New Horizons for Surfactant Science in Chemical Engineering

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Introduction

Applications of surfactant science (such as in household products, emulsion polymerization, and coating processes) and the underlying fundamental concepts (e.g., interfacial activity, solubilization, spreading, and wetting) have long been cornerstones of the chemical engineering discipline. While these applications and phenomena remain important, as chemical engineering diversifies into fields such as biotechnology, biomedical engineering, environmental engineering, and microelectronics processing, surfactant science is also changing its focus and significance in the hands of the chemical engineer.

The importance of surfactant science in modern chemical engineering is reflected in the education of the chemical engineer. For example, a technical presentation less than 15 years ago on surfactant science typically began with an answer to the question: "What is a surfactant?" This question is now largely obsolete, because the incorporation of courses and concepts on surfactant science into the modern undergraduate curriculum has undoubtedly increased the awareness of this field by chemical engineers. Indeed, surfactant science, which was largely housed in chemistry departments several decades ago, is now solidly headquartered in chemical engineering (at least, in the U.S.).

While the consolidation of research in surfactant science within chemical engineering has led to substantial progress in the development of a quantitative understanding of some properties of surfactant systems, and also to some innovative applications of surfactants, advances in the *chemistry* of surfactants do not seem to have progressed to the same extent under our stewardship. This fact defines a substantial opportunity that should be pursued by chemical engineers, because many of the emerging fields of chemical engineering appear ripe to benefit from the use of chemically functional surfactants.

The economics of past applications of surfactants in low-value, high-volume products (e.g., plastic films prepared by using continuous coating processes or latex particles prepared by emulsion polymerization for use in paints) substantially limits the range of chemistries that can be considered for use in these types of products. For this reason, chemical engineers have largely directed their past efforts toward understanding the properties and processing of a relatively narrow range of surfactant chemistries. The future, I suspect, will be different because a number of the emerging areas of interest to the chemical engineer lead to distinctly different classes of products, namely low-volume and high-value products. This future defines an opportunity to design, engineer, and apply surfactants that possess relatively exotic and varied chemistries. Novel chemistries offer the opportunity to engineer surfactants with specific chemical, biological, electrochemical and photochemical properties (Texter, 2001). While there appears to be no fundamental reason that the design, synthesis, and study of these types of surfactants could not have been pursued a decade or more ago, the technological opportunity did not exist previously as it obviously does now.

One of the main objectives of this article is to describe recent progress in surfactant science in a manner that defines areas that are suited for further study or technological exploitation. For the reasons already stated, a particular focus will be directed towards recent studies of chemically functional surfactants. This focus does not, however, mean that everything is understood in surfactant systems possessing relatively simple chemistries. In fact, as will be shown below, some extensively studied, conventional surfactants are still revealing unexpected properties and uses. This statement is particularly true for systems containing high concentrations of surfactants, multiple types of surfactants, or mixtures of surfactants and macromolecules. Below, I first address topics involving concentrated surfactants, polymer-surfactants mixtures, and macromolecular surfactants. The remainder of the article is devoted to chemically functional surfactants.

Concentrated Surfactant Systems and Drug Delivery

Early ideas regarding surfactants and drug delivery revolved around the use of micelles and vesicles (particularly, the notion of "encapsulation" within the aqueous interior of vesicles). The past decade, however, has seen thoughts turning also to the potential uses of concentrated surfactant phases—so called lyotropic liquid crystalline phases—including complex phases which go by names such as "hexagonal", "cubic", "intermediate", and "sponge" phases (Hyde et al., 1997). Whereas the microstructure of dilute surfactants systems (such as globular micelles) can be largely understood in terms of local constraints on the system (electrostatic interactions, chain packing, etc.), the structure of concentrated surfactant phases reflects a balance of local and global factors in the system. For this reason, understanding the microstructure of concentrated surfactant systems represents a substantial challenge relative to dilute ones. Although many fundamental questions remain regarding the identity and properties of concentrated phases, it is clear that differences in microstructures may translate into usefully different drug release characteristics. For example, the reversed hexagonal phase has been reported to be preferable over cubic phases for use in dental gels that release antimicrobial agents (Norling et al., 1992). Some commercial products are based on the reversed hexagonal phase, and it appears likely that concentrated surfactant phases will increasingly find application as materials to control the temporal delivery of active ingredients, such as drugs, pesticides and fragrances.

