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REFINED CONTINUOUS THERMODYNAMIC TREATMENT FOR THE LIQUID–LIQUID EQUILIBRIUM OF COPOLYMER SOLUTIONS

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ABSTRACT

Based on an improved calculation of activity coefficients, continuous thermodynamics using a generalized divariate Stockmayer distribution is applied to the liquid-liquid equilibrium of random copolymer solutions. The effects of the chemical polydispersity on the cloud-point curve, the shadow curve, the spinodal, and the critical point are discussed. The theory can account for the occurrence of three-phase equilibria as well as for the phase separation in pure copolymers.

INTRODUCTION

Random copolymers show polydispersity both with respect to molecular weight and with respect to chemical composition. The phase equilibrium can be influenced appreciability by both polydispersities. Continuous thermodynamics based on the divariate Stockmayer distribution is very useful for mathematical description. A simplified version of the lattice model due to Barker was used previously to calculate the activity coefficients [1, 2]. The present paper is based on an improved calculation of the activity coefficients. The phase separation of a pure polydisperse copolymer may be described in this way. Despite the improvement, the calculation of the cloud-point and shadow curves can be reduced to the numerical solution of only one equation that does not contain integrals. Equations for the spinodal, the critical point, and the double critical point are given. By using model calculations, it is shown how the chemical polydispersity influences the phase equilibrium of copolymer solutions. If the phase separations of the copolymer solution and of the pure copolymer are located in the same temperature range, a three-phase equilibrium may occur.

DIVARIATE DISTRIBUTION FUNCTION

A copolymer consisting of two kinds of monomer units, α and β, is considered. If a standard segment is chosen, the segment numbers r_α and r_β can be introduced. Then the total segment number r and the segment fraction Y of the α-monomer units within the molecules are defined by

$$r = r_\alpha + r_\beta \qquad \text{and} \qquad Y = r_\alpha / r. \tag{1}$$

Thus, the composition of a polydisperse copolymer sample may be described by the divariate distribution function $W(r, Y)$ in which $W(r, Y)\, dr\, dY$ gives the segment fraction of all copolymer species with segment numbers between r and $r + dr$ and α-monomer segment fractions between Y and $Y + dY$ [1]. Hence, $W(r, Y)$ has to fulfill the normalization condition

$$\int_r \int_Y W(r,Y)\, dY\, dr = 1 \text{; where } \int_r = \int_{r_0}^{r^0} ; \quad \int_Y = \int_0^1 . \tag{2}$$

The most important moments of this distribution function are

$$\widetilde{1/r} = \int_r \int_Y \frac{W(r,Y)}{r}\, dY\, dr = \frac{1}{\bar{r}}, \tag{3a}$$

$$\tilde{r} = \int_r \int_Y r W(r,Y)\, dY\, dr, \tag{3b}$$

$$\tilde{Y} = \int_r \int_Y Y W(r,Y)\, dY\, dr, \tag{3c}$$

$$\widetilde{Y^2} = \int_r \int_Y Y^2 W(r,Y)\, dY\, dr. \tag{3d}$$

The (-1)st moment $\widetilde{1/r}$ equals the reciprocal of the number-average segment number $\bar{r}$. And $\tilde{r}$, $\tilde{Y}$, $\widetilde{Y^2}$ are the segment-number averages of r, Y, and Y^2, respectively, which usually (i.e., if the densities of the two monomer units are not very different) roughly equal the corresponding weight averages.

For random copolymers, the distribution function obeys the following generalized expression due to Stockmayer [3] :

$$W(r, Y) = \left[\frac{k^{k+1}}{\bar{r}\Gamma(k+1)}\left(\frac{r}{\bar{r}}\right)^k \exp\left(-k\frac{r}{\bar{r}}\right)\right]\left[\sqrt{\frac{\bar{r}}{2\pi\epsilon}} \exp\left\{-\frac{\bar{r}(Y-\tilde{Y})^2}{2\epsilon}\right\}\right], \tag{4}$$

where Γ is the Γ-function. The first factor is a generalized Schulz-Flory distribution with respect to r ($r_0 = 0; r^0 = \infty$). The second factor is a Gaussian distribution with respect to Y. The limits of the domain of definition of a Gaussian function are $-\infty$ and $+\infty$, whereas Y is limited to the range 0 to 1. Nevertheless, the resulting error is very small because random copolymers possess a narrow distribution with respect to chemical composition. The parameters k and ϵ, characterizing the polydispersities of the copolymer, are given by

$$k = [\tilde{r}/\bar{r} - 1]^{-1}, \tag{5a}$$

$$\epsilon = \bar{r}[\widetilde{Y^2} - (\tilde{Y})^2]. \tag{5b}$$

ACTIVITY COEFFICIENTS

For a system containing a solvent A and a copolymer B, the solvent molecule is chosen as the standard segment, for simplicity. To calculate the activity coefficients, an expression for the segment-molar excess Gibbs free energy $\bar{\bar{G}}^E$ of the mixture is needed. Here, $\bar{\bar{G}}^E$ is the excess of Gibbs free energy per mole of segments with respect to a Flory-Huggins mixture (with $\chi = 0$) [1]. Based on a simplified version of Barker's lattice model [4], such an expression can be written on a molecular basis. The residual part of the change of Gibbs free energy of mixing Δg_{res}, i.e., the product of $\bar{\bar{G}}^E$ and the total number of segments of the mixture, reads

