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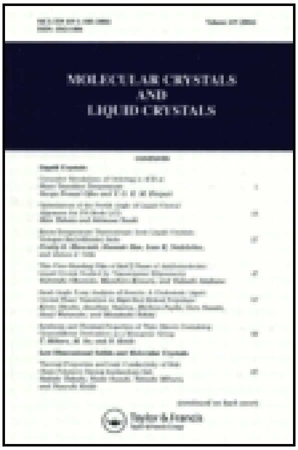

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Theory of Liquid Crystalline Phases in Amphiphilic Systems

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THEORY OF LIQUID CRYSTALLINE PHASES IN AMPHIPHILIC SYSTEMS

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Abstract: A variety of amphiphilic molecules reversibly aggregate to form polydisperse asymmetric particles that spontaneously align at sufficiently high concentrations. Such systems have been modeled using a lattice description of excluded volume effects and a phenomenological description of aggregate assembly. Our earlier calculations restricted to the formation of rod-like aggregates, have now been extended to include the formation of plate-like aggregates. Thus two types of aligned phases are possible: axial, in which the average length of particle edges parallel to the director is greater than perpendicular to the director, and planar, in which the opposite occurs. When rod and plate growth are equally favored the calculated phase diagram displays a sequence of first order transitions from isotropic to axial to planar phases. Additional sequences of phase transitions calculated from this model are reported.

INTRODUCTION

Surfactant molecules in aqueous solution spontaneously and reversibly assemble into micellar aggregates at a characteristic concentration, termed the critical micelle concentration (CMC). As the surfactant concentration is increased above the CMC the micelle population is modified

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from an initial monodisperse distribution of spherical aggregates of a definite minimum aggregation number to a polydisperse distribution of rod-like and/or plate-like aggregates. In more concentrated solutions these asymmetric micelles will align, forming a variety of liquid crystalline phases. The most common of these being the hexagonal, lamellar, and cubic. Nematic phases of both axial and planar symmetry are also reported. This general behavior is highly dependent upon both ionic strength and temperature. It is remarkable that such simple binary amphiphile-water systems display such complex physical behavior and thus these systems have been the subject of extensive experimental and theoretical study.[1-3]

The majority of the theoretical work has been directed towards an understanding of the aggregate assembly phenomena and the micelle size distribution in dilute isotropic systems.[4-7] There has also been theoretical interest in describing the low-water, perfectly ordered phases seen in these systems.[8,9] However there have been very few attempts to theoretically describe the formation of liquid crystalline phases from the polydisperse isotropic phase or the transitions between such aligned phases.[10,11] McMullen *et al*. have studied the isotropic to nematic transition in micellar systems restricted to the formation of rod-like aggregates.[12] They employed a truncated virial expansion and thus were only able to explore a limited range of particle volume fractions. Herzfeld *et al*. have carried out a similar study using a lattice model which can be used to describe the phase behavior of a polydisperse collection of reversibly assembling particles over the complete range of particle

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concentrations.[13]

In this paper we present some preliminary results from our recent theory of phase behavior in reversibly assembling systems when both rod-like and plate-like aggregates may be formed. A more detailed description of this work will be forthcoming.

THE MODEL

We consider a polydisperse system of particles which can reversibly associate into rod-like and plate-like aggregates of arbitrary size. The free energy of such a system can be expressed in terms of interparticle and intraparticle interactions. In the present model we limit the interparticle interactions to hard core steric repulsions, an approximation which should be reasonable for nonionic surfactants and surfactant systems at high ionic strengths. Lattice statistics can be utilized to calculate the excluded volume and thus the configurational free energy of such a population of particles. For this purpose particles are treated as rectangular parallelepipeds constrained to lie in the three mutually orthogonal directions of a cubic lattice: monomers are modeled as cubes of edge length one, minimum aggregates as DxDxD arrays of cubes, rod-like aggregates as $D \times D \times \ell$ ($\ell > D$) arrays of cubes, and plate-like aggregates as $D \times \ell_1 \times \ell_2$ ($\ell_1 > D$, $\ell_2 > D$) arrays of cubes (figure 1b). The complete particle size and orientation distribution is given by c_o, the number concentration of monomers, c_s, the number concentration of the quasi-spherical minimum aggregates, and $c_{i\ell_1\ell_2}$, the

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number concentration of aggregates of edge lengths D, ℓ_1 ($\ell_1 \geq D$) and ℓ_2 ($\ell_2 > D$) in the i, i+1, and i+2 lattice directions respectively, where i=1,2,3 is taken under cyclic permutation.

