

Translational and Rotational Contributions to the Size of Micelles in Dilute Surfactant Solutions

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Equilibrium theories of micellar self-assembly in dilute surfactant solutions are now well established. The fundamental thermodynamic quantity is μ_s , the chemical potential of an aggregate comprised of s surfactants: $\mu_s = \mu_s^\circ + kT \ln (X_s/s)$, where X_s is the mole fraction of surfactant molecules incorporated into s -micelles. The distribution of aggregate sizes ($\{X_s\}$) follows from the equilibrium condition $s'\mu_{s'} = s\mu_s$ (all s and s'), as soon as the s dependence of μ_s° is specified. But previous theories have implicitly interpreted the standard chemical potential μ_s° as the reversible work required to insert an s -micelle into aqueous solution at a particular point and with a particular orientation. In the present work we outline a simple but systematic derivation of μ_s . We show that the above μ_s° must be augmented by the translational and rotational contributions familiar from a statistical-thermodynamic treatment of the ideal (molecular) gas partition functions. Including these "new" terms in the micellar exchange equilibrium leads to new forms for the size distributions and relative stabilities of rodlike and disklike aggregates in dilute solution. The results of numerical calculations are presented for commonly accepted values of the micellar self-assembly parameters. Inclusion of translational and rotational degrees of freedom is shown in general to favor smaller aggregates, making finite disks still more likely than previously believed.

I. Introduction

Recent efforts to understand surfactant aggregation in dilute surfactant solutions have relied heavily on the theory of micellar self-assembly.¹⁻⁴ This approach probably represents the most successful to date at treating surfactant solutions as polydisperse systems of micellar aggregates. Regarding each micelle of specific size and shape as a distinct chemical species, one can calculate the distribution of surfactant molecules among the various micellar aggregates via the condition

$$s'\mu_{s'} = s\mu_s \quad (1)$$

One needs "only" know how the chemical potentials of the micelles—the μ_s 's—depend on their size and concentrations. Equation 1 is just the condition for chemical equilibrium between micelles having s surfactant molecules (monomers) and those having s' . Self-assembly theories describe these chemical potentials by writing them in the form of the usual ideal-solution expressions for the chemical potential of a solute

$$\beta\mu_s = \beta\mu_s^\circ + \ln x_s \quad (2A)$$

x_s , being the mole fraction of the solute, μ_s° its standard chemical potential, and β —as usual—the reciprocal of the product of Boltzmann's constant, k_B , and the absolute temperature, T . For micelles, the entropy of mixing— $\ln x_s$ —becomes $\ln (x_s/s)$ where x_s is now defined as the mole fraction of surfactant molecules contained in micelles of size s :

$$\beta\mu_s = \beta\mu_s^\circ + \ln (x_s/s) \quad (2B)$$

As we shall see, eq 2B is the correct starting point provided (i) interactions between various micellar aggregates are negligible and (ii) μ_s° properly includes all of the "ideal-gas" translational and rotational degrees of freedom.

The surfactant molecules that aggregate to form micelles are amphiphilic. A typical monomer consists of a hydrophilic (e.g., ionic or polar) "head" group bound to a hydrophobic "tail" (e.g., an alkyl chain of six or more carbons).⁵ Accordingly, μ_s°/s , the average μ° for a molecule in an aggregate, is considerably lower—by many $k_B T$ —than μ_1° , the μ° for a monomer in solution. That is, forgetting for a moment the "mixing" terms $\ln (x_s/s)$, these molecules lower their free energy by burying their alkyl tails in the hydrocarbon core of a micelle, with their heads in contact with the aqueous solution at the hydrocarbon-water interface. At low surfactant concentrations, the system free energy is minimized by dispersing the amphiphiles into monomers for entropic purposes. When the surfactant concentration is increased, however, the entropy of dispersing the surfactant into monomers—the entropy of mixing in eq 2B—becomes less important and micelles of some minimum size begin to form. The surfactant concentration at which micelles first begin to form is called the critical micellar concentration (cmc); the minimum micelle shape is often spherical. Unlike the spherical liquid-drop clusters encountered in nucleation theory,⁶ at least one of the dimensions of a micellar aggregate must not exceed the length of a fully extended surfactant tail. That is, all molecules must have their heads at the surface and no "holes" are tolerated in the core. For the micelles to grow, they must become more anisotropic in one of their other dimensions. These larger micelles may be either prolate (rodlike) or oblate (disklike) in shape.

In the conventional theory, free energy contributions from the alkyl chains of the surfactant molecules, from the hydrocarbon-water interface, and from the head-group repulsions are assumed separable. That coupling terms are important however can easily be appreciated by considering, for example, the fact that the conformations of the first few carbon-carbon bonds depend upon the curvature of the interface.⁷⁻⁹ Therefore, the above-mentioned

(1) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* 1976, 72, 1525. Israelachvili, J. N.; Marcelja, S.; Horn, R. G. *Q. Rev. Biophys.* 1980, 13, 121.

(2) Tanford, C. "The Hydrophobic Effect"; 2nd ed.; Wiley: New York, 1980.

(3) Mukerjee, P. In "Micellization, Solubilization, and Microemulsions"; Mittal, K., Plenum Press: New York, 1977; Vol. 1, p 171.

(4) For further basic references see: "Surfactants in Solution"; Lindman, B., Mittal, K. L., Eds.; Plenum Press: New York, 1984.

(5) See, for example, the recent review by: Lindman, B.; Wennerström, H. *Phys. Rep.* 1979, 52, 1.

(6) Abraham, F. F. "Homogeneous Nucleation Theory"; Academic Press: New York, 1974.

(7) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* 1980, 77, 3115; 1981, 78, 676.

(8) Gruen, D. W. R.; de Lacey, E. H. B. In "Surfactants in Solution"; Lindman, B., Mittal, K. L., Plenum Press: New York, 1984.

