improvements in selectivity. Such increases in selectivity must reflect a consolidation of the membrane skin region.

Coagulation behavior for the aromatic polyamides (polymers III and II) is similar. Rate of coagulation, as evidenced by the development of an opaqueness, occurs more rapidly for the aromatic polyamides than for the polyamide–hydrazide.

Conclusions

Typical flux-rejection data for the membrane systems described, with various feed solutions, are summarized in Table V. These aromatic polyamide membranes are characterized by their good mechanical strength, as illustrated in Figure 7. Here a comparison of flux-pressure response between polymer I and cellulose acetate is made. A straight line plot for flux is observed up to pressures of 1800 psi, with some departure from linearity evident after 1 hr. The deflection in the flux line for cellulose acetate is seen to coincide with a decrease in rejection, indicating development of a membrane defect.

Typical mechanical properties for asymmetric membranes prepared from these polymers are shown in Table VI. In addition to their good mechanical properties, these aromatic polyamides show remarkable chemical resistance, especially in the high-pH range. This is in marked contrast to the cellulose acetate systems.[9] Membrane reverse osmosis performance for aqueous salt rejections appears unaltered after 1 week of storage in 1 *N* solutions of H_2SO_4, HCl, HNO_3, CH_3COOH, NaOH, and NH_4OH.

Selectivity of these membranes to solutes other than NaCl is quite good, as illustrated by results for polymer III in Table VII.

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Liquid–Liquid Phase Separation in Multicomponent Polymer Systems. X. Concentration Dependence of the Pair-Interaction Parameter in the System Cyclohexane–Polystyrene

R. Koningsveld* and L. A. Kleintjens

Centraal Laboratorium, DSM, Geleen, The Netherlands. Received May 5, 1971

ABSTRACT: The classical lattice theory of polymer solutions contains a concentration function of the pair-interaction parameter, normally represented as a truncated power series. The present study deals with the simple closed expression itself, $g(\varphi, T) = \alpha + (\beta_{00} + \beta_{01}/T)(1 - \gamma\varphi)^{-1}$, the constants of which can be evaluated conveniently with the aid of critical miscibility data. For the system cyclohexane–polystyrene the closed expression compares favorably with the power series representation reported by the present as well as other authors. Within the scope of the lattice theory the number of nearest neighbors z approximates $2\gamma^{-1}$. The value of z calculated for this system on the basis of the volume fraction seems quite acceptable ($z = 8.5$). At relatively low molecular weights there are indications that g depends on chain length. The present data can be reconciled with literature data when g is assumed to decrease with increasing number-average molecule weight, which, at temperatures below the Θ point, may well be the case.

It has become widely accepted in the literature on thermodynamic properties of polymer solutions that the pair-interaction parameter generally depends on the polymer concentration. This parameter, here denoted by g, arises in the lattice treatment of fluid macromolecular mixtures developed by Flory[1,2] and Huggins[3,4] when it is endeavored to reach quantitative agreement between theory and experiment. For this purpose Tompa[5,6] suggested using a power series in concentration with empirical coefficients. Such a description has indeed proved to be useful.[2,5–9]

This has also appeared from a recent study on the critical miscibility of the system cyclohexane–polystyrene.[10] In this work, as well as in all experimental studies on correlation functions, the series must be truncated because higher terms cannot be established with sufficient accuracy owing to experimental errors. This is not serious in itself, since, at any rate within the range of the measurements, the description of the measured quantities will be satisfactorily precise.

Yet, a closed expression, if available, would seem more elegant and be preferable to a truncated series. Such expressions have of late come forward from more refined molecular theories[11–13] yielding g functions in which many molecular parameters are included. The latter can often be obtained from independent measurements, but such an approach renders the modern expressions for g rather impracticable for routine use in cases where a relatively large number of varying systems must be described. One would then be inclined to make do with a simple closed expression even if its parameters

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proved to be void of a physical meaning. The literature contains indications of the form of such a closed expression, which, in the present paper, is applied to critical miscibility data on the system cyclohexane–polystyrene. We have no other pretension than ordering the experimental data by means of a simple and convenient correlation function.

Theory

Orofino and Flory[7] have pointed out that a power-series development of the pair-interaction parameter g in the polymer volume fraction φ is, in fact, included in the lattice model itself. If the contribution of the molecular interactions to the free enthalpy (Gibbs free energy) of mixing is worked out properly, $g(\varphi)$ arises as the closed expression mentioned above. Series developement then yields a polynomial in which the coefficients have a definite significance related to characteristic parameters of the lattice model. In view of shortcomings of the lattice model, Orofino and Flory only mentioned the above feature as a justification of their using a power series for g in which they considered the coefficients as empirical quantities. In the present study we prefer to use the closed expression as such and, likewise, let the values of the parameters be determined by experimental critical data.

