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Micelle Formation in the Dilute Solution Mixtures of Block-Copolymers

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ABSTRACT: We have developed a theory for the micelle formation in dilute solution mixtures of two block-copolymers ($A-B$ and $C-B$) with very long soluble B-blocks and chemically identical insoluble blocks A and C differing in lengths. In this case spherical micelles with A, C, or A/C-core and B-corona are formed. The conditions for the formation of pure micelles and comicelles are determined by using the results of the calculation of the free energy of the core of the mixed micelles made previously by us and the theory of the micelle formation describing this process as a set of association−dissociation reactions with certain chemical constants. It is shown that the block-copolymers with longer blocks are normally the first to make aggregates (micelles). These micelles are enriched with shorter chains at the concentrations much smaller than cmc for these chains. There is a wide region on the phase diagram where the distribution function for the aggregation of block-copolymers in the micelles is bimodal, corresponding to the equilibrium coexistence of mixed micelles and pure micelles made of shorter block-copolymers. This is in good agreement with recent experimental findings by T. Nose et al.

1. Introduction

The problem of micelle formation in dilute solutions of block-copolymers in selective solvents has been attracting much attention in the literature.[1−4] The reason is that in addition to the fundamental interest, block-copolymer micelles in the solution are used in many practical applications (see e.g. refs 5 and 6). The micellization of these macromolecules is very similar to the analogous processes in the solutions of low molecular weight surfactants.[7−9]

One of the ways of modifying the properties of emerging micelles is to use the mixtures of block-copolymers with different block lengths. As a result, the possibility of forming micelles from pure components vs the comicellization should be explored, thus enriching this area of study. The micelle formation for such mixtures of block-copolymers in dilute solutions has been experimentally studied in the literature;[10,11] however, the corresponding theoretical consideration is still lacking; see, however, ref 12.

The aim of the present paper is just the development of the theory of micellization and comicellization for the dilute solution mixture of two diblock-copolymers ($A-B$ and $C-B$) with a very long B-block ($N_B \gg N_A$, N_C; N_i being the number of monomer units in the block i) and chemically identical blocks A and C, differing in length ($N_A < N_C$). The solvent is supposed to be extremely selective, i.e., poor for A- and C-blocks and good for B-blocks. As a result, since block-copolymers are very asymmetric (the length of A and C block is much shorter than the length of B-block) one can expect that the micelles of spherical shape with A, C, or A/C-core and B-corona are formed (see Figure 1).

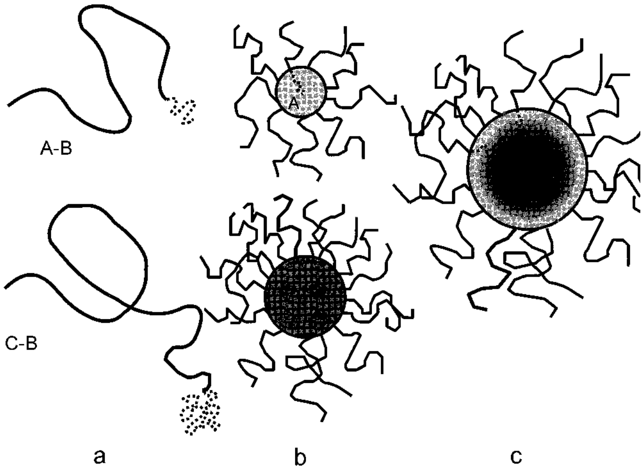

Figure 1. Two block-copolymer chains blended in the present system (a) and schematic representation of possible types of aggregates in the solution: (b) "pure" micelles and (c) "mixed" micelles.

For the theoretical viewpoint, we have previously described in refs 13 and 15, the two main points which we will use in the derivation. In ref 13 we have considered the microphase separation in the *melts* of two types of block-copolymers considered in the present paper. In particular, we have calculated in detail the free energy of A/C core in the comicelle, and we will use the result of this calculation for the present analysis. In ref 15 we proposed theoretical approach to describe the process of micelle formation in the solutions of block-copolymers with one polyelectrolyte and one uncharged block, describing this process as a set of association−dissociation reactions with certain chemical constants. We will use the same approach here for the more complicated situation when the micelle is characterized by two aggregation numbers (number of A- and C-blocks in the core), rather than by one aggregation number. In considering these points, present paper will follow the following plan: In the next section we will describe in detail the model, theoretical methods and present the theoretical calculations. The results following from these calculations are described in section 3, and section 4 contains the discussion of the results, comparison with experimental data, and conclusions.

