Polymer Fractionation Calculations Using Refined Free Energy Relations

M. T. Rätzsch[a]; S. Enders[a]; L. Tschersich[a]; H. Kehlen[a]

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

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M. T. RÄTZSCH,* S. ENDERS, L. TSCHERSICH, and H. KEHLEN

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

ABSTRACT

In an earlier paper, continuous thermodynamics was applied to calculate polymer fractionation procedures leading to lucid equations favorable for computer simulations. The present paper refines that treatment by applying more sophisticated Gibbs free energy relations. The simulation results agree closely with the experimental data, assuming the Flory-Huggins interaction parameter to be a function of the concentration.

INTRODUCTION

The molecular weight fractionation based on small solubility differences of the species was extensively used for many years as the main method for determining the molecular weight distribution (MWD) of synthetic polymers. The direct use of such continuous distribution functions (instead of the amounts of the individual species) forms the basic idea of continuous thermodynamics [2, 3], a version of thermodynamics which permits concise treatment of all complex multicomponent systems. Continuous thermodynamics was also applied to polymer systems [4, 5] (for a survey, see Ref. 6) and, in particular, to successive polymer fractionations on the basis of solubility differences [1]. In this way, equations clearly describing the fractionation procedures were obtained.

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In the paper referred to, the simple Huggins' χ-parameter concept was chosen for modeling the Gibbs free energy. However, to compare the calculated results with experimental fractionation data, the use of a more realistic expression for the free energy is necessary. Therefore, in this paper, various relations for the Gibbs free energy will be used to simulate successive solution fractionation (SSF) and successive precipitation fractionation (SPF). In particular, the polymer/solvent interaction parameter of Flory-Huggins' lattice theory [7, 8] will be assumed to be a function of the polymer contents, of the temperature, and/or a functional of the distribution function. Furthermore, the bridging theory, suggested by Koningsveld, Stockmayer, Kennedy, and Kleintjens [9], will be applied.

SUCCESSIVE SOLUTION FRACTIONATION (SSF)

A solution of a polymer (B) in a solvent (A) is cooled to obtain liquid–liquid phase separation into a polymer-lean Phase I and a polymer-rich Phase II. The polymer-lean phase is removed from the solution. The first polymer fraction is obtained from the polymer-lean phase by evaporating to dryness. Solvent is added to the polymer-rich phase up to the volume of the original feed phase, thus providing the mother solution for the next fractionation step, etc. The final fraction is obtained from the precipitate of the last step.

In SSF, to a very close approximation, the total number of segments is the same in the feed phases of all steps leading to the relation [1]

$$\psi_{j+1}^{F} W_{j+1}^{F}(r) = \phi_j \psi_j^{II} W_j^{II}(r) \tag{1}$$

The species of the polymer are identified by their segment numbers r, defined as the ratio of the hard-core volume of the species considered with relation to the hard-core volume of an arbitrarily chosen standard segment. The superscript F stands for feed phase, and the subscript j indicates the fractionation step j. The quantity ψ is the overall segment fraction of the polymer, and W is the continuous distribution function defined by the statement that $W(r)dr$ equals the (relative) segment fraction of all polymer species with segment numbers between r and $r + dr$. Furthermore, ϕ is the total amount of segments in Phase II divided by the total amount of segments in the feed. Treating polymer fractionation, the introduction of the precipitation rate $K(r)$ is favorable. $K(r)$ is defined in an analogous way as ϕ but refers to the amounts of segment

of the polymer species with segment numbers between r and $r + dr$. In continuous thermodynamics the precipitation rate K for the fractionation step j reads

$$K_j(r) = \phi_j \frac{\psi_j^{II} W_j^{II}(r)}{\psi_j^F W_j^F(r)} = \frac{\phi_j}{\phi_j + (1 - \phi_j) \exp \left[-r\rho_{Bj}(r)\right]} \tag{2}$$

where

$$\rho_{Bj}(r) = \frac{1}{\bar{r}_j^{II}} - \frac{1}{\bar{r}_j^I} + \ln \bar{\bar{f}}^I_{Bj}(r) - \ln \bar{\bar{f}}^{II}_{Bj}(r) \tag{3}$$

