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2 Surfactants and their applications

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Surfactants form a unique class of chemical compounds. This review provides an introduction to the nature and physical properties of surfactants, emphasizing their ability to radically alter surface and interfacial properties and to self-associate and solubilize themselves in micelles. These properties provide the means to apply surfactants in wettability modification, detergency, and the displacement of liquid phases through porous media on one hand, and to stabilize dispersions (including foams, froths and emulsions), or to destabilize dispersions (again including foams and emulsions) on the other hand. These in turn lead to a vast array of practical application areas which are illustrated in terms of mineral and petroleum processing, biological systems, health and personal care products, foods, and crop protection.

1 Introduction

The widespread importance of surfactants in practical applications, and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject. Good starting points for further basic information are classic books like those of Rosen,¹ Myers,² and Mittal.^{3,4} There are many other books on surfactants^{5–18} including Karsa's *Industrial Applications of Surfactants* series^{19–22} and the 109 volume *Surfactant Science Series*.²³ There are also glossaries and dictionaries covering terminology in surfactant science and technology.^{24,25} Most good colloid chemistry texts contain introductory chapters on surfactants; good starting points are references 26–29. For more detailed treatment of advances in specific surfactant-related areas the reader is referred to some of the chapters available in specialist books.^{30–35} For example, four recent books describe the principles and occurrences of surfactants, emulsions, foams, and suspensions in the petroleum industry.^{36–39} The most comprehensive source for surfactant information on the internet is probably Huibers' *The Surfactants Virtual Library*, which contains over 1000 links to surfactant and detergent related web sites.⁴⁰

The surfactant industry is dominated by several types: alkylbenzene sulfonates, alcohol ethoxylates, sulfates and ethersulfates.⁴¹ These are the major components of laundry detergents, household, and personal care products and account for over half of all use of surfactants. Interest in increasing performance in these areas has also led to research into mixed surfactant systems. Other commercial interests have also influenced the developments in surfactant science. For example in the 1970s, during the oil crisis, new methods of enhanced oil recovery, such as microemulsions, were heavily investigated. Scientific curiosity has also driven surfactant research into areas such as organization of surfactant molecules into interesting shapes and structures, all with unique properties.⁴² Surfactants have even been the subject of investigation into the origins of life, meteorites containing lipid-like compounds have been found to assemble into boundary membranes and may be an interstellar prebiotic earth source of cell-membrane material.⁴³

Over the past ten years, new surfactant molecules have been appearing at a relatively rapid pace. This growth in surfactant synthesis has, not surprisingly, paralleled the emphasis on increasing the basic performance of surfactant formulations and the provision of new surfactant technologies to a diverse range of disciplines. Although surfactant science is now a reasonably mature discipline, there is still room for new molecules designed for specific purposes and new applications (such as nanoparticle synthesis and more diverse and environmentally friendly consumer products). These new materials have spurred on the quest for improved molecular models, computer simulations, and improved structure–activity relationships. New functionalized surfactants depend critically on the nature and placement of additional functional groups. Slight modifications of the molecular structure with respect to conventional surfactants lead to a rich morphology of structures that are being explored by increasingly more sophisticated techniques and, in turn, enhancing our understanding of their properties at a molecular level. For some examples see references 44–47.

One of the original and predominant reasons for the ubiquitous deployment of surfactants is their remarkable ability to influence the properties of surfaces and interfaces, and to thereby have an impact on industrial processes and products, as will be discussed below. The applications of surfactants in industry area are quite diverse and have a great practical importance. Surfactants may be applied to advantage in the production and processing of foods, agrochemicals, pharmaceuticals, personal care and laundry products, petroleum (see Table 1), mineral ores, fuel additives and lubricants, paints, coatings and adhesives, and in photographic films. They can also be found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications.

This review provides examples of surfactants in action. It begins with a basic overview of the nature of surfactant molecules, their self-assembly in solutions, and their properties at interfaces. We then examine a range of surfactant applications from detergency to the stabilization of colloidal dispersions.

Table 1 Some examples of surfactant applications in the petroleum industry

Gas/liquid systems	Producing oil well and well-head foams Oil flotation process froth Distillation and fractionation tower foams Fuel oil and jet fuel tank (truck) foams Foam drilling fluid Foam fracturing fluid Foam acidizing fluid Blocking and diverting foams Gas-mobility control foams
Liquid/liquid systems	Emulsion drilling fluids Enhanced oil recovery in situ emulsions Oil sand flotation process slurry Oil sand flotation process froths Well-head emulsions Heavy oil pipeline emulsion Fuel oil emulsions Asphalt emulsion Oil spill emulsions Tanker bilge emulsions
Liquid/solid systems	Reservoir wettability modifiers Reservoir fines stabilizers Tank/vessel sludge dispersants Drilling mud dispersants

2 Surfactants and their solutions

Definition and classification of surfactants

Some compounds, like short-chain fatty acids, are amphiphilic or amphipathic, *i.e.*, they have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (*i.e.*, they lower the surface or interfacial tension of the medium in which they are dissolved). In some usage surfactants are defined as molecules capable of associating to form micelles. These compounds are termed surfactants, amphiphiles, surface-active agents, tensides, or, in the very old literature, paraffin-chain salts. The most commonly used term, surfactant, was originally registered as a trademark for selected surface-active products⁴⁸ and later released to the public domain.⁴⁹ Soaps (fatty acid salts containing at least eight carbon atoms) are surfactants. Detergents are surfactants, or surfactant mixtures, whose solutions have cleaning properties. That is, detergents alter interfacial properties so as to promote removal of a phase from solid surfaces.

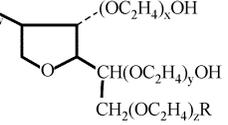
The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated *via* dipole–dipole or ion–dipole interactions.

In fact, it is the nature of the polar head group which is used to divide surfactants into different categories, as illustrated in Table 2. In-depth discussions of surfactant structure and chemistry can be found in references 1, 2, 19, 50 and 51. Compared with the commonly encountered hydrocarbon-based surfactants, substituting fluorocarbon into the structure creates a molecule that is resistant to oxidation, and, because of the smaller size of fluorine over hydrogen atoms, the surfactants are more rigid in structure thus having a strong surface tension lowering action, water and oil repellency, thermal resistance, chemical resistance and lubricating ability.⁵² An application of hybrid fluoride–hydrogen containing surfactants is in water-based paints. Adding silicone into fluorine-containing surfactants creates quality lubricants, good defoamers, and even molecules with a high anti-HIV activity.⁵² There is also an entire class of surfactants known as microbial, or biosurfactants, which have some very interesting and complicated structures, although being expensive to produce compared to chemically synthesized surfactants.^{53,54}

Despite the significant use of surfactants in many industries, it is somewhat surprising that the bulk of surfactant applications has been, until very recently, the domain of single-headed, single-tailed surfactants. Performance limitations of conventional sulfate and sulfonate surfactants, related to their hard water tolerance or their cold-water solubility, initiated some early interest in alternate surfactant structures. In the mid-1950s, Evans⁵⁵ began investigating sulfate surfactants in which the point of substitution of the sulfate surfactants was varied and the micellar properties were correlated to the point of substitution of the sulfate group. This was one of the earliest examples of the establishment of a structure–performance relationship in a family of surfactants. Stirton *et al.*^{56,57} outlined the synthesis of one of the first ‘tunable’ surfactants, the disodium α -sulfocarboxylates. These surfactants were found to have excellent properties in terms of hard water tolerance, foam stability, and detergency when compared to their single headed counterparts. They suffered from the drawback that they are irritating to the skin, a problem that is faced with most high critical micelle concentration (cmc) surfactants.⁵⁸ Interest in developing new amphiphiles waned as detergent formulators found they could enhance the performance of their commercial products by the judicious selection of additives. By the early 1980s however, interest in surfactants derived from non-linear alkylbenzene (non-LAB) sources began to increase as it became clear that consumer demand for “newer and better” detergents was outpacing the ability of detergent manufacturers to reformulate their products when the main component was still the conventional single-head, single-tail amphiphile. Hence the synthesis of novel surfactants has emerged as a viable and important topic in the literature. In modern surfactant papers it is not unusual to observe the investigation of the properties of vitamin E-based surfactants,⁵⁹ sugar-based surfactants,⁶⁰ and many others.⁶¹

One of the most exciting developments in the field of surfactant chemistry is the emergence of the Gemini surfactants in the late 1980s and early 1990s. The term Gemini surfactant, coined by Menger,⁶² has become accepted in the surfactant literature for describing dimeric surfactants, that is, surfactant molecules that have two hydrophilic (chiefly ionic) groups and two tails per surfactant molecule.^{62,63} These twin parts of the surfactants are linked by a spacer group of varying length (most commonly a methylene spacer or an oxyethylene spacer). A block diagram of a typical Gemini surfactant is shown in Fig. 1.

Table 2 Surfactant classifications

Class	Examples	Structures
Anionic	Na stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$
	Na dodecyl sulfate	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$
	Na dodecyl benzene sulfonate	$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3^-\text{Na}^+$
Cationic	Laurylamine hydrochloride	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+\text{Cl}^-$
	Trimethyl dodecylammonium chloride	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
	Cetyl trimethylammonium bromide	$\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
Non-ionic	Polyoxyethylene alcohol	$\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$
	Alkylphenol ethoxylate	$\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n\text{OH}$
	Polysorbate 80	$\text{HO}(\text{C}_2\text{H}_4\text{O})_x$
	$w + x + y + z = 20$ $\text{R} = (\text{C}_{17}\text{H}_{33})\text{COO}$	
Zwitterionic	Propylene oxide-modified polymethylsiloxane (EO = ethyleneoxy, PO = propyleneoxy)	$(\text{CH}_3)_3\text{SiO}((\text{CH}_3)_2\text{SiO})_x(\text{CH}_3\text{SiO})_y\text{Si}(\text{CH}_3)_3$ 
	Dodecyl betaine Lauramidopropyl betaine Cocoamido-2-hydroxypropyl sulfobetaine	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ $\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ $\text{C}_n\text{H}_{2n+1}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3^-$

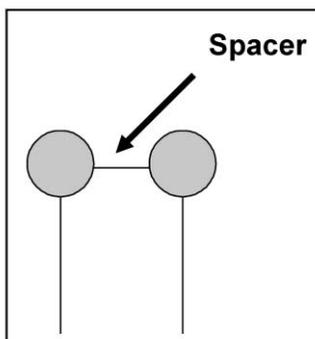


Fig. 1 Illustration of a Gemini surfactant.

A number of reviews cover the properties of cationic and anionic Gemini surfactants.^{64–66} Gemini surfactants possess a number of superior properties when compared to conventional single-headed, single-tailed surfactants, the Geminis tending to exhibit lower cmc values (by about an order of magnitude), increased surface activity (C_{20}) and lower surface tension at the cmc, enhanced solution properties such as hard-water tolerance, superior wetting times, and lower Krafft points. Given these performance advantages of Gemini surfactants one can anticipate their use in a myriad of surfactant applications (*e.g.*, soil remediation, oil recovery, and commercial detergents), given a favourable cost/performance ratio.

Phase behaviour

The hydrophobic effect and micelle formation. In aqueous solution dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. An illustration presented by Hiemenz and Rajagopalan²⁸ is given in Fig. 2. The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment.