$$\Delta g_{\text{res}} = N^*_{\text{A}\alpha}\Delta u_{\text{A}\alpha} + N^*_{\text{A}\beta}\Delta u_{\text{A}\beta} + (N^*_{\alpha\beta} - N^*_{\alpha\beta 1})\Delta u_{\alpha\beta}, \tag{6}$$

where $N^*_{\text{A}\alpha}$, $N^*_{\text{A}\beta}$, and $N^*_{\alpha\beta}$ are contact pair numbers for contacts between solvent segments A and/or between copolymer segments α and β, and $N^*_{\alpha\beta 1}$

is the contact pair number for the heterogeneous system formed by the pure copolymer species. The quantities $\Delta u_{\mathrm{A}\alpha}$, $\Delta u_{\mathrm{A}\beta}$, and $\Delta u_{\alpha\beta}$ are differences of interaction energies of the type

$$\Delta u_{\mathrm{A}\alpha} = u_{\mathrm{A}\alpha} - \frac{1}{2}(u_{\mathrm{AA}} + u_{\alpha\alpha}). \tag{7}$$

When the random mixture assumption is adopted, the contact pair numbers are given by

$$N^*_{\mathrm{A}\alpha} = (1 - \psi)z\sum_i\sum_j r_iY_jN_{ij}, \tag{8a}$$

$$N^*_{\mathrm{A}\beta} = (1 - \psi)z\sum_i\sum_j r_i(1 - Y_j)N_{ij}, \tag{8b}$$

$$N^*_{\alpha\beta} = \psi z\,\frac{\left[\sum_i\sum_j r_iY_jN_{ij}\right]\left[\sum_i\sum_j r_i(1 - Y_j)N_{ij}\right]}{\sum_i\sum_j r_iN_{ij}}, \tag{8c}$$

where N_{ij} is the number of copolymer molecules identified by the segment number r_i and the segment fraction of α-monomers Y_j. ψ is the total segment fraction of all copolymer species, and z is the coordination number of the lattice.

The improvement with respect to the earlier treatment [1, 2] consists in the calculation of $N^*_{\alpha\beta 1}$. In the earlier papers, $N^*_{\alpha\beta 1}$ was, as an approximation, set equal to the value of $N^*_{\alpha\beta}$ resulting from Eq. (8c) for the pure copolymer ($\psi = 1$) that is a mixture of the individual copolymer species. However, Δg_{res} has to refer to the heterogeneous system formed by the pure copolymer species and not to the mixture mentioned. Therefore, the improved expression for $N^*_{\alpha\beta 1}$ has to read

$$N^*_{\alpha\beta 1} = z\sum_i\sum_j r_iY_j(1 - Y_j)N_{ij}. \tag{9}$$

Applying a continuous description, the route outlined earlier [1] leads to

$$\bar{G}^E/RT = \psi(1 - \psi)\chi + \psi c[\widetilde{Y^2} - (\tilde{Y})^2]; \quad \chi = a + b\tilde{Y} + c(\tilde{Y})^2. \tag{10}$$

Here R is the gas constant and T is the absolute temperature, while a, b, and c are given by

$$\begin{aligned} a &= z\Delta u_{\mathrm{A}\beta}/k_{\mathrm{B}}T; \\ b &= z(\Delta u_{\mathrm{A}\alpha} - \Delta u_{\mathrm{A}\beta} - \Delta u_{\alpha\beta})/k_{\mathrm{B}}T; \\ c &= z\Delta u_{\alpha\beta}/k_{\mathrm{B}}T, \end{aligned} \tag{11}$$

where k_{B} is Boltzmann's constant. As a result of this improvement, the term $\psi c\,[\widetilde{Y^2} - (\tilde{Y})^2]$ occurs additionally in Eq. (10). For $\bar{\bar{G}}^E$ this additional term is only a small correction, but for the phase equilibrium calculations an important contribution may arise, as will be shown.

To simplify practical calculations, the abbreviations

$$\nu_b = b/a; \qquad \nu_c = c/a, \tag{12}$$

are introduced, and ν_b and ν_c are assumed to be independent of temperature and pressure. For the segment-molar activity coefficients, $\bar{\bar{\gamma}}_{\mathrm{A}}$ and $\bar{\bar{\gamma}}_{\mathrm{B}}$, the expressions result in

$$\ln \bar{\bar{\gamma}}_{\mathrm{A}} = a\psi^2\,[1 + \nu_b \tilde{Y} + \nu_c(\tilde{Y})^2], \tag{13}$$

$$\begin{aligned} \ln \bar{\bar{\gamma}}_{\mathrm{B}} = a\Big\{&(1-\psi)^2\,[1 + \nu_b\tilde{Y} + \nu_c(\tilde{Y})^2] + (1-\psi)(\nu_b + 2\nu_c\tilde{Y})\,(Y - \tilde{Y}) \\ &+ \nu_c\,(Y - \tilde{Y})^2\Big\} \end{aligned} \tag{14}$$

CLOUD-POINT CURVE AND SHADOW CURVE

The equilibrium between two phases, ′ and ″, is considered where phase ′ is assumed to be known, i.e., the total segment fraction of all copolymer species ψ' and the divariate distribution function of the copolymer $W'(r,Y)$ are given. Then the total segment fraction of the coexisting phase ″ and the equilibrium temperature T at a specified pressure are to be determined. The plot of T against ψ' is called the "cloud-point curve" and the plot of T against ψ'' is called the "shadow curve." Furthermore, one is interested in the distribution function $W''(r,Y)$ of the coexisting phase ″.

