Chemistry World

Surfactants: the ubiquitous amphiphiles

The surfactant industry is a huge and dynamic business, and soap is just the start, says Tony Hargreaves.

Most familiar of all surfactants is soap, a simple substance which, in water, clearly demonstrates two effects. It produces foam due to its action at the air-water interface, and it makes the grease transfer from grubby hands into the soapy water as a result of its activity at the water-oil (grease) interface. However, soap was probably not the first surfactant in the service of humankind.

Many plants produce significant quantities of saponins (steroid or triterpenoid glycosides) which have surfactant properties. One such plant is the soapwort Saponaria officianalis whose foliage yields a glycoside capable of wetting, foaming and grease dispersion - the very qualities that we recognise in a modern detergent. It is likely that the saponins provided our ancestors with our first useful surfactants. These natural glycosides are still in use today for specialised processes such as washing delicate fabrics.

Fig 1. The global surfactant market

Modern surfactants, however, are of many different chemical types and do far more than produce foams and disperse grease. The global surfactant industry is a multi-billion pound business (*Fig 1*), with markets everywhere from household detergents to explosives (*Table 1*). Surfactants (surface active agents) can be broadly defined as compounds which, when dissolved in water, concentrate at surfaces (interfaces) such as water-air or water- oil. The interfacial activity of these substances, which can be explained in terms of their molecular structure, gives rise to a wide range of surface chemistry functions: wetting, emulsifying, solubilising, foaming/defoaming, rheology-modifying, antistatic, 'glossing', lubricity and surface conditioning.

Seldom are surfactants on their own put directly into use. In the area of household cleaning preparations, the surfactant is normally blended with a range of ingredients such as other surfactants, thickeners, foaming or defoaming agents, alkalis/salts, chelating agents and so on. This is the province of specialist formulators such as Colgate Palmolive, Unilever, and Procter & Gamble.

Table 1. The major surfactant markets

	Value (£m)	Quantity (kt)
Household detergents	2800	4000
Industrial and institutional cleaning	420	530
Personal care	940	860
Crop protection	290	200
Oilfield	390	440
Paints and coatings	140	160
Textile spin finish	200	160
Textile auxiliaries	450	500
Construction	190	470
Emulsion polymerisation	240	290
Food	190	200
Leather	30	60
ORE/mineral	60	150
Plastic additives	60	40
Pulp and paper	100	120

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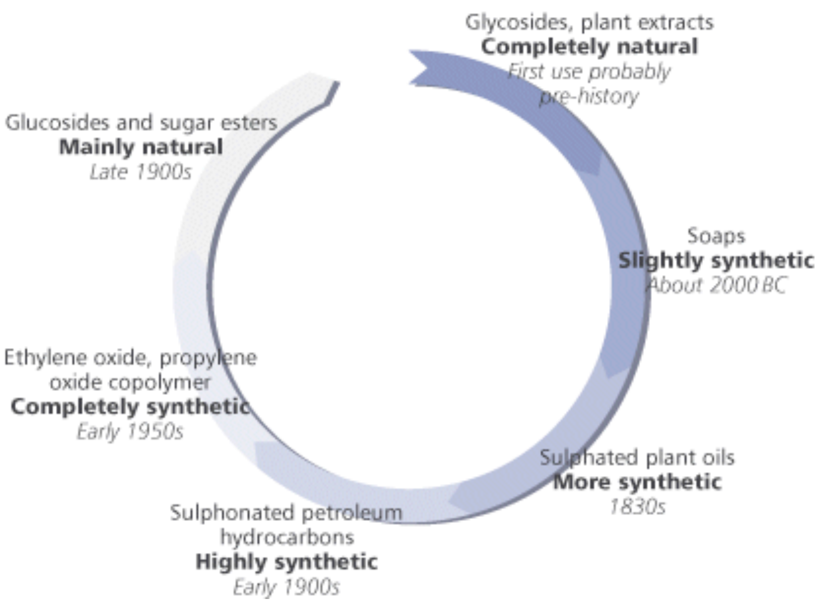
Explosives	10	10
Other	630	380
Total	*7140*	*8570*

Generally, these modern formulated products rely on man-made surfactants but there are exceptions. Certain foods, in particular, include natural surfactants such as lecithin, an emulsifier in chocolate and ice cream manufacture. Nature also relies heavily on surfactant chemistry: our liver produces surfactants, the bile acids; our lungs use surfactants to maximise the efficiency of gas exchange across the air-water interface; and in every cell in every organ in our bodies there is a complex membrane that functions due to surfactant chemistry.

