Micelles in Aqueous Solution

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1 Introduction

Micelles are molecular aggregates formed in solutions of detergents – molecules in which a non-polar 'tail' (usually an n-alkyl hydrocarbon chain containing 8 to 18 methylene groups) is joined to a polar head-group. Such molecules are also called amphiphiles, surfactants, and surface-active molecules; 'detergents' is our arbitrary choice for this review. At low concentrations in water, detergents exist mostly as monomers.[1] At higher concentrations, numbers of them aggregate to form more or less spherical micelles with the polar groups on the surface and the hydrocarbon chains forming a core (Figure 1). This minimizes the energetically unfavourable exposure of the hydrocarbon chains to water.

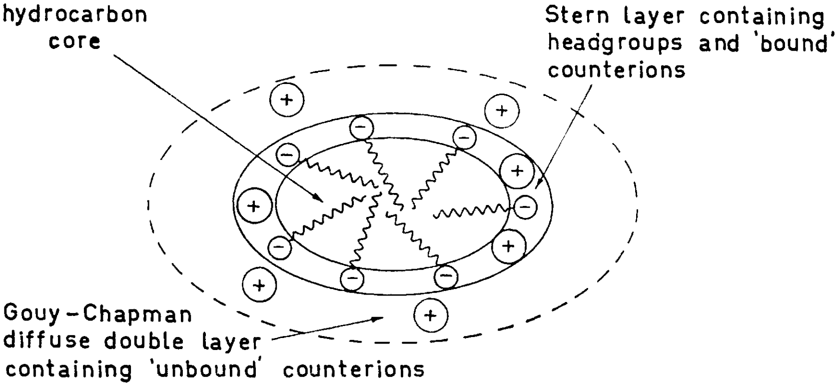

Figure 1 *Elliptical cross-section of an idealized anionic detergent micelle*

Detergents may have head-groups which are ionic (*e.g.* sulphates), zwitterionic (*e.g.* betaines), or non-ionic (*e.g.* polyoxyethylenes). The size of detergent micelles is limited by the balance of attractive forces between the non-polar portions and repulsive forces between the head-groups. Ionic detergents form smaller micelles [aggregation number (n) ~ 10—100] than non-ionic detergents

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[1] (*a*) G. S. Hartley, 'Aqueous Solutions of Paraffin Chain Salts', Hermann et Cie., Paris, 1936; (*b*) T. Drakenberg and B. Lindman, *J. Colloid Interface Sci.*, 1973, **44**, 184.

($n > 1000$). This is because the electrostatic repulsion between ionic head-groups is greater than the steric repulsion between non-ionic head-groups.

The concentration (actually an arbitrary concentration within a narrow range) above which micelles form is called the critical micelle concentration (CMC). Above the CMC, monomers and micelles exist in dynamic equilibrium.[2]

The most useful property of micelles is their ability to 'solubilize', *i.e.* to dissolve hydrophobic material in their interiors. This leads to the use of micelle-forming substances as detergents[3] and carriers for otherwise insoluble drugs,[4] and in organic synthesis *via* micellar catalysis.[5] The surface-active property of detergents is also valuable, especially in industrial processes such as froth flotation[6] and petroleum recovery.[7]

The interactions responsible for micelle stability are similar to those which stabilize biological membranes and the tertiary structure of proteins. Micelles have thus been used as models for these,[8,9] as well as in the study of such diverse processes as photosynthesis and vision,[10] electron-transport processes,[11] and lipid–protein interactions.[12]

In this review we discuss the properties of micelles in their simplest form, *i.e.* micelles in aqueous solutions of pure detergents at concentrations near the CMC. The emphasis is on ionic detergents with hydrocarbon tails, these detergents being most frequently studied. Despite considerable advances in the past decade,[13–15] understanding even in this restricted area is still fragmentary.

Our aim is to give a broad picture of recent developments. Detailed discussion of experimental results has been omitted for reasons of space. Reviews of 'reversed' micelles in non-polar solvents,[13] solubilization,[4] and micellar catalysis[5] have appeared recently, and these topics are not discussed.

2 Thermodynamics of Micelle Formation

Two simple models have long been used in the interpretation of micelle behaviour. Since their use is frequent, we summarize the main features of these models before proceeding to a discussion of recent experimental studies.

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[2] K. K. Fox, *Trans. Faraday Soc.*, 1971, **67**, 2802.

[3] J. W. McBain, *Adv. Colloid Sci.*, 1942, **1**, 99.

[4] P. H. Elworthy, A. T. Florence, and C. B. Macfarlane, 'Solubilization by Surface Active Agents', Chapman and Hall, London, 1968.

[5] E. Cordes, ed., 'Reaction Kinetics in Micelles', Plenum Press, New York, 1973.

[6] I. J. Lin, *Israel J. Technol.*, 1971, **9**, 621.

[7] W. B. Gogarty, U.S. P. 3 495 661. 1970.

[8] A. Ray and G. Némethy, *J. Amer. Chem. Soc.*, 1971, **93**, 6787.

[9] R. Smith and C. Tanford, *J. Mol. Biol.*, 1972, **67**, 75.

[10] S. C. Wallace and J. K. Thomas, *Radiation Res.*, 1973, **54**, 49.

[11] P. G. Westmoreland, R. A. Day, jun., and A. L. Underwood, *Analyt. Chem.*, 1972, **44**, 737.

[12] (*a*) V. G. Cooper, S. Yedgar, and Y. Barenholtz, *Biochim. Biophys. Acta*, 1974, **363**, 86; (*b*) C. Tanford, *Adv. Protein Chem.*, 1968, **23**, 121.

[13] H. F. Eicke and H. Christen, *J. Colloid Interface Sci.*, 1974, **46**, 417.

[14] P. Mukerjee, *Adv. Colloid Interface Sci.*, 1967, **1**, 241.

[15] (*a*) E. W. Anacker, in 'Cationic Surfactants', ed. E. Jungermann, Marcel Dekker, Inc., New York, 1970, p. 203; (*b*) C. Tanford, 'The Hydrophobic Effect', John Wiley and Sons, New York, 1973; (*c*) G. C. Kresheck, in 'Water; a Comprehensive Treatise', Vol. 4, ed. F. Franks, Plenum Press, New York, 1975, p. 95.

A. Mass-action Model.—This was the first thermodynamic approach to be developed.[16] As an illustration, consider the formation of micelles by an anionic detergent such as sodium dodecylsulphate (SDS) in water without added salt. Each micelle ($M^{(n-m)-}$) is assumed to contain n detergent ions (D^-) and m firmly bound counterions (C^+), so that a fraction m/n of the charge of the detergent ions in each micelle is neutralized. [Firmly bound counterions (see also Section 3F) are those which are intimately associated with the charged head-groups of the detergent ions in the Stern layer (Figure 1). They can be distinguished experimentally from the unbound counterions in the Gouy-Chapman diffuse double layer with which they are in dynamic equilibrium. For example, in response to an applied electrostatic field they move with the micelle, whereas unbound counterions migrate in the opposite direction.]

