

Mixed Micelles in a Bidisperse Solution of Diblock Copolymers

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ABSTRACT: This paper discusses theoretically the formation of micelles in a bidisperse solution of diblock copolymers. The two populations of copolymer chains are of identical chemical nature but have otherwise arbitrary different block asymmetries. We find that these asymmetries, or correspondingly the relative ratios of curvature of the diblocks, determine the micellization scenario and the type of aggregates coexisting in solution. If the asymmetries between the sizes of the blocks of the two copolymers are not too large, the short copolymers are incorporated continuously in the large copolymer micelles and only mixed micelles are stable. If the asymmetries are larger, the mixed micelles always contain a finite number of short copolymer chains; mixed micelles and large copolymer micelles can then coexist.

I. Introduction

Diblock copolymers often form micelles in a selective solvent.^{1–5} The assembly of these macromolecules is very similar to the micellization of low molecular weight surfactants in water or oil solutions:⁶ below the critical micellar concentration (the cmc), only isolated chains are observed, while above this concentration almost all the chains belong to micelles. Single chains in solution adopt a tadpole morphology, with a collapsed headblock and a swollen tail. The collapsed heads are the driving force for micellization: they greatly reduce the number of monomers exposed to the poor solvent by sharing a common space with other collapsed blocks in the core of the micelle. The onset of micellization requires a large enough concentration to overcome the entropic effects that favor dispersion. For strongly selective solvents and large molecular weights of the block in a poor solvent, the critical micellar concentrations can be very low, and, in practice, micelles are observed at all concentrations. However, by reducing the solvent selectivity or the size of the collapsed block or by adding a second solvent which platicizes the insoluble blocks, one can bring the critical micellar concentrations in the accessible experimental range. Of experimental interest are also the sizes and aggregation numbers of the micelles for which a number of theoretical predictions have been made.^{4,5,7} In the case where the molecules are very asymmetric, the number of molecules in the micelle p is predicted to increase almost linearly with the number of monomers N_A in the tadpole head and to decrease weakly with the number of monomers N_B in the tadpole tail ($p \approx N_A^{4/5}/(\log N_B)^{6/5}$). This is generally observed in experiments and has even been quantitatively checked for a number of cases.⁸

The size, aggregation number, critical micellar concentration, and other quantities which characterize a given micellar system can, in principle, be tuned by carefully tailoring the architecture and chemical nature of the macromolecules. In many experimental situations, this tuning is achieved by simply mixing molecules at different types. The mixing process is, however, not only a way to finely control the parameters of the system but may, in some cases, be necessary to

introduce a new, specific property: fluorescence, detergency, etc.

The formation of mixed micelles of diblock copolymers from a bidisperse solution has been previously addressed by Shim *et al.*,⁹ who considered the case where the copolymers have soluble blocks of the same chemical nature but different lengths and insoluble blocks of the same length but a different chemical nature. By varying the relevant parameters of the system (chain length, interaction between the chains in the core), these authors showed that it is possible to change the critical micellar concentration of the mixed micelles. They further showed that, depending on the concentration ratios of the two species in the solution, the mixed micelles can either form directly upon increasing the total concentration or be assembled in a two-stage process where micelles of one of the species are first created, and then polymers of the other species are progressively incorporated in the already formed micelles.

In this paper we present an extension of the study of ref 9 to the case where the soluble and the insoluble blocks of the two species have the same chemical nature but different chain lengths. More precisely, we consider A–B and C–D diblock copolymers, A being chemically identical to C and B chemically identical to D, but where all the chain lengths are different. By considering such mixtures, we hope not only to address on a more general basis the formation of mixed micelles but also to gain some insight into the behavior of mixtures of simple surfactants and diblock copolymers in the limit where the molecular weight of one of the copolymers is much smaller than the other one. Recent experimental results¹⁰ seem to show in certain conditions a bimodal distribution of the micellar sizes in mixtures of simple surfactants and triblock copolymers for which we give a qualitative explanation. Our study also provides a basis to understand polymers with a more complex architecture, such as polysoaps or multiblock copolymers.

The paper is organized as follows. In the next section we review the thermodynamics of the micellization of monodisperse solutions of diblock copolymers. In section III we present a model for the mixed micelles and analyze two limiting cases: the case where both coronas are much larger than the core sizes and the case where one of the coronas is much larger than the core size but the corona of the other species is much smaller than the core size. In the last section we summarize our

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main results and discuss experiments for which our approach is relevant.

II. Micellization in a Monodisperse Copolymer Solution

II.1. General Considerations. In this section we review the thermodynamics of micellization, which can first be described at a general, model-independent level, by recognizing that for large macromolecules aggregation sets in at low concentrations and that the aggregation numbers are large. Ignoring the interactions between micelles, it is then possible to write the free-energy density of the system as

$$F = c_1[\log(c_1/e) + F_1] + \sum_{p=2}^{\infty} c_p[\log(c_p/e) + F_p] \quad (1)$$

where F_p and c_p are respectively the free energy and concentration (number per unit volume) of micelles with p molecules. The free energies are measured in units where $k_B T = 1$. For clarity the energy has been split into the contributions of single chains $p = 1$ and of aggregates $p \geq 2$. The volume fraction of micelles with p molecules can be found by minimizing the free-energy density (1) with respect to c_p , under the constraint of conservation of the total chain concentration ϕ

$$c_1 + \sum_{p=2}^{\infty} p c_p = \phi \quad (2)$$

One finds

$$c_1 = \exp\{-F_1 + \mu\}; \quad c_p = \exp\{-F_p + \mu p\} \quad (3)$$

where μ is the chemical potential associated with the conservation of chain number. Equation 2 can then be rewritten as

$$1 + \sum_{p=2}^{\infty} p \exp\{-\Omega_p\} = \exp\{F_1 + \log \phi - \mu\} \quad (4)$$

with the grand potential Ω_p defined as $\Omega_p = F_p - F_1 - \mu(p - 1)$. The typical variation of the grand potential of a spherical micelle is sketched in Figure 1. At low concentrations Ω is everywhere larger than unity. This implies that the distribution c_p is strongly peaked around $p = 1$, and only single chains are present in the solution. The chemical potential can be written in this limit as

$$\mu = F_1 + \log \phi \quad (5)$$

When the chain volume fraction ϕ is increased, the chemical potential increases and a minimum appears in Ω_p at an aggregation number $p = \bar{p}$ larger than unity. Correspondingly, the distribution c_p develops a maximum around \bar{p} , indicating the presence of a finite concentration of micelles of aggregation number close to \bar{p} . In the following we show that, to a good approximation, the aggregation number and the critical micellar concentration can be determined from the two conditions:

$$\Omega_p = \partial \Omega_p / \partial p = 0 \quad (6)$$

Since the distribution is strongly peaked around \bar{p} , we can calculate the sum over the aggregation number in

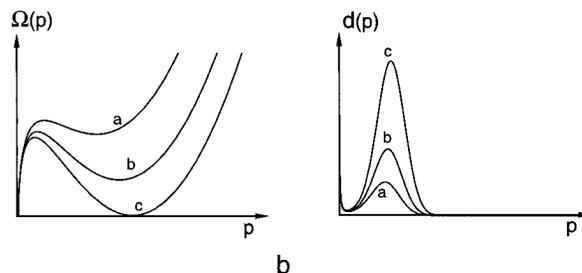
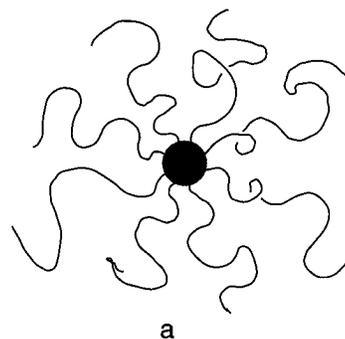


