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Liquid Crystalline States of Surfactant Solutions of Isotropic Micelles

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We consider micellar solutions whose surfactant molecules prefer strongly to form small, globular aggregates in the absence of intermicellar interactions. At sufficiently high volume fraction of surfactant, the isotropic phase of essentially spherical micelles is shown to be unstable with respect to an orientationally ordered (nematic) state of rodlike aggregates. This behavior is relevant to the phase diagrams reported for important classes of aqueous amphiphilic solutions.

KEY WORDS: Micelle; excluded volume; liquid crystallinity; self-assembly; isotropic–nematic transition; packing entropy.

1. INTRODUCTION

It is often tempting to treat micellized surfactant solutions as colloidal suspensions of particles of given size and shape. The "particles," however, are aggregates of large numbers of individual molecules, each in exchange equilibrium with all others in the solution. Accordingly, the aggregates do not in general maintain their integrity upon changes in temperature, concentration, or onset of long-range positional or orientational order. Rather, the self-assembly process is coupled to the system's thermodynamics, and the micelles vary their size and/or shape in response to any change in macroscopic state. Even in the dilute, ideal-solution, limit, for example, small globular ("spherical") aggregates are known to transform themselves into extended, cylinderlike micelles upon increase in concentration.(1) At higher concentrations, where repulsive interactions between micelles become important, the cylinders reorganize into a smaller number of larger

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aggregates, first to maximize the packing entropy(2) and then in response to the alignment arising at the isotropic–nematic (I–N) transition.(3)

In the present paper we consider an even more dramatic manifestation of coupling between micellar self-assembly and interaggregate interactions. Specifically, we treat the situation in which surfactant molecules form small, globular micelles throughout the *entire* concentration range of the isotropic phase; rodlike, extended structures appear *only* upon the onset of nematic order. In "ordinary" colloidal suspensions, of course, this possibility does not arise: the particles must be sufficiently anisotropic in the isotropic phase in order for liquid crystallinity to develop. In surfactant solutions, on the other hand, there are instances where no evidence of micellar anisotropy is seen in the isotropic phase, even as one approaches the long-range ordered hexagonal or lamellar states at high concentrations.(4)

In Section 2 we outline the free energy considerations necessary to describe interacting micelles in their isotropic and nematic phases. We include there the effects of the molecular exchange equilibrium, excluded-volume forces between aggregates, and long-range orientational ordering. Numerical results are presented in Section 3 and discussed in the context of both phenomenological and experimental studies of concentrated micellar solutions.

2. FREE ENERGY CONSIDERATIONS

2.1. Free Energies

Let $\tilde{A}_s$ denote the Helmholtz free energy per amphiphile in an aggregate comprised of s molecules. For present purposes it is sufficient to consider spherocylindrical micelles consisting of a body of length L capped at each end by a hemisphere of diameter D. ($L \to 0$ corresponds to the limit of spherical aggregates.) From earlier work(5) we can write (in units of $k_B T$)

$$\tilde{A}_s = \tilde{\mu}^0_{\text{cyl}} + \frac{\delta}{s} + \frac{1}{s}\left(\ln\frac{\phi_s}{s} - 1 + \sigma_s + \chi_s\right) \tag{1}$$

Here $\delta \equiv m\ (\tilde{\mu}^0_{\text{sph}} - \tilde{\mu}^0_{\text{cyl}})$, where $\tilde{\mu}^0_{\text{cyl}}$ and $\tilde{\mu}^0_{\text{sph}}$ are the standard chemical potentials per molecule in the body and cap, respectively, of an s-aggregate. m is the number of amphiphiles in the end caps and is given by $m = (4\pi/3)$ $(D/2)^3/v$, where v is the volume of each surfactant chain.(1) Note that positive (negative) δ values correspond to a natural preference for the amphiphilic species to pack into cylindrical (spherical) geometry. ϕ_s is the volume fraction of molecules incorporated into s-mers, and

$(1/s)[\ln(\phi_s/s)-1]$ describes the "entropy of mixing" contribution, which favors organization of the system into many aggregates of small size. The fourth term, $(1/s)\sigma_s$, arises from the loss of orientational entropy upon micellar alignment: $\sigma_s \equiv \int d\Omega\, f_s(\Omega) \ln 4\pi f_s(\Omega)$, where $f_s(\Omega)$ is the fraction of s-micelles having orientation Ω. (For an isotropic distribution of particles, where $f_s(\Omega)=1/4\pi$, $\sigma_s=0$.) Finally, χ_s incorporates the effects due to interactions between micelles. For sufficiently dilute solutions, with steric forces between micelles, χ_s can be approximated by the leading term in a virial expansion$^{(6)}$:

$$\chi_s = \frac{1}{2}\sum_r \int d\Omega \int d\Omega'\, v_{sr}(\Omega,\Omega')\, f_s(\Omega)\, f_r(\Omega')\, \frac{\phi_r}{vr}$$

where $v_{sr}(\Omega, \Omega')$ is the pair excluded volume between an s-mer and r-mer of orientation Ω and Ω', respectively.

