SURFACTANT SCIENCE
AND TECHNOLOGY
SURFACTANT SCIENCE
AND TECHNOLOGY

THIRD EDITION

Drew Myers

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To friends gone, but not forgotten—

Johnny B.
Paul G.
Alan B.
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Preface to the Third Edition

When a book reaches the third edition, it must be assumed that (1) the work has been useful to someone or (2) the publisher has lost its collective mind. As a simple matter of ego, I must assume that reason 1 is true in this case. For that reason, I have tried to maintain the same basic philosophy with regard to the style and content of the book, while endeavoring to incorporate new material where indicated. A good deal of the information presented is “old” in the sense that it represents work done many years ago by the virtual founders of the science of surface and colloid chemistry. In the mid-1950s a few names stood out as the “gurus” of the field—today the names are too numerous to mention, and the body of published literature is enormous. Surfactants and their applications continue to fill books and patents.

Important advances in the tools available for studying the activity of surfactants has significantly increased our understanding of what is happening at interfaces at the molecular level in both model and practical systems, although there is still a lot be learned. New knowledge obtained in the years since the publication of the second edition has added greatly to our understanding of the nature of the molecular interactions of surface-active materials and the consequences of their presence on system characteristics and performance. The basic concepts and principles, however, remain pretty much the same.

In this edition, some topics have been reduced or moved around and several new themes added. Two cases, those of phase transfer catalysis (PTC) and aerosols, are not directly related to surfactants, but their real or potential importance prompted me to include some introductory material related to them.

Without changing the fundamental philosophy and goals of the previous editions, this third edition was prepared with three major ideas in mind: (1) to maintain the basic content of the work, (2) to maintain the “readability” of the book for non-specialists, and (3) to improve the book’s utility as a source of basic concepts concerning surfactants and their applications. A limited number of problems are provided at the end of each chapter (except Chapter 1) to illustrate some of the concepts discussed. In some cases, the problems provided may not have a unique solution, but are posed to stimulate imaginative solutions on the part of the reader. Some may also require some searching on the part of the problem solver to find missing pieces. While exact literature references are not provided, the Bibliography at the end of the book includes many of the better resources for more detailed information on each specific subject. It should serve as a useful guide to more detailed coverage for the interested reader.
I would like to thank my two “best friends,” Adriana and Katrina, for their constant love and support, and the crew at ALPHA C.I.S.A.—Lucho, José, Guillermo, Lisandro, Gabriel, Soledad, Alberto, Carlos, Enrique, Rudi, and all the rest—for putting up with my presence and my absence. Gracias por haber soportado mi presencia y mi ausencia.

Drew Myers
An Overview of Surfactant Science and Technology

Rapid evolution in the chemical-based nature of our modern society has made it increasingly difficult for scientists, engineers, regulators, and managers to remain abreast of the latest in the technologies impacting their work. The scientific and technical journals published worldwide number in the thousands, and this number increases yearly. Paralleling the proliferation of the scientific literature in general has been an apparent divergence into fields of “pure” science—studies in which the principal goal is a general advancement of human knowledge with no particular “practical” aim in mind—and “applied” science and technology, in which the research is driven by some anticipated application, quite often, but not always, profit-related. Few areas of chemistry have exhibited this growing dichotomy of purpose more than the study of surface and colloid science, especially as applied to surface activity and surface-active materials. Even the nomenclature used in discussing materials showing surface activity is widely varied, depending on the context of the discussion. It is not surprising, then, that the world of surface activity and surface-active agents, or surfactants, can appear complex and confusing to those not intimately involved in it on a day-to-day basis.

When one considers the impact of surface science in general, and emulsions, dispersions, foaming agents, wetting agents, and other related compounds in particular, in our day-to-day routines, the picture that develops reveals the great extent to which these areas of chemistry and chemical technology permeate our lives. From the fundamental aspects of biological membrane formation and function in living cells, which vividly illustrates the spontaneity and importance of colloidal phenomena, to the more “far out” problem of how liquids wet the walls of a rocket’s fuel tank in a low-gravity environment, the physical chemistry of the interactions among various phases at interfaces lies at the root of much of our modern lifestyle.

