

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Cloud-Point Curves and Coexistence Curves of Several Polydisperse Polystyrenes in Cyclohexane

Margit T. Rätzsch^a; Bernd Krüer^a; Horst Kehlen^a

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

To cite this Article Rätzsch, Margit T. , Krüer, Bernd and Kehlen, Horst(1990) 'Cloud-Point Curves and Coexistence Curves of Several Polydisperse Polystyrenes in Cyclohexane', *Journal of Macromolecular Science, Part A*, 27: 6, 683 — 697

To link to this Article: DOI: 10.1080/00222339009349651

URL: <http://dx.doi.org/10.1080/00222339009349651>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CLOUD-POINT CURVES AND COEXISTENCE CURVES OF SEVERAL POLYDISPERSE POLYSTYRENES IN CYCLOHEXANE

MARGIT T. RÄTZSCH, BERND KRÜGER, and HORST KEHLEN

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

ABSTRACT

Cloud-point curves, critical points, and coexistence curves with feed concentrations close to the critical concentration were measured in three systems involving cyclohexane + different polydisperse polystyrenes. The shape of the coexistence curves is analyzed by using a scaling expression. In two systems the critical exponent β possesses values somewhat larger than in actual binary systems (where $\beta \approx 1/3$), whereas in the third system a somewhat smaller value is found. By using a three-parameter Gibbs free energy relation, cloud-point curves and coexistence curves are calculated from the critical point data and from the slope of the cloud-point curve at this point. To account for polydispersity, the method of continuous thermodynamics is applied. The cloud-point curves are well described, but the prediction of the coexistence curves is bad due to the mean-field character of the Gibbs free energy relation resulting in $\beta = 1/2$. Hence, the often used practice of fitting the parameters of a mean-field Gibbs free energy relation to the critical point and to some cloud points and then to calculate the coexistence data is to be considered with great care.

INTRODUCTION

For binary systems it is experimentally well recognized that near the critical miscibility point (c.p.) the binodal shows an extremely flat course [1]. This phenomenon can be described by using the following scaling expression:

$$X^{\text{II}} - X^{\text{I}} \approx \epsilon^\beta \quad (1)$$

$$\epsilon = \left| \frac{T^c - T}{T^c} \right| \quad (2)$$

The left-hand side in Eq. (1) is the difference of the mole fractions X (of one of the components) in the coexisting phases I, II at temperature T , and T^c is the critical point temperature. The quantity ϵ is the absolute value of the reduced temperature difference. Close to the c.p., β shows a value near 0.34 [1] whereas all mean-field Gibbs free energy relations predict β to be 0.5. In the neighborhood of the c.p., however, large fluctuations that occur in the order parameter are not adequately accounted for by the mean field model.

This phenomenon can be found both in low molecular weight mixtures and in polymer solutions. In the latter case, to account for the large differences in size between polymer and solvent molecules, the mole fractions in Eq. (1) are usually replaced by the mass fractions, the volume fractions, or the segment fractions. For polymer solutions, however, Dobashi et al. [2] reported the limit ϵ^c of the validity range $0 \leq \epsilon \leq \epsilon^c$ for scaling with $\beta \approx 1/3$ to be reduced with increasing molecular weight M of the polymer. For solutions of polystyrene in methylcyclohexane, the relation

$$\epsilon^c \approx M^{-0.7} \quad (3)$$

was presented, with $\epsilon^c \approx 0.002$ for $M = 719$ kg/mol.

In a polydisperse polymer solution, the behavior is expected to be more complicated for two reasons. First, the shorter and longer polymer molecules are influenced differently by the fluctuations occurring. Second, by using Eq. (1) only the variation of the overall polymer contents in both phases with changing temperature is discussed. But in reality, for a polydisperse polymer solution the binodal is a surface in a high-dimen-

sional hyperspace. In ternary polymer solutions (solvent + two monodisperse polymers), Dobashi et al. [3] found the critical exponent β to be shifted to values slightly higher than in binary systems. This corresponds to the prediction of Fisher [4] that impurities in binary systems (the second polymer of Dobashi's system can be regarded as an impurity in the first one) shift the critical exponent β to slightly higher values. Therefore, the overall effect on the β -value is not clear *a priori*. The effects caused by the polydispersity possibly cover the fluctuation effects. Hence, one aim of this work is to measure the coexistence curves in polydisperse polymer solutions and to estimate the β -values occurring.