Surfactants in antiquity

People first began to make surfactants, namely soap, in about 1500 BC, but soap-like substances have been found dating back to 2800 BC. Soap was, and still is, made by the alkaline hydrolysis of animal fats or vegetable oils - a process known as saponification. Soap is the most widely used single surfactant, accounting for around 30 per cent of the current surfactant market.

Moving on from soaps - and into the 19th century - the next surfactants to be developed were the sulphates and sulphonates of vegetable oils. The reaction of castor oil with sulphuric acid is a classic example from the late 1800s. In this reaction the product is a mixture of sulphates and sulphonates which, after neutralisation with sodium hydroxide, give a product known as Turkey Red oil useful in the dyeing of linen.



Soap going full circle?

Later, the development of sulphonation and sulphation processes using other oils as reactants led to a move away from natural and renewable plant oils and animal fats to the sulphonation of petroleum products. The introduction of alkyl benzene sulphonatis (ABSs), for example, was brought about by nucleophilic substitution in the benzene ring using oleum ($H_2S_2O_7$) or sulphur trioxide. The ABSs made a major contribution in changing the traditional soap powders to detergent powders for household laundry. One well-known example in the 1950s was the change in the composition of Lever Brothers' Persil, where the soap in the original formulation (PERborate+SILicate+soap) was replaced by ABS.

Other brands of washing powders followed suit and the word detergent is now a part of everyday vocabulary. Modern detergent powders now typically contain linear alkylbenzene sulphonates (LABSs), which biodegrade more quickly than the original ABSs.

Progress was not confined to the sulphonation of different oils, but was soon accompanied by ethoxylation, in which a few or many ethylene oxide (EO) molecules react with a fatty alcohol - which may be synthetic or plant derived - to make the surfactant molecule. Thus, alcohol ethoxylates, alcohol ether sulphates and alkyl phenol ethoxylates became available.

Along with the development of ether technology came the polymerisation of ethylene oxide with propylene oxide (PO) to give EO-PO copolymers - surfactants that are totally reliant on petrochemicals as raw materials.

But things may slowly be beginning to turn back around. Current pressure to move away from non-renewable petroleum feedstocks and towards plants as sources of raw materials has led to a lot of effort on developing surfactants from oleochemical feedstocks. Many recently-developed surfactants are an attempt to satisfy the modern consumers' desire for products to be 'more natural'.

Most important amongst these are surfactants derived from the carbohydrates sorbitol, sucrose, glucose and from plant oils such as coconut or palm kernel. Thus we have: sorbitan esters, sucrose esters, alkyl polyglucosides (AGs), alkyl glucamides (*Box 2*). Sorbitan esters are used as emulsifiers in cosmetics and the sucrose esters in food manufacture. The alkyl polyglucosides find application as detergents rather than as emulsifiers and are making inroads into some everyday products.

How surfactants work

A look through the surfactant literature presents us with a huge number of different surfactants, along with an even greater number of names. At the core of all this is some relatively simple chemistry.

All these surfactant molecules have in common the same basic molecular structure - a hydrophile attached to a lipophile - and it is this nature that makes them adsorb at surfaces. The hydrophile is attracted to water in preference to lipid-like substanoes (hydrocarbons such as oil and grease) whereas the lipophile is attracted to these in preference to water.

Other terms are sometimes used, for example, a hydrophile is a lipophobe and a lipophile is a hydrophobe. However, the use of 'phobe' is unfortunate because it implies repulsion whereas the true situation is one of only feeble attraction. Paraffin wax is lipophilic but it does not repel water, as is demonstrated by the fact that droplets of the liquid cling, somewhat precariously, to the underside of a wax block - the water must be attracted to the wax.