(9) Ben-Shaul, A.; Gelbart, W. M. *Proc. Natl. Acad. Sci. U.S.A.* 1984, 81, 4601.

separation is not strictly correct; nevertheless, this model does make several intuitively reasonable predictions about micellar growth and shape.

Because the alkyl chains comprising the hydrocarbon cores of micelles exhibit many of the physical properties characteristic of a liquid hydrocarbon, their free energy (per molecule) is commonly approximated by a bulk liquid term which we will call g . Consider next the hydrocarbon-water interface at the micelle surface. Because the heads shield only part of the hydrocarbon core from the aqueous solvent, a surface free energy, γa must be included in the micelle chemical potential for each head group: γ is an interfacial free energy, and a a local interfacial area per head group. Using simple surface-to-volume relationships, we can straightforwardly determine a as a function of the shape of the micelle surface. For example, $a_i = iv/l$ where v is the molecular (van der Waals, space-filling) volume per amphiphile, l is the alkyl length, and $i = 1, 2,$ and 3 for bilayers, right circular cylinders, and spheres, respectively. To account for the observed stability of various micellar shapes, a repulsive component inversely proportional to the local area per head group is also included in μ° . Collecting these contributions, we write for the free energy contribution per amphiphile (hence, the tilde)

$$\tilde{\mu}_i^\circ = \gamma a_i + C/a_i + g \quad (3)$$

In eq 3, C is a constant related to the work of charging up the surface—it is associated with the electrical double layer at the ionic head/counterion interface. [Most theories regard C (and γ) as independent of local curvature.^{1,2}]

To derive an expression for the micelle size distribution, we combine eq 2B for μ_1 and μ_s with eq 1 and find

$$x_s = s x_1^s \exp[s\beta(\mu_1^\circ - \tilde{\mu}_s^\circ)] \quad (4)$$

where $\tilde{\mu}_s^\circ = \mu_s^\circ/s$. Since we use eq 3 for each surfactant in a micelle to get $\mu_s^\circ (= \sum_i s_i \mu_i^\circ)$, we see that $\tilde{\mu}_s^\circ$ is a weighted average of the free energy contribution per amphiphile. s_i is the number of molecules in environment i (e.g., spherical "cap", cylindrical body, etc.) in a micelle of size s : $\sum_i s_i = s$. With this formulation one can easily show that¹⁰

$$\tilde{\mu}_s^\circ \text{rod} = \tilde{\mu}_\infty^\circ \text{r} + \delta_{\text{rod}}(1/s) + g \quad (5A)$$

$$\tilde{\mu}_s^\circ \text{disk} = \tilde{\mu}_\infty^\circ \text{d} + \delta_{\text{d}}(s) f_{\text{d}}(s) + g \quad (5B)$$

for spherocylinders and circular disks (enclosed by a hemitoroidal rim), respectively. $\tilde{\mu}_\infty^\circ \text{r}$ and $\tilde{\mu}_\infty^\circ \text{d}$ are the asymptotic forms of $\tilde{\mu}_s^\circ$ (rod) and $\tilde{\mu}_s^\circ$ (disk)—i.e., the free energy per amphiphile in an infinite cylinder or bilayer. δ_{rod} is a constant independent of s —it is proportional to the free energy difference between molecules in the caps and body of a rod and increases linearly with the interfacial free energy per unit area, γ ; $\delta_{\text{d}}(s)$, on the other hand, becomes constant (and proportional to γ) only as $s \rightarrow \infty$; in this same limit, $f_{\text{d}}(s) \rightarrow s^{-1/2}$. It can be shown that when γ is large enough (≈ 50 erg/cm²), expressions 5A and 4 predict broadly dispersed distributions of spherocylinders with large number and weight averages. According to eq 5B and 4, however, narrowly dispersed disk distributions centered around a small aggregation number can also prevail.^{2,10}

An important feature of these predictions is that they result not from the precise form of eq 3 but from the notion that $\tilde{\mu}_s^\circ$ is a weighted average of contributions from amphiphiles in the different environments of a micelle. This "averaging process" distinguishes self-assembly from other molecular theories of micelle formation.¹¹ Attempts to extend the above theory to cases where interactions between micelles are no longer negligible,¹² and to include curvature dependence of the chain free energies¹⁰— g in eq 3—change the model's qualitative predictions only slightly. In particular, interaggregate interactions enhance micelle size; and including the curvature dependence in the chain free energies

allows, under certain circumstances, significant concentrations of disklike micelles to form.

In the present paper, we will not challenge the averaging concept referred to above. Rather, we shall be concerned with how self-assembly fits into a more general statistical-mechanical framework. First, we will derive a general expression for the chemical potentials of micelles in an aqueous environment. After relating certain portions of these expressions to the standard chemical potentials given in eq 5A and 5B, it will become evident that important translational and rotational terms have been neglected in the prevailing self-assembly approach.¹³ Next, after taking the dilute (with respect to micelles) solution limit, we will use these results to derive a new size distribution in analogy to eq 4. We present some numerical calculations and discuss these in connection with those of the conventional theory of self-assembly.

II. General Derivation of Micellar Chemical Potentials

Chemical Potentials of Solutes in Solute Mixtures. According to the classic (McMillan-Mayer) theory of dilute solutions,¹⁴ the chemical potential of a solute species can be formally written as

$$\beta\mu_s = \ln(V\Psi_0/\Psi_1) + \ln\rho_s + \ln\gamma_s \quad (6)$$

where V is the system volume, ρ_s the number density of s -solute, and γ_s an activity coefficient with the property that $\gamma_s \rightarrow 1$ as the density of each solute, $\{\rho_s\} \rightarrow 0$. The quantity $V\Psi_0/\Psi_1$, as we will see below, contains the internal, rotational, and translational degrees of freedom of the s -solute, and also includes the solute-solvent interactions. (This latter contribution is closely related to the Henry's law constant for the system s -solute + pure solvent.) We will restrict our attention to situations where $\ln\gamma_s \rightarrow 0$ —the dilute-solution regime—but note that $\ln\gamma_s$ is the usual virial series for the logarithm of the activity coefficient of a multicomponent imperfect-gas mixture, with the potential energies replaced by potentials of mean force.