Micelles are considered to be formed in a single step in the following process:

$$n\,D^- + m\,C^+ \rightleftharpoons M^{(n-m)-} \tag{1}$$

The equilibrium constant for micelle formation is then:

$$K_M = \frac{[M^{(n-m-)}]}{[D^-]^n\,[C^+]^m} \tag{2}$$

The concentrations are expressed in mole fractions to simplify the subsequent thermodynamic equations. Activity coefficients are usually omitted, although even in dilute solutions ($< 10^{-2}$ mol l^{-1}) the departure from ideality is probably significant.[17,18]

From this model it can be shown[1,15a,19] that a relatively rapid increase in $[M^{(n-m)-}]$ occurs over a narrow range of $[D^-]$, provided that n is large. That is, the model predicts a CMC.

The equilibrium [equation (1)] can be broken down into its components, building up the micelle one molecule at a time. This multiple equilibrium model yields a similar expression to equation (2) (ref. 20), with

$$K_M = \prod_2^n K_q \tag{3}$$

where the K_q are stepwise association constants. Here K_M is no longer a true equilibrium constant.[20a]

We can calculate some thermodynamic functions from equation (2). The standard free energy of micelle formation per mole of monomer is given by the usual thermodynamic arguments as

$$\Delta G_{ma}{}^\circ = -\frac{RT}{n}\ln K_M \tag{4a}$$

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[16] E. R. Jones and C. R. Bury, *Phil. Mag.*, 1927, **4**, 841.

[17] (*a*) S. J. Dougherty and J. C. Berg, *J. Colloid Interface Sci.*, 1974, **48**, 110; (*b*) T. Sasaki, M. Hattori, J. Sasaki, and K. Nukina, *Bull. Chem. Soc. Japan*, 1975, **48**, 1397.

[18] T. Gilányi, *Acta Chem. Scand.*, 1973, **27**, 729.

[19] J. G. Watterson and H. G. Elias, *Kolloid-Z.*, 1971, **249**, 1136.

[20] (*a*) P. Mukerjee, *J. Phys. Chem.*, 1972, **76**, 565; (*b*) N. Muller, *ibid.*, 1975, **79**, 287.

$$= \frac{RT}{n} \{n \ln [\mathrm{D}^-] + m \ln [\mathrm{C}^+] - \ln [\mathrm{M}^{(n-m)-}]\} \qquad (4b)$$

taking unit mole fraction of monomer as the standard state. The subscript 'ma' refers to the mass-action model. Emerson and Holtzer[21] have shown that $\Delta G_{\mathrm{ma}}{}^\circ$ represents the free energy for the addition of a single monomer to a micelle with the most probable size, if the micelles are polydisperse.

At the CMC, $[\mathrm{D}^-] \simeq [\mathrm{C}^+] \simeq$ CMC. If the term containing $\ln [\mathrm{M}^{(n-m)-}]$ can be neglected,[22] we get the useful approximation

$$\Delta G_{\mathrm{ma}}{}^\circ \simeq RT(1 + m/n) \ln \mathrm{CMC} \qquad (5)$$

The micelles of non-ionic detergents do not have bound counterions, but otherwise a similar line of reasoning can be followed.

B. The Phase-separation Model.—In this approach the micelles of an ionic detergent such as SDS, together with their bound counterions, are considered as a separate phase, with phase separation occurring at the CMC.[22,23] We avoid for the moment the problem of defining a charged phase[24] by assuming that the number of counterions firmly bound to each micelle is equal to the number of detergent ions in the micelle, so that the micelles are electrically neutral.

From the phase rule it follows that monomers and micelles are in equilibrium only at a single monomer concentration, the CMC. Thus, above the CMC, monomer activity should remain constant.

An equation can be derived for $\Delta G_{\mathrm{ps}}{}^\circ$ (the subscript 'ps' stands for the phase-separation model) which is similar in form to that derived from the mass-action model. We obtain[22,23]

$$\Delta G_{\mathrm{ps}}{}^\circ = 2RT \ln \mathrm{CMC} \qquad (6)$$

The numerical values of $\Delta G_{\mathrm{ps}}{}^\circ$ and $\Delta G_{\mathrm{ma}}{}^\circ$ differ because the mole fractions are calculated differently. In the phase-separation approach the total number of moles is that of water plus monomer. In the mass-action approach micelles and free counterions are also included. At the CMC the two totals are approximately equal, and both models yield similar results.[15a]

C. Other Thermodynamic Parameters.—The standard enthalpy of micelle formation can be calculated from the differentiated Gibbs–Helmholtz equation:

$$\partial[\Delta G/T]/\partial T = -\Delta H/T^2 \qquad (7)$$

For the mass-action model, this gives, with equation (5),

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[21] M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, 1965, **69**, 3718.

[22] K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, 1962, **66**, 577.

[23] K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, 'Colloidal Surfactants', Academic Press, New York, 1962.

[24] D. G. Hall and B. A. Pethica, in 'Non-ionic Surfactants', ed. M. J. Schick, Marcel Dekker, Inc., New York, 1967.

$$\Delta H_{\mathrm{ma}}{}^{\circ} = -RT^2\,[(1 + m/n)\,\partial(\ln \mathrm{CMC})/\partial T + (\ln \mathrm{CMC})\,\partial(m/n)/\partial T] \tag{8}$$

Note that this expression includes the temperature coefficient of m/n as well as the temperature coefficient of the CMC.

The phase-separation model gives, from equations (6) and (7),

$$\Delta H_{\mathrm{ps}}{}^{\circ} = -2RT^2\,\partial(\ln \mathrm{CMC})/\partial T \tag{9}$$

This is formally the same as equation (8), with $m/n = 1$, which is implicit in the phase-separation model. As discussed above, the different methods of calculating mole fractions in the two models give different numerical values. Examples of values of the standard free energy, enthalpy, and entropy of micelle formation ($\Delta G_{\mathrm{mic}}{}^{\circ}$, $\Delta H_{\mathrm{mic}}{}^{\circ}$, and $\Delta S_{\mathrm{mic}}{}^{\circ}$, respectively) for the two models are given in Table 1 ($\Delta S_{\mathrm{mic}}{}^{\circ}$ is calculated from $\Delta G_{\mathrm{mic}}{}^{\circ}$ and $\Delta H_{\mathrm{mic}}{}^{\circ}$) together with experimental values of $\Delta H_{\mathrm{mic}}{}^{\circ}$. Clearly the entropy term is the major contributor to the negative free energy of micelle formation. It is reassuring that the calorimetric value of $\Delta H^{\circ}{}_{\mathrm{mic}}$ is in reasonable agreement with those calculated from the model s.

Table 1 *Comparison of thermodynamic parameters for micelle formation according to the mass-action and phase-separation models. The data are for SDS at* 20 °*C in aqueous solution*[a]. *All values are in units of* kJ mol^{-1}.