Consider in more detail now the *intra*micellar energy $\delta \equiv m(\tilde{\mu}^0_{\text{sph}} - \tilde{\mu}^0_{\text{cyl}})$. If $\tilde{\mu}^0_{\text{cyl}} < \tilde{\mu}^0_{\text{sph}}$, a surfactant molecule prefers the environment in the cylindrical body and there is a "push" for the micelles to grow beyond the minimum size m (that of the spherical aggregate). This is the well-studied situation$^{(7)}$ appropriate to surfactants such as cetyltrimethylammonium bromide (CTAB), where long, cylindrical micelles are found$^{(8)}$ to dominate shortly after the critical micelle concentration (CMC) is exceeded. That is, the δ/s term (with δ positive and large compared to kT) overwhelms the $(1/s)[\ln(\phi_s/s)-1]$ dispersion entropy contribution, and minimum-size micelles are not competitive. If $\tilde{\mu}^0_{\text{sph}} < \tilde{\mu}^0_{\text{cyl}}$, on the other hand, the aggregates will tend to retain their spherical shapes until interaction effects become important at much higher concentrations. Negative-δ behavior of this kind is expected in nonionic surfactants such as the large-m C_nEO_m polyoxyethylene ethers; there the $(OCH_2CH_2)_mOH$ head groups require more packing room than the $CH_3(CH_2)_{n-1}$ alkyl chains, and positive-curvature spheres are the strongly preferred micellar geometry.

Before proceeding to treat the alignment and interaction terms in the free energy, it is useful to simplify them by restricting the micellar orientations to lie along any of three mutually perpendicular axes.$^{(9)}$ We also suppress polydispersity and take s to be the single size characterizing the elongated micelles. These approximations have been shown to preserve all qualitative aspects of the liquid crystal phase transition.$^{(3)}$ It follows immediately that

$$\sigma_s \equiv \int d\Omega\, f_s(\Omega) \ln 4\pi f_s(\Omega) \to \sum_{i=1}^{3} X_i \ln 3X_i \tag{2}$$

where X_i is the mole fraction of rods pointing in the ith direction:

$\sum_{i=1}^{3} X_i = 1$. (Again, if $X_1 = X_2 = X_3 = 1/3$, i.e., in the isotropic case, $\sigma = 0$.) Similarly, the second virial term can be written as

$$\chi_s = \frac{\phi}{2} \int d\Omega \int d\Omega' \, \frac{v_{ss}(\Omega, \Omega')}{vs} f_s(\Omega) \, f_s(\Omega') \rightarrow \frac{\phi}{2} \sum_{i,j}^{3} \frac{v_{ss}(i, j)}{vs} X_i X_j \tag{3}$$

$v_{ss}(i, j)$ now refers to the pair excluded volume between an s-mer in the ith direction and one in the jth. Finally, we have

$$\tilde{A}_s = \tilde{\mu}^0_{\text{cyl}} + \frac{\delta}{s} + \frac{1}{s} \left(\ln 3 + \ln \frac{\phi}{s} - 1 + \sum_i X_i \ln X_i + \frac{\phi}{2} \sum_{i,j} \frac{v_{ss}(i, j)}{vs} X_i X_j \right) \tag{4}$$

The above, Onsager, expression, retaining only the linear term in ϕ, is quantitatively valid for sufficiently anisotropic particles.(6, 10) Since we want to treat, at the same time, concentrated phases of *spherical* particles, it is useful to include higher-order terms in ϕ. We do so by expanding the free energy in powers of, not the volume fraction ϕ, but the variable $y \equiv \phi/(1-\phi)$. Truncations of equations of state for several hard-particle geometries, written as summations in powers of y, have been shown to be rapidly convergent.(11) The free energy is transformed into a y expansion by simply recognizing that infinite-order series in ϕ and y must be identical and then by equating the coefficients of like powers in each. In the "Y_2" level of truncation, i.e., keeping only through quadratic terms in y in the pressure,

$$\tilde{A}_s = \tilde{\mu}^0_{\text{cyl}} + \frac{\delta}{s} + \frac{1}{s} \left(\ln 3 + \ln \frac{y}{s} - 1 - y + \sum_i X_i \ln X_i + \frac{y}{2} \sum_{i,j} \frac{v_{ss}(i, j)}{sv} X_i X_j \right) \tag{5}$$