The number of moles of lattice sites N_p adjacent to a polymer segment is given by

$$N_p = (z - 2)\Sigma n_i m_i + 2\Sigma n_i$$

where z is the coordination number of the lattice, n_i the number of moles of polymer species i, and m_i the chain length of polymer species i, expressed as the number of lattice sites occupied by macromolecule i. The number of moles of nearest neighbors N_0 of the solvent molecules is

$$N_0 = zn_0$$

where n_0 is the number of moles of solvent.

In the well-known approach,[2,4,6,14,15] the probability that a site adjacent to a solvent molecule is occupied by a polymer segment is assumed to be equal to the fraction $\vartheta_p = N_p/(N_0 + N_p)$. The probability that a solvent molecule is neighbor to a polymer segment is then given by $\vartheta_0 = N_0/(N_0 + N_p)$, so that the necessary identity for the total number of pairs P_{0p} of unlike neighbors in the mixture

$$P_{0p} = N_0\vartheta_p \equiv N_p\vartheta_0 = P_{p0}$$

is obeyed. This is not so if the probabilities mentioned above are assumed to be equal to the volume fractions φ, defined by $\varphi = \Sigma n_i m_i/N$ for the whole polymer, and by $\varphi_0 = n_0/N$ for the solvent. The total number of moles of lattice sites N is $n_0 + \Sigma n_i m_i$.

Several workers, *i.e.*, Flory[2] and Tompa,[6] have pointed out that only with $z \rightarrow \infty$ do the "site" or "interacting surface" fractions ϑ equal the volume fractions, as is evident from the relation between ϑ_p and φ.

$$\vartheta_p = [1 - 2(1 - m_n^{-1})/z][1 - 2(1 - m_n^{-1})\varphi/z]^{-1}\varphi \quad (1)$$

where m_n is the number-average chain length.

The usual line of reasoning[2,6,14,15] now leads straightforwardly to the free enthalpy of mixing ΔG

$$\Delta G/NRT = \varphi_0 \ln \varphi_0 + \Sigma\varphi_i m_i^{-1} \ln \varphi_i + \psi(\varphi) \quad (2a)$$

where

$$\psi(\varphi) = g\varphi_0\varphi \quad (2b)$$

and

$$g = \alpha + (z - 2)(\Delta w_{0p}/RT)(1 - 2\varphi/z)^{-1} \quad (2c)$$

The quantity Δw_{0p} stands for the difference between the interaction free enthalpy of unlike neighbors and the arithmetic mean of the values for identical neighbors, α is an empirical entropy correction of the form $\alpha\varphi_0\varphi$, φ_i is the volume fraction of polymer species i ($\Sigma\varphi_i = \varphi$), and R and T have the usual meanings. We have neglected the normally small influence of $1/m_n$ in eq 2c.

Abandoning the physical significance of the various parameters, we can write the interaction function as

$$g = \alpha + \beta_0/(1 - \gamma\varphi) \quad (3)$$

which is the closed expression for $g(\varphi)$ mentioned above.

The stability limit (spinodal) at constant pressure and temperature is defined by[16]

$$-\partial^2\psi/\partial\varphi^2 = (\varphi m_w)^{-1} + (1 - \varphi)^{-1} = 2X \quad (4)$$

and the consolute or critical state by

$$-\partial^3\psi/\partial\varphi^3 = -m_z/m_w^2\varphi_c^2 + 1/(1 - \varphi_c)^2 = 6Y \quad (5)$$

where m_z and m_w denote the z- and weight-average chain lengths and φ_c is the critical volume fraction of whole polymer.

Combining eq 2b and 3 with 4 and 5 we find

$$X = \alpha + \beta_0(1 - \gamma)/(1 - \gamma\varphi)^3 \quad (6)$$

$$Y = \beta_0\gamma(1 - \gamma)/(1 - \gamma\varphi_c)^4 \quad (7)$$

so that

$$X + \varphi_c Y = \alpha + Y/\gamma \quad (8)$$

The symbols X and Y stand for functions of measurable quantities. Hence, a set of critical miscibility data may be used for testing eq 8 and, hence, the form of the $g(\varphi)$ function 3. Such a set of data consists of critical concentrations and temperatures for a series of polymer samples differing in average molecular weight, all of them being dissolved in the same single solvent.