Mixtures of Polymers and Surfactants

In the past decade a second area of focus has been the engineering of interactions of surfactants and polymers in solution. Particular emphasis has been placed on understanding the balance of intermolecular interactions that govern microstructure and rheological properties. While the general phenomenon of polymer-surfactant complex formation is not new, the properties of these systems can now be tuned with useful predictability. Mixtures of surfactants and polymers modified with hydrophobic domains can serve to illustrate recent accomplishments (Nilsson et al., 1998).

Consider a series of such systems containing a fixed concentration of polymer (semi-dilute regime) and increasing concentrations of surfactant. At low concentrations of surfactant, the rheological properties of the mixtures are comparable to that of the polymer alone. At intermediate concentrations of surfactants, however, individual micelles of surfactant host hydrophobic domains from more than one polymer molecule. The micelles in these systems thus serve as links in a dynamic network of polymer and surfactant. The presence of the network is accompanied, for example, by a dramatic rise in viscosity. What happens next (with the addition of more surfactant) is less obvious. One possibility is that the additional surfactant leads to the formation of more micelles. If this occurs, the likelihood of a given micelle acting as host to hydrophobic domains from separate polymers will decrease. The transient network dissolves, and the viscosity plummets. On the other hand, if the surfactant system is designed such that the addition of surfactant leads to the growth of the existing micelles rather than to the formation of an additional number of micelles, the addition of surfactant can further increase the viscosity of the system. Whether or not the addition of surfactant leads to the nucleation of additional micelles or to the growth of existing micelles can be engineered with relatively high levels of predictability through the choice of the head groups of the surfactants (or addition of salt). Recent studies have demonstrated these effects using mixtures of anionic and cationic surfactants (Nilsson et al., 1998). This type of engineering of surfactant-polymer systems may prove to be useful, for example, in paint formulations where polymers are added to modify rheological properties and surfactants are present to stabilize latex particles and fillers.

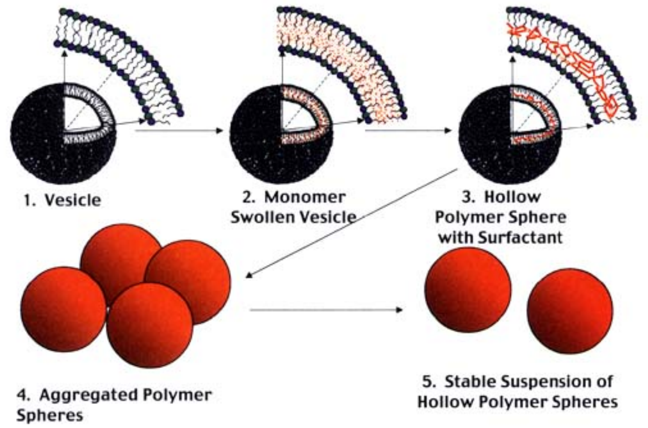

Figure 1. Synthesis of polymeric nanospheres using surfactant-based templates as vesicles.
Courtesy of Craig McKelvey and Eric Kaler, University of Delaware.

A second class of polymer-surfactant interactions that is receiving close attention from the surfactant science community is that of interactions of polyelectrolytes with ionic surfactants, particularly where the charges of the surfactant and polyelectrolytes are opposite in sign. One widely studied and important case is DNA and cationic surfactants (Safinya, 2001). Here, the addition of surfactant can lead to compaction of the DNA such that it facilitates transport of DNA across biological membranes and into cells. This area of research and technology is driven, in part, by the goal of replacing viruses as vehicles for the delivery of DNA when transfecting cells.

Surfactant-Based Templates for Materials Synthesis

A variety of equilibrium microstructures can be formed from surfactants, particularly at elevated concentrations. These microstructures are held together by weak intermolecular interactions. The fact that they are equilibrium structures has obvious appeal for processing (they form spontaneously), but it also means that the structures are susceptible to disruption by modest changes in solution conditions (e.g., temperature or by the introduction of a new component into the system). The microstructures formed in surfactant systems are also transient, with typical lifetimes ranging from milliseconds to hours.