2.2. Isotropic Suspensions

In the isotropic state, the mole fraction of spherocylinders pointing in each of the three allowed directions is 1/3 ($= X_i$); it follows that the $\ln 3 + \sum_i X_i \ln X_i$ terms cancel ($\sigma = 0$). Using the familiar $v_{ss} = 4\pi D^3/3 + 2\pi D^2 L + 2DL^2 \sin \gamma$ (where γ is the angle between the rod axes), we obtain for the excluded-volume term,

$$\frac{y}{2} \sum_{i,j} \frac{v_{ss}(i, j)}{sv} X_i X_j = \frac{8\pi + 12\pi\xi + 8\xi^2}{\pi(2 + 3\xi)} \, y$$

with $\xi \equiv L/D = \frac{2}{3}(s/m - 1)$. Substituting this into Eq. (5) and introducing $\sigma = 0$ yields the free energy per surfactant molecule

$$\tilde{A}^{\mathrm{I}}_s = \tilde{\mu}^0_{\text{cyl}} + \frac{\delta}{s} + \frac{1}{s} \left[\ln \frac{y}{s} - 1 - y + \frac{8\pi + 12\pi\xi + 8\xi^2}{\pi(2 + 3\xi)} \, y \right] \tag{6}$$

in the isotropic phase. Minimization with respect to s gives the optimum micellar size for a given y (or, equivalently, ϕ):

$$\bar{s} = y \exp\left[\delta + \left(3 - \frac{32}{9\pi}\right) y + \frac{32ym}{9\pi\bar{s}}\right] \tag{7}$$

A graphical solution to Eq. (7) indicates directly that there is a unique $\bar{s} > 0$ for any given y, δ pair. Furthermore, analysis of $\tilde{A}_s^{\mathrm{I}}$ shows that this single extremum $\bar{s}$ corresponds to a *minimum* in the free energy: $\tilde{A}_s^{\mathrm{I}}$ increases monotonically with s for $s > \bar{s}$, with

$$\lim_{s \to \infty} \tilde{A}_s^{\mathrm{I}} = \tilde{\mu}_{\mathrm{cyl}}^0 + \frac{16}{9\pi m} y$$

For fixed δ, $\bar{s}$ increases with y; the micellar size grows with concentration (in accord with previous work). With δ free and y fixed, on the other hand, the micelles are seen to get smaller as δ becomes more negative. Indeed, for sufficiently negative δ and small enough y, the solution to Eq. (7) appears at $\bar{s} < m$, in which case we need to set $\bar{s} = m$, since $\tilde{A}_s$ from Eqs. (5) and (6) holds only for $s \geqslant m$, i.e., $s = m$ is the smallest allowed aggregation number.

2.3. Aligned States and the Sphere–Nematic Transition

From the uniaxial symmetry of the nematic, $X_1 = X_2 = x$ and $X_3 = 1 - 2x$ for the mole fractions in Eq. (5), thereby obtaining, with inclusion of the appropriate $v_{ss}(i, j)$,

$$\tilde{A}_s^{\mathrm{N}} = \tilde{\mu}_{\mathrm{cyl}}^0 + \frac{\delta}{s} + \frac{1}{s}\left[\ln\frac{y}{s} - y - 1 + \ln 3 + 2x \ln x + (1 - 2x)\ln(1 - 2x)\right.$$
$$\left. + \frac{8\pi + 12\pi\xi + 48\xi^2 x - 72\xi^2 x^2}{\pi(2 + 3\xi)} y\right] \tag{8}$$

Setting $\partial\tilde{A}_s^{\mathrm{N}}/\partial x = 0$ gives the extremization equation for fixed ξ:

$$(1 - 3x)\, y = \frac{\pi(2 + 3\xi)}{24\xi^2} \ln\frac{1 - 2x}{x} \tag{9}$$

(The case in which ξ is *not* fixed, but rather is allowed to couple with alignment, is treated elsewhere$^{(3)}$; see also the discussion in Section 3 below.) Equation (9) leads to the familiar result that $x = 1/3$ (the isotropic distribution) is a solution for all y, and that at some critical value y_c two new solutions appear, one with x decreasing with increasing y, the other increasing. The first describes the stable thermodynamic situation corresponding to preferential alignment of the rods along a special direction [y_c turns out to be equal to $2.75\pi(2+3\xi)/24\xi^2$].