Mass-action Model			*Phase-separation Model*			*Experimental*
$\Delta G_{\mathrm{ma}}{}^{\circ}$	$\Delta H_{\mathrm{ma}}{}^{\circ b}$	$T\Delta S_{\mathrm{ma}}{}^{\circ}$	$\Delta G_{\mathrm{ps}}{}^{\circ}$	$\Delta H_{\mathrm{ps}}{}^{\circ}$	$T\Delta S_{\mathrm{ps}}{}^{\circ}$	$\Delta H_{\mathrm{exp}}{}^{\circ}$ (calorimetry)
−38.6	1.7	40.3	−43.1	1.9	45.0	1.3

(*a*) H. Kishimoto and K. Sumida, *Chem. and Pharm. Bull. (Japan)*, 1974, **22**, 1108;
(*b*) $\partial(m/n)/\partial T$ was assumed negligible in calculating this value.

Although these models are a useful framework for the interpretation of the experimental results discussed in the next section, the reader is warned that they represent an oversimplified picture of micelle formation. A number of assumptions are involved, not all of which are experimentally justifiable. Assumptions common to both models are:

(i) The micelles are of uniform size (monodisperse).

(ii) At the CMC, interactions between micelles are negligible.

(iii) For the micelles of ionic detergents, counterions may be regarded as either 'bound' or 'unbound', with no intermediate states.

(iv) The micelle does not contain solvent or ions other than counterions and surfactant ions.

For the mass-action model we also have:

(v) The problem that the CMC must be arbitrarily defined, since it is not sharp.

For the phase model we have to take into account, in addition to the validity of assumptions (i)—(iv):

(vi) The difficulty of extending the concept of a phase to cover the observed number of degrees of freedom.[24]

(vii) The assumptions of a sharp CMC and of constant monomer activity above the CMC.[17b,25]

Experimental tests of these assumptions are discussed in Section 3. More rigorous, though possibly less experimentally useful, models are examined in Section 4.

3 Experimental Aspects of Micelle Formation

A. Critical Micelle Concentration.—Experimentally, the CMC is found by plotting a graph of a suitable physical property as a function of concentration. An abrupt change of slope marks the CMC. Many physical properties have been used; Mukerjee and Mysels list 71 in their critical compilation of CMC's.[26]

The choice of CMC is never unambiguous, since the change in slope occurs over a more or less narrow range of concentrations. The value depends both on the nature of the data and on the way they are plotted. Since micelles are normally polydisperse, methods yielding a weight average (*e.g.* light scattering) give higher values than methods yielding a number average (*e.g.* dye solubilization).[19,27] The same raw data can also be plotted in different ways. For example, electrical conductivity can be plotted as specific conductance against concentration or as equivalent conductance against the square root of the concentration. The two plots give different, and equally arbitrary, values for the CMC.[26]

Several formal definitions of the CMC have been proposed in attempts to overcome this problem.[28–30] Of the experimentally applicable definitions, the least impractical is that of Phillips.[29] If ϕ is an ideal colligative property, Phillips defines the CMC as the concentration (c) at which the slope of a graph of ϕ *vs.* c is changing most rapidly; that is, $\mathrm{d}^3\phi/\mathrm{d}c^3 = 0$.* A less restrictive version, given by Hall,[28] uses the chemical potential of the solvent instead of ϕ, and is applicable to multicomponent solutions. Experimentally, very precise data are needed for these expressions to be useful (if ϕ is expressed as a polynomial in c, only the third- and higher-order terms determine the CMC).

The CMC can be affected by many variables, the most important of which are temperature and pressure. Detergents usually show a shallow minimum in the

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* Chung and Heilwell[30] have criticized this definition on the mistaken premise that it refers to the point of maximum rate of change of curvature rather than slope. This is not so, and the criticism is invalid. Their definition $[(\partial^2\phi/\partial c^2)_{\mathrm{CMC}} = 0]$ cannot be recommended, since few properties show an inflection at the CMC.

[25] P. H. Elworthy and K. J. Mysels, *J. Colloid Interface Sci.*, 1966, **21**, 331.

[26] P. Mukerjee and K. J. Mysels, 'Critical Micelle Concentrations of Aqueous Surfactant Systems', *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.* (*U.S.*) **36**, 1971.

[27] (*a*) P. Becher. in 'Non-ionic Surfactants', ed. M. J. Schick, Marcel Dekker, Inc., New York, 1967, p. 478; (*b*) P. Debye and E. W. Anacker, *J. Phys. Colloid Chem.*, 1951, **55**, 644.

[28] D. G. Hall, *J.C.S. Faraday I*, 1972, **68**, 668.

[29] J. N. Phillips, *Trans. Faraday Soc.*, 1955, **51**, 561.

[30] H. S. Chung and I. J. Heilwell, *J. Phys. Chem.*, 1970. **74**, 488.

CMC as a function of temperature,[31] with a consequent change in sign of $\Delta H_{\text{mic}}°$. In the case of ionic detergents the minimum (which usually occurs around 25 °C) can be explained by the opposing temperature dependences of the head-group and hydrocarbon chain interactions.[15b] In the case of non-ionic detergents, no satisfactory explanation exists. The minimum only occurs for non-ionic detergents with large head-groups,[31b] and usually at higher temperatures than for ionic detergents.

Pressure affects the CMC because micelle formation is accompanied by a volume change[32] (usually an increase) of the same sign as that for the transfer of hydrocarbon from water to an organic solvent.[33]

The CMC is also affected by the addition of both ionic and non-ionic solutes. Despite many attempts,[15c] there is still no coherent theory of these effects.

B. Premicellar Aggregation.—Small aggregates, usually dimers or trimers, are often formed in dilute aqueous solutions of molecules containing hydrophobic groups[34] (an example is the dimerization of carboxylic acids).[34b] It is therefore possible that small (premicellar) aggregates could form below the CMC in aqueous detergent solutions, although for ionic detergents electrostatic repulsion would oppose the formation of such aggregates, and there is little clear evidence for their existence.

Earlier evidence, summarized by Mukerjee in 1967,[14] indicated that premicellar aggregation could be a widespread phenomenon in solutions of ionic detergents. Recent evidence, although contradictory,[32b,35] has tended to oppose this view, and there is now no compelling evidence for the existence of premicellar aggregates except in solutions of ionic detergents with chain lengths greater than C_{16}.[36]

C. Size, Shape, and Size Distribution.—Micelles are generally assumed to be more or less spherical and of uniform size, at least at concentrations within an order of magnitude of the CMC. Neither of these assumptions is accurate; while they provide a good working model for the interpretation of much experimental data, it is now accepted that micelle populations are often polydisperse, and that micelles are not necessarily spherical.

(*i*) *Size and Size Distribution.* The average number of monomer units in a micelle

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[31] (*a*) H. Kishimoto and K. Sumida, *Chem. and Pharm. Bull.* (*Japan*), 1974, **22**, 1108; (*b*) E. H. Crook, G. F. Trebbi, and D. B. Fordyce, *J. Phys. Chem.*, 1964, **68**, 3592.

