

# Phase Behavior of Mixtures of Wormlike Micelles and Mixtures of Wormlike Micelles with Small Colloidal Particles

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Some surfactants form, in solution, long wormlike micelles. We study, theoretically, a binary solution of such surfactants which form micelles separately. For a wide range of intermicelle interactions, the surfactants are found to demix into two phases, one rich in each of the surfactants. We also study mixtures of wormlike micelles with small colloidal particles and again find that for a wide range of interactions there is demixing. The wormlike micelles behave in an analogous way to polymers; however, the length of micelles differs between phases which are surfactant rich and surfactant poor.

## 1. Introduction

A number of surfactant molecules form, in solution, micelles which are not of the familiar spherical shape but are cylindrical.<sup>1,2</sup> Whereas spherical micelles are restricted to have a volume roughly equal to the cube of the length of a surfactant molecule,<sup>3,4</sup> cylindrical micelles can grow almost indefinitely. Although their radius is restricted to the length of a surfactant molecule, there is no such restriction on their length. Cylindrical micelles have been studied which have a diameter of  $\approx 40$  Å and a persistence length of  $\approx 200$  Å and can grow to be micrometers in length.<sup>2</sup> Here, we will examine binary mixtures of surfactants in which both surfactants form cylindrical micelles. We show that if the different surfactants form micelles independently, or approximately independently, then it is probable that the surfactants will demix. Under the assumption that a binary solution of surfactants form the long wormlike micelles independently, we have two species of micelles. As with polymer mixtures,<sup>5</sup> only very slightly unfavorable interactions between the two micelles, i.e., the two surfactants, force demixing: phase separation into two phases, each of which is rich in one surfactant and poor in the other. However, unlike polymer mixtures, the micelles are of different lengths in the coexisting phases. The micelles formed by a surfactant are longer in the phase which is rich in this surfactant than in the phase which contains little of the surfactant.

As far as we are aware there have been no experimental studies of mixtures of surfactants which form wormlike micelles. However, there is experimental evidence for mixed surfactant solutions in which the two surfactants form spherical micelles independently.<sup>6,7</sup> The prediction of demixing of surfactant mixtures appears to be new; we hope it will stimulate experimental study of surfactant mixtures. It should be noted that in many of the surfactant mixtures studied the different surfactant molecules form only one type of micelle.<sup>8,9</sup> The behavior of such mixed micelles is outside the scope of the current work.

In addition, we study mixtures of wormlike micelles with small colloidal particles.<sup>10</sup> By small, we mean possessing a diameter no more than an order of magnitude or so larger than the diameter of the wormlike micelles. These mixtures show demixing behavior for wide ranges of the ratio of diameter of the particle to the micellar diameter. However, as only one component is growing to form very long objects, the demixing occurs at higher densities.

In the following section we derive a simple mean-field free energy for a mixture of wormlike micelles; it is a straightforward generalization to a mixture of a widely studied single-component free energy.<sup>2,11,12</sup> We derive expressions for the stability of micellar mixtures and present the results of some illustrative calculations. The phase boundaries we find are similar to those found for binary mixtures of polymers.<sup>5,13</sup> In the third section we consider mixtures of wormlike micelles and small colloidal particles, again using a simple mean-field free energy. Stability limits are found, and illustrative results are plotted.

## 2. Binary Mixtures of Wormlike Micelles

We consider a binary mixture of substances, each of which self-assembles into long, wormlike aggregates. Each of the two substances assembles independently; the aggregates are composed of molecules of one substance or the other, never a mixture of the two. An example would be a binary surfactant solution well above its critical micelle concentration. In order that the micelles of one component contain few molecules of the other component, the two surfactants should be very different; for example, one component could have a longer carbon chain or be fluorinated.<sup>6,7</sup> If the two components are similar they form mixed micelles; see ref 9 and references therein. Single-component analogues of our mixture have been studied extensively.<sup>2,3</sup>

The two components are labeled a and b; above both their critical micelle concentrations we assume that all the surfactant molecules are part of aggregates. These aggregates are of all lengths, from the smallest possible, approximately spherical, micelles to very long micelles whose length may be thousands of times larger than their diameter. We consider linear aggregation in which the diameter of the micelle is constant, independent of the length, so that the number of surfactant molecules and the volume of a micelle are proportional to its length. Micelles of component  $i = a, b$  have diameter  $D_i$ . Then, we specify the length of a micelle by an index  $s$ , where  $s$  is proportional to the length of a micelle and equal to 1 for a micelle which has a length equal to  $D_a$  or  $D_b$ , for components a or b, respectively. The number density of micelles of component  $i$  and length  $s$  is  $\rho_i(s)/v_i$ , for  $v_i = (\pi/4)D_i^3$ , the volume of a micelle with  $s = 1$ . Thus,  $\rho_i(s)$  is a reduced, dimensionless, number density. The number of surfactant molecules in a micelle is equal to  $s$  times the number in smallest possible, approximately spherical, micelles. Therefore, at fixed total concentration of surfactant  $i$

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$$\int_1^\infty \rho_i(s) s \, ds = \phi_i, \quad i = a, b \quad (1)$$

where  $\phi_i$  is the volume fraction of surfactant  $i$ . Setting the lower limit of the integration in eq 1 to 1 corresponds to restricting the micelles to be at least  $D_i$  long. The distribution of surfactant between micelles of different sizes,  $\rho_i(s)$ , varies as a function of temperature, salinity, etc., and this distribution will be found to be quite broad. The surfactant forms micelles with a large range of lengths. This is very different from a monodisperse polymer, where  $\rho_i(s)$  is a  $\delta$  function at a value of  $s$  fixed when the polymer is synthesised.