The segment-molar activity coefficients $\bar{\bar{f}}$ describe the deviations from a Flory-Huggins mixture (with $\chi = 0$). These coefficients are to be calculated according to the relation for the segment-molar Gibbs free energy $\bar{\bar{G}}$ since $\ln \bar{\bar{f}}_B$ and $\ln \bar{\bar{f}}_A$ are the partial segment-molar quantities with respect to G^E/RT, i.e., the segment-molar excess Gibbs energy $\bar{\bar{G}}^E$ divided by the gas constant R and the temperature T. The quantity $\bar{r}$ is the number-average segment number for the phase considered given by

$$\frac{1}{\bar{r}} = \frac{1 - \psi}{r_A} + \frac{\psi}{\bar{r}_{NB}}, \qquad \text{where} \quad \frac{1}{\bar{r}_{NB}} = \int_r \frac{W(r)}{r} \, dr \tag{4}$$

where r_A is the segment number of the solvent molecules.

Combination of Eqs. (1) and (2) with the equations describing the coexistence curves leads to the following system of equations [1, 5]:

$$1 - \psi_j^{II} = \frac{1 - \psi_j^F}{\phi_j + (1 - \phi_j) \exp (-r_A \rho_{Aj})} \tag{5}$$

$$\psi_j^{II} = \int_r \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} K_k(r) \psi_1^F W_1^F(r) dr \tag{6}$$

$$\frac{1}{\bar{r}_j^{II}} = \frac{1 - \psi_j^{II}}{r_A} + \int_r \frac{K_j(r)}{r\phi_j} \prod_{k=1}^{j-1} K_k(r) \psi_1^F W_1^F(r) dr \tag{7}$$

where

$$\rho_{Aj} = \frac{1}{\bar{r}_j^{II}} - \frac{1}{\bar{r}_j^{I}} + \ln \bar{\bar{f}}_{Aj}^{I} - \ln \bar{\bar{f}}_{Aj}^{II} \tag{8}$$

This system of equations permits the successive calculation of the unknown quantities ψ_j^{II}, $\bar{r}_j^{II}$, and ϕ_j (or T_j) for all fractionation steps j. The calculation has to be performed successively, i.e., at first for $j = 1$, then for $j = 2$, etc. Knowing these quantities, the distribution function of the ith polymer fraction $W_i^{I}(r)$ may easily be calculated from the initial polymer distribution $W_1^{F}(r)$:

$$\psi_i^{I} W_i^{I}(r) = \frac{1 - K_i(r)}{1 - \phi_i} \prod_{j=1}^{i-1} K_j(r) \psi_1^{F} W_1^{F}(r) \tag{9}$$

SUCCESSIVE PRECIPITATION FRACTIONATION (SPF)

When the temperature of the solution is lowered gradually, the precipitates are successively separated from the solution, leading to the polymer fractions $j = 1, 2, \ldots$. The final fraction is obtained by evaporating the precipitate of the last step. In SPF, Phase I from Step j is used directly as the feed phase for Step $(j + 1)$. Hence, the following relations apply:

$$\psi_{j+1}^{F} = \psi_j^{I} \tag{10}$$

$$W_{j+1}^{F}(r) = W_j^{I}(r) \tag{11}$$

$$\bar{r}_{j+1}^{F} = \bar{r}_j^{I} \tag{12}$$

With the aid of Eqs. (2), (3), (10)–(12), and of the equation describing the coexistence curve, a system of equations for the simulation of the successive precipitation fractionation [1] is obtained.

$$1 - \psi_j^{II} = \frac{1 - \psi_j^{F}}{\phi_j + (1 - \phi_j) \exp(-r_A \rho_{Aj})} \tag{13}$$

$$\psi_j^{II} = \int_r \frac{K_j(r)}{\phi_j} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi_1^F W_1^F(r)dr \tag{14}$$

$$\frac{1}{\bar{r}_j^{II}} = \frac{1 - \psi_j^{II}}{r_A} + \int_r \frac{K_j(r)}{r\phi_j} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi_1^F W_1^F(r)dr \tag{15}$$

These relations correspond to Eqs. (5)–(7) in the case of SSF. They permit the calculation of the unknown quantities ψ_j^{II}, $\bar{r}_j^{II}$, and ϕ_j (or T_j) from the composition of the initial polymer solution, i.e., from ψ_1^F and $W_1^F(r)$. If these unknowns are calculated, the distribution functions $W_i^{II}(r)$ of the polymer fractions may easily be obtained from

$$\psi_i^{II} W_i^{II}(r) = \frac{K_i(r)}{\phi_i} \prod_{j=1}^{i-1} \frac{1 - K_j(r)}{1 - \phi_j} \psi_1^F W_1^F(r) \tag{16}$$