2. Model and Theoretical Calculations

Let us characterize the solution of the micelles by the volume fraction $\Phi_{m,n}$ occupied by the *cores* of aggregates $A_{m,n}$ containing of m $A-B$ and n $C-B$ chains. One can imagine the process of micellization and comicellization in the present

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system as a set of reactions

$$A_{m,n} \leftrightarrow A_{m,n-1,n} + A_1^{\mathrm{A-B}} \qquad A_{m,n} \leftrightarrow A_{m,n-1,n} + A_1^{\mathrm{C-B}} \tag{1}$$

of associating (or dissociating) of single chains A_1^{A-B} and A_1^{C-B} to the micelle.

To define the volume fractions $\Phi_{m,n}$ of different aggregates, we consider the equilibrium conditions for the processes (1). These conditions are defined by the relation

$$\mu_{m,n} = m\mu_{A-B} + n\mu_{C-B} \tag{2}$$

where $\mu_{m,n}$ is the chemical potential of the corresponding m,n-micelle and μ_{A-B}, μ_{C-B} are the chemical potentials of the free floating chains.

In this paper we will stay, for the simplicity, within the framework of the Flory lattice theory,[14] i.e., we will assume that each monomer unit and each solvent molecule occupies one lattice site, the total number of available sites being equal to n_0. The volume of the solution is then $V = n_0a^3$, where a is the elementary lattice spacing. In all subsequent formulas we will express all the length scales in the units of a. In this model the free energy F of the dilute solution of micelles can be written as

$$\frac{\mathbf{F}}{n_0} = \frac{\Phi_{A-B}kT}{N_A}\ln\Phi_{A-B} + \Phi_{A-B}F_{A-B} + \frac{\Phi_{C-B}kT}{N_C}\ln\Phi_{C-B} + \Phi_{C-B}F_{C-B} + \sum_m\sum_n\left[\frac{\Phi_{m,n}kT}{N_A(1+pf_{m,n})Q_{m,n}}\ln\Phi_{m,n} + \Phi_{m,n}F_{m,n}\right] \tag{3}$$

where T is temperature, k is Boltzmann constant, $\Phi_{m,n}$ is the volume fraction occupied by the cores of aggregates formed by m $A-B$ and n $C-B$ chains, $Q_{m,n} = m + n$ and $f_{m,n} = n/(m+n)$ are the aggregation number and the fraction of the long chains of the micelle, parameter $p \equiv (N_C - N_A)/N_A$ shows the difference in the lengths of the blocks, and $F_{m,n}$ is the energy of the corresponding aggregate (per one lattice cell). We suppose that polymer concentration in the solution is low, so that different aggregates do not interact with each other. From eq 3 it follows that chemical potential of each solution component is given by

$$\begin{aligned}\mu_{m,n} &= kT\ln\Phi_{m,n} + N_AQ_{m,n}(1+pf_{m,n})F_{m,n}\\ \mu_{A-B} &= kT\ln\Phi_{A-B} + N_AF_{A-B}\\ \mu_{C-B} &= kT\ln\Phi_{C-B} + N_CF_{C-B}\end{aligned} \tag{4}$$

Keeping in mind eq 2, we obtain

$$\ln\Phi_{m,n} = -\frac{Q_{m,n}}{kT}[N_A(1+pf_{m,n})F_{m,n} - f_{m,n}N_CF_{C-B} - (1-f_{m,n})N_AF_{A-B}+] + m\ln\Phi_{A-B} + n\ln\Phi_{C-B} \tag{5}$$

and the volume fraction of the component m,n (the distribution function) is given by

$$\Phi_{m,n} = \xi_{A-B}^m\,\xi_{C-B}^n\exp\left[-\frac{N_AQ_{m,n}(1+pf_{m,n})F_{m,n}}{kT}\right] \tag{6}$$

where

$$\xi_{A-B} = \Phi_{A-B}\exp\left[\frac{N_AF_{A-B}}{kT}\right] \qquad \xi_{C-B} = \Phi_{C-B}\exp\left[\frac{N_CF_{C-B}}{kT}\right] \tag{7}$$