[32] (*a*) S. Kaneshina, M. Tanaka, T. Tomida, and R. Matuura, *J. Colloid Interface Sci.*, 1974, **48**, 450; (*b*) G. M. Musbally, G. Perron, and J. E. Desnoyers, *ibid.*, 1974, **48**, 494.

[33] W. L. Masterton, *J. Chem. Phys.*, 1954, **22**, 1830.

[34] (*a*) D. G. Oakenfull and D. E. Fenwick, *J Phys. Chem.*, 1974, **78**, 1759; (*b*) E. E. Schrier, M. Pottle, and H. A. Scherega, *J. Amer. Chem. Soc.*, 1964, **86**, 3444.

[35] (*a*) B. Lindman, H. Wennerström, and S. Forsén, *J. Phys. Chem.*, 1970, **74**, 754; (*b*) B. Lindman and B. Brun, *J. Colloid Interface Sci.*, 1973, **42**, 388; (*c*) B. Lindman, N. Kamenka, and B. Brun, *Compt. rend.*, 1974, **278**, *C*, 393; (*d*) P. Stenius and C.-H. Zilliacus, *Acta Chem. Scand.*, 1971, **25**, 2232; (*e*) P. Stenius, *ibid.*, 1973, **27**, 3435; (*f*) P. Stenius, *ibid.*, 1973, **27**, 3452.

[36] E. J. Bair and C. A. Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 1129.

(the aggregation number) can range from 10 to 100 in the case of the micelles of ionic detergents, to upwards of 1000[15b,27] for the micelles of non-ionic detergents. Methods of estimating this aggregation number can give different results, depending upon whether a weight-average (N_w) or number-average (N_n) result is obtained.[20a,26] This clearly indicates that at least some micellar systems are polydisperse,[37] the ratio of the two averages being a measure of the width of the size distribution. The width appears to be narrow for small micelles, broadening with increasing aggregation number.[20a]

Most recent theories take polydispersity as a premise.[20a,38,39] It has even been suggested on thermodynamic grounds that the CMC actually separates a region of low concentrations, where the size distribution is a monotonic decreasing function of size, from a region of higher concentrations, containing a maximum and minimum probable size.[39] If this model is substantiated, then the CMC is intimately related to the size distribution.

Within the limitations discussed above, several valuable studies of micelle size have been carried out. The techniques available have been described by Anacker.[15a] Light scattering is the most versatile and frequently used, but *X*-ray diffraction, diffusion, ultracentrifugation, flow birefringence, viscosity, and dye solubilization have also been applied.

Factors which can influence micelle size include temperature,[40] pressure,[32a] ionic strength,[15c] charge[41] hydrocarbon chain length,[42] the nature of the head-group,[43] and the type of counterion.[44] For example, the effect of the nature of the head-group has been studied using light scattering. Detergents such as the long-chain trimethylammonium halides and the pyridinium and quinuclidinium halides[43a,43c,44] (the latter corresponding to the trimethylammonium halides with the methyl groups 'tied') have been examined. Hydrogen bonding and head-group–water interactions are important, but the major effect comes from the distance of closest approach of the counterions. The shorter this is, the greater the mean micelle size, since the head-group charge is more effectively neutralized.

(*ii*) *Shape*. The *X*-ray diffraction work of Reiss–Husson and Luzatti[45] and subsequent authors[46] is most often quoted in support of the assumption that micelles of ionic detergents are more or less spherical. This work was done,

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[37] J. M. Corkhill and T. Walker, *J. Colloid Interface Sci.*, 1972, **39**, 621.

[38] (*a*) C. Tanford, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1811; (*b*) J. Rassing, P. J. Sams, and E. Wyn-Jones, *J.C.S. Faraday II*, 1974, **70**, 1247; (*c*) E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, 1974, **78**, 1024; (*d*) E. A. G. Aniansson and S. N. Wall, *ibid.*, 1975, **79**, 857.

[39] E. Ruckenstein and R. Nagarajan, *J. Phys. Chem.*, 1975, **79**, 2622.

[40] A. Holtzer and M. F. Holtzer, *J. Phys. Chem.*, 1974, **78**, 1442.

[41] J. M. Corkill, K. W. Gemmell, J. F. Goodman, and T. Walker, *Trans. Faraday Soc.*, 1970, **66**, 1817.

[42] S P Wasik and N. M. Roscher, *J. Phys. Chem.*, 1970, **74**, 2784.

[43] (*a*) R. D. Geer, E. H. Eylar, and E. W. Anacker, *J. Phys. Chem.*, 1971, **75**, 369; (*b*) E. W. Anacker and R. D. Geer, *J. Colloid Interface Sci.*, 1971, **35**, 441; (*c*) P. T. Jacobs and E. W. Anacker, *J Colloid Interface Sci.*, 1973, **44**, 505.

[44] W. P. J. Ford, R. H. Ottewill, and H. C. Parreira, *J. Colloid Interface Sci.*, 1966, **21**, 522.

[45] (*a*) F. Reiss-Husson and V. Luzzati, *J. Phys. Chem.*, 1964, **68**, 3504; (*b*) F. Reiss-Husson and V. Luzzati, *J. Colloid Interface Sci.*, 1966, **21**, 534.

[46] B. Svens and B. Rosenholm, *J. Colloid Interface Sci.*, 1973, **44**, 495.

however, at high detergent concentrations (> 5% w/w). Its interpretation depends upon the adoption of a simple spherical model and upon the assumptions that all counterions are firmly bound to the micelles, and that the micelles are monodisperse. Neither of these assumptions is likely to be correct (see Section 3F for a discussion of the first assumption).

Geometrical considerations[47] (see Section 4B) suggest that micelles are ellipsoids of revolution. However, hydrodynamic[48] and light-scattering depolarization evidence[27,37,44] shows that in most cases the axial ratio of the micelles of both ionic and non-ionic detergents is not greater than 6:1 at concentrations near the CMC, although a transition to rod-like micelles may occur at higher concentrations of detergent (the 'second CMC')[49] or in the presence of added salt.[48] Under these circumstances, estimates of aggregation number by light scattering (calculated using the assumption that micelles are spherical) at concentrations near the CMC are unlikely to be seriously in error.

D. Internal Viscosity.—The practical applications of micelles depend mostly on their ability to solubilize hydrophobic molecules. To understand this process we need to understand the nature of the interior of the micelle.

The intuitive view is that the interior of the micelle is like a liquid hydrocarbon droplet. Comparisons of the mobilities of fluorescence[50] and e.s.r.[51] probe molecules solubilized in micelles and dissolved in organic solvents have shown that this is largely true, although their motion is somewhat more restricted in the micelles than in the organic solvents.

E. Water Penetration.—The extent to which water penetrates the hydrocarbon core is another significant factor in determining the properties of solubilized molecules. Common sense suggests that not all of the hydrocarbon tail of the detergent ion is removed from contact with water in the formation of a micelle. The surface area per head-group is larger than the cross-sectional area of the hydrocarbon chain for both ionic and non-ionic detergents,[38a] which might allow water to penetrate between the chains.