We further rely on the model in that we assume the temperature dependence of g to be confined to β_0 so that T does not occur in eq 8. This equation can then be applied to a set of critical data which refer to various temperatures. When α and γ have been determined from a plot according to eq 8, $\beta_0(T)$ can be found either from eq 6 or eq 7.

Test of the Interaction Function

A series of critical data (φ_c and T_c) for nine polystyrene samples of different average molecular weight has been reported elsewhere.[10] The solvent was cyclohexane and in the power-series evaluation the polymer concentration φ was defined in various ways. We follow the same practice here and consider the volume fraction, the weight fraction, and the segment mole fraction x^* defined by[17]

$$x_p^* = 1/(1 + w_0M_m/w_pM_0)$$

where w_0 and w_p are the weight fractions of solvent and whole polymer and M_m and M_0 stand for the molecular weights of monomer and solvent. The relation between molecular weight and chain length of the polymer is affected by the choice of the concentration variable and must be appropri-

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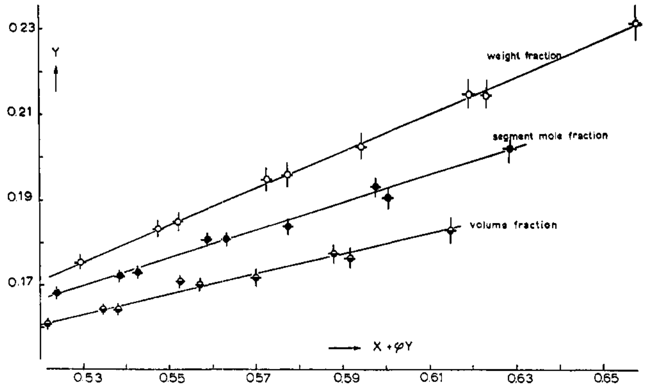

Figure 1. Plot of critical miscibility data according to eq 8. The magnitude of the effect of probable experimental errors is indicated. System, cyclohexane–polystyrene.

ately adapted. The "volume fraction" was calculated from the weight fraction on the assumption that the specific volume of the system is the sum total of the weighted specific volumes of the constituents.

Figure 1 shows that the $g(\varphi)$ function 3 can account satisfactorily for the concentration dependence of the pair-interaction parameter in cyclohexane–polystyrene. This conclusion is valid for any of the concentration variables, albeit that the best least-squares fit is obtained with the weight fraction.

In the present treatment we confine the temperature dependence of g to the parameter β_0. Upon calculation of β_0 with eq 6 and 7, we find that eq 6 gives more precise values. These are plotted *vs.* $1/T$ in Figure 2, which results in a relation of the form

$$\beta_0 = \beta_{00} + \beta_{01}/T \qquad (9)$$

Table I lists the values of the parameters.

It might be noted that, within the scope of the lattice theory, γ approximates $2/z$. Table I also contains the z values calculated from γ. As far as the volume fraction is concerned, the value of 8.5 found for the number of nearest neighbors seems quite acceptable. With regard to the weight fraction, which is the most practical concentration variable of the three, one might say that application hereof is least consistent with the concept of the lattice model. However, the present aim being purely phenomenological, we shall not pursue the matter any further here.[18]

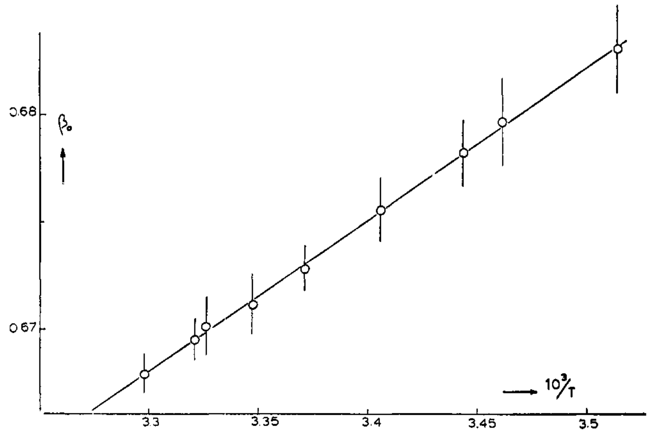

Figure 2. Temperature dependence of the pair-interaction parameter in cyclohexane–polystyrene. Basis, weight fraction; the volume and segment mole fractions give quite similar plots.