A thermodynamic description of the process of micelle formation will include a description of both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system. Hydrocarbons (*e.g.*, dodecane) and water are not miscible; the limited solubility of hydrophobic species in water can be attributed to the hydrophobic effect. The hydrophobic Gibbs energy (or the transfer Gibbs energy) can be defined as the Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water. In considering the transfer Gibbs energy in terms of its entropic and enthalpic contributions, a significant characteristic of the hydrophobic effect is that the entropy term is dominant, *i.e.*, the transfer of the hydro-

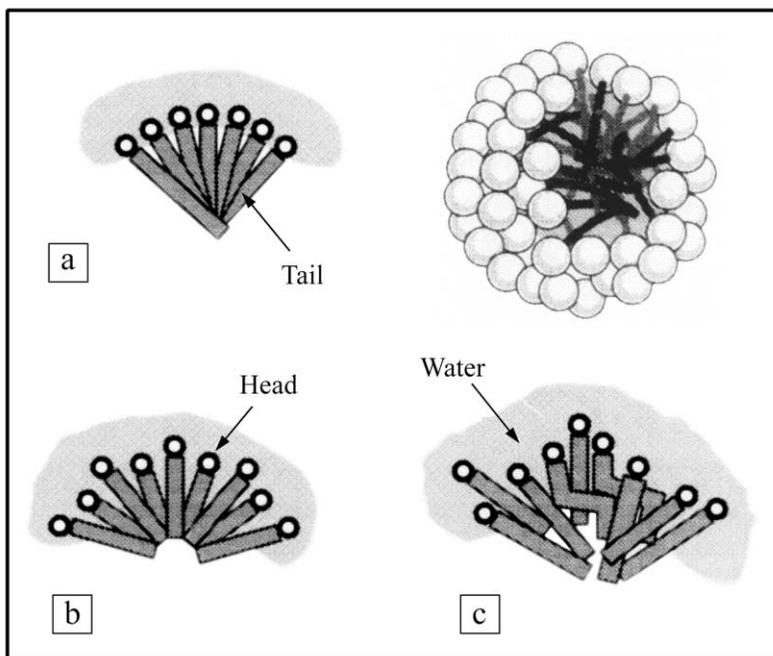


Fig. 2 Organization of surfactant molecules in a micelle. From Hiemenz and Rajagopalan.²⁸ (Reproduced with permission from *Principles of Colloid and Surface Chemistry*, Dekker.)

carbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy.⁶⁷ The decrease in entropy is thought to be the result of the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of differently structured water, often termed icebergs, around the hydrocarbon chain. The presence of the hydrophobic species promotes an ordering of water molecules in the vicinity of the hydrocarbon chain. To minimize the large entropy effect, the “icebergs” tend to cluster,⁶⁸ in order to reduce the number of water molecules involved; the “clustering” is enthalpically favoured, but entropically unfavourable. The overall process has the tendency to bring the hydrocarbon molecules together, which is known as the hydrophobic interaction. Molecular interactions, arising from the tendency for the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water “icebergs”, leading to an association of hydrophobic chains.

Due to the presence of the hydrophobic effect, surfactant molecules adsorb at interfaces, even at low surfactant concentrations. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. The surface activity of surfactants should therefore be considered a dynamic phenomenon. This can be determined by measuring surface or interfacial tensions *versus* time for a freshly formed surface, as will be discussed further below. At a specific, higher, surfactant concentration, known as the critical

micelle concentration (cmc), molecular aggregates termed micelles are formed. The cmc is a property of the surfactant and a number of other factors including the temperature, pressure, and the presence and nature of additives, since micellization is opposed by thermal and electrostatic forces. A low cmc is favoured by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte. Surfactant molecular masses typically range from a few hundreds up to several thousands. Although whimsically referred to as a critical concentration, it will be clear below that the transition between monomers and micelles occurs over a range of concentrations; the breadth of this range is determined primarily, but by no means limited to, the length and nature of the surfactant tails. The most commonly held view of a surfactant micelle is not much different than that published by Hartley in 1936^{67,69} (see Fig. 2). At surfactant concentrations slightly above the cmc value, surfactants tend to associate into spherical micelles, of about 50–100 monomers, with a radius similar to that of the length of an extended hydrocarbon chain. The micellar interior, being composed essentially of hydrocarbon chains, has properties closely related to the liquid hydrocarbon.

There are many examples of surfactant self-assembly. The ability of biological amphiphilic molecules to aggregate into spherical and nonspherical clusters, *i.e.*, vesicles, may have been important for the development of early living cells.⁷⁰ Cellular biological membranes in plants and animals share features with these colloidal systems, although the membrane structures and their properties are complex.^{70–72} The macroscopic nature of lubricating greases formed by dispersing short-chain surfactants, *e.g.*, lithium 12-hydroxystearate, in mineral oil,⁷³ is akin to the behaviour of biological amphiphiles, being also dependent on self-assembly mechanisms.

Critical micelle concentration. The physico-chemical properties of surfactants vary markedly above and below the cmc value.^{2–8,12,13,16,19,51,67–69,74–82} Below the cmc value, the physico-chemical properties of ionic surfactants like sodium dodecylsulfate, SDS, (*e.g.*, conductivities, electromotive force measurements) resemble those of a strong electrolyte. Above the cmc value, these properties change dramatically, indicating a highly cooperative association process is taking place. This is illustrated by Preston's⁸³ classic graph, shown in Fig. 3.

In terms of micellar models, the cmc value has a precise definition in the pseudo-phase separation model, in which the micelles are treated as a separate phase and the cmc value is defined as the concentration of maximum solubility of the monomer in that particular solvent. The pseudo-phase model has a number of shortcomings; however, its description of the cmc value is very useful when discussing the association of surfactants into micelles. It is for this reason that the cmc value is, perhaps, the most frequently measured and discussed micellar parameter.⁷⁶

The cmc values are important in virtually all of the process industry surfactant applications, from mineral processing to formulation of personal care products and foods, to drug delivery systems, and to new surfactant remediation technologies. In these processes, surfactant must usually be present at a concentration higher than the cmc because the greatest effect of the surfactant, whether in interfacial tension lowering,³⁷ emulsification, suspension stabilization, as a delivery vehicle, or in promoting foam stability,³⁸ is achieved when a significant concentration of micelles is present.

Table 3 Some common cmc methods

UV/Vis, IR spectroscopy
Fluorescence spectroscopy
Nuclear magnetic resonance spectroscopy
Electrode potential/conductivity
Voltammetry
Scattering techniques
Calorimetry
Surface tension
Foaming

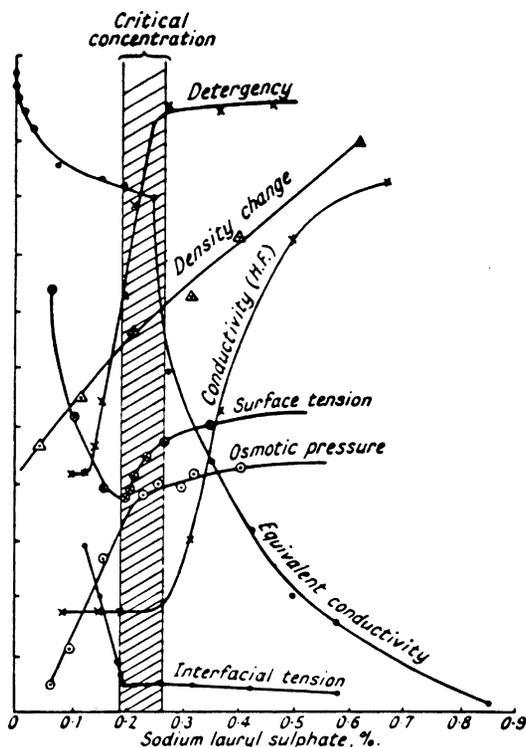


Fig. 3 Variation in physical properties of surfactant solutions below and above the cmc value.⁸³ (Reproduced with permission from *J. Phys. Colloid Chem.*, 1948, **52**, 84.)

The cmc is also of interest because at concentrations above this value the adsorption of surfactant at interfaces usually increases very little. That is, the cmc frequently represents the solution concentration of surfactant from which nearly maximum adsorption occurs.

The general way of obtaining the cmc value of a surfactant micelle is to plot an appropriate physico-chemical property *versus* the surfactant concentration and observe the break in the plot. Table 3 lists the most common cmc methods. Many

of these methods have been reviewed.^{10,84} For industrial process applications the conditions for which cmc values are needed can span the full range from ambient laboratory conditions to conditions of very high temperatures and pressures. It can be very difficult to accurately extrapolate ambient laboratory condition cmcs to elevated temperatures and pressures so an increasing number of new techniques and corresponding determinations have emerged over the past few decades. Most high temperature and pressure cmc studies have been by conductivity, calorimetry, or NMR, and have been limited to ionic surfactants.^{85–93} Conductometric techniques are unsuitable for non-ionic or zwitterionic surfactants, or for use where the background electrolyte concentrations are significant. In such cases specialized surface tension^{94,95} or dynamic foam stability^{95,96} measurements have been employed. For any of the techniques applied it appears⁸⁸ that the uncertainties in the experimental cmc determinations increase with increasing temperature because at the same time the surfactant aggregation number decreases and the aggregation distribution increases. That is, the concentration range over which micellization occurs broadens with increasing temperature. At any temperature and pressure different experimental techniques may give slightly different values for the cmc of a surfactant. However, Mukerjee and Mysels,⁸⁴ in their vast compilation of cmc values, have noted that the majority of values for a single surfactant (*e.g.*, sodium dodecyl sulfate, or SDS, in the absence of additives) are in good agreement and the outlying values are easily accounted for.

The values of cmcs show little variation with regards to the nature of the charged head group. The main influence appears to come from the charge of the hydrophilic head group. For example, the cmc of dodecyltrimethylammonium chloride (DTAC) is 20 mM, while for a 12 carbon non-ionic surfactant, hexaethylene glycol mono-*n*-dodecyl ether (C₁₂E₆), the cmc is about 0.09 mM;^{76,67,84} the cmc for SDS is about 8 mM, while that for disodium 1,2-dodecyl disulfate (1,2-SDDS) is 40 mM.⁹⁷ In addition to the relative insensitivity of the cmc value of the surfactant to the nature of the charged head group, cmcs show little dependence on the nature of the counter ion. It is mainly the valence number of the counter ion that affects the cmc. As an example, the cmc value for Cu(DS)₂ is about 1.2 mM, while the cmc for SDS is about 8 mM.^{84,98}

The cmc often exhibits a weak dependence on both temperature^{99–101} and pressure,^{102,92} although some surfactant cmcs have been observed to increase markedly with temperature above 100 °C.^{95,96} The effects of added substances on the cmc are complicated and depend greatly on whether the additive is solubilized in the micelle, or in the intermicellar solution. The addition of electrolytes to ionic surfactant solutions results in a well established linear dependence of log (cmc) on the concentration of added salt.^{103–107} For non-ionic micelles, electrolyte addition has little effect on cmc values. When non-electrolytes are added to the micellar solution, the effects are dependent on the nature of the additive. For polar additives (*e.g.*, *n*-alcohols), the cmc decreases with increasing concentration of alcohol, while the addition of urea to micellar solutions tends to increase the cmc, and may even inhibit micelle formation.^{108,109} Nonpolar additives tend to have little effect on the cmc.¹¹⁰

A mixed micelle is one which comprised of surfactant molecules of more than one type. Interest in mixed micelles has largely been driven by industry in search of prop-

erties that lie beyond that defined by each surfactant component. Applications include personal cleaning products, hair care and laundry aids.¹¹¹ The review by Hines¹¹¹ describes some of the recent advances in the theoretical evaluation of micellization in mixed surfactant systems.

The Krafft and cloud points. The solubilities of micelle-forming surfactants show a strong increase above a certain temperature, termed the Krafft point (Fig. 4). Below the Krafft point the solubility of the surfactant is too low for micellization so solubility alone determines the surfactant monomer concentration. Above the Krafft point a relatively large amount of surfactant can be dispersed in micelles and solubility increases greatly.¹⁰ Above the Krafft point maximum reduction in surface or interfacial tension occurs at the cmc because the cmc then determines the surfactant monomer concentration. Krafft points for a number of surfactants are listed in references 1 and 112. non-ionic surfactants do not exhibit Krafft points; their solubility decreases with increasing temperature and these surfactants may begin to lose their surface active properties above a transition temperature referred to as the cloud point. This occurs because above the cloud point a surfactant rich phase of swollen micelles separates; the transition is visible as a marked increase in dispersion turbidity. The addition of ionic surfactants increases the cloud points of their non-ionic counterparts, this increase being dependent on the composition of the mixed micelle. Recent studies¹¹³ suggest that an increase in cloud point can be attributed to surface charge of the micelle, therefore increasing electrostatic repulsion reduces micelle coalescence responsible for clouding.