Experimental evidence for water penetration is contradictory. There has always been an alternative explanation for any evidence suggesting water penetration into micelles, even to a depth of only two or three methylene groups,[52–54] as has been suggested for lipid bilayers.[55] Muller's conclusions,[52] for example,

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[47] C. Tanford, *J. Phys. Chem.*, 1972, **76**, 3020.

[48] (*a*) K. Granath, *Acta Chem. Scand.*, 1953, **7**, 297; (*b*) M. B. Smith and A. E. Alexander, *Proc. 2nd. Int. Conf. Surface Activity*, 1957, **1**, 349.

[49] M. Kodama, *J. Sci. Hiroshima Univ., Ser. A*, 1973, **37**, 53.

[50] U. Khuanga, B. K. Selinger, and R. McDonald, *Austral. J. Chem.*, 1976, **29**, 1.

[51] J. Oakes, *J.C.S. Faraday II*, 1972, **68**, 1464.

[52] N. Muller, J. H. Pellerin, and W. W. Chen, *J. Phys. Chem.*, 1972, **76**, 3012; see also ref. 1(*b*).

[53] (*a*) J. Clifford and B. A. Pethica, *Trans. Faraday Soc*, 1965, **61**, 182; (*b*) T. Walker, *J. Colloid Interface Sci.*, 1973, **45**, 372.

[54] D. Stigter. *J. Phys. Chem.*, 1974, **78**, 2480.

[55] O. H. Griffith, P. H. Dehlinger, and S. P. Van, *J. Membrane Biol.*, 1974, **15**, 159.

are based on the n.m.r. spectra of fluorinated surfactants. However, the CF_3 group has a dipole moment of 1.8 D, and is thus sufficiently polar to retain some water of hydration.[1b] Thus the issue remains open, pending more definite evidence.

F. Counterion Binding to Micelles of Ionic Detergents.—If the detergent molecules in ionic micelles were fully ionized, the equivalent conductance of the detergent ions in the micelles would be greater than the equivalent conductance of the monomeric detergent ions by a factor of $n^{2/3}$, where n is the aggregation number.[56] The equivalent conductance of a detergent solution would therefore increase above the CMC. The opposite is usually observed, the explanation being that part of the charge is neutralized by counterions bound in the Stern layer (Figure 1), whereas monomeric detergent ions are almost fully dissociated.[57]

The mechanism of counterion binding is a part of any complete theory of micelle formation, since the ratio of bound counterions to detergent ions in micelles (m/n) is needed to calculate thermodynamic quantities from the mass-action model (but see Section 4C).

Agreement between different experimental estimates of m/n is often poor.[15a] For example, e.m.f. measurements,[18] light scattering, conductance, and ultracentrifugation all give $m/n = 0.18 \pm 0.02$ for sodium dodecyl sulphate, but electrophoretic mobility gives 0.5, calculations from the effect on the CMC of adding a salt with a common ion give 0.54, different conductance experiments give 0.28, and corrected e.m.f. calculations give 0.5 (ref. 18).

These differences are mainly due to the different ways of handling the activity coefficient of the unbound counterions. In light scattering, for example, ideality is assumed, while in potentiometric studies it is assumed that micelles have no effect on the activity coefficient. Gilányi has suggested[18] that, if this latter assumption is invalid, it may involve over 100% error in values of m/n estimated from e.m.f. measurements.

In the study of counterion mobility, nuclear and electron magnetic resonance studies[58] have yielded three main conclusions. The first is that bound counterions are hydrated to much the same extent as their free counterparts. The second is that the mobility of bound counterions is reduced, but not dramatically. The third is that specific interactions involving the head-group, such as the hydrogen-bonding of water in the hydration shell of carboxylates, can be important. Most of these studies are interpreted in terms of a two-state model ('bound' and 'unbound' counterions). They do not, however, provide strong support for such a clear distinction.

G. Thermodynamics of Micelle Formation.—(*i*) *Free energy, enthalpy, and Entropy.* In Section 2 we described how the free energy of micelle formation

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[56] J. W. McBain, *Trans. Faraday Soc.*, 1913, **9**, 99.

[57] G. D. Parfitt and A. L. Smith, *J. Phys. Chem.*, 1962, **66**, 942.

[58] (*a*) H. Gustavsson and B. Lindman, *J. Amer. Chem. Soc.*, 1975, **97**, 3923; (*b*) J. Oakes, *J.C.S. Faraday II*, 1973, **69**, 1321; (*c*) I. D. Robb and R. Smith, *J.C.S. Faraday I*, 1974, **70**, 287.

($\Delta G_{mic}{}^\circ$) could be calculated from the CMC. It is a measure of the stability of the micelle. We can gain more information by splitting $\Delta G_{mic}{}^\circ$ into enthalpic and entropic contributions. The enthalpy change represents the *nett* change in intermolecular forces upon micelle formation (the small volume change makes the $P\Delta V$ term negligible). The entropy change includes changes in the degrees of freedom of both solvent and detergent molecules. The enthalpy change can be measured calorimetrically, but the entropy change (usually the main contributor to $\Delta G_{mic}{}^\circ$) can only be calculated from $\Delta G_{mic}{}^\circ$ and $\Delta H_{mic}{}^\circ$.

$\Delta G^\circ{}_{mic}$ is inevitably model-dependent. For example, values calculated from the phase- and mass-action models differ by 10% (Table 1). This is not the only difficulty; we have seen in earlier sections that most of the assumptions used in these models (as listed in Section 2) are not fully supported by experiment. Values of m/n, for example, can be grossly in error.

Enthalpies calculated from equations (8) or (9) do not always agree with those determined calorimetrically[31a,59] (see Table 1 also). This is probably mainly due to errors inherent in the calculation of enthalpies from the Van't Hoff equation.* A special problem in applying this equation to micelle formation is that the temperature coefficient of micelle size must be known.[40] It is usually assumed to be zero, but this assumption is probably wrong.[43b] Nevertheless, calculated enthalpies are normally within 10 kJ mol^{-1} of those found experimentally.[31a,59] This is sufficiently encouraging to suggest that calculated values of $\Delta G_{mic}{}^\circ$ may not be seriously in error.

