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Solution-Phase Equilibria for Block Copolymers in Selective Solvents

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ABSTRACT: Association equilibria, the spinodal equation, and the equation for critical points in solutions of block copolymers in selective solvents are calculated. It is shown that the association equilibrium is profoundly influenced by interactions between the several species in such systems. Model calculations show that in the transitional region between molecular and micellar block copolymer solutions, an immiscibility regime in a temperature-composition diagram can be expected.

Introduction

The phase behavior of systems containing block copolymers is more complex than that of systems containing homopolymers because the former involves two or more chemically different blocks. Interactions between the blocks usually are repulsive, causing some separation of the blocks within a polymer coil. As a result, a system may undergo a microphase as well as a macrophase separation. The formation of micelles is an example of microphase separation of block copolymers in selective solvents,[1] i.e., those which preferentially solvate one or other of the blocks.

In addition to the appearance of two phases (one of which is nearly pure solvent and the second a concentrated micellar solution),[2,3] in some cases large micellar aggregates[4,5] or a "closed" regime of immiscibility in a temperature-composition diagram is observed[6-11] in the transitional region between a solution of molecularly dissolved copolymer and a stable micellar solution; this phenomenon is usually denoted "anomalous micellization". A necessary condition for the occurrence of this phenomenon has been assumed to be the presence of some insoluble impurities in the block copolymer.[7,9,10]

A theoretical analysis of the phase behavior in systems containing a block copolymer has been presented by Hong and Noolandi.[12] Their results indicate the complexities of the phase behaviors in these systems relative to that of homopolymers. However, their analysis did not include interactions between all species in the system and did not explain the closed immiscibility regime at high temperature.

The goal of the present contribution is to analyze the phase behavior of block copolymer solutions in a selective solvent by using the simple Flory-Huggins theory and an association model for the micellization of block copolymers.

Association Equilibrium and the Spinodal Equation

The association of block copolymer chains in solution can be described as one of two extreme cases. The first is the formation of aggregates that are unlimited in size, i.e., open association:[13]

$$A_1 + A_m \rightleftarrows A_{m+1} \qquad m = 1, 2, 3, \ldots \tag{1a}$$

where A_1 denotes an unassociated copolymer chain. In the second case, the aggregates all contain a constant number n of chains (the association number) and are in equilibrium with the remaining molecularly dissolved (unassociated) copolymer chains, i.e., closed association:[13]

$$nA \rightleftarrows A_n \qquad n = \text{constant} \tag{1b}$$

Most of the observed cases of block copolymer micellization in selective solvents can be described as a closed association.[1]

In this analysis, we assume that three types of components exist in a micellar solution: unimers, or molecularly dissolved block copolymer molecules (denoted as component 1); micelles, or aggregates of n block copolymer molecules (denoted as component 2); and solvent molecules (denoted as component 0). The interactions between the species are described by the effective interaction parameters χ_1 (unimer-solvent), χ_2 (micelle-solvent), and χ_{12} (unimer-micelle). The Gibbs free energy of mixing per unit volume of solution for closed association can be expressed, following Flory's procedure,[14] as

$$\frac{\Delta G_v}{RT} = \phi_0 \ln \phi_0 + \frac{1}{r}\left\{\phi_1 \ln \phi_1 + \left(\frac{\phi_2}{n}\right)\left[\frac{\Delta G^\circ_n}{RT} + \ln \phi_2\right]\right\} + (\chi_1\phi_1 + \chi_2\phi_2)\phi_0 + \chi_{12}\phi_1\phi_2 \tag{2}$$

where ϕ_0 is the solvent volume fraction, ϕ_1 and ϕ_2 are the volume fractions of the unimers and the micelles, respectively, n is the association number, r is the degree of polymerization of the copolymer, and ΔG°_n is the change in the standard Gibbs free energy associated with the micellization described by eq 1b.