The calculation is performed in a way analogous to that described in previous papers [1, 2]. On the basis of a Stockmayer distribution of the type of Eq. (4) for the phase ′, all occurring double integrals may again be calculated analytically. The distribution function $W''(r, Y)$ also proves to be a generalized Stockmayer distribution of the type of Eq. (4) with the same values of k and ϵ. Instead of $\bar{r}'$ and $\tilde{Y}'$, now $\bar{r}''$ and $\tilde{Y}''$ occur, and they are related to $\bar{r}'$ and $\tilde{Y}'$ by

$$\bar{r}'' = \bar{r}' \left(\frac{\psi''}{\psi'} \right)^{1/(k+1)} \tag{15}$$

and

$$\tilde{Y}'' = \tilde{Y}' + \frac{\epsilon a(\nu_b + 2\nu_c \tilde{Y}')(\psi'' - \psi')}{1 - 2\epsilon a \nu_c \psi''}. \tag{16}$$

Two equations are obtained to calculate a, the only parameter in the $\bar{\bar{G}}^E/RT$ relation (Eq. 10) that depends on temperature, and ψ'':

$$\begin{aligned}[1 - 2\epsilon a \nu_c \psi'']^2 &\left\{ \ln \frac{1 - \psi''}{1 - \psi'} - \frac{k}{\bar{r}'} \left[1 - \left(\frac{\psi'}{\psi''} \right)^{1/(k+1)} \right] \right. \\ &\left. + 2a[1 + \nu_b \tilde{Y}' + \nu_c (\tilde{Y}')^2](\psi'' - \psi') \right\} \\ &+ \epsilon a^2 (\nu_b + 2\nu_c \tilde{Y}')^2 (\psi'' - \psi') \left\{ \frac{1}{2}(\psi'' - \psi') + \psi''(1 - 2\epsilon a \nu_c \psi'') \right\} = 0,\end{aligned} \tag{17}$$

$$\begin{aligned}[1 - 2\epsilon a \nu_c \psi'']^2 &\left\{ \ln \frac{1 - \psi''}{1 - \psi'} + \frac{\psi'}{\bar{r}'} \left[1 - \left(\frac{\psi''}{\psi'} \right)^{k/(k+1)} \right] + \psi'' - \psi' \right. \\ &\left. + a[1 + \nu_b \tilde{Y}' + \nu_c (\tilde{Y}')^2](\psi''^2 - \psi'^2) \right\} \\ &+ \epsilon a^2 (\nu_b + 2\nu_c \tilde{Y}')^2 \psi''^2 (\psi'' - \psi')[1 - \epsilon a \nu_c (\psi' + \psi'')] = 0.\end{aligned} \tag{18}$$

The temperature T may be calculated if the temperature dependence of the parameter a is known. Combination of the last two equations results in

$$\begin{aligned}\ln \frac{1 - \psi''}{1 - \psi'} &- \frac{k}{\bar{r}'} \left[1 - \left(\frac{\psi'}{\psi''} \right)^{1/(k+1)} \right] + 2a[1 + \nu_b \tilde{Y}' + \nu_c (\tilde{Y}')^2](\psi'' - \psi') \\ &+ \frac{2C^*}{\psi'' - \psi'} \left[1 + \frac{2\psi''}{\psi'' - \psi'} (1 - 2\epsilon a \nu_c \psi'') \right] = 0,\end{aligned} \tag{19}$$

where C^* and a are given by

$$C^* = \left[\frac{1}{2}(\psi' + \psi'') - 1\right] \ln \frac{1 - \psi''}{1 - \psi'} + \psi' - \psi''$$
$$- \frac{1}{2}\frac{k}{\bar{r}'}(\psi' + \psi'')\left[1 - \left(\frac{\psi'}{\psi''}\right)^{1/(k+1)}\right] - \frac{\psi'}{\bar{r}'}\left[1 - \left(\frac{\psi''}{\psi'}\right)^{k/(k+1)}\right], \quad (20)$$

$$a = 2/\left\{4\epsilon\nu_c\psi'' \pm (\nu_b + 2\nu_c\tilde{Y}')(\psi'' - \psi') \cdot \sqrt{\epsilon(\psi'' - \psi')/C^*}\right\}. \quad (21)$$

By replacing C^* and a in Eq. (19) according to Eqs. (20) and (21), a relation is obtained that contains only one unknown, ψ''. Hence, the phase equilibrium problem of polydisperse copolymer solutions reduces to the numerical solution of only one equation. Equations (19)-(21) may be used only if $\epsilon \neq 0$ because otherwise C^* vanishes. For $\epsilon = 0$, the parameter a has to be determined with the aid of Eq. (17) or Eq. (18).

