Cloud-Point Curve for the System Copoly(Ethylene-Vinyl Acetate) Plus Methyl Acetate. Measurement and Prediction by Continuous Thermodynamics

Margit T. Rätzsch[a]; Horst Kehlen[a]; Dieter Browarzik[a]; Michael Schirutschke[a]

[a] Chemistry Department, "Carl Schorlemmer" Technical University, Merseburg, German Democratic Republic

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MARGIT T. RÄTZSCH, HORST KEHLEN, DIETER BROWARZIK,
and MICHAEL SCHIRUTSCHKE

Chemistry Department
"Carl Schorlemmer" Technical University
DDR-4200 Merseburg, German Democratic Republic

ABSTRACT

The cloud-point curve for the system copoly(ethylene-vinyl acetate) plus methyl acetate has been measured by a simple visual method. The critical point was determined by using the phase volume ratio method. The method of continuous thermodynamics was applied for thermodynamic treatment. The composition of the copolymer is described by a divariate distribution function assumed as a generalized Stockmayer distribution. The activity coefficients were obtained with the aid of the Huggins χ-parameter concept assuming χ to be a quadratic polynomial with respect to the weight-average chemical composition of the copolymer. The three model parameters were calculated from the critical point and the slope of the cloud-point curve at the critical point. The cloud-point curve and the shadow curve were predicted from these parameters. The cloud-point curve shows qualitative agreement with experimental data.

INTRODUCTION

To describe phase equilibria of polymer systems better than pos-
sible in the framework of traditional thermodynamics, Kehlen and
Rätzsch [1], and later Salacuse and Stell [2], Gualtieri et al. [3], and
Briano and Glandt [4] established a version of thermodynamics based
directly on continuous distribution functions. This version is called
"continuous thermodynamics." In applications to homopolymers (see,
e.g., Refs. 5-8), the distribution function was assumed to depend on
only one variable.

However, copolymers show polydispersity with respect to the
chemical composition in addition to the usual polydispersity with re-
spect to the molecular weight. Therefore, "continuous thermodynam-
ics" was generalized to divariate distribution functions by Rätzsch,
Kehlen, and Browarzik [9]. By using a modified Huggins χ-parameter
concept, the problem of calculating the cloud-point curve, the shadow
curve, and the coexistence curves for a copolymer solution, including
the composition in the coexisting phases, may be reduced to the numer-
ical solution of a set of only three equations. Double integrals occur in
these equations. By using a generalized Stockmayer distribution, the
integrals for determining the cloud-point curve and the shadow curve
may be calculated analytically, reducing the calculation to numerical
solution of only two equations not containing integrals.

The influence of the chemical polydispersity on the phase equili-
brium may be estimated easily by variation of the model parameters.
If the monomer units forming the copolymer are very different in
their interactions with the solvent molecules, a considerable effect
may be expected. To demonstrate the validity of the expression for
χ, the calculated cloud-point curve will be compared with the mea-
sured cloud-point curve and the critical point for the system copoly-
(ethylene-vinyl acetate) plus methyl acetate. The parameters of the
χ expression were calculated from the critical data and from the slope
of the cloud-point curve at this point.

EXPERIMENT

Copoly(ethylene-vinyl acetate) produced in a high-pressure process
(VEB Leuna-Werke "Walter Ulbricht") was purified by dissolving in
benzene and precipitating by methanol. The purified product was frac-
tionated into two fractions with benzene and n-propyl alcohol. The
fraction used for turbidity measurements is characterized by $\overline{M}_n$ =
14 800, $\overline{M}_w$ = 41 500, and $\overline{M}_z$ = 79 200 (gel permeation chromatog-
raphy). Further, the vinyl acetate content amounts to 42.6 mol% and
the density is ρ_B = 0.9688 g/cm^3 (20°C). Methyl acetate (VEB Berlin-

TABLE 1. Cloud-Point Curve for Ethylene-
Vinyl Acetate Copolymer Plus Methyl Acetate

φ	T, K	φ	T, K
0.0051	311.1	0.0992	307.5
0.0117	314.9	0.1019	307.2
0.0152	315.9	0.1031	307.0
0.0300	314.9	0.1052	306.8
0.0453	313.9	0.1225	305.7
0.0579	312.4	0.1278	305.3
0.0740	310.3	0.1303	305.7
0.0817	309.3	0.1500	304.4
0.0843	309.0	0.1650	303.7
0.0875	308.7	0.1947	302.2
0.0943	308.0	0.2570	296.3

Chemie) was purified by calcium carbonate and water, and dried
thoroughly over calcium chloride and phosphorus pentoxide. The
product was distilled several times over phosphorus pentoxide with a
reflux ratio of 1/15. The gas chromatographic purity was 99.9%.