In deriving the free energy of the mixture we start from an assumed form of the free energy of an isolated micelle. We assume that this free energy has three parts: the translational free energy of a molecule of an ideal gas, a part which is extensive, i.e., proportional to  $s$ , and a part  $E_a$  (or  $E_b$ ), which is independent of  $s$ . The extensive part is irrelevant as it has no effect on the self-assembly<sup>2,3</sup> and is neglected.  $E_a$  and  $E_b$ , the so-called end-cap energies, are the free energy changes (over  $k_B T$ ) when a micelle of component  $a$  or  $b$ , respectively, breaks into two.  $T$  is the temperature, and  $k_B$  is Boltzmann's constant.  $E_a$  and  $E_b$  will be large and positive, representing a large free energy cost of forming two new micelle ends. The first and third parts of the free energy compete; many small micelles mean a high translational entropy, but a high free energy cost due to the large number of ends and, conversely, a few large micelles mean low translational entropy but few ends. This competition determines the functions  $\rho_a$  and  $\rho_b$  at equilibrium.

Treating micelles of different lengths as different components, we have for the free energy  $A$

$$\frac{\beta A v_a}{V} = \int_1^\infty \rho_a(s) [\ln \rho_a(s) - 1 + E_a] \, ds + v_r^{-1} \int_1^\infty \rho_b(s) [\ln \rho_b(s) - 1 + E_b] \, ds + \frac{1}{2} \chi_a \phi_a^2 + \frac{1}{2} \chi_b \phi_b^2 + \chi_{ab} \phi_a \phi_b \quad (2)$$

where  $V$  is the volume and  $v_r = v_b/v_a$ . The last three terms of eq 2 arise from interactions between micelles. The micelles are in usually aqueous solution, and so the  $\chi$ 's are effective interaction parameters (and not conventional Flory–Huggins interaction parameters). For example, the second virial coefficient for the interaction between two micelles of component  $a$ , of lengths  $s$  and  $s'$ , equals  $(1/2)\chi_a s s' v_a$ . Micelles are rather bulky; typically they have diameters  $\approx 40$  Å, and so there is a large excluded volume contribution to the  $\chi$  parameters. We assume that this contribution dominates and that the micelles interact like polymers in a good solvent.<sup>14,15</sup> The excluded volume interaction between micelles is then that between semiflexible rods.<sup>16,17</sup> Then, a micelle of component  $i$  and length  $s$  excludes a micelle of component  $i'$  and length  $s'$  from a volume  $(\pi/2) s s' D_i D_{i'} (D_i + D_{i'})$ . The  $\chi$  parameters may now be written in terms of the ratio  $D_b/D_a$

$$\chi_a = 2, \quad \chi_b = 2 \left( \frac{D_a}{D_b} \right)^3, \quad \chi_{ab} = \left( \frac{D_a}{D_b} + 1 \right) \frac{D_a}{D_b}, \quad v_r = \frac{\chi_a}{\chi_b} \quad (3)$$

There are three points that should be borne in mind when considering the range of validity of the free energy (eq 2). Firstly, this form for the intermicellar interaction free energy assumes that the interaction between two micelles is extensive, i.e., is proportional to the lengths of the micelles. This, together with our form of the free energy of a single micelle, defines our model of a micelle. The assumption is quite reasonable for flexible,<sup>5,14</sup> semiflexible,<sup>16</sup> and rodlike<sup>11</sup> micelles. Micelles

of the first two types, which will include all sufficiently long micelles,<sup>11,16</sup> will form coils.<sup>14</sup> As the interaction is extensive, it is proportional to the total density of surfactant and does not influence/is not influenced by the distribution of surfactant among micelles of different sizes. Secondly, and less importantly, the interaction part of the free energy is quadratic in density. Again, this is reasonable both for coils and rods providing the density is not too high.<sup>12,16</sup> Thirdly, the demixing will typically take place in the semidilute regime.<sup>14</sup> In this regime mean-field free energies require corrections due to scaling.<sup>15</sup> These are not too serious, however.<sup>2,18</sup>