Industrial concerns, whose very lifeblood may be intimately linked to application of the basic principles of interfacial interactions, often ignore the potential benefits of fundamental research in these areas in favor of an empirical trial-and-error approach, which may lead to a viable process but that possibly could be better understood and even significantly improved by the application of more fundamental science. In many cases the prevailing philosophy seems to be, to paraphrase an old
adage, “A dollar in the hand is worth two in the laboratory.” Unfortunately, such an approach often results in more dollars down the drain than many management-level decisionmakers care to admit. Academic researchers, on the other hand, are sometimes guilty of ignoring the potential practical aspects of their work in favor of experimental sophistication and the “Holy Grail” of the definitive theory or model. Neither philosophy alone truly satisfies the needs of our technological existence. Each approach makes its valuable contribution to the overall advancement of human knowledge; however, it sometimes appears that a great deal is lost in the communication gap between the two.

The science and the technology of surfactants have possibly suffered a double blow from the functional divergence of academic and applied research. Academic interest in surfactants, while increasing, has generally concentrated on highly purified, homogeneous materials [quite often limited to a few materials such as sodium dodecylsulfate (SDS), or cetyltrimethylammonium bromide (CTAB)] and elegant analytical techniques. While providing a wealth of useful information related to the particular system under investigation, the application of such information to more complex practical materials and processes is often less than obvious, and is sometimes misleading. The sad fact of life is that real surfactant systems are almost always composed of mixed chemical isomers, contaminants, and added materials that can dramatically alter the effects of a given surfactant on a system. High purity is necessary for the interpretation of delicate laboratory experiments, but requires the use of techniques that may be impractical at the industrial level.

In the results-oriented industrial environment, with some significant exceptions, surfactant research is often carried out on a “Make it work and don’t worry about why!” basis. The industrially interesting materials are usually complex mixtures of homologs and structural isomers, or contain impurities resulting from chemical side reactions, unreacted starting materials, residual solvents or byproducts, and so on. Such “contamination” of the desired product is not only common, but commonly variable from batch to batch. For example, particularly significant surface property changes can be induced by the presence of such impurities as inorganic salts or long-chain alcohols remaining after processing. While the presence of such impurities and mixtures will often produce superior results in practice, analysis of the process may be difficult because of the unknown or variable nature of the surfactant composition. Considering the limitations imposed by each school of surfactant research, it is not surprising to find that a practical fusion of the two approaches can be difficult to achieve.

The different views of surfactant science and technology have spawned their own distinctive terminologies and literatures. While the academic or fundamental investigator may probe the properties of surface-active agents, surfactants, tensides, or amphiphiles, the industrial chemist may be concerned with the characteristics of soaps, detergents, emulsifiers, wetting agents, and similar compounds. The former group may publish their results primarily in the *Journal of Physical Chemistry*, *Colloids and Surfaces*, *Langmuir*, or the *Journal of Colloid and Interface Science*, the latter in the *Journal of the American Oil Chemists Society*, the *Journal of Dispersion Science and Technology*, or one of the other technologically specialized...
publications aimed at specific areas of application (foods, cosmetics, paints, etc.). All too often, the value of the results to each community can become lost in the sea of manuscripts and the philosophical and operational gulf that sometimes develops between the two, not to mention the almost impossible task of being abreast of all the information published in all the relevant literature.

Before beginning a discussion of specific aspects of the chemistry of surface-active materials and surfactant action, it may be useful to have some idea of the history of surfactants and how their synthesis and use have evolved through the years. Because of parallel developments in various areas of the world, the secrecy of industrial research efforts, and the effects of two world wars, the exact details of the evolution of surfactant science and technology may be subject to some controversy regarding the specific order and timing of specific developments. In any case, the major facts are (hopefully!) correct.

1.1. A BRIEF HISTORY OF SURFACTANT SCIENCE AND TECHNOLOGY

The pedigree of the synthetic surfactant industry is reasonably well documented, unlike that of the more ancient “natural” alkali soaps. However, it is not an easy task to pinpoint the exact time when the industry came into being. In a strictly chemical sense, a soap is a compound formed by the reaction of an essentially water-insoluble fatty acid with an alkali metal or organic base to produce a carboxylic acid salt with enhanced water solubility, sufficient to produce useful surface activity. Since the soaps require some form of chemical modification to be useful as surfactants, they could be considered to be synthetic; however, custom dictates that they not be classified in the same category as the materials prepared by more “elegant” synthetic routes.