Let us look more carefully at $V\Psi_0/\Psi_1$. Ψ_0 is the grand partition function of pure solvent:

$$\Psi_0 = \sum_{N_w \geq 0} Q(N_w, V, T) \lambda_w^{N_w} \quad (7)$$

where $Q(N_w, V, T)$ is the canonical partition function of N_w solvent molecules at volume V and temperature T , and λ_w is their absolute activity. Similarly, Ψ_1 is a *semigrand* partition function for a single s -solute and any number of solvent molecules:

$$\Psi_1 = \sum_{N_w \geq 0} Q(1, N_w, V, T) \lambda_w^{N_w} \quad (8)$$

Because of the thermodynamic equivalence of the different ensembles, we can retain only the maximum terms in Ψ_0 and Ψ_1 and write

$$\frac{\Psi_1}{\Psi_0} = \frac{q_s \int \dots \int e^{-\beta u_{N,1}} d\{\bar{N}\} dr_s}{V \int dr_s \int \dots \int e^{-\beta u_{\bar{N}}} d\{\bar{N}\}} \quad (9)$$

In eq 9, q_s is the separable ideal-gas partition function for a single s -solute, $u_{N,1}$ the interaction potential energy of \bar{N} solvent molecules and a single s -solute, and $u_{\bar{N}}$ that for the solvent molecules only. q_s includes all momentum integrations and internal degrees of freedom associated with the solute particle. We assume that the solvent is isotropic and (as the micelles are very large compared to the molecules of the surrounding aqueous solution) that the interaction potential $u_{N,1}$ is independent of the rotational coordinates of our solute. Therefore, q_s is the partition function of a single s -solute under vacuum.

(10) McMullen, W. E.; Ben-Shaul, A.; Gelbart, W. M. *J. Colloid Interface Sci.* **1984**, *98*, 523.

(11) See discussion in ref 3-5.

(12) Ben-Shaul, A.; Gelbart, W. M. *J. Phys. Chem.* **1982**, *86*, 316. Gelbart, W. M.; Ben-Shaul, A.; McMullen, W. E.; Masters, A. *J. Phys. Chem.* **1984**, *88*, 861.

(13) For interesting exceptions see: Hoeve, C. A. J.; Benson, G. C. *J. Phys. Chem.* **1957**, *61*, 1149. Poland, D. C.; Scheraga, H. A. *J. Phys. Chem.* **1965**, *69*, 2431. Nagarajan, R.; Ruckenstein, E. *J. Colloid Interface Sci.* **1979**, *71*, 580.

(14) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276. See also: Hill, T. L. "Introduction to Statistical Thermodynamics"; Addison-Wesley: Reading, MA, 1960; Chapter 19.

Rewrite eq 9 in the slightly more convenient form

$$\frac{\Psi_1}{V\Psi_0} = \frac{q_s}{V} \langle e^{-\beta\phi_s} \rangle \quad (10)$$

where $\phi_s \equiv u_{N,1} - u_N$ is the "binding energy" of an s -solute (of fixed position and orientation) to pure solvent^{15,16} and $\langle \dots \rangle$ denotes a thermal average defined by $\int dr_s \int d\{N\} (\dots) P^N(\{N\})$. Returning now to eq 6 and putting in the result for $\Psi_1/V\Psi_0$ from eq 10 gives

$$\beta\mu_s = -\ln(q_s/V) + \ln\rho_s - \ln\langle e^{-\beta\phi_s} \rangle + \ln\gamma_s \quad (11)$$

Equation 11 states that the chemical potential of a solute consists of the usual ideal-gas contributions—the first two terms—and nonideal parts conveniently separated into a solvent-solute interaction portion and a solute-solute interaction in the presence of solvent.

We now specialize eq 11 to a polydisperse system of micellar aggregates. We regard any counterions or other nonamphiphilic species as part of the solvent. As mentioned earlier, q_s contains the ideal-gas contributions of a single s -solute to the overall solute chemical potential. So consider an s -aggregate executing free rotations and translations in an ideal-gas phase. As is well known, the polar heads of the s amphiphiles comprising each such aggregate are constrained to be at the micellar surface. Hence, we approximate a micelle by a rigid body of the same size and some average shape. That is, we ignore fluctuations from this average shape. (In principle we could include these fluctuations by allowing explicitly for many different shapes—i.e., all (size) subscripted quantities would carry an additional label describing their shape.) Within this approximation, one can separate a rotational partition function, $q_{rot}(s)$, from q_s . Other ingredients contained within q_s include head-group interactions, $q_h(s)$, and vibrational and torsional degrees of freedom, $q_{vib}(s)$, associated with the tails. (Strictly speaking, the head-group interactions are *not* separable from the solvent-micelle potential; however, as soon as we define the counterions as part of the solvent, we expect to see some Coulombic (or steric, for nonionic aggregates) repulsions between the heads even when we let the solvent become a vacuum. In any case, such subtleties will have no impact on the results that follow.) We thus write q_s/V as

$$q_s/V = q_h(s) q_{vib}(s) q_{rot}(s) q_{trans}/V \quad (12)$$

Recall now that $(q_{trans}(s)/V)^{-1}$ is just the cube of the thermal de Broglie wavelength Λ_s of an s -micelle. Using $\Lambda_s = s^{-1/2}\Lambda_1$, $\rho_s = (x_s/s)\rho$ (ρ = the overall number density), and eq 12 in eq 11 gives us

$$\beta\mu_s = -\frac{3}{2} \ln s + \ln(\Lambda_1^3 \rho) - \ln q_{rot}(s) + \ln(x_s/s) - \ln\langle e^{-\beta\phi_s} \rangle - \ln q_h - \ln q_{vib} + \ln\gamma_s \quad (13)$$

