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LIQUID-LIQUID EQUILIBRIUM OF COPOLYMER SOLUTIONS WITH BROAD AND ASYMMETRIC CHEMICAL DISTRIBUTIONS

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ABSTRACT

A solution of a random copolymer showing polydispersity only with respect to chemical composition is considered. A model distribution very flexible in its breadth and in its asymmetry is used to describe the polydispersity. Based on continuous thermodynamics, equations for the cloud-point curve, the shadow curve, the spinodal, the critical point, and the heterogeneous double critical point are derived. The activity coefficients are calculated with the aid of Huggins' χ-parameter concept assuming χ to depend linearly on the average chemical composition of the copolymer. The influence of the breadth and the asymmetry of the distribution on the liquid-liquid equilibrium of the copolymer solution is discussed.

INTRODUCTION

Kehlen and Rätzsch [1], and later Salacuse and Stell [2], Gualtieri et al. [3], and Briano and Glandt [4], developed continuous thermodynamics based directly on continuous distribution functions to describe phase equilibria of complex multicomponent systems, such as polydisperse polymer solutions, better than possible in the framework of traditional thermodynamics.

Since random copolymers show polydispersity with respect to the chemical composition in addition to the usual polydispersity with respect to the molecular weight, continuous thermodynamics was generalized to divariate distribution functions by Rätzsch, Kehlen, and Browarzik [5]. The double integrals for determining the cloud-point curve and the shadow curve of a copolymer solution may be calculated analytically by using a generalized Stockmayer distribution. Though the Stockmayer distribution is very narrow and symmetric with respect to chemical composition, a marked influence of the chemical polydispersity on the phase equilibria is found in many model calculations [5–8].

However, in reality, many copolymers show broad and asymmetric chemical distributions that are not of the Stockmayer type. The present paper aims at studying the effects of such distributions on the phase equilibrium of copolymer solutions. To show the principle clearly, the polydispersity with respect to the molecular weight is neglected.

CALCULATION OF CLOUD-POINT CURVE AND SHADOW CURVE

A copolymer consisting of two kinds of monomer units, α and β, is considered. By choosing a standard segment, the segment numbers r_α and r_β, respectively, may be defined. The total segment number r and the segment fraction Y of the α-monomer units within the molecules are introduced by

$$r = r_\alpha + r_\beta; \qquad Y = r_\alpha / r \tag{1}$$

For the sake of simplicity, the total segment number r is assumed to be the same in all molecules, i.e., there is no polydispersity with respect to the molecular weight. Thus, the chemical polydispersity of the copolymer may be described by the distribution function $W(Y)$ defined by the statement that $W(Y)dY$ equals the segment fraction of all copolymer species with chemical compositions between Y and $Y + dY$. Therefore, $W(Y)$ fulfills the normalization condition

$$\int_0^1 W(Y)dY = 1 \tag{2}$$

The moments of $W(Y)$ are defined by

$$\tilde{Y}^{(m)} = \int_0^1 Y^m W(Y) dY \tag{3}$$

For $m = 1$, the average chemical composition $\tilde{Y} = \tilde{Y}^{(1)}$ is obtained. Considering a system containing a Solvent A and a Copolymer B, the condition for phase equilibrium between two phases ′ and ″ reads

$$\mu'_{\mathrm{A}} = \mu''_{\mathrm{A}}$$

$$\mu'_{\mathrm{B}}(Y) = \mu''_{\mathrm{B}}(Y) \tag{4}$$

where μ indicates the chemical potential. The phase equilibrium condition for Copolymer B holds for all Y values between 0 and 1.

The relations for the chemical potentials read

$$\mu_{\mathrm{A}} = \mu^*_{\mathrm{A}} + RT\left[\ln(1-\psi) + 1 - r_{\mathrm{A}}\left(\frac{1-\psi}{r_{\mathrm{A}}} + \frac{\psi}{r}\right)\right] + r_{\mathrm{A}}RT\ln\bar{\bar{\gamma}}_{\mathrm{A}};$$

$$\mu_{\mathrm{B}}(Y) = \mu^*{}_{\mathrm{B,O}}{}^*(Y) + RT\left[\ln\psi W(Y) + 1 - r\left(\frac{1-\psi}{r_{\mathrm{A}}} + \frac{\psi}{r}\right)\right]$$
$$+ rRT\ln\bar{\bar{\gamma}}_{\mathrm{B}}(Y) \tag{5}$$

where R is the universal gas constant, T is the absolute temperature, ψ is the overall segment fraction of the copolymer, and r_{A} is the segment number of the solvent molecules. In Eqs. (5) the first terms on the right-hand side are standard terms independent of the composition of the mixture considered, i.e., independent of ψ and $W(Y)$. The second terms are the well-known Flory-Huggins terms, and the third terms describe the deviations from such a Flory-Huggins mixture containing the segment-molar activity coefficients $\bar{\bar{\gamma}}_{\mathrm{A}}$ and $\bar{\bar{\gamma}}_{\mathrm{B}}(Y)$. Expressing the chemical potentials in Eqs. (4) according to Eqs. (5) and rearranging leads to

$$1 - \psi'' = (1 - \psi')\exp r_{\mathrm{A}}\rho_{\mathrm{A}} \tag{6}$$

$$W''(Y) = \frac{\psi'}{\psi''}W'(Y)\exp r\rho_{\mathrm{B}} \tag{7}$$

where ρ_A and ρ_B are given by

$$\rho_A = (\psi'' - \psi')\left(\frac{1}{r} - \frac{1}{r_A}\right) - \ln \bar{\bar{\gamma}}''_A + \ln \bar{\bar{\gamma}}'_A \tag{8}$$

$$\rho_B = (\psi'' - \psi')\left(\frac{1}{r} - \frac{1}{r_A}\right) - \ln \bar{\bar{\gamma}}''_B(Y) + \ln \bar{\bar{\gamma}}'_B(Y) \tag{9}$$