The distribution of surfactant between micelles of different lengths is determined by minimizing the free energy (eq 2) with respect to variations in  $\rho_a$  and  $\rho_b$ , subject to the constraints in eq 1.<sup>2,11</sup> Then,

$$\rho_i(s) = \exp \left( -E_i - \frac{s}{(\phi_i \exp(E_i))^{1/2}} \right) \quad (4)$$

if only the leading order term is kept.<sup>2,11</sup> The terms dropped are of order  $(\phi_i \exp(E_i))^{-1}$  smaller than those retained; they are very small if the average micelle length is large. The average length of micelles of component  $i$  is  $\bar{s}_i = (\phi_i \exp(E_i))^{1/2}$ .<sup>3,11</sup>

Substituting eq 4 back into eq 2 and integrating

$$\frac{\beta A v_a}{V} = -2\phi_a^{1/2} e^{-E_a/2} - 2v_r^{-1} \phi_b^{1/2} e^{-E_b/2} + \frac{1}{2} \chi_a \phi_a^2 + \frac{1}{2} \chi_b \phi_b^2 + \chi_{ab} \phi_a \phi_b \quad (5)$$

As the two components form micelles independently, this is a straightforward generalization of the one-component result.<sup>2</sup>

**2.1. Demixing.** Wormlike micelles, also referred to as living polymers, behave in a similar way to conventional polymers in most but not all respects.<sup>1,2</sup> Due to the large size of polymer molecules, even weakly unfavorable interactions cause polymer mixtures to separate into two nearly pure phases.<sup>5,13</sup> We shall see that equilibrium polymers behave in a similar but not identical way, and for essentially the same reason—they are large objects.

Firstly, we find the limit of stability, the spinodal, of the mixture. This is given by a determinant  $\mathbf{D}$  whose elements are the second derivatives of the free energy (eq 5), with respect to the densities  $\phi_a$  and  $v_r^{-1} \phi_b$ .<sup>19,20</sup> The factor of  $v_r^{-1}$  is required as the two volume fractions  $\phi_a$  and  $\phi_b$  are made dimensionless using different characteristic volumes. When calculating the determinant, all dimensionless densities must contain the same characteristic volume:  $v_a$  in the case of  $\phi_a$  and  $v_r^{-1} \phi_b$ . So,  $\mathbf{D}$  is given by

$$\mathbf{D} = \begin{vmatrix} \frac{1}{2} \phi_a^{-3/2} e^{-E_a/2} + \chi_a & v_r \chi_{ab} \\ v_r \chi_{ab} & \frac{1}{2} v_r \phi_b^{-3/2} e^{-E_b/2} + v_r^2 \chi_b \end{vmatrix} \geq 0 \quad (6)$$

$$\frac{1}{4} (\phi_a \phi_b)^{-3/2} e^{-(E_a+E_b)/2} + \frac{1}{2} v_r \chi_b \phi_a^{-3/2} e^{-E_a/2} + \frac{1}{2} \chi_a \phi_b^{-3/2} e^{-E_b/2} + v_r \chi_a \chi_b - v_r \chi_{ab}^2 \geq 0 \quad (7)$$

The equality is the equation of the spinodal; the inequality is the condition for local stability.

The authors are not aware of any experimental data for wormlike-micelle mixtures, and so we consider just a few simple cases. If we impose symmetry between the two components we can obtain simple analytical expressions for the critical density and chain lengths. So, we will start by considering a symmetrical mixture. Of course, it is not possible to produce

a symmetrical mixture, but the trends in the critical density etc. will be the same for symmetrical and nonsymmetrical mixtures. We will then give the results of some calculations for nonsymmetrical mixtures, demonstrating the effect of changing the two components independently.

As an example of a mixture in which the two micelles do not differ too much in either diameter or end-cap energy, we will consider a symmetrical mixture. Then,  $v_r = 1$ ,  $E_a = E_b = E$ , and  $\chi_a = \chi_b = \chi$ . Now, eq 7 simplifies considerably. The critical point for demixing is on the spinodal curve, and therefore the critical volume fractions satisfy eq 7. For the symmetrical mixture, the two volume fractions at the critical point,  $\phi_a^*$  and  $\phi_b^*$ , are equal. Combining this condition with eq 7 yields

$$\phi_a^* = \phi_b^* = \frac{\exp(-E/3)}{(2(\chi_{ab} - \chi))^{2/3}} \quad (8)$$

Note the  $\exp(-E/3)$  dependence of  $\phi_a^*$ ;  $E$  can be as large as  $\sim 25$ ,<sup>2</sup> in which case  $\phi_a^*$  will be very low. However, the  $\bar{s}_i$ 's vary as  $(\phi_i \exp(E_i))^{1/2}$ , and so at the critical point  $\bar{s}_i \sim \exp(E/3)$  and so is very large if  $E$  is large. Conversely, increasing the difference  $\chi_{ab} - \chi$  decreases  $\phi_a^*$  and so reduces the length of the micelles at the critical point. As may be seen from eq 8, coexistence does not depend on  $\chi_{ab}$  and  $\chi$  separately, only on their difference.