Next we take the dilute-solution limit $\gamma_s \rightarrow 1$ and divide eq 13 by s so that

$$\beta\tilde{\mu}_s = -\frac{3}{2} \frac{1}{s} \ln s + \frac{1}{s} \ln(\Lambda_1^3 \rho) - \frac{1}{s} \ln q_{rot}(s) + \frac{1}{s} \ln \frac{x_s}{s} - \frac{1}{s} [\ln\langle e^{-\beta\phi_s} \rangle + \ln q_h(s) + \ln q_{vib}(s)] \quad (14)$$

Finally consider the averages (over all surfactants in a micelle) of the quantity given in eq 3. (As mentioned earlier, eq 5A and 5B are special cases of this.) We observe that this average must have its origin in the bracketed term in eq 14. For example, $-\ln\langle e^{-\beta\phi_s} \rangle$ can be thought of as the reversible work of inserting an s -micelle of fixed orientation and position into pure solvent from vacuum at constant V and T . Neglecting pressure-volume terms—which we can trivially show are very small and independent of size or shape—we find that

$$-\frac{1}{s} \ln\langle e^{-\beta\phi_s} \rangle - \frac{1}{s} \ln q_h(s) \leftrightarrow \left(\gamma a + \frac{C}{a} \right) \beta \quad (15A)$$

and similarly

$$-(1/s) \ln q_{vib}(s) \leftrightarrow \beta g \quad (15B)$$

i.e.

$$-(1/s)[\dots]_{eq 14} \leftrightarrow \beta\tilde{\mu}_s^\circ \quad (16)$$

Equations 15A,B and 16 show how the prevailing phenomenology—like that in eq 3—approximates the more rigorous expressions for portions of the chemical potential (eq 13). For example, to make the correspondence of eq 15B, $q_{vib}(s)$ must be $[q_{vib}(1)]^s$ where $q_{vib}(1)$ is the vibrational and torsional partition function of a single amphiphile tail embedded within a hydrocarbon core. (One might argue that even at this level of approximation we should write $q_{vib} = [q_{vib}(1)]^s/s!$. However, in an integration over the internal micelle configurational coordinates, $s!$ identical terms occur so $q_{vib} \rightarrow [q_{vib}(1)]^s$.) This assumes that each tail is the same and contributes equally to $q_{vib}(s)$. Of course, this statement is completely equivalent to the liquidlike approximation used to justify the presence of a g in $\tilde{\mu}_s^\circ$ given by eq 3. Similarly, $-\ln\langle e^{-\beta\phi_s} \rangle$ amounts to a surface free energy and any perturbation to $-\ln q_h(s)$ of a micelle. This justifies the correspondence of eq 15A. Obviously the most difficult interactions to quantify are the head group-solvent and head group-head group ones (e.g., the C/a approximation is purely phenomenological).

With these last observations in mind, we can rewrite eq 14 in the form

$$\beta\tilde{\mu}_s = \beta\tilde{\mu}_s^\circ + \frac{1}{s} \ln \frac{x_s}{s} \quad (17A)$$

where

$$\beta\tilde{\mu}_s^\circ = -\frac{3}{2} \frac{1}{s} \ln s + \frac{1}{s} \ln(\Lambda_1^3 \rho) - \frac{1}{s} q_{rot}(s) + \beta\tilde{\mu}_s^\ominus \quad (17B)$$

with

$$\tilde{\mu}_s^\ominus = \frac{1}{s} \sum_i \tilde{\mu}_i^\ominus \leftrightarrow -\frac{1}{s} [\ln\langle e^{-\beta\phi_s} \rangle + \ln q_h(s) + \ln q_{vib}(s)] \quad (17C)$$

so that eq 4, as applied to eq 17A,B, becomes

$$x_s = s^{3/2}(\Lambda_1^3 \rho)^{-1} q_{rot}(s) \{s x_1^s \exp[s\beta(\mu_1^\ominus - \tilde{\mu}_s^\ominus)]\} \quad (18)$$

The s dependence of the first three factors is new; the remaining quantities are identical with the x_s given by eq 4. We have replaced $\tilde{\mu}_s^\circ$ in eq 4 by $\tilde{\mu}_s^\ominus$ as in eq 17C. (One should note carefully that $\tilde{\mu}_s^\ominus$ ($\neq \tilde{\mu}_s^\circ$) is not a standard chemical potential or other thermodynamic quantity; rather, eq 17C and 3 define $\tilde{\mu}_s^\ominus$.) Equation 18 emphasizes the connection between x_s and the usual distribution (eq 4).

Before proceeding to the numerical calculations, we comment on the use of μ_1^\ominus —the chemical potential of an unassociated monomer—in eq 18. Rather than evaluating μ_1^\ominus via eq 11 with $\gamma_1 \rightarrow 1$, we take it as an experimentally measured quantity.² In fact, because the chain free energy contribution and the solvent-solute interactions for a monomer are not so easily estimated as eq 3 would imply (they are not separable at *any* level of approximation for monomers; i.e., eq 3 does not obtain for monomers), applying eq 11 to monomers would prove extremely cumbersome. Furthermore, a single surfactant molecule would not experience the "continuum" of solvent molecules that a micelle—by virtue of its large size—experiences. Hence, we would not expect to have a simple rotational partition function contained in q_1 (see eq 12). Even without a reliable value of μ_1^\ominus , however, we could still address the questions of most concern to us here: namely the size and shape of micelles at typical surfactant concentrations, and the shape of the micelle size distributions. As other workers have shown,¹ the precise value of μ_1^\ominus determines the critical micelle concentration (cmc), but does not affect the properties of the actual aggregates.

III. Numerical Calculations

We consider two classes of micellar aggregates: prolate and oblate. Furthermore, to make more tenable the packing arguments

(15) Ben-Naim, A. "Hydrophobic Interactions"; Plenum Press: New York, 1980.

(16) Widom, B. *J. Chem. Phys.* **1963**, *39*, 2808. Jackson, J. L.; Klein, L. S. *Phys. Fluids* **1964**, *7*, 228.