Further treatment depends on how the distribution function $W(Y)$ influences the segment-molar excess Gibbs energy $\bar{\bar{G}}^E$, where "excess" means the deviation from a Flory-Huggins mixture, because $\ln \bar{\bar{\gamma}}_A$ and $\ln \bar{\bar{\gamma}}_B$ are the partial segment-molar quantities with respect to $\bar{\bar{G}}^E/RT$. On applying Huggins' χ-parameter concept and assuming χ depends linearly on the average chemical composition $\tilde{Y}$ of the copolymer, $\bar{\bar{G}}^E$ is given by

$$\bar{\bar{G}}^E/RT = \psi(1 - \psi)\chi; \qquad \chi = a(T)(1 + \nu\tilde{Y}) \tag{10}$$

Then the distribution function $W(Y)$ influences $\bar{\bar{G}}^E$ only through its first moment $\tilde{Y}$. From a molecular point of view, Eqs. (10) corresponds to the neglect of interactions between the monomer units α and β of the copolymer [5, 7]. The parameter ν is a measure of the difference between the interactions of type Aα and of type Aβ, expressed by

$$\nu = \frac{\Delta u_{A\alpha} - \Delta u_{A\beta}}{\Delta u_{A\beta}}$$

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

$$\Delta u_{A\beta} = u_{A\beta} - \frac{1}{2}(u_{AA} + u_{\beta\beta}) \tag{11}$$

where u_{AA}, $u_{\alpha\alpha}$, $u_{\beta\beta}$, $u_{A\alpha}$, and $u_{A\beta}$ are interaction energies of segments AA, $\alpha\alpha$, $\beta\beta$, Aα, and Aβ, respectively. With the aid of Eqs. (10), the segment-molar activity coefficients $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B(Y)$ read

$$\ln \bar{\bar{\gamma}}_A = \psi^2 a(T)(1 + \nu\tilde{Y})$$

$$\ln \bar{\bar{\gamma}}_B(Y) = (1 - \psi)^2 a(T)(1 + \nu\tilde{Y}) + (1 - \psi)a(T)\nu(Y - \tilde{Y}) \tag{12}$$

Upon establishing the temperature equilibrium (at constant pressure) of a given phase ′, a second phase ″ (shadow phase) is formed. The plot of the equilibrium temperature T against the overall segment fraction ψ' of the copolymer in the phase ′ is called the cloud-point curve. The plot of the equilibrium temperature T against the total segment fraction ψ'' of the copolymer in the shadow phase ″ is called the shadow curve.

In order to calculate the cloud-point curve and the shadow curve, the three unknowns, T, ψ'', and $\tilde{Y}''$, have to be determined. For this purpose, two other equations are needed in addition to Eq. (6). They result from Eqs. (2) and (3) (with $m = 1$) as applied to phase ″ with the aid of Eq. (7):

$$\psi'' = \psi' \int_0^1 W'(Y) \exp(r\rho_B)dY \tag{13}$$

$$\tilde{Y}'' = \frac{\psi'}{\psi''}\int_0^1 YW'(Y) \exp(r\rho_B)dY \tag{14}$$

By using Eqs. (6), (8), (9), and (12), ρ_A and ρ_B may be rewritten

$$\rho_A = (\psi'' - \psi')(\left(\frac{1}{r} - \frac{1}{r_A}\right) + a(T)[(1 + \nu\tilde{Y}')(\psi')^2$$

$$- (1 + \nu\tilde{Y}'')(\psi'')^2] \tag{15}$$

$$\rho_B = \rho_{BO} + Y\rho_{BY} \tag{16}$$

where ρ_{BO} and ρ_{BY} are given by

$$\rho_{BO} = \frac{1}{r_A} \ln \frac{1 - \psi''}{1 - \psi'} + a(T)\{2(\psi'' - \psi')$$

$$+ \nu(\tilde{Y}''\psi'' - \tilde{Y}'\psi')\} \tag{17}$$

$$\rho_{BY} = a(T)\nu(\psi'' - \psi') \tag{18}$$

By combining Eqs. (13) and (14), $\bar{Y}''$ may be expressed by

$$\bar{Y}'' = I_2/I_1 \tag{19}$$

where

$$I_1 = \int_0^1 W'(Y) \exp\,(r\rho_{BY})dY \tag{20}$$

$$I_2 = \int_0^1 YW'(Y) \exp\,(r\rho_{BY})dY \tag{21}$$

Introducing

$$\lambda = (1 - \psi'')/(1 - \psi') \tag{22}$$

the combination of Eqs. (6) and (15) leads to

$$\nu(\bar{Y}'' - \bar{Y}')[a(T)]^2 + p^* a(T) + q^* = 0 \tag{23}$$

where p^* and q^* are given by

$$p^* = \frac{1}{r_A} \ln \lambda + \frac{2\rho_{BY}}{\nu(1 - \lambda)} [(1 + \nu\bar{Y}') - \lambda(1 + \nu\bar{Y}'')]$$

$$q^* = -\left(\frac{1}{r} - \frac{1}{r_A}\right)\frac{\rho_{BY}}{\nu} - \left[\frac{\rho_{BY}}{\nu(1 - \lambda)}\right]^2 [(1 + \nu\bar{Y}')$$
$$- \lambda^2(1 + \nu\bar{Y}'')] \tag{24}$$

Finally, Eqs. (13), (16), (17), (18), (20), and (21) result in

$$\frac{1}{r} \ln I_1 - \quad - \frac{1}{r} \ln \frac{a(T)\nu(1 - \lambda) - \rho_{BY}\lambda}{a(T)\nu(1 - \lambda) - \rho_{BY}} + \frac{1}{r_A} \ln \lambda$$
$$+ 2\frac{\rho_{BY}}{\nu} + a(T)\nu(\bar{Y}'' - \bar{Y}') - \frac{\rho_{BY}}{1 - \lambda} (\lambda\bar{Y}'' - \bar{Y}') = 0 \tag{25}$$