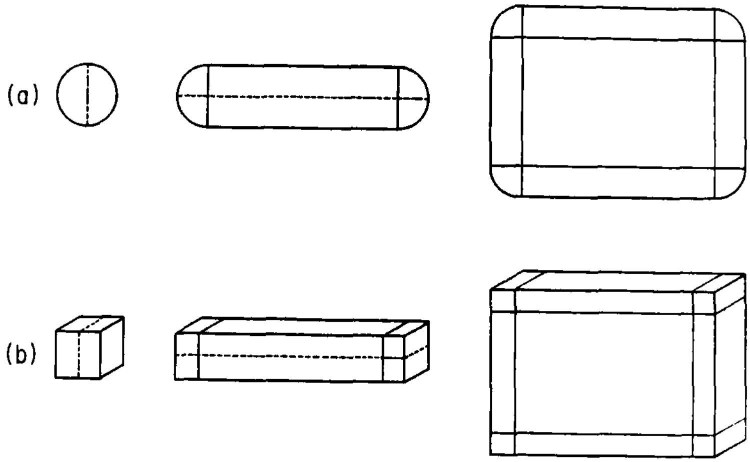

FIGURE 1. Aggregate geometry: (a) idealized particles in the form of spheres, rods and plates; (b) corresponding parallelepipeds for the cubic lattice.

Using the refined lattice of Herzfeld [14] we compute a configurational free energy per unit volume (in units of kT) of

$$f_{config} = c_o[\ln c_o - \xi] + c_s[\ln c_s - \xi] + \sum_{i=1}^{3} \sum_{\ell_1=D}^{\infty} \sum_{\ell_2=D+1}^{\infty} c_{i\ell_1\ell_2}\left[\ln c_{i\ell_1\ell_2} - \xi\right]$$

$$+ \sum_{i=1}^{3} \alpha_i \lambda_i \tag{1}$$

where $\xi = [\, 1 - 3 \ln \epsilon + \ln (1-v_p) \,]$, ϵ is the lattice mesh size, v_p is the volume fraction of solute particles, α_i is the total particle cross sectional area perpendicular to lattice axis i, and λ_i is the total particle edge length parallel to lattice axis i. The first three terms in eq. 1 arise from the entropy of mixing particles on the lattice and the last term accounts for the effects of excluded volume. ϵ is the ratio between edge lengths of the solvent and solute molecules on the refined lattice and thus gives a measure of the intrinsic translational entropy of the individual solute molecules in dilute solution.

A phenomenological free energy of association is used to describe the intraparticle interactions driving aggregate assembly by assigning a separate association energy to each particle geometry. Thus, imagining minimum aggregates as spheres, rod-like aggregates as cylinders with two hemispherical caps, and plate-like aggregates as rectangular plates with four half-cylinder edges and four quarter-sphere corners (figure 1a), three different energy parameters are required: one for spherical segments, one for cylindrical segments and one for plate-like segments. Accordingly, we define the average free energy of monomer addition to form spherical segments as $-\Phi_0 kT$, to form cylindrical segments as $-\Phi_1 kT$, and to form plate-like segments as $-\Phi_2 kT$. This leads to a total free energy of particle association per unit volume (in units of kT) of

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$$f_{assoc} = c_s \Phi_0 D^3 + \sum_{i=1}^{3} \sum_{\ell_1=D}^{\infty} \sum_{\ell_2=D+1}^{\infty} c_{i\ell_1\ell_2} \Big\{ \Phi_0 D^3 + \Phi_1 D^2 \big[(\ell_1-D)+(\ell_2-D)\big] + \Phi_2 D(\ell_1-D)(\ell_2-D) \Big\} \qquad (2)$$

This approach is completely phenomenological, yet it captures the essential results of the more detailed models of micelle assembly and growth.