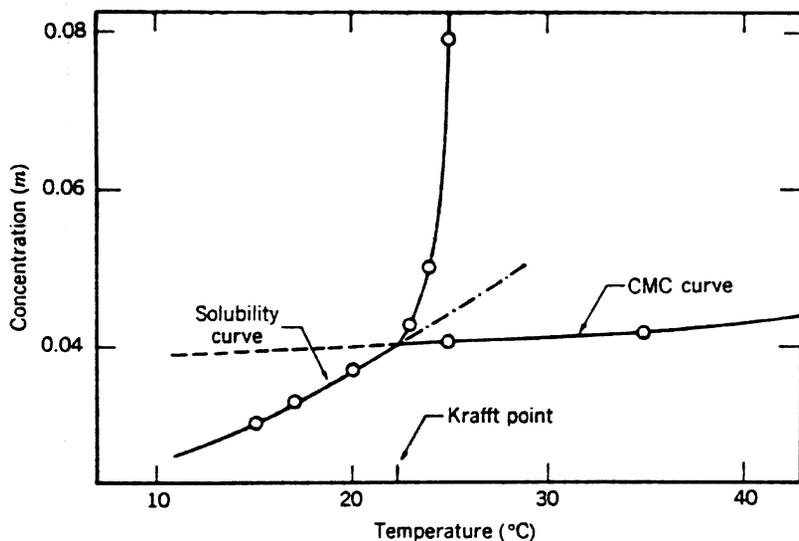


Fig. 4 Surfactant solubilities and the Krafft point.¹⁰ (Reproduced with permission from *Colloidal Surfactants, Some Physicochemical Properties*, Wiley.)

Surfactant adsorption and surface properties

Surfactant adsorption is a consideration in any application where surfactants come in contact with a surface or interface. Adsorption of surfactants may lead to positive effects, as in surface wettability alteration, or be detrimental, as in the loss of surfactants from solution. While many physical and compositional properties influence surfactant adsorption, for a given practical application, usually the main factor that is manipulated is the type of surfactant used. There are a number of areas of application where surfactant adsorption is important including ore flotation, improved oil recovery, *in situ* and *ex-situ* soil remediation, cleaning applications (detergency), surfactant based separation processes, and wetting. Surfactant adsorption may occur due to electrostatic interaction, van der Waals interaction, hydrogen bonding, and/or solvation and desolvation of adsorbate and adsorbent species.

Surface tension, elasticity and rheology. When surfactants concentrate in an adsorbed monolayer at a surface or interface the physical properties of the interface can be very important in all types of natural phenomena and industrial processing operations. For example, many industrial processes involve colloidal dispersions, such as foams, emulsions and suspensions, all of which contain large interfacial areas; the properties of these interfaces may also play a large role in determining the properties of the dispersions themselves. In fact, even a modest surface energy per unit area can become a considerable total surface energy.^{114,115}

When surfactant molecules adsorb at an interface they provide an expanding force and cause the interfacial tension to decrease (at least up to the cmc). This is illustrated by the general Gibbs adsorption equation, from which the packing density of surfactant in a monolayer and the area per adsorbed molecule can be calculated. Numerous examples are given by Rosen.¹ If the interface then undergoes a sudden expansion a surface tension gradient is established which induces liquid flow in the near-surface region, termed the Marangoni effect.³³ Related to these effects are the Gibbs and Marangoni surface elasticities^{27,116,117} and the surface dilational viscosity.^{117,118} Dynamic surface tensions, and related phenomena, are important in areas such as photography, where the dynamic surface tension is monitored to prevent film deformation and irregularities, in crop protection products where wettability rate is vital for pesticide spreading on leaves, biological processes, and in paper and textile production.¹¹⁹ For a detailed description of surface adsorption mechanisms and a discussion on the advancement of understanding adsorption kinetics, see the reviews by Eastoe and Dalton¹¹⁹ and Langevin.¹²⁰

Miller *et al.*¹²¹ provide a review of interfacial rheology. A high interfacial viscosity can contribute to emulsion or foam stability by reducing the rate of droplet/bubble coalescence.¹²²⁻¹²⁶ As drops approach each other the rate of oil film drainage will be determined, in part, by the interfacial viscosity which, if high enough, will significantly retard the final stage of film drainage and possibly even provide a viscoelastic barrier to coalescence. More detailed descriptions are given in references 127-129. The presence of mixed surfactant adsorption seems to be a factor in obtaining films with very viscous surfaces.³³ For example, in some cases, the addition of a small amount of non-ionic surfactant to a solution of anionic surfactant can enhance foam stability due to the formation a viscous surface layer could be a liquid crystalline

surface phase in equilibrium with a bulk isotropic solution phase.^{27,130} To the extent that viscosity and surface viscosity influence emulsion and foam stability one would predict that stability would vary according to the effect of temperature on the viscosity. Thus, some industrial processes exhibit serious foaming problems at low process temperatures, which disappear at higher temperatures.²⁷

Bulk solutions of surfactant can also exhibit interesting rheological properties, including viscoelasticity, yield stresses, gelation, and liquid crystal formation, as reviewed elsewhere.^{131,132}

Surface potential and dispersion stabilization. Most substances acquire a surface electric charge when brought into contact with a polar medium such as water. One mechanism for this involves the adsorption of ionic surfactants. In general, the nature and degree of surface charging is more complicated than this and surfactant adsorption may cause a surface electric charge to increase, decrease, or not significantly change at all. For example, an oil–aqueous interface can become negatively charged in alkaline aqueous solutions due to the ionization of surface carboxylic acid groups, the adsorption of natural surfactants present in the oil, and the adsorption of charged mineral solids.^{133–140}

The presence of a surface charge influences the distribution of nearby ions in a polar medium and an electric double layer (EDL) is formed, consisting of the charged surface and a neutralizing excess of counter-ions over co-ions, distributed near the surface. Most colloidal dispersions, including emulsions, suspensions and foams are not thermodynamically stable, but may possess some degree of kinetic stability. Encounters between dispersed species can occur due to Brownian motion, sedimentation, and/or stirring. The stability of the dispersion depends upon how the particles interact when this happens. More details are given in reference 141. Surfactants are frequently involved in the stabilization of colloidal dispersions of droplets, particles or bubbles by increasing the electrostatic repulsive forces.^{37–39}

Adsorption at S/L interfaces. In petroleum recovery³⁸ and environmental soil remediation processes,^{142,143} surfactant adsorption from solution onto solid surfaces most commonly occurs in porous media, either on the walls of pores or throats or else on fine particles in rock pores. This adsorption constitutes a loss of valuable surfactant so it directly affects, and may well dictate, the economics of an oil recovery or remediation process. The adsorption is also of considerable scientific interest because the surfactant can adsorb as individual molecules or as surfactant aggregates of various types.

Ionic surfactants tend to adsorb onto opposite-charged solid surfaces due to electrostatic interactions, most mineral surfaces in aqueous solution being charged. Adsorption of ionic surfactants on a like-charged substrate is less understood, but can occur *via* hydrogen bonding or attractive dispersion forces,^{1,144} as is the case for non-ionic surfactants. The interactions that cause adsorption are thought to be well understood, but there is active discussion of the nature of any surfactant surface aggregates that may form, as reviewed in references 145 and 146. Although they do not yet account for all of the underlying phenomena, several mathematical models have been developed to describe the adsorption isotherms.^{147–151}

The mechanisms driving surfactant adsorption are generally discussed in terms of specific regions in surfactant adsorption isotherms. At low surfactant concentrations the adsorption behaviour can usually be described by Henry's Law and is the region where the simple electrical double-layer model is often appropriate. Here ionic surfactant monomers adsorb as individual ions without mutual interaction^{152–154} while non-ionic surfactants adsorb with interactions involving hydrogen bonding between surface hydrogen atoms and proton acceptors in the polar groups and hydrophobic bonding between the surface and the hydrocarbon tails.^{148,149} At higher concentrations tail–tail interactions may begin to cause association of the adsorbed surfactants into aggregates, with the head groups facing the surface.^{148,154} The onset of this behaviour is marked by the hemimicelle concentration (HMC, in hemimicelles all the head groups are towards the surface)^{155–157} or as the critical admicelle concentration (CAC, in admicelles some of the surfactants are in an opposite orientation to the surface).^{149,158–160} Bilayer formation, with surfactant monomer headgroups in the first layer facing the surface while those of the second layer face the bulk solution, begins in this region.¹⁵⁴ The term admicelle was introduced in 1985 to describe surfactant surface aggregates which were bilayered in structure and which had formed without an intermediate hemimicelle structure existing at a lower surfactant concentration.¹⁴⁹ The HMC/CAC varies with surfactant chain length and branching in the same manner as cmc varies with these parameters.¹⁶¹ If the system contains ionic surfactants, the addition of an electrolyte will decrease the CAC in the same manner that electrolytes reduce the critical micelle concentration (cmc).¹⁶² Finally, plateau adsorption at near the critical micelle concentration (cmc) and is characterized by little or no increase in adsorption with increasing surfactant concentration. Here, micelles exist in bulk solution and the adsorbed surfactant has a bilayer structure. For more details, see references 17 and 163–166.

In addition to the hemimicelle and local bilayer, or admicelle, structures some others that have been proposed are surface micelles (spherical aggregates with only one surfactant monomer adhering to the solid surface¹⁶⁷ and hemicylinders and cylinders (cylindrical structures arranged with the surfactant headgroups facing outward).^{168,169} Debate over the exact structure of adsorbed surfactant aggregates has intensified with the advent of new techniques, such as atomic force microscopy (AFM). The term solloid has been introduced¹⁷⁰ to permit reference to surfactant aggregates at a surface without reference to morphology. It seems clear¹⁴⁶ that micelle-like aggregates form spontaneously at concentrations well below the bulk cmc and that a complete bilayer is formed at the maximum adsorption of ionic surfactants adsorbing onto surfaces of opposite charge.

An additional level of complexity in practical situations is due to the fact that many surfactant systems used in industry are mixtures. As adsorption behaviour from single surfactant systems mirrors the behaviour of micelle formation in solution, so too does adsorption from mixed surfactant systems mirror mixed micelle behaviour.¹⁷¹

The extent of adsorption of commercial surfactants developed for use in reservoir recovery processes can vary from near zero to as high as 2.5 mg g⁻¹. Surfactant adsorption on rock surfaces is usually measured by either static (batch) or dynamic (coreflood) experiments. The static adsorption method, employing crushed rock samples, is essentially the classical method for determining adsorption isotherms at the aqueous solution/solid interface and involves batch equilibrations of particles in

solutions of different initial surfactant concentration. The dynamic coreflood method is more involved but employs a greater solid to liquid ratio and is therefore more sensitive, see references 172–174. Temperature, brine salinity and hardness, solution pH, rock type, wettability, and the presence of a residual oil phase have all been found to influence the extent of adsorption of different surfactants.^{175–177}

Wettability alteration. Surfactant, by adsorbing at a solid surface, reduces interfacial tension and modifies the ability of water or oil to wet the solid surface. When the adsorbed surfactant orientation is such that its hydrophobic tail groups point away from the surface or along the surface there will result a decrease in water-wetting and an increase in oil-wetting. Likewise, if the orientation is with the polar head group away from the surface there will result an increase in water-wetting. In addition to the dual nature of surfactant molecules, specific structural characteristics can increase or decrease the packing of surfactant molecules and consequently influence surface wettability. A number of studies have shown wettability shifts from oil-wetting towards water-wetting due to surfactant adsorption.^{178,179} This topic is discussed in detail by Spinler and Baldwin.¹⁸⁰ An example of surfactant-induced wettability alteration can be found in the treatment of swelling clays, such as montmorillonite, with a cationic surfactant, such as dimethyl di(hydrogenated tallow) ammonium, in order to produce organophilic clay for use in non-aqueous drilling muds.^{181,182}

Rosen¹ and Spinler¹⁸⁰ provide some generalizations of the effect on adsorption behaviour and wettability of modifications to hydrophobic tail groups. Some specific studies of structure effects on adsorption and wettability include those of branching (branched vs. linear hydrophobic tails),¹⁸³ polar groups (e.g., ethoxylates vs. sulfates vs. ethoxysulfates),¹⁸⁴ and tail lengths.¹⁸⁵ Temperature can also alter wettability by affecting either the surfactant or the surfactant–surface adsorption characteristics.^{186,187}

Adsorption at L/L interfaces. It was pointed out earlier that surfactant adsorption at liquid interfaces can influence emulsion stability by lowering interfacial tension, increasing surface elasticity, increasing electric double layer repulsion (ionic surfactants), lowering the effective Hamaker constant, and possibly increasing surface viscosity. The nature of the surfactant can determine the arrangement of the phases in an emulsion, that is, which phase will form the dispersed *versus* continuous phase. For this there are several empirical predictive approaches based on anticipated surfactant positioning at the interface,^{115,188,189} including Bancroft's rule, the oriented wedge theory, the hydrophile–lipophile balance (HLB), and the volume balance value.¹⁹⁰ Of these the HLB has been the most used. This dimensionless scale ranges from 0 to 20 for non-ionic surfactants; a low HLB (<9) refers to a lipophilic surfactant (oil soluble) and a high HLB (>11) to a hydrophilic (water soluble) surfactant. Most ionic surfactants have HLB values greater than 20. Some examples of surfactant HLBs are given in Table 4. In general, water-in-oil (W/O) emulsifiers exhibit HLB values in the range 3–8 while oil-in-water (O/W) emulsifiers have HLB values of about 8–18. There exist empirical tables of HLB values required to make emulsions out of various materials.^{191,192} If the value is not known, then lab emulsification tests are required, using a series of emulsifying agents of known HLB values.¹⁹² There are various compilations and equations for determining emulsifier HLB values.^{188,191–194}

Table 4 Approximate surfactant HLB values^a

Surfactant	HLB
Oleic acid	1
Sorbitan tristearate (SPAN 65)	2
Sorbitan monooleate (SPAN 80)	4
Diethylene glycol monolaurate	6
Sorbitan monolaurate (SPAN 20)	9
Glycerol monostearate	11
Polyoxyethylene (10) cetyl ether (BRIJ 56)	13
Polyoxyethylene sorbitan monooleate (TWEEN 80)	15
Sodium octadecanoate	18
Sodium dodecanoate	21
Sodium octanoate	23
Dioctyl sodium sulfosuccinate	32
Sodium heptadecyl sulfate	38
Sodium dodecyl sulfate	40
Sodium octyl sulfate	42

^a Compiled from data in references 2, 29, 188 and 423.