The symmetry of our mixture makes finding coexistence between the a-rich and b-rich phases straightforward.<sup>21</sup> The equality of pressure is automatically satisfied, and the chemical potential of each component must be the same at coexistence. The chemical potentials are just the derivatives of the free energy density (eq 5) with respect to the  $\phi_i$ 's. Equating the two chemical potentials

$$-\phi_a^{-1/2} e^{-E/2} + \chi \phi_a + \chi_{ab} \phi_b = -\phi_b^{-1/2} e^{-E/2} + \chi \phi_b + \chi_{ab} \phi_a \quad (9)$$

which is the equation for the coexistence curve in the  $\phi_a$ - $\phi_b$  plane.

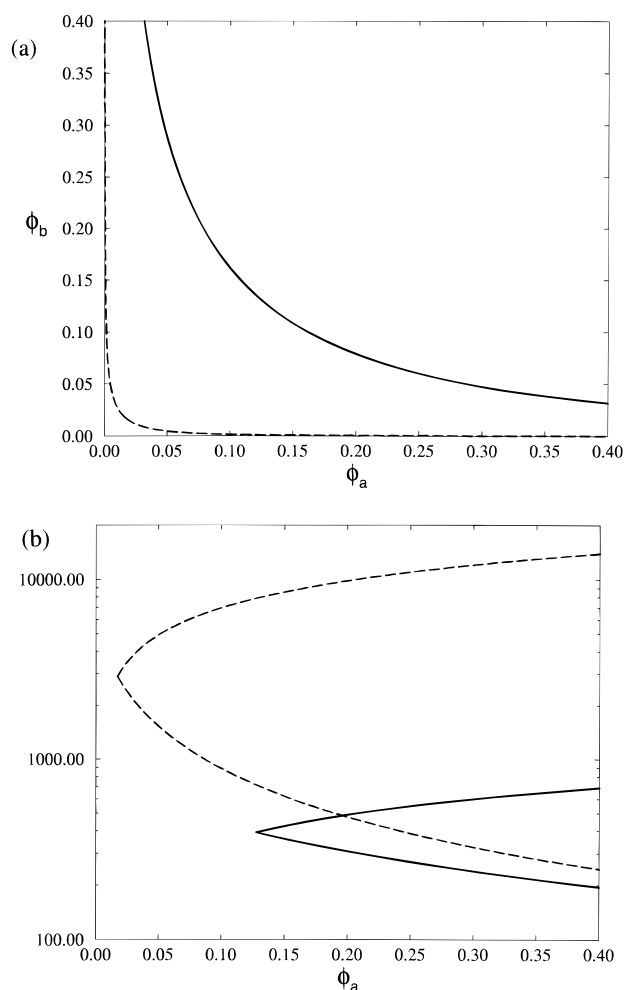
For definiteness, we consider the coexisting a-rich phase. The volume fractions  $\phi_a$  and  $\phi_b$  are equal at the critical point, and then  $\phi_a$  increases and  $\phi_b$  decreases at a rate which depends on  $\chi_{ab} - \chi$  and, very sensitively, on  $E$ . Indeed, if  $E$  is too small the demixing will be at such a high density that it will be preempted by a transition to an ordered phase, such as a nematic of columnar.<sup>11,12</sup> Living polymers differ from conventional polymers in that the size of the polymers changes in response to changes in temperature, density, etc.. Thus, the micelles of surfactant a will be longer, on average, in the a-rich phase than in b-rich phase, see Figure 1b. In Figure 1a, we see that the extent of the two-phase region is very sensitive to the value of  $E$ . For  $E = 20$  the coexisting phases are almost pure, and each phase consists of, on average, very long micelles of the majority component and a smaller number of much shorter micelles of the minority component. From eq 9 we can examine the asymptotic values of  $\phi_b$  and hence  $\bar{s}_a$  and  $\bar{s}_b$  in the a-rich phase far from the critical point. We take the limit of  $\phi_a \gg \phi_b$  in eq 9; this then simplifies to

$$\phi_b = (\chi_{ab} - \chi)^{-2} \phi_a^{-2} e^{-E} \quad (10)$$

Then, we have for  $\bar{s}_a$  and  $\bar{s}_b$ , in the a-rich phase at coexistence

$$\bar{s}_a = e^{E/2} \phi_a^{1/2}, \quad \bar{s}_b = \frac{1}{(\chi_{ab} - \chi) \phi_a} \quad (11)$$

and clearly  $\bar{s}_a \gg \bar{s}_b$ . Note that  $\bar{s}_b$  does not depend on  $E$ .



**Figure 1.** Densities and average micelle lengths of coexisting mixtures of micelles: (a) two coexistence curves in the  $\phi_a$ - $\phi_b$  plane; (b) the average micelle lengths  $\bar{s}_a$  and  $\bar{s}_b$  in the coexisting a-rich phase. The solid curves are for  $E = 14$  and the dashed for  $E = 20$ ; in both cases  $\chi_{ab} - \chi = 0.01$ .