The alkali metal soaps have been used for at least 2300 years. Their use as articles of trade by the Phoenicians as early as 600 B.C. has been documented. They were also used by the Romans, although it is generally felt that their manufacture was learned from the Celts or some Mediterranean culture. Early soap producers used animal fats and ashes of wood and other plants containing potassium carbonate to produce the neutralized salt. As the mixture of fat, ashes, and water was boiled, the fat was saponified to the free fatty acids, which were subsequently neutralized.

The first well-documented synthetic (nonsoap) materials employed specifically for their surface-active properties were the sulfated oils. Sulfonated castor oil, produced by the action of sulfuric acid on the castor oil, was originally known as “turkey red oil.” It was introduced in the late nineteenth century as a dyeing aid and is still used in the textile and leather industries today. The first surfactants for general application that have been traditionally classified as synthetic were developed in Germany during World War I in an attempt to overcome shortages of available animal and vegetable fats. Those materials were short-chain alkyl-naphthalene sulfonates prepared by the reaction of propyl or butyl alcohol with
naphthalene followed by sulfonation. The products, which proved to be only marginally useful as detergents, showed good wetting characteristics and are still in use as such. They are still sold under various trade names in Europe and the United States.

In the late 1920s and early 1930s, the sulfation of long-chain alcohols became common and the resulting products were sold as the sodium salt. Also in the early 1930s, long-chain alkylaryl sulfonates with benzene as the aromatic group appeared in the United States. Both the alcohol sulfates and the alkylbenzene sulfonates were used as cleaning agents at that time, but they made little impact on the general surfactant or detergent markets. By the end of World War II alkylaryl sulfonates had almost entirely overwhelmed the alcohol sulfates for use as general cleaning agents, but the alcohol sulfates were beginning to emerge as preferred components in shampoos and other personal care formulations.

In common with other chemical developments during that time, progress in the area of surfactants and detergents was not limited to one family of materials. The explosion of new organic chemical processes and the ready availability of new raw materials led to the development of a wide variety of new surface-active compounds and manufacturing processes. In a particular country, the limiting factor was almost always the availability of raw materials from which to prepare the desired product and the economics of each process.

Concurrent with the advance of alkylaryl sulfonates as economically viable surfactants, activities in the United States and Germany led to the development of the taurine (2-aminoethane-1-sulfonic acid) derivatives and the alkane sulfates, respectively. In the United Kingdom, secondary olefin sulfates derived from petroleum fractions were produced in large quantities. Each of those raw materials had its own special advantages and disadvantages; but in evaluating their feasibility, the producer had to consider such factors as the availability and cost of raw materials, ease of manufacture, the economics of manufacture and distribution, and overall product stability. As a result of their ease of manufacture and versatility, the propylene tetramer (PT)–based alkylbenzene sulfonates (ABS) very quickly gained a strong position in the world market. After World War II, the propylene tetramer, primarily a branched C_{9}H_{19} alkyl, C_{9}H_{19}–C_{6}H_{4}–SO_{3}Na^{+}, coupled to benzene became a predominant material. Thus, ABS materials very rapidly displaced all other basic detergents and for the period 1950–1965 constituted more than half of all detergents used throughout the world.

ABS materials held almost undisputed reign as the major ingredient used in washing operations until the early 1960s, with essentially 100% of the alkylbenzene detergents belonging to the PT family. Around that time it was noted that sewage effluents were producing increasing amounts of foaming in rivers, streams, and lakes throughout the world. In addition, where water was being drawn from wells located close to household discharge points, the water tended to foam when coming out of the tap. Such occurrences were naturally upsetting to many groups and led to investigations into the sources of the foaming agents. Such an undesirable phenomenon was ultimately attributed to the failure of the ABS materials to be completely degraded by the bacterial and other processes naturally present in wastewater treatment plants and effluents. It was further determined that it
was the branched alkyl (PT) chain that hindered attack by the microorganisms. Fatty acid sulfates, on the other hand, were found to degrade readily, and since all naturally occurring fatty acids from which fatty alcohols are produced are straight-chained, it seemed probable that a straight-chain alkylbenzene might prove more easily biodegradable.