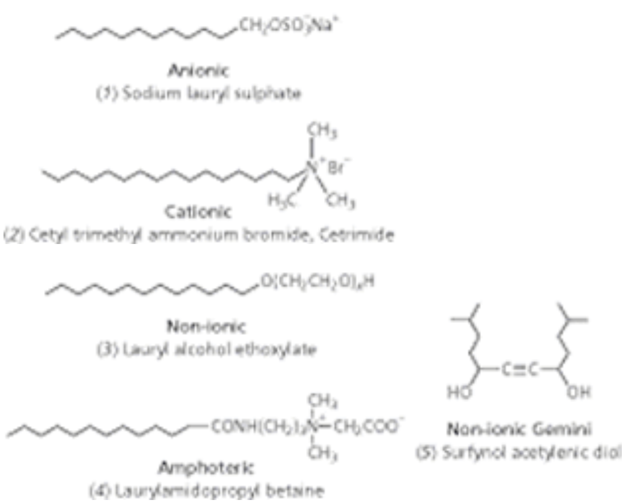
It is the amphiphilic nature of surfactant molecules that makes them bifunctional. This can be seen when oil/grease and water come together. No matter how much energy is expended in getting them to mix, the oil and water will always separate into two distinct phases. The intermolecular forces between water molecules and between oil molecules are stronger than the forces between water and oil molecules.

Added surfactant molecules adsorb at the oil-water interface, where they orient themselves such that the hydrophile is in the water and the lipophile is in the oil. With a little agitation the oil becomes dispersed in the water and the surfactant acts as an emulsifying agent.

Types of surfactants

Lipophiles are usually similar from one surfactant to another but hydrophiles show a range of chemical types and this is the basis for surfactant classification: anionic, cationic, non-ionic and amphoteric (Fig 2).

Fig 2. Structures of some common surfactants



Anionic surfactants, which include soap, are the most widely used for cleaning processes because many are excellent detergents. In anionic surfactants the hydrophile comprises some highly electronegative atoms, making these molecules strongly polar. The counterion is usually a small cation such as sodium but occasionally may be a larger cation such as ammonia or amines.

Cationic surfactants, in contrast, comprise a long chain hydrocarbon as the lipophile with a quaternary amine nitrogen as hydrophile, and a halide ion as counterion. An important property of cationics is that they are attracted to surfaces carrying a negative charge, upon which they adsorb strongly. Proteins and synthetic polymers can thus be treated with cationics to provide desirable surface characteristics. For example, hair conditioners and fabric softeners are cationic surfactants.

Amphoteric surfactants comprise a long hydrocarbon chain (lipophile) attached to a hydrophile containing both positive and negative charges, which give it the properties of a zwitterion. The simplest amphoterics can therefore behave as a cation or anion depending on pH. Mild and with low irritancy, amphoterics are widely used in shampoos.

Non-ionic surfactants are second to anionics in cleaning applications and are frequently used in conjunction with them. An important group of non-ionics includes those where the hydrophile comprises a chain of ethoxy groups and is known as the ethoxylates. Varying the number of ethoxy groups in the chain adjusts the amount of hydrophilic character in the final products.

Recent developments

Table 2 lists some of the major surfactant manufacturers and their products, along with some of their common applications. The whole adds up to a massive industry responding to the expanding technology of surfactants.

In all of the surfactants considered so far the basic structure is of a single lipophilic tail carrying a single hydrophilic head group and most surfactant development has been confined to this arrangement. However, a more radical approach is to use two lipophiles and two hydrophiles in the same molecule (eg 5, Fig 2).

Table 2. Major UK surfactant companies and some of their products

Croda	
anionic	Crodex, sodium lauryl sulphate, phosphate esters - emulsifiers for ointments and creams
cationic	Incroquats, stearalkonium chloride - hair conditioner
non-ionic	Crills, sorbitan stearate/oleate - cosmetics emulsifiers
amphoteric	Incronams - mild detergency for shampoos and bath products
Stepan	(formerly Manro)
anionic	Manro SDBS, sodium alkyl benzene sulphonate - dishwash liquids Manro BEC, sodium lauryl ether sulphate - primary surfactant in shampoos Manro SLS, sodium lauryl sulphate - dishwash liquids
non-ionic	Manromid, coconut monoethanolamide - foam stabiliser/booster in shampoos
amphoteric	Manroteric, cocoamidpropyl betaine - mild detergency for shampoos and bath products
Huntsman	(formerly Albright & Wilson)
anionic	Nansas, sodium dodecylbenzene sulphonate - dishwash liquids
cationic	Empigens, alkyl dimethyl benzyl ammonium chloride - disinfectants
non-ionic	Empilans, alcohol ethoxylates - cosmetics emulsifiers Empilan NPs, nonyl phenol ethoxylates - heavy duty degreasing detergents
amphoteric	Empigen CDs, cocoamphoacetate - non-irritant toiletries
ICI/Uniqema/Mona	
anionic	Atlas, isopropanolamine dodecylbenzene sulphonate - solvent/detergent degreasers
cationic	Atlas Gs, quaternary ammonium salts - emulsifiers and antistatics
non-ionic	Synperonic NPs, nonyl phenol ethoxylates - heavy duty degreasing detergents
amphoteric	Monaterics, 2-alkylimidazoline - mild detergency for shampoos and bath products