We have considered a symmetric mixture, and by doing so we have gained an understanding of the behavior of a binary mixture of surfactants which have similar end-cap energies. We now turn to consider more general mixtures. The critical point of a symmetrical mixture is given by eq 8. No such simple equation is available if there is no symmetry between the components. The critical point may, however, be found by solving two simultaneous equations: the first is eq 7; the second is formed from the determinant 6 by replacing the elements of one row with elements which are the derivatives of the determinant  $\mathbf{D}$  6 with respect to the  $\phi$ 's<sup>20</sup>

$$\mathbf{D}' = \begin{vmatrix} \partial \mathbf{D} / \partial \phi_a & \partial \mathbf{D} / \partial (v_r^{-1} \phi_b) \\ v_r \chi_{ab} & 1/2 v_r \phi_b^{-3/2} e^{-E_b/2} + v_r^2 \chi_b \end{vmatrix} = 0 \quad (12)$$

$$-(\phi_a^{-5/2} \phi_b^{-3/2} e^{-(E_a - E_b)/2} + 2 v_r \chi_b \phi_a^{-5/2} e^{-E_a/2}) (1/2 \phi_b^{-3/2} e^{-E_b/2} + v_r \chi_b) + (\phi_a^{-3/2} \phi_b^{-5/2} e^{-(E_a + E_b)/2} + 2 \chi_a \phi_b^{-3/2} e^{-E_b/2}) v_r \chi_{ab} = 0 \quad (13)$$

Results are tabulated in Table 1. As  $E_a$  increases  $\phi_a^*$  decreases rapidly, and as it does so  $\phi_b^*$  also decreases but less rapidly; correspondingly, as  $\phi_b^*$  shrinks at constant  $E_b$ , the value of  $\bar{s}_b$  at the critical point decreases. Increasing  $E_b$  at constant  $E_a$  has

**TABLE 1: Surfactant Volume Fractions and Average Micelle Lengths at the Demixing Critical Point for a Range of Values of the End-Cap Energies**

		$D_b/D_a = 1.25$			
$E_a$	$E_b$	$\phi_a^*$	$\phi_b^*$	$\bar{s}_a$	$\bar{s}_b$
14	14	$1.03 \times 10^{-1}$	$1.18 \times 10^{-1}$	$3.53 \times 10^2$	$3.77 \times 10^2$
14	20	$8.03 \times 10^{-2}$	$2.78 \times 10^{-2}$	$3.11 \times 10^2$	$3.67 \times 10^3$
20	14	$2.26 \times 10^{-2}$	$8.55 \times 10^{-2}$	$3.31 \times 10^3$	$3.21 \times 10^2$
20	20	$1.40 \times 10^{-2}$	$1.60 \times 10^{-2}$	$2.61 \times 10^3$	$2.79 \times 10^3$

an equivalent effect. The two components differ in that the volume fractions of *B* tend to be larger; see the results in Table 1 for  $E_a = E_b$ . This is due to the larger diameter of micelles of component *b*.

The shifting of the critical density is reflected in the coexistence curve. If we start from the  $E_a = E_b = 14$  symmetric mixture coexistence curve seen in Figure 1a and increase  $E_a$ , then the coexistence curve will be pulled to the left and  $\phi_a$  at coexistence will decrease. For fixed values of  $E_a$  and  $E_b$  the critical point density and coexistence curve are determined by the ratio  $D_b/D_a$ . Increasing  $D_b/D_a$  (assuming  $D_b > D_a$ ) increases the extent of the immiscibility, i.e., reduces the critical density; of course, for  $D_b = D_a$  the surfactants are completely miscible. This is true if the micelle–micelle interactions are excluded volume interactions. For modest ratios  $D_b/D_a$ ,  $\chi_{ab}$  is only just greater than the geometric mean of  $\chi_a$  and  $\chi_b$ ; for  $D_b/D_a = 1.25$ ,  $\chi_{ab} - (\chi_a\chi_b)^{1/2} \approx 0.009$ . Note that for  $D_b \neq D_a$  then necessarily  $\chi_{ab} > (\chi_a\chi_b)^{1/2}$ , although as  $D_b$  approaches  $D_a$  all three  $\chi$  parameters are equal. Below, just above eq 17, we show that  $\chi_{ab} > (\chi_a\chi_b)^{1/2}$  is a necessary precondition for phase separation. Indeed, it is a sufficient condition in the limit of  $E_a$  and  $E_b$  tending to infinity. For infinite end-cap energies the micelles are infinitely long and the translational entropy terms, the first two terms in eq 5 and the first three in eq 7, may be neglected. Thus a weakly favorable attractive interaction between micelles of components *a* and *b* will produce complete miscibility whereas an unfavorable interaction will greatly increase the extent of the immiscibility.