The turbidity measurements for the system ethylene-vinyl acetate
copolymer plus methyl acetate were performed by a simple visual
method. The equilibrium temperature T is given by Table 1 as a
function of the volume fraction φ of the copolymer.

The method of phase volume ratio due to Koningsveld [10] was ap-
plied for determination of the critical point. The critical parameters
are φ_{cr} = 0.1031 and T_{cr} = 307.0 K.

THEORY

Continuous Thermodynamics of Copolymer Solutions

Let us consider a copolymer consisting of two kinds of monomer
units, α and β. We choose a standard segment and define the segment
numbers, r_α and r_β, as the quotients of the hard core volumes of all
α-monomer units or all β-monomer units, respectively, in a molecule

and of this standard segment. Then we introduce the total segment number r and the segment fraction Y of the α-monomer units within the molecules by

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

Thus, segment number and composition of a polydisperse copolymer may be described by a divariate distribution function $W(r,Y)$, fulfilling the normalization condition

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

Here, the limits of the double integral characterize the total ranges of the r and Y values that occur.

Considering solutions of a Solvent A and a Copolymer B, a phase is characterized sufficiently by the total segment fraction of all copolymer species ψ' and the divariate distribution function of the copolymer $W'(r,Y)$. To calculate the cloud-point curve and the shadow curve, the total segment fraction ψ'' of the coexisting phase " and the equilibrium temperature T at a specified pressure are to be determined. Furthermore, we are interested in the distribution function $W''(r,Y)$ of the coexisting phase ". To calculate these quantities, we need expressions for the segment-molar Gibbs free energy $\overline{\overline{G}}^E$ and the distribution function $W'(r,Y)$. Introducing the weight average $\widetilde{Y}$ of the chemical composition Y of the copolymer:

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

The Huggins χ-parameter concept, assuming χ to be dependent on $\widetilde{Y}$ in the form of a quadratic polynomial, leads to

$$\frac{\overline{\overline{G}}^E}{RT} = \psi(1-\psi)\chi; \qquad \chi = a + b\widetilde{Y} + c\widetilde{Y}^2. \tag{4}$$

The parameters a, b, and c depend on the temperature. The relation for χ may also be justified by molecular considerations [9]. For the distribution function $W'(r,Y)$, we use an expression due to Stockmayer [11], reading in a generalized form

$$W'(r,Y) = \left[\frac{k^{k+1}}{\overline{r}_B' \, \Gamma(k+1)} \left(\frac{r}{\overline{r}_B'} \right)^k \exp\left(-k \frac{r}{\overline{r}_B'} \right) \right]$$
$$\left[\sqrt{\frac{r}{2\pi\epsilon}} \exp\left\{ -\frac{r(Y - \widetilde{Y}')^2}{2\epsilon} \right\} \right]. \tag{5}$$

The first factor is a generalized Schulz-Flory function with respect to r ($r_0 = 0$; $r^0 = \infty$). The parameters are k and $\overline{r}_B'$. Here $\overline{r}_B$ is is the number average of the segment numbers of all copolymer species, related to the distribution function of the phase considered by

$$\frac{1}{\overline{r}_B} = \int_r \int_Y \frac{W(r,Y)}{r} \, dY \, dr, \tag{6}$$

where Γ is the Γ-function. The second factor is a Gaussian distribution with respect to Y exhibiting the standard deviation $(\epsilon/r)^{1/2}$. The parameters are $\widetilde{Y}'$ and ϵ. For a Gaussian function the limits of the domain of definition are $-\infty$ and ∞, whereas in fact Y is limited to the range 0 to 1. Nevertheless, this leads to only a very small error as long as the copolymer distribution is sufficiently narrow with respect to the chemical composition Y. According to the approach described in a previous paper [9], the distribution function $W''(r,Y)$ of the phase '' proves also to be a generalized Stockmayer distribution of the type of Eq. (5) with the same values of k and ϵ. Instead of $\overline{r}_B'$ and $\widetilde{Y}'$, now $\overline{r}_B''$ and $\widetilde{Y}''$ occur related to $\overline{r}_B'$ and $\widetilde{Y}'$ by