At equilibrium, the condition

$$\left[\frac{\partial \Delta G_v}{\partial \phi_1}\right]_{T,P} = \left[\frac{\partial \Delta G_v}{\partial \phi_2}\right]_{T,P} \tag{3}$$

must be fulfilled.[15] The application of this condition to eq 2 leads to the relation between the equilibrium concentrations of unimers, ϕ_1, and micelles, ϕ_2:

$$\phi_2 = K\phi_1^{\,n} \exp(-rn\chi_{\text{eff}}) \tag{4}$$

where

$$K = \exp\left[(n-1) - \frac{\Delta G^\circ_n}{RT}\right] \tag{4a}$$

$$\chi_{\text{eff}} = (\chi_2 - \chi_1)\phi_0 + \chi_{12}(\phi_1 - \phi_2) \tag{4b}$$

$$\phi_1 + \phi_2 = \phi_P \tag{4c}$$

K is the equilibrium association constant and ϕ_P is the total volume fraction of copolymer in solution.

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By using a general thermodynamic procedure, Pouchlý and Sikora showed[15] that the conditions of the spinodal curve and the critical point for a binary system in which one component is aggregated are changed to conditions for a polydisperse mixture with a distribution of species determined by an association equilibrium. The condition of phase stability for a polydisperse system according to Gibbs[16] is

$$|G_{\mathrm{SP}}| = \left|\frac{\partial^2 \Delta G_v}{\partial \phi_i \partial \phi_j}\right|_{T,P} = 0 \qquad (5)$$

for the spinodal. Indexes i and j take the values of 0, 1, ..., $u-1$, where u is the number of components in the system (i.e., three in the system analyzed in this study). The partial derivatives are taken with respect to the $(u-1)$ independent concentration variables. At the critical point, the condition

$$|G_{\mathrm{C}}| = 0 \qquad (6)$$

must be fulfilled, where $|G_{\mathrm{C}}|$ is the determinant formed from the spinodal determinant $|G_{\mathrm{SP}}|$ by replacement of the elements in an arbitrary line by $\partial|G_{\mathrm{SP}}|/\partial\phi_1$, $\partial|G_{\mathrm{SP}}|/\partial\phi_2$, ..., $\partial|G_{\mathrm{SP}}|/\partial\phi_u$.

If we choose as the independent concentration variables ϕ_1 and ϕ_2, then the application of conditions (5) and (6) to eq 2 for an equivalent polydisperse polymer solution leads to the spinodal equation

$$\begin{aligned}\frac{1}{\phi_0} + \frac{1}{r(\phi_1 + n\phi_2)} - 2\left(\frac{\phi_0(\phi_1\chi_1 + n\phi_2\chi_2) + r(n\phi_1\phi_2\chi_{12})}{\phi_0(\phi_1 + n\phi_2)}\right) + \\ \frac{r(n\phi_1\phi_2)}{\phi_1 + n\phi_2}[2(\chi_1 + \chi_2)\chi_{12} - (\chi_1 - \chi_2)^2 - {\chi_{12}}^2] = 0 \qquad (7)\end{aligned}$$

and the equation of the critical point at composition ϕ_0^{c}, ϕ_1^{c}, ϕ_2^{c} is given by

$$\begin{aligned}&\frac{1}{\phi_0^{\mathrm{c}} r(\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}})}\Bigg\{(1-2\epsilon)\frac{(n-1)}{\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}}} + \\ &2r\left[(n\chi_{12} - \chi_1) - \frac{\bar{\chi}}{2}rn(\phi_1^{\mathrm{c}} - \phi_2^{\mathrm{c}})\right]\Bigg\} - \frac{1}{r^2(\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}})n\phi_2^{\mathrm{c}}} \times \\ &\Bigg\{(1-2\epsilon)\frac{1}{\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}}} + 2\left[r\chi_1 + \frac{\chi_{12}}{(\phi_0^{\mathrm{c}})^2} - \frac{\bar{\chi}}{2}(r^2 n) - \phi_2^{\mathrm{c}}\right] + \\ &\frac{1}{rn\phi_2^{\mathrm{c}}(\phi_0^{\mathrm{c}})^2} + \frac{1}{(\phi_0^{\mathrm{c}})^2}(\delta\chi - 2\chi_2) - \frac{(1-2\epsilon)}{r^2(\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}})^2} \times \\ &(n\delta\chi - 2\chi_2) - \frac{2}{r(\phi_1^{\mathrm{c}} + n\phi_2^{\mathrm{c}})}\Bigg[r(n\chi_2\delta\chi - 2\chi_1\chi_2) + \\ &\frac{\chi_{12}}{(\phi_0^{\mathrm{c}})^2}(\delta\chi - 2\chi_2)\Bigg] - \frac{r^2 n\bar{\chi}}{2}(\phi_1^{\mathrm{c}}\delta\chi - 2\phi_2^{\mathrm{c}}\chi_2)\Bigg\} = 0 \qquad (8)\end{aligned}$$

