Mixed versus Ordinary Micelles in the Dilute Solution of AB and BC Diblock Copolymers

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ABSTRACT: We predict the thermodynamic stability of mixed micelles of various morphologies (spheres, cylinders, lamellae) in the solution of AB and BC diblock copolymers in a selective solvent. The B blocks are assumed to be insoluble and form the core of the micelle, whereas soluble, incompatible (with each other) A and C blocks form the corona. A homogeneous mixing of the A and C blocks in the corona (mixed micelles) is possible if their incompatibility is relatively weak. Otherwise, a mixture of "pure" (ordinary) micelles consisting of either AB or BC copolymers is stable. Phase behavior of the solution, which depends on the relative and overall lengths of the blocks, and on the surface tension coefficients, is analyzed.

1. Introduction

Diblock copolymers are versatile materials with a wide range of applications.[1−3] In selective solvents, they tend to aggregate and form micelles. The insoluble blocks are incorporated into a dense core of the micelle and the soluble blocks form a corona. Depending on the relative lengths of the blocks, various micellar morphologies (spheres, cylinders, bilayers, etc.) can be stable. Intensive experimental[4−12] and theoretical[13−19] studies led to a construction of the phase diagrams of diblock copolymers in selective solvents.[10−12,19] In recent years, several new classes of micelles with intricately organized core and corona were obtained.[20] Their better tunability and wider range of characteristics make them valuable for such applications as drug delivery, particle modification, catalysis, etc.

One of the simplest possible ways to obtain complex micelles is a mixing of two different diblock copolymers. The natural question is whether these diblock copolymers will reside within a combined (mixed) micelle or not. For the systems of chemically identical diblock copolymers with different block lengths, a distribution of the molecules between micelles was studied in refs 21–23. The possibility of coexistence of "pure" and mixed micelles was shown. Shim and co-workers developed a theory of comicellization of diblocks with identical soluble blocks and different insoluble ones.[24] In this case, the authors studied equilibrium structures for different concentrations of the copolymers and found conditions for stability of the comicelles (mixed micelles in our terminology). The mixtures of diblock copolymers with different soluble and the same insoluble blocks were studied in recent experiments.[25−27] In these studies, successful preparation of the micelles with mixed corona was achieved.

To the best of our knowledge the only theoretical treatment of the latter system was done by Halperin.[28] He studied the behavior of the diblocks with very short soluble blocks (corona was assumed to be a flat grafted layer) and suggested that two processes can occur. The first one, called intramicellar microphase separation, involves segregation within a corona of a single micelle and leads to the formation of the Janus micelle, which was supposed to be metastable. The second one, called intermicellar microphase separation, results in formation of A-rich and C-rich (in our notations) micelles. The final state was expected to consist of micelles with continuously varying overall compositions. For one particular choice of parameters, it was shown that micelles are almost purely A-rich and C-rich. In other words, the equilibrium system is a solution of the mixture of the ordinary AB and BC micelles.