Cloud-points and critical points are easily measurable points of the liquid-liquid equilibrium for a polydisperse polymer solution. The determination of the coexistence points needs much more effort, but they are quantities of real interest in process designs based on liquid-liquid phase separation. Therefore, it is a practice often used to fit the model parameters of a Gibbs free energy expression to the experimentally determined critical point and to some cloud points and then to predict the coexistence curve by using this model. The parameter fitting generally works very well, although the Gibbs free energy expressions used are of some value. Therefore, the second aim of this work is to investigate how strongly the above-mentioned lack of Gibbs free energy relations influences the accuracy of the predicted coexistence curves in the polydisperse case.

EXPERIMENTAL

The cyclohexane used was refluxed for several hours over sodium, rectified, and kept dry over P_2O_5 . No measurable impurities were detected by gas chromatography. To avoid moisture, a special sample preparation technique using a dry nitrogen atmosphere was applied. The number-average molecular weight \bar{M}_n and the weight-average molecular weight \bar{M}_w characterizing the two relative narrow polystyrenes and the one large-distributed polystyrene are given in Table 1.

Cloud points were measured by using light-scattering equipment. The intensity of the light scattered by the sample under 30 and 90° (with respect to the incident beam) was determined simultaneously with the actual temperature of the sample. If the concentration of the sample is near the critical concentration, the cloud point is indicated by a maximum in the 90° scattered light intensity. A strong increase of the 30° scattered light intensity far away from the critical concentration marks

TABLE 1. Characterization Data of the Polystyrene Samples

Sample	\bar{M}_n , kg/mol	\bar{M}_w , kg/mol	$\bar{M}_w/\bar{M}_n - 1$
PS1	105.1	154.0	0.465
PS2	301.4	424.0	0.407
PS3	100.0	324.0	2.24

the cloud point. The measurements were started approximately 0.2 K above the expected cloud-point temperature. Then the temperature was lowered at a rate of 0.4 K/h. After passing the cloud point, indicated as described above, the temperature was raised at the same rate. In this way, two values, which differed by approximately 0.04 K, were obtained. The range between these two temperatures is considered to be the result of the experimental cloud-point determination.

The critical points were measured by means of the phase volume ratio method which dates back to Koningsveld and Staverman [5]. The critical concentration involved an interval of 0.1 weight % breadth.

Due to the polydispersity of a feed concentration equal to the critical concentration, the coexistence curve is a closed curve. For all other feed concentrations the coexistence curves are divided into two branches beginning at the corresponding points of the cloud-point curve and the shadow curve. (The shadow curve shows the temperature as a function of the overall polymer contents of the first droplets of the precipitated second phase.) Therefore, to permit a discussion on the basis of Eq. (1), coexistence curves with feed concentrations as close as possible to the critical concentration were investigated.

A refractive method was used to determine the coexistence curves. Calibration measurements showed the refractive index (at 32°C) to be a quadratic polynomial of the overall weight fraction of the polymer in the range up to a value of 0.3 of this weight fraction. Furthermore, this function was found to be independent of the molecular weight in the range $M > 20$ kg/mol. Since the molecular weight averages of the polymer samples used are much larger than this limit, fractionation during

phase separation has little influence on the refractive index function. Hence, it was possible to determine the overall polymer content in a phase by means of a simple refractive index measurement.

To determine a coexistence curve, the parent solution was divided into a number of samples. These samples were kept at different temperatures until there was no change in the phase volume ratio during 48 h. Then the coexisting phases were separated and the concentration of each phase was determined as described above.

The critical concentrations and the critical temperatures of the investigated systems are listed in Table 2. Figures 1 to 3 show the cloud points, the c.p.'s, and the coexistence curves of all the systems investigated.

CALCULATIONS

To account for the polydispersity of the polymers, continuous thermodynamics [6, 7] is used. Continuous thermodynamics is based on the direct application of the continuous molecular weight distributions density function in the thermodynamic equations. In this way the thermodynamic quantities become functionals of this distribution function (instead of functions of the mole fractions, etc., which describe the composition in traditional thermodynamics). Since detailed discussions were presented earlier [8, 9], only the necessary resulting system of equations is given here to calculate the cloud-point curves, the shadow curves, and the coexistence curves.

