1. Surfactant chemistry and general phase behaviour

1.1 SURFACTANTS IN COLLOIDAL SYSTEMS

The term *colloid* (which means "glue" in Greek) was first introduced in 1861 by Thomas Graham to describe the "pseudosolutions" in aqueous systems of silver chloride, sulfur, and Prussian blue which were prepared by Francesco Selmi in the mid-nineteenth century [1]. Such systems were characterised by a lack of sedimentation under the influence of gravity, as well as low diffusion rates. Graham thus deduced that the colloidal size range is approximately 1 μm down to 1 nm (i.e., 10^{-6} – 10^{-9} m). This characteristic still holds today and colloids are generally described as systems consisting of one substance finely dispersed in another. These substances are referred to as the dispersed phase and dispersion medium (or continuous phase) respectively, and can be a solid, a liquid, or a gas. Such combinations together with large surface areas associated with the characteristic size of colloidal particles give rise to a large variety of systems, practical applications and interfacial phenomena.

Amongst these systems, the most common and ancient class is probably the *lyophobic* ("liquid-hating") colloids, composed of insoluble or immiscible components. They can be traced back to the 1850's when Michael Faraday prepared colloidal gold sols, which involve solid particles in water [2]. More commonly encountered examples of lyophobic colloids are milk (liquid fat dispersed as fine drops in an aqueous phase), smoke (solid particles dispersed in air), fog (small liquid droplets dispersed in air), paints (small solid particles dispersed in liquid), jelly (large protein molecules dispersed in water), and bone (small particles of calcium phosphate dispersed in a solid matrix of collagen). A second and more recent class includes the *lyophilic* ("liquid-loving") colloids, which are solutions that form spontaneously and are thermodynamically stable. These systems consist of solute molecules that are polymers (i.e., of much larger size than the solvent molecules), and as such form a large and distinct area of research (polymer science).

Another major group of colloidal systems, also classified as lyophilic, is that of the so-called *association colloids*. These are aggregates of *amphiphilic* (both "oil and water-loving") molecules that associate in a dynamic and thermodynamically driven process that may be simultaneously a molecular solution and a true colloidal system. Such molecules are commonly termed "surfactants", a contraction of the term *surface-active agents*. As will be introduced below and described in more detail in Chapter 2, surfactants are an important and versatile class of chemicals. Due to their dual nature, they are associated with many useful interfacial phenomena, e.g., wetting, and as such are found in many diverse industrial products and processes.

1.2 CHARACTERISTIC FEATURES OF SURFACTANTS

Surface-active agents are organic molecules that, when dissolved in a solvent at low concentration, have the ability to adsorb (or locate) at interfaces, thereby altering significantly the physical properties of those interfaces. The term "interface" is commonly employed here to describe the boundary in liquid/liquid, solid/liquid and gas/liquid systems, although in the latter case the term "surface" can also be used. This adsorption behaviour can be attributed to the solvent nature and to a chemical structure for surfactants that combine both a polar and a non-polar (amphiphilic) group into a single molecule. To accommodate for their dual nature, amphiphiles therefore "sit" at interfaces so that their lyophobic moiety keeps away from strong solvent interactions while the lyophilic part remains in solution. Since water is the most common solvent, and is the liquid of most academic and industrial interest, amphiphiles will be described with regard to their “hydrophilic” and “hydrophobic” moieties, or “head” and “tail” respectively.

Adsorption is associated with significant energetic changes since the free energy of a surfactant molecule located at the interface is lower than that of a molecule solubilised in either bulk phase. Accumulation of amphiphiles at the interface (liquid/liquid or gas/liquid) is therefore a spontaneous process and results in a decrease of the interfacial (surface) tension. However, such a definition applies to many substances: medium- or long-chain alcohols are surface active (e.g., *n*-hexanol, dodecanol) but these are not considered as surfactants. True surfactants are distinguished by an ability to form oriented monolayers at the interface (here air/water or oil/water) and, most importantly, self-assembly structures (micelles, vesicles) in bulk phases. They also stand out from the more general class of surface-active agents owing to emulsification, dispersion, wetting, foaming or detergency properties.