### 3. Mixtures of Wormlike Micelles with Small Particles

We consider a binary mixture of a wormlike-micelles-forming surfactant (component *a*) and small, approximately spherical, particles (component *b*). A related system has been studied theoretically by Madden and Herzfeld.<sup>22</sup> These small particles could be small solid particles<sup>10</sup> or spherical micelles.<sup>23</sup> Our theory will assume that the interaction between a wormlike micelle and a particle is extensive in the length of the micelle, i.e., is proportional to the length of the micelle.<sup>24</sup> Thus, it will not be valid for all sizes of the particle. If the small particles have diameters  $D_b$  of order 1 or  $10D_a$  then our theory will be valid as long as  $\bar{s}_a \gg 1$ , which we are already assuming. However, if the micelles become very long, then the micelle–particle interaction is extensive even if the particle is much larger than this.

If a particle is so small that it interacts with only a small fraction of a micelle at a time, then the micelle–particle interaction is extensive.<sup>25–27</sup> However, if the particle is comparable in size to the radius of gyration of a coiled micelle<sup>25,26,28</sup> or the length of a rodlike micelle, then it simultaneously interacts with the whole micelle, and the micelle–particle interaction is not extensive.<sup>29–31</sup> So, the particles of the second component must be much smaller than the micelle’s radius of gyration.

The free energy of our mixture is

$$\frac{\beta A v_a}{V} = -2\phi_a^{1/2} e^{-E_a/2} + v_r^{-1} \phi_b [\ln \phi_a - 1] + \frac{1}{2} \chi_a \phi_a^2 + \frac{1}{2} \chi_b \phi_b^2 + \chi_{ab} \phi_a \phi_b \quad (14)$$

which is closely analogous to that for our mixture of wormlike micelles (eq 5). Because the *ab* interaction is extensive, the growth of the micelles of component *a* is unaffected by the presence of the small particles and  $\rho_a$  is given by eq 4. In eq 14,  $v_r = v_b/v_a$  where  $v_a$  is defined as in section 2 and  $v_b = (\pi/6)D_b^3$  is the volume of a particle. The volume fraction  $\phi_b$  is the number density of particles times  $v_b$ , and  $\phi_a$  is defined as in section 2. If all three interactions are excluded volume interactions, we can write the  $\chi$  parameters in terms of the diameter of the micelle  $D_a$  and the diameter of the particle  $D_b$

$$\chi_a = 2, \quad \chi_b = 12 \left( \frac{D_a}{D_b} \right)^3, \quad \chi_{ab} = \frac{3}{2} \left( \frac{D_a}{D_b} + 1 \right)^2 \left( \frac{D_a}{D_b} \right),$$

$$v_r = 4 \left( \frac{\chi_a}{\chi_b} \right) \quad (15)$$

As before, the excess part of the free energy contains only second virial coefficient terms.<sup>16</sup> This is more serious here than for binary mixtures of wormlike micelles as the densities we will encounter are higher. Our predictions should, however, remain qualitatively accurate.<sup>12,16</sup>

**3.1. Demixing.** As before, we require the equation of the spinodal; this is

$$\frac{1}{2} \phi_a^{-3/2} \phi_b^{-1} e^{-E_a/2} + \frac{1}{2} v_r \chi_b \phi_a^{-3/2} e^{-E_a/2} + \chi_a \phi_b^{-1} + v_r \chi_a \chi_b - v_r \chi_{ab}^2 = 0 \quad (16)$$

If we compare eqs 7 and 16 we see that the major difference is the lack of a factor of  $\exp(-E_b/2)$  in the third term of eq 16. This implies that the third term in eq 16 will tend to be much larger than the corresponding term in eq 7. In eq 7, as  $E_a$  and  $E_b$  increase, all but the last two terms become very small. The condition for stability then becomes

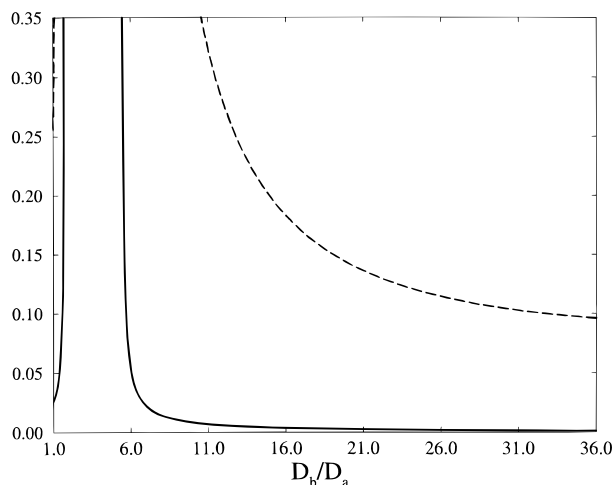
$$\chi_a \chi_b - \chi_{ab}^2 > 0 \quad (17)$$

In contrast, taking the high  $E_a$  limit in eq 16 yields

$$\chi_a \phi_b^{-1} + v_r \chi_a \chi_b - v_r \chi_{ab}^2 > 0 \quad (18)$$

if  $\phi_a$  is not too small. Essentially, any value of  $\chi_{ab}$  above the geometric mean of  $\chi_a$  and  $\chi_b$  causes a mixture of two long wormlike micelles to demix. However,  $\chi_{ab}$  has to be above the geometric mean by an amount given by eq 18 for the wormlike micelle plus small particle mixture to demix. These two situations are analogous to polymer–polymer and polymer–solvent demixing.<sup>5</sup> So, if the unlike interactions are unfavorable, a binary mixture of wormlike micelles will demix at very low volume fractions of both components, for  $E_a$  and  $E_b$  large.