The free energy of the micelle can be written as a sum of three terms

$$F_{m,n} = F_1 + F_2 + F_3 \tag{8}$$

where F_1 is the free energy of collapsed A- and C-blocks inside the core of the micelle, F_2 is the contribution due to the surface tension, and F_3 is the free energy of the swollen corona. We will write below the expressions for F_1, F_2, and F_3 using some assumptions. First, we will assume that the core does not contain any solvent molecules, so that we can apply our consideration of the mixed core developed for the melt in our previous work.[13] Second, we will suppose that the surface tension coefficient on the boundary of A/C-core and B-corona swollen with the solvent is always constant. Then, according to ref 13 the free energy of the core of the mixed micelle with aggregation number $Q = m + n$ and fraction of C-blocks $f = n/(m + n)$ can be written as

$$\frac{F_1}{kT} = \frac{Q^{2/3}(1+pf)^{2/3}}{N_A^{4/3}(1+p(1-\alpha)^{1/2})^5}\beta(\alpha,p) \tag{9}$$

where α is the dimensionless parameter varying in the range 0−1 connected with the fraction of C-blocks in the core via the relation

$$f = \left[(1+p(1-\alpha)^{1/2})((1-\alpha)^{1/2} - \alpha\,\mathrm{arcth}(1-\alpha)^{1/2}) - \frac{1}{3}(2+5p^2)(1-\alpha)^{3/2} - p\left(\frac{1}{3} - \alpha + \frac{2\alpha^{3/2}}{3}\right)\right]\Big/ \left[\frac{1}{3} - \frac{2}{3}p^2(1-\alpha^{3/2}) + p(1+p(1-\alpha)^{1/2})((1-\alpha)^{1/2} + \alpha\,\mathrm{arcth}(1-\alpha)^{1/2}) - \frac{p}{3}(1-\alpha)^{1/2}(1+2\alpha)\right] \tag{10}$$

and the function $\beta(\alpha,p)$ defines the dependence of the free energy F_1 on the composition of the micelle and is given by[13]

$$\beta(\alpha,p) = \frac{1}{15} + p(1-\alpha)^{1/2}\left(1 - \frac{5}{3}\alpha\right) + p(1+p(1-\alpha)^{1/2})\alpha\,\mathrm{arcth}[(1-\alpha)^{1/2}] + p^2(1-\alpha)\left(1+\frac{2}{3}\alpha\right) + p\left(\frac{p^2}{5} - \frac{2}{3}\right)(1-\alpha)^{5/2} - \frac{8}{15}p^2(1-\alpha^{5/2}) \tag{11}$$

The surface free energy can be written in the following form (cf. ref 13):

$$\frac{F_2}{kT} = \gamma\frac{1}{N_A^{1/3}Q^{1/3}(1+pf)^{1/3}} \tag{12}$$

where γ is the surface tension coefficient associated with the micellar boundary.

And to complete it all, the free energy of swollen corona for the case when the B-blocks are much longer in comparison with A- and C-blocks can be written in the form originally proposed by Birshtein and Zhulina (see ref 16):

$$\frac{F_3}{kT} = \frac{Q^{1/2}}{N_A(1+pf)}\ln\left[\frac{N_B}{Q^{2/9}(1+pf)^{5/9}N_A^{5/9}}\right] \tag{13}$$

Equations 6−13 completely define the distribution functions for the micelles of given size and composition.

3. Results

The investigation of distribution function 6 allows us make necessary conclusions about the micellization and comicellization in the solution mixture of block-copolymers. One can find five different regimes of the system.