The HLB is an indicator of the emulsifying characteristics of an emulsifier but not its efficiency. Thus, while all emulsifiers having a high HLB will tend to promote O/W emulsions, there will be a considerable variation in the efficiency with which those emulsifiers act for any given system. Often, for example, mixtures of emulsifying agents are more effective than single components, even if the final HLB is the same. It is thought that some mixed emulsifiers form a complex at the interface, thus yielding low interfacial tension and a strong interfacial film.

Just as solubilities of emulsifying agents vary with temperature, so does the HLB, especially for the non-ionic surfactants. A surfactant may thus stabilize O/W emulsions at low temperature, but W/O emulsions at some higher temperature. The transition temperature, at which the surfactant changes from stabilizing O/W to W/O emulsions, is known as the phase inversion temperature, PIT. At the PIT, the hydrophilic and oleophilic natures of the surfactant are essentially the same (another term for this is the HLB temperature). As a practical matter, emulsifying agents are chosen so that their PIT is far from the expected storage and use temperatures of the desired emulsions. In one method¹⁹⁵ an emulsifier with a PIT of about 50 °C higher than the storage/use temperature is selected. The emulsion is then prepared at the PIT where very small droplet sizes are most easily created. Next, the emulsion is rapidly cooled to the desired use temperature, where now the coalescence rate will be slow, and a stable emulsion results. Further details can be found in reference 196.

Analysis for surfactants

Numerous methods have been developed for the quantitative determination of each class of surfactants. The analysis of commercial surfactants is greatly complicated by the fact that these products are mixtures. They are often comprised of a range

Table 5 Typical methods of surfactant analysis

Surfactant class	Method
<i>Anionic</i>	
Alkyl sulfates and sulfonates	Two-phase or surfactant-electrode monitored titration
Petroleum and lignin sulfonates	Column or gel permeation chromatography
Phosphate esters	Potentiometric titration
Sulfosuccinate esters	Gravimetric or titration methods
Carboxylates	Potentiometric titration or two-phase titration
<i>Non-ionic</i>	
Alcohols	NMR or IR spectroscopy
Ethoxylated acids	Gas chromatography
Alkanolamides	Gas chromatography
Ethoxylated amines	HPLC
Amine oxides	Potentiometric titration
<i>Cationic</i>	
Quaternary ammonium salts	Two-phase or surfactant-electrode monitored titration, or GC or HPLC
<i>Amphoteric</i>	
Carboxybetaines	Low pH two-phase titration, gravimetric analysis, or potentiometric titration
Sulfobetaines	HPLC

of molar mass structures of a given structural class, may contain surface-active impurities, are sometimes intentionally formulated to contain several different surfactants, and are often supplied dissolved in mixed organic solvents or complex aqueous salt solutions. Each of these components has the potential to interfere with a given analytical method. Therefore surfactant assays may well have to be preceded by surfactant separation techniques. Both the separation and assay techniques can be highly specific to a given surfactant/solution system. This makes any substantial treatment beyond the scope of the present review. Good starting points can be found in the several books on surfactant analysis.^{197–202} The characterization and analysis of surfactant demulsifiers is discussed in reference 203. Table 5 shows some typical types of analysis methods that are applied to the different surfactant classes.

There are a number of reviews available for surfactants in specific industries,²⁰⁴ for specific surfactant classes, and for automation of surfactant titrations.²⁰⁵ References 197 and 206–208 discuss methods for the determination of anionic surfactants, which are probably the most commonly encountered in the petroleum industry. Most of these latter methods are applicable only to the determination of sulfate- and sulfonate-functional surfactants. Probably the most common analysis method for anionic surfactants is Epton's two-phase titration method^{209,210} or one of its variations.^{211,212} Related, single-phase titrations can be performed and monitored by either surface tension²¹³ or surfactant-sensitive electrode^{200,201,214,215,216} measurements. End-points have also been detected by turbidity and refractive index changes.²⁰⁵ non-ionic

surfactants may be analyzed by titration after the addition of an activator, such as barium chloride, which forms a charged complex, essentially a “pseudo-cationic” molecule, detectable by a surfactant-sensitive electrode.²⁰⁵ Gronsveld and Faber²¹⁷ discuss adaptation of the titration method to oleic phase samples.

Aqueous surfactant micellar systems have been utilized successfully in virtually every area of analytical chemistry. Separation applications, for example, have utilized micellar phases as mobile-phase additives in thin-layer chromatography, high performance liquid chromatography (HPLC), and capillary electrophoresis (CE). Reviews on the uses of surfactants in these areas are common and the reader is referred to the following sample review articles.^{218–220} In addition, a myriad of techniques have been developed that utilize the solubilization capacity of micelles for purification, pre-concentration, and extraction.²²¹ Despite the rich diversity of their phase properties, surfactant solutions have been somewhat ignored. This is somewhat surprising given the fact that these methods often utilize more environmentally friendly materials and have a significant cost/performance advantage over traditional liquid/liquid extractions. The main drawback with many of these techniques is the need for a suitable method of detection for the analytes.²²² Typically, micellar extractions have made use of the consolute temperature (cloud point) phenomenon that exists for non-ionic surfactants,²²³ where the increase in temperature above the critical temperature (cloud point) results in the separation of the aqueous surfactant solution into a surfactant-rich phase and an aqueous phase containing a significantly decreased concentration of surfactant. Any components that are solubilized originally by the micelles in the lower temperature solution can be extracted and concentrated in the small volume of the surfactant-rich phase.

Detergency and the displacement of dirt and oil

Surfactants and wetting. When a drop of liquid comes into contact with a solid surface it will form a bead on the surface if it has a weak affinity for the surface, *i.e.*, if its surface tension is above the critical surface tension of the surface (γ_c). Conversely, it will spread and form a film if it has a strong affinity for the surface, *i.e.*, if its surface tension is less than γ_c . The critical surface tensions of solids range from 18 mN m⁻¹ for Teflon® to about 46 mN m⁻¹ for nylon. Most fabric surfaces have critical surface tensions in this range; hence, the reduction of the surface tension of an aqueous solution to values below *ca.* 40 mN m⁻¹ by the addition of a suitable surfactants permits the wetting of most textile fabrics. Surfactants are often used as wetting agents in commercial applications, particularly where the wetting liquid is to be applied to a waxy or “wax-like” surface. Anionic surfactants are most often used in this regard. In pesticide or herbicide applications, a wetting agent is incorporated into the formulation to facilitate satisfactory surface coverage of the agent, and in the textile manufacturing industry in order to obtain even distributions of *e.g.*, textile dyes. Cationic surfactants are much less widely used than anionic surfactants as wetting agents, but they have found applications as oil-wetting agents in dry cleaning fluids and in road making operations. In addition to lowering the liquid/gas surface tension the wetting agent must also lower the solid/liquid surface tension. Bulky sur-

factants, *e.g.*, sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT), can be excellent wetting agents, since the formation of micelles (which leads to a surface tension minimum) is sterically hindered. Hence, the monomer concentration of this surfactant in solution can be made relatively high, resulting in extremely high surface pressures.

The ability of some siloxane surfactants to lower aqueous surface tensions to values (*ca.* 20 mN m⁻¹) lower than can be achieved using hydrocarbon surfactants, together with their ability to cause rapid spreading of aqueous solutions on hydrophobic surfaces (like polyethylene) remain topics of active research.^{224–229} The ability of siloxane surfactants to promote spreading plays an important role in their use in paints and coatings,²³⁰ personal care products,²²⁴ textiles,²³¹ the oil industry,²³² and as adjuvants for pesticides²³³ and herbicides.^{234,235}

Instead of promoting wetting of the surface, it is desirable in some cases to promote the exclusion of, *e.g.*, water from the solid interface. This is achieved by increasing the contact angle until it is substantially in the de-wetting range ($\theta > 90^\circ$). Long-chain cationic surfactants are often used in the textile industry to make fabrics water-repellent. The cationic headgroups adsorb on the anionic textile surface exposing the long hydrocarbon chain to the water, producing a hydrophobic surface ($\theta \approx 105^\circ$). In this case, a condition of negative capillary action is achieved and the pressure required to force water through the fabric is increased substantially, whereas the passage of air through the textile is not hindered.

Ore flotation. The flotation of solid particles on a liquid medium depends on the contact angle, which can be changed by the addition of surfactants. A familiar elementary chemistry demonstration consists of making a needle float on the surface of water by coating it in wax. Subsequent addition of a household detergent sinks the needle. The principles are the same as in the treatment of crude mineral ores by flotation, for which a small amount of collector oil is added during the grinding and slurring process. The collector oil, which is an anionic, cationic, or non-ionic surfactant, acts to alter the wettability of the ore particles. Organic xanthates and thiophosphates are often used for sulfide ores and long-chain fatty acids for oxide and carbonate ores. In practice, a foaming agent is usually also added so that when air is blown through the suspension the ore particles attach to the air bubbles. The ore particles then float to the surface where they are recovered by skimming.²³⁶ Flotation of this type is also used as a purification procedure for sludges and effluents.

Surfactants and detergency. Detergency is defined as “the action of surfactants that causes or aids in the removal of foreign material from solid surfaces by adsorbing at interfaces and reducing the energy needed to effect the removal”.²⁵ Usually wetting agents that rapidly diffuse and adsorb at appropriate interfaces are most effective. Soap, a surface active fatty acid salt containing at least eight carbon atoms,²⁵ has long been used as a detergent. Historically, soap has been obtained by the saponification of glyceride oils and fats with NaOH or KOH, giving glycerol as a by-product. Soaps are excellent detergents, but suffer from their sensitivity to acid pHs and the presence of hardness in the water (Ca²⁺ and Mg²⁺ ions), causing soap scum. Although the use of detergent builders will compensate for this deficiency, soaps have been essentially replaced by the synthetic detergents. The bulk of surfactant manufacturing is dedicated to those materials that are blended into commercial detergent formulations.

Alkyl sulfates, alkyl-aryl sulfonates and non-ionic polyethylene oxide derivatives still account for the bulk of surfactant manufacture.

Not all surfactants make acceptable detergents. For a surfactant to be considered a good detergent, it must be a good wetting agent, possess the ability to displace soil materials into the washing fluid, be a good solubilizing agent, and be a reasonable anti-redeposition agent. The solid surface to be cleaned may be a hard surface (plates, high density plastics, teeth) or a textile material (e.g. wool, cotton, synthetic fibres), or a part of the body (skin, hair, teeth). The dirt or soil may have variable chemical composition and particle sizes. In view of the possible surface/soil systems, theories of detergent action are limited in scope. For example, in detergent formulating a difference is observed between wetting of 'hard' surfaces (e.g. glass and metal) and 'soft' surfaces (e.g. textiles). In the case of hard surfaces, the equilibrium tends to be established rapidly, whereas, for soft surfaces, kinetic effects can cause complications. For specialized detergent applications, the situation is even more complex, since performance tends to be judged by criteria which are not wholly related to dirt removal. Surfactants that effectively adsorb at the solid/water and dirt/water interfaces make the best detergents. Adsorption at the air/water interface with the subsequent lowering of the surface tension and foaming are not necessarily an indication of detergency, advertising campaigns notwithstanding (hence the consumers' resistance to non-ionic formulations).