Now the cloud-point curve and the shadow curve may be calculated in the following way: By choosing a value for ρ_{BY}, the quantities I_1, and I_2, and $\tilde{Y}''$ may be determined with the aid of Eqs. (19)-(21). Only Eq. (25) has to be solved in an iterative way with respect to the unknown λ. The quantity $a(T)$ may be found as a solution of the quadratic Eq. (23):

$$a(T) = -\frac{p}{2} \pm \sqrt{\frac{p^2}{4} - q} \tag{26}$$

where

$$p = p^*/[\nu(\tilde{Y}'' - \tilde{Y}')]; \qquad q = q^*/[\nu(Y'' - Y')] \tag{27}$$

and p^* and q^* are given by Eqs. (24). Finally, using Eqs. (18) and (22), the quantities ψ' and ψ'' result from

$$\psi' = 1 - \frac{\rho_{BY}}{a(T)\nu(1 - \lambda)}; \qquad \psi'' = 1 - \frac{\rho_{BY}\lambda}{a(T)\nu(1 - \lambda)} \tag{28}$$

If the function $a(T)$ is specified, the equilibrium temperature may be calculated. The essential advantage of the algorithm described is the low expense in determining the integrals I_1 and I_2. To obtain a cloud point, these integrals have to be calculated only once.

In the monodisperse limit (all copolymer species possess the same composition $\tilde{Y}'$), the described algorithm may also be applied, but in a modified form. Then the quantities I_1, I_2, $\tilde{Y}''$, and $a(T)$ are given by

$$I_1 = \exp(r\rho_{BY}\tilde{Y}')$$

$$I_2 = \tilde{Y}' \exp(r\rho_{BY}\tilde{Y}')$$

$$a(T) = -q^*/p^* \tag{29}$$

Of course, in this limiting case there is no difference between the cloud-point curve and the shadow curve. Furthermore, because the segment-molar activity coefficients depend on T and $\tilde{Y}$ only by means of χ, a universal binodal $\chi^{-1}(\psi)$ may be found which is independent of the interaction parameters and $\tilde{Y}$.

CALCULATION OF SPINODAL AND CRITICAL POINT

There are two ways to obtain expressions for the spinodal and the critical point. First, the equilibrium condition, Eq. (6) or (13), is expanded into a series with respect to ψ'' about the critical point [7] by taking Eqs. (15)-(21) into account. Equating the first-order term to zero results in the spinodal condition. Furthermore, if the second-order term does vanish, there is a critical point. Analogously, the third-order term leads to a condition for a double critical point (heterogeneous double plait point). Second, the stability theory of continuous thermodynamics [9] may be applied to find expressions for the spinodal, the critical point, and the double critical point. The spinodal condition obtained reads

$$\frac{1}{r_A(1-\psi)} + \frac{1}{r\psi} - 2a(T)(1+\nu\tilde{Y}) - r[a(T)\nu]^2\psi(\tilde{Y}^{(2)} - \tilde{Y}^2) = 0 \tag{30}$$

At a critical point, the relation

$$\frac{1}{r_A(1-\psi)^2} - \frac{1}{r\psi^2} - 3r[a(T)\nu]^2(\tilde{Y}^{(2)} - \tilde{Y}^2) - r^2[a(T)\nu]^3\psi(\tilde{Y}^{(3)} - 3\tilde{Y}^{(2)}\tilde{Y} + 2\tilde{Y}^3) = 0 \tag{31}$$

has to be fulfilled. Analogously, at a heterogeneous double critical point the equation

$$\frac{2}{r_A(1-\psi)^3} + \frac{2}{r\psi^3} - 4r^2[a(T)\nu]^3(\tilde{Y}^{(3)} - 3\tilde{Y}^{(2)}\tilde{Y} + 2\tilde{Y}^3) - r^3[a(T)\nu]^4\psi(\tilde{Y}^{(4)} - 4\tilde{Y}^{(3)}\tilde{Y} - 3\tilde{Y}^{(2)2} + 12\tilde{Y}^{(2)}\tilde{Y}^2 - 6\tilde{Y}^4) = 0 \tag{32}$$

holds in addition to Eqs. (30) and (31).

DISTRIBUTION FUNCTION

To perform the calculation of phase equilibria, an expression for the distribution function $W(Y)$ is needed. In order to study the influence of breadth and asymmetry of the distribution function on the phase equilibrium, this expression has to be sufficiently flexible in these properties. These are met by the following relation:

$$W(Y) = \frac{\Gamma(s + t + 2)}{\Gamma(s + 1)\Gamma(t + 1)} Y^s(1 - Y)^t \tag{33}$$

where Γ is the Γ-function. The mth moment of $W(Y)$ reads

$$\bar{Y}^{(m)} = \frac{\Gamma(s + m + 1)\Gamma(s + t + 2)}{\Gamma(s + t + m + 2)\Gamma(s + 1)} \tag{34}$$

Then the integral I_1 given by Eq. (20) may be expressed by

$$I_1 = \sum_{i=0}^{\infty} \alpha_i \tag{35}$$

where

$$\begin{aligned} \alpha_k &= \alpha_{k-1} \frac{s + k}{s + t + k + 1} \frac{r\rho_{BY}}{k}; \qquad k = 1, 2, \ldots \\ \alpha_0 &= 1 \end{aligned} \tag{36}$$

The integral I_2 given by Eq. (21) may be expressed by

$$I_2 = \sum_{i=0}^{\infty} \beta_i \tag{37}$$

where

$$\begin{aligned} \beta_k &= \beta_{k-1} \frac{s + k + 1}{s + t + k + 2} \frac{r\rho_{BY}}{k}; \qquad k = 1, 2, \ldots \\ \beta_0 &= \bar{Y}' \end{aligned} \tag{38}$$

Practically, only a finite number of terms in the sums of Eqs. (35) and (37) has to be taken into account. Because of the rapid convergence behavior of these sums, even for large absolute values of the quantity ρ_{BY}, only a very few terms are actually needed. In such a way, the numerical integration may be performed rapidly and with high accuracy.