FREE ENERGY MODELS

On the basis of Flory-Huggins' lattice theory, a deviation of a polymer solution from an ideal-athermic mixture is characterized by the segment-molar excess Gibbs free energy $\overline{\overline{G}}^E$ according to

$$\overline{\overline{G}}^E = \frac{RT}{r_A} g(\psi, T; W)(1 - \psi)\psi \tag{17}$$

The dimensionless polymer/solvent interaction quantity g is assumed to be a function with respect to ψ and T and a functional with respect to the continuous distribution function W. The influence of the pressure on g is neglected.

The original Flory-Huggins theory [7, 8] assumes the interaction quantity g to be a function only of the temperature:

$$g = \chi_0(T); \quad \chi_0(T) = \beta_1 + \beta_2/T \tag{18}$$

Here χ_0 is assumed to be a linear function of $1/T$, i.e., β_1 and β_2 are empirical constants for a given polymer/solvent system.

It is well known that the original Flory-Huggins theory (Eq. 18) often fails in describing a real polymer solution. Experimental data show that the polymer/solvent interaction quantity g is usually a function of the polymer contents of the solution. Kamide and Sugamiya [10] formulated

$$g = \chi_0(1 + p\psi) \tag{19}$$

Here the parameter p expresses how strongly the polymer contents ψ influences the polymer/solvent interaction quantity g. More generally, p may be a function of $\bar{r}_{NB}$ of the polymer and of the temperature T of the solution. However, experimental results show that p can often be regarded approximately as a constant within the experimental uncertainties over a wide range of $\bar{r}_{NB}$ and T. In the calculations p was assumed to be constant throughout a fractionation run.

On the basis of theoretical considerations on the chain dimensions, Orofino and Flory [11] derived another relation reading

$$g = \frac{\chi_0(1 - \gamma)}{(1 - \gamma\psi)} \tag{20}$$

The parameter γ may be determined from the surface/volume ratio of the segments. In the calculations, γ was again assumed to be constant throughout a fractionation run. Koningsveld and Kleintjens [12] introduced an additional fitting quantity α:

$$g = \alpha + \frac{\chi_0(1 - \gamma)}{(1 - \gamma\psi)} \tag{21}$$

The parameter α accounts for the segment-molar excess entropy. Taking into consideration that g is also a function of the number-average segment number $\bar{r}_{NB}$, the experimental results suggest a linear relation between $\bar{r}_{NB}$ and the reciprocal segment number [13]. Since, according to Eq. (4), $\bar{r}_{NB}$ is a functional with respect to the distribution function $W(r)$, this also holds for g, i.e., $g = g(\psi, T; W)$. In this paper the relation [14]

$$g = \frac{\chi_0(1 - \gamma)}{(1 - \gamma\psi)}\left[1 + \frac{Q}{\bar{r}_{NB}}\right] \tag{22}$$

is used where Q is an additional fitting parameter. Since g is a functional of $W(r)$, the segment-molar activity coefficients must also be a functional.

In contrast to these ideas, Koningsveld, Stockmayer, Kennedy, and Kleintjens [9] used an interpolation procedure to provide continuity between the two extremes of polymer solution behavior; the concentrated-solution lattice formalism and the excluded-volume theory for dilute solutions. The authors proposed to write g for polymer solutions of arbitrary concentrations simply as a linear combination of the two extreme cases:

$$g = g_{DIL}P + g_{CONC}(1 - P) = g_{CONC} + P(g_{DIL} - g_{CONC}) \qquad (23)$$

The fraction P equals the probability that no polymer segment is found in a given small volume element in the solution. This may be written as

$$P = \exp(-\lambda_2\psi) \qquad (24)$$

where

$$\lambda_2 = \frac{4\pi a N_{AV} V_A^{1/2} b^3 \bar{r}_{wB}^{1/2}}{3 v_B^{1/2}} \qquad (25)$$

Here a is a geometrical factor near unity and b is the proportionality constant between the root-mean-square radius of gyration of the coil in its unperturbated state and the root of chain length. N_{AV} is Avogadro's number. V_A is the molar volume of the solvent and v_B is the partial specific volume of the polymer. The quantity $\bar{r}_{wB}$ means the mass-average segment number of the polymer. As a further approximation, $g_{DIL} - g_{CONC}$ is represented by its limiting value for vanishing ψ

$$g^+ = \lim_{\psi \to 0} (g_{DIL} - g_{CONC}) \qquad (26)$$

leading to

$$g = g_{CONC} + g^+ \exp(-\lambda_2\psi) \qquad (27)$$

with g^+ independent of concentration.