These structures, being twinned molecules, are known as Gemini, or dimeric, surfactants. They offer much greater surface activity at concentrations lower than those for regular surfactant molecules. A particular example of a Gemini surfactant is the acetylenic diol type which is used to formulate surface coatings because it offers excellent wetting characteristics at low concentrations with virtually no foaming. New Gemini structures are being researched by several companies, the extent of which is shown by the numerous patent applications. They include, for example, Surfynol, acetylenic diols from Air Products and Ceraluthion blends based on dicocoylethylenediamine PEG15 sulphate by Sasol.

Much of the research, particularly that of ENGEMS (European Network on Gemini Surfactants), is devoted to novel Gemini structures and their applications. Using Gemini molecules as drug delivery systems is one of the more active areas of research. Perhaps the most exciting research is aimed at using Gemini surfactants as synthetic vectors for introducing a selected gene into cells, as in gene therapy.

Clearly, surfactant technology is alive with exciting possibilities, working towards a healthier world from both a personal and environmental point of view.

Source: Chemistry in Britain

Acknowledgements

Tony Hargreaves is a consulting chemist working mainly in environmental monitoring for industry.

Further Reading

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1. Surfactants explained

Micelles

Surfactants have low solubility in water. A typical surfactant has a large lipophile (hydrophobe) which restricts its aqueous solubility. For example, sodium dodecylbenzene sulphonate has a solubility maximum of 0.04.mol l-1. Beyond this concentration the molecules associate to form colloidal aggregates known as micelles. This concentration is the critical micelle concentration (CMC). Different surfactants have different CMC values.

In a micelle the surfactant orients itself with its lipophiles towards the interior, thus presenting a hydrophilic surface to the water. The simplest micelles are spheres but as surfactant concentration increases the micelles grow and form rods.

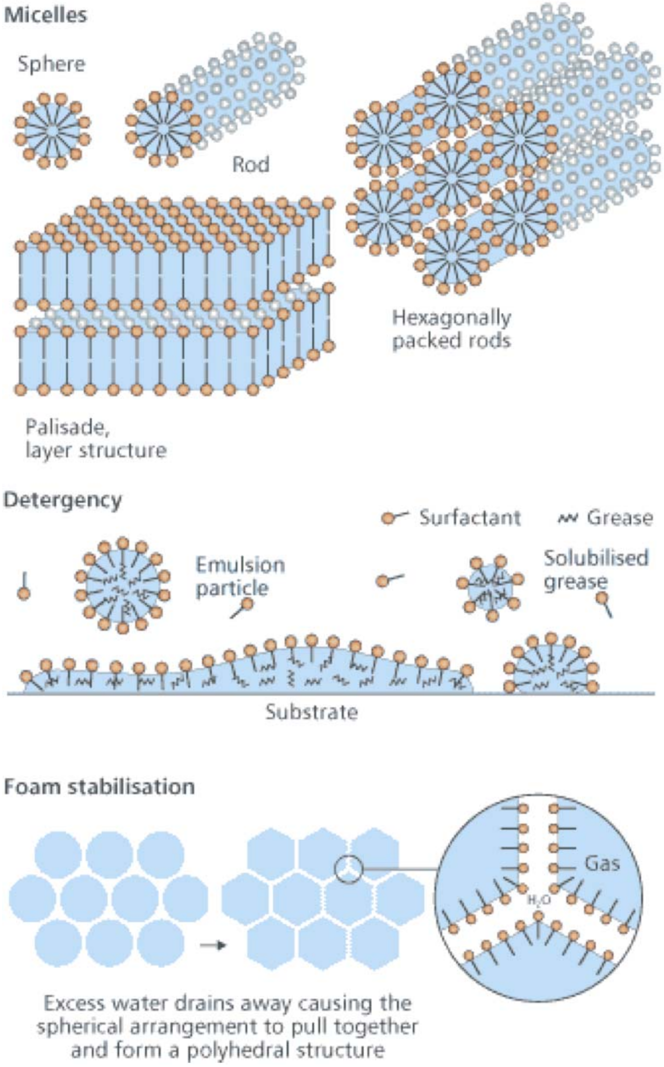
At high surfactant concentrations the rods form larger structures such as hexagonally packed rods and palisade arrangements. As these structures increase in size they take on a greater degree of order until, for the biggest structures, they occur as liquid crystals. These structural changes are reflected in the viscosity of the surfactant 'solution'.