where

$$\epsilon = r(\phi_1^{\mathrm{c}}\chi_1 + n\phi_2^{\mathrm{c}}\chi_2) + \frac{\chi_{12}}{(\phi_0^{\mathrm{c}})^2} - \frac{\bar{\chi} r^2 n \phi_1^{\mathrm{c}}\phi_2^{\mathrm{c}}}{2} \qquad (8a)$$

$$\bar{\chi} = 4\chi_1\chi_2 - (\chi_1 + \chi_2 - \chi_{12})^2 \qquad (8b)$$

$$\delta\chi = \chi_1 + \chi_2 - \chi_{12} \qquad (8c)$$

The matrix elements corresponding to $|G_{\mathrm{SP}}|$ are the same as those for an equivalent polymer–polymer–solvent ternary system.[17]

For a monodisperse copolymer forming micelles with constant association number n, the concentrations of unimers ϕ_1 and micelles ϕ_2 are not independent, but are related by eq 4 for the association equilibrium. Solving eqs 4 and 7, we can obtain the spinodal curves of the block copolymer micellar solution.

Discussion

For our model calculations, we shall consider a block copolymer with a total degree of polymerization $r = 100$ and monodisperse micelles with an association number $n = 10$. For our purposes, the form of the micelles is not critical. We can assume that the virial coefficients of the micelles and the unimer are different and allow interactions between particles in the system to be characterized by different effective interaction parameters χ_i.[19] The relations between these and the parameters characterizing interactions of the homopolymers with solvent and each other, χ_{AS}, χ_{BS}, and χ_{AB}, respectively, are very complex[20,21] for copolymers. Because the energy involved in the macroscopic phase separation is documented by interparticular interactions, it is not necessary to use these parameters, and we can use the simple effective interaction parameters χ_i in the range of values usually found for polymers. The effective interaction parameter χ_2 (micelle–solvent) is lower than the effective interaction parameter χ_1 (unimer–solvent) as a result of solvent expulsion from the micellar core. The parameter χ_1 generally depends on the composition of the copolymer, and its magnitude increases with increasing content of insoluble blocks. The parameter χ_{12} is assumed to be small and positive, as it generally is for two interacting nonpolar polymers. The temperature dependences of the χ's are expressed in the usual form

$$\chi = \alpha + \frac{\beta}{T} \qquad (9)$$

where α and β are constants. The micellization of block copolymers strongly depends on copolymer–solvent interaction;[18] therefore the value of the micellization equilibrium constant K should increase with increasing χ_1. We consider K in the general form

$$\ln K = \gamma + \frac{\delta}{T} \qquad (10)$$

The constants γ and δ are chosen so that micellization takes place in the temperature range 300–350 K.

