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Modelling solution entropy in the theory of micellization

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Abstract

In order to develop an equilibrium theory of surfactant solutions, one needs to estimate the entropy of the system consisting of the solvent, singly dispersed surfactant molecules and aggregates of all possible sizes and shapes. No fundamental approach for estimating this entropy taking into account such variations in the size, shape, flexibility and compactness of the constituent species is available in the literature. Currently available theories use entropy estimates that may lack a priori justification, but with the anticipation of obtaining useful practical results. The four widely used entropy estimates are based on the ideal solution model, the gas-like translation model, the Flory–Huggins model, and the translational entropy model. In this paper, we explore the consequences of using these entropy models to predict the properties of solutions in which globular and rodlike micelles are present. Specifically, we compare the theoretical predictions of the CMC, the average aggregation number of the micelles, the size polydispersity, the dependence of micelle size on concentration, the critical constants for incipient phase separation, the spinodal line and the osmotic compressibility resulting from the different entropy models. Our analysis shows that the different entropy estimates lead to widely differing predictions of aggregation characteristics and solution phase behavior. All four entropy estimates employed in the literature lead to predictions that disagree with one or more of the experimentally observed solution characteristics. We find however, that a simple modification to the translational entropy model based on the fact that the surfactant solution is a liquid and not gas-like, brings all theoretical predictions into consistency with the experiments.

Keywords: Critical micelle concentration; micellization; sphere-to-rod transition; surfactant phase behavior; surfactant solution theory.

Introduction

Some important characteristics of aqueous surfactant solutions learnt from experimental studies [1,2] can be summarized as follows. The CMC of a surfactant marking the onset of perceptible aggregation lies within a narrow range of concentrations, depending upon the technique employed for its determination. If the micelles formed are globular, then the micelle size distribution is narrow. In such solutions, the average micelle size does not change appreciably as the total surfactant concentration is increased. In contrast, if the micelles formed are rodlike, then the micelle size distribution is highly polydispersed. The average micelle size increases in proportion to the square root of the surfactant concentration. When surfactant solutions experience phase instability, the surfactant concentrations at the critical point are small and the coexistence curves are highly asymmetric analogous to the behavior displayed by solutions of high molecular weight polymers. All the above experimental features should be predicted by a theory of surfactant solutions, in order for the theory to be considered reasonable. Further, a reasonable theory should also provide quantitative results that are at least approximately comparable to those from the experiments.

Numerous theoretical studies of surfactant solutions have appeared in the literature and only a

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representative few that are discussed in this paper are cited as references [3–23]. A common framework adopted by these studies involves the visualization of the surfactant solution as a multicomponent system made up of the solvent, the singly dispersed amphiphile and aggregates of all possible sizes and shapes. Each of these, including aggregates of a given size and shape, is treated as a distinct chemical component which can be described by a characteristic chemical potential. The total Gibbs energy G of the surfactant solution is written as the sum of three parts: the free energy of the components in a suitably defined reference state G_r, the contribution from the entropy of the components constituting the solution G_e, and the free energy of mutual interactions among the various components G_i.

$$G = G_r + G_e + G_i \tag{1}$$

The total Gibbs energy of the solution is then examined using the general principles of equilibrium thermodynamics to obtain all the detailed characteristics of the surfactant solution.

In calculating the total Gibbs energy of the solution, there is some uncertainty involved in the estimation of each of the three component terms. Consequently, the method of estimating the Gibbs free energy is usually justified only a posteriori, by its success in being able to describe and/or predict various properties of the surfactant solution. The dominant emphasis of theoretical studies in the literature has been on developing improved models for the reference state free energy of an isolated micelle (and hence, G_r). These improvements are found to marginally affect the theoretical predictions of the CMC, micelle size, etc. The fact that more dramatic variations in the predicted properties are caused by how the entropic contribution G_e is calculated, has not been recognized adequately in the literature.

In developing an estimate for G_e, one has to take into account the fact that micelles of various aggregation numbers, the singly dispersed surfactant molecule and the solvent molecule are all different from one another in their sizes. Also, while micelles are large, because of their compact structure they are different from flexible macromolecules of comparable sizes. Further, the micelles are associated with distinct shapes. No fundamental approach for estimating the system entropy that takes into account such variations in the size, shape, flexibility and compactness of the constituent species is available in the literature. Consequently, four arbitrary expressions for the entropy developed for different situations have been employed for the theoretical study of surfactant solutions. Early statistical thermodynamic treatments of micellization utilized formulations applied to multicomponent gas mixtures [6,7]. In these treatments, the system entropy was taken to be the translational entropy of all the components, viewed as point molecules, in the total volume of the system. Such an entropy model, the gas-like translation model, has been used in treatments of micelle and vesicle formation [6–9], isotropic to nematic transition of aggregates [10], and phase separation in surfactant solutions [11]. A second entropy model is that involved in the treatment of ideal liquid mixtures. The ideal solution model has been used [12–14] in treatments of the CMC, the formation of micelles and vesicles, and to describe the transition between spherical and rodlike micelles. A third model of the solution entropy is that based on the work of Flory and Huggins applied to flexible linear macromolecules. The Flory–Huggins model has been used in treatments of micellization [15], formation of rodlike micelles [16] and vesicles [17] and phase separation in surfactant solutions [16,18]. The fourth model, referred to here as the translational entropy model is a variant of the gas-like translation model. In calculating the volume available for translation in this model, the size differences between the solvent and the singly dispersed surfactant molecule is neglected. The translational entropy model has been applied to the formation of globular and rodlike micelles and also to phase separation in surfactant solutions [19–22]. Although these four estimates for the system entropy have been utilized in various studies, there has been no systematic

comparison of the quantitative predictions that result from the different entropy estimates. The main goal of the present work is to undertake such a comparison. We show that the four models lead to widely differing predictions of micellar properties and that none of the models predicts quantitatively all the experimental observations summarized at the outset. Finally, we suggest a small modification to the translational entropy model based on the recognition that the surfactant solution is a liquid and not a gaseous mixture. Since this modification is found to eliminate the discrepancy between the predictions and the experiments, we propose the use of this expression for G_e in future theoretical studies.

Multicomponent solution treatment

Let us consider a surfactant solution made up of N_s solvent molecules, N_1 singly dispersed surfactant molecules and N_g aggregates of size g, all possible sizes and shapes of the aggregates being allowed. The total Gibbs energy of the solution is decomposed into three parts as in Eqn (1). The first contribution accounts for the standard state free energy of all the constituent species. The standard state for the solvent is defined to be that of pure solvent while the standard states for all the other species are defined to be those of infinitely dilute solution condition. The symbols μ_s°, μ_1° and μ_g° denote the reference state Gibbs energies of the solvent, the singly dispersed amphiphile and the aggregate of size g, respectively. Therefore, one may write

$$G_r = N_s\mu_s^\circ + \sum N_g\mu_g^\circ \tag{2}$$

The summation extends from 1 to ∞ and thus includes the singly dispersed surfactant as well as aggregates of all sizes and shapes. The second contribution to the total Gibbs energy is provided by the entropy of the components constituting the solution. Different models are used to calculate this entropic contribution as detailed below. The last contribution to the Gibbs energy of the surfactant system arises from the mutual interactions among all the species present in the solution. One may note that although the surfactant solution is a multicomponent system, all the components other than the solvent are related to one another through association–dissociation equilibria. Consequently, all the interspecies interactions in this multicomponent solution can be written as for binary mixtures in terms of solvent–solvent, solvent–surfactant, and surfactant–surfactant interactions [11,19]. The simplest treatment of interactions in binary solutions is that based on the random mixing approximation which gives rise to the well-known van Laar interaction energy. Both the regular solution theory of Hildebrand and Scatchard and the polymer solution theory of Flory and Huggins incorporate such a van Laar type interaction contribution in their respective models for the solution free energy. Thermodynamic treatments of phase separation in surfactant solutions, available in the literature [11,18–22] have utilized such an expression for the interaction energy. Therefore, we also adopt the van Laar form for this contribution to the system free energy

$$G_i = kT\chi N_s\phi \tag{3}$$

where ϕ is the total volume fraction of the surfactant in the system, T is the temperature, k is the Boltzmann constant, and χ is the interaction energy parameter of the kind appearing in the van Laar expression. The volume fraction ϕ is estimated from

$$\phi = \frac{\sum mgN_g}{N_s + \sum mgN_g} \tag{4}$$

where m is the ratio of the molecular volume of the singly dispersed surfactant to that of the solvent. As will be seen later, the size distribution of aggregates is unaffected by the interspecies interaction for this functional form of interaction energy. Obviously, Eqn (3) is not a unique representation of the interactions and it would be useful to explore other models for the interaction free energy as well. Especially, it is of interest to consider expressions for interspecies interactions which

would modify the micellar size distribution. However, since the main goal of this work is to focus on the consequences of the system entropy models, the van Laar form of the interaction energy is taken to be adequate for the present purposes.

The total Gibbs energy of the system G provides the basis for the evaluation of various characteristics of the surfactant solution. One may represent G formally in terms of the chemical potentials μ_i of the various species i present in the solution

$$G = N_s\mu_s + N_1\mu_1 + \sum_2^\infty N_g\mu_g \tag{5}$$

For a given total concentration of the surfactant, the equilibrium is defined by the condition of a minimum in the total Gibbs energy. Therefore, at equilibrium

$$\delta G = \delta N_s\mu_s + \delta N_1\mu_1 + \sum_2^\infty \delta N_g\mu_g = 0 \tag{6}$$

The mass conservation constraint implies

$$N_1 + \sum_2^\infty gN_g = \text{constant}$$

or

$$\delta N_1 = -\sum_2^\infty g\,\delta N_g \tag{7}$$

Recognizing $\delta N_s = 0$ and taking into account the mass conservation constraint, we can rewrite the equilibrium condition (Eqn (6)) as

$$\mu_g/g = \mu_1 \tag{8}$$

for all values of g.

Equation (8) represents a fundamental result for any system of associating molecules and stipulates that the chemical potential of the singly dispersed surfactant molecule is equal to the chemical potential per molecule of any aggregate irrespective of its size or shape. At this stage, in order to express the above equation in terms of concentrations, we need to formulate models for the system entropy. The following section summarizes the expressions for the system entropy and the resulting equations for the size distribution of aggregates for all the four entropy models employed in the literature as well as for the modified translational entropy model suggested in this paper.