These observations have driven a vigorous activity in recent years aimed at either preservation or replication of the complex microstructures formed by surfactants. Preservation, it has turned out, has presented many challenges. Initial attempts to incorporate polymerizable groups into surfactant structures were plagued by unwanted transformations of microstructure during polymerization. The process of polymerization changes, in general, the interactions between the surfactants that define the microstructure. The judicious choice of the location of the polymerizable group, however, appears to have addressed this issue in some surfactant systems, and functional materials with lamellar, inverted hexagonal, and bicontinuous cubic phases are now being synthesized by this approach (Reppy et al., 2001). Potential applications include catalysis, separations, and controlled release.

Whereas the approach to preservation described above requires the synthesis of new surfactants that incorporate polymerizable groups, it is interesting to note that a surprisingly simple alternative approach has also been demonstrated (McKelvey et al., 2000). This approach relies on impregnation of surfactant microstructure with monomer and subsequent polymerization (Figure 1). Although the rapid dynamics (short lifetimes of assemblies) of many surfactant systems would appear likely to undermine this approach, in mixed surfactant systems containing anionic and cationic surfactants hollow polymeric microspheres have been templated from vesicle-shaped surfactant assemblies. These hollow microspheres were synthesized using a mixture of commonly available surfactants and monomers. The result is a noteworthy one, because it suggests that it may be possible, in some cases, to preserve surfactant microstructures without resorting to custom-synthesized surfactants. Microspheres synthesized by this approach may find applications in encapsulation and controlled release.

Finally, we note the large and ongoing activity based on surfactant-templated synthesis of inorganic phases. While this topic has been covered by a number of recent perspectives in this journal (Texter and Tirrell, 2001; Ying, 2000), it is worthwhile to point out that much remains to be understood about the mechanisms of "templating" of inorganic phases by surfactants.

Macromolecular Surfactants

Polymer and surfactant science were largely distinct fields of study only a decade or two ago. The past ten years, however, has seen intense interest in the properties of aqueous and mixed solvent systems containing macromolecular surfactants. These systems differ from their low molecular-weight relatives in a number of interesting ways. For example, the cores of aggregates formed by macromolecular surfactants can vary enormously in their dynamic properties. Macromolecular surfactants containing polystyrene can form aggregates that possess glassy cores (Zhang and Eisenberg, 1996). These cores prevent the exchange of monomers between aggregates, which can be viewed as particles rather than micelles for this reason. In contrast, micelles with cores formed largely from polypropylene oxide (and water) are highly mobile, and the dynamics of these systems are not dissimilar from low molecular weight surfactants (other than being a bit slower; see Alexandridis and Hatton, 1995).

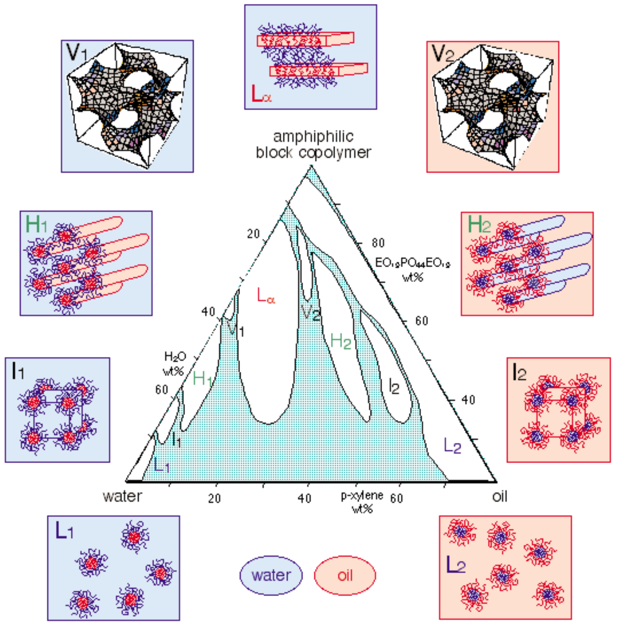

Figure 2. **Ternary phase diagram of system containing macromolecular surfactant, water, and oil.**
Courtesy of Paschalis Alexandridis, University of Buffalo