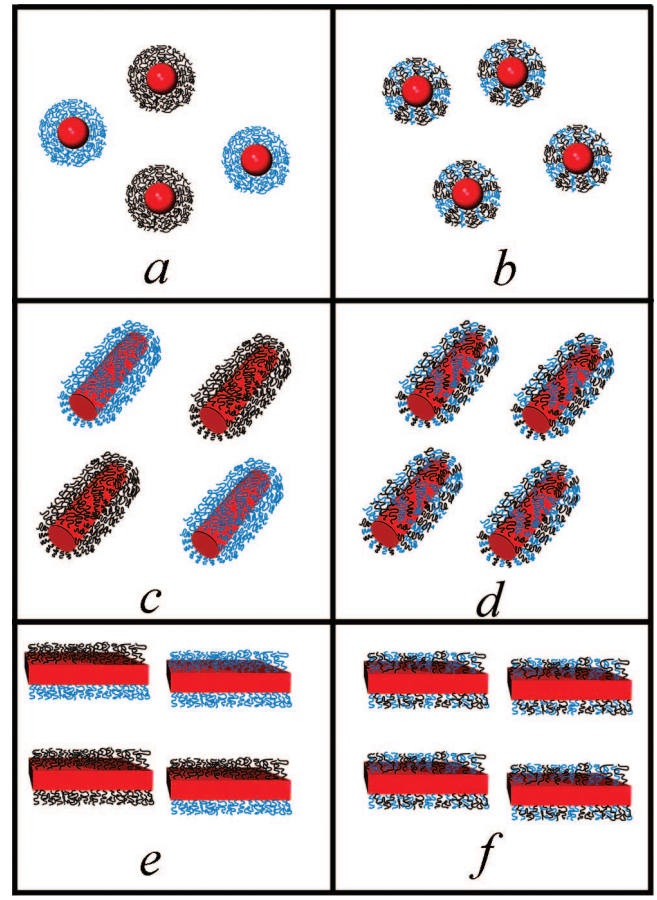

Figure 1. Ordinary micellar structures (left): (a) spheres (OS); (c) cylinders (OC); (e) lamellae (OL). Mixed micellar structures (right): (b) spheres (MS); (d) cylinders (MC); (f) lamellae (ML). In the case of ordinary lamellae (e), we do not make a distinction between the lamellae with AB−BA (CB−BC) bilayer and the lamellae with AB−BC bilayer.

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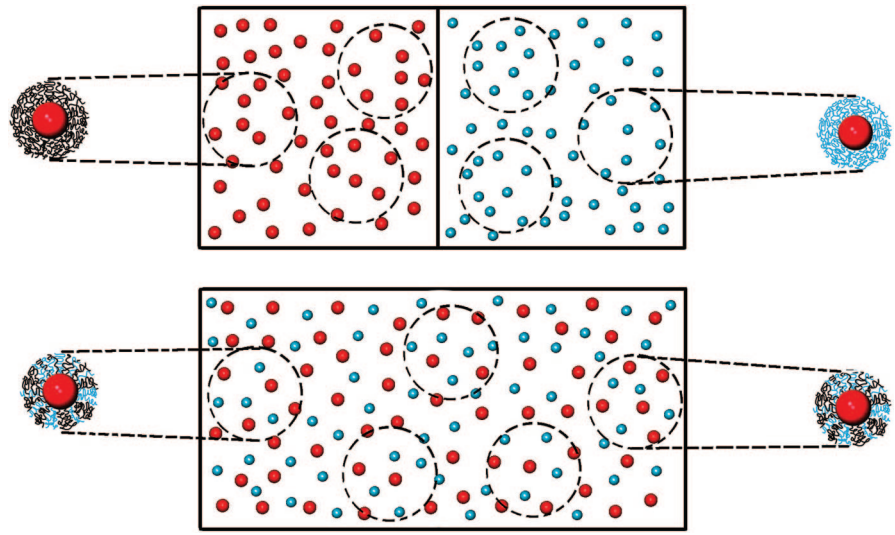

Figure 2. Top: the entropy of the segregated ideal gases corresponds to the entropy of translational motion of diblocks in ordinary ("pure") micelles. Bottom: the entropy of mixed ideal gases corresponds to the entropy of AB and BC diblocks in the mixed micelles.

In the present paper we will construct a phase diagram of the mixture of AB and BC diblock copolymers in selective solvent with insoluble B blocks and soluble A and C blocks. We will consider conventional micellar morphologies (spheres, cylinders, and bilayers) with "pure" and mixed coronae, Figure 1. We will show that the mixed micelles thermodynamically can be stable if incompatibility of A and C blocks is weak enough. Otherwise, the equilibrium state is a mixture of "pure" micelles. The physical reason for the stability of the mixed micelles is a gain in the entropy: AB and BC diblocks in the mixed micelles possess higher entropy of translational motion than in the ordinary micelles because of larger accessible volume. Indeed, if we deal with 1:1 ratio of AB and BC copolymers, they can form either k mixed micelles or $k/2$ AB and $k/2$ BC micelles (the aggregation numbers of all micelles are assumed to be equal). Thus, in the mixed micelles, the accessible volume for both AB and BC diblocks corresponds to the volume of k micelles. In the ordinary micelles, AB and BC diblocks can occupy the volume of only $k/2$ micelles. This effect is analogous to that of the mixing of two ideal gases, Figure 2. The segregated state, Figure 2a, possesses a lower entropy than the mixed state,[29] Figure 2b. One can say that the entropy of the diblocks in the ordinary micelles corresponds to the entropy of the segregated ideal gases, and the entropy of the mixed micelles corresponds to the entropy of the mixed gases.