It may be shown by the excluded-volume treatment [15] that

$$g^+ = \frac{(0.5 - \lambda_1)(1 - h(z))}{1 + \lambda_2} \tag{28}$$

Here λ_1 is a function of the temperature but not of the composition. From the several proposed relations for $h(z)$, the following one, dating back to Stockmayer [16], was selected:

$$h(z) = 1/(1 + 2.867z) \tag{29}$$

$$z = \left[\frac{v_B}{4\pi b^2}\right]^{-3/2} \left[\frac{1}{V_A}\right]^{1/2} \left[\frac{0.5 - \lambda_1}{N_{AV}}\right] \bar{r}_{WB}^{1/2} \tag{30}$$

To account for the polydispersity, the segment number r is replaced by the mass-average segment number $\bar{r}_{WB}$. For sufficiently concentrated solutions, g_{CONC} may be described by Eq. (21), leading finally to

$$g = \alpha + \frac{\chi_0(1 - \gamma)}{(1 - \gamma\psi)} \tag{31}$$

$$+ \frac{(0.5 - \lambda_1)[1 - \exp(-\lambda_2\psi)/(1 + 2.867z)]}{1 + \lambda_2}$$

SIMULATION

In the computer simulation of hypothetical fractionation runs [10, 17], equal amounts of the fractions were assumed. In experiments it is difficult to verify this condition. The amounts of the fractions are expressed with the quantities q_p and q_s being defined as the quotients of the overall amounts of polymer segments in Phase II or Phase I, n_{Bj}^{II} or n_{Bj}^{I}, respectively, of the considered separation step, and in the original polymer n_{B1}^{F}

$$q_p = n_{Bj}^{II}/n_{B1}^{F} \quad \text{and} \quad q_s = n_{Bj}^{I}/n_{B1}^{F} \tag{32}$$

To permit a comparison of the simulation calculations with experimental results, the experimental values q_{pj} or q_{sj} were used for all fractionation steps.
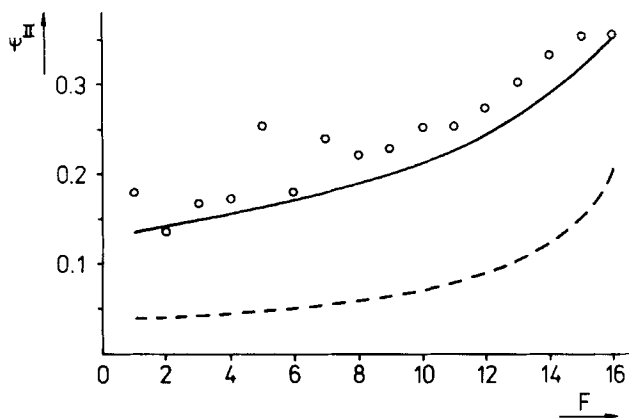
FIG. 1. SPF for polystyrene + methylcyclohexane: polystyrene segment fraction ψ^{II} in several fractions F. Circles are experimental values [13]; broken line is computer simulation with Eq. (18); full line is computer simulation with Eq. (20).

In this paper, SSF and SPF experiments for atactic polystyrene in methylcyclohexane and phase separations for atactic polystyrene in cyclohexane by Kamide, Miyazaki, and Abe [13] were chosen to compare the simulation calculations with experimental data. The computer simulations were performed for solutions with the initial overall polymer segment fraction $\psi^F = 0.0094$ of polystyrene described by a Schulz-Flory distribution with $\bar{r}_{WB} = 2400$ and $\bar{r}_{WB}/\bar{r}_{NB} = 2.8$.