These conclusions are subject to the reservation that a transition to an ordered phase does not intervene. Wormlike micelles can form a nematic phase<sup>11</sup> and even phases with translational ordering.<sup>12</sup> If the condition 17 is only just satisfied and the end-cap energies are not very large, then an isotropic–nematic transition may intervene, preempting isotropic–isotropic coexistence. Thus, for finite  $E_a$  and  $E_b$ , the left-hand sides of eqs 17 and 18 must be greater than zero by some margin in order to observe isotropic–isotropic coexistence.



**Figure 2.** Critical volume fractions  $\phi_a^*$  and  $\phi_b^*$  for a mixture of wormlike micelles and small particles, as a function of  $D_b/D_a$ . The end-cap energy of the micelles  $E_a = 18$ . The solid curve is  $\phi_a^*$ , and the dashed curve is  $\phi_b^*$ .

Rewriting eq 18 in terms of the  $D_i$  we obtain an expression for  $\phi_b$  on the spinodal in the limit of large  $E_a$  and not too small  $\phi_a$

$$\phi_b = \left( \frac{3}{4} \left( \frac{D_b}{D_a} \right) \left( \frac{D_a}{D_b} + 1 \right)^4 - 8 \right)^{-1} \quad (19)$$

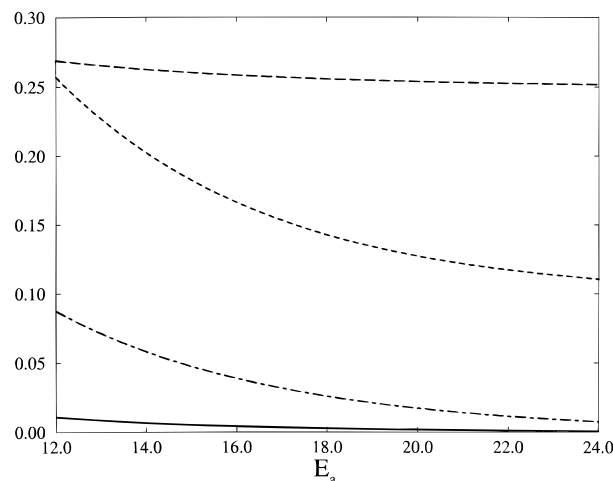
When the ratio  $D_b/D_a$  is large,  $\phi_b$  decreases linearly with  $D_b/D_a$ . However, the right-hand side of eq 19 diverges at  $D_b/D_a \approx 1.75$  and  $5.42$  and is negative between these two limits. Between  $D_b/D_a \approx 1.75$  and  $5.42$ , the micelle–particle excluded volume is smaller than the geometric mean of the micelle–micelle and particle–particle excluded volumes and so there is no driving force for demixing at the level of the second virial coefficient. Thus, the mixture will be completely miscible for  $D_b/D_a$  between  $1.75$  and  $5.42$ . This may be seen in Figure 2, where  $\phi_a$  and  $\phi_b$  at the critical point are plotted as a function of  $D_b/D_a$ . Finding the critical point requires eq 16 and ref 20

$$-\frac{3}{4}\phi_a^{-5/2}e^{-E_a/2}(\phi_b^{-1} + v_i\chi_b)^2 + \phi_b^{-2}v_i\chi_{ab}(\frac{1}{2}\phi_a^{-3/2}e^{-E_a/2} + \chi_a) = 0 \quad (20)$$

which is just eq 12 but for the micelle–particle mixture. The second virial coefficient approximation is not even qualitatively correct for mixtures of rods and spheres in the limit that the diameter of the spheres is much less than that of the rods. Equation 19 predicts, incorrectly, that  $\phi_b$  on the spinodal tends to 0 as  $D_b/D_a$  tends to 0. Thus, we have only shown, in Figure 2, results for  $D_b/D_a \geq 1$ .

In Figure 3 we plot the  $\phi_a^*$  and  $\phi_b^*$  as a function of  $E_a$ . As expected the critical volume fraction decreases as  $E_a$  increases. We can also see that for  $D_b/D_a = 1$ , the critical point is in the regime in which eq 19 is a reasonable approximation for all values of  $E_a$  shown. For  $D_b/D_a = 20$  and large values of  $E_a$ , the critical point is again in this regime. Equation 19 yields  $\phi_b^* \approx 0.098$  for  $D_b/D_a = 20$  and  $\phi_b^* = 0.25$  for  $D_b/D_a = 1$ .

