of products based on a broader range of feedstocks. The cost associated with installing and maintaining multiple feedstock and product storage facilities can easily rival or far exceed the cost of the primary reaction vessel. Since there are a limited number of processing hours, once a vessel is "sold out," demanding additional product variants can result in a shift to MTO production, where reactors end up as temporary hold tanks awaiting product transfer to tank trucks or drums, reducing throughput efficiency dramatically.

1.7.1 REGULATORY STANDARDS

Surfactants are used in a broad range of products that enter the environment through consumer use, and agricultural and industrial products. In recent years, there has emerged a consensus view about what tests should be conducted to evaluate both new and existing chemicals, particularly those that are manufactured in large quantities.

Legislation on chemicals was first adopted and implemented in Europe in 1967. However, only after 1979, the legislation systematically addressed the generation of a minimum set of information for chemicals. Under a 1979 EEC directive, an inventory was established comprising existing chemicals, with more than 100,000 substances. New chemicals not listed in the inventory and produced in annual volumes of more than 1 t had to be notified. The notification dossier included a base set of data covering certain environmental and toxicological properties. At annual production volumes more than 100 or 1000 t, additional data focusing on the effects of long-term exposure had to be provided. Since 1981, more than 3700 new chemicals have been notified in the EU, constituting ~3% of all marketed substances. In 1993, Council Regulation 93/793/EEC was adopted requiring the submission of available data for existing chemicals placed on the market in volumes of more than 10 t/year. Based on this information, authorities identified 141 high-priority chemicals for risk assessment. By 2004, the assessment had been completed for only 32 of these chemicals.

Owing to the slow progress, a critical review of the EU chemicals legislation was initiated in 1997, and in 1999, the council adopted conclusions requesting the EU Commission to review the existing legislation and to develop appropriate proposals for a new chemicals policy in the EU. Following an extensive discussion with all the involved stakeholders and the adoption of a white paper on a strategy for a future chemicals policy in 2001, the European Commission adopted a proposal for an European Parliament and Council Regulation on the Registration, Evaluation, Authorization and Restrictions of Chemicals (REACH) in October 2003.*

According to this proposal, after the new regulation comes into force, the industry would be obliged to register all marketed chemicals above 1 t annually within 11 years. A minimum dataset would be required for chemicals between 1 and 10 t and additional information—the extent depending on the tonnage—would have to be provided for chemicals exceeding 10, 100, and 1000 t. For chemicals exceeding 10 t, industry would in addition have to draw up a chemical safety report, which includes a risk assessment. The results of this assessment would be forwarded to the downstream users transformed into the traditional safety data sheet to enable them to meet their responsibilities.

The program was codified under the EU Existing Chemicals Regulation, which covered all European Inventory of Existing Chemical Substances (EINECS)-listed existing substances manufactured or imported at >10 t/annum. The available test data have been reported for 1408 substances supplied at >1000 t/annum. Of these, only 110 have been selected so far for complete testing and risk assessment.

REACH also applies to all chemicals that are considered to be of very high concern to health or the environment—regardless of volume. Depending on the substance in question and its use, producers and importers may be obliged to investigate its effects on human health and the environment. REACH applies to all chemicals imported or produced in the EU. The European Chemicals Agency will manage the technical, scientific, and administrative aspects of the REACH system. Highlights include the following:

- Establish one system for registration, evaluation, authorization, and restrictions of chemicals that will become immediately effective in all member states.
- Establish a central agency for the management of the system.
- Focus competent authorities on high-tonnage substances.
- Register 30,000 chemicals over 11 years.
- Scope is limited to industrial chemicals.
- Pharmaceuticals, pesticides, and biocides are covered by separate regulations and testing requirements.
- Polymers and nonisolated intermediates are excluded.
- At least 1 million more animal tests are expected to be conducted.
- Estimated costs of approximately 5 billion euros for business over 11 years.
- REACH legislation contains 1,000 pages of text, rising potentially to 15,000.
- By October 2006, there had been 1,000 amendments voted by the EU parliament.

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* AISE, the International Association for Soaps, Detergents, and Maintenance Products at www.aise-net.org.

The U.S. Toxic Substances Control Act (TSCA) was first enacted in 1976 and has been amended significantly three times. TSCA gives the U.S. Environmental Protection Agency (USEPA) broad authority to regulate the manufacture, use, distribution in commerce, and disposal of chemical substances. TSCA is a federally managed law and is not delegated to states. The law is overseen by the USEPA Office of Pollution Prevention and Toxics (OPPT).*

A major objective of TSCA is to characterize and evaluate the risks posed by a chemical to humans and the environment before the chemical is introduced into commerce. TSCA accomplishes this through the requirement that manufacturers perform various kinds of health and environmental testing, use quality control in their production processes, and notify EPA of information they gain on possible adverse health effects from use of their products. Under TSCA, "manufacturing" is defined to include "importing," and thus, all requirements applicable to manufacturers apply to importers as well.

TSCA requires manufacturers, importers, and processors of certain chemical substances and mixtures to conduct testing on the health and environmental effects of chemical substances and mixtures, unless they qualify for an exemption. Testing requirements cover existing chemicals (but not new chemicals, because these are addressed in the EPA premanufacturing notice process) and mixtures as well as individual substances. EPA has established a Master Testing List that lays out testing priorities based on risk and exposure potential.

