

On polymer solution thermodynamics

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On polymer solution thermodynamics*)

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Abstract: Various solution properties have been selected for testing the usefulness of the classic lattice model. The analysis leads to the inclusion of improvements such as different contact numbers for molecules and repeat units, distinction between concentration regimes, dilute and concentrated in polymer. The extensions of the simple model supply an adequate description of the data provided the free enthalpy of mixing in the concentrated region is made temperature- and molar mass-dependent. Part of the latter contribution can be attributed to the chains bending back on themselves. The other part is not easily accommodated in the model and might be related to free volume effects that have been left out of the present consideration. The resulting free enthalpy expression quantitatively covers independent data like osmotic pressure measurements by Krigbaum and binodals in near ternary systems by Hashizume et al.

Key words: Free energy, interaction function, partial miscibility, prediction.

Introduction

Since its origination the rigid lattice model of polymer solutions has been the subject of much criticism [1]. It is the objective of the present paper to investigate the limits to which the applicability of the model can be stretched, in particular from the point of view of its predictive power. It is obvious that the main point of criticism — the inability to deal with excess volumes — cannot be removed in the present context, but we shall restrict ourselves to systems at constant, ambient pressure.

A further restriction is that we avoid the serious complications presented by polymolecularity [2-4] and limit the analysis to near binary systems in which the polymeric constituent has a very narrow molar mass distribution. The system studied is cyclohexane/polystyrene and we use light scattering and ultracentrifuge data by Scholte et al. [5-9], near binary binodals by Hashizume et al. [10], spinodal points [7, 11-13] and

critical miscibility data [14-18]. 'Predictive' calculations will then be tested i. a. with data on systems with moderate polymolecularity, viz. Krigbaum's osmotic pressure measurements on polystyrene fractions [19] and Hashizume et al.'s [10] near ternary coexistence curves. Prediction means calculation within experimental error of properties on the same system, not used in the data fitting.

The free enthalpy (Gibbs free energy ΔG) of mixing n_1 moles of solvent with n_2 moles of polymer with a single molar mass M_2 was derived independently by Flory [20, 21], Huggins [22, 23] and Staverman and Van Santen [24, 25]. We write

$$\Delta G/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + I \quad (1)$$

where RT has its usual meaning, $\phi_1 = n_1/N$, $\phi_2 = n_2 m_2/N$, $N = n_1 + n_2 m_2$, m_2 = number of lattice sites occupied by a polymer chain. The term I is used to describe all conceivable corrections needed to amend the first two combinatorial terms so that ΔG conforms with actual thermodynamic properties. In the following we develop I , starting from the simple Van Laar expression, led by the selected experimental data.

*) Affectionately dedicated to Prof. Dr. H.-G. Kilian on the occasion of his 60th birthday.

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Within the framework of the model ϕ_i is the volume fraction of component i . It is in the spirit of the present study to calculate volume fractions from mass fractions on the assumption of additivity of volume on mixing, we ignore the obvious problems with the volume fraction [26]. Then, the 'relative chain length' m_2 is given by

$$m_2 = v_2 M_2 / V_1 \quad (2)$$

where v_2 and V_1 are the specific volume of the polymer in the liquid state, and the molar volume of the solvent, respectively.

Shultz-Flory method

The Van Laar expression for Γ reads

$$\Gamma/N = g\phi_1\phi_2 = (g_s + g_H/T)\phi_1\phi_2. \quad (3)$$

The simplest interpretation of the interaction function g defines it in terms of the interchange energy (see ref. [27]). Experimental data suggest interpretation as a free enthalpy to be preferable [28,29]. Thus we have an entropic contribution g_s to g , in addition to the enthalpic term g_H (in a first approximation [30]).