Regardless of how it is obtained, $\Delta H_{mic}{}^\circ$ is usually small compared to $\Delta G_{mic}{}^\circ$. The nett change in intermolecular forces upon micelle formation is thus negligible compared to the contribution to $\Delta G_{mic}{}^\circ$ from the change in entropy,† Conventional wisdom attributes this change to the rearrangement of neighbouring water molecules when the hydrocarbon part of the detergent is transferred from water to the micelle core.[15b] An alternative view is that changes in the type of chain motion can sufficiently account for the observed entropy change.[62] This hypothesis, although not widely held, has never been refuted and has recently received support.[63]

(ii) Head-group and Hydrocarbon-chain Contributions to the Free Energy. Numerous attempts have been made to separate $\Delta G_{mic}{}^\circ$ for the micelles of ionic detergents into electrostatic repulsion ($\Delta G_{el}{}^\circ$) and hydrocarbon chain attraction ($\Delta G_{hc}{}^\circ$) parts.[15a,15b]

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* The Van't Hoff equation [$\Delta H_{mic}{}^\circ = (-RT^2/n)\,\partial(\ln K_M)/\partial T$] is derivable directly from equations (4a) and (7). It should also be noted that the Van't Hoff equation gives a differential heat, while calorimetry gives an integral heat. These may be quite different.[60]

† It is best to calculate entropy so as to obtain [(molar entropy of micelle at the CMC) − (molar entropy of monomer at the CMC)]. It is common, however, to calculate $\Delta H_{mic}{}^\circ$ from equations (8) or (9) and substitute in $\Delta S_{mic}{}^\circ = \Delta H_{mic}{}^\circ/T$. This gives a value of $\Delta S_{mic}{}^\circ$ which contains an unknown mixing term, and can be misleading.[61]

[59] M. N. Jones and J. Piercy, *Kolloid-Z.*, 1973, **251**, 343.

[60] (*a*) L. Benjamin, *Canad. J. Chem.*, 1963, **41**, 2210; (*b*) F. Franks and D. S. Reid, in 'Water; A Comprehensive Treatise', Vol. 2, ed. F. Franks, Plenum Press, New York, 1974, p. 337.

[61] R. E. Lindstrom and J. Swarbrick, *J. Phys. Chem.*, 1970, **74**, 2033.

[62] R. H Aranow and L. Witten, *J. Phys. Chem.*, 1960, **64**, 1643.

[63] O. W. Howarth, *J. C. S. Faraday I*, 1975, **71**, 2303.

Two ways of calculating ΔG_{el}° have been used, although neither is completely satisfactory. The more exact is to solve the non-linearized Poisson–Boltzmann equation for the electrostatic potential at the micelle surface. This equation cannot be solved analytically for spherical particles, and approximate solutions so far obtained have been criticized.[64] A recent closed solution[65] has not yet been applied to micelles.

An alternative is to use the Gouy–Chapman model of the electrical double layer. This model treats the micelle surface as flat; a good approximation for large colloidal particles but undoubtedly invalid for most micelles. It has been thoroughly explored by Stigter.[66]

The hydrocarbon contribution to ΔG_{mic}° can be calculated as $\Delta G_{mic}^{\circ} - \Delta G_{el}^{\circ}$. Alternatively, ΔG_{mic}° can be plotted against hydrocarbon chain length (n_c) for a series of homologous detergents, and ΔG_{hc}° can be calculated from the slope. For ionic detergents at constant (high) ionic strengths, and for non-ionic and zwitterionic detergents, such plots are linear, with a slope of about 3 kJ mol^{-1} per methylene group as ΔG_{hc}°.[15b] The slope is different for ionic detergents without added salt[15b] (about 1.7 kJ mol^{-1} per methylene group) because the ionic strength at the CMC is just the CMC, and is different for each member of the series. A rough correction for ionic-strength effects makes this value agree with that above.

Values of ΔG_{el}° and ΔG_{hc}° calculated by various methods are given by Anacker.[15a] Tanford[15b] has compared ΔG_{hc}° with the free energy of transfer of detergent from water to a non-polar solvent. These differ, possibly because head-group and hydrocarbon-chain contributions are not completely independent. Increasing the chain length affects the micelle packing, and hence both head-group and hydrocarbon-chain interactions.

4 Recent Advances in Equilibrium Theories of Micelle Formation

A. Multiple-equilibrium Models.—Multiple equilibrium models are a natural extension of the mass-action approach to micelle formation. A range of micelle sizes is considered to exist.[37,67] These micelles may be built up from detergent monomers (D) in a single process[19a,38c,68] [equation (10)]* or by a series of

$$\begin{array}{l}
\mathrm{D} + \mathrm{D} \underset{k_{2,1}}{\overset{k_{1,2}}{\rightleftharpoons}} \mathrm{D}_2 \\
\mathrm{D} + \mathrm{D}_2 \rightleftharpoons \mathrm{D}_3 \\
\vdots \qquad \vdots \qquad \vdots \\
\mathrm{D} + \mathrm{D}_{n-1} \underset{k_{n,n-1}}{\overset{k_{n-1,n}}{\rightleftharpoons}} \mathrm{D}_n
\end{array} \tag{10}$$

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* The detergent may be ionic or non-ionic. For convenience we omit counterions from the equations in the case of ionic detergents.

[64] P. Mukerjee, *J. Phys. Chem.*, 1969, **73**, 2054.

[65] S. L. Brenner and R. E. Roberts, *J. Phys. Chem.*, 1973, **77**, 2367.

[66] D. Stigter, *J. Phys. Chem.*, 1975, **79**, 1015.

[67] J. M. Corkhill, J. F. Goodman, T. Walker, and J. A. Wyer, *Proc. Roy. Soc.*, 1969, **A312** 243.

[68] C. Tanford, *J. Phys. Chem.*, 1974, **78**, 2469.

processes equivalent to equation (1).[20a,38a] All species are in rapid equilibrium, and for micelles of ionic detergents the counterions are assumed to equilibrate with the micelles virtually instantaneously.

In practical terms, multiple-equilibrium models have only limited application. For example, they do nothing to remove the ambiguities inherent in calculations of $\Delta G_{\text{mic}}°$. However, they can give relationships between such quantities as monomer concentration $[\mathrm{D}_1]$, total micelle concentration $\sum_1^n [\mathrm{D}_i]$, and total micelle concentration expressed as monomer concentration $\sum_1^n i[\mathrm{D}_i]$. These relationships agree well with experimental results; but these experimental results can often equally well be described by a simple mass-action model. We have found, for example, that Figure 6 of Corkill and Walker[37] is fitted equally well by equation (2), modified for the case of a non-ionic detergent, with $n = 18$, $K_{\mathrm{M}} = 2 \times 10^{-8}$.

Thus the strength of multiple-equilibrium models is that they may provide information about the distribution of micelle sizes, given some simplifying assumptions about the relationships between the equilibrium constants.[20a,38c] Number-average (N_{m}) and weight-average (N_{w}) aggregation numbers can be calculated as functions of the total detergent concentration, and this dependence compared with experiment. The ratio N_{w}/N_n can be deduced, for example, from the dependence of N_{w} on concentration, and is a measure of the spread of micelle sizes. Its value is one for monodisperse micelles and increases with polydispersity. Experimental estimates of N_{w}/N_n are not always reliable, since correction factors of unknown size can completely change their interpretation. For example, light-scattering results for very similar non-ionic detergents have been interpreted as indicating both monodisperse[23] and polydisperse[37] micelles for different, though overlapping, concentration ranges.