3. RESULTS AND CONCLUSIONS

Since the quantity $\phi\tilde{A}_s$ is proportional to the system's free energy per unit volume, its ϕ dependence in each of the (isotropic and nematic) phases can be used to locate a first-order transition via the common-tangent construction. For a given choice of δ and m—and ξ for the nematic, we simply determine $\tilde{A}_s^{\mathrm{I}}$ and $\tilde{A}_s^{\mathrm{N}}$ as functions of ϕ by minimizing with respect to size (s) and degree of alignment (x), respectively. Figure 1 shows the results for the corresponding free energy densities in the case of $\delta = -3kT$, $m = 20$, and $\xi = 5$. It is important to note that the optimum size $\bar{s}$ in the isotropic phase begins to exceed the minimum (spherical) value m only for large ϕ; specifically, for this choice of δ, m spherical micelles give way to (isotropically distributed) rods iff $\phi \geqslant 0.64$. But this ("sphere-to-rod") "transformation" is preempted by the I–N transition: as pictured, the isotropic and nematic phases coexist for volume fractions in the range $0.57 < \phi < 0.81$. Accordingly, the transition is seen to take place from a system of *spheres* to one of *aligned rods* (and is strongly first order). We stress that such a transition is possible only when the interacting

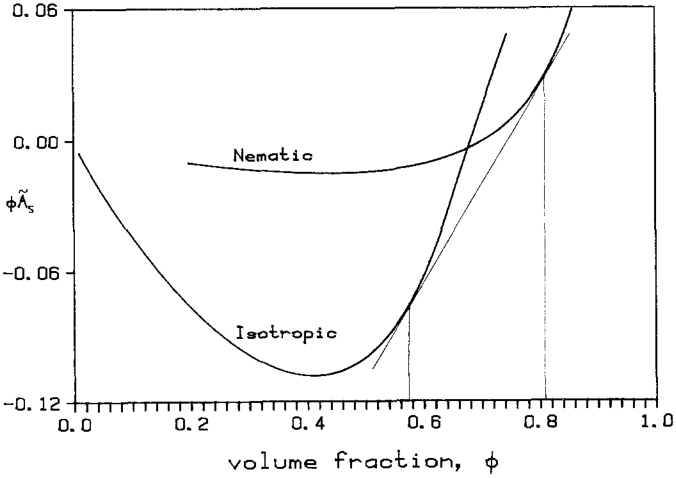

Fig. 1. Plots of $\phi\tilde{A}_s^{\mathrm{I}}$ and $\phi\tilde{A}_s^{\mathrm{N}}$ versus ϕ for $\delta = -3kT$, $m = 20$, $\xi = 5$ (for the nematic). The common-tangent construction shows the coexistence of isotropic and nematic phases for volume fraction $0.57 < \phi < 0.81$; spherical micelles give way to rods in the isotropic phase only for $\phi \geqslant 0.64$.

particles—here micelles—are able to change their size and shape in response to thermodynamic state.

As mentioned in the Introduction and in Section 2.1, there are many surfactant molecules which prefer the stronger curvature of a globular ($\approx$spherical) aggregate to that of more extended structures. Our object in the present work has been to point out how a nematic state arises in such systems at sufficiently high volume fraction. The competing free energy terms which we have featured are the same as those discussed in previous studies(2,3): the $(1/s)[\ln(\phi_s/s)-1]$ mixing entropy favors a large number of small aggregates, the $(1/s)\sigma$ orientational entropy is maximized by an isotropic distribution of particles, and the $(1/s)\chi$ packing entropy prefers (growth and) alignment of the micelles. Note that, although we have fixed for simplicity the nematic rod axial ratio ξ, minimization of $\tilde{A}_s^{\mathrm{N}}$ with respect to (alignment *x and*) size ξ ($\sim s$) would only stabilize further the nematic state. Accordingly, our prediction of a sphere-to-nematic transition would not be qualitatively changed: we conclude that aggregate anisotropy is *not* necessary for the onset of liquid crystallinity in micellar systems.

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