TABLE I
PARAMETERS OF THE INTERACTION FUNCTION (EQ 3 AND 9)
SYSTEM, POLYSTYRENE–CYCLOHEXANE

	Wt fraction	Vol fraction	Segment mol fraction
α	0.1290	−0.1597	0.0276
β_{00}	0.4212	0.4987	0.3899
β_{01}	72.91	111.74	98.55
γ	0.4373	0.2365	0.3365
z	4.6	8.5	5.9
Θ (°C)	32.9	32.7	32.85

The g function can be checked to some extent by comparing the Θ value it involves with that found by other methods. If Θ is defined as the temperature at which the osmotic second virial coefficient vanishes,[2] we must have at $T = \Theta$

$$\alpha + \beta_0(1 - \gamma) = 0.5 \qquad (10)$$

This follows from the activity a_0 of the solvent

$$\ln a_0 = \ln(1 - \varphi) + (1 - m_n^{-1})\varphi + \chi\varphi^2$$

where

$$\chi = g - \varphi_0\partial g/\partial\varphi = \alpha + \beta_0(1 - \gamma)/(1 - \gamma\varphi)^2$$

Series development of $\ln(1 - \varphi)$ and $(1 - \gamma\varphi)^{-2}$ leads to condition 10.

Evaluation of eq 10 yields the Θ values listed in Table I. These values compare favorably with the experimental value of 33–34° found from light-scattering measurements and ultracentrifugal equilibrium data on the same set of samples.[19]

A further check of the $g(\varphi)$ function is possible by comparing the spinodals calculated by means of eq 4 with those deduced from light-scattering measurements at temperatures slightly above the miscibility gap.[20] In the latter study the scattered light intensity $I(\vartheta)$ is measured as a function of the scattering angle ϑ and extrapolated to $\vartheta = 0$. If now $1/I(0)$ is plotted *vs.* $1/T$, extrapolation to $1/I(0) = 0$ yields the spinodal temperature for the polymer concentration considered. Figure 3 shows a comparison for three of the samples. For the upper two spinodals the agreement can be considered to be satisfactory; with the lower molecular weight sample, however, the deviation is too large to be attributed to experimental errors alone. Possibly, g depends on molecular weight in this region, which was left out of consideration in the present approach.

If eq 3 is expanded into a power series in φ, β_0 occurs in every coefficient. In the previous polynomial description[10] the temperature dependence of g was limited to the leading, concentration-independent term, so that there is no point in comparing the coefficients as such. If we calculate spinodals with the present g function and with the previous polynomial expression, we do not find significant deviations. These do arise, however, if we compare spinodals calculated with g functions originating from various sources. Figure 4 gives examples for two polystyrene samples for which the cloud-point curve in cyclohexane had been measured in part. With the molecular weight distributions of the employed samples, cloud-point curve and spinodal should pass through the

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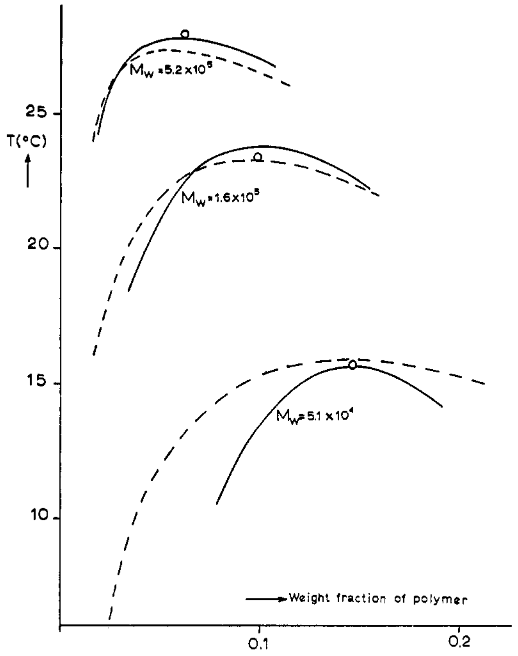

Figure 3. Spinodals for three samples of polystyrene in cyclohexane: calculated with the present g(φ) function (——), determined by light scattering[20] (- - - -), measured critical points (○).