TABLE 2. Critical Point Data for the Systems Cyclohexane + Polystyrene with Different Polystyrene Samples

Polystyrene sample	Critical polystyrene mass fraction	T^c , K
PS1	0.113	293.4
PS2	0.078	298.6
PS3	0.094	300.0

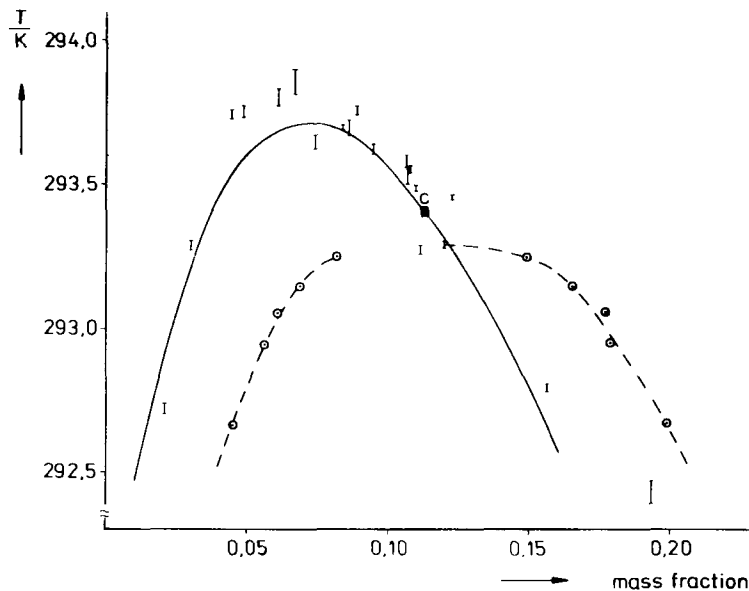


FIG. 1. Cyclohexane + Polystyrene PS1: experimental cloud points (I), experimental critical point (■), and experimental coexistence data (-O-); cloud-point curve (—) calculated by using parameters of Table 3.

To calculate the cloud points (F) and the related shadow points (S) the equations

$$1 - \psi^S = (1 - \psi^F) \exp(\rho_A^F - \rho_A^S) \quad (4a)$$

$$1 = \int \frac{\psi^F}{\psi^S} W^F(M) \exp \left[\frac{M}{M_{\text{seg}}} (\rho_B^F - \rho_B^S) \right] dM \quad (4b)$$

$$\frac{1}{\bar{M}_n^S} = \int \frac{1}{M} \frac{\psi^F}{\psi^S} W^F(M) \exp \left[\frac{M}{M_{\text{seg}}} (\rho_B^F - \rho_B^S) \right] dM \quad (4c)$$

with

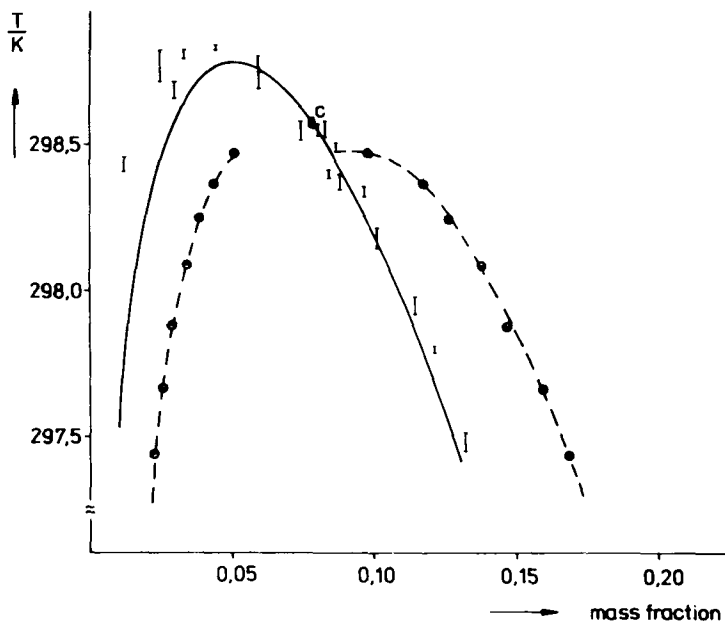


FIG. 2. Cyclohexane + Polystyrene PS2: symbols as in Fig. 1.