RESULTS AND DISCUSSION

Original Lattice Theory

Here the g-parameter is given by Eq. (18). In Fig. 1 for SPF of the system polystyrene + methylcyclohexane, the calculated polymer segment fractions in the polymer-rich phase are compared with experimental values. For SPF and also for SSF, the calculated values are always too small. The phase volume ratio $R = V^I/V^{II}$ also proves to be too small (Fig. 2). Other quantities are also not calculated correctly, as shown in Fig. 3 for the number-average molecular weight of the polymer in the Phase II in SPF. The correct description of the number-average
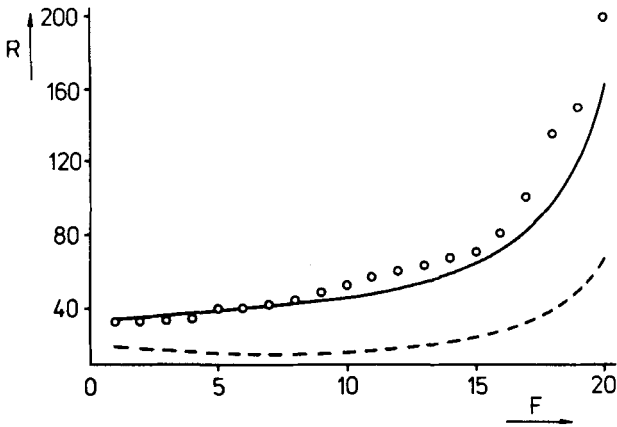
FIG. 2. SSF for polystyrene + methylcyclohexane: phase volume ratio R in several fractions F. Circles are experimental values [13]; broken line is computer simulation with Eq. (18); full line is computer simulation with Eq. (20).

FIG. 3. SPF for polystyrene + methylcyclohexane: number-average molar mass $\overline{M}_{NB}^{II}$ of polymer-rich phases in several fractions F. Circles are experimental values [13]; broken line is computer simulation with Eq. (18); full line is computer simulation with Eq. (20).
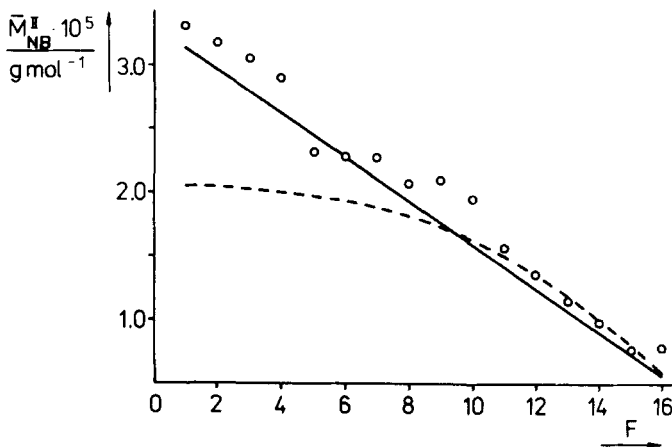
molecular weight is important since the determination of the distribution function of the original polymer is the aim of analytical fractionations. This function is obtained from the number-average molecular weights of the fractions. Hence, the result of the comparison is that the experimental fractionation data of the system polystyrene + methylcyclohexane can be described only qualitatively by the original lattice theory, Eq. (18).

g depends on Concentration

In Eqs. (19)–(21) the g-parameter is assumed to be a function of the concentration ψ. Applying Eq. (19), Kamide, Miyazaki, and Abe [13] proposed $p = 0.7$ for the system polystyrene + methylcyclohexane and $p = 0.6$ for the system polystyrene + cyclohexane. In Eqs. (20) and (21) the parameter γ was fitted to the first fraction. As a result, in the calculations γ was assumed to be 0.3 for the system polystyrene + methylcyclohexane and 0.24 for the system polystyrene + cyclohexane. The parameter α in Eq. (21) is known in the existing literature only for the system polystyrene + cyclohexane [12]. The experimental spinoidal points [12] describe the theoretical curve well, assuming $\alpha = -0.1597$.

Applying Eqs. (19)–(21) to calculate the spinoidal curve or the critical point, drastic differences between the results occur. But in applying these equations to simulate polymer fractionation, no marked differences are found. The differences become perceptible only if large q_p– or q_s–values are considered.

