Self-assembling surfactant molecules give rise to a large variety of structures

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Surfactant Systems

Surfactant molecules possess both an hydrophilic (water soluble) and an hydrophobic (water insoluble) part. They adsorb at air-water or oil-water interfaces and form monolayers with the hydrophilic part lying in water. They also self-assemble in water solutions to hide their hydrophobic part from the water. The self-assembly process gives rise to micelles, vesicles, sponge phases, liquid crystal lyotropicphases (hexagonal, cubic, lamellar) among others. Micelles and lamellarphases are perhaps the most extensively studied systems, but the whole variety of structures observed with surfactants has also attracted considerable interest. In this short paper, we recall the main ideas in understanding the physical chemistry of molecular organization. We will mainly focus on aqueous surfactant solutions, although surfactant self-assembly also occurs in other solvents. Surfactants also help to stabilize dispersions of water-insoluble liquids such as oils in water (emulsions, microemulsions).

Dilute surfactant solutions

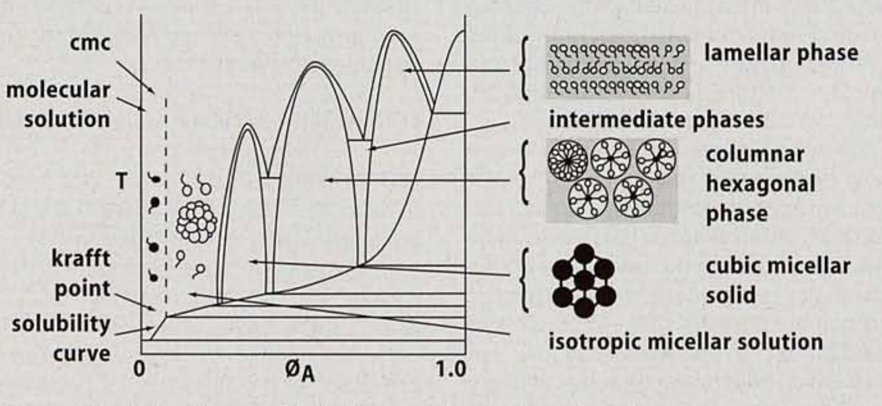
Surfactant aggregation

Surfactant molecules are dispersed as monomers in water when their concentration c is very low. When the solubility limit is reached, either the excess surfactant precipitates (the Krafft point), or it forms aggregates in which the hydrophobic part of the molecule is hidden in the interior, to minimize contact with water. These aggregates are in equilibrium with monomers, and the monomer concentration remains close to the solubility limit called the "cac"(for critical aggregation concentration). When the hydrophobic part of the surfactant is made of CH_2 chains, one can evaluate simply the difference in chemical potential of the surfactant in the aggregates and as a monomer, from the free enthalpy gain Δg when a CH_2 group is removed from water and incorporated in an alkane environment ($\Delta g \sim kT$ per CH_2 group). This leads to the relation: $\ln \mathrm{cac} = a - bn$ (1) where a is a constant, n is the number of CH_2 units and $b = \Delta g / kT$. Since $b \sim 1$, an increase in n by two units approximately leads to a decrease of the cac by a factor of 10.

Shape of the aggregates

This important issue was first addressed by Tanford and later on by Israelachvili, Mitchell and Ninham who compared the relative bulkiness of the polar and non-polar parts of the surfactant molecule. A surfactant "parameter" V/AL can be introduced, where V is the volume of the non-polar part, L its length and A the area occupied by the molecule at the hydrocarbon-water interface. If $V/AL < 1/3$, the relative bulkiness of the polar part dominates, the aggregates show a strong curvature towards water, and spherical micelles are formed. For DTAB (dodecyl trimethyl ammonium bromide), for instance, $A \sim 50$ Å^2 and $V/AL \sim 1/3$: sphericalmicelles are indeed formed above the cac, in this case called the "cmc" (for critical micellar concentration).

If $1/2 > V/AL > 1/3$, cylindrical aggregates are favoured and if $2 > V/AL > 1/2$, flat aggregates are favoured. This last case frequently corresponds to double chain lipids: above the cac, the solution becomes turbid because there is not enough surfactant to form a lamellar phase and the portions of lamellae close up into vesicles. Vesicles are larger than micelles and give rise to an appreciable scattering, even close to cac. For $V/AL > 2$, the formation of aggregates into non-polar solvents is favoured (reversed micelles, for instance)



Schematic phase diagram; $Ø_A$ is the surfactant volume fraction

Surfactant layers bending energy

Recently, the notion of "spontaneous" curvature of surfactant layers has been generalized by Helfrich to include the notion of curvature elasticity. If the surfactant layer is replaced by a mathematical surface (the neutral surface) of principal curvatures C_1 and C_2, one can write the elastic energy perunit area of the system as:

$$F = 1/2\, K\, (C_1 + C_2 - 2C_0)^2 + \overline{K} C_1 C_2 \quad (2)$$

where C_0 is the spontaneous curvature of the layer, by convention positive if the curvature is against water ($V/AL < 1$); flat aggregates correspond to $C_0 = 0$ ($V/AL = 1$). The elastic constants K and $\overline{K}$ are related respectively to deviations from mean curvature and from gaussian curvature. This energy explains the behaviour of the systems for which $C_0 \sim 0$. When the elastic constants are large compared to kT, flat lamellae are formed; when they are comparable to kT, the layers are undulated because of thermal fluctuations. The lamellar phase is no longer stable and a "sponge" phase, with no long range order is obtained. Whereas the meaning of K is rather straightforward, the role of $\overline{K}$ is more difficult to assess. If $\overline{K}$ is negative, the second term of *equation* 2 is smaller if C_1 and C_2 have the same sign, *ie* favouring vesicles. If $\overline{K}$ is positive, structures with saddles (regions where C_1 and C_2 have opposite signs) are favoured: these are the "sponge" phases. The actual structure is determined not only by the two terms of *equation* 2, but also by the many other contributions to the free energy of the system: dispersion entropy, interaction between aggregates, *etc*. In particular, dilute lamellar phases are only stable if there are long range repulsions between the surfactant bilayers.