If $\psi'' \approx 1$, the second phase contains practically no solvent, and it proves appropriate to neglect the phase equilibrium condition for solvent A and to base the calculations only on the phase equilibrium condition for the copolymer. This results in a single equation giving the quantity a as a function of ψ'. Mathematically, this equation can be obtained by subtracting Eq. (17) from Eq. (18), which gives a quadratic polynomial in a. The interesting solution reads

$$a = \left\{\frac{K}{2} + \sqrt{\frac{K^2}{2} - L}\right\}^{-1}, \quad (22)$$

where

$$K = \frac{1}{M}\left[1 + \nu_b\tilde{Y}' + \nu_c(\tilde{Y}')^2\right](1 - \psi')^2 + 2\epsilon\nu_c, \quad (23a)$$

$$L = \frac{\epsilon}{2M}\left\{4\nu_c\left[1 + \nu_b\tilde{Y}' + \nu_c(\tilde{Y}')^2\right] - (\nu_b + 2\nu_c\tilde{Y}')^2\right\}(1 - \psi\ )^2. \quad (23b)$$

The expression for M reads

$$M = \frac{k}{\bar{r}'}\left[1 - (\psi')^{1/(k+1)}\right] + 1 - \psi' + \frac{\psi'}{\bar{r}'}\left[1 - (\psi')^{-k/(k+1)}\right]. \quad (23c)$$

For a pure copolymer ($\psi' = \psi'' = 1$) and with Eq. (11) for the interaction energies, which are assumed to be independent of temperature, Eqs. (22) and (23) result in

$$T = 2\epsilon z \Delta u_{\alpha\beta}/k_B. \tag{24}$$

For ideal random copolymers and $\tilde{Y} = 0.5$, ϵ equals 0.25. If the interaction energy $\Delta u_{\alpha\beta}$ multiplied by Avogadro's number lies between 500 and 1000 J/mol (the coordination number z can take values between 4 and 12), a phase separation is to be expected for pure liquid copolymers. As more detailed considerations [5] show, the temperature given by Eq. (24) equals the critical temperature of the pure copolymer.

SPINODAL AND CRITICAL POINT

The relations for the spinodal and for the critical point may be derived by the methods presented earlier [6, 7], but these equations can also be derived in a simple way from a series expansion [5]. On denoting the left-hand side of Eq. (17) or (18) by the symbol F and forming the partial derivative with respect to ψ'', the spinodal condition is obtained. The second and the third partial derivatives of F with respect to ψ'' yield conditions for the critical point and for a double critical point. A double critical point occurs if a stable and an unstable critical point merge. (A detailed discussion of multiple critical points is presented in a paper by Solc, Kleintjens, and Koningsveld [8]). Hence, the following relations apply:

$$\frac{\partial F}{\partial \psi''} = 0 \qquad \text{spinodal} \tag{25a}$$

$$\frac{\partial F}{\partial \psi''} = 0; \frac{\partial^2 F}{\partial \psi''^2} = 0 \qquad \text{critical point} \tag{25b}$$

$$\frac{\partial F}{\partial \psi''} = 0; \frac{\partial^2 F}{\partial \psi''^2} = 0; \frac{\partial^3 F}{\partial \psi''^3} = 0 \qquad \text{double critical point} \tag{25c}$$

In detail, the spinodal condition reads

$$[1 - 2\epsilon a\nu_c\psi]\left\{\frac{1}{1-\psi} + \frac{1}{\bar{r}}\frac{k}{k+1}\frac{1}{\psi} - 2a[1 + \nu\tilde{Y} + \nu_c(\tilde{Y})^2]\right\}$$

$$- \epsilon_a{}^2(\nu_b + 2\nu_c\tilde{Y})^2\,\psi = 0, \tag{26}$$

where $a = a(T)$. The critical point may be calculated by additionally taking into account the following condition:

$$[1 - 2\epsilon a\nu_c\psi]^2\left\{\frac{1}{(1-\psi)^2} - \frac{1}{\bar{r}}\frac{k(k+2)}{(k+1)^2}\frac{1}{\psi^2}\right\} - 3\epsilon a^2(\nu_b + 2\nu_c\tilde{Y})^2 = 0. \tag{27}$$

For a double critical point, a further condition has also to be fulfilled:

$$[1 - 2\epsilon a\nu_c\psi]^3\left\{\frac{1}{(1-\psi)^3} + \frac{1}{2\bar{r}}\,\frac{k(k+2)(2k+3)}{(k+1)^3}\,\frac{1}{\psi^3}\right\}$$

$$- 12\epsilon^2 a^3\nu_c(\nu_b + 2\nu_c\tilde{Y})^2 = 0. \tag{28}$$

The common slope of the cloud-point curve and of the spinodal at the critical point (subscript *cr*) is given by

$$\left(\frac{\partial T}{\partial\psi}\right)_{cr} = \frac{a(T_{cr})}{\left(\dfrac{da}{dT}\right)_{cr}}\;\frac{\dfrac{2}{(1-\psi_{cr})^2} - \dfrac{1}{\bar{r}}\dfrac{k(2k+1)}{(k+1)^2}\dfrac{1}{\psi_{cr}{}^2}}{\dfrac{3-2\psi_{cr}}{(1-\psi_{cr})^2} + \dfrac{1}{\bar{r}}\dfrac{k(2k+1)}{(k+1)^2}\dfrac{1}{\psi_{cr}}}. \tag{29}$$

According to Eq. (29), the slope $(\partial T/\partial\psi)_{cr}$ for a given copolymer depends only on the critical concentration ψ_{cr}, on $a(T_{cr})$, and on the derivative $(da/dT)_{cr}$.