$$\overline{r}_B'' = \overline{r}_B' \left(\frac{\psi''}{\psi'} \right)^{1/(k+1)} \tag{7}$$

and

$$\widetilde{Y}'' = \widetilde{Y}' + \frac{\epsilon(b + 2c\widetilde{Y}')(\psi'' - \psi')}{1 + 2\epsilon c(1 - \psi'')}. \tag{8}$$

The quantities ψ'' and T may be calculated by numerical solution of the relations

$$[1 + 2\epsilon c(1 - \psi'')]^2 \left\{ \frac{1}{r_A} \ln \frac{1 - \psi''}{1 - \psi'} - \frac{1}{\bar{r}_B'} k \left[1 - \left(\frac{\psi'}{\psi''} \right)^{1/(k+1)} \right] \right.$$

$$\left. + 2[a + b\tilde{Y}' \quad c\tilde{Y}'^2](\psi'' - \psi') \right\} + \epsilon(b + 2c\tilde{Y}')^2 (\psi'' - \psi')$$

$$\left\{ \frac{1}{2}(1 + 2\epsilon c)(\psi'' - \psi') + \psi''[1 + 2\epsilon c(1 - \psi'')] \right\} = 0 \qquad (9)$$

$$[1 + 2\epsilon c(1 - \psi'')]^2 \left\{ \frac{1}{r_A} \ln \frac{1 - \psi''}{1 - \psi'} + \frac{1}{\bar{r}_B'} \psi' \left[1 - \left(\frac{\psi''}{\psi'} \right)^{k/(k+1)} \right] \right.$$

$$\left. + \frac{1}{r_A}(\psi'' - \psi') + (a + b\tilde{Y}' + c\tilde{Y}'^2)(\psi''^2 - \psi'^2) \right\}$$

$$+ \epsilon(b + 2c\tilde{Y}')^2 \psi''^2 (\psi'' - \psi')[1 + \epsilon c(2 - \psi' - \psi'')] = 0, \qquad (10)$$

where r_A is the segment number of the solvent.

To calculate the cloud-point curve and the shadow curve, only Eqs. (9) and (10) are needed. The plot of T against ψ' represents the cloud-point curve, and the plot of T against ψ'' gives the shadow curve.

In practice, the parameters a, b, and c are determined from experimental data. As a simplification in this paper, all three parameters, a, b, and c, are assumed to depend on the temperature in the same way. Thus, we write

$$\chi = a(T)(1 + \nu_b \tilde{Y} + \nu_c \tilde{Y}^2); \qquad \nu_b = b/a; \qquad \nu_c = c/a, \qquad (11)$$

where ν_b and ν_c are considered to be independent of temperature.

Critical Point

The relations for the critical point may be obtained by expanding Eqs. (9) and (10) into power series at the critical point [12, 13]. Furthermore, these expansions result in relations for the cloud-point curve and the shadow curve valid in the vicinity of the critical point.

Applying Eq. (11), the series expansion is performed with respect to ψ', ψ'', and a. Eliminating ψ'', the first-order terms lead to the spinodal equation as applied to the critical point:

$$\frac{1}{r_A} \frac{1}{1 - \psi_{cr}} + \frac{1}{\bar{r}_B'} \frac{k}{k+1} \frac{1}{\psi_{cr}} - 2a_{cr} [1 + \nu_b \tilde{Y}' + \nu_c \tilde{Y}'^2]$$

$$- \psi_{cr} a_{cr} (\nu_b + 2\nu_c \tilde{Y}') \lambda = 0. \qquad (12)$$

The subscript cr denotes the critical point, where $a_{cr} = a(T_{cr})$, and λ is given by

$$\lambda = \frac{a_{cr}(\nu_b + 2\nu_c \tilde{Y}')\epsilon}{1 + 2a_{cr}\nu_c(1 - \psi_{cr})\epsilon}. \qquad (13)$$