2. Model

Let us consider a mixture of AB and BC block copolymers in a selective solvent. Insoluble B blocks can aggregate and form dense cores of the micelles whereas soluble A and C blocks form coronae. We assume that all blocks of different kinds are incompatible with each other. The swelling and incompatibility of A and C blocks in corona will be described in terms of the second virial coefficients, B_0 and B. Here B_0 quantifies A−A and C−C repulsions between monomer units, i.e., the solvent power is assumed to be the same for A and C blocks. The coefficient B describes repulsion between A and C monomer units. To provide incompatibility of A and C blocks, one has to fulfill inequality $B > B_0$. For the sake of simplicity we will develop a theory for the mixture where AB and BC diblocks have equal contour lengths and compositions, i.e., each B block consists of N_B segments and the numbers of segments in A and C blocks are equal, $N_A = N_C$. Also we assume that the segments of all kinds are geometrically identical; each of the linear size a and of the excluded volume $v = a^3$.

2.1. Mixed Micelles. Let us assume that A and C blocks are homogeneously mixed in the corona. The total free energy of the micelle per chain comprises the elastic free energy of the core, F_B, the free energy of the swollen A and C blocks, F_{AC}, the surface energy of the core, F_{sur}, and the free energy of the translational motion of the chains within the micelles, F_{tr} (the entropy of the translational motion of micelles is small and can be omitted):

$$F_{mix} = F_B + F_{AC} + F_{sur} + F_{tr} \tag{1}$$

In the limit of strong insolubility of the B blocks, F_B can be approximated as that of the micelles in the melt[30] ($k_BT \equiv 1$):

$$F_B = \lambda_d \frac{R^2}{a^2 N_B}, \quad \lambda_1 = \frac{\pi^2}{8}, \quad \lambda_2 = \frac{\pi^2}{16}, \quad \lambda_3 = \frac{3\pi^2}{80} \tag{2}$$

where $d = 1, 2,$ and 3 corresponds to the lamella (bilayer), cylinder, and sphere, respectively, and R is the radius (semi-thickness) of the core.

Denote by φ a fraction of BC diblocks in the system. Then the numbers of BC and AB molecules in the spherical micelle are φQ and $(1 - \varphi)Q$, respectively, where Q is the aggregation number. Keeping in mind that the cylindrical micelles and lamellae have infinite aggregation numbers, $Q_{cyl} = Q_{lam} = \infty$, we will deal with the aggregation numbers per unit length (cylinders), $Q = Q_{cyl}a/L$, and unit area (lamellae), $Q = Q_{lam}a^2/S$, which are finite. With these aggregation numbers, the dense packing conditions for the cores of the micelles take the following form:

$$2R = QN_Ba \quad R^2 = QN_Ba^2 \quad \frac{4\pi}{3}R^3 = QN_Ba^3 \tag{3}$$

The free energy of A and C blocks in the corona will be calculated on the basis of the blobs picture.[14,15,19,31] However, to distinguish A−C from A−A (C−C) interactions of monomer units, let us begin with the mean-field description. First, we consider a homogeneous semidilute mixture of A and C chains, $n_A = (1 - \varphi)n$ and $n_C = \varphi n$ being the concentrations of monomer units. The density of the mean-field energy of the excluded volume interactions in a good solvent takes a standard form:

$$F_{m-f} = B_0(n_A^2 + n_C^2) + 2Bn_An_C = B_0n^2 + 2(B - B_0)\varphi(1-\varphi)n^2 = B_en^2 \quad (4)$$

where $B_e = B_0 + 2(B - B_0)\varphi(1 - \varphi)$ is an effective second virial coefficient, and n is the average concentration of monomer units. The semidilute mixture can be imagined as a set of densely packed blobs, each of the size ξ comprising g monomer units. Inside the blobs, the chains fragments are swollen,[32,33] $\xi \simeq g^{3/5}a^{2/5}B_e^{1/5}$. It is known that the density fluctuations are strong on the length scales smaller than the correlation radius (blob size) ξ and the mean-field approach breaks down. Nevertheless, these fluctuations can be taken into account within the framework of the mean-field theory if each blob can be treated as a Gaussian chain with monomer units characterized by the renormalized parameters:[34,35] the size $\hat{a} = \xi/g^{1/2}$ and the virial coefficient $\hat{B}_e$. It is easy to find the $\hat{B}_e$ from condition for parameter z, which is introduced in the perturbation theory of a polymer chain:[33]