Figure 1. (a) Schematic representation of a diblock copolymer micelle in a selective solvent. The solvent does not penetrate the micelle core. (b) Free energy $\Omega(p)$ and micelle size distribution $d(p)$ as a function of the aggregation number p . The lines a , b , and c correspond to increasing chemical potentials. The line c corresponds to the critical micellar concentration.

the conservation equation (2) using a steepest descent approximation and then solve for the two concentrations c_1 and $c_{\bar{p}}$. By defining the critical micellar concentration ϕ_{cmc} as

$$\phi_{\text{cmc}} = (\bar{p}\Delta)^{1/(1-\bar{p})} \exp\left\{-\frac{\bar{p}F_1 - F_{\bar{p}}}{\bar{p} - 1}\right\} \quad (7)$$

with $\Delta^2 = 2\pi/(\partial^2 F_p/\partial p^2|_{p=\bar{p}})$, the concentrations of unimers and micelles are determined from

$$\frac{c_1}{\phi_{\text{cmc}}} + \left[\frac{c_1}{\phi_{\text{cmc}}}\right]^{\bar{p}} = \frac{\phi}{\phi_{\text{cmc}}} \quad (8)$$

Well below the cmc almost no aggregate is formed and all the chains are isolated. Above the cmc almost all the chains belong to micelles:

$$\begin{cases} \phi \ll \phi_{\text{cmc}} & c_1 \approx \phi; & c_{\bar{p}}\Delta \approx \frac{\phi_{\text{cmc}}}{\bar{p}} \left[\frac{\phi}{\phi_{\text{cmc}}}\right]^{\bar{p}} \\ \phi \gg \phi_{\text{cmc}} & c_1 \approx \phi_{\text{cmc}} \left[\frac{\phi}{\phi_{\text{cmc}}}\right]^{1/\bar{p}}; & c_{\bar{p}}\Delta \approx \phi/\bar{p} \end{cases} \quad (9)$$

Note that, due to the finite width in the micelle size distribution c_p , the concentration of micelles with aggregation number close to \bar{p} is $c_{\bar{p}}\Delta$ rather than $c_{\bar{p}}$, the value of the distribution at the peak. From eqs 9 and 3 we can now calculate the chemical potential below and above the cmc:

$$\begin{cases} \phi \ll \phi_{\text{cmc}} & \mu = F_1 + \log \phi \\ \phi \gg \phi_{\text{cmc}} & \mu = F_1 + \frac{\bar{p}-1}{\bar{p}} \log \phi_{\text{cmc}} + \frac{1}{\bar{p}} \log \phi \end{cases} \quad (10)$$

The chemical potential at the cmc is given by $\bar{\mu} = F_1 + \log \phi_{\text{cmc}}$ and coincides with the chemical potential at the cmc obtained from eq 6, up to a small correction of order $\sim (\log \Delta \bar{p})/\bar{p}$. Above the cmc, the chemical potential (and

thus the aggregation number) varies slowly with the concentration and can for practical purposes be considered as constant: $\mu(\phi \geq \phi_{\text{cmc}}) = \mu(\phi_{\text{cmc}})$.

II.2. Models for the Micellar Assembly. The actual calculation of the chemical potential and aggregation numbers from this description requires a model for the micellar assembly, that allows the determination of the free energies F_p . Hereafter, we study asymmetric diblock copolymer chains, in the asymmetry range $N_A \ll N_B^{3/2}$ (N_A and N_B being respectively the polymerization indices of the collapsed and swollen blocks) where spherical micelles are formed.¹¹ Throughout the paper, we assume that the insoluble block of the copolymer is in so poor a solvent that it has a tendency to form molten regions where neither the solvent nor the other block penetrates. Micelle formation in a monodisperse copolymer solution has been studied in this limit in refs 4 and 5; we summarize here the essential results. Figure 1 depicts a representation of the structure of the micelle. The incompressibility of the core leads to a simple relationship between the number p of chains in the micelle and the core radius: $R = (3pN_A/(4\pi))^{1/3}b$, where b is the size of one monomer. For simplicity we choose in the following a unit length where $b = 1$ and we assume that monomers A and B have equal sizes. The chains in the outer corona form a starlike object, a configuration first described by Daoud and Cotton.¹² In the corona the chains follow locally the statistics of a semidilute polymer solution. They can thus be described by a local, position-dependent correlation length. Pictorially one associates a blob with the correlation length and describes the external shell as a succession of blobs of increasing size. At a given distance r from the center of the micelle (with $r > R$), there are p blobs occupying a surface $4\pi r^2$. This gives a blob size which varies as $\xi(r) \approx rp^{-1/2}$. The external radius of the micelle $R + h$ can then be obtained by the conservation constraint $pN_A = 4\pi \int_R^{R+h} c(r) r^2 dr$, where the monomer concentration in the corona decays as $c(r) \approx p^{2/3}r^{-4/3}$. When the corona is much larger than the core, this gives $R + h \approx h = N_B^{3/5}p^{1/5}$. The chains in the corona are thus extended by a factor $p^{1/5}$ with respect to their free radius in the solution. The free energy associated with these stretched configurations can be calculated by integrating the local free-energy density of an equivalent semidilute solution $f_0 = 4\pi k_B T \int_R^{R+h} \phi^{9/4} r^2 dr \approx k_B T p^{3/2} \log[1 + h/R]$. The other important contribution to the free energy of the micelle is the interfacial energy between the core and the solvent: $f_s = 4\pi R^2 \gamma = \gamma c N_A^{2/3} p^{2/3}$, where γ is the relevant interfacial tension and c is the numerical constant $c = (36\pi)^{1/3}$. The potential Ω_p can now be written as

$$\Omega_p = f_0 + f_s - \mu p \quad (11)$$

We show below that the contribution $-F_1 + \mu$ is negligible.

In the case where the corona is much larger than the core, the conditions (6) lead to the following values for the aggregation number and the chemical potential

$$\bar{p} = \left(\frac{2c\gamma}{3A}\right)^{6/5} N_A^{4/5}; \quad \bar{\mu} = \frac{5}{2} A \left(\frac{2c\gamma}{3A}\right)^{3/5} N_A^{2/5} \quad (12)$$

where $A = \log(1 + h/R)$ is in a first approximation taken as a constant, evaluated at $p = \bar{p}$.

When the corona is much smaller than the core radius, the swollen tails form a planar grafted layer also

known as a brush, with grafting density $\sigma = p/(4\pi R^2)$. The osmotic contribution to the free energy can then be expanded in powers of h_0/R , leading to $f_c = p^{3/2}(h_0/R)(1 - \xi_1 h_0/R + \xi_2 (h_0/R)^2)$. The numerical constants are given by $\xi_1 = 5/6$ and $\xi_2 = 25/26$, and the brush thickness for a flat layer is $h_0 \sim N_B \sigma^{1/3}$. Notice that the expansion coefficients for the mean-field version of a brush in a curved geometry have been previously calculated in refs 13 and 14. Our expansion, extracted from a scaling form for the free energy, gives obviously different coefficients but does preserve the correct scaling forms for a brush in good solvent.

In this limit the aggregation number and chemical potential, calculated from (6) are given by

$$\bar{p} = \left(\frac{6c}{5\tilde{c}} \frac{\gamma}{N_B}\right)^{18/11} N_A^2; \quad \bar{\mu} = 11 \left(\frac{c\gamma}{5}\right)^{5/11} \left(\frac{\tilde{c}}{6} N_B\right)^{6/11} \quad (13)$$

where \tilde{c} is another numerical factor; $\tilde{c} = 24^{2/3}/c^{4/3}$.

The leading neglected contribution to the potential would introduce a relative correction of the order of $1/\bar{p}^{2/3}$, negligible for typical aggregation numbers. We have also neglected the stretching contribution from the hydrophobic blocks in the core. In the asymmetry range where the corona is much larger than the core, this contribution, on the order of R^2/N_A , is negligible. For $N_A^{11/18} \ll N_B \ll N_A^{11/15}$, the size of the corona is smaller than the size of the core. However, in this range, it can also be checked that the elastic contribution is still much smaller than the energy of the brush.