$$\rho_A^i = \psi^i \left(1 - \frac{M_{\text{seg}}}{\overline{M}_n^i} \right) + r_A \ln \overline{\gamma}_A^i \quad (5a)$$

$$\rho_B^i = \psi^i \left(1 - \frac{M_{\text{seg}}}{\overline{M}_n^i} \right) + r_A \ln \overline{\gamma}_B^i \quad (5b)$$

$i = F, S$

have to be solved. ψ is the overall polystyrene segment fraction. $W^F(M)$ is the polystyrene distribution density function in the feed phase, defined by the statement that $W^F(M)dM$ is the relative segment fraction (or relative mass fraction) of all polymer species with molar masses between M and $M + dM$. Here the term "relative" means: with respect to the overall polymer contents in this phase. M_{seg} is the molecular weight of a polymer segment. r_A is the segment number of the solvent. $\overline{\gamma}_A^i$ and $\overline{\gamma}_B^i$ are the

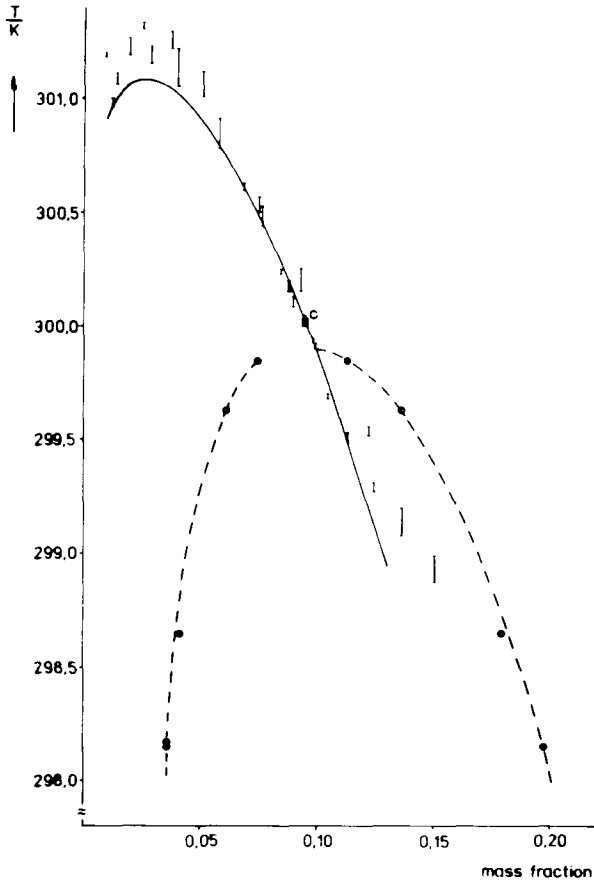


FIG. 3. Cyclohexane + Polystyrene PS3: symbols as in Fig. 1.

segment molar activity coefficients in Phase i of the Solvent A and of the Polystyrene B, respectively. In Eqs. (4) the unknown quantities are ψ^s , \bar{M}_n^s , and the temperature T (since the segment molar activity coefficients are functions of T) which are to be determined by numerical solution of the system of three equations.

To calculate the branches (I, II) of the coexistence curves, the system of equations to be solved reads

$$1 - \psi^{\text{II}} = \frac{1 - \psi^{\text{F}}}{\phi + (1 - \phi) \exp \left[-(\rho_{\text{A}}^{\text{I}} - \rho_{\text{A}}^{\text{II}}) \right]} \quad (6a)$$

$$1 = \int \frac{\psi^{\text{F}} W^{\text{F}}(M)}{\psi^{\text{II}} \left\{ \phi + (1 - \phi) \exp \left[-\frac{M}{M_{\text{seg}}} (\rho_{\text{B}}^{\text{I}} - \rho_{\text{B}}^{\text{II}}) \right] \right\}} dM \quad (6b)$$

$$\frac{1}{\bar{M}_n^{\text{II}}} = \int \frac{\psi^{\text{F}} W^{\text{F}}(M)}{M \psi^{\text{II}} \left\{ \phi + (1 - \phi) \exp \left[-\frac{M}{M_{\text{seg}}} (\rho_{\text{B}}^{\text{I}} - \rho_{\text{B}}^{\text{II}}) \right] \right\}} dM \quad (6c)$$