$$z \equiv \hat{B}_e g^{1/2}\hat{a}^{-3} \approx 1 \quad (5)$$

This equality is equivalent to the condition that the energy per blob is equal to unity ($k_BT \equiv 1$). Indeed, if we deal with the renormalized parameters (Gaussian chain), the energy per blob in the second virial approximation is $\hat{B}_e ng \approx 1$, where concentration $n = g/\xi^3$ and $\xi = \hat{a}g^{1/2}$. Taking into account that the polymer volume fraction $\phi = na^3 \simeq ga^3/\xi^3$ and introducing dimensionless second virial coefficients, $B_0 = a^3\tau_0$, $B = a^3\tau$, and $B_e = a^3\tau_e$

$$\tau_e = \tau_0 + 2(\tau - \tau_0)\varphi(1-\varphi) \quad (6)$$

we find the following expressions:

$$\hat{B}_e \simeq a^3\phi^{1/4}\tau_e^{3/4} \quad \xi \simeq \frac{a}{\phi^{3/4}\tau_e^{1/4}} \quad (7)$$

Substituting $\hat{B}_e$ instead of B_e in eq 4, we get the scaling form for the free energy density of the semidilute mixture:

$$F_{sc} \simeq \frac{1}{a^3}(\tau_0 + 2(\tau - \tau_0)\varphi(1-\varphi))^{3/4}\phi^{9/4} \simeq \frac{1}{\xi^3} \quad (8)$$

Returning to the mixed micelles, each block of the corona can be imagined as a set of blobs differing in the size (spheres and cylinders) or having the fixed size (lamellae).[14,15,19,31] The dependence of the blob size ξ on the radial coordinate r is found from the dense packing condition for the blobs

$$Q\xi^2 = 2a^2 \quad \text{(lamellae)} \quad Q\xi^2 = 2\pi ra \quad \text{(cylinders)} \quad Q\xi^2 = 4\pi r^2 \quad \text{(spheres)} \quad (9)$$

The free energy of the blocks in the corona can be calculated via integration of eq 8 over the volume V of the corona:

$$F_{AC} \simeq \frac{1}{Q}\int\frac{dV}{\xi^3} = \begin{cases} \sqrt{\frac{Q}{2}}\frac{R_0 - R}{A} & \text{(lamellae)} \\ 2\sqrt{\frac{Q}{2\pi}}\left(\sqrt{\frac{R_0}{a}} - \sqrt{\frac{R}{a}}\right) & \text{(cylinders)} \\ \sqrt{\frac{Q}{4\pi}}\ln\left(\frac{R_0}{R}\right) & \text{(spheres)} \end{cases} \quad (10)$$

where R_0 is the outer radius of the corona (the thickness of one layer in the lamella). This parameter is determined through the space filling condition, $\int dV\, \phi = a^3QN_A$, and takes the form:

$$R_0 = R + \left(\frac{\tau_eQ}{2}\right)^{1/3}N_Aa \quad \text{(lamellae)}$$

$$R_0^{4/3} = R^{4/3} + \frac{4}{3}\left(\frac{\tau_eQ}{2\pi}\right)^{1/3}N_Aa^{4/3} \quad \text{(cylinders)}$$

$$R_0^{5/3} = R^{5/3} + \frac{5}{3}\left(\frac{\tau_eQ}{4\pi}\right)^{1/3}N_Aa^{5/3} \quad \text{(spheres)} \quad (11)$$

The surface energy of the interface between the core and corona of the micelle can be chosen in the following form

$$F_{sur} = (\gamma_{AB}(1-\varphi) + \gamma_{BC}\varphi))\frac{dN_Ba^3}{R} \quad (12)$$

where $d = 1$, 2, and 3 corresponds to the lamellae, cylinders, and spheres, respectively. The surface tension coefficients γ_{AB} and γ_{BC} describe incompatibility of the B blocks with the solvent and A (C) blocks. Taking into account that the polymer volume fraction of A and C blocks at the interface is small, one can expect that the values of γ_{AB} and γ_{BC} are close to each other.