Entropy models and micelle size distributions

Ideal solution model

The entropy of an ideal solution can be estimated by visualizing a lattice with $N_s + \sum N_g$ sites or cells in which the $N_s + \sum N_g$ species can be equivalently placed. Thus, this model ignores the differences in the sizes of the various species present in the solution. The total number of distinguishable arrangements possible is

$$\Omega = \frac{\left(N_s + \sum N_g\right)!}{N_s! \prod_g N_g!} \tag{9}$$

Correspondingly, the contribution of the system entropy to the total Gibbs energy is calculated from

$$G_e = -kT\ln\Omega = -kT\left[N_s\ln\left(\frac{N_s}{N_s + \sum N_g}\right) + \sum N_g\ln\left(\frac{N_g}{N_s + \sum N_g}\right)\right] \tag{10}$$

Introducing Eqn (10) in the expression for the total Gibbs energy, we can find the chemical potentials of the various constituent species. For species of aggregation number g (including $g = 1$)

$$\mu_g = \mu_g^\circ + kT\ln\left(\frac{N_g}{N_s + \sum N_g}\right) + kT\chi\left(\frac{N_s}{N_s + \sum mgN_g}\right)^2 mg \tag{11}$$

Applying the equilibrium condition (Eqn (8)), we obtain the aggregate size distribution equation

$$X_g = X_1^g \exp - \left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right)$$
$$X_g = \frac{N_g}{N_s + \sum N_g} \tag{12}$$

where X_i denotes the mole fraction of species i.

Given the size distribution function X_g, one can compute the number-average, weight-average and the z-average aggregation numbers (g_n, g_w and g_z, respectively) of the micelles from

$$g_n = \frac{\sum gX_g}{\sum X_g} \qquad g_w = \frac{\sum g^2 X_g}{\sum gX_g} \qquad g_z = \frac{\sum g^3 X_g}{\sum g^2 X_g} \tag{13}$$

The change in the average aggregation number for a change in the total surfactant concentration can be estimated from the following equations:

$$\frac{\partial \ln g_w}{\partial \ln \sum gX_g} = \frac{g_z}{g_w} - 1$$
$$\frac{\partial \ln g_n}{\partial \ln \sum gX_g} = 1 - \frac{g_n}{g_w} \tag{14}$$

The mean square deviations σ^2 of the aggregation numbers from either the weight- or the number-average value (σ_n and σ_w, respectively) are given by

$$\sigma_w^2 = \frac{\sum (g - g_w)^2 X_g}{\sum X_g} = g_w^2\left(1 - \frac{g_n}{g_w}\right)$$
$$\sigma_n^2 = \frac{\sum (g - g_n)^2 X_g}{\sum X_g} = g_n^2\left(\frac{g_w}{g_n} - 1\right) \tag{15}$$

Equation (15) indicates that a deviation from unity of the ratio g_w/g_n is a measure of the size dispersion of the aggregates. This ratio is commonly known as the polydispersity index. Equation (14) suggests that for relatively monodispersed systems, the average aggregation number is practically unaffected by a change in the total surfactant concentration. In contrast, the average aggregation number in polydispersed micellar solutions changes appreciably with changing surfactant concentration.

Gas-like translation model

In this model, the various species constituting the surfactant solution are treated like point molecules free to translate over the entire volume of the solution. In defining the system volume V, the size differences between the various species are taken into account. The canonical partition function Q for the translation of various species is given by

$$Q = \frac{V^{N_s}}{N_s!} \prod_g \frac{V^{N_g}}{N_g!} \qquad V = N_s + \sum mgN_g \tag{16}$$

where V is the total volume of the system expressed as multiples of the volume V_s of a solvent molecule. The Gibbs energy associated with this translational entropy can be written as

$$G_e = A + PV = -kT \ln Q + \left(N_s + \sum N_g\right) kT \tag{17}$$

where A is the Arrhenius free energy related directly to the canonical partition function of a gas with molecules translating over a fixed volume V at constant temperature T, P is the total pressure and PV in the above equation is expressed in terms of the ideal gas equation of state. Consequently

$$G_e = kT\left[N_s \ln\left(\frac{N_s}{N_s + \sum mgN_g}\right) + \sum N_g \ln\left(\frac{N_g}{N_s + \sum mgN_g}\right)\right] \tag{18}$$

Introducing this expression in the equation for the Gibbs energy of the surfactant solution, we can determine the chemical potentials of various species. For species of aggregation number g (including the case when $g = 1$)

$$\mu_g = \mu_g^\circ + kT\left[\ln\left(\frac{N_g}{N_s + \sum mgN_g}\right) + 1 - mg\left(\frac{N_s + \sum N_g}{N_s + \sum mgN_g}\right)\right]$$

$$+ kT\chi\left(\frac{N_s}{N_s + \sum mgN_g}\right)^2 mg \tag{19}$$

At equilibrium the equivalence of chemical potentials per molecule of the aggregate and the singly dispersed amphiphile yields

$$\rho_g = \rho_1^g \exp(g-1)\exp-\left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right)$$
$$\rho_g = \left(\frac{N_g}{N_s + \sum mgN_g}\right) \tag{20}$$

where ρ_i is the number density (number per unit dimensionless volume) of species i. From the size distribution function the various average aggregation numbers are computed as

$$g_n = \frac{\sum g\rho_g}{\sum \rho_g} \qquad g_w = \frac{\sum g^2\rho_g}{\sum g\rho_g} \qquad g_z = \frac{\sum g^3\rho_g}{\sum g^2\rho_g} \tag{21}$$

The dependence of the average aggregation numbers on the total surfactant concentration is calculated from the expressions

$$\frac{\partial \ln g_w}{\partial \ln \sum g\rho_g} = \frac{g_z}{g_w} - 1$$
$$\frac{\partial \ln g_n}{\partial \ln \sum g\rho_g} = 1 - \frac{g_n}{g_w} \tag{22}$$

The index of polydispersity is taken, as before, to be the ratio g_w/g_n.

Flory–Huggins model

Flory and Huggins independently formulated expressions for the entropy of mixing of flexible linear macromolecules with a low molecular weight solvent. The polymer is assumed to be composed of a number of segments, each comparable in size to that of the solvent. The solution is visualized as a lattice and the number of ways of arranging the polymer segments and solvent molecules in the lattice is estimated by combinatorial calculations. The total number of arrangements is then reduced by a factor which represents the number of ways that a pure polymer can be arranged in the lattice in the absence of any solvent. The entropy of mixing of a solution of polydispersed flexible polymers obtained in the above manner is taken as being equivalent to the system entropy of the micellar solution. This entropy of the micellar solution is provided by the relationship

$$G_e = kT\left[N_s \ln\left(\frac{N_s}{N_s + \sum mgN_g}\right) + \sum N_g \ln\left(\frac{mgN_g}{N_s + \sum mgN_g}\right)\right] \tag{23}$$

The above equation differs from that for the ideal solution model in the replacement of the mole fractions by volume fractions. It differs from that for the gas-like translation model in that while both models refer to the same total volume, the latter refers to the translational entropy of point molecules while Eqn (23) refers to the entropy of mixing of molecules of various sizes.

Introducing Eqn (23) in the expression for the total Gibbs energy, the chemical potentials of species containing g molecules (including $g = 1$) can be found.

$$\mu_g = \mu_g^\circ + kT\left[\ln\left(\frac{mgN_g}{N_s + \sum mgN_g}\right) + 1 - mg\left(\frac{N_s + \sum N_g}{N_s + \sum mgN_g}\right)\right] + kT\chi\left(\frac{N_s}{N_s + \sum mgN_g}\right)^2 mg \tag{24}$$

Correspondingly, the equilibrium aggregate size distribution can be written as

$$\phi_g = \phi_1^g \exp(g-1)\exp-\left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right)$$
$$\phi_g = \left(\frac{mgN_g}{N_s + \sum mgN_g}\right) \tag{25}$$

where ϕ_i denotes the volume fraction of species i. From the size distribution function we can compute the various average aggregation numbers as follows:

$$g_n = \frac{\sum \phi_g}{\sum \phi_g/g} \qquad g_w = \frac{\sum g\phi_g}{\sum \phi_g} \qquad g_z = \frac{\sum g^2\phi_g}{\sum g\phi_g} \tag{26}$$

The dependence of the average aggregation numbers on the total surfactant concentration is given by the relationship

$$\frac{\partial \ln g_n}{\partial \ln \sum \phi_g} = 1 - \frac{g_n}{g_w}$$
$$\frac{\partial \ln g_w}{\partial \ln \sum \phi_g} = \frac{g_z}{g_w} - 1 \tag{27}$$

The polydispersity index in this case is again given by the ratio g_w/g_n.

Translational entropy model

This model is a minor variant of the gas-like translation model. The various species constituting the surfactant solution are treated like point molecules translating over the system volume $V_0 = N_s + \sum gN_g$. Thus, the size difference between the solvent molecule and the singly dispersed surfactant molecule is ignored while defining the system volume in this model when compared to the gas-like translation model. The canonical partition function Q describing the translation of various species is

$$Q = \frac{V_0^{N_s}}{N_s!}\prod_g \frac{V_0^{N_g}}{N_g!} \qquad V_0 = N_s + \sum gN_g \tag{28}$$

The Gibbs energy associated with this translational entropy is calculated, as before, to be

$$G_e = A + PV_0 = -kT\ln Q + \left(N_s + \sum N_g\right)kT \tag{29}$$

where the term PV_0 representing the difference between the Gibbs and Arrhenius free energies is written as for an ideal gas mixture. Consequently

$$G_e = kT\left[N_s \ln\left(\frac{N_s}{N_s + \sum gN_g}\right) + \sum N_g \ln\left(\frac{N_g}{N_s + \sum gN_g}\right)\right] \tag{30}$$

Taking into account the above expression for G_e in the equation for the total Gibbs energy G, the chemical potential of a species of aggregation number g (including $g = 1$) can be written as

$$\mu_g = \mu_g^\circ + kT\left[\ln\left(\frac{N_g}{N_s + \sum gN_g}\right) + 1 - g\left(\frac{N_s + \sum N_g}{N_s + \sum gN_g}\right)\right] + kT\chi\left(\frac{N_s}{N_s + \sum mgN_g}\right)^2 mg \tag{31}$$

Therefore, the aggregate size distribution is given by

$$Z_g = Z_1^g \exp(g-1)\exp - \left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right)$$
$$Z_g = \left(\frac{N_g}{N_s + \sum gN_g}\right) \tag{32}$$

where Z_i is the ratio between the true moles of a species i and the total stoichiometric moles of all species present in the solution. From the size distribution function, the various average aggregation numbers are computed as

$$g_n = \frac{\sum gZ_g}{\sum Z_g} \qquad g_w = \frac{\sum g^2 Z_g}{\sum gZ_g} \qquad g_z = \frac{\sum g^3 Z_g}{\sum g^2 Z_g} \tag{33}$$

The dependence of the average aggregation numbers on the total surfactant concentration is calculated from the expressions

$$\frac{\partial \ln g_w}{\partial \ln \sum g Z_g} = \frac{g_z}{g_w} - 1$$
$$\frac{\partial \ln g_n}{\partial \ln \sum g Z_g} = 1 - \frac{g_n}{g_w} \quad (34)$$

The index of polydispersity is taken, as before, to be the ratio g_w/g_n.