The polymer segment fraction in a polymer-rich phase at a given fractionation step increases strongly with p or γ. Comparison of simulated and experimental data shows that the consideration of the interaction quantity as a function of concentration leads to a better agreement of the segment fractions in polymer-rich phases (Fig. 1). The experimental points are in reasonable consistency with the calculated points by applying $p = 0.7$ or $\gamma = 0.3$.

The phase volume ratio R increases markedly with increasing p or γ, particularly in higher fractionation steps of SSF and in lower steps of SPF, i.e., in the steps yielding fractions with low molecular weights. The value of R in SPF is always larger than that in SSF. In Fig. 2 the effect of p or γ on R by SPF is demonstrated. The difference between the experimental and calculated R values at $p = 0.7$ or $\gamma = 0.3$ for polystyrene + methylcyclohexane is within the experimental error, independent of the fractionation run (SPF or SSF).
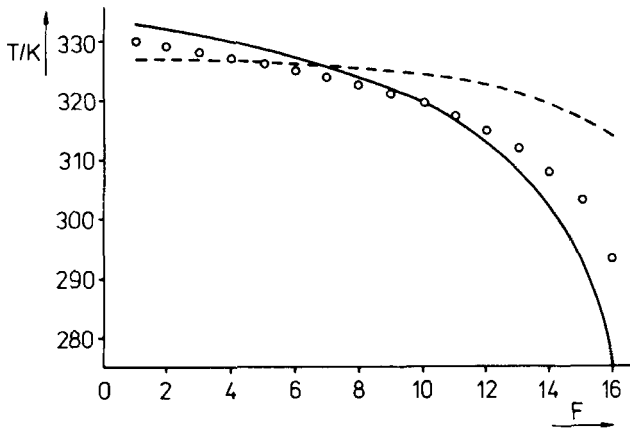
FIG. 4. SPF for polystyrene + methylcyclohexane: phase separation temperatures T in several fractions F. Circles are experimental values [13]; broken line is computer simulation with parameters obtained from spinoidal data [14]; full line is computer simulation with parameters obtained from SSF.

Figure 3 shows that a good description of the experimental number-average molecular weight is achieved. The molecular weight distribution curve depends markedly on the p — or γ — values chosen. The polydispersity of the fractions, as expressed by $\bar{r}_{WB}/\bar{r}_{NB} - 1$, decreases gradually with increasing p or γ, irrespective of the fractionation schemes. In other words, larger p or γ gives narrower fractions. It is noticeable that the maximum of the distribution function in the first fractions shifts to the higher molecular masses region with increasing p or γ as shown in Fig. 3, where the number-average molecular masses are plotted versus the fractionation step j. In the higher fractionation steps, no shift of the maximum occurs (Fig. 3). The effect of p or γ on $\bar{r}_{NB}^{II}$ for the fractions separated by SSF is much smaller than that in SPF.

The values of χ_0 in the fractionation calculations may be converted to T by Eq. (18). For the system polystyrene + methylcyclohexane, Kamide, Sugamiya, Ogawa, Nakaywa, and Baba [18] suggested the use of following parameter values:

$$\beta_1 = -0.759 \quad \text{and} \quad \beta_2 = 438 \text{ K}$$

These values were obtained by fitting to spinoidal data. Figure 4 illustrates the change of T during a given SPF process. The phase separation

temperatures obtained by computer simulation with these parameters differ essentially from the experimental temperatures. Therefore, the parameters β_1 and β_2 were fitted to temperatures from SSF, resulting in

$$\beta_1 = 0.468 \quad \text{and} \quad \beta = 85.459 \text{ K}$$

By using these values, the accuracy of the simulation of SPF is greatly improved (Fig. 4). But the difference between experimental and calculated phase separation temperatures is still large for the fractions containing the short polymer chains, independent of the fractionation run (SPF or SSF).

g Depends on Distribution Function

The dependence of g on the continuous distribution function is taken into consideration by Eq. (22). Calculations with Eq. (22) show that the polystyrene segment fraction ψ^{II} in the polymer-rich phase increases if Q has a positive value and decreases if Q is negative. Due to the large experimental errors, it seems to be senseless to fit Q to fractionation data. Hence, the parameter Q was arbitrarily chosen to equal 20 or -20. Applying Eq. (22) only, the phase separation temperatures of SSF in the first fractions could be improved. The parameter g proves to be approximately independent of $\bar{r}_{NB}$ for small q_p − or q_s − values. For large q_p values, the parameter g decreases a little with increasing $\bar{r}_{NB}$. But the constancy of g over the whole $\bar{r}_{NB}$ range can be regarded as a good approximation.