In an analogous way, the second-order terms together with the third-order terms result in the second equation for the critical point, expressing the condition of identical coexisting phases:

$$\frac{1}{r_A} \frac{1}{(1 - \psi_{cr})^2} - \frac{1}{\bar{r}_B'} \frac{k(k+2)}{(k+1)^2} \frac{1}{\psi_{cr}^2} - \frac{3}{\epsilon} (1 + 2\epsilon a_{cr}\nu_c)\lambda^2 = 0. \qquad (14)$$

Comparison of Eqs. (12) and (14) with the corresponding equations for the critical point in solutions of homopolymers (cf., e.g., Refs. 10, 12, and 13) shows that they coincide with the exception of the additional occurrence of the last terms in Eqs. (12) and (14), i.e., the terms containing λ. These terms describe the influence of the polydispersity with respect to chemical heterogenity on the critical point. Hence, these terms vanish either if there is no chemical polydispersity ($\epsilon \rightarrow 0$) or if it has no influence on the thermodynamic behavior ($\nu_b = 0$; $\nu_c = 0$).

Furthermore, the second-order terms and the third-order terms of the series expansion yield a relation between a and ψ', valid in the vicinity of the critical point:

$$
a = a_{cr} \left\{ 1 + \frac{\dfrac{1}{\overline{r}_B'} \dfrac{k}{(k+1)^2} \dfrac{1}{\psi_{cr}^2} + \dfrac{2}{\epsilon}(1 + 2\epsilon a_{cr}\nu_c)\lambda^2}{\dfrac{1}{r_A} \dfrac{1}{1-\psi_{cr}} + \dfrac{1}{\overline{r}_B'} \dfrac{k}{k+1} \dfrac{1}{\psi_{cr}} + \dfrac{1}{\epsilon}\psi_{cr}\lambda^2} (\psi' - \psi_{cr}) \right\}.
$$

$$(15)$$

Prediction of the Cloud-Point Curve and the Shadow Curve for Ethylene-Vinyl Acetate Copolymer Plus Methyl Acetate

For this purpose, first the segment number r_A characterizing the solvent and the parameters $\overline{r}_B'$, $\widetilde{Y}'$, k, and ϵ characterizing the co-polymer distribution (Eq. 5) in the specified phase have to be determined. As a standard segment we choose the ethylene monomer unit (α) occurring in the copolymer. According to Bondi's increments of (molar) van der Waals volumes [14], the standard segment has the value $V_{w,\alpha} = 20.46$ cm^3/mol. For the vinyl acetate monomer unit (β) in the copolymer, the van der Waals volume is $V_{w,\beta} = 45.88$ cm^3/mol, and for methyl acetate $V_{w,A} = 42.54$ cm^3/mol. The quotient $V_{w,A}/V_{w,\alpha}$ yields $r_A = 2.08$. The number average $\overline{r}_B'$ of the segment number of the copolymer (B) in the phase ' may be calculated by

$$
\overline{r}_B' = \frac{M_n}{\widetilde{Y}'M_\alpha + (1 - \widetilde{Y}')M_\beta \dfrac{V_{w,\alpha}}{V_{w,\beta}}} .
$$

$$(16)$$

where M_α and M_β are the molecular weights of the monomer units α and β of the copolymer. $\widetilde{Y}'$ may be obtained from

$$
\widetilde{Y}' = \frac{(1 - X_\beta)V_{w,\alpha}}{(1 - X_\beta)V_{w,\alpha} + X_\beta V_{w,\beta}} ,
$$

$$(17)$$

where X_β is the (average) mole fraction of the vinyl acetate monomer units in the copolymer. From Eqs. (16) and (17) we

get $\widetilde{Y}' = 0.375$ and $\overline{r}_B' = 429$. To calculate k, we use the relation

$$k = \frac{1}{(M_w/M_n) - 1} \cdot \qquad (18)$$

The quantity ϵ may be calculated according to

$$\epsilon = \widetilde{Y}'(1 - \widetilde{Y}') \sqrt{1 - 4\widetilde{Y}'(1 - \widetilde{Y}')(1 - q_\alpha q_\beta)}, \qquad (19)$$

where $q_\alpha = 1.07$ and $q_\beta = 1.08$ [15] are the kinetic parameters of the copolymerization, leading to $\epsilon = 0.25$.