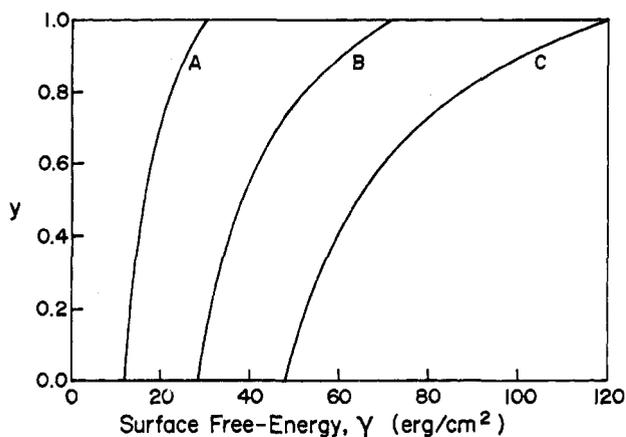


Figure 1. "Phase diagram" for micellar rods in " y, γ space". That is, (y, γ) values to the right of each curve imply that the average size of aggregate will exceed 100 when the total mole fraction of amphiphile equals 0.005. Curve A is the plot obtained for rods from the "usual" self-assembly theory (see text); B includes translational degrees of freedom, but no rotations; and C includes both.

that go along with eq 3 we restrict the prolate particles to spherocylinders and the oblate ones to circular bilayers surrounded by hemitoroidal rims. In a recent paper¹⁰ we showed that (see eq 5A)

$$\beta \bar{\mu}_s^{\ominus} \text{rod} = \beta \bar{\mu}_{\infty}^{\ominus} \text{rod} + \delta_{\text{rod}}(1/s) + g \quad (19A)$$

with

$$\bar{\mu}_{\infty}^{\ominus} \text{rod} = 2\gamma a_0 [1 + (1-y)^2 / 4(1+y)] \quad (19B)$$

$$\delta_{\text{rod}} = \frac{m\gamma a_0}{6(1+y)k_B T} (5 - 2y - y^2) \quad (19C)$$

Here $a_0 \equiv (C/\gamma)^{1/2}$ is the value of a which minimizes $\gamma a + C/a + g$ (eq 3), m is the minimum micelle size ($= 4/3\pi l^3/v$), and $y \equiv a_0 l/v - 1$ is a parameter which sets the lengths of the alkyl chains relative to the value which would give a_0 . (Recall $a_i = iv/l$, $i = 1, 2, 3$ for bilayers, cylinders, and spheres.) [Because in the liquidlike approximation^{1,2} each chain is allowed to adjust to give $a_i = a_0$ in each particular i environment, we would never expect to see anisotropic micelles! This is because $\bar{\mu}_s^{\ominus}$ would be the same for all micelles, making the minimum (i.e., spherical) aggregates favored via the entropy of mixing terms. The y -parameter approach¹⁰ resolves this difficulty.] For disks, the equations analogous to eq 19A-C are

$$\beta \bar{\mu}_s^{\ominus} \text{disk} = \beta \bar{\mu}_{\infty}^{\ominus} \text{disk} + \delta_d(s) f_d(s) \quad (20A)$$

$$\bar{\mu}_{\infty}^{\ominus} \text{disk} = 2\gamma a_0 [1 + y^2 / 2(1+y)] \quad (20B)$$

$$\delta_d(s) = \left(\frac{3m}{32}\right)^{1/2} \frac{\pi\gamma a_0}{k_B T(1+y)} \left[1 - \frac{y(2+y)}{1 + \frac{m}{s_{\text{rim}}}} \right] \quad (20C)$$

$$f_d(s) = \left(\frac{32m}{3\pi^2}\right)^{1/2} \frac{1}{s} \left(\frac{1 + \frac{s_{\text{rim}}}{m}}{1 + 2\frac{s_{\text{rim}}}{m}} \right)^2 \quad (20D)$$

$$s_{\text{rim}} = \frac{\pi}{2} \left(\frac{3m}{2}\right)^{1/2} \left[s + m \left(\frac{3\pi^2}{32} - 1\right) \right]^{1/2} - m \left(\frac{3\pi^2}{16} - 1\right) \quad (20E)$$

Note that (cf. eq 20A-D vs. 5A,B) we have absorbed a factor of β into δ_{rod} and δ_d and dropped the additive constant g .

Writing $\Lambda_1 = h^2 / (2\pi m_1 k_B T)$ for the DeBroglie wavelength of a monomer (with $m_1 =$ the mass of a monomer and $h =$ Planck's constant), and

$$q_{\text{rot}}(s) = \pi^{1/2} \left[\frac{8\pi^2 k_B T}{h^2} \right]^{3/2} [(m_1 l^2)^3 R_A(s) R_B(s)^2]^{1/2} \quad (21)$$

for the rotational partition function of symmetric tops like our micelles, we find from eq 18

$$x_s = s^{3/2} \pi^{1/2} \left[\left(\frac{16\pi^3 (k_B T)^2 m_1^2 l^2}{h^4} \right)^{3/2} \frac{1}{\rho} \right] R_A(s)^{1/2} R_B(s) \times \{s x_1^s \exp[s\beta(\mu_1^{\ominus} - \bar{\mu}_s^{\ominus})]\} \quad (22)$$

Here $R_A(s) = I_A(s)/m_1 l^2$ and $R_B(s) = I_B(s)/m_1 l^2$ are dimensionless moments of inertia about the symmetry axis and other two identical principal axes, respectively. For spherocylinders

$$R_A(s) = (5s - m)/10 \quad (23A)$$

$$R_B(s) = \frac{3}{20}m + \frac{s}{4} + \frac{4}{9m^2} \left[\frac{(s-m)^3}{3} + (s-m)^2 \right] + \frac{s-m}{2m} \quad (23B)$$

while for disks

$$R_A(s) = \frac{\pi}{v} \left[\frac{r_0^4}{l} + \pi r_0^3 + 4r_0^2 l + \frac{3}{4}\pi r_0 l^2 + \frac{8}{15}l^3 \right] \quad (24A)$$

$$R_B(s) = \frac{\pi}{v} \left[\frac{r_0^4}{2l} + \frac{\pi r_0^3}{3} + \frac{8}{3}r_0^2 l + \frac{5\pi}{8}r_0 l^2 + \frac{8}{15}l^3 \right] \quad (24B)$$

$$r_0 = \frac{\pi l}{4} \left\{ \left[1 + \frac{16}{\pi^2 l^2} \left(\frac{sv}{2\pi l} - \frac{2l^2}{3} \right) \right]^{1/2} - 1 \right\} \quad (24C)$$