Modified translational entropy model

The four entropy models discussed above are shown later to predict one or more characteristics of the surfactant solutions at variance with the experimental observations. Here we suggest a simple modification to the translational entropy model that is found to bring all theoretical predictions into better agreement with experiments. One may note that in writing Eqn (29), the difference between the Gibbs free energy and the Arrhenius free energy, namely PV_0, has been taken to be equal to $\left(N_s + \sum N_g\right) kT$. This is valid if the system being considered is an ideal gas mixture. But surfactant solutions are in the liquid state and for liquids PV is negligibly smaller than $\left(N_s + \sum N_g\right) kT$. This is a restatement of the well-known fact that the compressibility factor for liquids at atmospheric pressure is practically zero, while it is unity for ideal gases. Hence, the Gibbs free energy should be practically equal to the Arrhenius free energy in the case of surfactant solutions. Therefore, Eqn (30) should be modified to

$$G_e = kT\left[N_s \ln\left(\frac{N_s}{N_s + \sum g N_g}\frac{1}{e}\right) + \sum N_g \ln\left(\frac{N_g}{N_s + \sum g N_g}\frac{1}{e}\right)\right] \quad (35)$$

Consequently, the chemical potential μ_g is given by

$$\mu_g = \mu_g^\circ + kT\left[\ln\left(\frac{N_g}{N_s + \sum g N_g}\right) - g\left(\frac{N_s + \sum N_g}{N_s + \sum g N_g}\right)\right] + kT\chi\left(\frac{N_s}{N_s + \sum mg N_g}\right)^2 mg \quad (36)$$

The aggregate size distribution Eqn (32) is thus transformed into

$$Z_g = Z_1^g \exp - \left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right) \quad (37)$$

where the mole ratio Z_i has already been defined. The average aggregation numbers are calculated from Eqn (33) while their dependence on the surfactant concentration is determined using Eqn (34).

In order to proceed further and compute the size distribution of micelles, the CMC, the average aggregation number and the polydispersity index for the models of system entropy discussed above, we need explicit expressions for the standard chemical potential difference term $\mu_g^\circ - g\mu_1^\circ$. A detailed molecular approach to the calculation of $\mu_g^\circ - g\mu_1^\circ$ developed in our recent work [23] is used in the present study. Appendices A, B and C briefly summarize the expression for the standard free energy of micelle formation, as well as the relevant geometrical properties of micelles.

Results for systems forming globular micelles

The size distributions of micelles have been calculated for a non-ionic surfactant, decyl methyl sulfoxide (designated $C_{10}SO$) and an anionic surfactant sodium dodecyl sulfate (designated SDS) for illustrative purposes. The calculated CMCs, the weight- and number-average aggregation numbers at the CMC and the index of polydispersity are summarized in Table 1. Here, we define the CMC as the total surfactant concentration at which a sharp transition is observed in a plot of the total

TABLE 1

CMC, average aggregation numbers and polydispersity index for non-ionic $C_{10}SO$ and ionic SDS surfactants

Entropy model	CMC (mM)	g_w	g_n	g_w/g_n
Non-ionic surfactant $C_{10}SO$				
Experimental data [24]	1.7	–	–	–
Ideal solution model	1.76	92.6	95.2	1.028
Gas-like translation model	0.638	92.4	94.9	1.027
Flory–Huggins model	0.044	102.0	105.0	1.029
Translational entropy model	0.638	92.4	94.9	1.027
Modified translational entropy model	1.76	92.6	95.2	1.028
Ionic surfactants SDS				
Experimental data [2]	8.12	–	–	–
Ideal solution model	7.46	73.4	69.0	1.064
Gas-like translation model	4.24	52.0	44.5	1.169
Flory–Huggins model	0.856	18.0	16.0	1.125
Translational entropy model	4.24	52.0	44.5	1.169
Modified translational entropy model	7.46	73.4	69.0	1.064

surfactant concentration versus the singly dispersed surfactant concentration. Also included in the table are the experimental CMC data [2,24] for the two surfactants considered here. The solution conditions for which the calculations have been performed give rise only to small globular micelles.

For the non-ionic surfactant, all the entropy models predict comparable aggregation numbers. The weight- and the number-average aggregation numbers are practically equal to one another. Therefore, the size dispersion index is close to unity, indicating a virtually monodispersed population of aggregates. Consequently, the calculated average aggregation numbers are found to change very little with a change in the total concentration of the surfactant. The calculated CMCs, however, are very different for the different entropy models. The gas-like translation model and the translational entropy model yield a smaller CMC compared with the experimental CMC while the Flory–Huggins model gives rise to an exceptionally smaller CMC. The ideal solution model and the modified translational entropy model provide identical results that are in good agreement with the experiments.

In the case of ionic surfactants, both the CMC and the average aggregation number are affected by the choice of the entropy model. The CMC values predicted by the different entropy models differ from one another, the relative trend being the same as for the results mentioned above for non-ionic surfactants. As before, the gas-like translation model, the translational entropy model and the Flory–Huggins model predict smaller values for the CMC while the ideal solution model and the modified translational entropy model predict CMCs that agree with the experiments. The average aggregation numbers of SDS micelles predicted by the models are substantially different from one another. Models that predict lower CMC also predict smaller average aggregation numbers. This is in marked contrast to the previous results for the non-ionic surfactant. All the entropy models predict size dispersion indices close to unity and thus virtually monodispersed micellar aggregates.

The above results can be simply interpreted starting from the size distribution equations derived earlier. Recognizing that the total surfactant concentration is rather small near the CMC, one can write approximate expressions for the CMC corresponding to the different entropy models (Table 2). The standard chemical potential μ_g° in the expressions for the CMC corresponds to that of the equilibrium aggregate having an area a_e per surfactant molecule. For non-ionic surfactants, the area a_e per surfactant molecule is virtually unaffected by the choice of the entropy model. Consequently, the predicted average aggregation number is independent of the entropy models. The CMC values are comparable between measurements and the predictions of the ideal solution model and the modified translational entropy model, but smaller by a factor 1/e for the gas-like translation model and the translational entropy model and by a factor $1/me$ for the Flory–Huggins model. In contrast, for ionic surfactants, the area

TABLE 2

Approximate expressions for the CMC

Entropy model	Expression[a]
Ideal solution model	$X_1 = \frac{N_1}{N_s} = \exp\left[\frac{(\mu_g^\circ/g) - \mu_1^\circ}{kT}\right]$
Gas-like translation model	$\rho_1 = \frac{N_1}{N_s} = \frac{1}{e}\exp\left[\frac{(\mu_g^\circ/g) - \mu_1^\circ}{kT}\right]$
Flory–Huggins model	$\frac{1}{m}\phi_1 = \frac{N_1}{N_s} = \frac{1}{me}\exp\left[\frac{(\mu_g^\circ/g) - \mu_1^\circ}{kT}\right]$
Translational entropy model	$Z_1 = \frac{N_1}{N_s} = \frac{1}{e}\exp\left[\frac{(\mu_g^\circ/g) - \mu_1^\circ}{kT}\right]$
Modified translational entropy model	$Z_1 = \frac{N_1}{N_s} = \exp\left[\frac{(\mu_g^\circ/g) - \mu_1^\circ}{kT}\right]$

[a] All the equality signs should be read as approximate equalities.

a_e is affected by the choice of the entropy models. This is because, in the absence of any added electrolyte, the ionic strength is determined primarily by the concentration of the single amphiphiles. Consequently, entropy models that predict a lower CMC are characterized by lower ionic strengths. Correspondingly, the electrostatic repulsions among the head groups are larger and the predicted equilibrium micelle sizes are smaller. This is seen in the lower aggregation number obtained for the gas-like translation and the translational entropy models, and the substantially smaller aggregation number resulting for the Flory–Huggins model in comparison with the predictions of the ideal solution model and the modified translational entropy model. Obviously, in the presence of a sufficient amount of added electrolyte (e.g. 0.1 *M*), this difference between non-ionic and ionic surfactants will diminish. In summary, theoretical predictions of the ideal solution and the modified translational entropy models are identical and in good agreement with experiments for solutions in which globular micelles are formed. The other three models disagree with experimental data in their predictions of the CMC and the micelle size.

Formation of rodlike micelles

Rodlike micelles with large aggregation numbers are formed under conditions that contribute to an increase in the attractive component or a decrease in the repulsive component of the free energy of micellization. For example, longer surfactant tail lengths, smaller polar head groups and larger ionic strengths of the surfactant solution are conditions favorable to the formation of rodlike micelles. Many experimental studies [25–33] have been conducted to measure the average size of rodlike micelles, their size dispersion and the dependence of the average size on the total surfactant concentration. Also, whether their structures are rigid or flexible has been explored. These studies suggest that when rodlike micelles form, they are generally polydisperse. The average aggregation numbers of the micelles are found to vary with the square root of the total concentration of the surfactant. The micellar structures are rigid when the rods are of small length but are considerably flexible when the aggregation numbers are extremely large. Whereas the above observations are most frequently encountered in the literature, there have been a few conflicting reports as well. Some reports suggest that there are concentration ranges of surfactant where the rodlike micelles may be monodispersed, with their average size being less dependent on the total surfactant concentration [31]. Also, it has been reported that in some systems, the micelle aggregation number is proportional to the total surfactant concentration at moderate concentrations of the surfactant and becomes independent of the concentration at larger amounts of surfactant in solution [30].

Theoretical treatment of the transition from small globular micelles to large rodlike micelles was first formulated by Mukerjee [4,5,34]. He predicted that rodlike micelles should be highly polydispersed and that their average aggregation number should be proportional to the square root of the total surfactant concentration. Also, Mukerjee demonstrated how subtle variations in the free energy of micellization dramatically influence whether globular or rodlike micelles will be

formed in solution. Mukerjee's treatment has been presented in alternative but equivalent forms in many subsequent discussions of the transition from spherical to cylindrical micelles [14,26–28,35]. Implicit in the model used by Mukerjee is the assumption that the entropy of the micellar system can be estimated as for an ideal solution. This is reflected in the representation of equilibrium constants of micellization as ratios of mole fractions of various species.