The experimental values for the copolymer concentration are given by the volume fraction φ, but, in the theoretical treatment, the segment fraction ψ is used. To transform φ into ψ and inversely, the relation

$$\psi = \frac{\rho_B \dfrac{\overline{r}_B}{M_n} \varphi}{\rho_A \dfrac{r_A}{M_A}(1 - \varphi) + \rho_B \dfrac{\overline{r}_B}{M_n}\varphi} \qquad (20)$$

has to be applied. Here, M_A and ρ_A are the molecular weight and the density of methyl acetate, respectively. We use the value $\rho_A = 0.9244$ g/cm^3 (20°C) [16].

To apply Eq. (11) for χ, the further simplification

$$a(T) = \frac{a_{cr} T_{cr}}{T} \qquad (21)$$

is used with T_{cr} as the temperature of the critical point. Equation (21) may be justified by molecular considerations (cf. Ref. 9, Appendix). Using Eq. (21), we get, by combining Eqs. (14) and (15),

$$\lambda^2 = \frac{\epsilon}{\psi_{cr}^2} \left\{ \frac{T_{cr}/\psi_{cr}}{(dT/d\psi')_{cr}} \left[\frac{2}{3} \frac{1}{\bar{r}_B'} \frac{k(k+2)}{(k+1)^2} - \frac{2}{3} \frac{1}{r_A} \left(\frac{\psi_{cr}}{1-\psi_{cr}} \right)^2 \right. \right.$$

$$\left. \left. - \frac{1}{\bar{r}_B'} \frac{k}{(k+1)^2} \right] - \frac{1}{\bar{r}_B'} \frac{k}{k+1} - \frac{1}{r_A} \frac{\psi_{cr}}{1-\psi_{cr}} \right\} . \tag{22}$$

This relation permits the calculation of λ^2 from the experimental critical values ψ_{cr} and T_{cr}, together with the slope $(dT/d\psi')_{cr}$ of the experimental cloud-point curve at the critical point. This slope was calculated with the help of the experimental cloud points in the φ-range from 0.0992 to 0.1052, leading to $(dT/d\psi')_{cr} = 113.1$ K.

Applying Eq. (22), we obtain from Eqs. (12)-(14) the following relations:

$$a_{cr}\nu_c = \frac{1}{6\lambda^2} \left\{ \frac{1}{r_A} \frac{1}{(1-\psi_{cr})^2} - \frac{1}{\bar{r}_B'} \frac{k(k+2)}{(k+1)^2} \frac{1}{\psi_{cr}^2} \right\} - \frac{1}{2\epsilon} \tag{23}$$

$$a_{cr}\nu_b = \frac{\lambda}{\epsilon} \left\{ 1 + 2\epsilon a_{cr}\nu_c (1-\psi_{cr}) \right\} - 2\tilde{Y}' a_{cr}\nu_c \tag{24}$$

$$a_{cr} = \frac{1}{2} \left\{ \frac{1}{\bar{r}_B'} \frac{k}{k+1} \frac{1}{\psi_{cr}} + \frac{1}{r_A} \frac{1}{1-\psi_{cr}} - \frac{\lambda^2}{\epsilon} \psi_{cr} \right.$$

$$\left. [1 + 2\epsilon a_{cr}\nu_c (1-\psi_{cr})] \right\} - \tilde{Y}' a_{cr}\nu_b - \tilde{Y}'^2 a_{cr}\nu_c , \tag{25}$$

permitting the calculation of a_{cr}, ν_b, and ν_c from the experimental data mentioned above. Since two λ-values result from Eq. (22), we also obtain two parameter sets:

$$a_{cr} = -0.2547; \quad \nu_b = -8.0078; \quad \nu_c = 7.5447 \tag{26a}$$

$$a_{cr} = 0.1941; \quad \nu_b = 4.3433; \quad \nu_c = -9.9022, \tag{26b}$$

leading to exactly the same cloud-point curve. Considering the molecular background of the parameters in the framework of the lattice model (cf. Ref. 9, Appendix), the Parameter Set (26b) is to
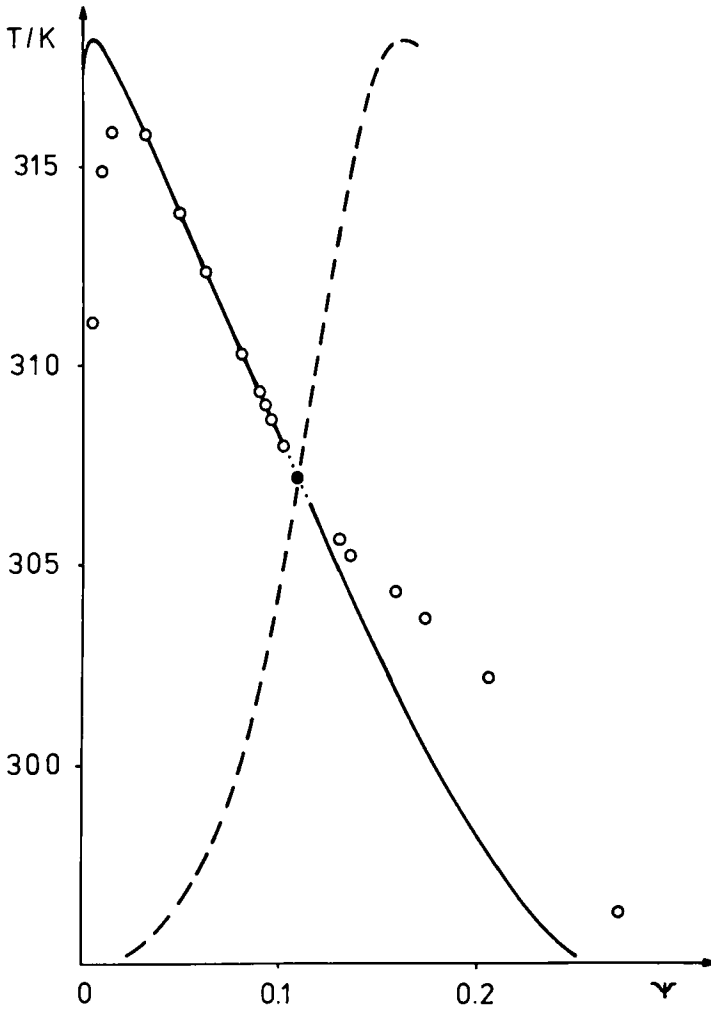
FIG. 1. Copoly(ethylene-vinyl acetate) plus methyl acetate. Cloud-point curve: experimental (○), calculated (——), range of parameter fit (···). Shadow curve: calculated (- -). Critical point: Experimental (●).

be preferred (the vinyl acetate monomer unit in the copolymer and
the methyl acetate molecule should not be too different in their inter-
molecular interactions).

Having obtained all quantities needed in this way, the phase equilib-
rium of the copolymer solution considered may be predicted complete-
ly. Figure 1 shows the cloud-point curve and the shadow curve calcu-
lated with the aid of Eqs. (9) and 10). (Regarding the calculation
of coexistence curves, cf. Ref. 9.)

COMPARISON OF EXPERIMENT AND THEORY

A comparison between calculated and experimental results for the
cloud-point curve is now possible. Therefore (Fig. 1), the experi-
mental cloud points are also plotted. Taking into account the simpli-
city of the assumptions introduced, the agreement between calculated
and experimental results is qualitatively good. The prediction of the
maximum of the cloud-point curve is not quite satisfactory as is also
often the case for solutions of homopolymers. In the region $\psi > \psi_{cr}$,
the agreement between calculated and experimental results is unsatis-
factory. Perhaps the shape of the experimental cloud-point curve in
this region is caused by the tendency to form a three-phase equilib-
rium. Solc [17] studied this phenomenon for homopolymer solutions
in detail. According to his results, the tendency to form three-phase
equilibria corresponds to very asymmetric molecular weight distri-
butions. Therefore, in future work we will substitute the more asym-
metric Wesslau distribution for the Schulz-Flory distribution in the
molecular-weight (or segment-number) dependent part of Eq. (5). A
further modification planned consists in assuming the χ parameter
to depend on the total segment fraction ψ of the copolymer, but then
additional parameters occur which have to be fitted to the experi-
mental cloud-point curve. Hence, the possibilities for comparison
of calculation and experiment are reduced because there is a lack of
additional experimental data.

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