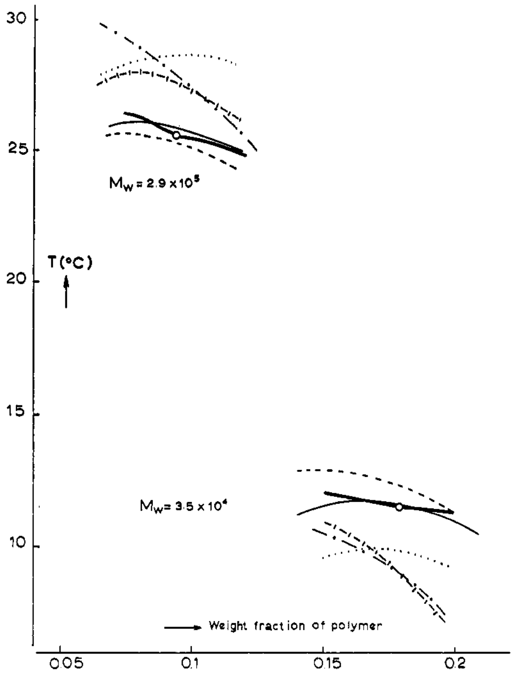

Figure 4. Cloud-point curves (▬▬) and spinodals for two samples of polystyrene in cyclohexane: calculated with g(φ) functions from osmotic data of Krigbaum and Geymer[9] (····) and Rehage and Palmen[23] (–|–|–|–|–), ultracentrifugal equilibrium data of Scholte[24] (–·–·–), light-scattering data of Scholte[20] (- - - -), and critical-miscibility data of this work (——); critical points (○).

critical point and also have a common tangent there.[21,22] The other g functions were taken from the work of Krigbaum and Geymer[9] (osmotic and vapor pressure), Palmen and Rehage[23] (osmotic pressure), Scholte[24] (ultracentrifugal equilibrium), and Scholte[20] (light scattering). On the basis of the criterion mentioned above one would infer that the critical-miscibility and light-scattering data yield the more accurate information on the pair-interaction parameter.

Finally, it should be mentioned that the form of the present $g(\varphi)$ function resembles that of the expression arising from Huggins' recent theory of polymer solutions, which is based upon a detailed consideration of interacting contact surfaces.[25] It is now being examined whether critical and light-scattering data may serve to estimate some of the molecular parameters in Huggins' g(φ) function.

Molecular Weight Dependence of the Interaction Parameter

In testing the present $g(\varphi)$ function, it was observed that g might depend on chain length. This dependence, if existing, would reveal itself in particular at low molecular weights. In this range only few data are available at present. Accounting for a molecular weight dependence of g makes equations like (4) rather complicated. A complete analysis being carried out currently, we restrict ourselves here to some preliminary remarks.

The stability limit of the system at constant pressure and temperature, as formulated by Gibbs,[26] reads

$$J_{sp} = |\partial^2 \Delta G / \partial \varphi_i \partial \varphi_j| = 0 \qquad (11)$$

where φ_i and φ_j stand for the independent concentration variables (the volume fractions of all macromolecular species). If eq 11 is worked out upon substitution of ΔG expression 2, we find eq 4. However, if g is a function of m_n, we must account for the dependence of m_n on φ_i. Equation 11 then yields

$$1 + L\varphi m_w + (B^2L - A^2)\varphi^2 u + 2A\varphi + B^2\varphi/m_n \underset{\text{(spinodal)}}{=} 0 \qquad (12)$$

where

$$L = (1 - \varphi)^{-1} + \partial^2\psi/\partial\varphi^2 + 2(1 - 2\varphi)m_n\varphi^{-1}(\partial g/\partial m_n) + 2\varphi_0 m_n(\partial^2 g/\partial m_n\partial\varphi) + \varphi_0 m_n^2\varphi^{-1}(\partial^2 g/\partial m_n^2)$$

$$A = -[(2 - 3\varphi)(\partial g/\partial m_n) + \varphi_0\varphi(\partial^2 g/\partial m_n\partial\varphi) + \varphi_0 m_n(\partial^2 g/\partial m_n^2)]m_n^2\varphi^{-1}$$

$$B^2 = [m_n(\partial^2 g/\partial m_n^2) + 2\,\partial g/\partial m_n]m_n^3\varphi_0\varphi^{-1}$$

$$u = (m_w/m_n) - 1$$

For the moment we only want to check qualitatively whether a possible m_n dependence of g might be responsible for the deviation between the two lower spinodals in Figure 3. It is not likely that the dependence neglected in eq 2c is to be considered as such. On the other hand, an analysis on the basis of the various numbers of pairs of nearest neighbors, as carried out above, may indicate the form of the $g(m_n)$ function. This analysis could be made by attributing different interaction free enthalpies to end and middle segments.[6,27] The resulting equations are complicated, and we use a first approximation, which may be written as follows

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$$g = \alpha + (1 - \gamma\varphi)^{-1}(\beta_0 + \beta_1/m_n) \tag{13}$$

where β_1 shows a similar temperature dependence as β_0 (eq 9). Without loss of qualitative generality of the conclusions, β_1 may be considered to be independent of T.