To examine the formation of rodlike micelles, one can visualize the micelle as having a structure consisting of a cylindrical portion of length L and two spherical endcaps. The radii of the cylindrical portion and the spherical endcaps are allowed to differ from one another. The reference state Gibbs energy of the micelle is then written as the sum of two parts, one denoting the spherical endcaps and the other representing the cylindrical middle portion of the micelle. In a micelle of aggregation number g, the number of molecules in the two endcaps are denoted by g_{sp} while the remaining $g - g_{sp}$ molecules are in the cylindrical middle part. Therefore

$$\mu_g^\circ = (g - g_{sp})\mu_{cy}^\circ + g_{sp}\mu_{sp}^\circ \tag{38}$$

In the above expression, μ_{sp}° and μ_{cy}° denote the standard chemical potential of a molecule in the spherical and the cylindrical portions, respectively, of the micelle. Consequently, the standard free energy of micellization can be written as

$$\begin{aligned}\frac{\mu_g^\circ - g\mu_1^\circ}{kT} &= g\left(\frac{\mu_{cy}^\circ - \mu_1^\circ}{kT}\right) + g_{sp}\left(\frac{\mu_{sp}^\circ - \mu_{cy}^\circ}{kT}\right) \\ &= g\left(\frac{\mu_{cy}^\circ - \mu_1^\circ}{kT}\right) + \ln K\end{aligned} \tag{39}$$

The parameter K is a measure of the preference for the rodlike micelles compared to the spherical micelles. For rodlike micelles to form at reasonable surfactant concentrations, K should lie within the range of 10^7–10^{11} [4,14,35]. Introducing the above expression in the equations for micelle size distributions, we can predict the characteristics of rodlike micelles based on the different entropy models.

Entropy models and sphere-to-rod transition

Ideal solution model

The micellar size distribution (Eqn (12)), when combined with Eqn (39) for the free energy of micellization, yields

$$X_g = \frac{Y^g}{K} \qquad Y = X_1 \exp - \left(\frac{\mu_{cy}^\circ - \mu_1^\circ}{kT}\right) \tag{40}$$

Here Y must be smaller than unity to ensure that the micellar concentration X_g is bounded and finite. For simplifying the mathematical analysis, we assume that micelles in the size range $2 < g < g_{sp}$ are in negligible concentrations and may be ignored [14,26–28]. This is reasonable in view of the expected preponderence of aggregates of larger sizes in solution. To evaluate the sums of discrete variables like X_g, we replace the summation by an integral, treating X_g as a continuous function. Further, Y should be close to unity if large micelles are to form at reasonable total surfactant concentrations. In the limit $Y \to 1$, $\ln(Y) = -(1 - Y)$. Also, $g_{sp}(1 - Y) \ll 1$. Consequently, we obtain

$$\sum X_g = \int_{g_{sp}}^{\infty} \frac{Y^g}{K} dg = -\frac{1}{K}\frac{Y^{g_{sp}}}{\ln Y} = \frac{1}{K}\frac{1}{(1 - Y)} \tag{41}$$

$$\begin{aligned}\sum g X_g &= \int_{g_{sp}}^{\infty} g\frac{Y^g}{K} dg \\ &= -\frac{1}{K}\left[g_{sp}\frac{Y^{g_{sp}}}{\ln Y} - \frac{Y^{g_{sp}}}{(\ln Y)^2}\right] = \frac{1}{K}\frac{1}{(1 - Y)^2}\end{aligned} \tag{42}$$

$$\begin{aligned}\sum g^2 X_g &= \int_{g_{sp}}^{\infty} g^2\frac{Y^g}{K} dg \\ &= -\frac{1}{K}\left[g_{sp}^2\frac{Y^{g_{sp}}}{\ln Y} - 2g_{sp}\frac{Y^{g_{sp}}}{(\ln Y)^2} + \frac{2Y^{g_{sp}}}{(\ln Y)^3}\right] \\ &= \frac{1}{K}\frac{2}{(1 - Y)^3}\end{aligned} \tag{43}$$

$$\sum g^3 X_g = \int_{g_{sp}}^{\infty} g^3 \frac{Y^g}{K} dg = -\frac{1}{K}\left[g_{sp}^3 \frac{Y^{g_{sp}}}{\ln Y} - 3g_{sp}^2 \frac{Y^{g_{sp}}}{(\ln Y)^2} + 6g_{sp} \frac{Y^{g_{sp}}}{(\ln Y)^3} - 6\frac{Y^{g_{sp}}}{(\ln Y)^4}\right] = \frac{1}{K}\frac{6}{(1-Y)^4} \quad (44)$$

In order to determine how the average aggregation numbers depend on the total surfactant concentration, we relate $(1 - Y)$ to the total amount of surfactant through Eqn (42)

$$\frac{1}{(1-Y)} = \left(K \sum g X_g\right)^{1/2} = \left(K \frac{\sum g N_g}{N_s + \sum N_g}\right)^{1/2} = \left(\frac{K}{m}\frac{\phi}{1-\phi}\right)^{1/2} \quad (45)$$

In writing the last equality above, we have considered the fact that $N_s \gg \sum N_g$, even when the total amount of surfactant in solution is large. Using Eqns (41)–(44) and the definitions of the number-, weight- and z-average aggregation numbers given by Eqn (13), we obtain the results that are summarized in Table 3. One may note that the expression for the CMC in the table is obtained from Eqn (40) corresponding to the condition $Y \to 1$.

Gas-like translation model

The micelle size distribution (Eqn (20)) incorporating Eqn (39) for the free energy of micellization yields

$$\rho_g = \frac{Y^g}{eK} \qquad Y = e\rho_1 \exp -\left(\frac{\mu_{cy}^\circ - \mu_1^\circ}{kT}\right) \quad (46)$$

As in the previous case, $Y \to 1$ for the appearance of rodlike micelles. Following the procedure identical to that discussed for the ideal solution model, we find that the total surfactant concentration is related to $(1 - Y)$ via

$$\frac{1}{(1-Y)} = \left(eK \sum g\rho_g\right)^{1/2} = \left(eK \frac{\sum g N_g}{N_s + \sum mg N_g}\right)^{1/2} = \left(\frac{eK}{m}\phi\right)^{1/2} \quad (47)$$

Consequently, one can write down the results summarized in Table 3 for the average aggregation number, polydispersity index and the CMC.

Flory–Huggins model

The equation for the micelle size distribution (Eqn (25)), when combined with the free energy of micellization (Eqn (39)), gives the result

$$\phi_g = \frac{Y^g}{eK} \qquad Y = e\phi_1 \exp -\left(\frac{\mu_{cy}^\circ - \mu_1^\circ}{kT}\right) \quad (48)$$

As mentioned already, the condition for the formation of large micelles coincides with the limit $Y \to 1$. One obtains, in a manner identical to that discussed earlier, the relationship between the total surfactant concentration and $(1 - Y)$

$$\frac{1}{1-Y} = eK \sum \phi_g = eK\phi \quad (49)$$

Utilizing this relationship, the dependence of the various average aggregation numbers on the total concentration of the surfactant are determined. The predictions of the Flory–Huggins model are also listed in Table 3. One may note that for deriving the expression for g_n, we need the summation

$$\sum_{g_{sp}}^{\infty} \frac{\phi_g}{g} = \frac{1}{eK}\left(\sum_1^{\infty} \frac{Y^g}{g} - \sum_1^{g_{sp}-1} \frac{Y^g}{g}\right) \quad (50)$$

The second term, which is a summation of a finite series, is approximated using numerical calculations, taking $Y = 1$

$$\sum_1^{g_{sp}-1} \frac{Y^g}{g} \approx \ln(1.8 g_{sp}) \quad (51)$$

TABLE 3

Predicted characteristics of rodlike micelles

Entropy model	g_w	g_w/g_n	g_z/g_w	$(N_1/N_s)_{CMC}$
Ideal solution model	$2\left(\frac{K}{m}\frac{\phi}{1-\phi}\right)^{1/2}$ 2334[a]	2	1.5	$\exp\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right)$
Gas-like translation model	$2\left(\frac{eK\phi}{m}\right)^{1/2}$ 3807[a]	2	1.5	$\frac{1}{e}\exp\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right)$
Flory–Huggins model	$eK\phi$ $5.4\cdot 10^{7}$[a]	$\ln\left(\frac{g_w}{1.8g_{sp}}\right)$	2	$\frac{1}{em}\exp\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right)$
Translational entropy model	$2\left(\frac{eK}{m}\frac{\phi}{1-\phi}\right)^{1/2}$ 3848[a]	2	1.5	$\frac{1}{e}\exp\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right)$
Modified translational entropy model	$2\left(\frac{K}{m}\frac{\phi}{1-\phi}\right)^{1/2}$ 2334[a]	2	1.5	$\exp\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right)$

[a]Illustrative numerical values for g_w, calculated taking typical values of $m = 15$, $K = 10^9$ and $\phi = 0.02$.

Therefore

$$\sum_{g_{sp}}^{\infty}\frac{\phi_g}{g} = \frac{1}{eK}[-\ln(1-Y)-\ln(1.8g_{sp})]$$

$$= \frac{1}{eK}\ln\left[\frac{1}{1.8g_{sp}(1-Y)}\right] = \frac{1}{eK}\ln\left(\frac{g_w}{1.8g_{sp}}\right) \quad (52)$$

Hence the results for g_w/g_n listed in Table 3.

Translational entropy model

Equation (32) for the micelle size distribution incorporating Eqn (39) for the reference state free energy difference leads to

$$Z_g = \frac{Y^g}{eK} \qquad Y = eZ_1\exp-\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right) \quad (53)$$

Following the same procedure as in the previous models, the total surfactant concentration is related to $(1-Y)$ through the equation

$$\frac{1}{(1-Y)} = \left(eK\sum gZ_g\right)^{1/2} = \left(eK\frac{\sum gN_g}{N_s+\sum gN_g}\right)^{1/2}$$

$$= \left[eK\frac{\phi/m}{(1-\phi)+\phi/m}\right]^{1/2} \quad (54)$$

Recognizing $\phi/m \ll (1-\phi)$ in the above equation, we obtain the results summarized in Table 3.