Both adsorption and aggregation phenomena result from the hydrophobic effect [3]; i.e., the expulsion of surfactant tails from water. Basically this originates from water–water intermolecular interactions being stronger than those between water–tail. Finally another characteristic of surfactants, when their aqueous concentration exceeds approximately 40%, is an ability to form liquid crystalline phases (or lyotropic mesophases). These systems consist of extended aggregation of surfactant molecules into large organised structures.

Owing to such a versatile phase behaviour and diversity in colloidal structures, surfactants find application in many industrial processes, essentially where high surface areas, modification of the interfacial activity or stability of colloidal systems are required. The variety of surfactants and the synergism offered by mixed-surfactant systems [4] also explains the ever-growing interest in fundamental studies and practical applications. Listing the various physical properties and associated uses of surfactants is beyond the scope of this chapter. However, a few relevant examples are presented in the following section, giving an idea of their widespread industrial use.

1.3 CLASSIFICATION AND APPLICATIONS OF SURFACTANTS

1.3.1 Types of surfactants

Numerous variations are possible within the structure of both the head and tail group of surfactants. The head group can be charged or neutral, small and compact in size, or a polymeric chain. The tail group is usually a single or double, straight or branched hydrocarbon chain, but may also be a fluorocarbon, or a siloxane, or contain aromatic group(s). Commonly encountered hydrophilic and hydrophobic groups are listed in Tables 1.1 and 1.2 respectively.

Since the hydrophilic part normally achieves its solubility either by ionic interactions or by hydrogen bonding, the simplest classification is based on surfactant head group type, with further subgroups according to the nature of the lyophobic moiety. Four basic classes therefore emerge as:

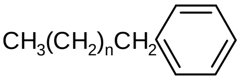
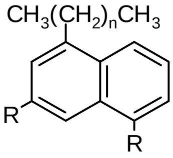
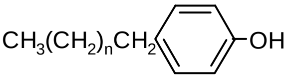
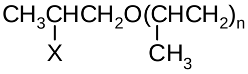
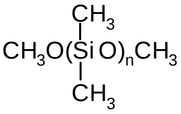
- the anionics and cationics, which dissociate in water into two oppositely charged species (the surfactant ion and its counterion),
- the non-ionics, which include a highly polar (non charged) moiety, such as polyoxyethylene ($-OCH_2CH_2O-$) or polyol groups,
- the zwitterionics (or amphoterics), which combine both a positive and a negative group.

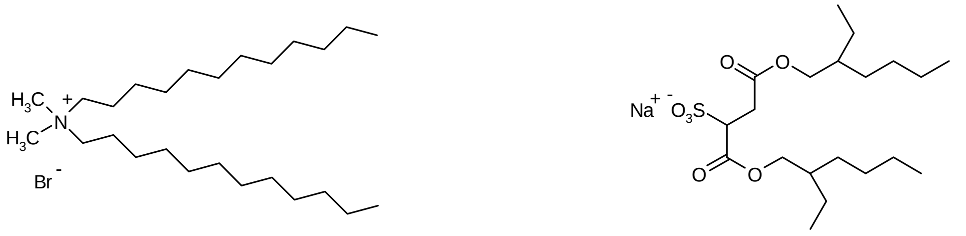
With the continuous search for improving surfactant properties, new structures have recently emerged that exhibit interesting synergistic interactions or enhanced surface and aggregation properties. These novel surfactants have attracted much interest, and include the catanionics, bolaforms, gemini (or dimeric) surfactants, polymeric and polymerisable surfactants [5, 6]. Characteristics and typical examples are shown in Table 1.3. Another important driving force for this research is the need for enhanced surfactant biodegradability. In particular for personal care products and household detergents, regulations [7] require high biodegradability and non-toxicity of each component present in the formulation.