Equation 4 describes the influence of interactions between species in a system on the association equilibrium. It is obvious that even small differences in the interactions result, in a polymer system, in a large displacement of the association equilibrium because of the large magnitudes of r and n. This effect is demonstrated in Figure 1, where the dependence of the weight fraction of the copolymer in unimer form, $w_1 = \phi_1/\phi_{\mathrm{P}}$, on the total copolymer concentration in solution is shown for different values of χ_{eff} at 306 K. For $\chi_{\mathrm{eff}} = 0$ (curve 1, Figure 1), eq 4 is transformed into the familiar quasi-chemical equilibrium equation. For the selected value of $K = 8.6 \times 10^{-25}$, no association takes place; all the copolymer is dissolved in the form of unimers ($w_1 = 1$). More advantageous interaction of aggregates with the solvent ($\chi_2 < \chi_1$) shifts the equilibrium toward micelle formation (curve 2, Figure 1). The critical micellar concentration (cmc) is shifted to a lower concentration range. The influence of the inter-

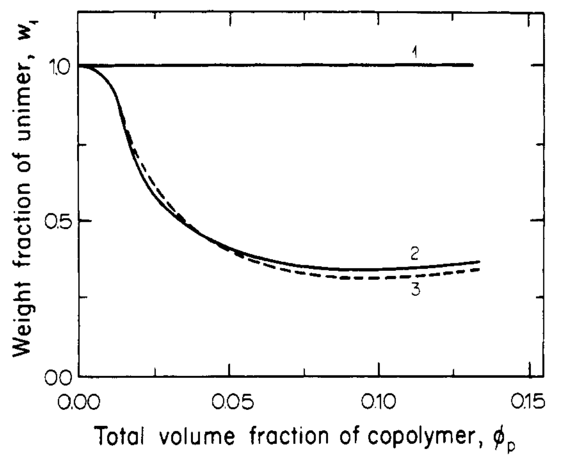

Figure 1. Dependence of the weight fraction of copolymer forming in micelles, w_1, on the total concentration of copolymer in solution, ϕ_P. $T = 306$ K, $\ln K = -395.1 + 105340/T$, $r = 100$, $n = 10$; curve 1, $\chi_1 = \chi_2 = \chi_{12} = 0$; curve 2, $\chi_1 = 0.4684 + 45.75/T$, $\chi_2 = 0.3776 + 45.75/T$, $\chi_{12} = 0$; curve 3, χ_1 and χ_2 are the same as for curve 2, $\chi_{12} = 0.0075$.

action between unimers and micelles (χ_{12}) depends on the difference in their actual concentrations in the solution. Below the cmc (where ϕ_1, = ϕ_P and $\phi_2 = 0$), a repulsive interaction $\chi_{12} > 0$ acts against micellization, whereas above the cmc ($\phi_2 > \phi_1$), the same interaction shifts the micellization equilibrium toward higher concentrations of micelles (curve 3, Figure 1). However, in the region of low total copolymer concentration, the influence of χ_{12} is relatively small. The influence of the term containing χ_{eff} on the micellization equilibrium decreases as the equilibrium association constant K increases.

The theoretical analysis of diblock copolymer micellization by Munch and Gast[18] shows a decrease in the cmc and the association number n as the value of the equilibrium association constant K increases. However, previous results[1] show that the cmc of micellar solutions of block copolymers usually lies at very low concentrations of the copolymer and the association numbers are relatively high, from several tens to several hundreds.[1] This difference between theory and experiment can be explained as a consequence of the influence of effective repulsive interactions between unimers and micelles, characterized by χ_{eff} (eq 4b), on the micellization equilibrium. The effect is pronounced for polymers as a result of the high values of r. Even for low values of K, which according to the theory correspond to high n, a negative value of $(\chi_2 - \chi_1)$ shifts the cmc into the region of low copolymer concentrations (Figure 1).