EPA has the authority to ban the manufacture or distribution in commerce, limit the use, require labeling, or place other restrictions on chemicals that pose unreasonable risks. Among the chemicals EPA regulates under TSCA are asbestos, chlorofluorocarbons (CFCs), and polychlorinated biphenyls (PCBs).

By the early 1990s, it was evident that many of the existing major industrial chemicals had not been evaluated completely, although in 1989 the Organization for Economic Cooperation and Development (OECD) countries had initiated their voluntary testing program aimed at providing this data by developing Screening Information Data Sets (SIDS) on high production volume (HPV) chemicals.

Later in the decade, concern over chemical safety prompted the USEPA, in collaboration with the American Chemical Council (ACC) and the U.S.-based nongovernmental organization the Environmental Defense Fund, to launch the Chemical Right-to-Know initiative. A key element to this was the HPV challenge program, which was designed to obtain SIDS information on ca. 2800 HPV chemicals supplied in the United States at >1 million pound annually according to the 1990 TSCA Inventory Update. More than 300 companies and consortia volunteered to develop and supply data on a completion schedule targeted at the end of 2004.

In March 2005, the ACC, in cooperation with U.S.–based Soap and Detergents Association (SDA) and Synthetic Organic Chemical Manufacturers Association (SOCMA), announced a joint initiative to extend the industry's work on HPV chemicals—those produced in the United States or imported in quantities greater than 1 million pound annually. The Extended HPV (EHPV) Program was designed to publish health and environmental information on 574 newly designated HPV chemicals. These are substances that did not qualify as HPV chemicals at the start of the original program, but now meet the volume threshold according to EPA's 2002 inventory. In addition to gathering health and environmental information, companies will be asked to provide information on use and exposure for both the "extended" HPV as well as the original Challenge Program substances. In this way, the EHPV Program will provide EPA and the public with an extensive source of chemical safety information on HPV chemicals.

Collaboration between national and regional industry organizations representing surfactant chemical manufacturers have attempted to avoid redundant testing through consortia organized to support specific groups or families of products.

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* ChemAlliance, a resource organization funded by USEPA and private industry to provide current information on environmental regulations to the chemical industry, accessible at www.ChemAlliance.org.

Cost sharing and data ownership issues have been negotiated in attempts to achieve equitable distribution of burden. As national and regional chemical inventories are translated from developed regions to developing regions, the expenditures borne by the consortia will create opportunity for the local production of surfactants.

As a result of regional testing and registration, the use of certain surfactants have been restricted to specific areas of the world, such as the EU, although these products continue to find acceptance and use in other regions. A well-established example is DHTDMAC.

Regulatory challenges that face production of surfactants include

1. The primary surfactant ingredient (and possibly coproducts) must appear on the regional chemical inventories of approved chemicals such as TSCA in the United States, Canadian Designated Substance List (DSL) or Canadian Non-Designated Substance List (NDSL), and EINECS in Europe.
2. When the product is ultimately discharged to the environment, it must meet biodegradability requirements, the results of which vary by test method and the acceptable levels of which vary from region to region.
3. The presence of some unreacted starting materials, by-products, or impurities may cause concerns around chronic exposure due to results generated for the concentrated isolate, and by modes of exposure that are irrelevant to the use of the product, for example, concerns for the carcinogenicity of nitrosamines from unreacted DEA found in shampoos and body washes based on results of oral testing.

In the CEFIC Pan European Survey "Image of the Chemical Industry 2006,"* the summary report notes several expected trends.

> At pan European level, the development shows a trend back towards a more business-critical climate, namely publics' declining belief in the benefits of modern technology and publics' increasing feeling of companies' profits being too high.
>
> Publics' belief in a sacrosanct value of nature is, despite the measurable decline, still very strong and a potential barrier to the implementation of new technologies such as genetically modified plants or nano-technology.*

It is clear that the chemical industry up and down the supply chain will continue to be scrutinized and judged, and our "right to practice" will continue to be challenged in various quarters, but can be maintained by complying with the evolving and ever harmonizing standards for safety, health, and environmental (SHE) performance. More than compliance, there is an expectation by stakeholders surrounding the industry that the tenets of responsible care and product stewardship will be embraced and advanced at more than a symbolic level, and that real, tangible, continuous improvement will be the standard to which we are held and against which we are judged.

The good news is that the chemical industry in Europe as a whole continues to gain positive ground in the public's eyes.

> Most detailed ratings of the chemical industry on qualitative aspects have improved too, slightly on items related to "Importance & Benefits" and "SHE-Performance", more significantly on "Social Responsibility".
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> Practically unchanged from 2004, publics' perceptions of "chemical products" are more positive than negative and focus on cleaners, detergents, toiletries, pharmaceuticals, cosmetics, pesticides, paints.
>
> There is no measurable effect from media reports or NGO-campaigns related to REACH.*

Clearly, consumers recognize they have a high level of interaction with chemicals in the form of laundry detergents, household cleaning, personal cleansing, and health and beauty products. Thus,

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* CEFIC, the European Chemical Industry Council, from the Cefic Pan-European Survey, Image of the Chemical Industry 2006, accessible at www.cefic.org.