To give an idea of how the chemical polydispersity influences the critical quantities, the relations for ψ_{cr} and T_{cr} will be expanded with respect to ϵ at $\epsilon = 0$, assuming $\Delta u_{A\beta}$ to be independent of the temperature. If one considers only the first-order terms, the result reads

$$\psi_{cr} = \psi_{cr}(\epsilon = 0) + \frac{3}{8}\left(\frac{1 + \sqrt{\dfrac{1}{\bar{r}}\dfrac{k}{k+2}}}{1 + \sqrt{\dfrac{1}{\bar{r}}\dfrac{k(k+2)}{(k+1)^2}}}\right)^2 \sqrt{\frac{1}{\bar{r}}\frac{k(k+2)}{(k+1)^2}}\cdot D\epsilon, \tag{30}$$

$$T_{cr} = T_{cr}(\epsilon = 0) \left\{ 1 + \frac{1}{8} \frac{1 + \sqrt{\frac{1}{\bar{r}} \frac{k}{k+2}}}{1 + \sqrt{\frac{1}{\bar{r}} \frac{k(k+2)}{(k+1)^2}}} \left[\frac{2k+1}{k+2} \right.\right.$$

$$\left.\left. + 2\sqrt{\frac{1}{\bar{r}} \frac{k(k+2)}{(k+1)^2}} \right] \sqrt{\frac{1}{\bar{r}} \frac{k(k+2)}{(k+1)^2}} \cdot D\epsilon \right\}, \tag{31}$$

where

$$D = \left(\frac{\nu_b + 2\nu_c \tilde{Y}}{1 + \nu_b \tilde{Y} + \nu_c (\tilde{Y})^2} \right)^2 . \tag{32}$$

It is seen that the critical concentration ψ_{cr} and the critical temperature T_{cr} of the copolymer increase with increasing chemical polydispersity. The effect of chemical polydispersity decreases with increasing number-average $\bar{r}'$ of the segment number of the copolymer. This result is to be expected because the Stockmayer distribution is narrower with respect to chemical composition if the copolymer molecules are shorter. Obviously, the parameter D is very important in discussing the effect of chemical polydispersity on the phase equilibrium. With the aid of Eqs. (10) and (12), D may also be expressed by the relation

$$D = \left(\frac{\partial \bar{\bar{G}}^E / \partial \tilde{Y}'}{\bar{\bar{G}}^E} \right)^2_{\epsilon = 0} \tag{33}$$

Hence, if $\bar{\bar{G}}^E$ is small and depends strongly on the average $\tilde{Y}'$ of the chemical composition, a large effect on the chemical polydispersity will occur.

MODEL CALCULATIONS

A solution of an ideal random copolymer with relatively short chains will be considered. Therefore, the following parameter values for the Stockmayer distribution, Eq. (4), were chosen: $\bar{r}' = 20$, $k = 1$, $\tilde{Y}' = 0.5$, $\epsilon = 0.25$. Furthermore, $\Delta u_{A\beta}$ is assumed to be positive and independent of the temperature. The following three cases will be studied:

I. $\Delta u_{\mathrm{A}a} = -\frac{1}{2}\,\Delta u_{\mathrm{A}\beta}$; $(\nu_b + \nu_c = -1.5)$

II. $\Delta u_{\mathrm{A}a} = 0$; $(\nu_b + \nu_c = -1)$

III. $\Delta u_{\mathrm{A}a} = \frac{1}{2}\,\Delta u_{\mathrm{A}\beta}$; $(\nu_b + \nu_c = -0.5)$.

The critical concentration of the copolymer, ψ_{cr}, and $1/\chi_{cr}$ (according to Eq. 10) are shown as functions of the parameter ν_c for the three cases in Figs. 1 and 2. As a result of the assumptions introduced, the reciprocal of χ is proportional to the temperature and, hence, $1/\chi_{cr}$ corresponds to the critical

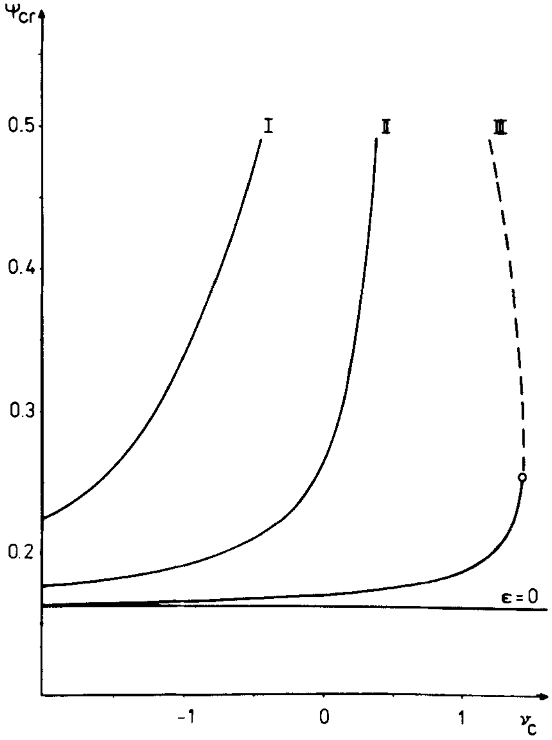

FIG. 1. Critical concentration ψ_{cr} versus ν_c for Cases I, II, and III: (—) stable critical points, (- -) unstable critical points, (○) double critical point.