Rheology

The flow characteristics of the surfactant in water is an important feature of many surfactant formulations. For surfactant systems these characteristics are explained in terms of the micelles. Where unassociated molecules are present the viscosity is virtually that of water.

The formation of spherical micelles has little effect, but where the sphere-to-rod changes occur there is a marked increase in viscosity. The hexagonal packing of rods causes viscosity to climb further but, surprisingly, the formation of the largest palisade structures results in a dramatic fall in viscosity.

The latter effect is due to the large layer-like structures being able to slide over each other so that there is little intermolecular friction. In surfactant technology the micelle structure can be manipulated to give a product with the desired properties such as a shampoo gel rather than a runny liquid.



Solubilisation
Micelles can act as solubilisers in which oily molecules of oil/grease/hydrocarbon are taken into the lipophilic core of the micelle and retained by the lipophile-to-lipophile attractive forces. By this means it is possible to make colloidal emulsions or microemulsions -sometimes called swollen micelles. An important application is to make a solvent such as a hydrocarbon 'dissolve' in water and surfactant.

Detergency
Washing dirty dishes or clothes involves a complex mechanism comprising many physical and chemical effects resulting from a variety of soil types and a range of substrate materials. However, the most important cleaning action is a result of surface chemistry and surfactants. Detergent action to remove oily/greasy soiling involves wetting, emulsification, solubilisation and micelles.

Emulsification
Adsorption at the water-oil interface results in dispersion of one phase into the other depending on the properties of the system. These dispersions are emulsions and of two types: oil-in-water (o/w) or water-in-oil (w/o).

Wetting
Water is not attracted on an oily/greasy surface, but with a surfactant present wetting occurs because the molecules adsorb at the oil-water interface in a manner similar to that seen for emulsification.

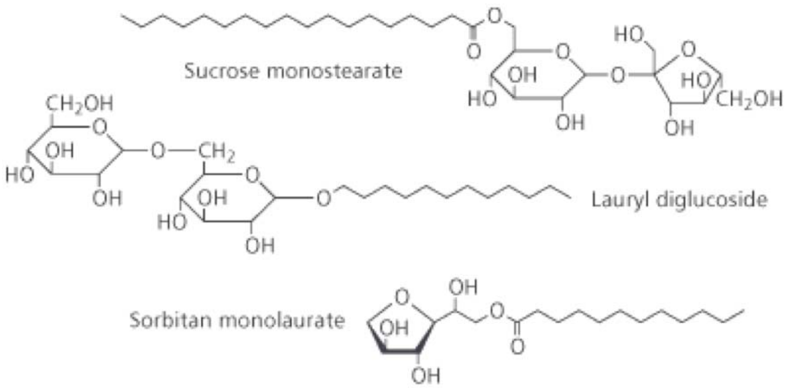
Foaming
A foam is a dispersion of gas in liquid, generally air in water, where there is only a small volume of liquid compared with the large volume of gas. Each gas space, or cell, has walls made up of a thin layer of water with surfactant molecules adsorbed at the surfaces. Adsorption of a suitable

surfactant creates a foam that gets its mechanical stability from surface elasticity and just the right amount of drainage in the water between the surfaces of the film.

2. 'Natural surfactants'

Carbohydrate-based surfactants, being based on plant-derived chemicals, use renewable resources, are readily biodegradable, non toxic and do not add to the Earth's CO_2 burden.

Structures of three common carbohydrate-based surfactants are shown below:



A few of the currently available carbohydrate-based surfactants include:

Alkyl polyglucosides - Triton APGs (Union Carbide), Plantcare (Cognis/Henkel), Lauryl glucoside, Monatrope (ICI/Uniqema)

Sorbitan esters - Crills (Croda) and Spans (ICI/Uniqema)

Sucrose esters - Crodestas (Croda)

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