Finally, the mixing entropy (translational motion of the diblocks in the mixed micelle) contributes

$$F_{tr} = \varphi\ln\frac{\varphi}{N_B} + (1-\varphi)\ln\frac{1-\varphi}{N_B} \quad (13)$$

which has the same form for all kinds of the morphologies. The equilibrium free energies of the mixed micelles are calculated by minimization of eq 1 over the radius R. In eqs 10 and 11, dependence of Q on R is taken from the space filling conditions, eq 3.

2.2. Mixture of the Ordinary Micelles. The free energy of a mixture of the ordinary micelles consisting of either AB or BC diblocks is calculated using eq 1:

$$F_{ord} = (1-\varphi)F_{mix}(\varphi = 0) + \varphi F_{mix}(\varphi = 1) \quad (14)$$

Here $F_{mix}(\varphi = 0)$ and $F_{mix}(\varphi = 1)$ mean that all contributions to the free energy F_{mix} are taken at $\varphi = 0$ and $\varphi = 1$, respectively.

3. Results and Discussion

The phase diagram of the mixture of AB and BC diblock copolymers is constructed via numerical solution of equations $F_{ord} = F_{mix}$ where all possible morphologies (spheres, cylinders, bilayers) are analyzed. Also transitions between different morphologies in solution of ordinary micelles and in solution of mixed micelles are calculated using equations $F_{ord}|_{lam} = F_{ord}|_{cyl}$, $F_{mix}|_{lam} = F_{mix}|_{cyl}$, etc. The typical phase diagrams are plotted in Figure 3. Here f is the fraction of the soluble block in the copolymer, $f = N_A/(N_A + N_B)$, and τ is a measure of incompatibility between A and C monomer units: the larger the τ, the stronger the incompatibility. Taking into account that A−A and C−C repulsions are quantified by the parameter τ_0, the incompatibility implies that $\tau > \tau_0$. For systems with the upper critical solution temperature, τ_0 has a meaning of the dimensionless temperature,[33] $\tau_0 = (T - \Theta)/T$, where Θ is the theta-temperature for polymers A and C. Figure 3 shows that the mixed micelles are stable if the parameter τ is relatively small. In this case, a gain in the entropy of translational motion of the mixed diblocks overcomes a penalty in the energy of the excluded volume interactions. A mixture of the ordinary micelles becomes stable at larger values of τ. Similarly with one-component diblock copolymer solutions,[19] the nonspherical morphologies of both mixed and "pure" micelles occur in the so-called crew-cut micelle regime, i.e., when the soluble blocks are shorter than the insoluble ones. In the opposite limit (hairy micelle regime) only spherical micelles are stable. Unusual (at the first glance) behavior comprises an expansion of the stability region of the spherical mixed micelles with f, i.e., the longer the soluble blocks are, the larger values of τ are needed to induce formation of the ordinary micelles, Figure 3. On the contrary, one can expect that the increase of the length of the soluble blocks has to increase the A−C volume interactions in corona region and decrease the transition value of τ. However, due to the decrease