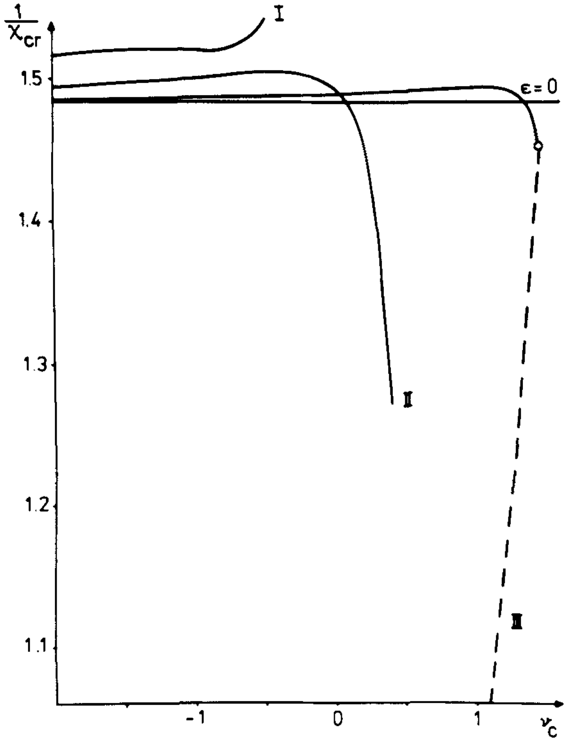

FIG. 2. $1/\chi_{cr}$ (proportional to the critical temperature) versus ν_c. Symbols as in Fig. 1.

temperature T_{cr}. For vanishing chemical polydispersity ($\epsilon = 0$), the values $\psi_{cr} = 0.1622$ and $1/\chi_{cr} = 1.4840$ are obtained. This result does not depend on the choice of ν_b and ν_c.

Generally, the critical concentration is higher for chemical polydispersity ($\epsilon \neq 0$) than for zero polydispersity, due to the symmetry of the chemical part of the Stockmayer distribution. The magnitude of this effect is determined by the decrease of the parameter D from Case I to Case III. The critical temperature may take higher or lower values than for zero chemical polydispersity. In Case III, a stable and an unstable critical point exist. These critical points merge, forming a double critical point for $\nu_c = 1.4364$. Furthermore, in Case III, two additional critical points, not shown in Figs. 1 and 2,

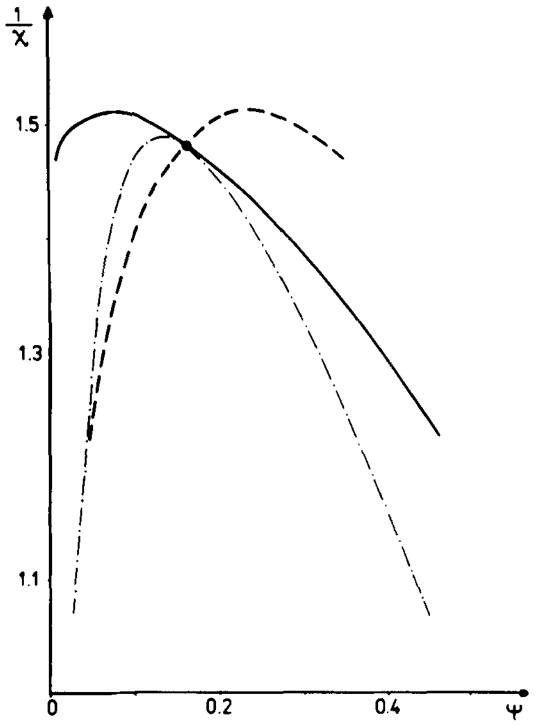

FIG. 3. Phase diagram for vanishingly small chemical polydispersity ($\epsilon = 0$): (—) cloud-point curve, (- -) shadow curve, (- • -) spinodal, (●) critical point.

occur: the critical point of the pure copolymer and an unstable critical point situated at low temperatures, where the liquid state cannot be expected to exist.

The next figures demonstrate the influence of chemical polydispersity on the cloud-point curve, the shadow curve, and the spinodal. The quantity $1/\chi$, which is proportional to the temperature, is plotted versus the segment mole fraction of the copolymer ψ for zero chemical polydispersity in Fig. 3. The phase diagram is the same for all values of ν_b and ν_c. Figures 4 and 5 present the phase diagrams for representative examples of Cases I and II. The diagrams do not show any pecularities. The maxima of the cloud-point curves are shifted to lower concentrations ψ as a result of the chemical polydispersity.

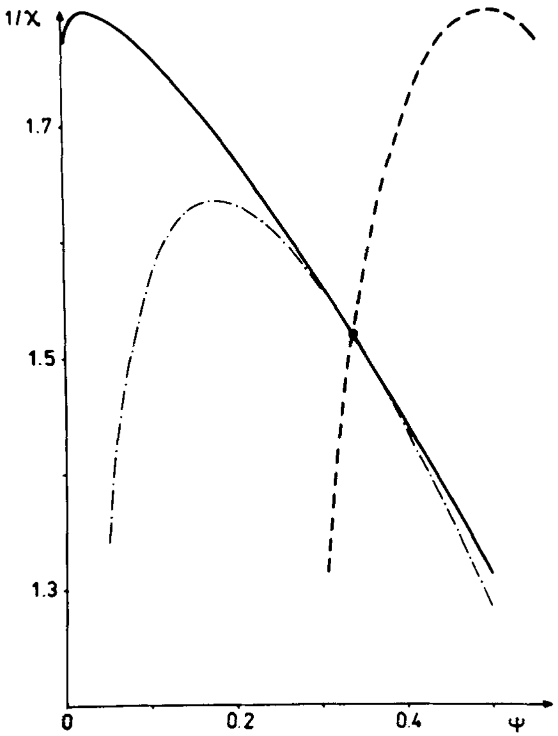

FIG. 4. Phase diagram for Case I with $\nu_c = -1$. Symbols as in Fig. 3.