A second broad difference between molecular and macromolecular surfactants lies in the complexity of their phase diagrams (Alexandridis et al., 1998). The hydrophilic and hydrophobic domains of molecular surfactants are strongly segregated within their assemblies. In contrast, the level of segregation of the blocks of macromolecular surfactants is often weak and readily changed by swelling with solvents. The effects of solvent penetration, when combined with the long-ranged interactions of polymers, gives rise to complex liquid crystalline phases over a wide range of concentrations (Figure 2). These facts also make predicting the properties of systems containing macromolecular surfactants particularly challenging. Although the science of macromolecular surfactants with well-defined structures has advanced rapidly over the past few years, the technological applications have been relatively few to date, presumably because the cost of synthesis doesn't yet justify the benefits. However, macromolecular surfactants with less well-defined architectures are being explored and may find technological applications in the short term.

Functional Surfactants with Tailored Chemical Structures

See Figure 3. As described in the introduction, the low selling price of many surfactant-based products will always restrict the range of surfactants that can be considered as plausible constituents. However, emerging uses of surfactants in applications such as biotechnology and microscale processing (e.g., microscale separations) are likely to permit inclusion of a more diverse set of surfactant chemistries. Such chemistries offer the possibility of higher levels of physical and biological functionality. For example, chemically tailored surfactants make possible both spatial and temporal control of surfactant-based systems using a variety of independently controlled variables, including electrical potential and illumination.

Chemically-Reactive Surfactants

A first example of a surfactant that is chemically tailored is one that incorporates a chemically reactive group (e.g., acetal, siloxane, azo, and disulfide) and is triggered to undergo a transformation upon exposure to a particular chemical environment (Jong and Abbott, 2000). The oldest class of surfactants that fall into this category are the so-called chemodegradable surfactants. These surface-active compounds can undergo specific chemical reactions and thereby lose their surface activity. These surfactants have attracted interest in the recent past for several reasons. For example, the capability to transform water-soluble molecules from surface-active states to surface-inactive states can be used to break emulsions or foams. Chemodegradable surfactants are also useful as emulsifiers in emulsion polymerizations, because their subsequent conversion to fragments can be exploited to eliminate the presence of charged surfactant head groups at surfaces of latex particles. The presence of charged groups at the surfaces of the latex particles reduces the water resistance of resultant polymer films. Finally, chemodegradable surfactants are potentially useful in procedures such as those used for the isolation, purification, and reconstitution of proteins in lipid environments. They can be used to solubilize membrane proteins, but can then be transformed into fragments that are readily displaced by natural phospholipids. As illustrated by the above examples, past interest in chemodegradable surfactants has been largely driven by the aim of making the surfactant "invisible" by reaction. A recent and promising area of research, in contrast, now focuses on the *in situ* synthesis of surfactants by a variety of chemical transformations. Demonstrations of spontaneous emulsification of oil and aqueous phases that are catalyzed by enzymes, or driven by the complexation of dications with organic receptors, have been recently reported (Nishimi and Miller, 2001).

Surfactants with Biological Function

Whereas the polar head groups of many surfactants studied in the past possess an ionic moiety such as a sulfate group, or a nonionic moiety such as an oligomer of ethylene glycol, more recent studies illustrate the opportunities that arise from the design of surfactants with head groups that, in addition to providing a hydrophilic domain, perform a biomimetic function. For example, peptide-based surfactants have been exploited to perform chiral separations (Billiot et al., 2001). These surfactants were evaluated for their enantioselectivity by using them as psuedo-stationary phases in electrokinetic capillary chromatography. A second example can be found in peptide-based amphiphiles that are under study as the basis of biomimetic membrane surfaces. These surfaces are designed to regulate the interactions of receptors found on cells (integrins) with surfaces (Pakalns et al., 1999). Knowledge gained from the study of these materials suggests approaches for modification of biomedical implant surfaces that possess tailored interactions with cells. Other types of peptide-based amphiphiles are also under investigation, where one domain of the peptide confers on the molecule an ability to permeate a biological membrane, whereas the second domain performs a function such as bind to a protein or protein aggregate to modify its surface properties.