ϕ is the overall amount of segments in Phase II divided by the overall amount of segments in the feed. The quantities $\rho_{\text{A}}^{\text{I}}$, $\rho_{\text{A}}^{\text{II}}$, $\rho_{\text{B}}^{\text{I}}$, and $\rho_{\text{B}}^{\text{II}}$ can be calculated by Eqs. (5) with $i = \text{I}, \text{II}$. Equations (6) are three equations interrelating the four quantities ψ^{II} , \bar{M}_n^{II} , T , and ϕ . One of these quantities may be specified and then the others are to be calculated by numerical solution of Eqs. (6). The following equations resulting from the mass balance permit the calculation of the related quantities in the coexisting Phase I:

$$\psi^{\text{F}} = (1 - \phi) \psi^{\text{I}} + \phi \psi^{\text{II}} \quad (7)$$

$$\frac{\psi^{\text{F}}}{\bar{M}_n^{\text{F}}} = (1 - \phi) \frac{\psi^{\text{I}}}{\bar{M}_n^{\text{I}}} + \phi \frac{\psi^{\text{II}}}{\bar{M}_n^{\text{II}}} \quad (8)$$

The distribution of all investigated polystyrenes is well described by using the (generalized) Schulz-Flory relation

$$W^{\text{F}}(M) = \left(\frac{kM}{\bar{M}_n^{\text{F}}} \right)^k \frac{1}{\bar{M}_n^{\text{F}} \Gamma(k)} \exp \left(-k \frac{M}{\bar{M}_n^{\text{F}}} \right) \quad (9)$$

with

$$k = \left[\frac{\bar{M}_w^{\text{F}}}{\bar{M}_n^{\text{F}}} - 1 \right]^{-1} \quad (10)$$

For high polymers (but not for oligomers), $\bar{\gamma}_B$ is usually assumed not to be a function of M . According to the characterization data of the polystyrenes (Table 1), this assumption is made for further calculations. Then, in describing the feed distribution by Eq. (9), the integrals in Eqs. (4b) and (4c) may be calculated analytically. Presuming $\bar{M}_n^F(\rho_B^F - \rho_B^S)/M_{\text{seg}}k < 1$, these equations result in

$$\psi^S = \frac{\psi^F}{\left(1 - \frac{\bar{M}_n^F (\rho_B^F - \rho_B^S)}{M_{\text{seg}} k}\right)^{k+1}} \quad (4b)$$

$$\frac{\psi^S}{\bar{M}_n^S} = \frac{\psi^F}{\bar{M}_n^F} \frac{1}{\left(1 - \frac{\bar{M}_n^F (\rho_B^F - \rho_B^S)}{M_{\text{seg}} k}\right)^k} \quad (4c')$$

In the calculations, segment number r_A of the solvent is set equal to 1, resulting in the value 0.10294 kg/mol for the molecular weight M_{seg} of a polymer segment.

To calculate the segment molar activity coefficients $\bar{\gamma}_A$ and $\bar{\gamma}_B$, a free energy relation is needed [8, 9]. In this paper, for the Gibbs free energy per mole of segments an equation is used resulting from the classic Flory-Huggins relation by replacing the χ -term by (R means the gas constant)

$$\frac{\bar{G}^E}{RT} = (1 - \psi)\psi \left\{ \frac{d}{T} (1 - e) \frac{1}{C} - \frac{1}{\psi} \ln A - \frac{1}{(1 - \psi)} \ln B \right\} \quad (11)$$

with $C = 1 - e\psi$

$$A = K_A(1 - e)\psi/C + 1$$

$$B = K_B(1 - \psi)/C + 1$$

$$e = 1 - (\sigma_B/\sigma_A)$$

This relation is obtained by replacing the empirical entropy correction term in the well-known Koningsveld-Kleintjens relation [10] by an orientational entropy correction first presented by Huggins [11] (the two last terms in the braces of Eq. 11). This expression is used because of its high flexibility. σ_A and σ_B are the quotients of the surface and the volume of a molecule of Solvent A and of a segment of Polymer B, respectively. Using

Bondi's data [12] for the calculation of molecular surfaces and volumes, e equals 0.0772 in all systems investigated. Hence, Eq. (11) contains the three parameters d , K_A , and K_B . The parameter d can be calculated independently of K_A and K_B by using the experimentally determined slope of the cloud-point curve at the critical point. This slope is equal to the slope of the spinoidal curve in the critical point related to d by

$$\left(\frac{dT}{d\psi}\right)_{\text{spinoidal}}^c = -\left(\frac{\bar{M}_z}{\bar{M}_w} - 1\right) \frac{T^c C^{c^3}}{2d(1-e)^2 \psi^{c^2}} \frac{M_{\text{seg}}}{M_w} \quad (12)$$