Test methods for determining degradability were developed and showed that, in fact, linear alkylbenzene sulfonates (LABS) were significantly more biodegradable and hence ecologically more acceptable. In most of the industrialized world, detergent producers, voluntarily or by legislation, have switched from ABS to LABS as their basic detergent building block. By the 1980s, more than 75% of synthetic detergents were of the LABS family.

The change to LABS feedstocks gave some rather surprising results. It was found that detergency in many heavy-duty cleaning formulations using LABS was approximately 10% better than when ABS were used. Solutions of the neutralized acid had a lower cloud point (see glossary in Section 1.8), and pastes and slurries had a lower viscosity. The first two results were obviously advantageous, and a lower viscosity in slurries had an advantage when the product was processed into a powder. When the LABS product was to be sold as a liquid or paste detergent, however, the lower viscosity was seen as a detriment to sales appeal and had to be overcome.

Today, even though many of the application areas such as detergents and cleaning products are considered to be "mature" industries, the demands of ecology, population growth, fashion, raw-materials resources, and marketing appeal have caused the technology of surfactants and surfactant application to continue to grow at a healthy rate overall, with the usual ups and downs that accompany most industries.

While a large fraction of the business of surfactants is concerned with cleaning operations of one kind or another, the demands of other technological areas have added greatly to the enhanced role of surfactants in our modern existence. Not only are personal care products becoming an even greater economic force in terms of dollar value and total volume; applications as diverse as pharmaceuticals, petroleum recovery processes, high-tech applications, and medicine are placing more demands on our ability to understand and manipulate interfaces through the action of surface-active agents. As a result, more and more scientists and engineers with little or no knowledge of surface chemistry are being called on to make use of the unique properties of surfactants.

1.2. THE ECONOMIC IMPORTANCE OF SURFACTANTS

The applications of surfactants in science and industry are legion, ranging from primary production processes such as the recovery and purification of raw materials in the mining and petroleum industries, to enhancing the quality of finished products such as paints, cosmetics, pharmaceuticals, and foods. Figure 1.1 illustrates a few of the major, high-impact areas of application for surfactants and other amphiphilic
materials. As the economic, ecological, and performance demands placed on product and process additives such as surfactants increase, it seems obvious that our need to understand the relationships between the chemical structures of those materials and their physical manifestations in particular circumstances becomes more important.

The properties and applications of surfactants are, as we shall see, determined by the balance between the lyophilic (“solvent-loving”) and lyophobic (“solvent-hating”) portions of the molecules. The desired properties will vary significantly for many of the applications noted in Figure 1.1. For that reason, such characteristics as solubility, surface tension reducing capability, critical micelle concentration (cmc), detergency power, wetting control, and foaming capacity may make a given surfactant perform well in some applications and less well in others. The “universal” surfactant that meets all the varied needs of surfactant applications has yet to emerge from the industrial or academic laboratory. The following chapters will

Figure 1.1. Some important, high-impact areas of surfactant applications.
provide more detail on the molecular structural features that determine the various functional characteristics of surfactants. For now, suffice to say that each application will have specific requirements that will determine a specific surfactant’s utility in a given system. Some of the fundamental characteristics that must be evaluated for a surfactant proposed for some specific applications are listed in Table 1.1.

The fast-paced, highly competitive nature of modern industrial developments often demands the fastest, most economical possible solution to a problem, consistent with the needs of the product. In the area of surfactant science and technology, it might often be the case that the fastest marginally acceptable solution could be replaced by a superior, possibly more economical, alternative if only the right minds and information could be brought together. Unfortunately, the world of surfactants and surface science historically has not received wide coverage in most academic training situations, and most workers have limited familiarity with the basic concepts and processes involved.

1.3. SOME TRADITIONAL AND NONTRADITIONAL APPLICATIONS OF SURFACTANTS

A comprehensive discussion of the myriad applications of surfactants in our daily activities is well beyond the scope of this work. Nevertheless, it is important to have a good concept of the impact, very often overlooked by those outside the field, of surfactants in our everyday lives—personally, professionally, socially, economically, and just about every other “-ly” word we can imagine. For that reason, the following notes will try to introduce some of those impact areas, without getting into too much detail for the moment.