Shultz and Flory used equations (1) and (3) to analyse miscibility gaps in several solvent/polymer systems for a series of polymer chain lengths [31]. At a critical point both spinodal and critical conditions are obeyed. In a binary system one has

$$\{(\partial^2 \Delta G / NRT) / \partial \phi_2^2\}_{p,T} = 0 \text{ (spinodal)} \quad (4)$$

$$\{(\partial^3 \Delta G / NRT) / \partial \phi_2^3\}_{p,T} = 0 \text{ (critical point)}. \quad (5)$$

Application of conditions (4) and (5) to equations (1) and (3) leads to

$$g_H/T_m = \frac{1}{2} - g_s + (m_2^{-1/2} + 1/(2m_2)). \quad (6)$$

Shultz and Flory identified the maximum separation temperature T_m with the critical point and plotted $1/T_m$ vs. the expression between brackets in equation (6) to find the parameters g_s and g_H .

Shultz-Flory plots are often found to be linear, in spite of the fact that the underlying assumptions (strictly binary systems and validity of eqs. (1) and (3)) are probably never realistic. It can be explained that, nevertheless, linearity is observed frequently, but slope

and intercept cannot be interpreted in terms of equation (6) [30,32].

It is therefore not surprising that Shultz and Flory noted the 'predictive' power of their treatment to be extremely poor. This aspect is illustrated in figure 1 which shows the miscibility gaps calculated with equations (1) and (3), with the parameters from a Shultz-Flory plot. The maximum separation temperatures check with the experimental ones for obvious reasons, but the calculated gaps are much narrower and more

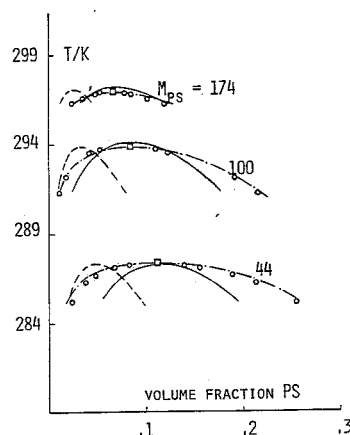


Fig. 1. Experimental binodals (coexisting phase compositions: O) as a function of temperature for indicated molar masses (kg/mole), and their representation by the Shultz-Flory method (eqs. (3) and (6): ---), by equation (8) (—) and by equations (18) and (19) (-·-·-). Data from Hashizume et al. [10]. Critical points: □. System cyclohexane/polystyrene

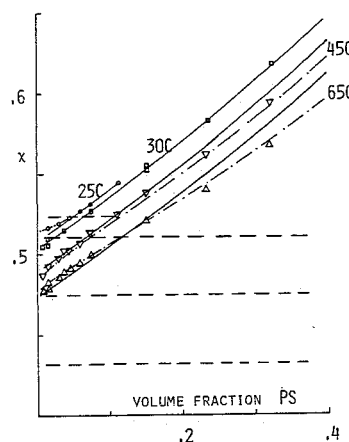


Fig. 2. Experimental values of $\chi (= g - \phi_1 \partial g / \partial \phi_2)$ at indicated temperature and their representation by the Shultz-Flory method (eqs. (3) and (6): ---), by equation (8) (—) and by equations (18) and (19) (-·-·-). Data from Scholte et al. [5-9]. Molar mass: 166 kg/mole. System cyclohexane/polystyrene

asymmetric than the experimental curves. The discrepancy is illustrated even more clearly if measured values of the quantity $(g - \phi_1 \partial g / \partial \phi_2)$ are compared with those calculated with equations (1) and (3). The inadequacy of the procedure is demonstrated in figure 2.

In the present examples polymolecularity can hardly be expected to cause the discrepancy. Figure 2, however, indicates a major reason for the failure. Evidently, the parameter g depends markedly on concentration.

The quantity $(g - \phi_1 \partial g / \partial \phi_2)$ is usually known by the symbol χ , representing the interaction parameter in the expression for the chemical potential of the solvent.