EXAMPLES

In all examples considered, the parameters r_A, r_B, and ν are given by

$$r_A = 1; \qquad r_B = 100; \qquad \nu = 1 \tag{39}$$

In the simplest case $a(T)$, and hence $\chi(T)$, are assumed to be proportional to T^{-1}. Then, in the framework of model calculations, $a(T)$ does not have to be specified considering simply the functions $\chi^{-1}(\psi')$ and $\chi^{-1}(\psi'')$ as the cloud-point curve and the shadow curve, respectively. (In the monodisperse limit there exists a common binodal $\chi^{-1}(\psi)$, independent of ν and $\bar{Y}$. The demixing temperature is proportional to $1 + \nu\bar{Y}$. For $\nu > 0$ (i.e., $\Delta u_{A\alpha} > \Delta u_{A\beta}$; $\Delta u_{A\beta} > 0$) the miscibility decreases if $\bar{Y}$ increases, corresponding to the increasing number of interactions of the more repulsive type Aα).

First, the influence of the breadth of the distribution function on the critical point and on the cloud-point curve shall be studied. To separate the effects of the breadth from those of the asymmetry of the distribution function, symmetric distributions ($t = s$) are considered.

In Table 1 the quantity $\bar{Y}^{(2)} - \bar{Y}^2$, which measures the breadth of the

TABLE 1. The Influence of the Breadth of the Distribution on the Critical Quantities

s	$\bar{Y}^{(2)} - \bar{Y}^2$	ψ_c	χ_c^{-1}
∞	0	0.0909	1.6529
20	0.0058	0.1021	1.6637
10	0.0109	0.1149	1.6709
4	0.0227	0.1682	1.6661
2	0.0357	0.2972	1.5783
1	0.0500	0.4287	1.4885
0.5	0.0625	0.4933	1.4705
0	0.0833	0.5532	1.4942

distribution function, and the critical quantities ψ_c and χ_c^{-1} are listed for some values of the parameters s. With increasing breadth of the distribution (the monodisperse case is given by $s \rightarrow \infty$, the critical concentration increases in a considerable degree. The critical temperature, i.e., χ_c^{-1}, at first shows a slight increase, but then it decreases with increasing breadth of the distribution. To illustrate, some representative examples of the distribution functions used are plotted in Fig. 1. Figure 2 shows the influence of the breadth of the distribution function on the cloud-point curves. Whereas the general shape of the cloud-point curves in all the cases considered (except $s \rightarrow \infty$) is nearly the same, the equilibrium temperature increases with increasing breadth of the distribution function

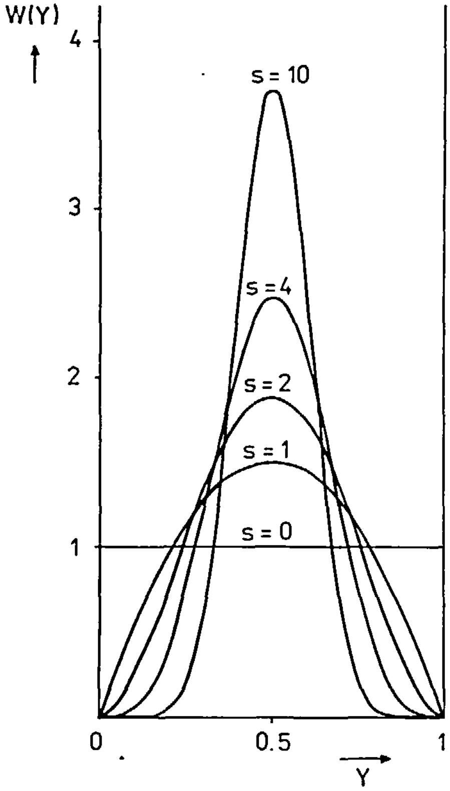

FIG. 1. Symmetric distributions for s = 0, 1, 2, 4, and 10.

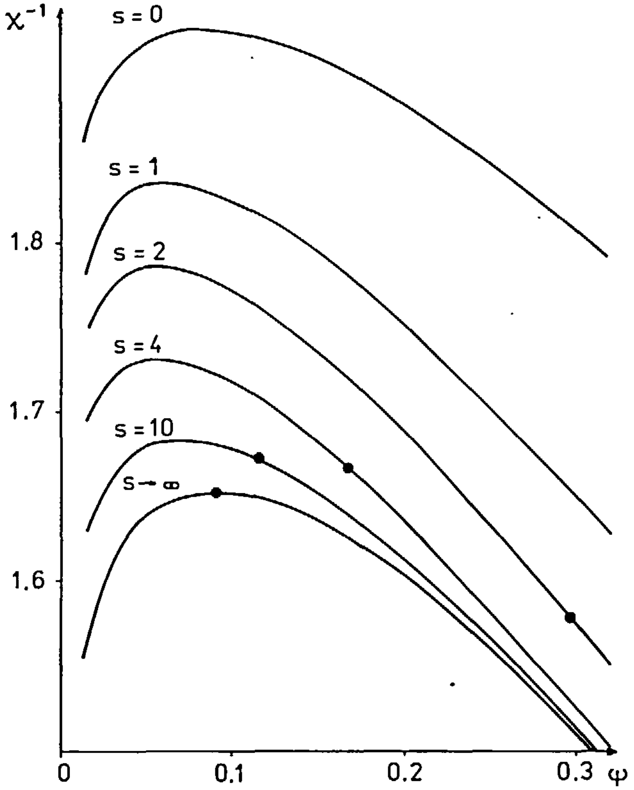

FIG. 2. Cloud-point curves for different breadths of the symmetric distribution, critical point (●).

(decreasing miscibility). In the case of broad distributions, the critical concentration is very large. (For $s = 0$ and $s = 1$, the critical point lies outside the concentration range considered in Fig. 2). Of course, there is a corresponding effect on the shadow curves as shown by comparing Figs. 3(a) and 3(b).