Present multiple-equilibrium models have two major drawbacks. All assume ideality, although this is unlikely, especially when comparing prediction with experiment at high concentrations such as those used in light scattering. Most also assume that the micelle distribution is unimodal. A more recent model does assume a bimodal distribution, but the basis of this assumption is not clearly stated.[38c,d]

B. Geometric Models.—Because no holes may exist within a micelle, one or more dimensions must be limited by the maximum possible extension of a hydrocarbon chain. Simple geometric calculations[15b,38a,47,69] show that, given experimentally measured aggregation numbers, most micelles cannot be spherical under this constraint. The simplest alternative are oblate and prolate ellipsoids of revolution; for most micelles an axial ratio of less than 2:1 is required to explain observed aggregation numbers.[70]

The surface area per head-group (A/n) is a key parameter, since it measures the

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[69] (*a*) H. Schott, *J. Pharm. Sci.*, 1971, **60**, 1594; (*b*) H. Schott, *ibid.*, 1973, **62**, 162.
[70] H. V. Tartar, *J. Phys. Chem.*, 1955, **59**, 1195

distance between adjacent head-groups and is inversely related to their free energy of interaction. Tanford has calculated A/n for ellipsoidal models as a function of aggregation number. A graph of his results clearly demonstrates a gradual change from spherical through oblate or prolate ellipsoid of revolution, with the eventual formation of rod-shaped micelles, as n increases.[47] This calculation depends on the implicit assumption that micelle volume increases with chain length. Recent Russian work has suggested that the opposite is true.[71] This conclusion, being so contrary to normal expectation, must be regarded with caution.

The optimum value of A/n is set by thermodynamic considerations. Tanford has used semi-empirical estimates of $\Delta G_{\text{el}}{}^{\circ}$ and $\Delta G_{\text{hc}}{}^{\circ}$, calculated from various values of A/n, to calculate $\Delta G_{\text{mic}}{}^{\circ}$. Reasonable values of A/n lead to consistent values of the CMC and mean size for different types of detergent. An important consequence of Tanford's calculations is that both $\Delta G_{\text{el}}{}^{\circ}$ and $\Delta G_{\text{hc}}{}^{\circ}$ depend on A/n. Thus $\Delta G_{\text{hc}}{}^{\circ}$ is not linearly proportional to chain length nor is $\Delta G_{\text{el}}{}^{\circ}$ completely independent of chain length, contrary to the assumptions of many other models.

Another important result from Tanford's calculations is that oblate, rather than prolate, ellipsoids of revolution are generally energetically preferred, although the experimental evidence for this is controversial.[47] The theory also predicts micelle size distributions, but these are not yet subject to experimental test.

C. Statistical-thermodynamic Models.—Statistical thermodynamics relates bulk thermodynamic properties to molecular interactions. Little progress has been made in its application to micelles because it is difficult to apply to strongly interacting particles, and it is strong interactions that limit micelle size.

Most attempts so far[30,72–74] use the normal approach of defining a partition function (Q), with appropriate assumptions, and calculating thermodynamic quantities from Q. All have used at least one experimentally unjustified assumption,[30] and some are only applicable to unassociated solvents,[30] and thus useless for aqueous solutions. Within these limitations, all models predict a minimum in free energy per monomer at some large aggregation number, *i.e.* micelle formation. Few other predictions are experimentally testable at present; for example, Aranow's formulae relating micelle size fluctuations to monomer activity and mean micelle size.[74] A prediction that is testable is a maximum in N_n as a function of temperature.[73] Experiments over a wide enough temperature range to test this have not been done.[75,76]

[71] G. A. Simakova, V. M. Pankov, S. A. Nikitina, A. E. Chalykh, and K. V. Zotova, *Kolloid. Zhur.*, 1974, **36**, 592.

[72] C. A. T. Hoeve and G. C. Benson, *J. Phys. Chem.*, 1957, **61**, 1149.

[73] (*a*) D. C. Poland and H. A. Scheraga, *J. Phys. Chem.*, 1965, **69**, 2431; (*b*) D. C. Poland and H. A. Scheraga, *J. Colloid Interface Sci.*, 1966, **21**, 273.

[74] R. H. Aranow, *J. Phys. Chem.*, 1963, **67**, 556.

[75] R. R. Balmbra, J. S. Clunie, J. M. Corkhill, and J. F. Goodman, *Trans. Faraday Soc.*, 1962, **58**, 1661.

[76] D. Attwood, P. H. Elworthy, and S. B. Kayne, *J. Phys. Chem.*, 1970, **74**, 3529.

An alternative approach has been developed by Hall,[77] using the Kirkwood–Buff theory of solutions, which is an exact statistical-mechanical theory relating thermodynamic properties to the distribution of solute species. The results obtained agree with the rigorous predictions of small-systems thermodynamics in the limit of infinite dilution. The advantage of Hall's approach is that unbound counter-ions are implicitly allowed for in the expression for the partial molar free energy. Thus, the artificial division between 'bound' and 'unbound' counter-ions is eliminated. This approach is superior to the suggestion[78] that *all* counter-ions be regarded as part of the micelle 'phase'.

D. Small-systems and Surface Thermodynamics.—Small-systems thermodynamics[79] applies to systems in which there are likely to be large fluctuations from the mean value of thermodynamic quantities. The distinguishing feature of small-systems thermodynamics is that normally intensive variables (such as the mean energy) depend on the size of the system. Using small-systems thermodynamics, it is possible to calculate thermodynamic quantities for a single micelle rather than an ensemble of micelles.

In the application of small-systems thermodynamics to micelles, it has so far proved necessary to assume ideality. With this assumption, Hall and Pethica[24] have presented rigorous derivations of the various thermodynamic quantities for micelles of non-ionic detergents. Hall has also presented alternative derivations[80] and has extended the theory to cover micelles of ionic detergents.[81] As may be expected, these quantities (such as $\Delta H_{\text{mic}}{}^\circ$ and $\Delta V_{\text{mic}}{}^\circ$) are derivable from the mean size, the size distribution, and the variation of these with temperature, pressure, and other intensive variables. Data are not available to test these predictions; such comparisons should at least provide a good test of the assumption of ideality.

5 Dynamic Aspects of Micelle Formation

Micelles form and break up very rapidly (estimated relaxation times range from 10^{-2} to 10^{-9} s). The rates of these processes, when studied by the methods used to study fast chemical reactions, can always be interpreted in terms of a single relaxation time (τ), although it should be noted here that it is often impossible to distinguish between an exponential decay with a single time constant and the sum of several exponential decays with different time constants.[82] The observed process is probably exchange of detergent molecules between aggregated and monomeric states[15c,83] although it has been argued that, when applied to the micelles of ionic detergents, some experimental methods measure the rate of exchange of counterions between 'bound' and 'unbound' environments.[81]

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[77] D. G. Hall, *J.C.S. Faraday II*, 1972, **68**, 1439.

[78] P. F. Mijnlieff, *J. Colloid Interface Sci.*, 1970, **33**, 255.

[79] T. L. Hill, 'Thermodynamics of Small Systems', Vols. 1 and 2, Benjamin, New York, 1963–4.

[80] D. G. Hall, *Trans. Faraday Soc.*, 1970, **66**, 1351, 1359.

[81] D. G. Hall, *Kolloid Z.*, 1972, **250**, 895.

[82] A. E. W. Knight and B. K. Selinger, *Austral. J. Chem.*, 1973, **26**, 1.