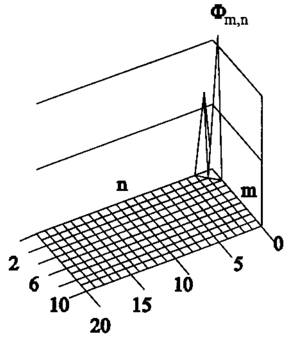


Figure 2. The schematical representation of the two-dimensional volume fraction distribution function corresponding to regime I. Two peaks show existence of unimers of both sorts of block-copolymers in the solution.

Regime I. The polymer volume fraction is extremely low, so all the chains are floating independently (unimers). The distribution function in this regime corresponds to that schematically shown in Figure 2.

The numbers of the chains of both types in the micelle, m and n, are shown on the horizontal axes of the hystogram. The volume fraction $\Phi_{m,n}$ of the aggregate of given content is shown on the vertical axis. For regime I, due to the presence in the solution of unimers only, the distribution function has two peaks centered at $m = 0, n = 1$ and $m = 1, n = 0$.

Regime II. When the concentration of the $C-B$ component is increased, the "pure" micelles containing long chains are first formed in the solution. Most of the short chains are floating independently in the form of unimers. (Here and below the statement like "aggregates of one sort or another exist" should be understood in the sense that the local maximum of the distribution function corresponds to the micelles of this type. For instance in this particular case some $A-B$ chains can form comicelles with $C-B$, but the fraction of these aggregates is less than fraction of "pure" micelles.) The distribution functions corresponding to this regime are shown in the Figures 3a and 4a.

Regime III. When "pure" $C-B$ micelles are already formed, upon further increase of the overall solution concentration at the fixed ratio of short and long chains, shorter $A-B$ chains are being included into the mixed micelles at the concentrations below the cmc for these chains (Figure 3b).There are two maxima of the distriburion function corresponding to the coexistence of comicelles and the unimers of short $A-B$ chains. Long $C-B$ chains do not form "pure" micelles but all of them are included into the comicelles.

Regime IV. Above the cmc for $A-B$ chains, they are partly included into the "mixed" micelles and the excess of the chains form "pure" $A-B$ micelles. So, one can observe the micelles of two different types in the solution (Figure 3c). In this regime the possibility of forming pure aggregates containing short chains is of great importance. Therefore, the distribution function exhibits two maxima corresponding to the coexistence of comicelles and micelles including only short $A-B$ chains. The distribution functions characteristic for this regime are shown in the Figures 3c and 4b.

Regime V. In this situation chains of two sorts form comicelles of approximately equal size and composition. The two-dimensional distribution function for this case is shown in Figure 5. It should be noted that this