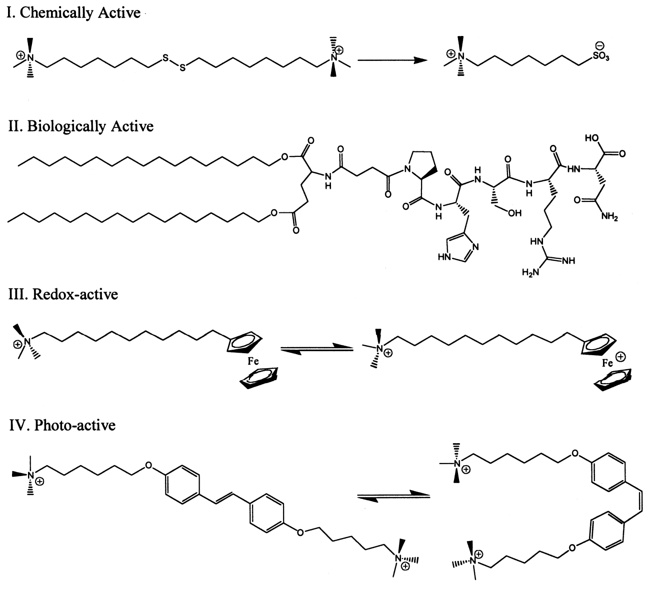

Figure 3. Examples of functional surfactants with tailored chemical structures

Redox-Active Surfactants

A third class of chemically-tailored surfactants are those that incorporate redox-active species (such as ferrocene), and thus can be tuned by using electrochemical methods. These types of surfactants have recently been demonstrated to permit both spatial and temporal control over the interfacial properties of aqueous solutions (Gallardo et al., 1999). Large (>20 mN/m) and reversible changes in the surface tensions of aqueous solutions have been demonstrated. This capability has been exploited to actively control the motion and positions of aqueous and organic liquids on millimeter and smaller scales. By using electrochemical methods to generate surface-active species at one electrode, and by using a second electrode to consume these surface-active species, the magnitude and direction of spatial gradients in surface tension can be controlled between electrodes. This effect can be used to guide droplets of organic liquids through simple fluidic networks. Electrochemical control of the position of surface-active species within aqueous films of liquid supported on energetically homogeneous surfaces has also been used to direct these films into periodic arrays of droplets having deterministic shapes and sizes (Gallardo et al., 1999) (see front cover). These results suggest new principles that might be exploited for active control of microfluidic or decorative coating processes.

A second area of research addresses the potential use of redox-active surfactants in microscale separations (Rosslee and Abbott, 2001). This research makes use of electrochemical control of the oxidation state of redox-active surfactants to achieve reversible control over the assembly/disassembly of micelles in solution. Closed-loop separations processes that exploit selective solubilization and release of organics into micellar solutions of redox-active surfactants have been demonstrated.

The separations processes consist of two essential steps. First, micelles are assembled at a microelectrode submerged in a solution of redox active surfactant. The electrode is located near a mixture of compounds that are partially solubilized into the micelles. Second, these solubilizate-laden micelles are disassembled at a second electrode, thereby releasing the solubilized material from the solution and capturing it on the electrode. By repeating the process of solubilization and deposition several times, high levels of selectivity can be achieved. It also appears feasible to perform these electrochemical separations on very small scales (Rosslee and Abbott, 2001). Such separations processes might be integrated into microreactor systems used for synthesis or analysis.