[83] T. Yasunga, H. Takeda, and S. Harada, *J. Colloid Interface Sci.*, 1973, **42**, 457.

Transient methods, such as pressure-jump and temperature-jump, give values of τ ranging from 10^{-2} to 10^{-5} s, while steady-state methods, such as n.m.r., e.s.r., and ultrasonic absorption, always give values less than 10^{-5} s.[15c,84] This wide range of relaxation times suggests that at least two different relaxation processes are being observed. Muller has suggested that transient methods follow the slow complete breakdown of micelles whereas steady-state methods observe fast single steps, as in equation (10).[85] Folger, Hoffmann, and Ulbricht[86] have found two relaxation times from their pressure-jump and shock wave measurements on SDS solutions. They have identified these relaxation times with the fast and slow processes suggested by Muller.

$1/\tau$ is normally found to increase linearly with concentration, although this may not be universal.[86,87] The relaxation time and its concentration dependence are the only experimental parameters available. On their own, they are not particularly informative. To relate them to rate constants for micelle association and dissociation, a model must be used. If a distribution of micelle sizes is accepted, the multiple-equilibrium model is appropriate and is the one most often adopted. Since this model contains a large number of rate constants, drastic simplifying assumptions about the relations between them must be made. A common assumption (originally proposed by Kresheck, Hamori, Davenport, and Scheraga)[88] is that the rate-limiting (slow) step is the loss of the first monomer from the micelle. In other words, the micelle reluctantly parts with one monomer molecule and then 'explodes'. Since polydispersity implies a range of micelle sizes with similar stabilities, this model seems physically unreasonable (it has been criticized in detail by Muller[85]). Its main appeal is mathematical tractability; it yields a simple relationship between relaxation time and rate constants:

$$1/\tau = k_{n,n-1} + k_{n,n-1}n^2\,([\mathrm{D}_n]/[\mathrm{D}]^2) \qquad (11)$$

An alternative assumption is that micelle distintegration may be treated as a random-walk process with equal forward and backward rate constants for each step.[85] This leads to the relationship (12). This fails to account for the observed

$$1/\tau \simeq 2k_{n,n-1}/n^2 \qquad (12)$$

concentration dependence of τ, and also leads ultimately to a flat size distribution, but it does give values of $k_{n,n-1}$ compatible with steady-state relaxation times, and also with relaxation times from transient methods if total micelle disintegration is being observed by these methods.

A collision model for micelle association and dissociation has been developed by Sams, Wyn-Jones, and Rassing.[38b,89] In its simplest form this contains the

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[84] T. Nakagawa, *Colloid Polymer Sci.*, 1974, **252**, 56.

[85] N. Muller, *J. Phys. Chem.*, 1972, **76**, 3017.

[86] R. Folger, H. Hoffmann, and W. Ulbricht, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 986.

[87] U. Herrmann and M. Kahlweit, *Ber. Bunsengesellschaft Phys. Chem.*, 1973, **77**, 1119.

[88] G. C. Kresheck, E. Hamori, G. Davenport, and H. A. Scheraga, *J. Amer. Chem. Soc.*, 1966, **88**, 246.

[89] (*a*) P. J. Sams, J. E. Rassing, and E. Wyn-Jones, *Adv. Mol. Relaxation Processes*, 1975, **6**, 255; (*b*) J. E. Rassing and E. Wyn-Jones, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 651.

assumptions that monomer–micelle collision frequency is proportional to the cross-sectional area of the micelle and that the dissociation rate is proportional to the aggregation number. These authors also make the unreasonable assumption that the cross-sectional area is proportional to the aggregation number (n).* Geometric models (Section 4B) take the *volume* as proportional to n, making the cross-sectional area proportional to $n^{2/3}$. The model of Sams, Wyn-Jones, and Rassing amounts to the alternative, and not unreasonable, assumption that the rate constants for both association and dissociation are proportional to n, *i.e.*

$$k_{n,n-1} = k_b n;\ k_{n-1,n} = k_f(n - 1) \tag{13}$$

If dimerization is fast, this leads to:

$$1/\tau = k_f C - k_b;\ k_b/k_f = [\mathrm{D}] \simeq \mathrm{CMC} \tag{14}$$

as found by these authors. CMC values calculated from equation (14) are usually within 50% of experimental values. In using these equations, it should be remembered that k_b and k_f are not true rate constants.

These and other models have been summarized by Nakagawa.[84] There is a measure of agreement between values of $k_{n,n-1}$ found from different models (Muller[85] finds values of $3 \times 10^6\ \mathrm{s}^{-1}$ and $11 \times 10^6\ \mathrm{s}^{-1}$ for sodium dodecyl sulphate and dodecyl pyridinium bromide respectively; Sams, Rassing, and Wyn-Jones[38b] find $(1.6 \times 10^6 n)\ \mathrm{s}^{-1}$ and $(3 \times 10^6 n)\ \mathrm{s}^{-1}$ for sodium decyl sulphate and decyl pyridinium iodide, respectively. However, Folgar, Hoffmann, and Ulbricht[86] find $1.9 \times 10^4\ \mathrm{s}^{-1}$ for SDS, and Kresheck, Hamori, Davenport, and Scheraga[87] find $50\ \mathrm{s}^{-1}$ for dodecyl pyridinium iodide). There is still no fully convincing explanation for the difference between results found from steady-state and transient methods.

6 Conclusions

Many features of micelles are well established. Micelles of ionic detergents have aggregation numbers ranging from 10 to 100, and are slightly flattened spheres with interiors resembling those of liquid hydrocarbon droplets. Both the detergent molecules and the counter-ions of the micelles are in dynamic equilibrium with their surroundings, with the detergent molecules having a mean residence time in a micelle of about 10^{-5} s. Micelles of non-ionic detergents are much larger ($n > 1000$) and less spherical than those of ionic detergents. For both types of detergent the existence of a CMC can be predicted from simple equilibrium models, and thermodynamic quantities can be calculated from these models.

However, there are large areas which are not well understood. In particular, theoretical progress at the moment is hindered by a lack of adequate experimental data in four key areas:

(*i*) *Non-ideality.* Activity coefficients of the components of micelle solutions are needed to calculate the properties of micelles from theoretical models.

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* The same authors have proposed an alternative derivation based on the Langmuir adsorption isotherm.[89a] This derivation involves the same assumption.

Although these activity coefficients are usually assumed to be unity, this assumption could be grossly in error.

(*ii*) *Polydispersity.* Recent theories of micelle formation all predict polydispersity and in some cases its variation with temperature and concentration. Experimental data are needed to test these predictions.

(*iii*) *Specific interactions between detergent molecules.* Development of statistical-thermodynamic theories of micelle formation requires a much more detailed knowledge of the specific interactions of detergent molecules than is currently available.

(*iv*) *Identification of specific relaxation processes.* In dynamic studies, most workers use guesswork to identify the species involved in the relaxation processes observed experimentally. It should prove possible in the near future to identify these processes with more certainty.