Modified translational entropy model

The micelle size distribution (Eqn (37)) incorporating Eqn (39) for the free energy of micellization yields

$$Z_g = \frac{Y^g}{K} \qquad Y = Z_1\exp-\left(\frac{\mu_{cy}^{\circ}-\mu_1^{\circ}}{kT}\right) \quad (55)$$

Consequently, we obtain in place of Eqn (54), the following relationship between $(1-Y)$ and the total surfactant concentration.

$$\frac{1}{(1-Y)} = \left(K\sum gZ_g\right)^{1/2} = \left[K\frac{\sum gN_g}{N_s+\sum gN_g}\right]^{1/2}$$

$$= \left[\frac{K}{m} \frac{\phi}{(1-\phi)+\phi/m} \right]^{1/2} \quad (56)$$

The predictions of the model are presented in Table 3. One may observe that in arriving at these results we have used the fact that $\phi/m \ll (1-\phi)$ in Eqn (56).

Results for systems forming rodlike micelles

The predicted weight-average aggregation number g_w, the polydispersity indices g_w/g_n and g_z/g_w, and the CMCs summarized in Table 3 show how the choice of the entropy model significantly influences the theoretical predictions of all important aspects of rodlike micelles. The CMC values predicted by the models follow the same trends as has been observed in solutions where small globular micelles are formed. The ideal solution and modified translational entropy models predict practically the same CMCs which agree with the experiments [23,27], while the CMCs predicted by the gas-like translation model and the translational entropy model are smaller by the factor 1/e, and that predicted by the Flory–Huggins model is smaller by the factor $1/me$.

Concerning the micelle size, earlier results for solutions containing globular micelles showed that all the models predict comparable (though different) values for the average aggregation number. Markedly contrasting results are obtained when solution conditions favor the formation of rodlike micelles. The average aggregation numbers predicted by the ideal solution model and the modified translational entropy model are practically the same. However, the average micelle size predicted by the gas-like translation model and the translational entropy model are larger by a factor $(e)^{\frac{1}{2}}$. In these four models, the average aggregation numbers are proportional to the square root of the total volume fraction of the surfactant. In contrast, remarkably large average aggregation numbers are predicted by the Flory–Huggins model, as can be seen from the illustrative numerical results provided in Table 3. This model also predicts that the average aggregation number is proportional to the total surfactant concentration. This is a much stronger dependence than that suggested by the other models. All the entropy models predict that the size distribution of micelles must be quite broad. We conclude that the ideal solution model and the modified translational entropy model which provide practically identical predictions are in good quantitative agreement with experimentally observed characteristics [23,27] of the rodlike micellar solutions.

Phase separation in surfactant solutions

Surfactant solutions undergo phase separation when the solution conditions are modified. For example, an increase or a decrease in the solution temperature or an increase in the concentration of electrolytes added to the solution can cause a phase separation of the surfactant solution [36–39]. Recently, considerable attention has been paid to the temperature-induced phase separation, known as the clouding phenomenon, in non-ionic surfactant solutions. In these studies, the question of whether phase separation occurs in solutions where micelles remain spherical or where micelles grow into larger cylinders has been explored [40–49].

A few theoretical treatments of phase separation in surfactant solutions have appeared in the literature. Kjellander [18] has used the formalism of the Flory–Huggins model to describe phase separation in solutions of non-ionic surfactants having polyoxyethylene-type polar head groups. Using a detailed interaction free energy model representing solvation interactions of the polyoxyethylene groups with water, the experimentally determined phase boundaries have been reproduced in this treatment. By comparing the predicted and calculated critical surfactant volume fractions, Kjellander ruled out the presence of spherical micelles in the phase separating surfactant solution, and concluded that the micelles present must be rodlike and flexible. Both micellization as well as

phase separation have been treated in an unitary way by Blankschtein and co-workers [16,19–22]. In their work on solution phase behavior, the micelles are considered to be rodlike. The entropy of the system is described through the translational entropy model and an interaction energy term equivalent to Eqn (3) is used to account for the intermicellar interactions. Also, the Flory–Huggins model for system entropy has been examined by them [6]. An essentially similar treatment using the gas-like translation model of system entropy has been presented by Goldstein [11] for a surfactant solution containing spherical micelles.

Here, we examine systematically how the theoretically predicted phase stability characteristics of surfactant solutions depend on the manner in which one accounts for the entropy of the surfactant system. Specifically, we investigate how the critical point, the spinodal line and the osmotic compressibility are affected for surfactant solutions containing practically monodispersed globular micelles, as well as for those containing highly polydispersed rodlike micelles. As mentioned earlier, even though the micellar solution is made up of a large number of distinct components, the equilibrium condition stipulates the equality of chemical potential per molecule, for aggregates of all sizes and shapes. Thus, if the solvent chemical potential and that of any one of the remaining species is known, then the chemical potentials of all the components in the solution are completely characterized. In this sense, the multicomponent surfactant solution is amenable to visualization as a binary solution. Consequently, the phase stability conditions for a surfactant solution can be conveniently analyzed through an examination of the solvent chemical potential μ_s. The analysis of phase behavior in multicomponent surfactant solutions is thus greatly simplified compared with that in non-associating multicomponent systems commonly encountered in solution thermodynamics.

Choosing the volume fraction of the surfactant as the composition variable, one may obtain the critical conditions $\phi = \phi_c$ and $\chi = \chi_c$ for incipient phase separation from

$$\frac{\partial \mu_s}{\partial \phi} = 0 \quad \text{and} \quad \frac{\partial^2 \mu_s}{\partial \phi^2} = 0 \tag{57}$$

The spinodal curve which provides the coexisting phase compositions at metastable equilibrium conditions is defined by $\partial \mu_s / \partial \phi = 0$. The binodal curve which provides the coexisting phase compositions at stable equilibrium conditions is defined by $\mu_s(\phi_a) = \mu_s(\phi_b)$, where ϕ_a and ϕ_b are the volume fractions of the surfactant in the two coexisting phases. The spinodal and binodal curves practically coincide if the kinetics of the phase demixing process is very rapid, and in such situations the experimentally determined coexistence curves could be compared against the calculated spinodal curves. Another variable, directly accessible from light or neutron scattering experiments, is the osmotic compressibility $(\partial \pi / \partial c)^{-1}$, where π denotes the osmotic pressure and c is the mass concentration of the surfactant

$$\pi = \frac{\mu_s^\circ - \mu_s}{V_s}$$
$$c = \frac{\phi M}{m V_s N_{AV}} = \frac{\phi}{\bar{V}} \tag{58}$$

where V_s is the molecular volume of the solvent, M is the molecular weight of the surfactant, $\bar{V}$ is the specific volume or reciprocal density of the surfactant and N_{AV} is Avogadro's number. Using the definitions for π and c given above, we can calculate the osmotic compressibility from the solvent chemical potential via

$$\left(\frac{1}{RT}\frac{\partial \pi}{\partial c}\right)^{-1} = \frac{M}{m}\left(-\frac{1}{kT}\frac{\partial \mu_s}{\partial \phi}\right)^{-1} \tag{59}$$

where R is the universal gas constant ($R = kN_{AV}$). It is evident from Eqn (57) that osmotic compressibility diverges towards infinity at the spinodal line. To proceed further and calculate the critical point, the spinodal line and the osmotic compressibility, we need to develop explicit expressions for the solvent chemical potential μ_s as a function of the surfactant concentration.

Entropy models and phase separation behavior

Ideal solution model

Combining Eqns (1)–(3), and (10), we obtain the following expression for the solvent chemical potential μ_s

$$\mu_s = \left.\frac{\partial G}{\partial N_s}\right|_{N_g} = \mu_s^\circ + kT\ln\left(\frac{N_s}{N_s + \sum N_g}\right) + kT\chi\phi^2 \tag{60}$$

Using definitions for the total volume fraction of the surfactant ϕ and for surfactant present in micelles of size $g(\phi_g)$, the above expression can be rewritten as a function of ϕ

$$\mu_s = \mu_s^\circ + kT\ln\left(\frac{1-\phi}{1-\phi+\sum\frac{\phi_g}{mg}}\right) + kT\chi\phi^2 \tag{61}$$

Denoting the quantity $\left(1-\phi+\sum\frac{\phi_g}{mg}\right)$ by ϵ, we obtain

$$\frac{1}{kT}\frac{\partial\mu_s}{\partial\phi} = 2\chi\phi - \frac{1}{1-\phi} - \frac{1}{\epsilon}\frac{\partial\epsilon}{\partial\phi} \tag{62}$$

$$\frac{1}{kT}\frac{\partial^2\mu_s}{\partial\phi^2} = 2\chi - \frac{1}{(1-\phi)^2} - \frac{1}{\epsilon}\frac{\partial^2\epsilon}{\partial\phi^2} + \left(\frac{1}{\epsilon}\frac{\partial\epsilon}{\partial\phi}\right)^2 \tag{63}$$

The derivatives $\partial\epsilon/\partial\phi$ and $\partial^2\epsilon/\partial\phi^2$ are evaluated from Eqn (12) for the size distribution of micelles, which is rewritten below in terms of the volume fractions

$$\sum\frac{\phi_g}{mg} = c + \phi - 1 = \sum\left(\frac{\phi_1}{m}\right)^g \epsilon^{1-g}\exp-\left(\frac{\mu_g^\circ - g\mu_1^\circ}{kT}\right) \tag{64}$$

After some tedious algebra one obtains

$$\frac{1}{\epsilon}\frac{\partial\epsilon}{\partial\phi} = \frac{1-mg_w}{\phi+(1-\phi)mg_w} \tag{65}$$

$$\frac{1}{\epsilon}\frac{\partial^2\epsilon}{\partial\phi^2} = \frac{1-(g_z/g_w)}{mg_w\phi\left[\frac{\phi}{mg_w}+(1-\phi)\right]^3} \tag{66}$$

The critical constants are obtained by the simultaneous solution of Eqns (62) and (63), both equated to zero, in conjunction with the derivatives defined through Eqns (65) and (66). Eliminating χ from these four equations, we obtain a polynomial expression for the critical volume fraction

$$\left(\frac{\phi_c}{1-\phi_c}\right)^3(-1) + \left(\frac{\phi_c}{1-\phi_c}\right)^2(1-3mg_w) + \left(\frac{\phi_c}{1-\phi_c}\right)(2-3m^2g_w^2+m^2g_wg_z) + (3mg_w - 3m^2g_w^2 + 2m^2g_wg_z) + \left(\frac{\phi_c}{1-\phi_c}\right)^{-1}(m^2g_wg_z) = 0 \tag{67}$$

Since $\frac{\phi_c}{1-\phi_c}$ is of the order of unity or less and $g_w, g_z \gg 1$, we need to retain only the last three dominant terms in the above equation, thus transforming the equation to a quadratic one in the variable $\frac{\phi_c}{1-\phi_c}$. We further simplify the coefficients of the quadratic equation by eliminating the smaller terms, namely, 2 in the coefficient of $\left(\frac{\phi_c}{1-\phi_c}\right)$ and 3 mg_w in the coefficient of $\left(\frac{\phi_c}{1-\phi_c}\right)^0$.