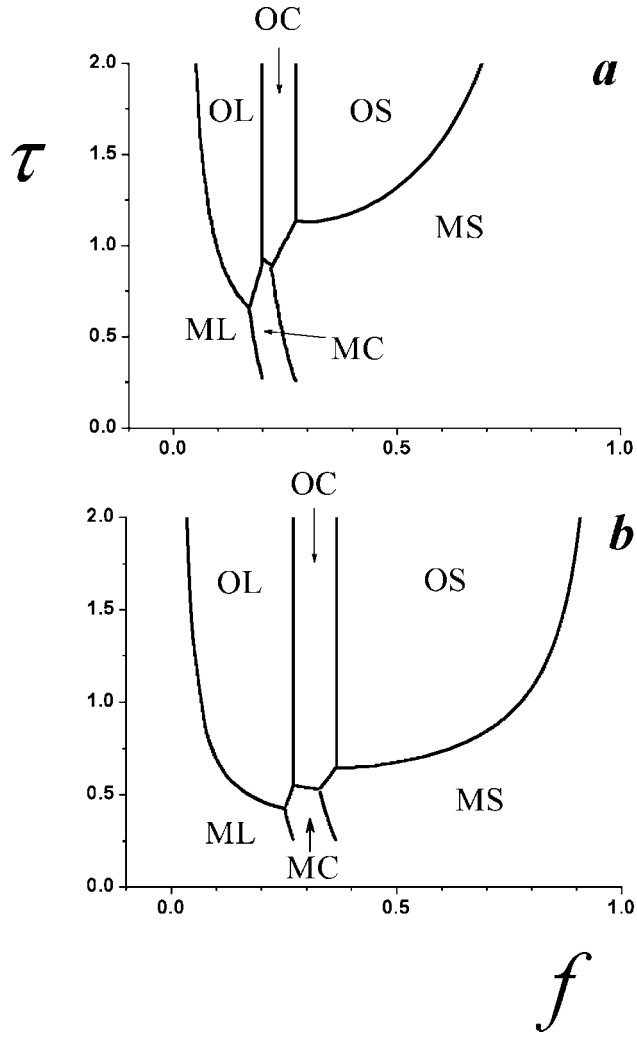

Figure 3. $\tau-f$ phase diagrams at fixed values of $\varphi = 0.5$, $\tau_0 = 0.25$, and $N = 400$. The values of the surface tension coefficients between core and corona of the ordinary micelles, γ_{AB}, γ_{BC}, are assumed to be equal: $\bar{\gamma} = \gamma_{AB}a^2 = \gamma_{BC}a^2 = 0.2$ (a) and $\bar{\gamma} = 0.6$ (b). Abbreviations OL, OC, etc., correspond to those in Figure 1.

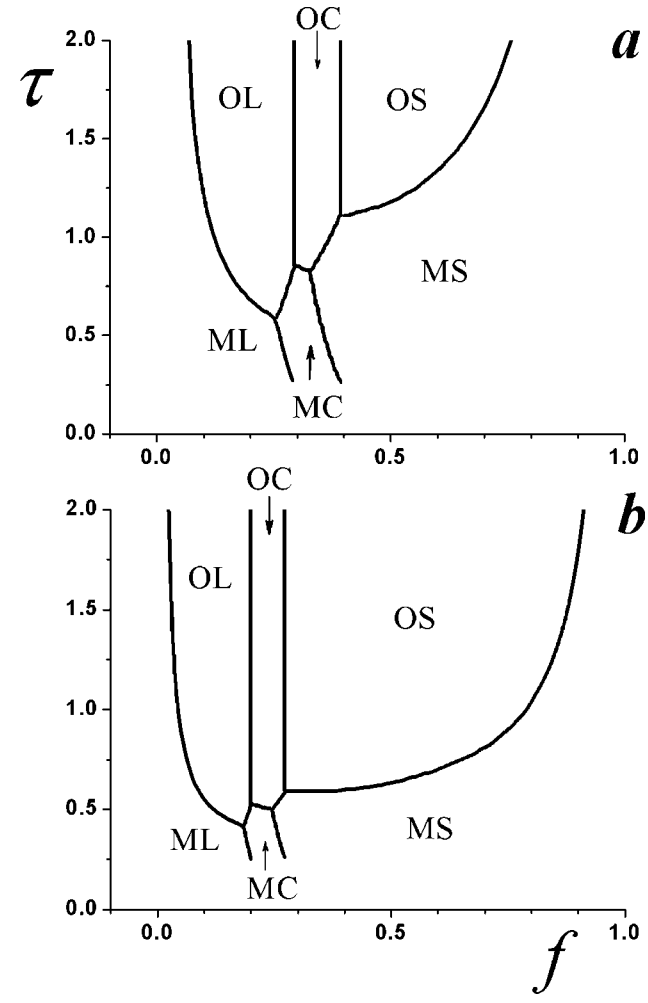

Figure 4. $\tau-f$ phase diagrams for two different values of the contour length of the diblock copolymers: $N = 200$ (a) and $N = 800$ (b). $\varphi = 0.5$, $\bar{\gamma} = 0.4$, $\tau_0 = 0.25$.

of the aggregation number of the spherical micelles with f, the density of the corona decreases too and the A−C interactions weaken. That is why τ is the increasing function of f.