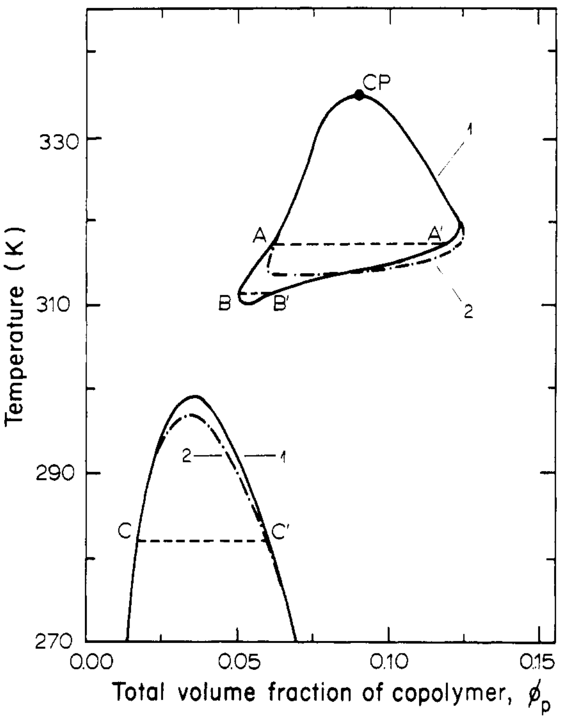

Figure 2. Spinodal curves for a block copolymer in a selective solvent. $\ln K = -395.1 + 105340/T$, $r = 100$, $n = 10$; curve 1, $\chi_1 = 0.4684 + 45.75/T$, $\chi_2 = 0.3776 + 45.75/T$, $\chi_{12} = 0$; curve 2, χ_1 and χ_2 are the same as for curve 1, $\chi_{12} = 0.0075$. CP locates the critical point; dashed lines, e.g., A,A′, connect isothermal points on the spinodals.

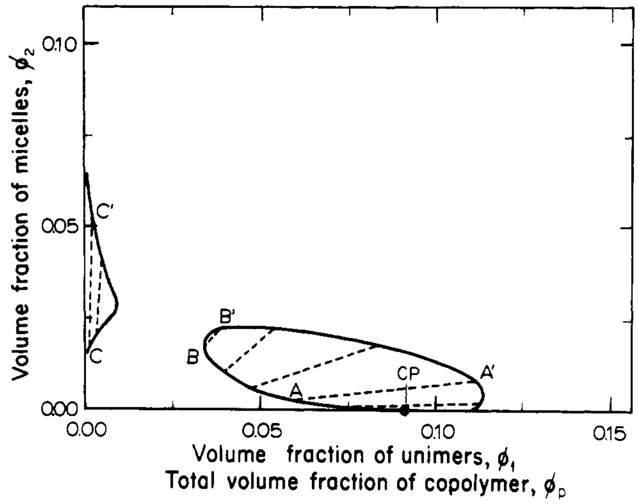

Figure 3. Distribution of a block copolymer between unimer and micelles along the spinodal curves. The parameters and labels are the same as in Figure 2.

Figure 2 shows the calculated spinodal curves for this model. It is important to note that the spinodal curves for aggregated block copolymers in solution are in fact curves in a three-dimensional coordinate system in which the coordinates are temperature T, the total concentration of copolymer ϕ_P (or the concentration of unimer ϕ_1), and the concentration of micelles ϕ_2. The curves in Figure 2 are projections of these spinodal curves onto the plane T,ϕ_P. A closed regime of immiscibility is seen at higher temperatures, and a more typical regime of immiscibility with a UCST (upper critical solution temperature) is apparent at lower temperatures. The total concentration of copolymer on the spinodal is given by the concentration ϕ_P, but the distribution of copolymer between unimers and micelles changes with temperature. The change in the distribution along the spinodal curves is shown in Figure 3. The curves are obtained as the projection of the spinodal curves onto the plane ϕ_1,ϕ_2. These curves are not isothermal cross sections; however, points connected by a dashed line lie at the same temperature (A–A′, B–B′,...). The separated phases differ from each other by the micellar concentration but not by the micellar size.

We now discuss how a copolymer solution in a selective solvent behaves with changing temperature. Above $T = 335$ K in the present model (the critical temperature of the molecularly dissolved copolymer chains), a homogeneous solution exists (Figure 2). As the temperature decreases, phase separation takes place. The separated phases consist of dilute and concentrated unimer solutions (axis ϕ_P, Figure 3). As the temperature continues to decrease, micellization begins in both phases. The concentration of copolymer and its distribution between unimer and micelles on the spinodal curve are given by the points A,A′, B,B′, etc. (Figure 3). The formation of micelles decreases the combinatorial entropy of mixing