Table 1.1 Common hydrophilic groups found in commercially available surfactants

Class	General structure
Sulfonate	$R–SO_3^- M^+$
Sulfate	$R–OSO_3^- M^+$
Carboxylate	$R–COO^- M^+$
Phosphate	$R–OPO_3^- M^+$
Ammonium	$R_xH_yN^+X^-$ (x = 1-3, y = 4-x)
Quaternary ammonium	$R_4N^+X^-$
Betaines	$RN^+(CH_3)_2CH_2COO^-$
Sulfobetaines	$RN^+(CH_3)_2CH_2CH_2SO_3^-$
Polyoxyethylene (POE)	$R–OCH_2CH_2(OCH_2CH_2)_nOH$
Polyols	Sucrose, sorbitan, glycerol, ethylene glycol, etc
Polypeptide	$R–NH–CHR–CO–NH–CHR'–CO–...–CO_2H$
Polyglycidyl	$R–(OCH_2CH[CH_2OH]CH_2)_n –...–OCH_2CH[CH_2OH]CH_2OH$

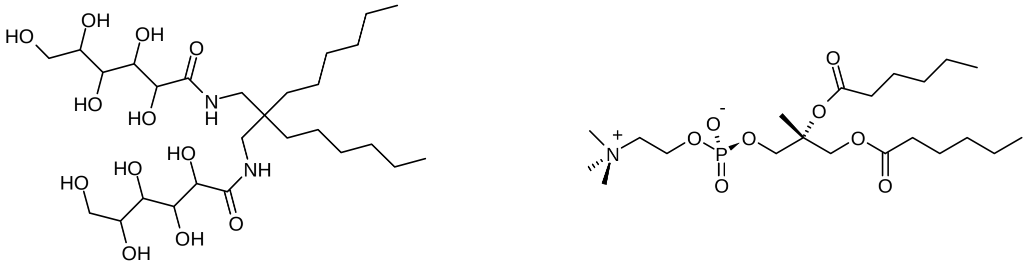
Table 1.2 Common hydrophobic groups used in commercially available surfactants

Group	General structure	
Natural fatty acids	$CH_3(CH_2)_n$	n = 12-18
Olefins	$CH_3(CH_2)_nCH = CH_2$	n = 7-17
Alkylbenzenes		n = 6-10, linear or branched
Alkylaromatics		n = 1-2 for water soluble, n = 8 or 9 for oil soluble surfactants
Alkylphenols		n = 6-10, linear or branched
Polyoxypropylene	 $CH_3\underset{X}{C}HCH_2O(\underset{CH_3}{C}HCH_2)_n$	n = degree of oligomerisation, X = oligomerisation initiator
Fluorocarbons	$CF_3(CF_2)_nCOOH$	n = 4-8, linear or branched, or H-terminated
Silicones	 $CH_3O(\overset{CH_3}{\underset{CH_3}{Si}}O)_nCH_3$	



Cationic: *n*-didodecyldimethylammonium bromide (DDAB)

Anionic: Sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT or AOT)

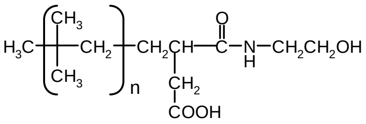
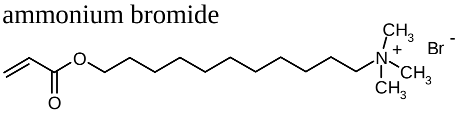


Non-ionic: di(hexyl)glucamide (di-(C6-Glu))

Zwitterionic: di-hexylphosphatidylcholine ((diC6)PC)

Figure 1.1 Chemical structure of typical double-chain surfactants.