III. Mixed Micelles

In this section we consider mixtures of diblock copolymers with different polymerization indices. For the sake of simplicity, we study the formation of mixed micelles in these mixtures in two different limits. First, we consider diblock copolymers with large tails, in the limit where the sizes of both tails are much larger than the size of the core of the micelle. We refer to this case as a copolymer mixture. Then we study mixtures of diblock copolymers where the tails of one of the species are much larger than the size of the core, the tail of the other species being smaller than the size of the core. Since we hope to mimic in this limit the behavior of mixtures of macromolecular diblocks and small surfactant molecules, we refer to this case as a copolymer-surfactant mixture.

In both cases the formalism for studying mixed micellization is a straightforward extension of that presented in the previous section. There are now two species in the solution, and we need, in general, to describe the content of a micelle by the number of short and long chains, respectively p_s and p_l . The aggregation number of the micelle is thus $p = p_s + p_l$, and the relative composition of short chains in the micelle is $x_m = p_s/(p_s + p_l)$. There are also two chemical potentials associated with the conservation of ϕ_s and ϕ_l , the total concentrations of chains of the two species. Within the same approximations as above, we can write the free energy

$$\Omega_p = f_0(p_s, p_l) + f_s(p_s, p_l) - \mu_s p_s - \mu_l p_l \quad (14)$$

and derive the aggregation numbers and the chemical potentials at the critical micellar concentration from the conditions

$$\Omega_p = \frac{\partial \Omega_p}{\partial p_s} = \frac{\partial \Omega_p}{\partial p_l} = 0 \quad (15)$$

Note that there are four unknown quantities to be determined (two aggregation numbers and two chemical potentials) from three conditions. This implies that in a bidisperse copolymer solution the micellization process is described by a line $\mu_s = \mu_s(\mu_l)$ in the $[\mu_l, \mu_s]$ phase diagram (or, equivalently, by a line $\phi_s = \phi_s(\phi_l)$ in the $[\phi_l, \phi_s]$ phase diagram).

III.1. Copolymer Mixtures. When the soluble blocks of both chains are larger than the core size of the micelle, one can easily describe the structure of the corona by a concentric two-shell picture, with radii $R + h_s$ and $R + h_l$ as shown on Figure 2a. The largest tails extend from the core to the micelle radius $R + h_l$, whereas the smallest tail extends from the core to the radius of the first shell $R + h_s$. The osmotic contribution of the corona is written as

$$f_0 = (A - B)p_l^{3/2} + B(p_l + p_s)^{3/2} \quad (16)$$

with $A = \log(1 + h_l/R)$ and $B = \log(1 + h_s/R)$. The sizes of the coronas are given as above by $h_l = N_{Bl}^{3/5} p_l^{1/5}$ and $h_s = N_{Bs}^{3/5} (p_l + p_s)^{1/5}$ where N_{Bl} and N_{Bs} are the degrees of polymerization of the soluble blocks of the large and small copolymers, respectively. As before we consider in a first approximation A and B as constants, calculated from the aggregation numbers at the cmc.

The interfacial tension contribution reads

$$f_s = c\gamma(N_l p_l + N_s p_s)^{2/3} \quad (17)$$

N_s and N_l being respectively the number of monomers of the collapsed blocks of the chains with the shortest and longest tails. For each of the copolymer species we define the reference aggregation numbers p_s° and p_l° and the reference chemical potentials μ_s° and μ_l° as the values obtained at the cmc for the pure solutions. They are obtained from eq 12 with A and N_l for the copolymers with the large tails and B and N_s for copolymers with the small tails.

The precise determination of the critical concentration for the formation of mixed micelles and of the aggregation numbers can only be achieved by a numerical solution of eq 15. However, a global picture can be drawn from the study of a few particular paths in the chemical potential (or concentration) phase diagram. Of special interest are the situation where micelles of the large copolymers are already formed in the solution, and one increases progressively the concentration of the small copolymers, or the situation where a few large copolymers are added to a solution of small copolymers.

III.1.a. Incorporation of Small Copolymers in a Large Copolymer Micelle. We first assume that micelles of the large copolymers have already formed in the solution. The chemical potential of the large copolymers is μ_l° . We now add a small amount of short copolymers and study the conditions under which these molecules can form mixed micelles, by assembling into the micelles of the large diblock copolymer. If the small copolymer concentration is very low, no mixed micelles are formed; the critical micellar concentration is that of a pure large copolymer solution. Above a critical concentration of short chains or equivalently above a critical value μ_s^* of the chemical potential of the short chains, the short copolymers are incorporated into the micelles.

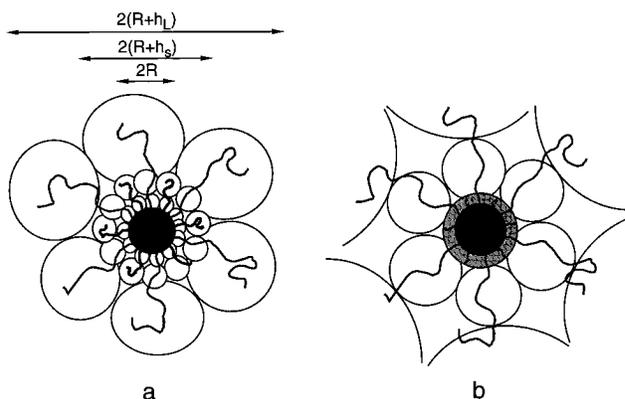


Figure 2. Schematic representation of a bidisperse micelle in (a) copolymer mixtures ($h_l \gg h_s \gg R$) and (b) copolymer surfactant mixtures ($h_l \gg R \gg h_s$).

Just above the threshold, $\mu_s = \mu_s^* + \delta\mu_s$, we look for the cmc by expanding the equilibrium equations 15, $p_l = p_l^\circ + \delta p_l$, $p_s = \delta p_s$, and $\mu_l = \mu_l^\circ + \delta\mu_l$. The zeroth-order term in the expansion gives the critical value of the chemical potential for mixed micelle formation

$$\mu_s^* = \left(\frac{2}{3}c\gamma\right)^{3/5} (AN_l)^{2/5} \left(\frac{3}{2}b + n\right) = \frac{2}{5} \left(\frac{3}{2}b + n\right) \frac{1}{(bn)^{2/5}} \mu_s^\circ \quad (18)$$

We have introduced here two parameters that characterize the asymmetry in molecular weights of the two copolymers: $n = N_s/N_l$ is the ratio of the molecular weights of the insoluble parts and $b = B/A$ is related to the difference in the heights of the corona and characterizes the asymmetry in the soluble blocks of the two copolymers. In the derivation of the free energy, we have implicitly assumed that $b < 1$; note also that, in principle, b varies with the aggregation numbers of the short and large blocks; this variation is very smooth, and b is considered here as a constant.

The critical chemical potential for mixed micelle formation is meaningful only if it is smaller than the chemical potential at the cmc of the pure short polymers. If it is larger than this cmc value, the short copolymer forms micelles before being incorporated into the large copolymer micelles. The chemical potential of the short copolymer then saturates at the cmc value, and no mixed micelles can form. This condition for the existence of mixed micelles reads

$$\frac{3}{2}b + n < \frac{5}{2}(bn)^{2/5} \quad (19)$$

In particular, this criterion predicts that, for a given value of one of the asymmetry parameters n or b , mixed micelles do not form if the other asymmetry parameter is too small. This reflects the fact that mixed micelles are not formed by surfactants with very different spontaneous curvature.