1.3.1. Detergents and Cleaners

The primary traditional application for surfactants is their use as soaps and detergents for a wide variety of cleaning processes. As already noted, soaps have been
used in personal hygiene for well over 2000 years with little change in the basic chemistry of their production and use. New products with pleasant colors, odors, and deodorant and antiperspirant activity have crept into the market since the early twentieth century or so, but in the end, soap is still soap.

On the other hand, the synthetic detergents used in cleaning our clothes, dishes, houses, and so on are relative newcomers. "Whiter than white" and "squeaky clean" commercials notwithstanding, the purpose of detergents is to remove unwanted dirt, oils, and other pollutants, while not doing irreparable damage to the substrate. In the past, due primarily to the shortcomings of available surfactants, such cleaning usually involved energy-intensive treatments—very hot water and significant mechanical agitation. Modern surfactant and detergent formulations have made it possible for us to attain the same or better results with much lower wash temperatures and less mechanical energy consumption. Improved surfactants and detergent formulations have also resulted in less water use and more efficient biological degradation processes that help protect our environment. Even with lower wash temperatures and lower energy consumption, extensive studies have shown that equivalent or improved hygiene is maintained. It is only in instances where particularly dangerous pathogenic agents are present, as in hospital laundries, for example, that additional germicidal additives become necessary to obtain efficient cleaning results.

More and more detergents and cleaners are being produced using feedstocks from "natural" or renewable sources, mainly vegetable oils and animal fats. The emotional or sociological impact of the "natural" label aside for the moment, that trend is important for several more practical standpoints—local availability, more constant prices (in general), relative ease of processing, and, of course, flexibility of production. The naturalness of the materials also helps out in terms of the ultimate biodegradation of the products, of course, since the building blocks fit naturally into the biological chain of life.

1.3.2. Cosmetics and Personal Care Products

Cosmetics and personal care products make up a vast multi-billion-dollar market worldwide, a market that continues to grow as a result of improved overall living standards in areas such as Asia and Latin America and continuing cultural driving forces in the already developed economies. Traditionally, such products have been made primarily from fats and oils, which often are perceived to have the advantage of occurring naturally in the human body and therefore present fewer problems in terms of toxicity, allergenicity, and so on. That perception is, of course, totally false, as shown by the large number of quite nasty allergens and toxins that come from the most "natural" of sources. Nonetheless, natural surfactants and other amphiphilic materials have been used in cosmetics since their "invention" in ancient Egypt (or before). The formulators of the day had no idea why certain things worked; they were interested only in the end results.

It is probably safe to say that few, if any, cosmetic products known to women (or men, for that matter) are formulated without at least a small amount of a surfactant
or surface-active component. That includes not only the more or less obvious creams and emulsions but also such decorative products as lipstick; rouge; mascara; and hair dyes, tints, and rinses. An important aspect of such products is, of course, the interaction of the components of the cosmetic formulation with the human skin, membranes, and other tissues or organs with which it will come into contact during use. As mentioned above, merely because a product is “natural” or is derived from a natural source does not guarantee that it will not produce an adverse reaction in some, if not all, users. Just look at the poor peanut, a long-term staple for American kids and airline passengers for more than a century, banished from planes, schools, and other bastions of civilization because a few unlucky individuals have an allergic reaction to some component of that natural product. But that’s another story.

The possible adverse effects of surfactants in cosmetics and personal care products must, of course, be studied in depth for obvious safety reasons as well as for questions of corporate liability and image. Unfortunately, our understanding of the chemical reactions or interactions among surfactants, biological membranes, and other components and structures is not sufficiently advanced to allow the formulator to say with sufficient certainty what reaction an individual will have when in contact with a surfactant. In the end, we unfortunately still need the rabbit’s assistance.

1.3.3. Textiles and Fibers

Surfactants have historically played an important role in the textile-and-fibers industry. The dyeing of textiles is an obvious application of surfactants. The added surfactants serve to aid in the uniform dispersion of the dyes in the dying solution, the penetration of the dying solution into the fiber matrix, the proper deposition of the dyes on the fiber surface, and the proper “fixing” of the dye to that surface.