Considering a cloud point, there is an equilibrium between the phase ′, characterized by the overall segment fraction ψ' of the copolymer and by its mean chemical composition $\bar{Y}'$, and of the phase ″, characterized by the quantities ψ'' and $\bar{Y}''$, Considering the quantity $\bar{Y}'' - \bar{Y}'$ (in the cases discussed above, $\bar{Y}' = 0.5$) as a function of ψ', information about the

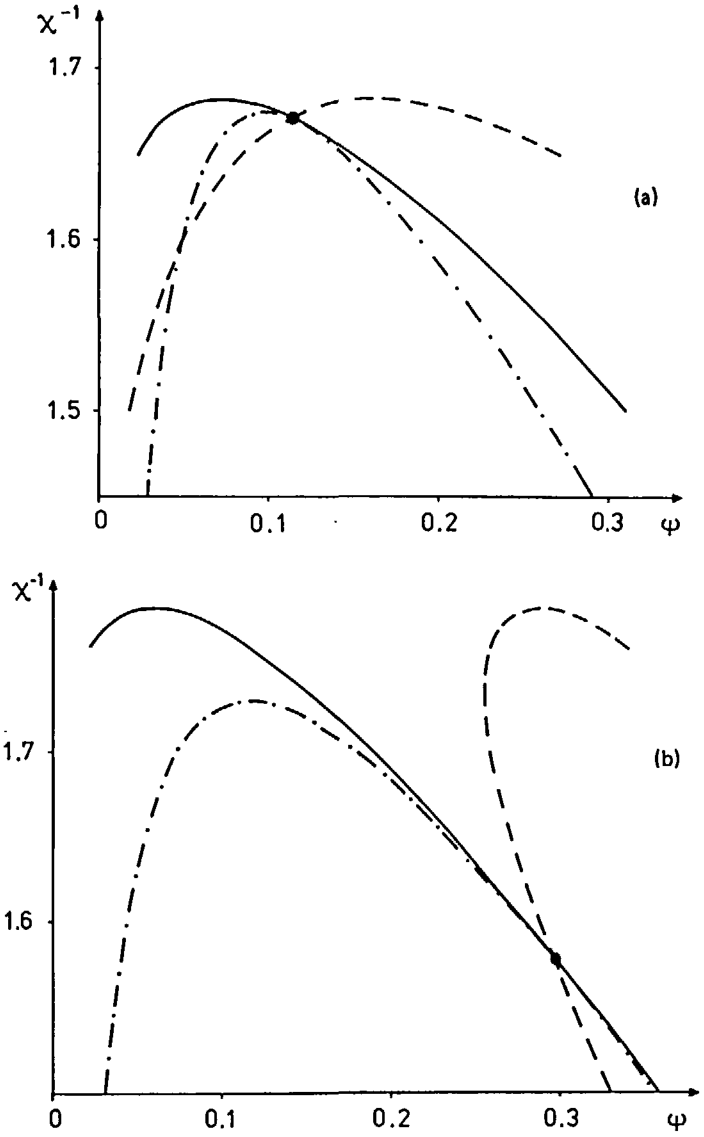

FIG. 3. Phase diagram for a symmetric distribution with (a) $s = 10$ and with (b) $s = 2$: cloud-point curve (——), shadow curve (- -), spinodal (- · · -), critical point (●).

fractionation of the copolymer with respect to its chemical composition may be obtained. As expected, there is an increase of the fractionation effect with increasing breadth of distribution, i.e., decreasing value of *s* (Fig. 4).

The influence of the asymmetry of the distribution function on the phase equilibrium shall now be studied. To separate the effects of the asymmetry from those of the breadth of the distribution, some distribu-

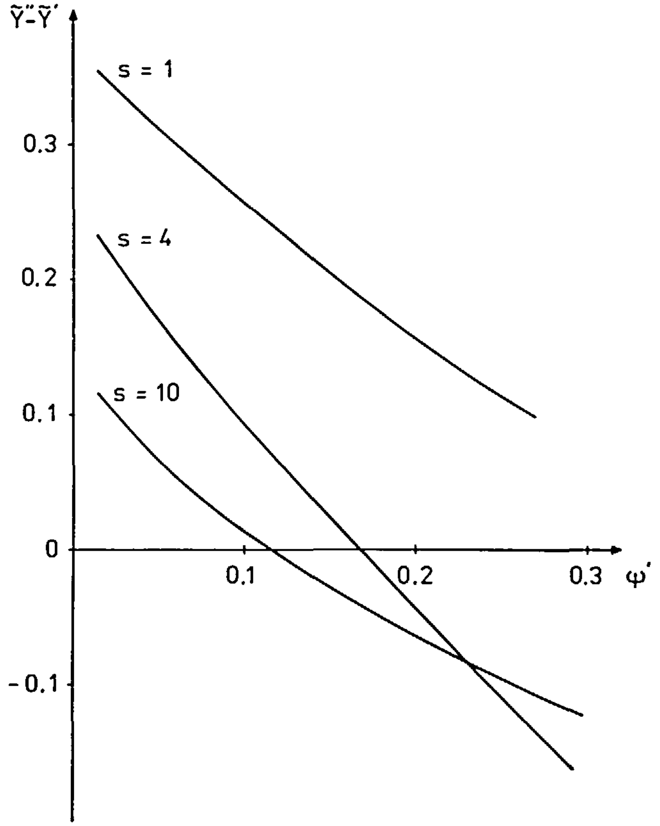

FIG. 4. Fractionation effect $\tilde{Y}'' - \tilde{Y}'$ for different breadths of the (symmetric) distribution.

tion functions with the same standard deviation $\bar{Y}^{(2)} - \bar{Y}^2$ but different asymmetries are considered. For a given symmetric distribution function with the parameters $s = t = s^*$, the parameters s and t of an asymmetric distribution function with the same standard deviation may be calculated by

$$s = \frac{1}{2}\left\{\tau + \delta(\tau + 2)\sqrt{1 - \frac{\tau + 3}{2s^* + 3}}\right\}; \qquad \delta = \pm 1$$

$$t = \tau - s \tag{40}$$

applying different τ values. In the limit $\tau = 2s^*$, the symmetric case is obtained. If τ decreases, the asymmetry of the distribution function increases. Furthermore, the relations

$$s_1 = t_2; \qquad s_2 = t_1 \tag{41}$$

apply where the subscripts 1 and 2 correspond to the two possible values of δ. If $\delta = +1$, then $\bar{Y} > 0.5$, and if $\delta = -1$, then $\bar{Y} < 0.5$. Therefore, the quantity τ measures the degree of asymmetry and the sign of δ gives information about the direction of asymmetry. To illustrate, Fig. 5 presents some examples of distribution functions $W(Y)$ with the same breadth (measured by s^*) but different asymmetries.