Just above the threshold, we obtain the cmc and the aggregation numbers at the cmc by a first-order expansion of the equilibrium equations (15)

$$\begin{aligned} \delta p_s &= \frac{50}{3D} \frac{p_l^\circ}{\mu_l^\circ} \delta\mu_s \\ \delta p_l &= -\frac{10(9b - 4n)}{3D} \frac{p_l^\circ}{\mu_l^\circ} \delta\mu_s \quad \delta\mu_l = 0 \end{aligned} \quad (20)$$

where D is a function of the asymmetry parameters n

and b

$$D = 5b - 9b^2 + 8bn - 4n^2 \quad (21)$$

Whenever D is positive, the aggregation number of the small copolymer p_s increases with the chemical potential or equivalently with the concentration and small copolymers are introduced progressively inside the mixed micelles. The aggregation number p_l decreases as small chains are incorporated when $n < 9/4b$ and increases otherwise. Interestingly, the total aggregation number increases when $n > 9/4b - 5/4$ and decreases otherwise. This leads to three distinct regions in the $[b, n]$ diagram, separated by the two lines $n = 9/4b - 5/4$ and $n = 9/4b$. The change in the chemical potential of the large chains at the critical concentration for mixed-micelle formation $\delta\mu_l$ vanishes at linear order in $\delta\mu_s$. If the phase diagram of the mixture is represented in a plane $[\mu_l, \mu_s]$, the mixed micellization line has thus a vertical tangent at the point $[\mu_l^0, \mu_s^*]$. The chemical potential of the large copolymer on the micellization line then decreases as μ_s increases.

In this case where $D > 0$, the typical variation of the grand-canonical free energy Ω with the aggregation number p_s is shown in Figure 3a. The different curves correspond to different chemical potentials around the critical potential where mixed micelles are formed. The grand-canonical free energy has a single minimum at a finite value of p_s . The value of p_s at the minimum increases when the chemical potential of the short copolymer increases. As for a monodisperse solution, the micelle size distribution given by eq 3 is proportional to $\exp(-\Omega)$. It only has one strong peak corresponding to mixed micelles.

In the opposite case where $D < 0$, the perturbation calculation for the cmc leads to a negative value of δp_s when the chemical potential of the short chains is increased above the critical value μ_s^* . This is clearly unphysical. The linearization around the pure large copolymer micelle is not possible in this case, and the short copolymers are incorporated discontinuously in the mixed micelles which always contain a finite number of short copolymer chains. Mixed micelles are formed in this case at a chemical potential smaller than μ_s^* .

We have numerically determined the solution of the equilibrium equations for the cmc in the case where $D < 0$. We start from a solution of large copolymers at the cmc and increase the chemical potential of the short chains. At a small value of the chemical potential μ_s , the short copolymers do not aggregate and the solution contains only micelles of the long copolymer chains. At a critical value $\mu_s^c < \mu_s^*$ mixed micelles are formed which contain a finite number of short chains. If the chemical potential μ_l of the large chains is smaller than the cmc value, mixed micelles are stable for a chemical potential of the short chains, μ_s , larger than μ_s^c . At the concentration where mixed micelles are first formed, the grand-canonical free energy shows a potential barrier between a state corresponding to mixed micelles and a state corresponding to pure large copolymer micelles ($p_s = 0$)—see Figure 3b. The micelle size distribution shows thus two peaks, one for mixed micelles and a second for pure large copolymer micelles. We show on Figure 4a an example of the micelle size distribution calculated numerically. The potential barrier is high in this case, and one expects a sharp distribution of micelle sizes around the peaks. At larger values of μ_s along the mixed-micelle stability line, the peak corresponding to the

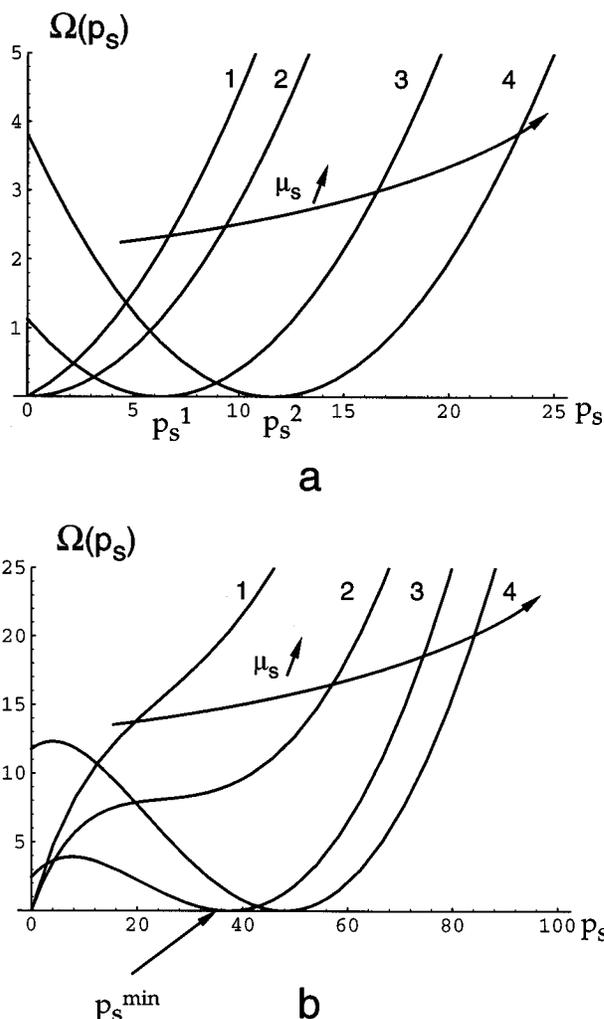


Figure 3. Variation of the grand-canonical free energy with the aggregation number p_s of the short chains in the mixed micelles for increasing chemical potentials μ_s for (a) $D > 0$ and (b) $D < 0$. If $D > 0$, a single minimum appears at a critical chemical potential μ_s^* (line 2) and moves toward increasing p_s continuously as μ_s is increased. For $D < 0$ the minimum appears at a finite aggregation number p_s^{\min} (line 3) for a chemical potential $\mu_s^c < \mu_s^*$. The curves have been drawn for the following values of the parameters: $A = 6$, $N_l = 100$, $B = 1$, $\gamma = 1$, and $N_s = 50$ for $D > 0$, $N_s = 80$ for $D < 0$, or equivalently $b = 1/6$ and $n = 1/2$ ($D > 0$) or $b = 1/6$ and $n = 4/5$ ($D < 0$).

monodisperse micelles disappears and the micelle size distribution shows only the mixed-micelle peak.

In this limit where D is negative, the formation of mixed micelles is only possible if the threshold chemical potential μ_s^c is smaller than μ_s^0 , the chemical potential at the cmc of the pure short copolymer. If one increases (say) n at constant b , the smallest aggregation number of small chains in mixed micelles (for $\mu_s = \mu_s^c$) increases with n and the number of large chains decreases. Along a vertical line in the $[b, n]$ diagram, the mixed micelles crossover smoothly to micelles of the short copolymer with $p_l = 0$. This condition corresponds to a boundary line in the $[b, n]$ diagram, above which no mixed micelles can form. This boundary can be calculated by requesting the peak position of the size distribution for mixed micelles at $\mu_s = \mu_s^c$ to coincide with the peak position of the size distribution for single short copolymer micelles ($\mu_s = \mu_s^0$). The linearization of eq 15 near $p_l = 0$, $p_s = p_s^0$, μ_l^0 , and μ_s^0 leads to a condition for the formation of mixed micelles