Bridging Theory

In applying the bridging theory to polymer fractionation, Eq. (31) has to be used. $\overline{\overline{G}}^E$ depends on the mass-average segment number $\bar{r}_{WB}$ (Eqs. 25 and 33). The mass-average segment number forms an additional functional (first moment) of the distribution function

$$\bar{r}_{WB} = \int_r rW(r)dr \tag{33}$$

i.e., in the calculations the additional unknown $\bar{r}_{WB}$ occurs. Hence, an additional equation is necessary which may be obtained from the mass balance and reads

$$\bar{r}_{WB}^{F} = (1 - \phi)\,\bar{r}_{WB}^{I} + \phi\bar{r}_{WB}^{II} \tag{34}$$

Applying the bridging theory, the mathematical expense and the computer time grow drastically. The computer time increases by 30%. The molecular characteristics for the calculation of the segment molar activity coefficients are found in the literature only in connection with the system polystyrene + cyclohexane. The following values were used for the calculations:

$$\alpha = -0.1597,\, \beta_1 = 0.4987,\, \beta_2 = 111.74\,K,\, \gamma = 0.2365,$$
$$v_B = 0.925\,cm^3/g,\, V_A = 108\,cm^3/mol,\, b^2 = 7.6 \times 10^{-10}\,cm^2,$$
$$\lambda_2 = 0.57,\, a = 1$$

The parameters α, β_1, β_2, and γ were fitted by Koningsveld, Stockmayer, Kennedy and Kleintjens [9] to the spinoidal curve. The molecular characteristics, e.g., the partial specific volume of the polymer in the solvent, are taken from standard sources [19]. Experimental fractionation data for the system polystyrene + cyclohexane are found in the literature only for the first fraction, i.e., simple phase separation. Therefore, a comparison with the experiment could be made only for these data (Fig. 5). In order to make a comparison, analogous computer simulations were also carried out by using Eqs. (19)–(21), showing that these equations provide similar results (Fig. 5). For q_p values with practical interest (<0.1), the bridging theory, Eq. (31), provides practically the same results as the refined lattice theory. Furthermore, the bridging theory does not permit calculation of the phase separation temperatures using parameters obtained from spinoidal data. These results do not justify the larger numerical expense of the bridging theory. Its application results only in a further increase of the number of parameters and of computing time.

CONCLUSION

In computer simulation of SSF and SPF for the system polystyrene + cyclohexane or polystyrene + methylcyclohexane, the $\overline{\overline{G}}^E$ relation

$$\overline{\overline{G}}^E = RT\psi(1 - \psi)\frac{(1 - \gamma)(\beta_1 + \beta_2/T)}{(1 - \gamma\psi)} \tag{35}$$
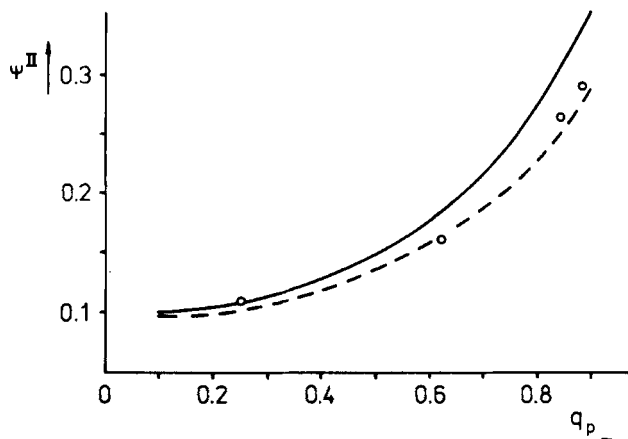
FIG. 5. Phase separation for polystyrene + cyclohexane: polystyrene segment fractions ψ^{II} for various amounts q_p of the fractions. Circles are experimental values [13]; broken line is computer simulation with Eq. (21); full line is computer simulation with Eq. (31).

which describes the g parameter as a function of ψ, according to the theory by Orofino and Flory [11], should be used. The parameter γ may be determined from molecular data. To calculate the phase separation temperatures, the parameters β_1 and β_2 are needed. These should be fitted to the coexistence curve, neglecting the critical area.

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