The most successful detergents are those forming surfactant micelles; hence, micelles were long thought to be an intimate part of the detergency mechanism. However, we now know that detergent action is dependent upon the concentration of monomeric surfactant and is practically unaffected by the presence of micelles. The formation of micelles is secondary to the detergent process, and the main function of the surfactant micelles appears to be providing a reservoir for replenishing unassociated surfactant adsorbed from solution, and for solubilizing greases and oils. The chemical properties of surfactant molecules that are associated with good detergent action, will, in most cases, lead to micelle formation as a competing process. Finally, detergents cannot work by themselves in practical situations; the business of detergent additives is huge. Common additives include builders, anti-redeposition agents, brighteners, and co-surfactants. The function of each of these and trends in their developments and is discussed on an annual basis in the *Chemical and Engineering News – Soaps and Detergents* special issues.

Oil recovery. In primary oil recovery from underground reservoirs, the capillary forces described by the Young and Young-Laplace equations are responsible for retaining much of the oil (residual oil) in parts of the pore structure in the rock or sand. It is these same forces that any secondary or enhanced (tertiary) oil recovery process strategies are intended to overcome.^{32,35,37,237}

The relative oil and water saturations depend upon the distribution of pore sizes in the rock. The capillary pressure, P_c , in a pore is given by,

$$P_c = 2\gamma \cos\theta/R \quad (1)$$

where R is the pore radius, and at some height h above the free water table, P_c is fixed at $\Delta\rho h$, where $\Delta\rho$ is the density difference between the phases. Therefore, as the

interfacial tension and contact angle are also fixed, and if the rock is essentially water-wetting (low θ), the smaller pores will tend to have more water in them (less oil) than larger pores.²³⁸ One generally attempts to reduce the capillary forces restraining the oil and/or alter viscosity of the displacing fluid in order to modify the viscous forces being applied to drive oil out of the pores. The ratio of viscous forces to capillary forces actually correlates well with residual oil saturation and is termed the capillary number. One formulation of the capillary number is,

$$N_c = \eta v / (\gamma \phi) \quad (2)$$

where η and v are the viscosity and velocity of the displacing fluid, γ is the interfacial tension and ϕ is the porosity. After even the most efficient waterflooding, N_c is about 10^{-6} and the residual oil saturation is still around 45%.²³⁹ To recover additional oil requires increasing the capillary number by several orders of magnitude. In practice this is most readily accomplished by adding a suitable surfactant to decrease the interfacial tension to ultralow values.^{37,36} In some systems the addition of a fourth component to an oil/water/surfactant system can cause the interfacial tension to drop to near-zero values, *ca.* 10^{-3} to 10^{-4} mN m⁻¹, allowing spontaneous emulsification to very small drop sizes, *ca.* 10 nm or smaller (microemulsions).²⁴⁰ Microemulsions have some special qualities, and can have important applications in areas such as enhanced oil recovery, soil and aquifer remediation, foods, pharmaceuticals, cosmetics, herbicides and pesticides.^{36,37,189,241-243}

Soil remediation. The contamination of groundwater by non-aqueous phase liquids (NAPLs) is a cause for concern throughout the world. Typical NAPLs like tetrachloroethylene (PCE), trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA) can easily invade the subsurface, are difficult to remove, have sufficiently high solubilities to be of concern with respect to drinking water standards, and have low biodegradability.²⁴⁴ For these reasons, NAPLs can persist in the soil for many decades and present a long term threat to groundwater quality.²⁴⁵ The use of surfactants to remediate groundwater contaminated by non-aqueous phase liquids has been under significant development and field testing over the past two decades, especially for dense non-aqueous phase liquids such as chlorinated solvents^{246,247} because they are otherwise very difficult to remediate. The techniques used to achieve the displacement, solubilization, and flushing of the NAPLs are adapted from surfactant-based enhanced oil recovery technology^{248,249} as are the surfactant selection criteria.²⁴⁷ New surfactants can be tailored to meet specific goals, such as improving their microemulsion forming ability for specific situations by changing the numbers of ethylene oxide or propylene oxide units in the surfactant.²⁵⁰⁻²⁵² Kimball²⁵³ has applied this technology and found that surfactants were effective at removing hexadecane, *o*-cresol and phenanthrene by changing the surface wetting state and desorbing the contaminants during flushing of the soil. With a good surfactant formulation based upon good phase behaviour, up to 99.9% of the NAPL can be recovered from a soil column in as little as 1.0 to 2.0 pore volumes of surfactant flooding.²⁴⁷ A major constraint for such processes is that surfactants, if left behind must not impose an environmental threat.²⁵⁴ A recent review of surfactant-enhanced soil remediation²⁴⁹ lists various classes of biosurfactants, some of which have been used in enhanced oil recovery, and

discusses their performance on removing different type of hydrocarbons, as well as removal of metal contaminants such as copper and zinc. In the latter area, the application of heavy metal ion complexing surfactants to remediation of landfill and mine leachate is showing promise.²⁵⁵

Surfactant stabilized dispersions

An emulsion, foam or suspension can be made by simply mixing oil, gas or solids into another phase (often water or an aqueous solution) with sufficient mechanical shear. The additional interfacial area created between the two phases is important because, as shown by the Laplace equation, even a modest interfacial energy per unit area can become a considerable total interfacial energy requirement if many small droplets, bubbles or particles are formed. In practise, the energy requirement is even greater due to the need for droplets, bubbles or particle aggregates to deform before being disrupted.^{256,257} If this energy requirement cannot be provided, say, by mechanical shear, then another alternative is to use surfactant chemistry to lower the interfacial free energy, or interfacial tension. This can lower the amount of mechanical energy needed for dispersion by several orders of magnitude. Every metastable emulsion or foam, and many of the suspensions, that will be encountered in practise contain a surface-active stabilizing agent. The stabilizing surfactant makes the dispersion easier to form and may create an interfacial film that helps keep the system from breaking or separating.^{37,38,189,260–266} Although surfactants and surface free energies are very important to the stability of dispersions, there are a considerable number of factors involved in determining their stability.

As stated at the outset, the number of industrial applications of surfactants is huge, and represents the subject of several book series. In the petroleum industry alone, applications of surfactants include,^{38,258}

- wettability alteration,
- enhanced microdisplacement of oil
- stabilizing foams for mobility control or foam drilling fluids,
- stabilizing emulsions or foams for acid stimulation,
- separation and flotation aids in oil sands processing, heavy oil transportation as aqueous emulsion,
- surfactant enhanced aquifer remediation, and
- breaking of oil spill emulsions.

Foams and froths

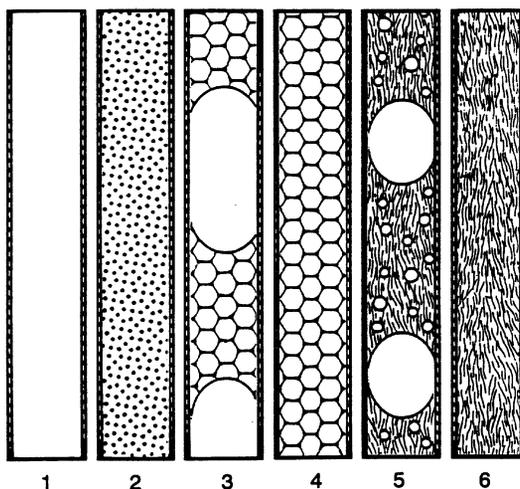
Practical foams comprise a mixture of gas with either oil or water, where the gas phase occurs in the form of bubbles dispersed within the liquid. The bubble diameters are typically on the order of 10 to 1000 μm , but may be as large as several centimetres. Although both aqueous and oleic foams may be encountered, the former are by far the most common. Foam drainage is an important element in the formation and early development of a foam, as reviewed by Weaire *et al.*²⁵⁹ Foams and emulsions may also

be encountered simultaneously.³⁸ Industrial occurrences of foams are long-standing and widespread. Indeed, foams may be applied or encountered at all stages in the processing industries and have important properties that may be desirable in some process contexts and undesirable in others.^{38,260–262}

Although the drainage half-life of a typical foam is of the order of tens of minutes, some foams can have much greater stability. In carefully controlled environments, it has been possible to make surfactant-stabilized foam bubbles and films having lifetimes of from months to years.²⁶³ A review by Prins and van Kalsbeek²⁶⁷ shows the growing interest in studying foam behaviour, particularly foam making and stabilizing. Although many factors such as film thickness and adsorption behaviour, have to be taken into account, the ability of a surfactant to reduce surface tension and contribute to surface elasticity are among the most important features of foam stabilization. The relation between Marangoni surface elasticity and foam stability^{116,117,268,269} partially explains why some surfactants will act to promote foaming while others reduce foam stability (foam breakers or defoamers), and still others prevent foam formation in the first place (foam preventatives, foam inhibitors). Continued research into the dynamic physical properties of thin liquid films and bubble surfaces is necessary to more fully understand foaming behaviour. Schramm *et al.*¹⁷⁶ discuss some of the factors that must be considered in the selection of practical foam-forming surfactants for industrial processes, Kerner²⁷⁰ describes several hundred different formulations for foam inhibitors and foam breakers, and Pugh²⁷¹ reviews both foaming and defoaming phenomena. Although most foams are not thermodynamically stable, in practise they can be quite stable and may resist explicit antifoaming and defoaming treatments.

Industrial foams. Fire fighting foams were first introduced in the early 1900s and have since evolved into specialized and widely adopted systems²⁷² that may be found in any of the many industrial operations involving the transportation, processing, or handling of flammable petroleum liquids, including refineries and offshore production platforms. Fire fighting foams function by smothering the fire, preventing air from mixing with flammable vapours, separating flames from the fuel surface, and cooling the fuel and its surface.^{273,274} Typically, the foams used for fire fighting contain 75–97% air and are known as “low expansion” foams. Foam selection criteria include classical properties such as static half lives, salinity tolerance, toxicity and stability to decomposition, but also properties like expansion and fire extinguishing performance.^{274,275} The practical formulations may contain numerous other additives to control freezing, viscosity, bacterial degradation, oxidation, corrosion, and so on.²⁷⁴ These foams are often formulated to contain fluorocarbon surfactants, sometimes blended with hydrocarbon surfactants and/or polymers. Foams that can be effective on hydrocarbon fuel fires are typically characterized as protein (hydrolyzed protein surfactants), fluoro-protein (hydrolyzed protein and perfluorinated surfactants), aqueous film-forming (AFFF, blend of perfluorinated surfactants), alcohol resisting aqueous film forming (AFFF-AR), high expansion, or alcohol (polar-solvent) foams.²⁷³

Several types of foams have been utilized as drilling fluids.^{276–281} Fig. 5 shows some possible flow regimes corresponding to the use of air, mist, foam, or liquid as a drilling fluid.²⁸² Foams have been used to remove formation brine that has entered a well while



1. Air or gas flow
2. Mist flow
3. Stable foam with gas slugs
4. Stable foam
5. Liquid flow with gas slugs and interspersed bubbles
6. Liquid flow

Fig. 5 Some possible flow regimes corresponding to the use of air, mist, foam, or liquid as a drilling fluid.²⁸² (Reproduced with permission from *World Oil*, 1980, June, 187.)

air drilling, this is sometimes called mist drilling because the fluids are injected as a mist (although the mist changes to foam before returning up the annulus of the well). Since foams can exhibit a high carrying capacity (viscosity), they can also be used for sand or scale clean-outs. Foam drilling fluids are now of much interest for under-balanced, low annular velocity drilling of horizontal wells in the petroleum industry,^{283,284} a method in which the drilling fluid is kept at lower pressure than the reservoir so that the drilling fluid and cuttings will neither erode nor penetrate and potentially damage the reservoir. Air, mist, and foam can also yield superior drilling penetration rates compared with conventional mud systems. Such foams are typically based on alpha-olefin sulfonate or alcohol ether sulfate surfactants. Polymer-thickened foams (incorporating, for example, guar and xanthan gums) have also been used for enhanced cuttings carrying capacity.^{285,286} Although the foam generation methods used in the field can be quite primitive, quite sophisticated foam generators have also been developed, especially for the generation of shear-sensitive, polymer-thickened foams.²⁸⁷ When a foam drilling fluid is brought to the surface a defoaming strategy is needed, such as the addition of a defoamer such as a polydimethylsiloxane or low molar mass aliphatic alcohol. Borchardt²⁸⁶ reviews defoamers that have been used.