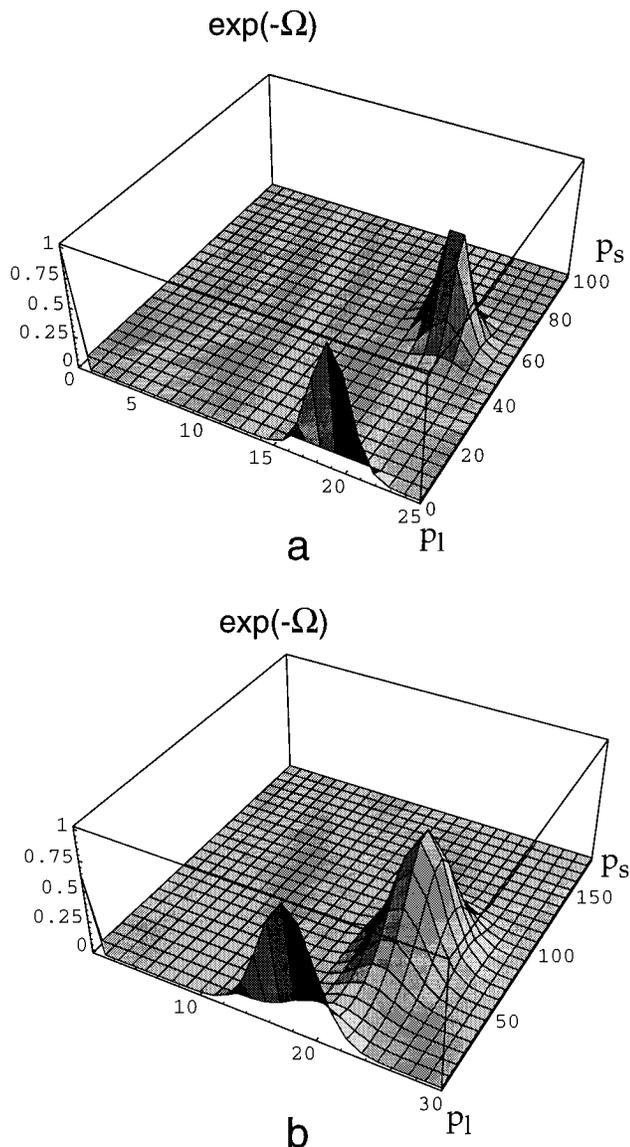


Figure 4. Micelle size distribution for $D < 0$ in the case of (a) copolymer mixtures and (b) copolymer/surfactant mixtures. The parameters are as follows: (a) $A = 6$, $B = 1.4$, $N_1 = 100$, $N_s = 120$, $\gamma = 1$; (b) $A = 2$, $N_s^B = 9$, $N_1 = 50$, $N_s = 35$, $\gamma = 0.5$.

$$\frac{1}{(bn)^{2/5}} > \frac{2}{5n} + \frac{3}{5} \quad (22)$$

We display in Figure 5 the $[b, n]$ diagram showing the possibility of mixed-micelle formation as a function of the asymmetry of the mixture. Inside the line $D = 0$, the small copolymers are incorporated continuously in the micelles formed by large copolymers and the micelle size distribution has only one peak corresponding to the mixed micelles. In the region where $D < 0$, the short copolymers are incorporated discontinuously in the mixed micelles, leading to the possibility of a bimodal micelle size distribution. The line beyond which no mixed micelles are formed is also shown on this diagram.

The region of the diagram around $b = 0.9$ and $n = 0.5$ has been enlarged to show the existence of two special points. These points are obtained by noting that the border line $\mu_s^* < \mu_s^\circ$ is meaningful only in the region where $D > 0$, while the corresponding boundary for $D < 0$ ($\mu_s^c < \mu_s^\circ$) is meaningless in the $D > 0$ zone. Between the two intersection points defined by $\{\mu_s^\circ = \mu_s^c, D = 0\}$ and $\{\mu_s^\circ = \mu_s^*, D = 0\}$ which are located

respectively at $[b = 0.94, n = 0.69]$ and $[b = 0.89, n = 0.54]$ the boundary line has a zigzag shape. The micelle population at these two intersecting points combines the features of both lines, namely, the existence of pure micelles of each species (for the conditions involving the chemical potentials), and a strong tendency for a degenerate distribution (on the line $D = 0$). This results in a "ridged" distribution, running across the $[p_s, p_1]$ plane; mixed micelles are therefore observed with a composition that continuously varies between the large ($p_s = 0$) and the small ($p_1 = 0$) copolymer micelles.

The point $n = 1, b = 1$ on this diagram is a trivial point corresponding to a mixture of identical copolymers. It is interesting to notice that starting from this point we obtain very different behaviors when either b or n is varied. If the ratio of the molecular masses of the insoluble blocks of the copolymers n is fixed to 1, when b is decreased below 1, mixed micelles are formed and the small diblock copolymers are incorporated continuously into the micelles. When b is fixed to 1, any small variation of n to a lower value brings one into a region of the diagram where no mixed micelles are formed. It would be interesting to check whether this is a general feature for surfactants with identical head groups and different tails or whether it is very specific to our copolymer model that considers only the asymptotic limit of infinite molecular weights and thus neglects corrections to the free energy such as the free energy of mixing of the two surfactants in the micelle that could turn out to be important for small surfactants.

III.1.b. Decoration of the Large Copolymers by Small Copolymers. We now consider a copolymer mixture where the concentration of the large copolymers is extremely small and discuss the decoration of the large copolymer by short copolymers that would aggregate around its collapsed insoluble block. The grand-canonical free energy of one large copolymer chain decorated with short copolymers is obtained directly from eqs 14, 16, and 17 with $p_1 = 1$ and $\mu_1 = 0$.

$$\Omega = B(p_s)^{3/2} + c\gamma N_1^{2/3}((1 + np_s)^{2/3} - 1) - \mu_s p_s \quad (23)$$

$$n = N_s/N_1 \ll 1$$

In this case we keep the reference terms in the energy, because the addition of one large diblock copolymer into the micelle might not be a small perturbation to the micelle shape. If the volume of the core is mainly occupied by the small diblocks ($np_s \gg 1$), this free energy is the same as the free energy that describes the micellization of a monodisperse solution of small diblock copolymers and no aggregation of the small block is possible below the cmc. If $np_s > 1$, decoration occurs thus above the cmc of the small diblock copolymer and is not relevant. If $np_s < 1$, the surface tension contribution to the free energy can be expanded

$$\Omega = Bp_s^{3/2} + \frac{2}{3}c\gamma N_1^{2/3} \left(np_s - \frac{1}{6}(np_s)^2 \right) - \mu_s p_s \quad (24)$$

The free energy has no minimum, and there is no decoration when $\mu_s < \mu_s^d = \frac{2}{3}c\gamma N_1^{2/3}n$. When $\mu_s > \mu_s^d$, the free energy has a minimum for a finite value $p_s = ((\mu_s - \mu_s^d)/B)^2$. Decoration actually occurs if the chemical potential threshold value is smaller than the cmc value μ_s° , i.e., when $N_s < N_1^{5/9}$ or $n < N_1^{-4/9}$. When this is the case, the number of small chains decorating a large chain increases from zero at μ_s^d and reaches its maximum value p_s° at the cmc of the short chains.