Combining the above interparticle and intraparticle contributions leads to an expression for the total free energy of the system as a function of the complete particle size and orientation distribution. The actual equilibrium distribution of particles is determined by minimizing this total free energy over the set of all possible distributions. The resulting equilibrium distribution can be expressed in terms of a small number of parameters [15] as follows:

$$c_{i\ell_1\ell_2} = c_s \, P_{i+1}^{(\ell_1-D)} \, P_{i+2}^{(\ell_2-D)} \, Q_i^{(\ell_1-D)(\ell_2-D)} \qquad (3)$$

where P_i is the probability of unidirectional growth in the i-th lattice direction and Q_i is the probability of bidirectional growth in the lattice plane perpendicular to the i-th lattice axis. This full equilibrium distribution is usually best computed using an iterative procedure similar to that previously employed for systems of monodisperse nematogens.[16] However, in certain cases, this iteration is not well behaved and a non-linear minimization routine is used. The double infinite sums in

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(1) and (2) are evaluated using either a direct partial summation or by a double application of the Euler-Maclaurin summation formula.[17] By determining the complete equilibrium particle size and orientation distribution, we are able to compute chemical potentials and thus determine the theoretical phase boundaries for this system.

RESULTS

In figure 2 we present a phase diagram, calculated with the above model, as a function of particle volume fraction and $\Phi_1-\Phi_0$ where D=4, $\Phi_0=24$ and $\Phi_2=\Phi_1$. D=4 corresponds to a minimum aggregation number of $4^3=64$. Φ_0 has been chosen by its relation to the CMC. Specifically, the mole fraction of surfactant at the CMC is ~ $\exp(-\Phi_0) \approx 10^{-11}$, a value of the order of magnitude of those observed experimentally for large surfactants.[1] Again, with large surfactants in mind, we have taken $\epsilon=0.1$.

The general features of this diagram are as follows: (a) In the region $0.10\le(\Phi_1-\Phi_0)\le0.15$ we have only an isotropic phase composed of an approximately equal mixture of small rod-like and plate-like micelles. For example at $\Phi_1-\Phi_0=0.15$, $v_p=0.5$ the number average particle anisotropy is (1 : 1 : 1.3) for rods and (1 : 1.3 : 1.3) for plates. (b) In the region $0.15\le(\Phi_1-\Phi_0)\le0.30$ there is a first order transition between an isotropic micellar phase at low volume fraction and an aligned planar phase at higher volume fractions. The coexistence region becomes markedly broader with increasing Φ_1. The average aggregate anisotropies at $\Phi_1-\Phi_0=0.25$ are (1 : 2.5 : 2.5) on the

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isotropic side of the I-P transition ($v_p=0.58$) and (1 : 3.3 : 3.3) for particles in the preferred orientation on the planar side of the I-P transition ($v_p=0.68$). (c) In the region $0.30 \leq (\Phi_1-\Phi_0) \leq 0.40$ we have a first order transition from an isotropic micellar phase to an aligned axial phase, via a very narrow two phase region, followed by a second first order transition, through a much broader mixed phase region, into an aligned planar phase. For $\Phi_1-\Phi_0=0.35$ the average particle anisotropies are (1 : 4.9 : 6.0) at the narrow I-A transition ($v_p=0.18$), (1 : 3.2 : 17.3) for particles in the preferred orientation on the axial side of the A-P transition ($v_p=0.32$), and (1 : 10.5 : 10.5) for particles in the preferred orientation on the planar side of the A-P transition ($v_p=0.50$).

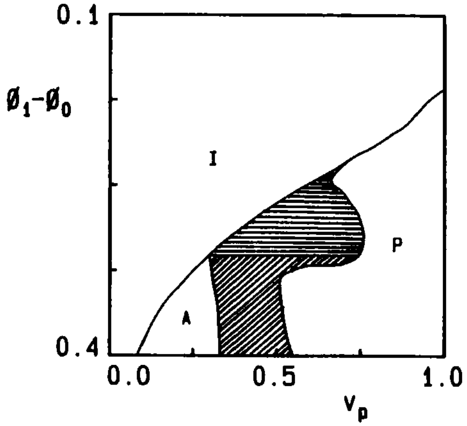

FIGURE 2. Calculated phase diagram for $\Phi_0=24$, $\Phi_2=\Phi_1$, $D=4$ and $\epsilon=0.1$. Phases are identified as I for isotropic micellar, A for axial anisotropic (average particle edge length parallel to the director greater than perpendicular), and P for planar anisotropic (average particle edge length perpendicular to the director greater than parallel).