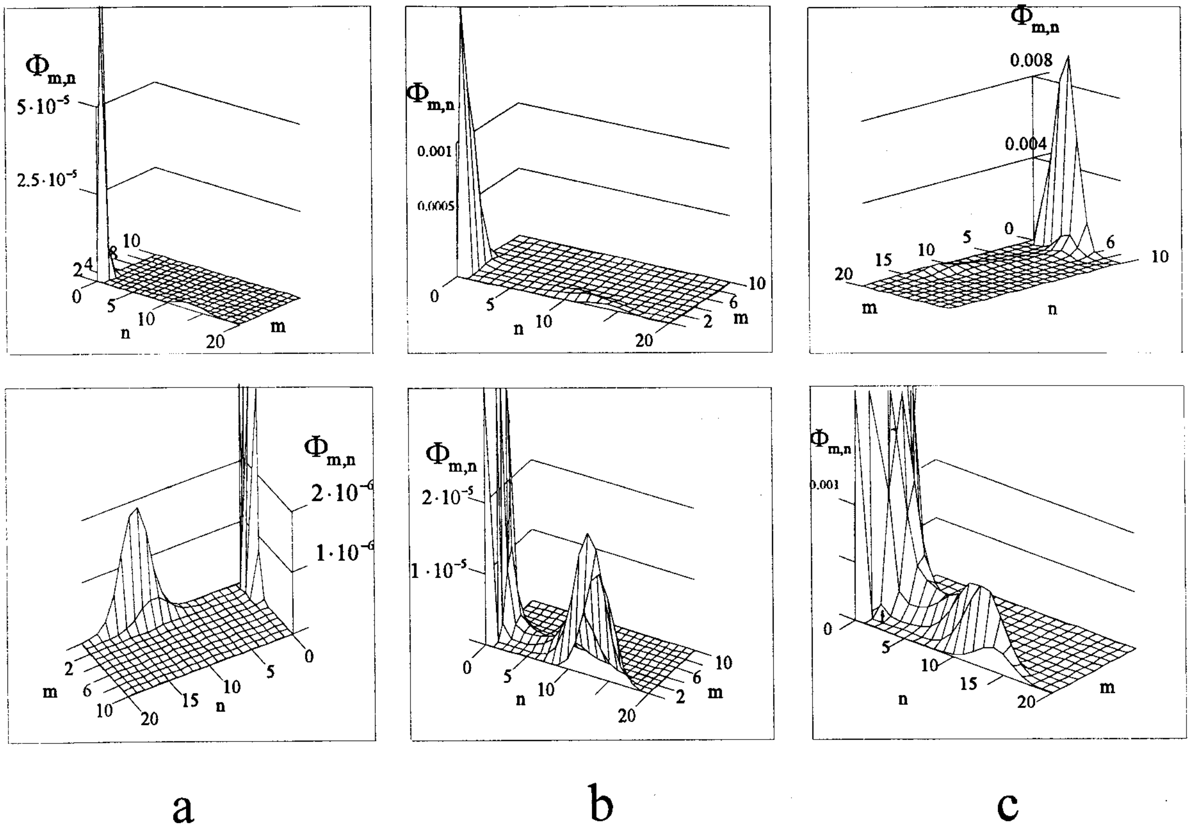
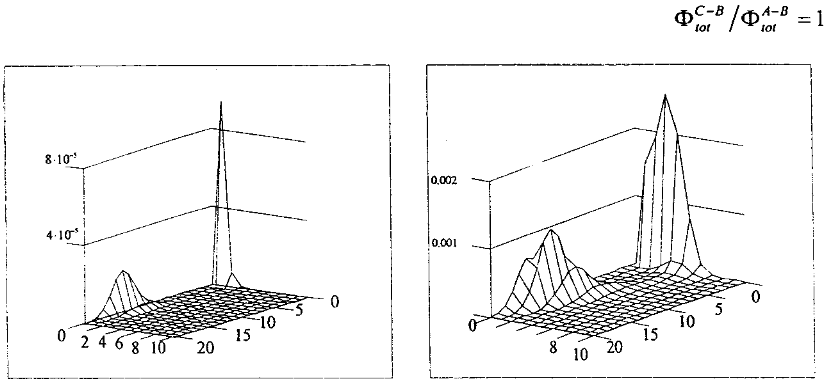


Figure 3. The evolution of the volume fraction distribution function with the increase of the total polymer concentration for the composition $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 1/10$. Part a corresponds to regime II (point A in Figure 3); parts b and c correspond to regimes III and IV (points A′ and A″ in Figure 3). All the distribution functions are shown with the use of two different scales on the vertical axis, and occasionally from two different viewpoints for the sake of better displaying of different peaks.



$\Phi_{total} = 2 \cdot 10^{-4}$
a

$\Phi_{total} = 2 \cdot 10^{-2}$
b

Figure 4. The evolution of the two-dimensional volume fraction distribution function with the increase of the total polymer volume fraction for the composition $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 1/1$. These two distributions correspond to the points B (a) and B′ (b) in Figure 3.

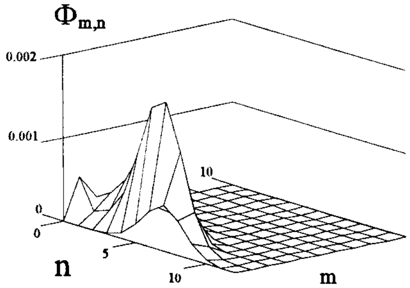


Figure 5. The two-dimensional volume fraction distribution function corresponding to regime V. The peak shows existense of comicelles in the solution.