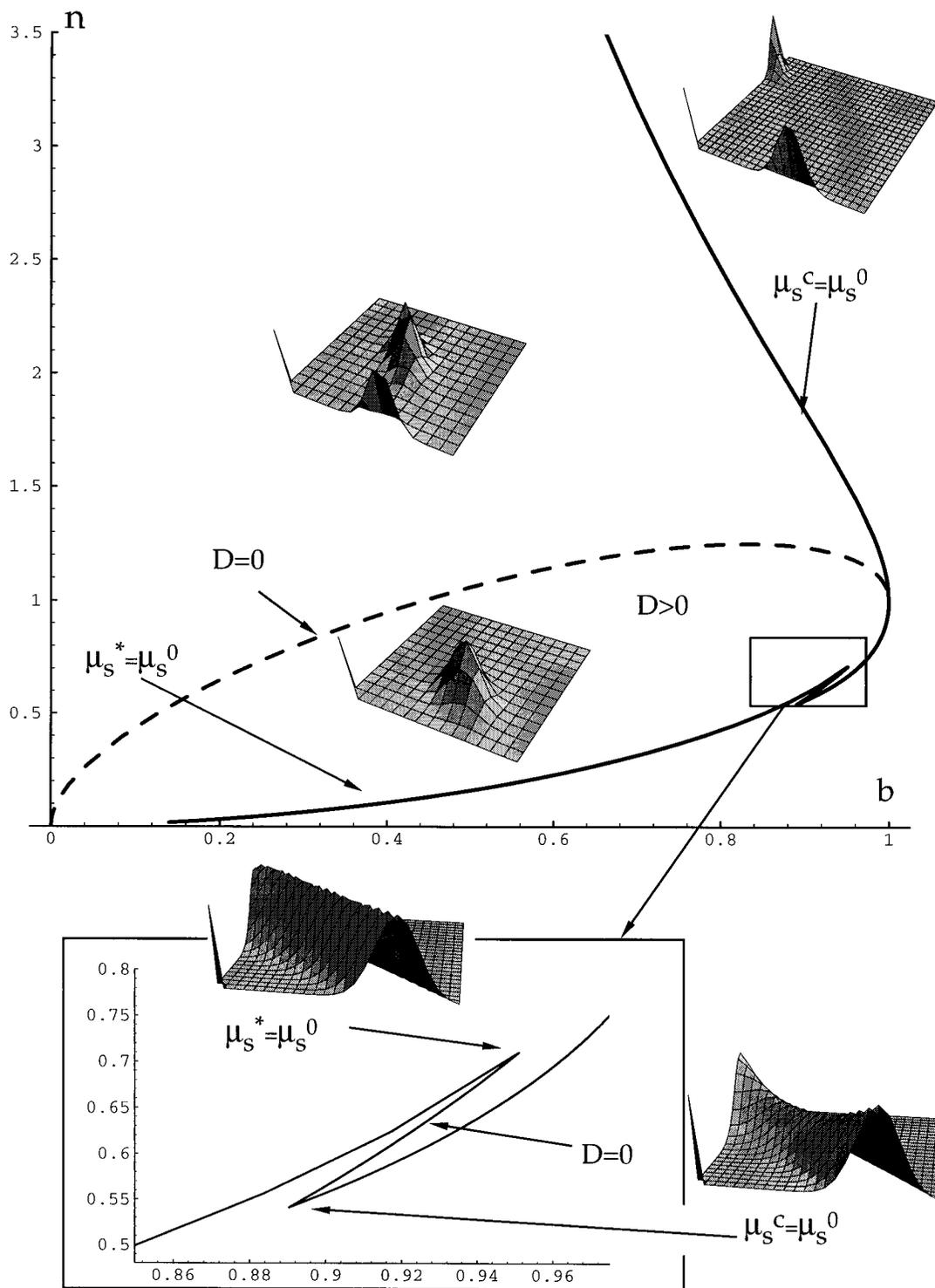


Figure 5. Stability diagram of the mixed copolymer micelles in the $[b, n]$ plane. Mixed micelles are stable above the line $\mu_s^* = \mu_s^0$ and in the left side of the line $\mu_s^c = \mu_s^0$. In the region $D > 0$, the small copolymers are continuously incorporated in the long copolymer micelle. The region of the diagram around $b = 0.9$, $n = 0.6$ has been enlarged. The reasons for such a rather unusual form of the phase diagram are given in the text. Also depicted are typical size distributions for the different regions.

When the concentration of large chains is increased, if $n < N_l^{-4/9}$, one must keep in mind that the objects that aggregate to form the mixed micelles can be the decorated chains and not the isolated large chains. This does not change the critical chemical potentials for mixed-micelle formation but will slightly change the cmc for the large chains; in the following, we ignore this decoration effect. Therefore, a linearization scheme can also be carried out from the equilibrium equations to describe the incorporation of large diblock copolymer chains in micelles of small chains. The threshold

corresponding to eq 18 is given now in the chemical potential representation by

$$\mu_1^* = \frac{2}{5} \left(\frac{3}{2} + \frac{1}{n} \right) (bn)^{2/5} \mu_1^0 \quad (25)$$

III.1.c. Critical Micellar Concentration of a Copolymer Mixture. We have determined the phase diagram of the copolymer mixture by solving numerically the equilibrium equations (14). An example of the phase diagram in the chemical potential plane $[\mu_l, \mu_s]$

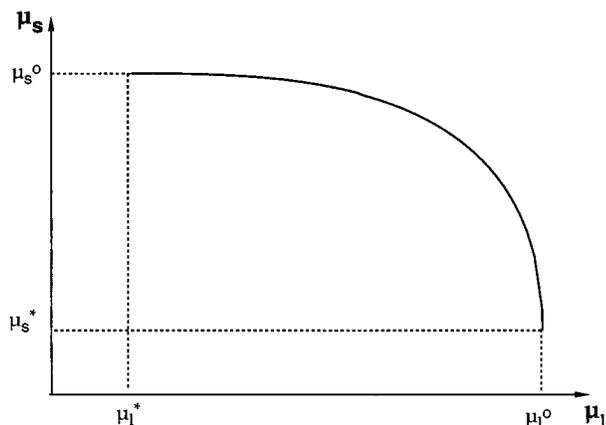


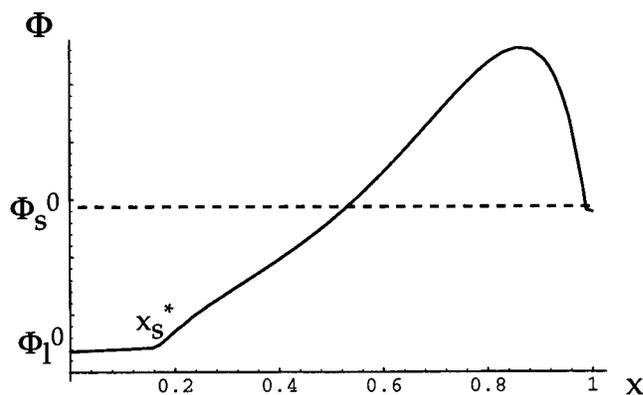
Figure 6. Phase diagram in the plane $[\mu_1, \mu_s]$ for $D > 0$ ($A = 3$, $B = 1.5$, $N_l = 75$, $N_s = 50$, $\gamma = 0.5$). With this choice of parameters, there is no decoration of large copolymer chains by the small copolymers in the vicinity of $\mu_s = \mu_s^0$. The chemical potential threshold μ_1^* is thus relevant.

is shown in Figure 6. This particular case corresponds to asymmetries such that short chains are continuously embedded in the micelles of a large copolymer ($D > 0$) and such as there are no decoration effects. A diagram where $D < 0$ would have a similar shape provided that μ_s^* is replaced by μ_s^c . In the following the onset of mixed-micelle formation in this chemical potential variable is called the micellization line. We now discuss this diagram for two types of experiments: (i) when the concentration of large chains is fixed and the concentration of short chains progressively increased; (ii) when the composition of the solution is fixed and the total copolymer concentration increased.

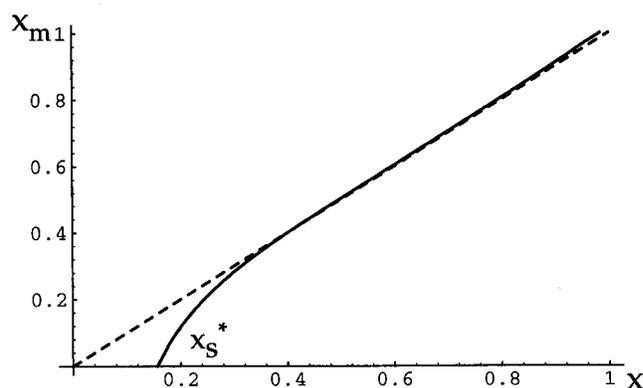
(i) We first fix the chemical potential μ_1 or the concentration of the large copolymers below the cmc value and increase the concentration of the short chains (or the chemical potential μ_s). At very low values of μ_s there is no aggregation. Provided that $\mu_1 > \mu_1^*$, the micellization line is reached when the concentration of short chains is increased and mixed micelles are formed with a finite aggregation number of both large and short chains. If the concentration of short chains is further increased, the chemical potentials remain on the micellization line, the concentration of isolated short chains increases, and thus the chemical potential of the short chains increases; the concentration and the chemical potential of the large chains decrease as the large chains are incorporated into the mixed micelles.