In Table 2 for $s^* = 4$, the critical quantities for different values of τ and δ are listed. For $\bar{Y} > 0.5$, increasing the asymmetry of the distribution function results in a decrease of the critical concentration ψ_c and in an increase of the critical χ^{-1} value. Therefore, such an asymmetry reduces the effect arising from the breadth of the distribution function. However, there is only a small influence. On the contrary, for $\bar{Y} < 0.5$ the critical concentration ψ_c increases and the critical χ^{-1} value decreases drastically with increasing asymmetry of the distribution function. To illustrate, some of the cloud-point curves corresponding to the distributions shown in Fig. 5 are represented in Fig. 6. Again, in all cases the phase separation temperatures are higher than in the monodisperse limit considering the same average chemical composition, i.e., the solubility of the copolymer is decreased by the chemical polydispersity. The effect of the standard deviation may be decreased ($\delta = +1$) or increased ($\delta = -1$) by the asymmetry of the distribution function.

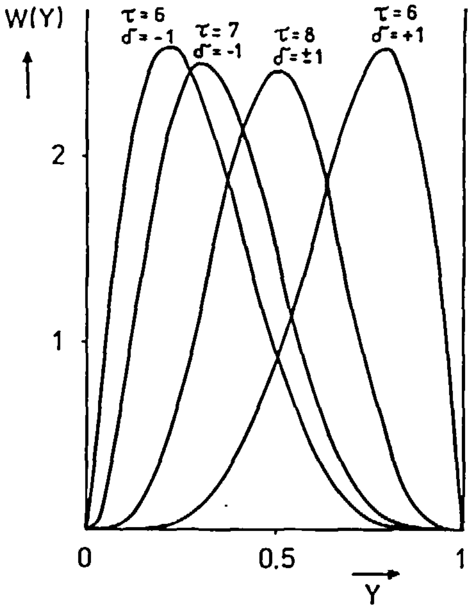

FIG. 5. Asymmetric distributions with the same standard deviation ($s^* = 4$).

TABLE 2. The Influence of the Asymmetry of the Distribution on the Critical Quantities for $s^* = 4$

τ	δ	ψ_c	χ_c^{-1}
6	+1	0.1291	1.6803
7	+1	0.1368	1.6791
8	±1	0.1682	1.6661
7.5	−1	0.2370	1.6061
7	−1	0.3668	1.4426
6.75	−1	0.5869	1.1009
6	−1	0.9018	0.4601

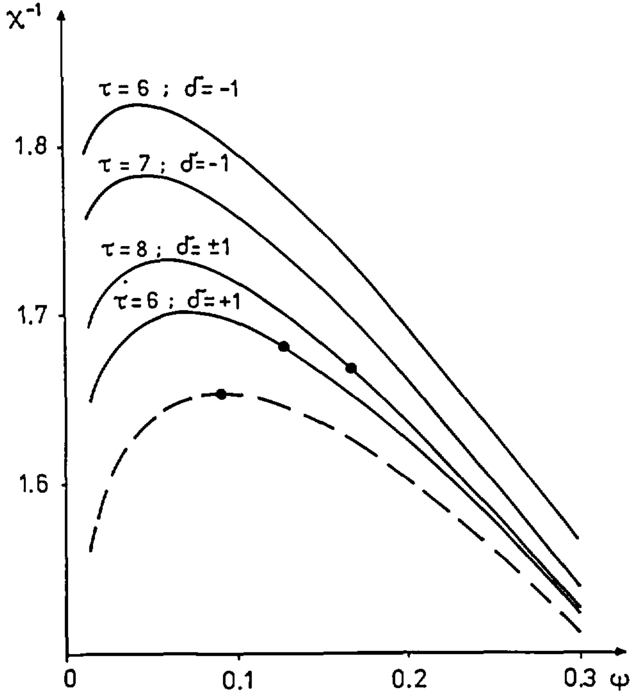

FIG. 6. Cloud-point curves for different asymmetries of the distribution ($s^* = 4$): polydisperse case (—), monodisperse case (- -), critical point (●).

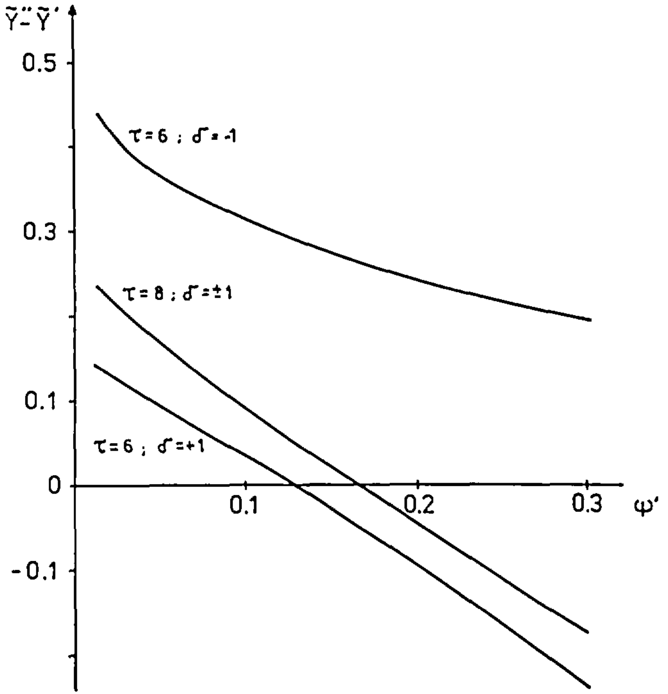

FIG. 7. Fractionation effect $\tilde{Y}'' - \tilde{Y}'$ for distributions with different asymmetries but the same breadth ($s^* = 4$).

In Fig. 7 the fractionation effect is shown for different asymmetries of the distribution function. Again, all distribution functions possess the same standard deviation $\tilde{Y}^{(2)} - \tilde{Y}^2$. Two asymmetric distribution functions ($\tau = 6$, $\delta = \pm 1$) characterized by the same absolute value $|\tilde{Y} - 0.5|$ but different in the direction of the asymmetry are compared with the symmetric distribution function ($\tau = 8$). The largest effect is found for $\tau = 6$, $\delta = -1$ arising from the very large critical concentration.