It must be stressed that the description in terms of *equation* 2 is only valid for surfactant layer thicknesses much smaller than the inverse curvatures and it is not suitable for spherical micelles.

Concentrated surfactant solutions

The interactions between aggregates can play an important role in more concentrated solutions. Interactions can affect both size and polydispersity of the micelles. They can also promote transitions from spherical to cylindrical micelles in ionic surfactant solutions, because when c is increased, the ionic concentration is increased and the spontaneous curvature is decreased (see *shape of the aggregates*). The growth of cylindrical micelles with surfactant concentration can be extremely fast if particular ions are added to CTAB solutions, for instance salicylate ions. When the cylinders are long enough, the micelles can entangle, and the solutions become viscoelastic as semi-dilute polymer solutions.

In still more concentrated solutions, the excluded volume interactions among others, can promote the appearance of liquid crystalline phases. They occur generally in the order hexagonal then lamellar, with sometimes cubic phases before and/or after the hexagonal phase. The cubic phase can be either made of isolated micelles in a cubic lattice, or have a bicontinous structure (such as those described by the Schwartz surface). Nematic and rectangular phases have also been observed. In each phase, the packing conditions are only optimal for a given concentration c. In the range of existence of this phase and away from this concentration, there is some degree of geometrical frustation which is released by the production of topological defects. The amount of defects is obviously larger at the phase boundaries and could promote the transition between the different phases.

Surfactant aggregates are transient because the surfactant constantly changes between the aggregates and the solvent. The exchange time τ is related to the solubility of the surfactant in the solvent. When the non-polar part is made of CH_2 groups, this solubility is related to the free enthalpy cost Δg of transfer of a CH_2 group from an alkane environment to an aqueous environment. As the cac, the exchange time τ decreases by a factor 10 when two CH_2 groups are added to the chain. For surfactants with chains of 16 carbons, $\tau \sim 10^{-5}$ seconds. For lipids with two carbon chains, τ is much larger, and can be up to hours. The rheological behaviour of these systems is strongly affected by the exchanges. An extreme case is the sponge phase for which viscosity is only slightly larger than that of water although the structure is connected over a macroscopic scale. The entangled solutions of giant micelles are also less viscous than expected from their equilibrium length.

Polymerization in surfactant systems

Many attempts to use surfactant structures as templates for the synthesis of small colloidal particles and mesoporous materials have been made in the past. The main problem encountered is that first, the monomers introduced in the systems might adsorb at the surface of the aggregates and change therefore their curvature. The change of spontaneous curvature can also be produced by the polymer, once formed. The polymer also strongly affects the elastic bending moduli of the surfactant layers. Changes in spontaneous curvature and in bending moduli produced by polymers are dependent on the way in which the polymer is connected to the layer: anchored, adsorbed, *etc.* Electrostatic interactions also play an important role in the complexation of surfactant aggregates and polyelectrolytes with charges of opposite signs.

The study of aqueous mixed solutions of polymers and surfactants is itself presently a very active field of research.

In conclusion, we have briefly described several key ideas in the understanding of structure and dynamic properties of surfactant solutions. The structure properties are now relatively well understood, but more work is needed for a better understanding of the dynamic properties, the rheology in particular. The field of mixed polymer-surfactant systems is expanding, with promising developments both for practical applications and biology.

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Further reading

Micelles, Membranes, Microemulsions and Monolayers edited by W.M. Gelbart, A. Ben-Shaul, D. Roux (Springer, New York, 1994) • D. Langevin *Current Opinion in Colloid & Interface Science* **3** 600 (1998) • Mesoporous Molecular Sieves 1998 edited by L. Bonneviot, F. Beland, C. Danumah, S. Giasson, S. Kaliaguine (Elsevier, Amsterdam, 1998) • Interaction of Surfactants with Polymers and Proteins E.D. Goddard, K.P. Ananthapadmanabhan (CRC Press, Boca Raton, 1993)

Denis Weaire and Stefan Hutzler,

Ireland

Making, Modelling and Measuring Foams

There is a long history of interest in soap films, bubbles and foams among leading scientists. A bibliography compiled by Mysels, Shinoda and Frankel in 1959 comprises over three hundred references, spanning many centuries

The ephemeral nature of bubbles has commended them to poets and prophets in every age. The ambitious student of the physics of foams should recall Shakespeare's characterisation of the young man seeking "the bubble reputation, even in the cannon's mouth".

Connotations of mortality are compounded with the attractive visual aspect of bubbles in many famous pictures, of which a selection is presented by Michele Emmer in his delightful book Bolle di Sapone: un viaggio tra arte, scienza a fantasia (which awaits, and deserves, a republication in English.)

In this century, scientific interest in bubbles at first receded—Sir James Dewar was one of the last of the old generation to study them. Industrial companies recognized the practical importance of foams and applied research, in the spirit of engineering, developed on a wide front. The books and papers from that mid-century period offer a plethora of empirical data but only minimal insight at a basic level.

Recently, we have begun to rectify this imbalance. Specialized foam conferences have appeared. The proceedings of the most recent meeting in Cargese have just been published by Kluwer. At least two physics networks under the TMR programme and its predecessors have brought together small groups from throughout the European Union, and there have been contributions from East-