If we start from a concentration of large chains larger than the cmc, the chemical potential of the large chains is fixed at the cmc value μ_1^0 . When the short chains are incorporated continuously in the micelles ($D > 0$), the scenario is the same as below the cmc. If the short chains are incorporated discontinuously ($D < 0$), each mixed micelle contains a finite number of short chains and a small increase of the concentration above the value where mixed micelles appear cannot transform all the large-chain micelles into mixed micelles. There remains thus an excess of large-chain micelles in equilibrium with the mixed micelles.

(ii) The experiments are often performed by fixing the solution composition $x = \phi_s/(\phi_l + \phi_s)$ and increasing the total concentration. We first discuss the case where the short copolymers are incorporated continuously into the micelles $D > 0$. At low concentration, the path followed in the chemical potential $[\mu_1, \mu_s]$ plane when increasing the concentration at fixed composition x is a straight line of slope 1. As the total concentration increases,



a



b

Figure 7. Variation on the micellization line of (a) the total copolymer concentration $\phi = \phi_l + \phi_s$ and (b) the micelle composition $x_m = p_s/(p_l + p_s)$ with the solution composition $x = \phi_s/(\phi_l + \phi_s)$ for $A = 3$, $B = 1.5$, $N_l = 75$, $N_s = 50$, $\gamma = 0.5$. Mixed micellization only occurs for x between $x_s^* = \phi_s^*/(\phi_l^0 + \phi_s^*)$ where $x_m = 0$ and $x_l^* = \phi_s^*/(\phi_l^* + \phi_s^0)$ where $x_m = 1$. In the present case $x_l^* = 0.99 \approx 1$ and can hardly be seen.

both chemical potentials increase and the first micelles form in the solution. The composition $x_m = p_s/(p_l + p_s)$ of the first micelles depends on the imposed concentration ratio and, in general, $x_m \neq x$ (for example, if $x_m < x$, there is an excess of small copolymer in the bulk). This excess of the free chains of one species changes the composition of the free chains in the bulk, which is the important parameter for the evolution of the composition of the mixed micelles. At higher concentration the chemical potential follows the micellization line until the micelle composition matches the imposed solution composition at high enough concentration. (The chemical potential of the small chains increases along the micellization line if $x_m < x$ since the concentration of free chains increases.) The variation of the micelle composition at the cmc x_m with x is shown in Figure 7. Over a broad range of x the micelles form with a composition x_m virtually identical to the imposed composition x ; for these values of x , the composition of the micelles remains approximately constant when the total concentration increases. A difference between x and x_m is, however, observed at small and large values of x . For these compositions, the micelle composition increases with the polymer concentration from x_m when the micelles form to x .

If x is very small, the chemical potential of the large chains reaches the cmc value μ_1^0 while the chemical

potential of the short chains is smaller than the value where mixed micelles are formed. This occurs when $x < x_s^* = \phi_s^*/(\phi_1^\circ + \phi_s^*)$ where ϕ_s^* is the short-chain concentration when the chemical potential of the short chains is μ_s^* . Micelles containing only the large copolymer are then formed. As the concentration is increased further, more large-chain micelles are formed and the chemical potential of the large chains remains approximately constant at the cmc value; the concentration of the small chains increases and the chemical potential of the short chains increases until it reaches the critical value where mixed micelles are formed μ_s^* . The chemical potentials increase then up to the point where the fraction of short chains in the micelle is equal to x . Note that a similar effect occurs in the vicinity of the cmc of the pure short copolymer micelles, but the corresponding composition x_1^* in Figure 7 is very close to 1 and is hardly visible.

We display also in Figure 7 a phase diagram showing the total concentration where mixed micelles appear ($\phi = \phi_1 + \phi_s$) as a function of x . Note that this cmc has a nonmonotonic variation with x . Although the mixed micellization cannot in our case be described by the regular solution theory for mixed surfactants,¹⁵ the shape of the cmc in Figure 7 suggests a similarity with surfactant systems which fall in the class of positive β . In the surfactant theory mentioned above this parameter expresses the average interaction of the two different species in the micelle. A positive β in surfactant theory indicates effective repulsive interactions between the chains in the micelle. In our case they arise solely from the asymmetry of the different blocks, the two chemical species in the core or in the corona being identical.

The case $D < 0$, where the short chains are incorporated discontinuously into the mixed micelles, is more complex. For most values of the imposed solution composition x , as the total concentration is increased, one reaches the critical line where mixed micelles are formed. At higher concentration, the chemical potentials change along the micellization line and the micelle composition changes. Different scenarios are possible depending on the value x_m° of the micelle composition on the micellization line at the chemical potential μ_1° , which is the smallest composition that can be achieved in mixed micelles. If x_m° is smaller than x , the behavior of the solution is similar to the $D > 0$ case. After the formation of the first micelles, the micelle composition changes and approaches the imposed solution composition x . In the case where x_m° is larger than x , there is always an excess of large copolymer chains in the solution as compared to the imposed composition, because even the mixed micelles with the smallest fraction of small copolymers have a small-chain fraction larger than that available from the bulk. At high enough concentration, the chemical potential of the large chain reaches the cmc value μ_1° at which the large chains also form micelles. There is then always coexistence between mixed micelles and large copolymer micelles.

III.2. Copolymer-Surfactant Mixtures. In the limit where the small copolymer can be considered as a simple surfactant, the height of the small corona is smaller than the radius of the core of the mixed micelles and the small corona cannot be considered as a star polymer but must rather be considered as a flat (or slightly curved) grafted polymer layer. The equivalent grafting density is $\sigma = (p_s + p_l)/(4\pi R^2)$, and the thickness

of a flat grafted layer with this grafting density is

$$\frac{h_0}{R} \simeq \frac{N_{Bs}(p_l + p_s)^{1/3}}{(N_l p_l + N_s p_s)^{5/9}} \quad (26)$$

The actual size h_s and the free energy of the curved inner corona can then be expanded in powers of h_0/R to account for the effect of curvature. The osmotic free energy can still be written in the form of eq 16, but B is no longer a constant and explicitly depends on the values of the aggregation numbers p_s and p_l .

$$B \simeq \frac{h_0}{R} \left(1 - \xi_1 \frac{h_0}{R} + \xi_2 \left(\frac{h_0}{R} \right)^2 \right) \quad (27)$$

In order to investigate the formation of mixed micelles, as for the copolymer mixtures, we start from a solution of copolymers at the cmc ($\mu_l = \mu_l^\circ$) and increase the concentration or the chemical potential of the surfactant. There is here also a finite chemical potential threshold μ_s^* above which the surfactant molecules are incorporated inside the large copolymer micelles. The threshold is obtained by linearizing the equilibrium equations around the point $[\mu_1^\circ, \mu_s^*]$ in the chemical potential phase diagram. The critical potential for the formation of mixed micelles is still given by eq 18 where B is calculated from eq 27 at the value H_0 of the grafted layer thickness which corresponds to $p_s = 0$ (this is the height of the small corona when the first surfactant molecule is incorporated inside the mixed micelle).

$$\frac{H_0}{R} \simeq \frac{N_s^B (p_l^\circ)^{1/3}}{(N_l p_l^\circ)^{5/9}} \quad (28)$$