\bar{M}_z is the z -average molecular weight. K_A and K_B can be calculated from the critical point data ψ^c , T^c by the equations

$$\begin{aligned} 0 = & \frac{1}{1-\psi^c} + \frac{M_{\text{seg}}}{\bar{M}_w \psi^c} + \frac{2(1-e)}{C^{c^3}} \left[\frac{K_A}{A^c} (1-e) + \frac{K_B}{B^c} \right] \\ & + \frac{(1-e)^2}{C^{c^4}} \left[\frac{K_A^2}{A^{c^2}} (1-\psi^c) + \frac{K_B^2}{B^{c^2}} \psi^c \right] \\ & - \frac{2d(1-e)^2}{T^c C^{c^3}} \quad (\text{spinoidal condition}) \end{aligned} \quad (13)$$

$$\begin{aligned} 0 = & \frac{1}{(1-\psi^c)^2} - \frac{\bar{M}_z M_{\text{seg}}}{\bar{M}_w^2 \psi^{c^2}} + \frac{6e(1-e)}{C^{c^4}} \left[\frac{K_A}{A^c} (1-e) + \frac{K_B}{B^c} \right] \\ & + \frac{3(1-e)^2}{C^{c^5}} \left[\frac{K_B^2}{B^{c^2}} (1+e\psi^c) - \frac{K_A^2}{A^{c^2}} (1-2e+e\psi^c) \right] \\ & + \frac{2(1-e)^3}{C^{c^6}} \left[\frac{K_B^3}{B^{c^3}} \psi^c - \frac{K_A^3}{A^{c^3}} (1-\psi^c) \right] - \frac{6de(1-e)^2}{T^c C^{c^4}} \end{aligned} \quad (14)$$

For the systems investigated, the parameter values obtained in this way are given in Table 3.

TABLE 3. Slope $(dT/d\psi)^c$ of the Cloud-Point Curve Determined Experimentally and the Values of the Parameters d , K_A , and K_B Calculated from This Slope and from the Experimental Critical Point Data (Table 2)

System	$(dT/d\psi)^c$, K	d , K	K_A	K_B
Cyclohexane + PS1	-15.25	77.36	-0.8604 ₅	0.1704 ₆
Cyclohexane + PS2	-16.63	52.05	-0.8227 ₈	0.0656 ₉
Cyclohexane + PS3	-30.69	60.36	-0.8244 ₇	0.0936 ₈

DISCUSSION

Since it was not possible to measure a coexistence curve with a feed concentration exactly equal to the critical concentration, the quantity ϵ for scaling was defined by

$$\epsilon = \left| \frac{T_{\max} - T}{T_{\max}} \right| \quad (15)$$

where T_{\max} is the maximum temperature occurring when the two coexistence curve branches are interpolated to form a closed curve. In all cases T_{\max} differs from the related cloud-point temperature by only a very small amount since the polymer concentrations of the feeds applied were close to the critical concentrations. A least-squares fit using Eqs. (1) and (15) yields the β values listed in Table 4. The critical exponents in the systems with PS2 and PS3 tend to be slightly higher values compared to that of true binary systems. This is in agreement with the behavior in ternary systems as discussed above. The reason for the deviation to a smaller value in the system with PS1 is not known. Deviation from the scaling expression (1) over the whole range of determinations was not observed, i.e., a log-log plot of $(\bar{X}^{II} - \bar{X}^I)$ versus ϵ yields a straight line.

The experiments show clearly that the polydispersity does not cover the fluctuation effects near the c.p., i.e., in all cases the quantity β deviates substantially from the classic mean field value $1/2$ in the total range investigated.