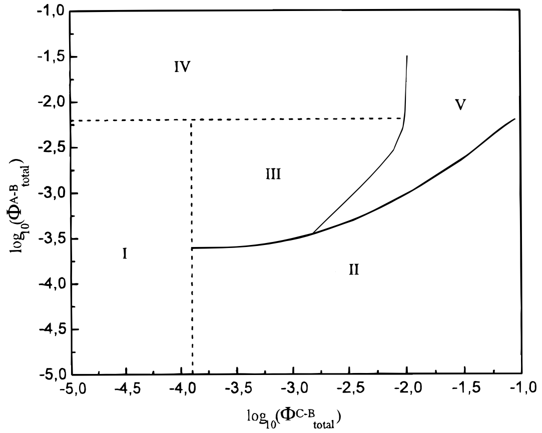


Figure 6. The diagram of possible regimes for the solution of block-copolymers at $N_A = 25$, $N_B = 1000$, $p = 0.7$, and $\gamma = 3$. Dash vertical and bold horizontal lines show the volume fraction of both types of chains corresponding to the appearance of “pure” micelles.

regime of the solution can exist if the difference in the lengths of *A*- and *C*-blocks is not so great and the concentration of polymer in the solution is relatively high (see Figure 6 for the location of this regime in the diagram of states). This regime cannot be observed when the difference in the lengths of insoluble blocks is large.

The state diagrams of Figures 6 and 7 show different possible regimes of the solution for two different sets of parameters of the chains. The volume fractions Φ^{total}_{A-B} and Φ^{total}_{C-B} corresponding to the axes of the diagrams

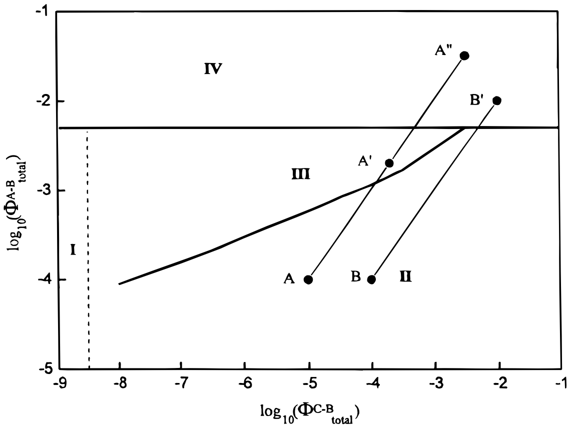


Figure 7. The diagram of possible regimes for the solution of block-copolymers at $N_A = 25$, $N_B = 1000$, $p = 2$, $\gamma = 3$. Line **A**−**A′**−**A**" corresponds to the composition $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 1/10$; line **B**−**B′** corresponds to the composition $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 1/1$.

are given by

$$\begin{aligned} \Phi^{total}_{A-B} &= \sum_m \sum_n \Phi_{m,n} \frac{(1+p)n}{m+(1+p)n} \\ \Phi^{total}_{C-B} &= \sum_m \sum_n \Phi_{m,n} \frac{m}{m+(1+p)n} \end{aligned} \tag{14}$$

The volume fractions (14) are proportional to the concentration of the core-building components of the corresponding block-copolymers in the solution.