Table 1.3 Structural features and examples of new surfactant classes

Classes	Structural characteristics	Example
Catanionic	Equimolar mixture of cationic and anionic surfactants (no inorganic counterion)	*n*-dodecyltrimethylammonium *n*-dodecyl sulfate (DTADS) $C_{12}H_{25}(CH_3)_3N^+\ {}^-O_4S\,C_{12}H_{25}$
Bolaform	Two charged headgroups connected by a long linear polymethylene chain	Hexadecanediyl-1,16-bis(trimethyl ammonium bromide) $Br^-(CH_3)_3N^+–(CH_2)_{16}–N^+(CH_3)_3Br^-$
Gemini (or dimeric)	Two identical surfactants connected by a spacer close to or at the level of the headgroup	Propane-1,3-bis(dodecyldimethyl ammonium bromide) C_3H_6 -1,3-bis$[(CH_3)_2N^+C_{12}H_{25}Br^-]$
Polymeric	Polymer with surface active properties	Copolymer of isobutylene and succinic anhydride  $H_3C\left[C(CH_3)_2-CH_2\right]_n-CH_2CH(CH_2COOH)-C(=O)-NH-CH_2CH_2OH$
Polymerisable	Surfactant that can undergo homo-polymerisation or copolymerisation with other components of the system	11-(acryloyloxy)undecyltrimethyl ammonium bromide 

A typical example of a double-chain surfactant is sodium bis(2-ethylhexyl)sulfosuccinate, often referred to by its American Cyanamid trade name Aerosol-OT, or AOT. Its chemical structure is illustrated in Figure 1.1, along with other typical double-chain compounds within the four basic surfactant classes.

1.3.2 Surfactant uses and development

Surfactants may be from natural or synthetic sources. The first category includes naturally occurring amphiphiles such as the lipids, which are surfactants based on glycerol and are vital components of the cell membrane. Also in this group are the so-called “soaps”, the first recognised surfactants [8]. These can be traced back to Egyptian times; by combining animal and vegetable oils with alkaline salts a soap-like material was formed, and this was used for treating skin diseases, as well as for washing. Soaps remained the only source of natural detergents from the seventh century till the early twentieth century, with gradually more varieties becoming available for shaving and shampooing, as well as bathing and laundering. In 1916, in response to a World War I-related shortage of fats for making soap, the first synthetic detergent was developed in Germany. Known today simply as detergents, synthetic detergents are washing and cleaning products obtained from a variety of raw materials.

Nowadays, synthetic surfactants are essential components in many industrial processes and formulations [9-11]. Depending on the precise chemical nature of the product, the properties of, for example emulsification, detergency and foaming may be exhibited in varying degree. The number and arrangement of the hydrocarbon groups together with the nature and position of the hydrophilic groups combine to determine the surface-active properties of the molecule. For example C12 to C20 is generally regarded as the range covering optimum detergency, whilst wetting and foaming are best achieved with shorter chain lengths. Structure-performance relationships and chemical compatibility are therefore key elements in surfactant-based formulations, so that much research is devoted to this area.

Amongst the different classes of surfactants, anionics are often used in applications, mainly because of the ease and low cost of manufacture. They contain negatively charged head group, e.g., carboxylates ($-CO_2^-$), used in soaps, sulfate ($-OSO_3^-$), and sulfonates ($-SO_3^-$) groups. Their main applications are in detergency, personal care products, emulsifiers and soaps.

Cationics have positively charged head groups – e.g., trimethylammonium ion ($-N(CH_3)_3^+$) – and are mainly involved in applications related to their absorption at surfaces. These are generally negatively charged (e.g., metal, plastics, minerals, fibres, hairs and cell membranes) so that they can be modified upon treatment with cationic surfactants. They are therefore used as anticorrosion and antistatic agents, flotation collectors, fabric softeners, hair conditioners and bactericides.

Non-ionics contain groups with a strong affinity for water due to strong dipole-dipole interactions arising from hydrogen bonding, e.g., ethoxylates ($-(OCH_2CH_2)_mOH$). One advantage over ionics is that the length of both the hydrophilic and hydrophobic groups can be varied to obtain maximum efficiency in use. They find applications in low temperature detergents and emulsifiers.

Zwitterionics constitute the smallest surfactant class due to their high cost of manufacture. They are characterised by excellent dermatological properties and skin compatibility. Because of their low eye and skin irritation, common uses are in shampoos and cosmetics.

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