The excluded volumes of eq 15 are general for mixtures of spheres and long rods. Therefore, at the level of the second virial coefficient hard rods and spheres demix providing  $D_b/D_a$  is not in the range  $1.75$ – $5.42$ . However, as  $D_b/D_a$  approaches  $1.75$  or  $5.42$  the critical volume fraction increases sharply, to the extent that it is far too high for the second virial coefficient approximation to be accurate. This approximation is only reasonable if  $D_b/D_a$  is not too small and the volume fraction is



**Figure 3.** Critical volume fractions  $\phi_a^*$  and  $\phi_b^*$  for a mixture of wormlike micelles and small particles, as a function of the end-cap energy of one component. The solid and dot-dashed curves are  $\phi_a^*$  (the micelles), and the long- and short-dashed curves are  $\phi_b^*$  (the particles);  $D_b/D_a = 1$  for the dot-dashed and long-dashed curves, and  $D_b/D_a = 20$  for the solid and short-dashed curves.

not too high. So, we are led to conclude that sphere plus long rod mixtures demix if  $D_b/D_a$  is greater than approximately 10 or is near 1 and also that mixtures with  $D_b/D_a$  in the range  $1.75$ – $5.42$  do not demix at low densities. The prediction of demixing for  $D_b/D_a \sim 1$  is a little suspect as it lies between two regions within which we know the second virial coefficient approximation is inadequate. If  $D_b/D_a$  is not near 1 or greater than 10 we are unable to describe the behavior of the mixture with our simple theory. Calculations incorporating the higher virial coefficients are required.

#### 4. Conclusion

To summarize, a binary solution of surfactants which form separate micelles will demix if the interaction between them is even slightly unfavorable. The large end-cap energy induces rapid growth of the wormlike micelles with increasing surfactant concentration. As the micelle grows, its interactions with other micelles grow linearly but its translational entropy remains  $1 - \ln \rho(s)$ ; the interactions then dominate the translational entropy, and even marginally unfavorable interactions induce demixing. By unfavorable interactions we mean, essentially, interactions such that  $\chi_{ab} > (\chi_a\chi_b)^{1/2}$ ; see eq 17. Although the demixing is a straightforward consequence of the micelle–micelle interactions, the growth of the micelles greatly magnifies the effect of these interactions. The solutions of wormlike micelles and small colloidal particles behave analogously, with the obvious difference that only one of the components grows to form the long micelles. This difference is reflected in the higher critical volume fractions found.

Our mixtures of micelle-forming surfactants show very little miscibility if the end-cap energies are large; only a small difference in diameters is enough to induce demixing. This is just as in mixtures of high molecular weight polymers.<sup>5</sup> Both mixtures demix so readily because they are composed of very large and strongly interacting objects: molecules in the case of polymers and molecular aggregates in the case of the micelles. However, if we examine the coexisting phases we see that polymer and micellar mixtures differ. Far from the demixing critical point, we find very long micelles of species a in the a-rich phase coexisting with much shorter micelles of type a in the b-rich phase (the same is, of course, true for species b). In a mixture of monodisperse polymers, the density of polymer

molecules of species b in the a-rich phase will be much lower than the density of b-type micelles in the a-rich phase of a demixed micellar mixture but they will, of course, have the same length as in the b-rich phase. Also, as the end-cap energies are sensitive functions of the salinity (for charged surfactants), the size of the micelles and thus how immiscible they are may be controlled in a way that is not possible for polymer mixtures.

It is perhaps useful to comment on the sensitivity of our results to the concentration of surfactant molecules of one component in micelles of the other. Of course, in a mixed solution of surfactants no micelle will be completely pure. The qualitative features of the phase behavior we have found, in particular the demixing, are relatively robust to 'impure' micelles; only if the difference in stability between nearly pure<sup>7</sup> and mixed micelles<sup>9</sup> is small would the demixing disappear. However, in phases in which the volume fraction of one component is much higher than that of the other, a large fraction of the minority component could be incorporated into micelles of the majority component. Therefore, in relation to experiment, our predictions concerning the minority component in coexisting phases far from the critical point are probably not realistic. This applies to Figure 1b, particularly to  $\bar{s}_b$  and to the expression for  $\bar{s}_b$  in eq 11. Of course, if the two surfactant species form only one<sup>8,9</sup> (mixed) species of micelle, then our results do not apply.

Finally, we remark that the linear aggregation we have studied here is quite common. Simple hydrogen-bonding substances such as hydrogen fluoride, carboxylic acids, etc. associate to form chains of molecules.<sup>19</sup> This undoubtedly contributes to the immiscibility of many of these substances with non-hydrogen-bonding substances. This is analogous to the mixtures of micelles with small particles studied above; the free energy (eq 14) is a crude but reasonable phenomenological free energy for a binary mixture in which the molecules of one species hydrogen bond to each other forming long chains. There is an extensive literature treating such mixtures<sup>32</sup> using theoretical approaches closely related to that taken here.<sup>33–36</sup>

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