This quadratic equation in $\left(\frac{\phi_c}{1-\phi_c}\right)$ is then readily solved to obtain ϕ_c. Using this value for ϕ_c, we can determine the critical interaction parameter χ_c from either Eqns (62) or (63), equated to zero. The resulting expressions for the critical constants are summarized in Table 4.

These expressions are general and are valid for surfactant solutions containing either globular micelles or rodlike micelles. For globular micelles, it has been shown earlier that the micelles are

TABLE 4

Expressions for the critical constants

Entropy model	ϕ_c	χ_c
Ideal solution model	$\frac{1}{3}\left(\frac{g_z}{g_w}\right)$	$\{2\phi_c(1-\phi_c)[\phi_c+(1-\phi_c)mg_w]\}^{-1}$
Gas-like translation model	$\left(\frac{g_z}{g_w}\right)^{1/2}(mg_w)^{-1/2}$	$\frac{1}{2}+\frac{1}{2}(mg_w)^{-1/2}\left[\left(\frac{g_z}{g_w}\right)^{1/2}+\left(\frac{g_z}{g_w}\right)^{-1/2}\right]$
Flory–Huggins model	$\left(\frac{g_z}{g_w}\right)^{1/2}(mg_w)^{-1/2}$	$\frac{1}{2}+\frac{1}{2}(mg_w)^{-1/2}\left[\left(\frac{g_z}{g_w}\right)^{1/2}+\left(\frac{g_z}{g_w}\right)^{-1/2}\right]$
Translational entropy model	$\frac{\left[\frac{1}{4}+\frac{1}{3}\left(\frac{g_w}{m}-2\right)\frac{g_z}{g_w}\right]^{1/2}-\frac{1}{2}}{\left(\frac{g_w}{m}-2\right)}$	$\frac{1}{2m^2}\left[\frac{1}{(1-\phi_c)^3}+\frac{m}{g_w\phi_c(1-\phi_c)^2}\right]$
Modified translational entropy model	$\frac{\left[\frac{1}{4}+\frac{1}{3}\left(\frac{g_w}{m}-2\right)\frac{g_z}{g_w}\right]^{1/2}-\frac{1}{2}}{\left(\frac{g_w}{m}-2\right)}$	$\frac{1}{2m^2}\left[\frac{1}{(1-\phi_c)^3}+\frac{m}{g_w\phi_c(1-\phi_c)^2}\right]$

narrowly dispersed. In such a case all the average aggregation numbers g_n, g_w and g_z are practically equal to one another. The critical constants are thus reduced to the expressions provided in Table 5. Some typical numerical values are also given in Table 5, taking $m=15$ and $g_w=90$. Similarly, for rodlike micellar solutions, the ideal solution model has been shown to predict (see Table 3)

$$\frac{g_z}{g_w}=\frac{3}{2} \qquad g_w=2\left(\frac{K}{m}\frac{\phi}{1-\phi}\right)^{1/2} \tag{68}$$

where K is the constant representing the thermodynamic preference for the formation of rodlike micelles over spherical micelles. Correspondingly, the critical conditions reduce to those shown in Table 5 where the illustrative numerical results have been obtained taking $m=15$ and $K=10^9$.

The spinodal curve is obtained by equating Eqn (62) to zero, incorporating in it the derivative given by Eqn (65). Table 6 summarizes the predicted equation for the spinodal line. The osmotic compressibility is calculated by introducing Eqns (62) and (65) in Eqn (59)

$$\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right)^{-1}=\frac{M}{m}\left[-2\chi\phi+\frac{1}{1-\phi}+\frac{1-mg_w}{\phi+(1-\phi)mg_w}\right]^{-1} \tag{69}$$

This expression is simplified by noting that $\phi \ll (1-\phi)mg_w$, and $c\bar{V}=\phi$. Also, one can expand $(1-\phi)^{-1}$ as a power series in ϕ. Thus one obtains

$$\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right)^{-1}=\left[\frac{1}{Mg_w}+c\bar{V}\left(\frac{2}{Mg_w}-\frac{2m\chi}{M}\right)+c^2\bar{V}^2\left(\frac{1}{Mg_w}\right)\right]^{-1} \tag{70}$$

Expressions for osmotic compressibility predicted by various entropy models are summarized in Table 7 for comparative purposes.

Gas-like translation model

Combining Eqns (1)–(3) and (18) we obtain the following expression for the solvent chemical

TABLE 5

Reduced expressions for critical constants, and illustrative magnitudes

Entropy model	ϕ_c	χ_c
Globular micelles		
Ideal solution model	$\frac{1}{3}$	$\frac{27}{8mg_w}$
	0.333[a]	$2.5 \cdot 10^{-3}$[a]
Gas-like translation model	$(mg_w)^{-1/2}$	$\frac{1}{2}+(mg_w)^{-1/2}$
	0.0272[a]	0.5272[a]
Flory–Huggins model	$(mg_w)^{-1/2}$	$\frac{1}{2}+(mg_w)^{-1/2}$
	0.0272[a]	0.5272[a]
Translational entropy model	$\frac{\left[\frac{1}{4}+\frac{1}{3}\left(\frac{g_w}{m}-2\right)\right]^{1/2}-\frac{1}{2}}{\left(\frac{g_w}{m}-2\right)}$	$\frac{1}{2m^2}\left[\frac{1}{(1-\phi_c)^3}+\frac{m}{g_w\phi_c(1-\phi_c)^2}\right]$
	0.1895[a]	$7.15 \cdot 10^{-3}$[a]
Modified translational entropy model	$\frac{\left[\frac{1}{4}+\frac{1}{3}\left(\frac{g_w}{m}-2\right)\right]^{1/2}-\frac{1}{2}}{\left(\frac{g_w}{m}-2\right)}$	$\frac{1}{2m^2}\left[\frac{1}{(1-\phi_c)^3}+\frac{m}{g_w\phi_c(1-\phi_c)^2}\right]$
	0.1895[a]	$7.15 \cdot 10^{-3}$[a]
Rodlike micelles		
Ideal solution model	$\frac{1}{2}$	$\frac{2}{(mK)^{1/2}}$
	0.50[a]	$0.163 \cdot 10^{-4}$[a]
Gas-like translation model	$\left(\frac{9}{16meK}\right)^{1/5}$	$\frac{1}{2}+\frac{5}{6}\left(\frac{9}{16meK}\right)^{1/5}$
	0.00675[a]	0.5056[a]
Flory–Huggins model	$\left(\frac{2}{meK}\right)^{1/3}$	$\frac{1}{2}+\left(\frac{27}{32meK}\right)^{1/3}$
	$0.366 \cdot 10^{-3}$[a]	0.50028[a]
Translational entropy model	$\left(\frac{m^3}{16eK}\right)^{1/5}$	$\frac{1}{2m^2}(1+5\phi_c)$
	0.0379[a]	$2.64 \cdot 10^{-3}$[a]
Modified translational entropy model	$\left(\frac{m^3}{16K}\right)^{1/5}$	$\frac{1}{2m^2}(1+5\phi_c)$
	0.046[a]	$2.73 \cdot 10^{-3}$[a]

[a]Illustrative numerical values for the critical constants, calculated taking $m = 15$, $g_w = 90$ for globular micelles, and $m = 15$, $K = 10^9$ for rodlike micelles.

TABLE 6

Expressions for the spinodal curve

Entropy model	Expression
Ideal solution model	$2\chi\phi = \frac{\phi}{1-\phi} + \frac{1+\phi(1-mg_w)}{mg_w+\phi(1-mg_w)}$
Gas-like translation model	$2\chi\phi = \frac{\phi}{1-\phi} + \frac{1}{mg_w}$
Flory–Huggins model	$2\chi\phi = \frac{\phi}{1-\phi} + \frac{1}{mg_w}$
Translational entropy model	$2\chi\phi(1-\phi+\phi/m)^2 = \frac{1}{m^2}\frac{\phi}{1-\phi} + \frac{1}{mg_w}$
Modified translational entropy model	$2\chi\phi(1-\phi+\phi/m)^2 = \frac{1}{m^2}\frac{\phi}{1-\phi} + \frac{1}{mg_w}$

TABLE 7

Expressions for osmotic compressibility, referring to the equation $\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right)^{-1} = \left(\frac{1}{Mg_w} + \alpha_1 c\bar{V} + \alpha_2 c^2\bar{V}^2\right)^{-1}$

Entropy model	α_1	α_2
Ideal solution model	$\frac{2}{Mg_w} - \frac{2m\chi}{M}$	$\frac{1}{Mg_w}$
Gas-like translation model	$\frac{m}{M} - \frac{2m\chi}{M}$	$\frac{m}{M}$
Flory–Huggins model	$\frac{m}{M} - \frac{2m\chi}{M}$	$\frac{m}{M}$
Translational entropy model	$\frac{2}{Mg_w} + \frac{1}{mM} - \frac{2m\chi}{M}$	$\frac{1}{Mg_w} + \frac{3}{mM}$
Modified translational entropy model	$\frac{2}{Mg_w} + \frac{1}{mM} - \frac{2m\chi}{M}$	$\frac{1}{Mg_w} + \frac{3}{mM}$

potential μ_s

$$\mu_s = \left.\frac{\partial G}{\partial N_s}\right|_{N_g} = \mu_s^\circ + kT\left[\ln\left(\frac{N_s}{N_s+\sum mgN_g}\right) + 1 - \left(\frac{N_s+\sum N_g}{N_s+\sum mgN_g}\right)\right] + kT\chi\phi^2 \quad (71)$$

We can rewrite the above equation as a function of the volume fraction of the surfactant

$$\mu_s = \mu_s^\circ + kT\left[\ln(1-\phi) + \phi - \sum\frac{\phi_g}{mg}\right] + kT\chi\phi^2 \quad (72)$$

We now follow the procedure detailed for the previous model to obtain expressions for the critical constants, the spinodal line and the osmotic compressibility presented in Tables 4–7.