Three diagrams of Figures 6 and 7 show the change in the solution behavior with varying of the parameter *p*. The increase of this value leads to the deterioration of the mixing ability of the *A* and *C* chains inside the aggregates, i.e., to the coexisting of the aggregates of two sorts. Two lines **A**−**A′**−**A″** and **B**−**B′** shown in Figure 7 correspond to the fixed compositions of the system $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 0.1$ and $\Phi^{total}_{C-B}/\Phi^{total}_{A-B} = 1$ and to the increase of polymer volume fraction. As one moves along these lines toward the region of higher concentrations, one can see the changes in the behavior of the solution. Figures 3 and 4 display the characteristic forms of the two-dimensional distributions of the micellar aggregation numbers corresponding to the different regions of the diagrams. Figure 3 corresponds to the situation when the volume fraction of the long chains is much less than the volume fraction of $A-B$ chains (curve $\mathbf{A}-\mathbf{A}'-A''$ in Figure 7). In this case, as the total polymer concentration rises, the long chains are the first to form micelles, while short chains are still not aggregated (regime II, Figure 3a). Short chains then start to be included into the micelles of long chains (regime III, Figure 3b). Finally, the micelles including only short chains are also formed, and they coexist with mixed micelles (regime IV, Figure 3c). Figure 4 corresponds to the situation when both block-copolymers are dissolved at the equal proportion. As is seen, in this case regime III is missing, since the aggregation of the chains into the comicelles is supressed by active forming of “pure” $A-B$ micelles. There are ′pure′ micelles consisting of long chains and comicelles with low content of short chains at the point **B** (Figure 4a). The distribution function maximum corresponds to the “pure” $C-B$ micelles. Figure 4b corresponds to the point **B′** in the Figure 7. In this case total concentration of $A-B$ chains is higher than cmc for these chains, and the distribution function has two maxima. One of them corresponds to the “pure” $A-B$ micelles, while another to the comicelles with low content of short chains. At the same time the relative content of unimers of $A-B$ chains in the solution decreases. (This can be seen from Figure 4, since the peak of volume fraction of “pure” $A-B$ micelles “moves” toward the larger micelles.)

4. Discussion

We have developed the theory for the micelle formation in dilute solution mixtures of two block-copolymers ($A-B$ and $C-B$) with very long soluble B-blocks and chemically identical insoluble blocks A and C differing in length. Due to the difference in the lengths of hydrophobic blocks A and C, the micelles of two different sizes can be formed in the solution. Presence of longer $C-B$ chains in the system leads to the inclusion of $A-B$ chains in the mixed micelles below the cmc for these chains. These conclusions are in good agreement with the experimental results of T. Nose et al. in refs 10 and 11. Namely, in these papers the micelle formation in the mixture of poly(α-methylstyrene)-*block*-poly(*p*-vinylphenethyl alcohol)s (Pα MS−PVPA) differing in the lengths of Pα MS blocks in the benzyl alcohol was studied by means of static an dynamic light scattering. The critical micellization temperature of one sort of copolymer was found to be lower than that of another. The characteristics of the micelles were measured after single-step and double-step temperature jumps from the unimer region. The authors of refs 10 and 11 reached the following conclusions. In the region where only long chains could form micelles, while short chains alone are nonaggregating (at the temperature T_1), comicelles were observed for the mixture of copolymers. In the region where both copolymers formed micelles in their respective pure solutions (at the temperature $T_2 < T_1$), the two different ways of comicellization were observed. If copolymers were mixed in the equal proportion, comicelles with the average composition equivalent to that for the overall solution were observed. For the case of high relative fraction of short chains in the mixture the excess part of short chains formed “pure” micelles. Figure 6 of ref 11 displays the schematic representation of the conclusions made from the experimental data. The data of this figure are in qualitative agreement with our theoretical results (see distributions shown in Figures 3−5). In our investigation we consider the micellization process which occurs upon variation of concentrations of the components rather than temperature; however, the parameters of the aggregates at the temperature T_2 qualitatively correspond to those of regimes III−V in the Figure 6 of the present paper. The geometrical proportions of the $A-B$ and $C-B$ chains we set for the Figure 6 are close to the parameters of the samples KT-326 and KT-327 of the ref 11, except we increased the length of the soluble block N_B. However, this change of parameters did not play a significant role, since the dependence on the length of the soluble B block was weak due to presence of the factor ln N_B in the eq 13.

In the case of varying temperature the situation should be qualitatively similar, since by changing the temperature we change the relative distance to cmc. In principle, regimes I−V on the phase diagram should remain, although the critical micellization concentrations differ with temperature. This means that there should be a wide region on the phase diagram where the distribution function for the aggregation of block-copolymers in the micelles is bimodal, corresponding to the equilibrium coexistence of mixed micelles and pure micelles made of shorter block-copolymers. This is in agreement with the experimental findings of refs 10 and 11.

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