Micro-foams (colloidal gas aphrons)

The terms micro-foam and colloidal gas aphrons refer to a dispersion of aggregates of very small foam bubbles in aqueous solution.^{288–290} They can be formed by dispersing gas into surfactant solution under conditions of very high shear^{289,291} creating very small gas bubbles (bubble diameters \approx 50–300 μm), each surrounded by a bimolecular film of stabilizing surfactant molecules (Sebba termed this film a soapy shell). There is some evidence that such micro-foams tend to be more stable than comparable foams that do not contain the bimolecular film structure.^{288,289,291} Other claims for special properties have been made,^{292–298} but are less well supported, or even conflicting within the literature. Potential applications that have been reported in the literature include micro-foam flushing for soil remediation^{292–296} and micro-foam injection for reservoir oil recovery.^{297,298} Despite the fact that these papers make conflicting claims regarding the physical properties of these foams, and, although their results should be interpreted with caution pending additional independent studies, these papers provide interesting reading and suggest that micro-foams may well find useful application.

Oil flotation. Whereas mineral ore flotation relies on wettability alteration and bubble attachment, oil and bitumen flotation rely more on attachment and filming to create an oleic foam. In the hot water flotation process for recovering bitumen from oil sands (used commercially in Canada) surfactants play key roles in separating bitumen from mineral particles and then floating the former. As reviewed elsewhere^{36,38} alkaline conditions are used to produce (saponify) from the bitumen a class of natural surfactants that are predominantly aliphatic carboxylates of chain length typically C_{15} to C_{17} , and also aliphatic sulfonates with chain lengths greater than C_5 . These surfactants adsorb at surfaces and interfaces, increasing their electric charge and the increased disjoining pressure helps drive disengagement of the oil from the solids. The adsorbed surfactants also reduce surface tensions, causing spontaneous filming of the oil over gas bubbles which drives the flotation and leads to the formation of an oleic foam (froth) that is recovered by skimming.^{36,38,299}

Foams in harsh environments. Foams can be injected in to a petroleum reservoir to control the mobility of injected fluids or for the blocking of selected zones or channels with consequent diversion of injected fluids into other regions of the reservoir. Suitable foams can be formulated for injection with a wide range of gases, from air/nitrogen,^{300–303} to hydrocarbons,^{303–307} to carbon dioxide,^{303,308,309} or steam.^{303,310–312} A major challenge is the proper selection of foam-forming surfactants, and there have been several hundred papers published in the past 35 years on appropriate foam characteristics. Some of the characteristics thought to be necessary for a foaming agent to be effective (including cost-effective) in porous media under reservoir conditions are reviewed elsewhere.³¹³ These requirements can severely limit the number of surfactant candidates, especially if the operating environment involves high salinity, hardness, and temperature. In one study with such restrictions, from an initial set of 157 commercially available foaming surfactants recommended by suppliers around the world, solubilities were determined³¹⁴ at different salinity, hardness, pH and temperature conditions and it was found that only 9 had sufficient solubility and thermal stability

under such conditions. The most salinity and hardness tolerant surfactants were mostly betaines and sulfobetaines. Borchardt²⁸⁶ lists a number of foaming surfactants that have been used in less demanding environments.

Surfactant selection for practical foam performance relates to both foam formation and foam persistence, which in turn depend on the alteration of surface properties including surface tension lowering, surface elasticity, surface viscosity and disjoining pressure.^{114,315,316} Beyond the nature of the surfactant, compositions of the liquid and gas phases, temperature and pressure, practical foam performance in porous media depends on additional factors such as the nature of the porous medium, the presence and nature of other phases (including oil), foam quality, texture, and flow rate.^{313,314,317,318} To economically propagate foam through any kind of confining media one has to minimize the amount of surfactant loss through partitioning into the crude oil phase and/or through adsorption on the porous medium surfaces. Surfactant loss through partitioning into an oil phase can be responsible for surfactant losses of as much as 30%, although for very hydrophilic surfactants the partitioning into crude oil is very nearly zero. More serious are the results of a number of systematic studies of the adsorption properties of surfactants suitable for foam injection,^{177,319,320} which have shown that effective foaming surfactants may exhibit adsorption levels from near zero up to quite high levels on the order of 2.5 mg g^{-1} .

Much work has also been done on the development and selection of surfactants for making foams that can be used to increase the injectivity or productivity of wells by fracturing or acidizing the matrix rock. In either case, the goal is to increase flow capacity in the near-well region of a reservoir. Fracturing fluid foams have been used since the 1970s.^{321–328} They are typically 20–40% liquid phase, comprising water, water–methanol, aqueous gel, or oleic gel, and containing the surfactants and any other stabilizers. Acidizing foams, which improve the productivity of reservoirs by dissolving fine particles from flow channels, are aqueous foams in which the continuous phase is usually hydrochloric acid (carbonate reservoirs) or hydrofluoric acid (sandstone reservoirs), or a blend, together with suitable surfactants and other stabilizers.^{286,329} Chambers provides a useful review of the applications of foam stimulation fluids.³³⁰

Defoaming. Some agents will act to reduce the foam stability of a system (termed foam breakers or defoamers) while others can prevent foam formation in the first place (foam preventatives or foam inhibitors). There are many such agents, Kerner³³¹ describes several hundred different formulations for foam inhibitors and foam breakers. Although these materials are not usually surfactants themselves, their relevance to surfactants is that in all cases the cause of the reduced foam stability can be traced to various kinds of changes in the nature of the surfactant-stabilized interface. The addition to a foaming system of any soluble substance, that can become incorporated by co-solubilization or by replacement of the original surfactants into the interface, may decrease dynamic foam stability if the substance acts against the formerly present stabilizing factors. Some branched, reasonably high molecular mass alcohols can be used for this purpose. Not being very soluble in water, they tend to be adsorbed at the gas/liquid interface, displacing foam promoting surfactant and breaking or inhibiting foam. Alternatively, a foam can be destroyed by adding a chemical that actually reacts with the foam-promoting agent(s). Foams may also be destroyed

or inhibited by the addition of certain insoluble substances. Such hydrophobic compounds include waxes, hydrophobic silica, metal soaps, polypropylene glycols, amides and polyurethanes.³³² A review of defoaming mechanisms is given by Pugh.²⁷¹

Emulsions

Emulsions comprise a mixture of oil and water in which one of the phases, the dispersed phase, occurs as droplets dispersed within the other, the continuous phase. The droplet diameters are typically of the order of 0.1 to 100 μm , but may be as small as a few nanometres or as large as many hundreds of micrometres. The two most familiar types of emulsion are readily distinguished, O/W and W/O. However, emulsion characterization is not always so simple and it is not unusual to encounter multiple emulsions, O/W/O, W/O/W, and even more complex types.³⁷ Developments in and applications of double emulsions have been reviewed by Garti and Bisperink.³³³ As is the case with foams, occurrences of emulsions in industry are long-standing and widespread. Emulsions may be applied or encountered at all stages in the processing industries and have important properties that may be desirable in some process contexts and undesirable in others. Double emulsions have applications in cosmetics, agriculture, food, photography, leather, and drug-delivery.³³³ A number of books provide very useful introductions to the properties, importance, and treatment of emulsions^{37,189,264–266} in the petroleum industry. Although most emulsions are not thermodynamically stable, in practise they can be quite stable and may resist explicit demulsification treatments.

Discussions of surfactant applications in drilling fluids are given in references 334–336. Two types of oilwell drilling fluid (or “drilling mud”) are emulsion based, water-continuous and oil-continuous (invert) emulsion drilling fluids. Just as with classical suspension drilling muds, careful formulation is needed in order to minimize fluid loss into the formation, cool and lubricate the cutting bit, and to carry drilled rock cuttings up to the surface.³³⁷ The oil-continuous (invert) emulsion fluids are typically stabilized by long chain carboxylate or branched polyamide surfactants. Borchartd²⁸⁶ lists a number of other emulsion stabilizers that have been used. In the case of carboxylate surfactants, the calcium form is often used to ensure stabilization of the water-in-oil emulsion type (involving the oriented-wedge mechanism).

Emulsions in petroleum production. In oilfields, after the primary and secondary cycles of oil recovery, chemicals may be injected to drive out additional oil in an enhanced oil recovery process, which may involve creating *in situ* emulsions in the reservoir.¹¹⁵ In a petroleum reservoir the relative oil and water saturations depend upon the distribution of pore sizes in the rock. The capillary pressure, or pressure difference across an oil/water interface spanning a pore, is given by,

$$P_c = 2\gamma \cos\theta/r \quad (3)$$

where γ is the oil/water interfacial tension, θ is the contact angle, measured through the water phase at the point of oil/water/rock contact, and r is the effective pore

radius. In a water-wet reservoir the water will have been imbibed most strongly into the smallest radius pores, while the largest pores will retain high oil contents. As water is injected during a secondary recovery process the applied water pressure increases and the larger pores will imbibe more water, displacing oil which may be recovered at producing wells. There is a practical limit to the extent that the applied pressure can be changed by pumping water into a reservoir however, so that after waterflooding some residual oil will still be left in the form of oil ganglia trapped in the larger pores where the viscous forces of the driving waterflood could not completely overcome the capillary forces holding the oil in place.

The ratio of viscous forces to capillary forces correlates well with residual oil saturation and is termed the capillary number. One formulation of the capillary number is,

$$N_c = \eta v / \gamma \quad (4)$$

where η and v are the viscosity and velocity of the displacing fluid. The functional form of the correlation is illustrated in reference 239. During waterflooding N_c is about 10^{-6} and at the end of the waterflood the residual oil saturation is still around 45%. In order to recover the remaining oil one must increase the capillary number. This could be done by raising the viscous forces, *i.e.* viscosity and velocity, but in practise does not achieve the desired orders of magnitude increase.

Chemical flooding involves the injection of a surfactant solution which can cause the oil/aqueous interfacial tension to drop from about 30 mN m^{-1} to near-zero values, on the order of 10^{-3} to $10^{-4} \text{ mN m}^{-1}$, allowing spontaneous or nearly spontaneous emulsification and displacement of the oil.^{338,339} Sharma³⁴⁰ has reviewed the types of surfactants used for enhanced oil recovery processes. The exact type of emulsion formed can be quite variable, ranging from fine macroemulsions, as in alkali/surfactant/polymer flooding,²³⁹ to microemulsions.^{341,342} Microvisualization studies suggest that with such low interfacial tensions, multiple emulsions may form, even under the low flow rates that would be produced in a reservoir. Fig. 6 shows an

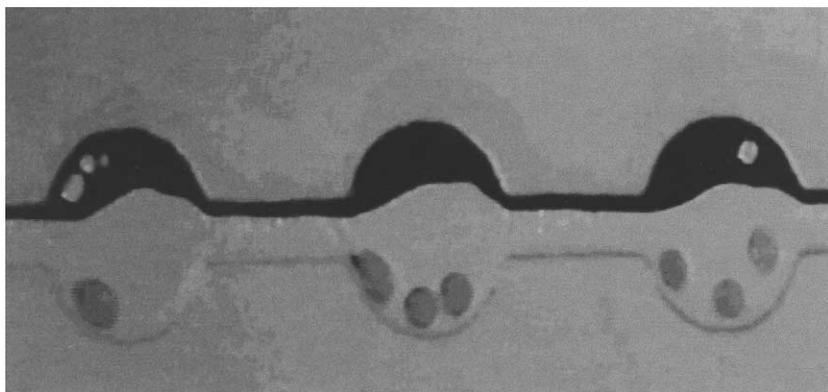


Fig. 6 Example of multiphase flow in an etched glass micromodel. Crude oil is being displaced by an alkali/surfactant/polymer solution. The droplets in the upper field of view are W/O while the lower droplets are W/O/W.⁴²² (Reproduced with permission from *Surfactants, Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press.)

example of multiphase flow in an etched glass micromodel wherein crude oil is being displaced by an alkali/surfactant/polymer solution at low flow rate (advance rate of about 2 m day^{-1}). Even at such a low flow rate, the displacement and tortuous flow have combined to produce both water-in-oil emulsion (top of the pores) and water-in-oil-in-water multiple emulsion (lower regions of the pores). Details of the chemical formulation are given in reference 343.