For natural fibers, the role of surfactants begins at the beginning—with the washing and preparation of the crude fiber in preparation for spinning. Once the crude material is ready for spinning, the use of surfactants as internal lubricants and static discharge agents allows the industry to produce yarns in extremely long and fine filaments that would be impossible to handle otherwise. Extremely fast modern spinning and weaving equipment requires that the fibers pass through the process without breaking or jamming, events that would produce very expensive production line stoppages. Sewing equipment that may work at more than 6000 stitches per minute requires that the fibers and needles pass in the night with a minimum of friction that could produce a significant amount of frictional heat and even burn the fibers. That interaction is controlled by the use of the proper surfactant and surfactant dosification.

Synthetic fibers also require surfactants at various steps in their evolution from monomeric organic chemicals to finished cloth. Depending on the type of polymer involved, the process may require surfactants beginning with the polymer synthesis, but certainly once the first extrusion and spinning processes begin. Even after the textile is “finished,” it is common to apply a final treatment with a surface-active material to define the final characteristics of the product. In woven polyester rugs,
for example, a final finish with an antistatic surfactant reduces or eliminates problems with static discharge (those shocking doorknobs in winter) and retards the adhesion of dirt to the fibers. The applications of fluorinated materials produces the stain repelling “Scotch Guard” effect by coating the fibers with a Teflonlike armor.

1.3.4. Leather and Furs

Surfactants are an important part of the manufacture of leather and furs, starting with the original untreated skin or hide and ending with the finished product. In leather tanning, for example, it is normal to treat the leather with a surfactant to produce a protective coating on the skin and hide fibers. This helps prevent the fibers from sticking together and keeps the fiber network flexible or supple while increasing the tensile strength of the finished leather product. Surfactants may also help the penetration of dyes and other components into the fiber network thereby improving the efficiency of various stages of the tanning process, saving time, energy, and materials while helping to guarantee a higher-quality, more uniform finished product.

The final surface finish of leather goods is now commonly applied in the form of lacquerlike polymer coatings that can be applied as emulsions and suspensions, using suitable surfactants, of course. Similar applications are found in the fur industry.

1.3.5. Paints, Lacquers, and Other Coating Products

It is probably not surprising to find that surfactants are required in many capacities in the production of paints and lacquers, and in related coating systems. In all paints that carry pigment loads, it is necessary to prepare a uniform dispersion that has reasonable stability to flocculation and coalescence. (See the glossary in Section 1.8 if those terms have slipped your mind.) In addition, the preparation of mineral pigments involves the process of grinding the solid material down to the desired particle size, which is an energy-intensive process. In general, it is found that a smaller, more uniform particle size results in a higher covering power for the same weight load of pigment, that is, a more efficient use of material and consequently a reduction in cost—always a nice effect in commerce.

The grinding process is helped by reducing the surface energy of the solid pigment, an effect achieved by the addition of surfactants. Since pigment solids are far from smooth surfaces at the molecular level, the raw material will have small cracks and holes that serve as initiation points for the rupture of the structure. In the presence of the proper surfactant, the molecules penetrate into the cracks and crevices, adsorb onto the solid surface, and significantly reduce the surface energy of newly exposed solid, facilitating the continued breaking of the large particles into smaller units. The adsorbed surfactant molecules also create a barrierlike coating that helps prevent the small particles from adhering or agglomerating. It is estimated that the use of surfactants in the grinding process can save up to 75% of the energy needed to achieve the same result without added surfactant.
Once the pigment is properly ground, it must be mixed into the basic liquid carrier and maintained stable or easily redispersible for an extended period of time, much against the natural driving force of thermodynamics. For the dispersion of the pigment in the final coating formulation, it may be necessary to add additional surfactant of the same or another class. In organic coating systems, the surfactant may in fact be a polymeric system that doubles as the final dried binder for the pigment. On the other hand, there are available low-molecular-weight surfactants specifically designed to act in organic solvents.