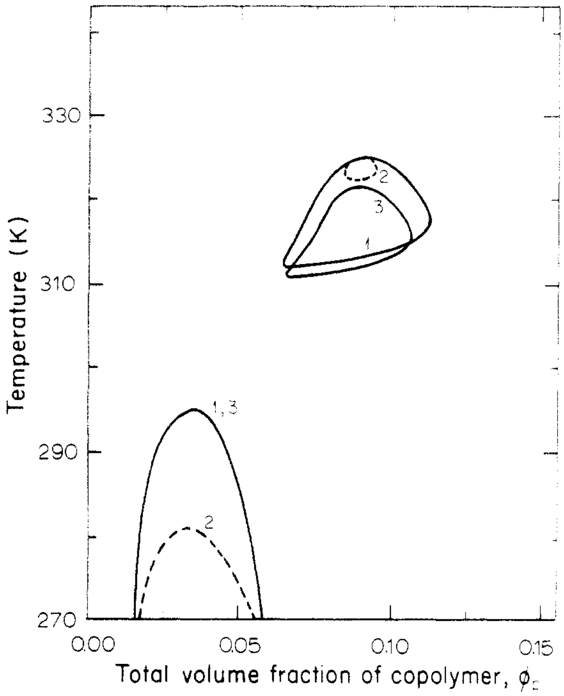

Figure 4. Influence of interaction parameters χ_i on the spinodal curves for a block copolymer solution in a selective solvent. $\ln K = -395.1 + 105340/T$, $r = 100$; $n = 10$; $\chi_{12} = 0$; curve 1, $\chi_1 = 0.4643 + 45.75/T$, $\chi_2 = 0.3762 + 45.75/T$; curve 2, $\chi_1 = 0.4643 + 45.75/T$, $\chi_2 = 0.3695 + 45.75/T$; curve 3, $\chi_1 = 0.4625 + 45.75/T$, $\chi_2 = 0.3762 + 45.75/T$.

and therefore opposes mixing, but the increasing fraction of micelles leads to a favorable enthalpic contribution to the Gibbs free energy of mixing $(\chi_2 - \chi_1)$. As a result of the competition between entropic and enthalpic contributions, the system will homogenize at $T = 311$ K, but in this regime it will be a homogeneous micellar solution. A further temperature drop results in an increase in χ_2; and after the temperature of the system reaches a critical value, phase separation again takes place. The separated phases will now consist of dilute and concentrated micellar solutions (points C–C′, Figure 3).

The influence of interaction parameters χ_i on the spinodal curves is shown in Figures 4 and 5. An increase in the interaction parameter χ_2 (increasingly unfavorable interaction between solvent and micelles) enlarges the high-temperature immiscibility regime (curves 1 and 2, Figure 4); and ultimately, this regime merges with the region of immiscibility at lower temperature (Figure 5). The decrease in the interaction parameter χ_1 (increasingly favorable interaction between solvent and unimer) diminishes the size of the high-temperature immiscibility regime (cf. curves 1 and 3, Figure 4), and eventually, it disappears. We note also that a repulsive interaction between unimer and micelles ($\chi_{12} > 0$) shifts the association equilibrium toward micelle formation and, as a result the closed regime of immiscibility, becomes smaller (curve 2, Figure 2).

The influence of the association equilibrium constant K and the association number n on the spinodal curves of a block copolymer in a selective solvent is shown in Figure 6. Increasing K (i.e., increasing micellization) removes the closed immiscibility regime at higher temperature (see progression in curves 1–3, Figure 6), and the same result is obtained with an increasing value of the association number n (see progression in curves 1, 4, and 5, Figure 6).

Conclusion

The micellization equilibrium in block copolymer solutions is profoundly influenced by interactions between the different species in solution. Even for very weak association forces and low magnitudes of the association equilibrium constant K, micelle formation at low copolymer concentrations can be expected.