Microemulsions are stable emulsions of hydrocarbons and water in the presence of surfactants and co-surfactants. They are characterized by spontaneous formation, ultra-low interfacial tension, and thermodynamic stability. The widespread interest in microemulsions and use in industrial applications are based mainly on their high solubilization capacity for both hydrophilic and lipophilic compounds, their large interfacial areas and on the ultralow interfacial tensions achieved when they coexist with excess aqueous and oil phases. The properties of microemulsions have been extensively reviewed elsewhere.³⁴⁴⁻³⁵⁰ The ultralow interfacial tension achieved in microemulsion systems has application in several phenomena involved in oil recovery as well as in other extraction processes (*i.e.*, soil decontamination and detergency).

As with alkali/surfactant/polymer formulations, microemulsions are injected into reservoirs as part of enhanced oil recovery (EOR) processes which use interfacial tension lowering to mobilize the residual oil left trapped in the reservoirs after waterflooding. The optimum surfactant formulation for a microemulsion system is dependent on many variables (*e.g.*, pH, salinity, temperature, *etc.*). Some of the components in a typical formulation are listed in reference 422. The surfactants and co-surfactants must be available in large amounts at a reasonable cost. In addition, they should also be chemically stable, brine soluble and compatible with the other formulation components. Common surfactants used are petroleum sulfonates and ethoxylated alcohol sulfates.^{239,340} The degree of interfacial tension lowering depends on the phase behaviour of the oil/brine/surfactant mixture. Surfactants are generally used at concentrations much higher than their critical micelle concentration (cmc). Phase behaviour will depend on the surfactant partition coefficient between the oil and brine. The advent of new and more cost-effective surfactants and polymers, along with improved reservoir characterization, should lead to substantial design improvements.

Although producing a more efficient oil displacement than alkali/surfactant/polymer flooding, microemulsion flooding has developed slowly so far because of its complex technology and higher costs. Nevertheless, numerous field pilot tests, has been reported, primarily using previously waterflooded reservoirs.^{351,352} Many field experiments have failed or have displayed poor performances because of inadequate well patterns, poor knowledge of reservoir characteristics, or degradation of chemicals, leading to loss of mobility control. Some pilot tests, with better reservoir characterization and properly designed chemicals, have been reported to be technically successful with recoveries in the order of 50% of the oil at the start of the flood, recovering two-thirds of the residual oil.^{353,354} Further information on chemical flooding for reservoir oil recovery and for environmental soil remediation can be found in reference 36.

Some emerging applications involve the possible use of macroemulsions, as opposed to the microemulsions discussed in the previous section. These emulsions would be injected or produced *in situ* in order to either for blocking and diverting, or

for improved mobility control. Broz *et al.*³⁵⁵ and French *et al.*³⁵⁶ have proposed the use of oil-in-water emulsions for blocking and diverting of injected steam. For mobility control, there is some evidence to suggest that the *in situ* formation of heavy water-in-oil emulsions, such as sometimes happens during cyclic steam stimulation of heavy oil reservoirs, can improve the oil mobility, and hence recovery, in water-wet reservoirs.³⁵⁷ This apparently only occurs for certain conditions of emulsion properties, flow conditions, and rock wettability, because the improved oil mobility in the reservoir has to occur despite the fact that the bulk phase emulsion viscosity would be greater than that of the oil alone.

Other applications. Oil spills at sea can cause significant environmental damage. If the spill cannot be contained and removed mechanically, then chemical treatment agents must often be incorporated into the clean-up procedures. Following the actual spill of an oil onto the sea some of the slick will break into an O/W emulsion and disperse.³⁵⁸ Otherwise, the oil will pick up water to form a high water content and very viscous water-in-oil “mousse” emulsion, probably stabilized by mechanically strong films^{359,360} comprised of asphaltenes and/or natural surfactants.^{360–363} This complicates the use of dispersants and/or demulsifiers.³⁶⁴ A fairly large number of demulsifying/dispersing formulations have been created for application to marine oil spills.^{358,365,366} These are usually formulated to have a tendency to promote oil-in-water emulsion formation, and tend to be moderately hydrophilic, having hydrophile-lipophile balances (HLBs) in the range 10 to 12.^{365,367} Such values can be obtained, for example with an appropriate blend of Span® and Tween® surfactants. Some surfactant dispersants include sulfosuccinates, sorbitan esters of oleic or lauric acid, polyethylene glycol esters of oleic acid, and ethoxylated fatty alcohols. Determining effectiveness of a chemical agent is a complex issue because it is a function of the oil type, composition, the amount of oil present and how long it has weathered. This has been a major stumbling block in the development of a universal treatment agent.³⁶⁸

Asphalt emulsions are used to produce a smooth, water-repellant surface in road paving. First, an asphalt oil-in-water emulsion is formulated which has sufficiently low viscosity to be easy to handle and apply, and which has sufficient stability to survive transportation, brief periods of storage, and the application process itself. After application the emulsion needs to break quickly. The asphalt emulsions are usually stabilized either by natural naphthenic surfactants released by treatment with alkali (for a somewhat similar situation involving bitumen processing see also reference 140) or else by the addition of anionic or cationic surfactant.³⁶⁹ When stabilized by cationic surfactant, the positive charge may facilitate binding of the asphalt droplets to the gravel or rock surfaces.¹⁸⁹

Demulsification. Some emulsions are undesirable when they occur. In process industries chemical demulsification is commonly used to separate water from oil in order to produce a fluid suitable for further processing. The specific type of emulsion treatment required can be highly variable, even within the same industry. The first step in systematic emulsion breaking is to characterize the emulsion in terms of its nature (O/W, W/O, or multiple emulsion), the number and nature of immiscible phases, the presence of a protective interfacial film around the droplets, and the sensitivity of the emulsifiers.^{370–372} Based on an emulsion characterization, a chemical addition can be

prescribed to neutralize the effect of the emulsifier, followed by mechanical means to complete the phase separation. A wide range of chemical demulsifiers are available in order to effect this separation.^{373–377} Selecting the best demulsifier however, is complicated by the wide range of factors that can affect demulsifier performance, including oil type, the presence and wettability of solids, oil viscosity, and the size distribution of the dispersed water phase.

Demulsifiers are frequently surfactants; the relationship between demulsifier structure and performance has been studied for over 50 years.³⁷⁸ Mikula *et al.*²⁰³ trace the historical evolution of demulsifier chemistry and effective concentration range, and several reviews of demulsifier chemistry and properties are also available.^{379–383} A demulsifier must displace or counteract the emulsifying agent stabilizing the emulsion, and promote aggregation and coalescence of the dispersed phase into large droplets that can be separated.^{376,377}

Examples of the primary active agents in commercial demulsifiers include ethoxylated (cross-linked or uncross-linked) propylene oxide/ethylene oxide polymers or alkylphenol resins. These products are formulated to provide specific properties including hydrophile–lipophile balance (HLB), solubility, rate of diffusion into the interface, and effectiveness at destabilizing the interface.^{266,384}

The classification of surfactants as demulsifiers is usually based on chemical structure.^{385,386} Demulsifier surfactants include soaps,^{380,387} glyceryl esters, fatty acid esters, fatty alcohols, and alkylphenol ethoxylates; alkyl sulfonates, alkyl aryl sulfonates, and alkyl aryl sulfates;^{379,380} alkylpolyoxyethylene glycol ethers and alkylphenol (ethylene oxide) ethers; derivatives of alkyltrimethylammonium salts and alkylpyridium salts, and polyester amines,^{380,383} among others. Several families of chemicals can be tailor-made to accommodate different emulsion types by adjusting surface activity and the rate at which the demulsifiers move to the interface. For example, the addition of ethylene oxide and/or propylene oxide to formaldehyde resins and to diamines or higher functional amines yields a variety of modified polymers that perform well at relatively low concentrations. The low molecular weight demulsifiers can be transformed into high-molecular-weight products by reactions with diacids, diepoxides, diisocyanates, and aldehydes.^{380,385–388} A wide range of properties and parameters are used to characterize surfactant demulsifiers and predict their performance, from physical properties to compositional and structural analyses,^{203,383,389} although in practice the degree of characterization needed to tailor a demulsifier based on first principles is prohibitive.

3 Other surfactant applications

Surfactants in biological systems

The understanding of the pulmonary surfactant system, although discovered in 1929, has only been applied clinically since about 1990 for the treatment of respiratory distress syndrome. Surfactant replacement therapy may also be used in treating other forms of lung disease, such as meconium aspiration syndrome, neonatal pneumonia and congenital diaphragmatic hernia.³⁹⁰ Lung surfactants, composed of phospholipids and proteins,^{391,392} is necessary to maintain a low surface tension at the

alveolar air-liquid interface. When there is a deficiency of surfactant the high surface tension of the thin aqueous layer lining the respiratory epithelium of the lungs would cause alveolar collapse at the end of expiration. Conversely, a reduced surface tension tends to keep alveolar spaces small, it counteracts alveolar expansion during inspiration and supports alveolar retraction during expiration.^{390,392} In fact, the surface tension responds dynamically to changes in alveolar radius, to a plateau value of below 10 mN m^{-1} , in order to maintain constant alveolar pressure throughout the ventilatory cycle.³⁹² The lung surfactant system may also protect the lung from injury and infection caused by inhalation of particles and micro-organisms.^{390,392} Details of lung surfactant composition, function and clinical studies are given in several reviews.^{390–392}

The formulation ingredients of therapeutic drugs includes amphiphilic molecules and polymers. Polymer-based colloidal drug delivery carriers include micelles, liposomes, nano- and micro-particles, and hydrogels.^{393,394} Polymeric micelles have emerged as drug delivery carriers for poorly water soluble drugs (often protein-based) because they can solubilize the active component in their inner core, protecting it from contact with the surrounding aqueous environment. The micelle shell provides stabilization in the aqueous environment and interacts with plasmatic proteins and cell membranes. Micelle formation of block copolymers is driven not only by hydrophobic effects, but by electrostatic interaction or intermolecular hydrogen bonding, leading to the formation of polyion and polypeptide micelles.³⁹³ Surface properties of the block copolymer micelle carrier can also be optimized to selectively improve properties such as biocompatibility, biodistribution, and residence time.³⁹³ Drug-release kinetics must be modified so that once below the cmc, the micelle will still be stable enough to reach the target tissue before dissociating. Details of polymer-based colloidal drug systems can be found in several reviews.^{393–395}

Other drug-delivery systems may include double emulsions, usually W/O/W, for transporting hydrophilic drugs such as vaccines, vitamins, enzymes and hormones.³⁹⁶ The multiple emulsion also allows for slow release of the delivered drug and the time release mechanism can be varied by adjusting the emulsion stability. Conversely, in detoxification (overdose) treatments, the active substance migrates from the outside to the inner phase.

Surfactants in health and personal care products

Quaternary ammonium surfactants (quats) provide an example of cationic surfactants that have potent germicidal activity in addition to their use as fabric softeners in detergents. The best known fabric softener and antistatic agent is ditallow dimethyl ammonium chloride (DTDMAC). Emulsifiers commonly have a *N*-alkyltrimethylammonium chloride or *N*-alkylimidazoline chloride configuration, and germicides, such as benzalkonium chloride, typically have a *N*-alkyldimethylbenzylammonium chloride structure.

The popularity of “natural” cosmetics stems from the perception of better purity, safety and efficacy. Although many products have the label “natural” or “herbal,” many of these merely contain herbal extracts, which have been added for marketing

value. Formulating a shampoo generally meets the following criteria: mild detergency, good foaming, good conditioning, adequately preserved and aesthetically appealing.³⁹⁷ Although there are no standards for a “natural” shampoo, it may incorporate the following, no hazardous chemicals, use of plant or plant-based surfactants, and only natural additives (*e.g.*, a viscosity builder such as xanthan gum) and preservatives (*e.g.*, an antimicrobial such as alkylpolyglucosides).³⁹⁷ The meaning of the phrase “natural surfactant” may also be stretched to mean not just a surfactant taken directly from a natural source, but that one that was derived from a natural source *via* chemical reaction(s).