Contrary to Cases I and II, the phase diagram for Case III is more complicated. The parameter ν_c may take values that cause phase separation of the pure copolymer and of the copolymer solution to occur in the same temperature range. Then, three critical points CP1, CP2, and CP3 occur in the interesting temperature range. Depending on the parameter ν_c, different possibilities can occur.

Figure 6 shows the case of a three-phase equilibrium with the three-phase point, *T*. The cloud-point curve is subdivided into three branches: 1, 2, 3. The transitions from Branch 1 to Branch 2 (not shown in Fig. 6) and from Branch 2 to Branch 3 take place in a cusp point *C*. Branch 1 is stable for $\psi \leqslant \psi_T$, where ψ_T is the concentration of the three-phase point, *T*; it is metastable for $\psi_T < \psi \leqslant \psi_{S1}$, where ψ_{S1} means the concentration of the intersection point of the spinodal and Branch 1 of the cloud-point curve; and

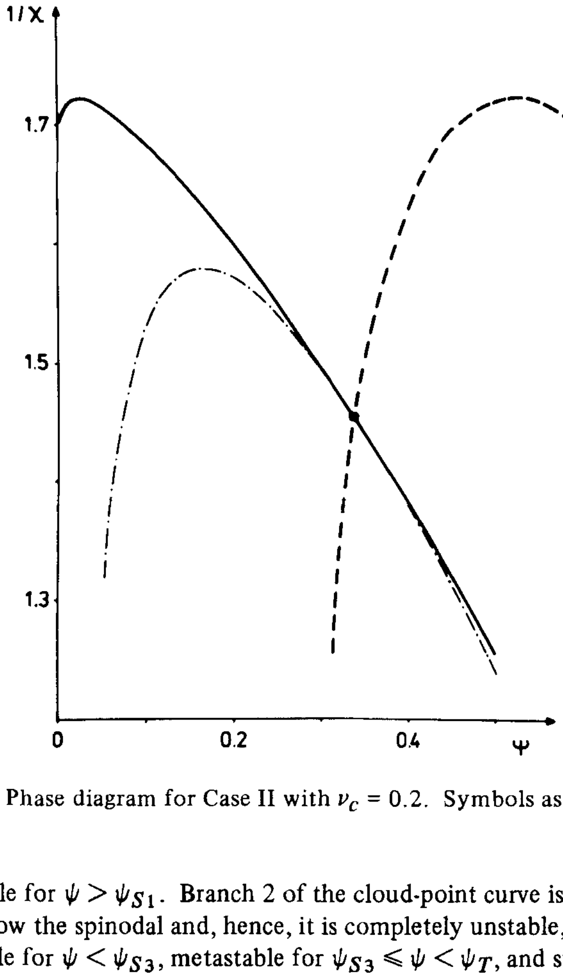

FIG. 5. Phase diagram for Case II with $\nu_c = 0.2$. Symbols as in Fig. 3.

it is unstable for $\psi > \psi_{S1}$. Branch 2 of the cloud-point curve is situated completely below the spinodal and, hence, it is completely unstable, while Branch 3 is unstable for $\psi < \psi_{S3}$, metastable for $\psi_{S3} \leqslant \psi < \psi_T$, and stable for $\psi \geqslant \psi_T$. The three branches 1, 2, and 3 of the shadow curve are related to the three branches 1, 2, and 3 of the cloud-point curve, respectively. They intersect the related branches of the cloud-point curves at the critical points CP1, CP2, and CP3, respectively. Here CP1 is a stable critical point, CP2 is an unstable critical point, and CP3 is the critical point of the pure copolymer and again a stable critical point. At those temperatures where the cloud-point curve goes from Branch 1 to Branch 2, and from Branch 2 to Branch 3, the shadow curve goes from the related Branch 1 to the related Branch 2 (not shown in Fig. 6), and from the related Branch 2 to the related Branch 3. The three-phase point, I, is the intersec-

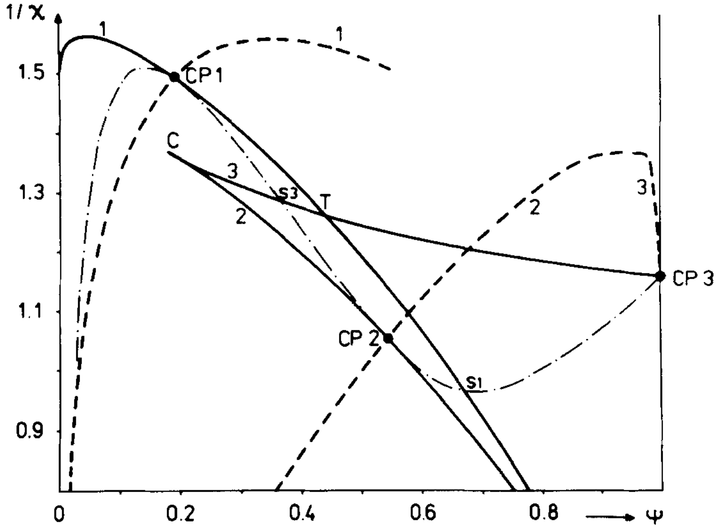

FIG. 6. Phase diagram for Case III with $\nu_c = 1.1$, exhibiting a three-phase equilibrium: (—) Branches 1, 2, and 3 of the cloud-point curve; (- -) Branches 1, 2, and 3 of the shadow curve; (- • -) spinodal; (●) critical points CP1, CP2, and CP3; (*C*) cusp point; (*S*1, *S*2, *S*3) intersection points of the spinodal with the branch of the cloud-point curve indicated; (*T*) three-phase point.