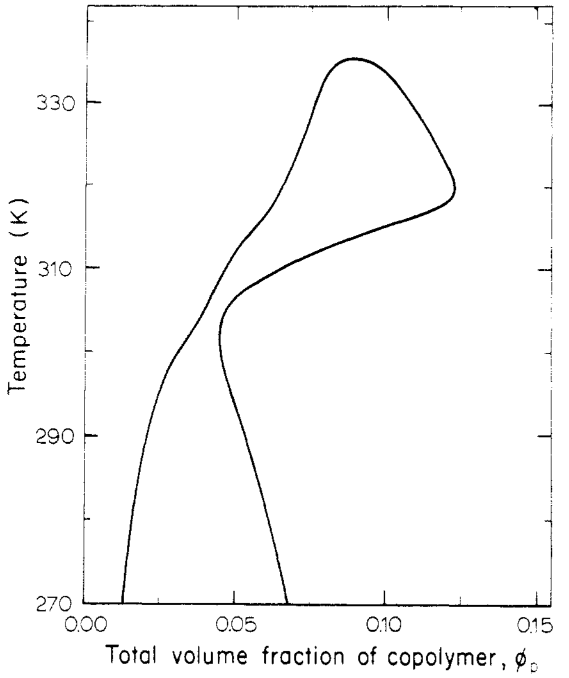

Figure 5. Spinodal curve for a block copolymer solution in a selective solvent. $\ln K = -395.1 + 105340/T$, $r = 100$, $n = 10$; $\chi_1 = 0.4684 + 45.75/T$; $\chi_2 = 0.3784 + 45.75/T$; $\chi_{12} = 0$.

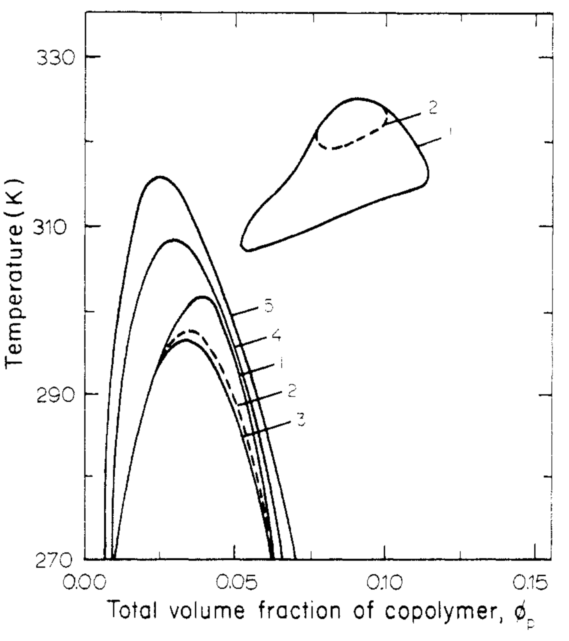

Figure 6. Effect of different values of K and n on spinodal curves for a block copolymer in a selective solvent. $r = 100$, $\chi_1 = 0.4643 + 45.75/T$, $\chi_2 = 0.3776 + 45.75/T$; $\ln K = A + 105340/T$; curve 1, $A = -395.1$, $n = 10$; curve 2, $A = -388.2$, $n = 10$; curve 3, $A = -381.1$, $n = 10$; curve 4, $A = -395.1$; $n = 15$; curve 5, $A = -395.1$, $n = 20$.

As in the case of low-molecular-weight associating systems,[22] a closed regime of immiscibility can be expected even in solutions of monodisperse block copolymers in a selective solvent. The existence of this region is influenced by the upper critical solution temperature of the copolymer solution at the transitional region from molecular to micellar solution (the region of weak association). An experimentally observed phenomenon, anomalous micellization,[6-11] can be identified with the closed immiscibility regime and can be explained as a consequence of the influence of block copolymer aggregation on the macrophase equilibrium in a copolymer solution. The appearance of this regime is most sensitive to the value of the effective interaction parameter χ and to the value of the association constant K or temperature T. The closed immiscibility regime (anomalous micellization) can be expected only for weak association. The observed anomalous micellization has these traits.[7]

On the other hand, the immiscibility regime with a UCST only occurs in the case of a strong association (high values of the association constant K). The separated phases contain different amounts of micelles, but the micellar size is the same in both phases.

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