Flory–Huggins model

Combining Eqns (1)–(3) and (23), we obtain the following equation for the chemical potential μ_s of the solvent molecule

$$\mu_s = \left.\frac{\partial G}{\partial N_s}\right|_{N_g} = \mu_s^\circ + kT\left[\ln\left(\frac{N_s}{N_s+\sum mgN_g}\right) + 1 - \left(\frac{N_s+\sum N_g}{N_s+\sum mgN_g}\right)\right] + kT\chi\phi^2 \quad (73)$$

In the above equation, the variables denoting the numbers of various species present in solution may be expressed alternatively in terms of the volume fraction of the surfactant in solution. We thus obtain

$$\mu_s = \mu_s^\circ + kT\left[\ln(1-\phi) + \phi - \sum\frac{\phi_g}{mg}\right] + kT\chi\phi^2 \quad (74)$$

Starting from this expression, one obtains the results listed in Tables 4–7.

Translational entropy model

Combining Eqns (1)—(3) and (30), we obtain the following equation for the chemical potential of the solvent

$$\mu_s = \left.\frac{\partial G}{\partial N_s}\right|_{N_g} = \mu_s^\circ + kT\left[\ln\left(\frac{N_s}{N_s+\sum gN_g}\right) +\right.$$

$$1-\left(\frac{N_s+\sum N_g}{N_s+\sum gN_g}\right)\Bigg] + kT\chi\phi^2 \qquad (75)$$

Expressing μ_s as a function of the volume fraction ϕ of the surfactant, we rewrite Eqn (75) in the form

$$\mu_s = \mu_s^\circ + kT\Bigg[\ln\left(\frac{1-\phi}{1-\phi+\phi/m}\right) + 1-\left(\frac{1-\phi+\sum \phi_g/mg}{1-\phi+\phi/m}\right)\Bigg] + kT\chi\phi^2 \qquad (76)$$

One can now derive the expressions for the critical constants, the spinodal line and the osmotic compressibility presented in Tables 4–7.

Modified translational entropy model

Combining Eqns (1)–(3) and (35), the following expression for the solvent chemical potential μ_s can be obtained

$$\mu_s = \left.\frac{\partial G}{\partial N_s}\right|_{N_g} = \mu_s^\circ + kT\Bigg[\ln\left(\frac{N_s}{N_s+\sum gN_g}\right) - \left(\frac{N_s+\sum N_g}{N_s+\sum gN_g}\right)\Bigg] + kT\chi\phi^2 \qquad (77)$$

Expressing μ_s as a function of the volume fraction of the surfactant, we can write

$$\mu_s = \mu_s^\circ + kT\Bigg[\ln\left(\frac{1-\phi}{1-\phi+\phi/m}\right) - \left(\frac{1-\phi+\sum \phi_g/mg}{1-\phi+\phi/m}\right)\Bigg] + kT\chi\phi^2 \qquad (78)$$

We now follow the same procedure used in previous models to obtain the results summarized in Tables 4–7.

Results for solution phase behavior

Expressions for the critical constants, the spinodal line and the osmotic compressibility resulting from the five entropy models reveal important differences in the predicted phase behavior. In Table 4, the general expressions for the critical constants are given, while in Table 5 the expressions are reduced to the specific cases of solutions containing either globular or rodlike micelles. To derive the reduced expressions for globular micelles, we take the size dispersion indices to be equal to unity. The numerical results reported have been obtained by assuming $m = 15$ and $g_w = 90$, similar to the results shown in Table 1 for the nonionic surfactant $C_{10}SO$. For the case of rodlike micelles, the reduced expressions are derived by incorporating the results in Table 3 while the numerical results are obtained with the use of $m = 15$ and the sphere-to-rod transition parameter $K = 10^9$. The chosen value for K is typical of a number of non-ionic, zwitterionic and ionic surfactant systems [35].

The ideal solution model predicts large values of ϕ_c both when the micelles are globular and when they are rodlike. This is in conflict with the measured values of ϕ_c for many surfactant solutions which lie in the range 0.005–0.10 [22]. The critical interaction parameter is correspondingly smaller. Because of the large value of ϕ_c, this model cannot describe the asymmetric coexistence curves observed experimentally. We will not comment on this model any further with respect to the solution phase behavior.

All the remaining entropy models predict lower values of ϕ_c and thus can describe at least qualitatively the asymmetric coexistence curves. However, for solutions containing rodlike micelles, the Flory–Huggins model predicts values of ϕ_c that are more than an order of magnitude smaller than those predicted by the other models. Further, as we have already noted, the aggregation characteristics of rodlike micelles predicted by the Flory–Huggins model are greatly in error. Consequently, the Flory–Huggins model cannot quantitatively describe the coexistence curves.

The expressions for the spinodal line predicted based on the different models are summarized in Table 6. From these, one can observe that the

magnitude of both χ and $\partial\chi/\partial T$, needed to describe the experimental coexistence curve based on the gas-like translation and the Flory–Huggins models must be larger approximately by a factor of m^2 compared with those based on the translational entropy model and its modification. This can also be seen from a comparison of the values of the critical interaction parameters χ_c listed in Table 5. Consequently, the osmotic compressibility calculated from the different models (Table 7) will differ significantly, even if the models can predict equally satisfactorily both ϕ_c and the coexistence curves. To illustrate this, we compare the osmotic compressibility along the critical isochore very near the critical point predicted by the different entropy models. At the critical point, the osmotic compressibility diverges, or the inverse osmotic compressibility is zero. Near the critical point we can evaluate the inverse osmotic compressibility by carrying out a perturbation expansion around the critical point. Thus, for a temperature deviation of $\delta T = T - T_c$ along the critical isochore, let g_w, ϕ, α_1 and α_2 change by δg_w, $\delta\phi$, $\delta\alpha_1$ and $\delta\alpha_2$, respectively. Note that α_1 and α_2 have been defined as the coefficients of the terms containing $c\bar{V}$ and $(c\bar{V})^2$ in the expressions for osmotic compressibility (see Table 7). Therefore, the inverse osmotic compressibility along the critical isochore can be written as

$$\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right) = \frac{1}{M(g_w + \delta g_w)} + \left[\alpha_{1c} + \left(\frac{\partial\alpha_1}{\partial T}\right)_c (T - T_c)\right](\phi_c + \delta\phi) + \left[\alpha_{2c} + \left(\frac{\partial\alpha_2}{\partial T}\right)_c (T - T_c)\right](\phi_c + \delta\phi)^2 \quad (79)$$

where the subscript c refers to the critical point. Expressions for α_1 and α_2 are summarized in Table 7 for the various models. Taking $\delta\phi$ to be very small, one can approximate $\delta g_w = 0$. Further, the temperature derivative of g_w can also be approximated to zero. This implies that α_2 is temperature invariant ($\partial\alpha_2/\partial T = 0$) in the proximity of the critical point since α_2 depends only on g_w. The temperature dependence of α_1 emerges solely from the temperature dependence of the interaction parameter χ, i.e. $\partial\alpha_1/\partial T = (-2m/M)\partial\chi/\partial T$. Further, as already noted, the inverse osmotic compressibility is zero at the critical point

$$\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right)_c = 0 = \left(\frac{1}{Mg_w}\right)_c + \alpha_{1c}\phi_c + \alpha_{2c}\phi_c^2 \quad (80)$$

Thus, Eqn (79) for the inverse osmotic compressibility along the critical isochore reduces to

$$\left(\frac{1}{RT}\frac{\partial\pi}{\partial c}\right) = \phi_c\left(\frac{2m}{M}\right)\frac{\partial\chi}{\partial T}(T_c - T) \quad (81)$$

The above equation has been presented in a different form already in the literature [16] where it has been shown that $\partial\chi/\partial T$ can be taken to be a constant in order to describe experimental coexistence curves [16,19–22]. If $\partial\chi/\partial T$ is equal to η for the gas-like translation and the Flory–Huggins models, then we can write approximately that $\partial\chi/\partial T = \eta/m^2$, for the translational entropy model and its modified version. Therefore, Eqn (81) shows that even if all the models predict comparable values of ϕ_c, the osmotic compressibility, which is proportional to $(\partial\chi/\partial T)^{-1}$, will be smaller by a factor of approximately $1/m^2$ for the gas-like translation and the Flory–Huggins models when compared to the translational entropy and the modified translational entropy models. The latter two models predict comparable osmotic compressibilities along the critical isochore, and are also in good agreement with the experiments [16,19–22].

Conclusions

Theoretical treatments of surfactant solutions require the estimation of the entropy of the system consisting of the solvent, singly dispersed surfactant molecules and aggregates of all sizes and shapes. This estimation is complicated because of the compact nature of the aggregates, their shape

variations, their rigidity or flexibility and the wide disparity in their sizes with respect to the other species present in the surfactant solution. No fundamental approach addressing this problem is available in the literature. Theories of surfactant solutions available in the literature have employed four entropy expressions associated with the ideal solution model, the gas-like translation model, the Flory–Huggins model and the translational entropy model. In this paper, we present a systematic comparison of the theoretical predictions of micelle size distribution, CMC, average aggregation number, its dependence on surfactant concentration, polydispersity of the micelles, critical points for incipient phase separation, spinodal line and osmotic compressibility, that result from the various entropy models. Also, we examine a model that incorporates a small modification to the translational entropy model based on the liquid-like and not gas-like state of the surfactant solution. Illustrative calculations have been carried out for both non-ionic and ionic surfactant systems under conditions when small globular micelles or large rodlike micelles are formed. All the principal results of this study, summarized in Tables 1–7, reveal that different entropy models lead to dramatic differences in the predicted aggregation and phase separation characteristics of surfactant solutions.

In applying the entropy estimate based on the ideal solution model, one completely ignores all size variations among the species constituting the surfactant solution. The model provides predictions of the CMC, the micelle size, its dependence on surfactant concentration and the polydispersity index in good agreement with experiments, irrespective of whether the micelles are globular or rodlike. However, the model fails in its predictions of the solution phase behavior. The model leads to very large values for the critical volume fraction, in disagreement with experiments. Hence, the model cannot reasonably describe the experimental coexistence curve.