tion of Branches 1 and 3 of the cloud-point curve. Here, three phases do coexist: the given phase with the concentration ψ_T and two other phases characterized by those points of the related Branches 1 and 3 of the shadow curve that exhibit the same ordinate value as *T*. When measuring the cloud-point curve, the experiment provides Branch 1 if $\psi \leqslant \psi_T$ and Branch 3 if $\psi \geqslant \psi_T$. Hence, the experimental cloud-point curve shows a break at the three-phase point, *T*. Behavior of this kind is well known from the calculations of Solc [8-10] concerning solutions of homopolymers with logarithmic normal molecular weight distribution.

In performing the numerical calculations, the computation of Branch 3 of the cloud-point curve and of the shadow curve may become difficult if the concentration ψ'' of the shadow phase approaches unity. Then the cloud-point curve may be calculated by Eqs. (23) and (24).

The phase diagram shown in Fig. 7 refers to a higher value of ν_c. According to Eqs. (11) and (12), this corresponds to a higher value of $\Delta u_{\alpha\beta}$ and,

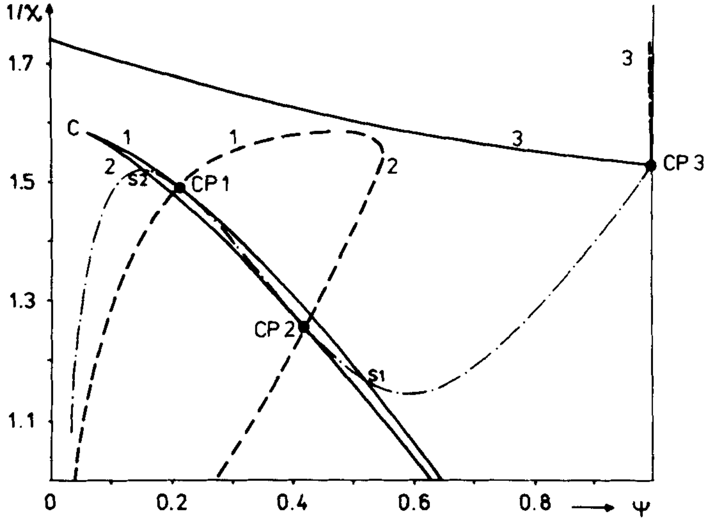

FIG. 7. Phase diagram for Case III with $\nu_c = 1.3$. Symbols as in Fig. 6.

according to Eq. (24), to the occurrence of phase separation for the pure copolymer at higher temperatures. Now, Branch 3 of the cloud-point curve belonging to the critical point CP3 of the pure copolymer is always stable. Branch 1 of the cloud-point curve is metastable for $\psi \leqslant \psi_{S1}$ and unstable otherwise. Analogously, Branch 2 of this curve is metastable for $\psi \leqslant \psi_{S2}$ and unstable otherwise. Correspondingly, now the critical point CP1 is a metastable critical point and the cusp point, *C*, shown in the figure arises from Branches 1 and 2 of the cloud-point curve (instead of Branches 2 and 3). There is no longer a three-phase point.

A further increase of ν_c results in a further reduction of the distance between the two critical points CP1 and CP2. For $\nu_c = 1.4364$, the distance equals zero, i.e., the initially stable critical point CP1 and the unstable critical point CP2 merge, forming a double critical point. The phase diagram for this situation is given in Fig. 8. The coincidence of the two critical points also means that Branches 1 and 2 of the cloud-point and of the related shadow curve vanish.

The phase diagrams presented in Figs. 6-8 show that a relatively simple Gibbs energy relation that requires very small computational expense in the context of continuous thermodynamics can explain complicated phase behavior of copolymer solutions, including a three-phase equilibrium.

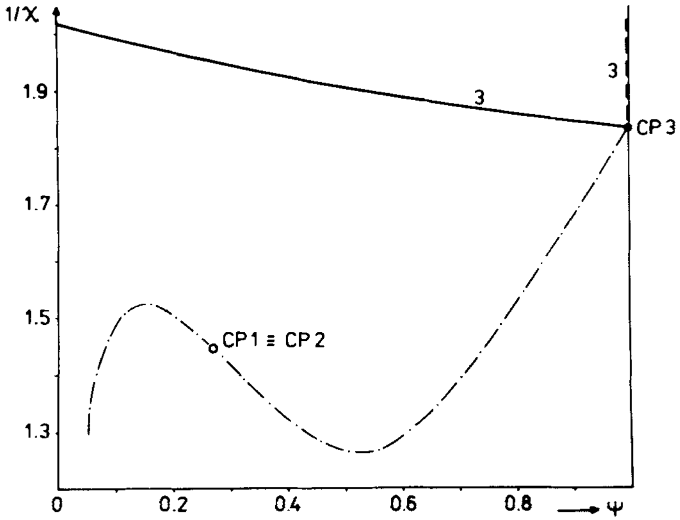

FIG. 8. Phase diagram for Case III with $\nu_c = 1.4364$ exhibiting a double critical point (○). Symbols as in Fig. 6.

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