The phase diagrams in Figure 3 are plotted under assumption that both surface tension coefficients, γ_{AB} and γ_{BC}, are equal. Such assumption is reasonable because main contribution to the surface tension coefficients comes from incompatibility of polymer B with the solvent, and the difference between γ_{AB} and γ_{BC} is expected to be small. Figure 3a corresponds to $\bar{\gamma} = \gamma_{AB}a^2 = \gamma_{BC}a^2 = 0.2$, whereas Figure 3b is plotted at $\bar{\gamma} = 0.6$. The increase of $\bar{\gamma}$ results in a shrinkage of the stability regions of the mixed micelles and in a shift of the boundaries of the cylindrical phases toward larger values of f. The latter tendency was already observed in several experimental studies for ordinary micelles (for example, PS−PI in mixtures of DBP/DEP and DEP/DMP[12] or PS−PAA in mixtures of water/dioxane[10] and water/DMF[36]). The shrinkage is explained by the increase of the aggregation number and the corona density with $\bar{\gamma}$ that enhances the A−C repulsion. Parts a and b of Figure 3 demonstrate also that variation of τ can be responsible for a number of morphological transitions such as ML−MC−OL, MC−MS−OC, etc.

The variations of the contour length (molecular weight) of the copolymers lead to the monotonous shift of the lines on the phase diagram. The stability regions of the mixed structures become smaller with the increase of the length of the copolymers, Figure 4. It again implies the increase of the repulsion between A and C units in the corona. In contrast with the Figure 3, the stability regions of the ordinary lamellae and cylinders become smaller with N displaying the importance of the overall molecular weight of diblock copolymers even for the systems with the same composition f. The latter is consistent with the conclusions of experiments by Jain and Bates for ordinary micelles.[11]

Taking into account that variation of the surface tension coefficient $\bar{\gamma}$ shifts the phase diagram, Figure 3, one can expect that analysis of different γ_{AB} and γ_{BC} can enrich phase behavior. Indeed, a coexistence of the ordinary micelles having different morphologies is possible already at small difference in the surface tension coefficients, Figure 5. In the coexistence region, different diblocks form different morphologies. For example, OC + OL in Figure 5 means that the ordinary cylinders consisting of AB diblocks are mixed with the ordinary lamellae consisting of BC copolymers.

Considering mixed micelles, one can imagine that a homogeneous mixing of A and C blocks in the corona is not the only option realizing thermodynamic equilibrium. At the first glance intramicellar segregation of A and C blocks leading to the formation of the Janus micelles[37–39] is also possible. However, more careful analysis shows that the Janus micelles are not stable in the mixture of AB and BC block copolymers. To provide their stability, some additional interactions between the blocks in the core are needed. We will report this case in a forthcoming publication.

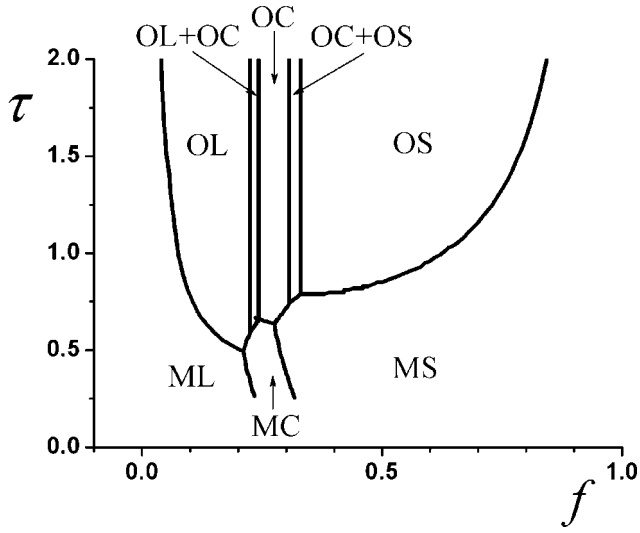

Figure 5. $\tau-f$ phase diagram for different values of the surface tension coefficients: $\gamma_{AB}a^2 = 0.4$ and $\gamma_{BC}a^2 = 0.3$. Abbreviations OL+OC and OC+OS mean coexistence of different morphologies. $\varphi = 0.5$, $\tau_0 = 0.25$, $N = 400$.

4. Conclusions

We have developed a theory that predicts micellization in a mixture of AB and BC diblock copolymers in a selective solvent. The B blocks were considered to be insoluble. We have shown that soluble and incompatible (with each other) A and C blocks are homogeneously mixed within one corona (the so-called mixed micelles) or they form "pure" A- and C-coronae (the so-called ordinary micelles). The mixed micelles are formed if incompatibility between the A and C blocks is weak enough. Otherwise, the ordinary micelles are stable. Phase diagrams including spherical, cylindrical and lamellar morphologies were plotted.

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