In the last examples the effects of distribution functions, which are broad and asymmetric, were considered. The influence of asymmetry on the phase behavior for narrower distribution functions shall now be studied. For this purpose the parameter s^* is chosen to equal 10. In Figs. 8(a) and 8(b) the critical quantities ψ_c and χ_c^{-1} are plotted against τ for $\delta = -1$. For $8.082 \leq \tau \leq 11.466$, three critical points occur, and at least one of them is stable. For $\tau = 9.7865$ and $\tau = 11.4115$, heterogeneous double plait points occur that separate the branch of stable critical points and the branch of unstable critical points. Whereas the asymmetry corresponding to $\tilde{Y} < 0.5$ essentially influences the phase behavior, the effect of the asymmetry corresponding to $\tilde{Y} > 0.5$ is very small. To give an idea of the degree of asymmetry connected with the τ values considered in Figs. 8, some representative distribution functions are plotted in Fig. 9.

In Fig. 10 the influence of the asymmetry of narrower distributions on the cloud-point curve is shown. The results are similar to those of Fig. 6. However, for τ values leading to the occurrence of three critical points, the phase behavior is much more complex. The cloud-point curve splits into different branches which may be stable, metastable, or unstable. In such cases a three-phase point often occurs, resulting in a break of the stable part of the cloud-point curve [7, 10, 11]. In Fig. 10 this behavior can be seen for $\tau = 9.7865$, $\delta = -1$. The slopes of the two plotted (stable) branches of the cloud-point curve differ at the three-phase point. In order to explain this, Fig. 11 shows that part of the cloud-point curve situated near the three-phase point in detail. The heterogeneous double plait point occurring for $\tau = 9.7865$ is located exactly in the cusp point formed by the metastable and the unstable branches of the cloud-point curve.

Finally, in Fig. 12 the fractionation effect for different asymmetries of distribution with the same (smaller) breadth is shown. The very asymmetric case $\tau = 7$ results in a considerable fractionation effect. The three-phase point for $\tau = 9.7865$ corresponds to a finite discontinuity of the fractionation effect.

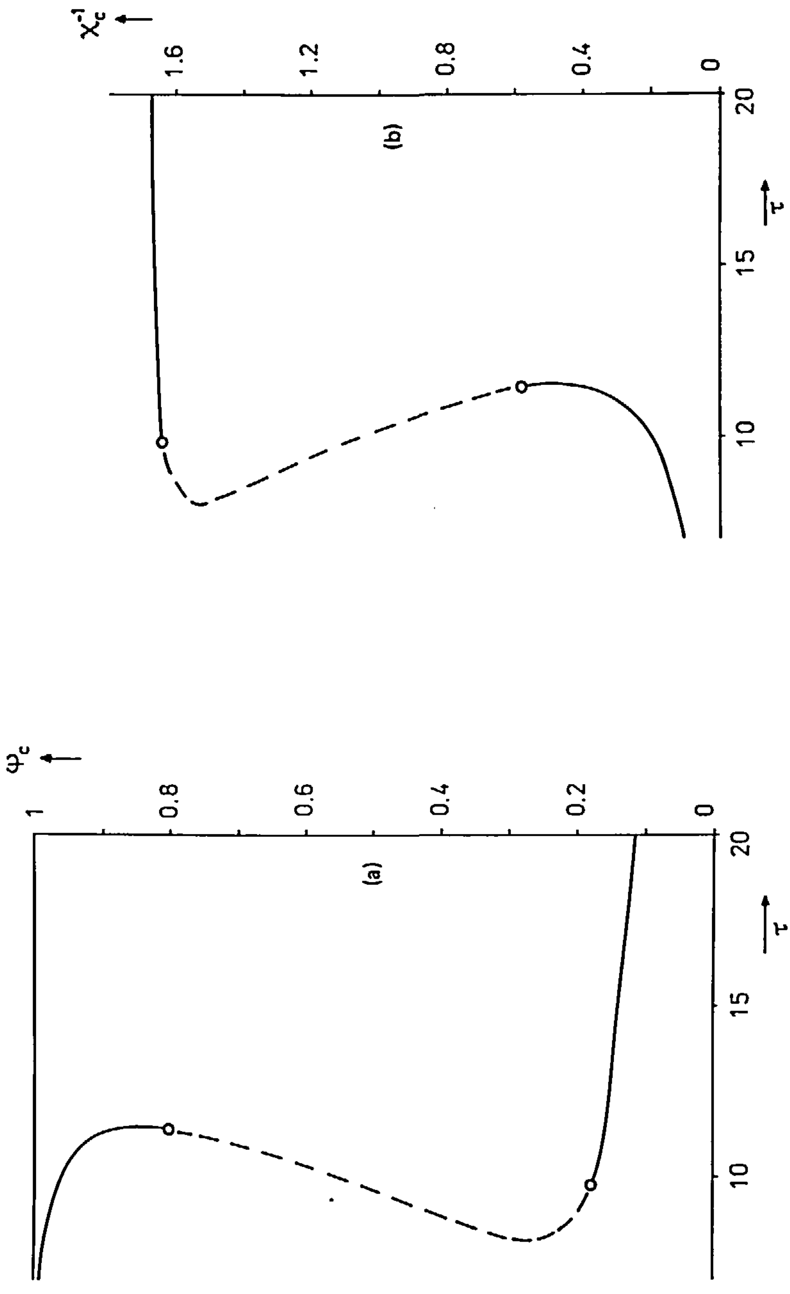

FIG. 8. Critical quantities (a) ψ_c and (b) χ_c^{-1} as functions of the asymmetry τ of the distribution ($s^* = 10$); $\delta = -1$): stable branch (—), unstable branch (- -), heterogeneous double plait point (○).