Then, eq 12 and 13 yield

$$\begin{aligned}2(1 - \gamma)(1 - \gamma\varphi)^{-3}(\beta_{00} + \beta_{01}/T) = (1 - \varphi)^{-1} + (\varphi m_w)^{-1} - \\ 2\alpha - \beta_1(1 - \gamma)\varphi(1 - \gamma\varphi)^{-3} m_w^{-1}[(1 - \gamma) \times \\ u(1 - \gamma\varphi)^{-1}\beta_1 + 2(1 + \gamma\varphi u)\varphi^{-1}]\end{aligned} \tag{14}$$

It follows from eq 14 that β_1 must be positive in order to cause the spinodal temperature at given φ to shift to higher T values (Figure 3). This would involve that $\partial g/\partial m_n < 0$, which, at first sight, appears rejectable. However, the temperatures considered are below the Θ point of the system. From Krigbaum's[28] measurements at T around Θ one could infer[20] that the usual m_n dependence of the interaction parameter changes sign upon passing Θ. It is true that Krigbaum's data refer to infinite dilution, but Scholte[20] as well as Rietveld, *et al.*,[29] found the same trend at relatively high polystyrene concentrations in light-scattering and ultracentrifugal studies, respectively. Hence, $\beta_1 > 0$ would seem to be qualitatively consistent with these authors' findings.

Further support may be derived from a paper by Breitenbach and Wolf,[30] who studied the fractionation of polystyrene and measured the phase–volume ratio in some liquid–liquid separations. They also determined the molecular weight distributions of the fractions in the two phases in order to check the distribution coefficient. For a ΔG function of the form of eq 2a, in which g may be any function of φ, the distribution coefficient reads[2]

$$\varphi_i''/\varphi_i' = \exp\sigma m_i \tag{15}$$

which can be rearranged[30] into

$$\ln(w_i'w_i'') = \ln r - \sigma m_i \tag{16}$$

where $w_i'(\varphi_i')$ and $w_i''(\varphi_i'')$ are the masses (volume fractons) of macromolecules i in the dilute and concentrated phases, and r is the ratio of the volumes of these. The partition factor σ contains the pair-interaction parameter and the whole polymer concentrations in the two phases.

A plot of $\ln(w_i'/w_i'')$ *vs.* m_i should yield a straight line. Breitenbach and Wolf indeed found straight lines, but noted that the intercept at $m_i = 0$ was a factor of 10 smaller than that following from the measured value of r.

If g depends on m_n, eq 15 is no longer valid and the distribution coefficient is given by

$$\varphi_i''/\varphi_i' = \exp(\sigma m_i + \tau) \tag{17}$$

where $\tau = (\varphi_0 m_n^2 \partial g/\partial m_n)'' - (\varphi_0 m_n^2 \partial g/\partial m_n)'$. The double and single primes indicate the values of the quantity between brackets for the polymer-rich and dilute phases. Equation 16 now becomes

$$\ln(w_i'/w_i'') = \ln r - \tau - \sigma m_i \tag{18}$$

so that the same linear relation should be obeyed, albeit that the intercept at $m_i = 0$ does not equal $\ln r$.

Introduction of eq 13 for $g(m_n)$ yields

$$\tau = \beta_1(\varphi'' - \varphi')(1 - \gamma)(1 - \gamma\varphi'')^{-1}(1 - \gamma\varphi')^{-1} \tag{19}$$

where φ'' and φ' denote the whole polymer volume fractions in the two phases. For the γ values listed in Table I, it follows from eq 19 that $\tau > 0$ if $\beta_1 > 0$, so that the discrepancy reported by Breitenbach and Wolf gives further support to the observation that β_1 must be positive.

A rough estimate of the various quantities in eq 14 and 19 indicates that all measured data described here might well be reconcilable with the same value of β_1. For a quantitative comparison, the complete treatment of critical data, which is being developed at present, must be available.

Acknowledgment. The authors are indebted to Dr. B. A. Wolf (University of Mainz) for drawing their attention to the problem of the distribution coefficient.

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