By using the parameters of Table 3, the cloud-point curves were calcu-

TABLE 4. Critical Exponents β for the Coexistence Curves of Several Polystyrenes in Cyclohexane

Polystyrene sample	Polystyrene mass fraction of the feed	β
PS1	0.1179	0.289
PS2	0.0800	0.381
PS3	0.0994	0.398

lated and are shown in Figs. 1 to 3 for comparison with the experimental results. The prediction is quite good. Contrary to this result, the prediction of the coexistence curves on this basis is always bad. As an example, the calculated and the experimental coexistence curves in the system with PS1 are compared in Fig. 4. This bad prediction clearly results from the mean field character of the model used ($\beta = 1/2$). A question arises of how to explain the good ability of the \bar{G}^E relation to describe the cloud-point curve when the relation is not correct, as the bad description of the coexistence curves shows. The answer is: In fitting the parameters, data on the cloud-point curve but not on the related shadow curve are used since this curve is not known. Hence, there is an additional degree of freedom to shift the shadow curve in such a way that the cloud-point curve is well described. Similar calculations were carried out using other possible \bar{G}^E relations besides that given in Eq. (11). The result was always the same. It is possible to describe the cloud-point curve in more or less good agreement with the experiment, but if these parameters are used to predict the coexistence curves, a similar bad correspondence between experiment and prediction, as shown in Fig. 4, is always obtained.

The conclusion is that the usual mean-field Gibbs free energy relations permit a good modeling of the cloud-point curve. But there is no hope of obtaining in this way a Gibbs free energy relation that permits a realistic prediction of the coexistence curves or of the related shadow curve, at least not near the c.p. Hence, the often-used practice of fitting the parameters of a mean-field \bar{G}^E relation by using the c.p. data and then calculating the coexistence curves is a doubtful procedure.

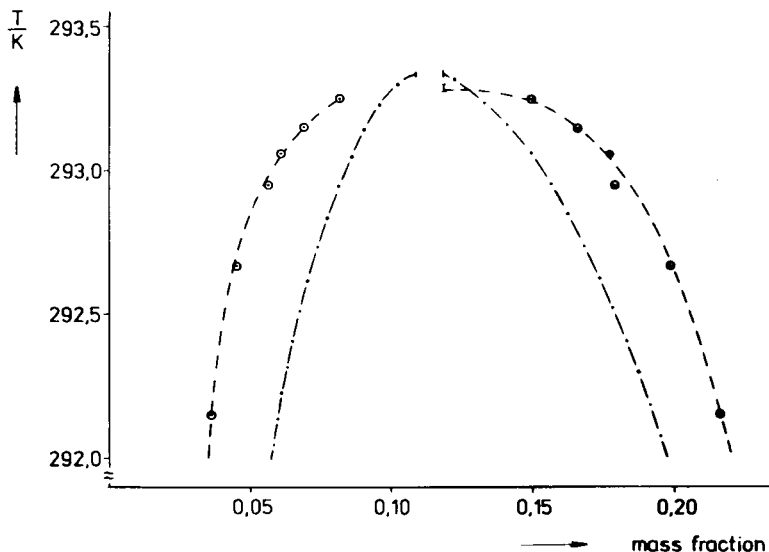


FIG. 4. Comparison of experimental ($-\odot-$) and calculated ($- \cdot -$) coexistence curve for the system cyclohexane + Polystyrene PS1; (\triangle) related experimental cloud point.

REFERENCES

- [1] A. Stein and G. F. Allen, *J. Phys. Chem. Ref. Data*, **2**, 443 (1973).
- [2] T. Dobashi, M. Nakata, and M. Kaneko, *J. Chem. Phys.*, **72**, 6685, 6692 (1980).
- [3] T. Dobashi, M. Nakata, and M. Kaneko, *Ibid.*, **80**, 948 (1984).
- [4] M. E. Fisher, *Phys. Rev.*, **176**, 257 (1968).
- [5] R. Koningsveld and A. J. Staverman, *J. Polym. Sci., Part C*, **16**, 1715 (1967).
- [6] H. Kehlen and M. T. Rätzsch, *Proceedings of the 6th International Conference on Thermodynamics, Merseburg 1980*, p. 41.
- [7] M. T. Rätzsch and H. Kehlen, *Fluid Phase Equilibria*, **14**, 225 (1983).
- [8] H. Kehlen and M. T. Rätzsch, *Z. Phys. Chem. (Leipzig)*, **264**, 1153 (1983).
- [9] M. T. Rätzsch and H. Kehlen, *J. Macromol. Sci. - Chem.*, **A22**, 323 (1985).

- [10] R. Koningsveld and L. A. Kleintjens, *Macromolecules*, **4**, 637 (1971).
- [11] M. L. Huggins, *J. Phys. Chem.*, **75**, 1255 (1971).
- [12] A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, 1968.

Received June 30, 1989

Revision received September 25, 1989