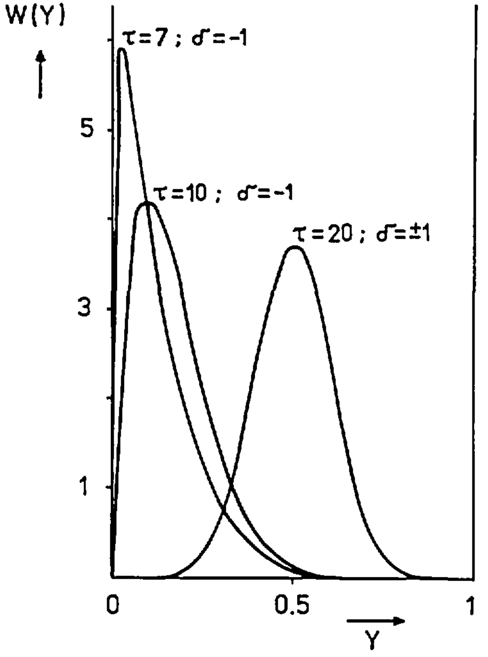

FIG. 9. Asymmetric distributions with the same standard deviation ($s^* = 10$).

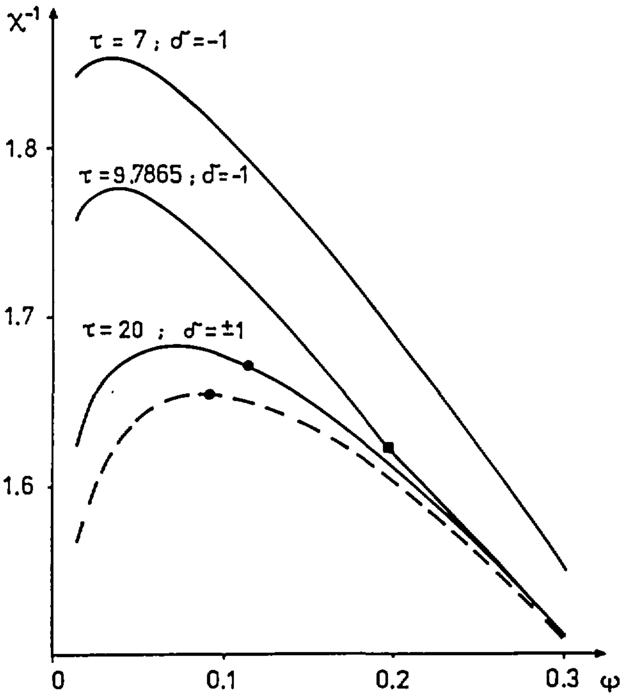

FIG. 10. Cloud-point curves for different asymmetries of the distribution ($s^* = 10$): polydisperse case (—), monodisperse case (- -), critical point (●), three-phase point (■).

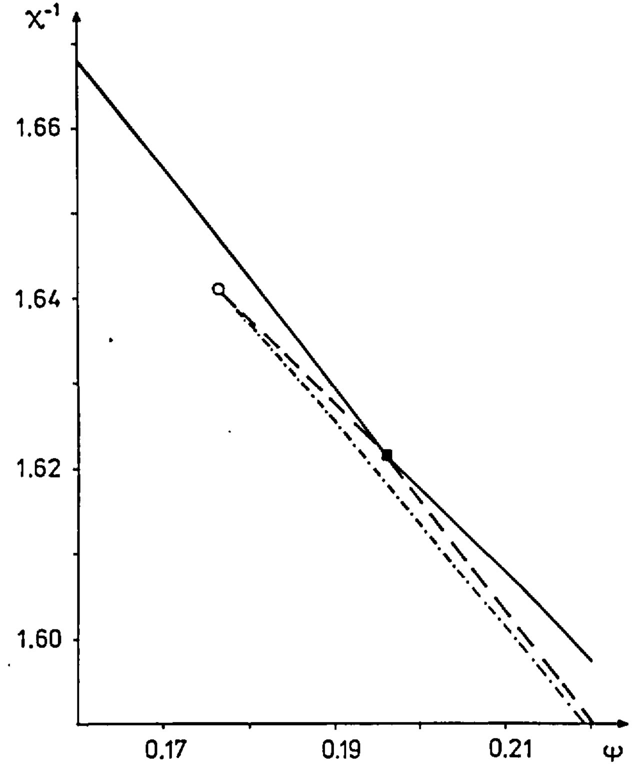

FIG. 11. Cloud-point curve for $s^* = 10$ and $\tau = 9.7865$, $\delta = -1$ near the three-phase point: stable branch (—), metastable branch (- -), unstable branch (- · -), heterogeneous double plait point (○), three-phase point (■).

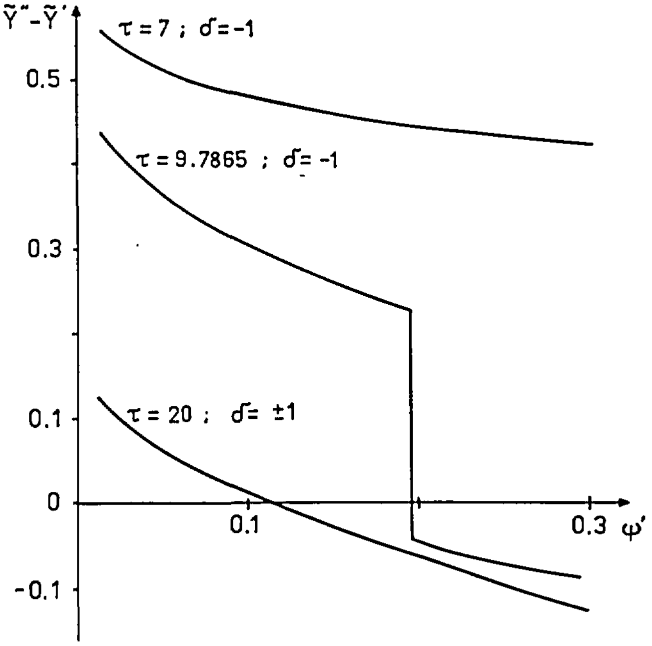

FIG. 12. Fractionation effect $\tilde{Y}'' - \tilde{Y}'$ for distributions with different asymmetries but the same breadth ($s^* = 10$).

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