With eq 22, 19A-C, and 23A,B for rods and eq 22, 20A-E, and 24A-C for disks we calculate the micelle size distributions. From the definitions of the number and weight averages— \bar{s}_N and \bar{s}_W , respectively

$$\bar{s}_N = \frac{\sum_{s=m}^{\infty} x_s / \sum_{s=m}^{\infty} (x_s/s)}{\quad} \quad (25A)$$

$$\bar{s}_W = \frac{\sum_{s=m}^{\infty} s x_s / \sum_{s=m}^{\infty} x_s}{\quad} \quad (25B)$$

we can also determine the average sizes (and variances).

Figure 1A is a plot obtained for rods from the usual self-assembly theory; Figure 1B includes micelle translations but no rotations ($q_{\text{rot}}(s) \rightarrow 1$ in eq 18); and Figure 1C includes all of the ideal-gas terms (rotation and translation). This figure shows the values of y and γ necessary to bring about large anisotropic rods. More precisely, for any y, γ pair to the right of the relevant curve, the monomers will be organized predominantly into aggregates with $\bar{s} \geq 100$ when the mole fraction equals 0.005. Here

$$\text{mole fraction} \equiv x_r = \frac{\sum_{s=m}^{\infty} x_{s,\text{rod}}}{\quad} \quad (26)$$

Having fixed μ_1^{\ominus} , l , v , m , g , and ρ to values of typical surfactant monomers (e.g., SDS—see figure caption), the calculations (for rods) depend on only two parameters, y and γ . Recall that, in terms of v and l , y and a_0 are given by¹⁰

$$(1+y)v/l = a_0 \quad (27)$$

so that knowing either y or a_0 implies the other. We treat γ as a parameter, consistent with the interfacial free energy being an item of some controversy.¹⁷ Again we emphasize the tendency of the alkyl tail length to depend on the shape of the micellar interface: the rather subtle connections between this effect and the use of y above is discussed elsewhere.¹⁰

Figure 2A-C shows the analogous plots for disks using the same molecular constants and $x_d = \sum_{s=m}^{\infty} x_s(\text{disk}) = 0.005$. For either

(17) See: ref 1 and 2; Jonsson, B.; Wennerström, *J. Colloid Interface Sci.* **1982**, *80*, 482.

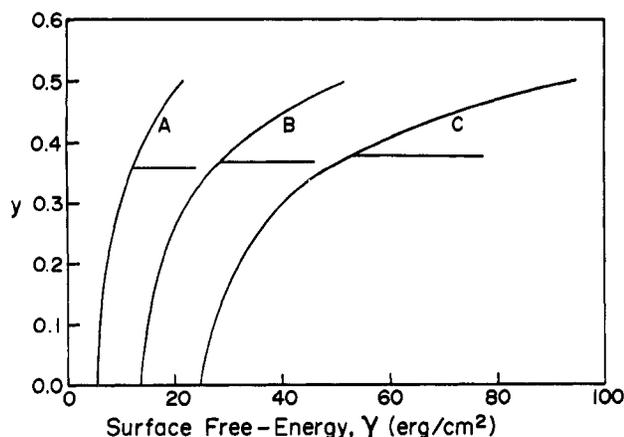


Figure 2. Same as in Figure 1, but for micellar disks. The horizontal line for each curve shows the value of y below which a direct transition to bilayers is observed.

set of plots, low values for γ lead to spheres instead of rods or disks. Below $y \approx 0.38$ (see Figure 2C), we observe the usual monomer \rightarrow bilayer transition before big disks can form: such a transition to an "infinite" phase is not possible for rods—i.e., the finite micelles grow continuously to larger and larger rods.¹⁰

As one would expect, including the additional rotational and translational degrees of freedom forces one to go to higher interfacial free energies before micelles can grow. This is because these "new" terms can be seen (see eq 17B and discussion in section IV) to make $\beta\bar{\mu}_s^\circ$ decrease more slowly with increasing s (size). For example, when $y = 0.5$, rods with a weight average of ≈ 200 will form at $x_{\text{rod}} = 0.005$ when $\gamma = 17$ erg/cm² in the conventional theory (Figure 1A), when $\gamma = 38$ erg/cm² when just translation is included, and when $\gamma = 64$ erg/cm² upon including both translation and rotation. A short glance at Figure 2A–C will reveal a similar trend ($y = 0.4$: $\gamma = 14, 33,$ and 60 erg/cm²) for disks.

IV. Discussion

In the usual self-assembly approach,¹ rodlike (disklike) micelles can grow from monomers only when the mole fraction of monomer, x_1 , approaches the quantity

$$[A_{\text{rod(disk)}}]^{-1} = e^{\beta[\mu_1^\circ - g - \bar{\mu}_\infty^\circ \text{rod(disk)}]} \quad (28)$$

Alternatively, for rods

$$x_1 A_{\text{rod}} \rightarrow 1 \quad (29A)$$

and disks

$$x_1 A_{\text{disk}} \rightarrow 1 \quad (29B)$$

These conditions on the monomer mole fractions have interesting consequences: for $A_{\text{rod}} > A_{\text{disk}}$, rods will form and dominate up to $x_{\text{rod}} \sim 1$ (an unphysical situation) before x_1 can get large enough for disks to occur. The reverse situation— $A_{\text{disk}} > A_{\text{rod}}$ —obviously causes disks to swamp out rods provided y is not too small. (If $y \leq 0.38$, bilayers form instead of disks or rods;¹⁰ i.e., x_{disk} jumps from approximately 0 to ∞ —the disk sum diverges—before rods or disks can be seen). From eq 28, then, we see that $\bar{\mu}_\infty^\circ \text{disk} > \bar{\mu}_\infty^\circ \text{rod}$ will favor rods while $\bar{\mu}_\infty^\circ \text{disk} < \bar{\mu}_\infty^\circ \text{rod}$ will favor disks. In terms of y , the transition occurs¹⁰ at $y = 2^{1/2} - 1 \approx 0.41$ (see eq 19B and 20B). That is, for $y < 2^{1/2} - 1$ we have dominantly disks (or bilayers), while for $y > 2^{1/2} - 1$, we have rods.