Photo-Active Surfactants

The final class of chemically-tailored surfactants that is mentioned here is a surfactant that changes its structure upon exposure to light. This class is illustrated by a water-soluble surfactant that hosts the azobenzene moiety (Shin and Abbott, 1999). Azobenzene is a widely studied photo-active group that can assume one of two isomeric states (*cis* or *trans*), depending on the wavelength of light used to illuminate the compound. Although a number of past studies have reported water-soluble and water-insoluble amphiphiles containing azobenzene, past studies based on water-soluble surfactants have been largely unsuccessful in driving useful changes in surface tension upon illumination with light. Recently, a surfactant system containing a mixture of a cationic surfactant that hosts azobenzene and an anionic surfactant was demonstrated to permit large changes in the dynamic surface tension of aqueous solutions upon illumination with UV light (Shin and Abbott, 1999). This capability was used to control the release of selected droplets of liquid from an array of capillaries. Because light is relatively easy to pattern and direct to spatially localized regions of a solution on millimeter and smaller scales, these surfactants appear to be particularly promising ones for microscale applications. One constraint on the use of these surfactants in large volumes (long optical path lengths) is their high specific absorbances (in the UV) which lead to limited depths of penetration of light into their solutions.

Other Opportunities and Challenges

Synthetic detergents were among the first class of synthetic organic chemicals to create an environmental problem (Rittmann and McCarty, 2000). Alkylbenzene sulfonate surfactants synthesized in Europe during and after the Second World War, while not toxic to humans, did not readily degrade in the environment. Their accumulation lead to pollution of some groundwater supplies. Although this problem was addressed by engineering, the extent of branching of the hydrocarbon tail (leading to so-called linear alkylbenzene sulfonate surfactants that are used today), our understanding of the life cycle of surfactants (and other materials) is still incomplete. This is evidenced by the recent focus on perfluorocarbon-containing surfactants. Engineering the complete life cycle of a surfactant—from its synthesis from renewable resources through to the engineering of its rapid degradation—remains a substantial challenge. Surfactants belonging to the class of alkylglucosides, for example, have been investigated recently for these types of reasons (Ryan and Kaler, 2001).

A second broad challenge, which is both fundamental and technologically important, relates to the development of an understanding of the dynamic properties of surfactant systems. Although there are very few instances where surfactants are used in equilibrium, our general understanding of the origin of the dynamic properties of surfactants is remarkably limited. The problem appears to be experimental and theoretical, and can be illustrated by considering the seemingly simple phenomenon of the time-dependent adsorption or desorption of surfactants from the surface of water. Experimental measurements of kinetic constants vary by many orders of magnitude (for the same system) and no theoretical methodology exists to relate the molecular structure of a surfactant to its kinetic behavior at the surface of an aqueous solution. A better understanding of surfactant dynamics will likely lead to new approaches for the engineering of surfactant-based properties, such as those that emphasize the use of dissipative structures rather than equilibrium ones. Here, it also appears likely that chemically functional surfactants—particularly surfactants that can be driven reversibly between states that differ in structure and properties on time-scales that are short compared to the characteristic relaxation times of solutions—may offer a powerful tool for fundamental studies.

Concluding Remarks

The main messages are three-fold. First, surfactant science (and, more broadly, colloid and interfacial phenomena) is playing an important role in a substantial number of the technological fields into which chemical engineering is now diversifying (e.g., life science-based technologies, microelectronics, and micrometer-scale and smaller chemical technologies). For this reason, I believe that surfactant science is going to become more important to the future of chemical engineering. We should therefore continue to integrate modern courses (i.e., with relevant examples) on surfactant and interfacial phenomena into the standard education of the chemical engineer. Second, the time is ripe for the chemical engineer to direct attention to the design and engineering of chemically functional surfactants. These types of surfactants offer substantial opportunities to tailor the properties of surfactant systems when processing/preparing low-volume, high-value products by performing functions that go beyond the passive reduction of surface or interfacial tension. Novel chemistries offer the opportunity to engineer surfactants with specific chemical, biological, electrochemical and photochemical functions. These surfactants can be prepared using routine methods of organic synthesis that are well within reach of the chemical engineer. Third, chemical engineers should also keep doing what they have doing in surfactant science for the past 20 years. Past contributions of U.S. chemical engineers to fundamental and quantitative studies of surfactant-based systems (in recent years, for example, focusing on concentrated surfactant systems, microemulsions, and systems containing polymers and surfactants) are admirable and distinct from accomplishments in other parts of the world where surfactant science is typically housed in departments of chemistry, applied mathematics, or physics. Chemical engineers also appear well-positioned to pursue future investigations that address some of the unresolved issues in surfactant science, such as understanding the molecular origins of dynamic properties of surfactant-based systems.

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