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Our identification of the aligned phases in this diagram simply as axial and planar is due to the fact that we can only determine the orientation dependence of the particle size distribution. No account is taken of possible positional order and thus we can not distinguish between the highly ordered hexagonal and lamellar phases and their less ordered nematic counterparts. The average particle sizes reported can not be used to make such a distinction either since the hexagonal and lamellar phases are not necessarily composed of "infinite" cylinders and bilayers, but may indeed consist of ordered arrays of finite aggregates.[18] We should also note that the aggregate dimensions given above are averages over a polydisperse size distribution (as seen from eq. 3).

While the results in figure 2 are for the single case of $\Phi_1=\Phi_2$, by varying the difference between these two parameters we find a wide variety of phase behaviors. For example when $\Phi_2<\Phi_1$ (rod growth favored over plates) we see the following sequences of first order transitions: $I \to A' \to A$, $I \to P \to A$, and $I \to A$. Whereas for $\Phi_2>\Phi_1$ (plate growth favored over rods) we see the sequences: $I \to A' \to P' \to P$, $I \to P' \to P$, and $I \to P$. We also note that when Φ_0 is small and $\Phi_1=\Phi_2$ we see a direct transition from monomer to a planar phase.

DISCUSSION

The calculated phase diagram in figure 2 is qualitatively representative of the phase behavior of many binary surfactant-water systems. In figure 3 we reproduce a schematic temperature-concentration phase diagram typical of such systems.[3,19,20] In the schematic diagram we note temperature regions displaying the following behaviors: (a) isotropic solution of micelles, (b) first order isotropic to lamellar (planar) transition, (c) first order isotropic to hexagonal (axial) transition followed by a cubic phase followed by a first order transition into a lamellar (planar) phase. Of course the similarities between figures 2 and 3 rest on the assumption that our phenomenological parameters Φ_0 and Φ_2-Φ_1 represent physical quantities which are relatively temperature insensitive. But in terms of concentration behavior our model does give a correct progression of phases with increasing surfactant volume fraction (noting that a cubic phase can not exist in our model).

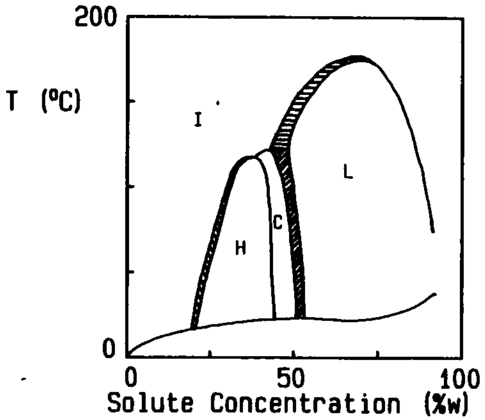

FIGURE 3. Schematic temperature-concentration phase diagram of a typical binary surfactant-water system. Phases are denoted as I for isotropic micellar, H for hexagonal, C for cubic, and L for lamellar.

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The values we have used for our aggregation parameters (Φ_0, Φ_1 and Φ_2) accord well with theoretically derived quantities. In particular, detailed models of micelle formation yield values corresponding to $\Phi_0 \sim 10\text{-}20$.[4-7] These same theories also give values of $(\Phi_1-\Phi_0) < \sim 1$, in agreement with the range we have considered. In addition, for $\Phi_1, \Phi_2 < \Phi_0$ we predict that no particle growth occurs beyond the minimum aggregate, in further agreement with the above theories.

CONCLUSIONS

We have presented a model describing reversibly assembling systems that contain polydisperse aggregates which can undergo alignment transitions to form liquid crystalline phases. Using a specific set of reasonable phenomenological parameters we have calculated a phase diagram qualitatively representative of many binary surfactant-water systems. More generally, this model gives rise to a wide variety of phase behaviors which we are currently exploring.

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