Cosmetic formulations are dependent on new formulation techniques for emulsions, particularly for storage properties.³⁹⁸ The phase inversion temperature (PIT) emulsion and microemulsion are characterized by fine droplet sizes which are highly stable; microemulsions are useful for creating a clear formulation of O/W and also appear to create a less irritating product.³⁹⁹ In a PIT system, the water/oil emulsion is cooled below the inversion range temperature, yielding an oil/water emulsion which generally has droplet sizes less than 200 nm, resulting in high kinetic stability. These may be called “blue emulsions” because of their blue glimmer. This formulation technique has found use in deodorant emulsion preparation.³⁹⁸ Microemulsions may also be formed directly, but they are only stable over a limited temperature range. Stabilizers in the form of new surfactants (*e.g.*, alkyl polyglycosides) may extend the stability range over increased temperature ranges. Stability is also dependent on HLB, so a precise co-emulsifier concentration must be selected.³⁹⁸ Good cosmetic formulations also yield good skin-product interactions and therefore good penetration of active ingredients into the skin layers. A hand cream, for instance, may be an O/W macro-emulsion with a 10–25% oil phase, or a W/O emulsion, which has a greasier feel and leaves a longer-lasting residue.³⁹⁹ The emulsifier chosen in each formulation is usually determined by its HLB or PIT. Phase behaviour as the product dries on the skin is an important factor in producing an effective product.³⁹⁸

Surfactants in foods

Surfactants are involved in the production of many common food items and can be found in the extraction of cholesterol, solubilization of oils, liquor emulsification, prevention of component separation, and solubilization of essential nutrients. One popular example is ice cream, a partially frozen foam that is 40–50% air (by volume). The first step in formulating ice cream is to create an emulsion. The homogenization step forces the hot ingredients (milk fats, milk solids-no-fat, sweeteners, corn-syrup solids, stabilizers/emulsifiers, other dry solids) through small orifices under moderate pressure (about 15 to 19 MPa). Fat droplet diameters decrease to 0.4 to 2.0 μm , allowing a large surface area for adsorption of proteins (which in turn stabilize the emulsion to coalescence), and the uniformity of droplet sizes result in greater stability of fat droplets during ageing, a better whipping ability and a smoother, more uniform final product. The adsorption of emulsifiers (such as egg yolk, sorbitan esters, diglycerides) decreases the interfacial tension between fat globules and the surrounding liquid phase, or serum, even more than does just mere adsorption of proteins (to about 2.2 mN m^{-1}). Ice cream stabilizers (such as guar, carboxymethyl cellulose,

xanthan, *etc.*) are used to produce smoothness in body and texture, reduce ice and lactose crystal growth during storage, provide product uniformity and resist melting.⁴⁰⁰

The second stage in ice cream production is foaming and emulsion destabilization. This is analogous to the foaming step in whipped cream.^{401,402} Air is incorporated by whipping or by air injection. The added shear causes controlled partial coalescence (enhanced by the adsorbed emulsifier), causing air to be trapped in clumped fat globules, and also ice formation. When whipping and freezing occur simultaneously, good fat destabilization is achieved and a complex internal structure is achieved.⁴⁰⁰

Beer quality is often judged by the foam of the dispensed beer. Desirable visual qualities include stability, quantity, lacing (adhesion), whiteness, creaminess and strength.⁴⁰³ Foam stability is the perceived best indicator of a good beer. Foam-stabilization comes from amphipathic polypeptides from malt and bitter compounds, particularly iso- α -acids, and from the absence of lipophilic materials.⁴⁰⁴ Unlike champagne, where foam film lifetimes are short (hydrodynamic control), beer foam has a slower drainage rate due to the effect of disjoining pressure of two interfaces in close proximity.⁴⁰⁵ A beer that has smaller bubbles of uniform size tends to have a more stable foam. Several reviews have been written on this aspect of beer (and champagne) foams.^{403,404,406}

Surfactants are a key component in the manufacture of edible coatings. A finish coat or polish may be added to chocolate- and sugar-panned confectionery products to produce an aesthetically pleasing gloss. These are commonly ethanol-based shellac and corn zein coatings, but may also include water-based whey proteins.⁴⁰⁷ Surfactants are added to create a dispersion of the coating particles, which then allows for proper wetting and adhesion over the candy surface. A problem with chocolate blend coating is "bloom" where the fat crystallizes and the cocoa butter separates.⁴⁰⁸ Crystal modifiers, emulifiers such as distilled monoglycerides, lactic acid esters of monoglycerides, sorbitan monostearate and polysorbate 60, are added to stabilize the fat. The latter may also be used to increase the palatability of the confection by forming an emulsion between the fat and mouth saliva, which minimizes the waxy mouthfeel.⁴⁰⁸

Margarine is an example of a W/O emulsion. Consisting of 80% fat, the hot homogenized mixture of fat crystals, liquid oil and water does not have to be a stable emulsion since the emulsion is quickly set by rapid chilling. Lecithin, a typical ingredient in margarine, enhances the solubility of monoglycerides in the oil blend, and monoglycerides reduce the interfacial tension between the oil and water phases. Emulsifiers also lend to a creamier product.⁴⁰⁸ Mayonnaise is an example of an O/W emulsion in which the emulsifier is egg yolk (a source of phospholipids).⁴⁰⁸

Surfactants in crop protection

Crop protection products refer to pesticides, herbicides, fungicides and insecticides. The formulation of pesticides is significant in terms of product stability and product performance. The current trend in crop protection is towards products that are more potent, safer to user, having less impact on the environment, more convenient to use and improved efficiency of the applied product. A review of how science and technology optimizes the physical properties of the product and maintains/improves product

performance is given in reference 409 In the case of sprayed products, colloid and interface science impacts all aspects of application. First, spray droplets impact the leaf surface, creating a foliar deposit from which the pesticide moves into the leaf or contacts the pest. The spray pattern is influenced by the applicator nozzle, the physical properties of the spray fluid and the movement of sprayer vehicle. The formulation influences impact and retention of the droplets, the residence time of the deposit, and the availability of the active ingredient to move into the plant. External factors such as temperature, humidity, wind, sunlight and rainfall also play roles in efficacy.⁴⁰⁹

Typical surfactants used in pesticide formulations are ethoxylated alcohols, alkylphenols, sorbitan and alkylamines.⁴¹⁰ Organosilicone surfactants have begun appearing in commercial spray-application products.⁴¹⁰ The latter show improved surface tension lowering (for improved leaf wetting) and a low dynamic surface tension (for spray-drop retention on leaves).⁴¹⁰ The organosilicone surfactants easily break down, which is an environmental bonus, but the lack of stability poses difficulty in product storage as ready-to-use products.⁴¹⁰

Surfactant toxicity and persistence

Surfactants are so common in everyday household use that they are widely considered to be quite safe. Britton⁴¹¹ points out that this comfort zone with commercial surfactants should not be extended to situations where they enter surface waters, because surfactants exhibit considerable toxicity to aquatic organisms. There is a need to understand the environmental properties and risks associated with any large volume chemicals. The mass of surfactants that could ultimately be released into the environment, for example, is significant. A 1995 estimate of the global use of linear alkylbenzenesulfonates, alcohol ethoxylates, alkylphenol ethoxylates, alcohol sulfates, and alcohol ether sulfates totaled 3 million tonnes.⁴¹² Surfactant usage in industry will probably increase as new applications are found. In addition to products, many industries produce waste containing significant amounts of suspended matter for which treatment incurs significant technological challenges and costs.⁴¹³⁻⁴¹⁵

The toxicity and persistence of surfactants is now fairly predictable for a variety of environmental situations and several reviews are available.^{411,412,416-420} Much of the available information deals with surfactant release into surface waters and soil. Under aerobic conditions many surfactants are readily biodegraded, while anaerobic biodegradation generally proceeds more slowly. An illustration of possible aerobic and anaerobic pathways for the biodegradation of alcohol ethoxylate surfactants is shown in Fig. 7 (see Britton⁴¹¹ for further discussion). Studies of the long term stability of surfactants are now starting to appear, including conditions relevant to industrial usage.⁴²¹

The toxicity of surfactants naturally depends greatly upon their structure. Increasing alkyl chain length in the hydrophobic group will generally increase toxicity, whereas increasing ethylene oxide (EO) numbers with the same hydrophobic group will generally decrease toxicity. These trends are understandable when one considers the toxicity mechanism of surfactants, namely membrane disruption and protein denaturation, is a function of the surface-active properties of surfactants.⁴¹¹ There-

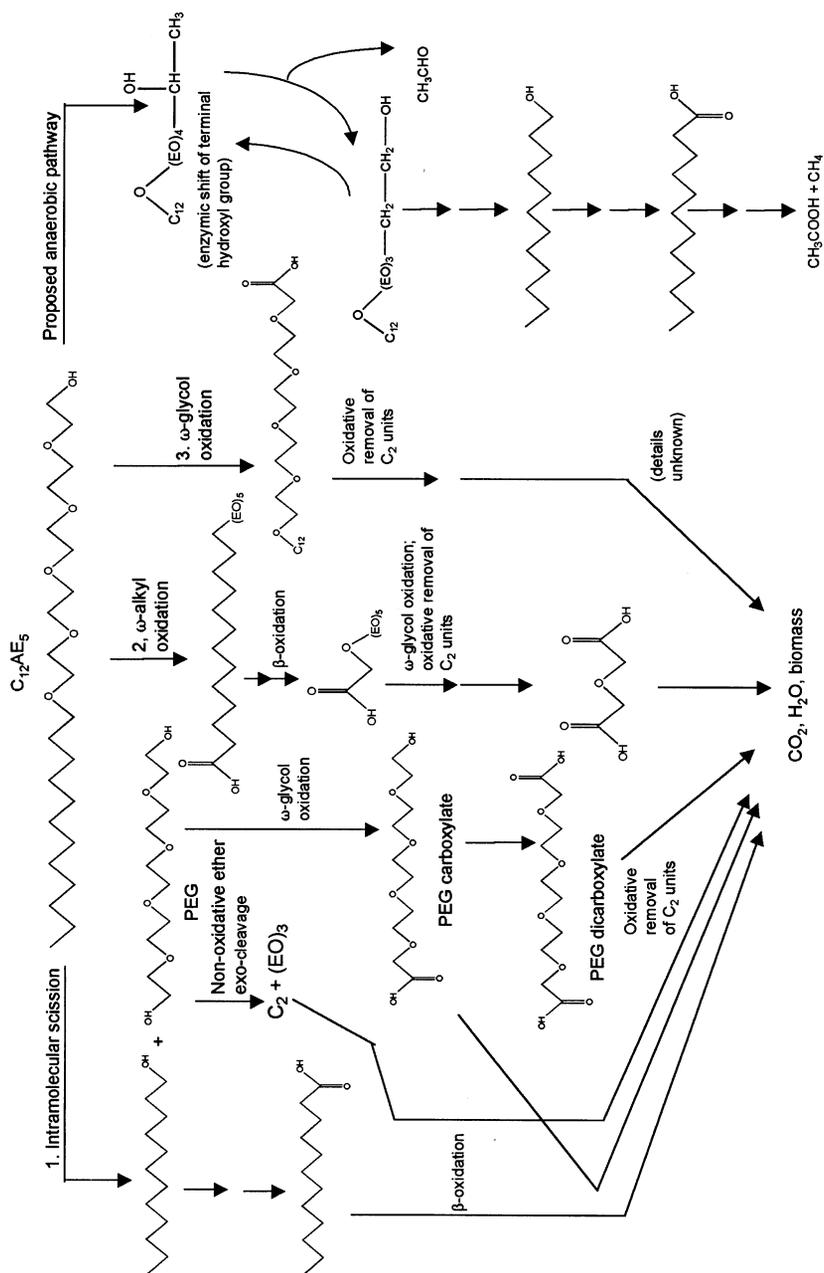


Fig. 7 Some possible biodegradative pathways for linear alcohol ethoxylate surfactants.⁴¹¹ (Reproduced with permission from *Surfactants, Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press.)

fore, the alteration of surface-active properties *via* structure changes should affect toxicity.

As with all chemicals, the use of surfactants brings with it the need to understand the environmental fate and effects of these chemicals, both in normal applications and in accidental releases. An obvious constraint for surfactant-based soil and aquifer remediation, for example, is that any surfactants left behind must not impose an environmental threat, and the environmental issues concerned with the transport of surfactants through the subsurface must be addressed as part of the advancement of this technology.²⁵⁴ The regulatory environment for surfactant usage has evolved considerably over the past several decades, and environmental risk assessment requires knowledge of biodegradation and toxicity of these chemicals.⁴¹¹ There are some common themes in surfactant biodegradation, such as mechanisms for degrading the alkyl chains that form the hydrophobic groups of all commercial surfactants, and toxicity of surfactants is also reasonably predictable, so that it is possible to arrive at reasonably sound judgments on the environmental safety of surfactants.⁴¹¹ As with other colloidal species, continued research is needed to understand the health hazards linked to surfactants.

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