In aqueous or latex paints, the surfactant is important not only in the pigment grinding process but also in the preparation of the latex polymer itself. The chemistry of emulsion polymerization (i.e., latex formation) is a complex and interesting phenomenon and cannot be treated here. Very few emulsion polymers are produced without the addition of surfactants, and most of those so prepared are interesting laboratory novelties that never see the light of commercial exposure. In addition to surfactants for pigment grinding and dispersion and latex preparation, they are also important in the control of the wetting and leveling characteristics of the applied paint.

In painting applications that use lacquers such as the automobile industry, application and drying times are important. In such situations, wetting and leveling are also important. In powdered lacquers, the presence of the proper surfactants produces a net electrical charge on the surface of the particles, which allows them to be applied quickly and evenly by electrophoretic processes.

A potential drawback to rapid paint or lacquer application is that such speed can facilitate the introduction of air into the material resulting in foam formation at the time and point of application. If foam is produced, the drying bubbles on the painted surface will produce indentations and perhaps even bare spots that will significantly degrade the aesthetic and protective properties of the coating. To help prevent such foaming it is sometimes useful to add surfactants that also serve as antifoaming agents. Although it is common to relate surfactants with increased foam—as in beer, shaving cream, whipped toppings, and firefighting foams—we will see in Chapter 8 that surfactants can be either foam stabilizers or foam breakers, depending on the chemical structure and/or conditions of use.

### 1.3.6. Paper and Cellulose Products

Surfactants play several important roles in the papermaking industry. Several components of paper such as pigments for producing white or colored paper and sizing agents, often emulsion polymers that bind the cellulose fibers in the finished product and incorporate strength and dimensional stability, require surfactants in their preparation. In addition, the water-absorbing capacity of paper is often controlled by the addition of the proper surfactants.

Surfactants are also important in the process of recycling paper. A major step in the process is the removal of the ink and pigments present (deinking). That process is what is termed a flotation process (see Section 1.3.7), in which a surfactant is added to an aqueous slurry of old paper. The surfactant is chosen so that it will
adsorb on the surfaces of pigment particle and ink droplets, causing them to become very hydrophobic. Air is then bubbled through the slurry. As the bubbles rise through the system, they become preferentially attached to the hydrophobic pigment and ink particles, acting like lifejackets and causing the particles to rise to the surface. At the surface they are skimmed off and separated from the cellulose slurry.

1.3.7. Mining and Ore Flotation

As just mentioned, the addition of the proper surfactant to a dispersion can produce a situation in which the solid particles, having a specific gravity much greater that that of water, can be made to float to the top and be easily (relatively speaking) separated from the aqueous phase. In the deinking mentioned above, there is no particular interest in being selective with respect to what is removed. It is essentially an “all out” proposition. In the mining industry the situation is quite different.

The flotation process has been important in mining for much longer than has deinking. In many instances, the desired mineral is present in small amounts that would be difficult or impossible to isolate and process while still “mixed” with the bulk of the mined rock. In that industry, therefore, it is necessary to have a more selective flotation process in which the desired mineral can be separated from the bulk of the ore in a continuous and relatively inexpensive process. Because different minerals tend to have slightly different surface properties, especially with regard to electrical charge characteristics, it is possible (with luck and perseverance) to design or formulate a surfactant system that will preferentially “float” a specific class of mineral while having little effect on other materials present. The selective surfactant or “collector” formulation allows the desired mineral to be skimmed from the top of the foaming slurry and thereby concentrated. The unwanted material can then be further processed or disposed of as slag.

While the theory of the adsorption of surfactants onto solid surfaces is highly developed and well understood in ideal systems, the reality of the universe is that in such complex multicomponent systems as mining ores, theory soon runs out of steam and success ultimately depends on hands-on laboratory and field trials, intuition, and art (or perhaps black magic).

Surfactants are also becoming more important in the coal mining industry. Aside from flotation processes, they are also employed as binders for the suppression of coal dust, and as dispersal aids and antifreezes for coal slurries that are pumped through pipelines.

1.3.8. Metal-Processing Industries

Surfactants are as important to the metal processing as to the mining industry. In order to perform as needed, metal surfaces must be cleaned and freed from deposits of oxides, oils, and other contaminants. Welding, painting, and other machining and surface treatments require a well-prepared surface. Even before that stage of