When eq 5A, 22, 23A, 23B, and 28, and the approximation $R_A(s)^{1/2} \approx (s^{1/2}/2^{1/2})(1 - m/10s)$ are used, the expression for x_{rod} can easily be cast in the form

$$x_{\text{rod}} = \sum_m x_{s,\text{rod}} \sim \sum_{s \geq m} h(s) e^{-\delta_r(x_1 A_r)^s} \quad (30)$$

where $h(s)$ is a polynomial in s . Equation 30 is "simply" a sum of various geometric series and can be evaluated in closed, analytic form;¹⁸ it converges for $x_1 A_r < 1$, varying very rapidly only when

$x_1 A_r$ gets close to 1.0. Israelachvili et al. have shown that the weight average (eq 25B) and dispersion (variance) of the distribution can be written as

$$\bar{s}_{\text{rod(disk)}} = \partial \ln x_{\text{rod(disk)}} / \partial \ln x_1 \quad (31)$$

$$\sigma_{\text{rod(disk)}}^2 = \partial^2 \ln x_{\text{rod(disk)}} / \partial (\ln x_1)^2 \quad (32)$$

Now as $x_1 A_r$ approaches 1, x_{rod} varies rapidly with x_1 so \bar{s}_{rod} gets large. Also, as part of the analysis of the geometric series in eq 30, x_{rod} can be shown asymptotic to the line $x_1 = 1/A_r$. Hence, the curvature of $\ln x_{\text{rod}}$ vs. $\ln x_1$ must get large, as must σ_{rod}^2 . Then when anisotropic rods do form, we expect to see a broad distribution of them.

Because of the complicated form of eq 20C–E as well as the moments of inertia (eq 24A,B), the analysis for disks is much more difficult. Nevertheless, for the large s tail of the distribution

$$x_{\text{disk(tail)}} \approx \sum_{s > k} b(s) e^{-\delta_d(\infty) s^{1/2}} (s_1 A_d)^s \quad (33)$$

where $b(s)$ is a power series in s , $\delta_d(\infty) = \lim_{s \rightarrow \infty} \delta_d(s)$, and k is an arbitrary lower limit [large, so that $\delta_d(k) f_d(k) \approx \delta_d(\infty) (1/s^{1/2})$]. The circle of convergence of this sum is $x_1 A_d = 1$: for $x_1 A_d$ infinitesimally larger than 1, the sum does not converge. From $x_{\text{disk}} = \sum_m k^{-1} x_{s,\text{disk}} + x_{\text{disk(tail)}}$, we see that the overall sum converges for $x_1 A_d \leq 1$. Furthermore, since x_{disk} does not have the asymptote that x_{rod} has, we expect the disk distribution to be narrowly dispersed about some small aggregation number (compared to \bar{s}_{rod}). For moderate values of s in $\bar{\mu}_s^\circ \text{disk}$, $\delta_d(s) f_d(s)$ falls off even faster than $1/s$ (as in the rod case). So if medium-sized rods can be observed, so can medium-sized disks.

The transition of the y vs. γ plots in Figures 1A–C and 2A–C to higher values of γ can be explained in terms of the large numerical prefactor in eq 22 that also occurs in the sums for x_{disk} and x_{rod} (eq 30 and 33); for the values of ρ , m_1 , l , and T (300 K) assumed in the numerical work, this constant has the value 7.3×10^{13} . Note that before \bar{s}_{rod} —and presumably \bar{s}_{disk} also—can get large, $x_1 A_{\text{rod(disk)}}$ must approach 1. (Some preliminary calculations indicate that fairly large disks begin to form when $x_1 A_{\text{disk}} \approx 0.8$ —significantly less than 1—if y is about 0.5. However, rods would overwhelm the disks here because $A_{\text{disk}}/A_{\text{rod}} < 0.8$ for values of γ of interest ($\gamma > 25$ erg/cm².) Only when γ (and hence δ_r and $\delta_d(\infty)$ in eq 30 and 33, respectively) is large enough so that x_{rod} and x_{disk} are not unphysically large (≈ 0.005) will this occur. Of course, when one includes only translation in the chemical potentials, the effect is less pronounced (Figures 1B and 2B).

To establish evidence for the existence of rods and rule out the possibility of disks, Israelachvili et al. took $y = 1$ for rods, $y = 0$ for disks, and $\gamma \approx 50$ erg/cm². Consistent with the analysis here and elsewhere they found only bilayers when searching for disks. On the other hand, we see that when the correct ideal-gas degrees of freedom are included, rods only get big in the $y = 1$ case when γ is 2–3 times larger than their value. Since γ for bulk hydrocarbon–water interface is not much greater than 50 erg/cm², we must suspect that rods are not as ubiquitous as previously accepted. Furthermore, at $y = 0.38$, it takes only a surface term of 54 erg/cm² to generate disks with a weight average of 100 at $x = 0.005$. At slightly larger y values the necessary interfacial tension rises rapidly. However, for $y \leq 0.41$ (disk regime), γ is never unphysically large.