The change in the aggregation numbers δp_s and δp_l of the mixed micelle can also be determined when the chemical potential of the surfactant molecules is increased slightly above the critical value for mixed-micelle formation $\mu_s = \mu_s^* + \delta \mu_s$

$$\delta p_s \propto -\frac{1}{D} \frac{p_l^\circ}{\mu_1^\circ} \delta \mu_s$$

$$\delta p_l \propto \frac{\left(\frac{H_0}{AR} \left(1 - \frac{\xi_1}{5} \frac{H_0}{R} - \frac{3\xi_2}{5} \left(\frac{H_0}{R} \right)^2 \right) - \frac{4}{5}n \right) p_l^\circ}{D} \frac{p_l^\circ}{\mu_1^\circ} \delta \mu_s \quad (29)$$

where

$$D = -36n^2 + 15 \frac{H_0}{AR} (7 - 4n) - \left(\frac{H_0}{AR} \right)^2 (25 + (165 - 192n)A\xi_1) + \left(\frac{H_0}{AR} \right)^3 (10A\xi_1 + (225 - 324n)A^2\xi_2) \quad (30)$$

The results are qualitatively similar to those obtained for the copolymer mixtures, and one must distinguish two types of behaviors according to the sign of D . The surfactant molecules are incorporated continuously into the large copolymer micelles when D is positive and discontinuously when D is negative; in this last case, the formation of mixed micelles occurs at a chemical potential smaller than μ_s^* . We display in Figure 8 a diagram showing the possibility of formation of mixed

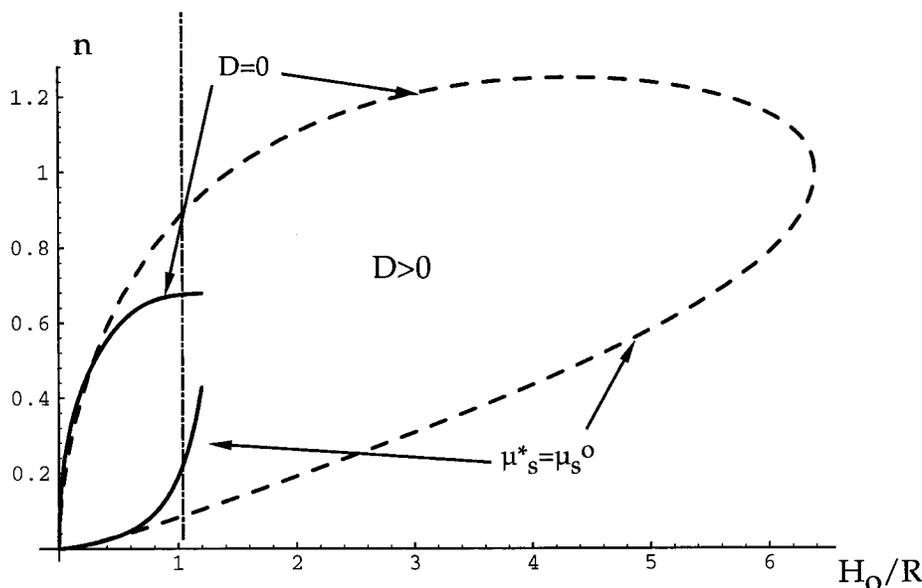


Figure 8. Stability diagram of the mixed micelle in surfactant/copolymer mixtures in a plane $[H_0/R, n]$ for $A = 2$. The lines of the diagram for copolymer mixtures have been added in order to check the continuity between the two models when $H_0/R \approx 1$.

micelles as a function of the relative molecular weights of the copolymer and the surfactants. In order to characterize the asymmetry of the soluble block of the copolymer, we use here the variable H_0/R instead of b and with A fixed. We have explicitly checked that this diagram crosses over smoothly to the similar diagram for copolymer mixtures when $B \approx 1$ —see Figure 8.

When the surfactant molecules are incorporated discontinuously in the large copolymer micelles, the micelle size distribution is bimodal, with one peak corresponding to mixed micelles and one peak corresponding to a pure copolymer micelle. An example of the size distribution calculated numerically is shown in Figure 4b. For the chosen values of the parameters the potential barrier between the two peaks is less pronounced than that for the copolymer mixture, and we expect a broader distribution of the size of the micelles in this case. As in section III.1.b, one can also show that decoration of one large diblock head by small diblocks can always occur for large enough concentrations of the small diblock chains.

IV. Discussion

We have discussed in this paper the formation of mixed micelles in mixtures of long block copolymers or in mixtures of surfactant and long block copolymers. This has been done by extending the work of Shim *et al.*⁹ to diblock copolymers where both the soluble and insoluble sequences are chemically identical but have different molecular weights.

Our main result is the existence of two scenarios for the formation of mixed micelles. The choice of scenario is driven by the relative asymmetries of the copolymer blocks, measured by the quantity D , which is positive for relatively small asymmetries and negative when the asymmetries are large. In the first scenario, when D is positive, the small copolymers are incorporated continuously into the micelles formed by the large copolymer and the micelle size distribution has a sharp peak corresponding to the mixed micelles. In the second scenario ($D < 0$) which is expected when the spontaneous curvatures of the two copolymers are very different, even at the cmc of the large copolymer chains, the mixed micelles contain a finite number of short copolymer

chains. In this case the micelle size distribution is bimodal, with one peak corresponding to mixed micelles and one peak corresponding to pure large copolymer micelles. One also expects above the cmc of the large copolymer an equilibrium between mixed micelles and large copolymer micelles. In the case where $D < 0$, the formation of mixed micelles is thus very similar to a first-order transition.

Our study was motivated by the work of Hecht *et al.*,¹⁰ who have observed a bimodal micelle size distribution in a mixture of pluronic triblock copolymers and simple surfactants. Our results when $D < 0$ may provide a qualitative explanation of this experimental result. Although in these experiments the nature of the two hydrophobic moieties is different, the existence of a bimodal distribution suggests that they do not have large negative excess enthalpies of mixing. It can be checked that such a contribution of the form $-\chi(p_s N_s) - (p_l N_l)/(p_s N_s + p_l N_l)$ increases the region of the phase diagram (5) where mixed micelles are observed.

An important issue is then the generality of the result which is based theoretically on an expression for the free energy of the micelles where the molecular weight both of the hydrophilic group and of the hydrophobic core can be considered as extremely large. When this is not the case, several other contributions to the free energy of a micelle which are subdominant for copolymers are relevant. The entropy of mixing of the junction points on the surface of the core or the stretching of the tails inside the core could change somewhat our conclusions. For instance, the entropy contribution can broaden the border lines in the phase diagram (5). Another limitation of our study is the range of asymmetries which are accessible experimentally; we have assumed that the asymmetry parameters n and b can be varied without any limitations, but in certain cases this would lead to extremely large molecular weights. We are not aware of any other experiment than that of ref 10 on simple surfactants or on copolymer mixtures that would study quantitatively the micellar size distribution and would thus allow for confrontation with our predictions. Available self-consistent-field calculations on the specific case of polydisperse PEO-PPO-PEO triblock copolymers¹⁶ do not report the coexistence of micelles with

different sizes, but this could be due either to the limited range of parameters explored or to the more continuous nature of the assumed polydispersity.

Another surprising result is the difference in the role of the asymmetry parameters b and n . If the hydrophobic groups are identical ($n = 1$), a slight difference in the hydrophilic blocks always leads to the formation of mixed micelles. This is not the case if the hydrophilic groups are identical ($b = 1$), even a slight difference between the molecular weights of the hydrophobic blocks can lead to a situation where no mixed micelles are formed. This effect (which again could only be valid for asymptotically large molecular weights) may, however, be difficult to observe for two reasons. First, two micelle populations with the same hydrophilic blocks but slightly different hydrophobic blocks will be indistinguishable to most of the available techniques. Second, diblock copolymer solutions always have some polydispersity in both block lengths. One could, for instance, check that a system with fixed, monodisperse composition but presenting a total mass polydispersity would be represented by a line in the phase diagram which lays *inside* the region where mixed micelles are formed.

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