Topic 2770

Surfactants and Micelles

'Nonsense, McBain'. The story is told that with these words an eminent scientist, chairman of a meeting of the Royal Society in London in the early 20th Century, reacted to the proposal by J. W. McBain that surfactants [= **surf**ace **act**ive **a**ge**nts]** might aggregate in aqueous solution [1]. Subsequent events confirmed that the nub of McBain's model is correct.

The enormous industry based on 'soaps' and detergents [2] prompts intensive studies of these complicated systems, supported by monographs [3-5] and detailed reviews [6-11].

In the context of aqueous solutions, surfactant molecules are amphipathic meaning that the solutes have dual characteristics : amphi ≡ dual and pathi ≡ sympathy. These dual characteristics emerge because a solute molecule contains both hydrophobic and hydrophilic parts. The subject is complicated because there is no general agreement concerning the nature-structure of these solute aggregates in aqueous solutions. Amphipathic molecules are broadly classified as either ionic or non-polar. Ionic surfactants are typified by salts such as sodium dodecylsulfate ($C_{12}H_{25}OSO_3^-Na^+$) and hexyltrimethylammonium bromide ($C_{16}H_{33}N^+Me_3Br^-$; CTAB). Non-ionic surfactants are typified by those based on ethylene oxide; e.g. hexaethylene glycol dodecylether, ($C_{16}H_{25}(OCH_2CH)_6OH$).

When small amounts of a given surfactant are gradually added to a given volume of water (ℓ), the properties of the aqueous solutions are unexceptional until the concentration of the surfactant exceeds a characteristic concentration of surfactant (at defined T and p) called the critical micellar concentration, cmc. At this point further added surfactant exists in solution as aggregates of generally 20 to 100 monomers, which are called micelles. The formation of micelles is often signalled by a change in the pattern of the dependence of a given property P of a solution on surfactant concentration. The property can be surface tension, molar conductance of an ionic surfactant, uv-visible absorption spectra of water

soluble dyes (or, an iron complex [12]). When more surfactant is added, the micelles cluster to form more complicated aggregates [13].

Micelles are not formed by the gradual association of monomers, forming dimers, trimers…..[14] . Rather micelles are examples of organised structures spontaneously formed by simple molecules [15]. A quoted aggregation number is not a stoichiometric number. The quoted number (e.g. approx. 90 for CTAB at 298 K) is taken as an 'average' over the micelles in a given system.

In terms of the structure of micelles in aqueous solutions, key questions centre on (i) the extent to which water penetrates into a micelle, and (ii) the organisation of alkyl chains in a given micelle [16]. The two questions are linked by the question – to what extent does the terminal group in, for example, the hexadecyl chains of CTAB come into contact with the aqueous solution? If the answer is 'never', micelles have a structure in which there is a well organised hydrophobic core. If the answer is 'frequently' the micelles are very dynamic assemblies with continuous changes in organisation/structure. We do not become involved in this debate. However we note that there is such a debate over what precisely the thermodynamic analysis is asked to describe.

Description of micellar-surfactant systems emerges from the Phase Rule. The number of phases = 3; vapour, aqueous solution and micelle. The number of components = 2 ; water and surfactant. Hence having defined the temperature, the remaining intensive variables are defined; i.e. vapour pressure, mole fraction of surfactant monomer in aqueous solution, and mole fraction of surfactant in micellar phase.

The starting point for a thermodynamic analysis is the assumption of an equilibrium between surfactant monomers and micelles in solution (at defined T and p). A key feature of these systems is that above the cmc when more surfactant is added the concentration of monomers remains essentially constant, the added surfactant existing in micellar form. Two models for micelle formation are discussed; (i) phase equilibrium [17], and (ii) closed association model , often called the mass-action model.

Here we assume that the closed system containing solvent and surfactant is at equilibrium at defined T and p. Each system is at a unique

minimum in Gibbs energy. The system is at ambient pressure, which for our purposes is effectively the standard pressure p^0. We characterise micelle formation using thermodynamic variables describing monomers and micelles. Then $\Delta_{mic}G^0$ is the standard Gibbs energy of micelle formation which is dependent on temperature. The latter dependence is characterised by the standard enthalpy of micelle formation, $\Delta_{mic}H^0$, where,

$$\Delta_{mic}G^0 = \Delta_{mic}H^0 - T \cdot \Delta_{mic}S^0 \qquad \text{(b)}$$

Clearly the definition of $\Delta_{mic}G^0$ is directly associated with the definition of standard states for both the simple salt in solution and the micelles in the aqueous system. These thermodynamic variables together with aggregation numbers are extensively documented [18].

Footnotes

[1] F. M. Menger, Acc. Chem.Res.,1979,**12**,111; and references therein.

[2] E. M. Kirshner, Chem. Eng. News, 1998,**76**,39

[3] J. H. Clint, Surfactant Aggregation, Blackie, Glasgow, 1992.

[4] Y. Mori, Micelles, Plenum Press, New York, 1992.

[5] D. F. Evans and H. Wennerstrom,
The Colloidal Domain, VCH, New York, 1994.

[6] B. Lindman and H. Wennerstrom,
Top. Curr. Chem., 1980, **87**,1.

[7] G. C. Kresheck in, Water: A Comprehensive Treatise, ed. F. Franks,
Plenum Press, New York, 1973, volume **4**,chapter 2.

[8] J. E. Desnoyers, (a) J. Surface Sci. Technol., 1989,**5**,289;
(b) Pure Appl. Chem.,1982,**54**,1469.

[9] Polymer-surfactant interactions;
(a)E.D.Goddard, JAOCS, 1994,**71,**1.
(b)J. Kevelam, J. F. L. van Breemen, W. Blokzijl
and J. B. F. N. Engberts, Langmuir, 1996, **12**, 4709.

[10] Solubilisation by micelles; C. Treiner, Chem. Soc. Rev.,1994,**23**,349.

[11] Alcohol-micelle interactions;
R. E. Verrall, Chem. Soc. Rev.,1995,24,79.

[12]

(a) N. M. van Os, G. J. Daane and G. Haandrikman,
J.Colloid Interface Sci.,1991,**141**,199.

(b) M. J. Blandamer, B. Briggs, J. Burgess, P. M. Cullis and G. Eaton,
J. Chem. Soc. Faraday Trans.,1991,**87,**1169.

[13] S. Backlund, H. Hoiland, O. J. Krammen and E. Ljosland,
Acta Chem. Scand,,Ser. A, 1982, **87**,1169.

[14] But see D. Schuhman, Prog. Colloid Polym. Sci.,1989,**71**,338.

[15] See for example, K. Shinoda, Langmuir, 1991,**7**,2877.

[16] F. Menger and D. W. Doll , J. Am. Chem.Soc.,1984,**106**,1109.

[17] S. Puvvada and D. Blankschtein, J.Phys.Chem.,1992,**96**, 5567.

[18] N. M. van Os, J. R. Haak and L A. M. Rupert,
Physico-Chemical Properties of Selected Anionic, Cationic
and Non-Ionic Surfactants, Elsevier, Amsterdam,1993.