The fundamental reason for the differences between the results of conventional self-assembly theory and the calculations reported here is that, in the present treatment, rotation and translational have been included in the micelle chemical potentials. From eq 17B and 21 we see that the s -dependent parts of the translational and rotational contributions to the micelle chemical potential per surfactant molecule can be written as $-(3/2)(1/s) \ln s$ and $-(1/2)(1/s) \ln [R_A(s) R_B(s)^2]$, respectively. Both of these functions are negative and decrease monotonically in magnitude with s : they make less negative contributions to $\bar{\mu}_s$ for big micelles, thereby favoring small spherelike micelles. At any given y , the

(18) McMullen, W. E., unpublished notes.

micelles can grow only when the driving force for growth is large enough. We also note that the new constant terms in the chemical potentials, which bring about the effects discussed in the preceding paragraphs, are a measure of the loss in entropy attendant upon going from a dispersion of s monomers to an s -micelle.

V. Conclusion

Ignoring portions of the size dependence of micelle chemical potentials could cause serious disagreement and misinterpretation upon comparing experimental results to theoretical predictions. Neglecting the translational and rotational degrees of freedom of micelles, for example, allows one to make the rather strong prediction^{1,10} that rodlike micelles should dominate the isotropic phases of soap solutions provided the interfacial free energy of a particular amphiphile-water interface γ is large enough (≈ 50 erg/cm²). On the other hand, when one properly includes these contributions, unphysically large interfacial free energies are required to observe rods. Under the right conditions, though ($0.38 \leq \nu \leq 0.41$), dislike micelles may occur at the same values of γ previously thought to guarantee only rod formation. In other important respects, the more rigorous treatment does not differ qualitatively from the usual approach. We still obtain a critical micelle concentration and ensuing growth into broadly dispersed rod and narrowly dispersed disk distributions.

We have seen that the principal qualitative effect of the "new" translational and rotational free energy contributions is to favor small (vs. large) aggregates. Thus, we conclude that any mechanism which drives the growth of micelles will be opposed by the effect of these terms. For example, the growth induced by the decrease of $\bar{\mu}_s^\circ$ with s —which accounts for the sphere \rightarrow rod and disk transitions referred to above—has been shown to be "stunted" by the translational and rotational terms which become *more positive* with s . Similarly, consider the growth of rodlike aggregates which is brought about by their alignment in nematic phases.¹⁹ It is easy to show for this case that—in the absence of the translational and rotational contributions—the finite rods

are destabilized by their long-range orientational ordering; i.e., the nematic state does not even correspond to a *local* thermodynamic minimum. Under these circumstances the rods "explode" into infinite, perfectly aligned cylinders: the isotropic phase is transformed directly into the hexagonal state. When terms like $-(3/2)(1/s) \ln s$ are included, however, the system free energy can be shown to take on a minimum for a *partially* ordered, *small-rod* configuration. This example of the stunting of micellar growth via the translational and rotational contributions is discussed at length elsewhere.²⁰

It is interesting to remark in closing on the formal equivalence between the treatment of translations and rotations in this paper and the "replacement free energy" paradox in nucleation theory.²¹ Historically, for nucleating systems, the internal degrees of freedom of a liquid drop were implicitly suppressed. The drop free energy was described by a bulk binding energy term (scaling with the volume, i.e., s) and a surface tension contribution (going as $s^{2/3}$). In distinguishing between statistical mechanical "clusters" and phenomenological "drops", Reiss^{21,22} showed explicitly how the thermodynamic treatment neglected fluctuations in the center of mass of the molecules comprising nucleation spheres, and made contact with the earlier attempts by Lothe and Pound²³ to incorporate translational and rotational degrees of freedom. Within the context of micellized soap solutions we have seen a similar historical development. That is, initial efforts have concentrated on thermodynamic descriptions in which the free energies of aggregates are accounted for phenomenologically. In building on this zero-order starting point we have neglected center-of-mass fluctuations (consistent with the molecules being constrained to the surface) and treated directly the translational and rotational degrees of freedom of rigid particles of specified sizes and shapes.

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(20) Gelbart, W. M.; McMullen, W. E.; Ben-Shaul, A. submitted for publication in *J. Phys. (Orsay, Fr.)*.

(21) Reiss, H. In "Nucleation"; Zettlemoyer, A. C., Ed.; Elsevier: Amsterdam, 1977; Adv. Colloid Interface Sci. Vol. 7, pp 1-66.

(22) Reiss, H.; Katz, J. L.; Cohen, E. R. *J. Chem. Phys.* **1968**, *48*, 5553.

(23) Lothe, J.; Pound, G. M. *J. Chem. Phys.* **1962**, *36*, 2080.

(19) Gelbart, W. M.; Ben-Shaul, A.; Masters, A.; McMullen, W. E. "Proceedings of the Enrico Fermi School, Varenna, Italy; Degiorgio, V.; Corti, M., Eds.; North-Holland Publishing Co.: Amsterdam, 1984.

Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions. 8. Mixtures of Counterions, Species Selectivity, and Valence Selectivity

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The equations of the territorial binding model of counterion condensation theory are presented in general form. The unknown variables are taken as the binding fractions of the different counterion species, and there are as many equations as variables. The equations accommodate any number of counterion species, each of general valence. They are written for any proportion of polyion to added salt concentration. We derive the familiar condensation rules for binding fractions as "limiting laws" valid at infinite dilution. The equations themselves, however, may be solved numerically for the binding fractions at any fixed concentration. The parameters of the equations allow us to characterize ion-specific short-range interactions and, in particular, species selectivity effects among counterions of the same valence.

The phenomenon of *selectivity* is observed in a dilute polyelectrolyte solution that contains a mixture of counterion species. Species of higher valence predominate in the population of bound counterions even in the face of larger stoichiometric concentrations of species of lower valence. Among different counterion species of the same valence the ratio of their bound concentrations is not

equal to the ratio of their stoichiometric concentrations. Long-range ionic forces are the dominant mechanism for *valence selectivity*, while short-range forces account for *species selectivity* if the valences are the same.

Counterion condensation theory has been almost exclusively concerned with a description of the large effects of ionic charge