In employing the Flory–Huggins model, one accounts for the size variations among the various species present in the surfactant solution. But the use of this model implies that the micelles are equivalent to flexible polymers for the purposes of statistically enumerating how the various species can be arranged on a lattice. One can expect such statistical enumeration to be greatly in error because of the compactness of the micelles. Indeed, for solutions containing spherical compact species, calculations based on the hard sphere equation of state suggest that the system entropy is closer to that provided by the ideal solution model than that provided by the Flory–Huggins model [50]. Our analysis shows that the predictions of all the aggregation characteristics of globular and rodlike micelles resulting from the application of the Flory–Huggins model are in disagreement with the experiments. In particular, the predicted CMCs are very small, the average size of the rodlike micelles is unreasonably large and this average size is predicted to vary in direct proportion to the surfactant concentration ϕ, rather than to $\phi^{\frac{1}{2}}$. The solution phase behavior predicted based on the Flory–Huggins entropy estimate is in qualitative agreement with the experiments in the sense that low critical volume fractions result from this model. However, quantitatively, the predicted values for ϕ_c are too small by one order of magnitude compared with the experimental values in systems containing rodlike micelles. Further, since the model leads to very large rodlike micelles having a size proportional to ϕ, the predicted coexistence curve and osmotic compressibility are in poor quantitative agreement with the experiments.

The ideal solution model and the Flory–Huggins model provide two limiting estimates for the system entropy. All other models yield intermediate entropy estimates and thus their predictions lie in between those of the two limiting models. Both the gas-like translation and the translational entropy models account for size variations among the species while defining the volume available for translation. Both models view the system to be gas-like and thus attribute an extra free energy of 1 kT per species. As a result, both models predict CMCs that are smaller by the factor 1/e compared

with the experimental values. The predicted aggregation numbers of the rodlike micelles are larger by the factor $e^{\frac{1}{2}}$. However, the predictions pertaining to the size of globular micelles as well as the concentration dependence of the micelle sizes are in good agreement with the experiments. Further, both models predict solution phase behavior in qualitative agreement with the experiments. The agreement is quantitative with respect to the critical volume fraction and the coexistence curves. But the osmotic compressibility calculated along the critical isochore is smaller when the gas-like translation model is used compared with when the translational entropy model is used.

Finally, the entropy estimate based on a small modification to the translational entropy model is explored. The modification stems from the fact that the surfactant solution is a liquid and not a gaseous mixture and hence both Gibbs and Arrhenius free energies must be practically equal. Thus the extra free energy of $1\ kT$ per species introduced by the translational entropy model is eliminated. The predictions of all the aggregation characteristics of globular and rodlike micelles provided by the modified translational entropy model are identical to those from the ideal solution model and in good agreement with the experiments. The phase behavior predicted by the modified translational entropy model coincides with that predicted by the translational entropy model and is in reasonable agreement with the experiment. Thus Eqn (35) can be used for estimating the entropic contribution in future theoretical studies of surfactant solutions.

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Appendix A: molecular characteristics of surfactant tail with $(n_c - 1)CH_2$ groups and a terminal CH_3 group

Volume of a CH_3 group $V(CH_3) = 54.6 + 0.124\,(T - 298)$ Å^3, where T is temperature (K); volume of a CH_2 group $V(CH_2) = 26.9 + 0.0146\,(T - 298)$ Å^3; extended length of surfactant tail $l_t = 1.50 + 1.265 n_c$ Å; volume of surfactant tail $V_t = V(CH_3) + (n_c - 1)V(CH_2)$; number of effective segments per surfactant tail $N = \frac{n_c + 1}{3.6}$; $NL^3 = V_t$; $L^3 = 3.6V(CH_2)$ and a_p is the cross-sectional area of the polar head (40 Å^2 for $C_{10}SO$; 17 Å^2 for SDS).

Appendix B: geometrical properties of micelles

The aggregate shapes considered in this study are shown in Fig. B1. In the equations given below,

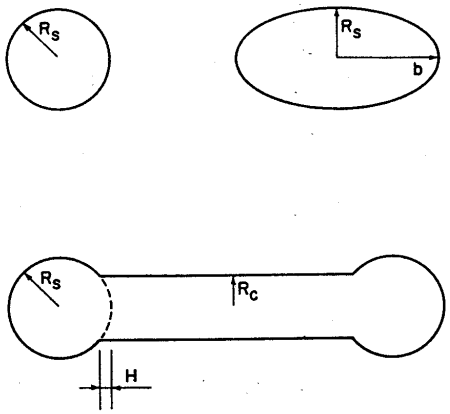

Fig. B1. Geometrical variables defining the structures of surfactant aggregates considered in this study. The prolate ellipsoidal shape is used to define the average properties of non-spherical but globular aggregates. The rodlike micelle is allowed to have differing radii for the cylindrical middle and the spherical endcaps.

V_g is the hydrophobic core volume of the aggregate, A_g is the surface area of the hydrophobic core, P is a molecular packing parameter, and δ denotes the distance from the hydrophobic core surface of the micelle to the center of the counterions at closest approach and is relevant for ionic surfactants. The dimensions R_s, R_c, b, and H are defined in Fig. B1.

Spherical micelle

$$V_g = gV_t = \frac{4\pi R_s^3}{3}$$

$$A_g = ga = 4\pi R_s^2$$

$$A_{g\delta} = ga_\delta = 4\pi(R_s + \delta)^2$$

$$P = \frac{V_g}{A_g R_s} = \frac{V_t}{aR_s}$$

Globular micelle — prolate ellipsoid of eccentricity E

$$V_g = gV_t = \frac{4\pi R_s^2 b}{3}$$

$$A_g = ga = 2\pi R_s^2\left[1 + \frac{\sin^{-1} E}{E(1-E^2)^{1/2}}\right]$$

$$A_{g\delta} = ga_\delta = 2\pi(R_s+\delta)^2\left[1 + \frac{\sin^{-1} E_\delta}{E_\delta(1-E_\delta^2)^{1/2}}\right]$$

$$P = \frac{V_g}{A_g R_s} = \frac{V_t}{aR_s}$$

$$E = [1-(R_s/b)^2]^{1/2}$$

$$E_\delta = \{1-[(R_s+\delta)/(b+\delta)]^2\}^{1/2}$$

$$R_{eq} = \left(\frac{3V_g}{4\pi}\right)^{1/3}$$

Infinite cylinder per unit length

$$V_g = gV_t = \pi R_c^2$$

$$A_g = ga = 2\pi R_c$$

$$A_{g\delta} = ga_\delta = 2\pi(R_c+\delta)$$

$$P = \frac{V_g}{A_g R_c} = \frac{V_t}{aR_c}$$

Endcaps of spherocylindrical micelle

$$V_g = gV_t = \left[\frac{8\pi R_s^3}{3} - \frac{2\pi}{3}H^2(3R_s - H)\right]$$

$$A_g = ga = (8\pi R_s^2 - 4\pi R_s H)$$

$$A_{g\delta} = ga_\delta = [8\pi(R_s+\delta)^2 - 4\pi(R_s+\delta)(H+\delta)]$$

$$P = \frac{V_g}{A_g R_s} = \frac{V_t}{aR_s}$$

$$H = R_s\{1-[1-(R_c/R_s)^2]^{1/2}\}$$

Appendix C: contributions to free energy of micelle formation

The free energy of micelle formation can be decomposed into a number of contributions by considering the changes in the state of a singly dispersed surfactant molecule when it is transferred from water to the micelle. Firstly, the hydrophobic tail of the surfactant is removed from contact with water and transferred to the micellar core, which is like a hydrocarbon liquid. Secondly, the surfactant tail in the micelle is subjected to conformational constraints because of the requirement that the polar head group remains at the micelle–water interface. This gives rise to a free energy contribution associated with the deformation of the surfactant tail. Thirdly, the formation of the micelle is accompanied by the creation of a micelle–water interface. Fourthly, the surfactant head groups are brought to the micellar surface, giving rise to steric interactions among them. Finally, if the head groups are ionic, electrostatic interactions between them at the micellar surface also arise. Detailed quantitative modelling of each of the above contributions to the free energy of micelle formation has been carried out in Ref. [23] and only the final expressions used in the present calculations are summarized below.

$$\Delta\mu_g^\circ = (\mu_g^\circ/g - \mu_1^\circ)$$
$$= (\Delta\mu_g^\circ)_{tr} + (\Delta\mu_g^\circ)_{def} + (\Delta\mu_g^\circ)_{int} + (\Delta\mu_g^\circ)_{steric} + (\Delta\mu_g^\circ)_{ionic}$$

where the subscripts tr, def, int, steric and ionic indicate transfer, deformation, interface, steric and ionic, respectively.

Transfer free energy

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{tr} = 5.85\ln T + \frac{896}{T} - 36.15 - 0.0056T$$

for CH_2 groups and

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{tr} = 3.38\ln T + \frac{4064}{T} - 44.13 + 0.02595T$$

for the CH_3 group.

Tail deformation free energy

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{def} = \frac{9P\pi^2}{80}\frac{R_s^2}{NL^2}$$

for spheres, ellipsoids, endcaps of spherocylinders

and

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{def} = \frac{10P\pi^2}{80}\frac{R_c^2}{NL^2}$$

for middle cylindrical part of spherocylinders.

Aggregate core–water interfacial free energy

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{int} = \frac{\sigma_{agg}}{kT}(a - a_0)$$

where $\sigma_{agg} \approx 50$ dyn cm^{-1} at 298 K, and a_0 is the smaller of a_p or L^2.

Head group steric interactions

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{steric} = -\ln\left(1 - \frac{a_p}{a}\right)$$

Head group ionic interactions

$$\left(\frac{\Delta\mu_g^\circ}{kT}\right)_{ionic} = 2\left(\ln\left\{\frac{s}{2} + \left[1 + \left(\frac{s}{2}\right)^2\right]^{1/2}\right\} - \frac{2}{s}\left\{\left[1 + \left(\frac{s}{2}\right)^2\right]^{1/2} - 1\right\} - \frac{2C}{\kappa s}\ln\left\{\frac{1}{2} + \frac{1}{2}\left[1 + \left(\frac{s}{2}\right)^2\right]^{1/2}\right\}\right)$$

where $s = \frac{4\pi e^2}{\epsilon\kappa a_s kT}$, $\kappa = \left(\frac{8\pi n_0 e^2}{\epsilon kT}\right)^{1/2}$, $C = \frac{2}{R_s + \delta}$ for spheres and endcaps of spherocylinders, $C = \frac{2}{R_{eq} + \delta}$ for ellipsoids, $C = \frac{1}{R_c + \delta}$ for cylindrical middle of spherocylinders, ϵ is the dielectric constant of water ($\epsilon = 78$ at 298 K), n_0 is the number density of counterions in solution, and e is the electronic charge ($e = 4.8 \cdot 10^{-10}$ e.s.u.).