Disparity of contact numbers

The major reason for g to depend on concentration is to be sought in the disparity in size and shape between solvent molecules and repeat units in the polymer. Staverman [33], working out earlier suggestions by Langmuir [34] and Butler [35], assumed the number of nearest neighbour contacts a molecule or segment can make to be proportional to its accessible surface area. Thus he obtained an expression for the enthalpy of mixing which, in terms of g , reads

$$g = B(T)/(1 - \nu\phi_2) \quad (7)$$

where $B(T)$ summarizes the temperature dependence and $\sigma_2/\sigma_1 (= 1 - \nu) =$ the ratio of the surface areas of polymer segments and solvent molecules.

The idea has been applied by other authors, with or without reference to the unit cell volume of the lattice [36, 37]. The viability of Staverman's straightforward approach is illustrated in figure 3. It is interesting to note that the curve in figure 3b was calculated with Bondi's [38] σ_2/σ_1 value of 1.35, and passes right through the experimental points. Whether one uses the surface area ratio as such, or corrected for the cell volume, depends on how close one wishes to adhere to the notion of a rigid lattice. Remembering Rowlinson's remark that the lattice model might prove more useful than is often thought, provided it is seen as an abstraction, useful for the purpose of calculation, the straightforward treatment would not seem objectionable [39]. We shall adhere to it in this paper.

Fitting critical points for various molar masses in the system cyclohexane/polystyrene to equations (1), (3),

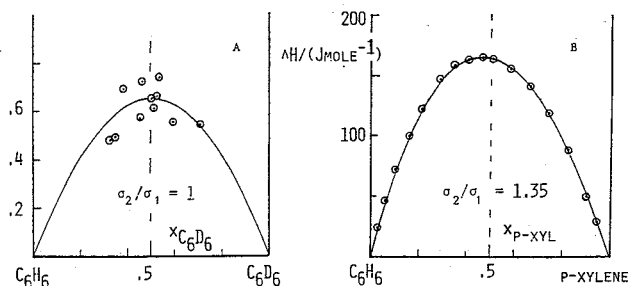


Fig. 3. Enthalpies of mixing (ΔH) for benzene with perdeutereous benzene (a, ref. [64]) and with p-xylene (b, ref. [65]). The curves were calculated according to Staverman [33] with molecular surface ratios of 1 (a) and 1.35 (b)

(4), (5) and (7) reveals the need of an extra, empirical parameter [40], viz.

$$g = B(T)/(1 - \nu\phi_2) + C \quad (8)$$

where $B(T)$ is expressed as $B(T) = B_0 + B_1/T$.

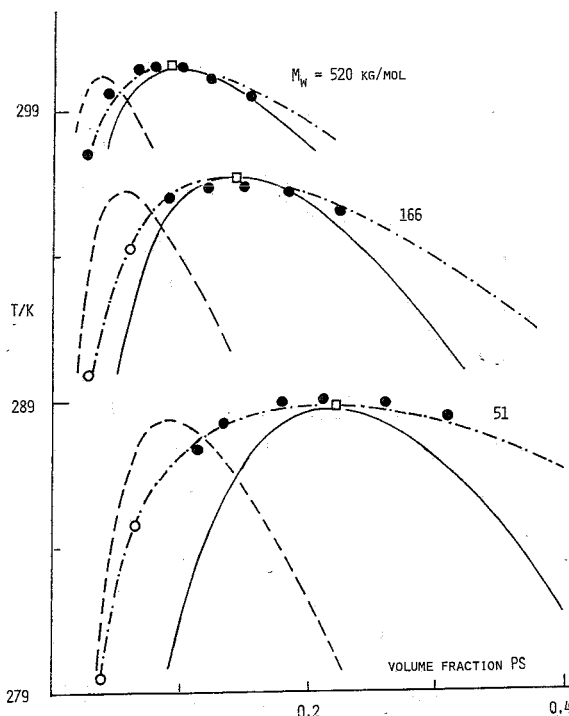


Fig. 4. Experimental spinodals and their representation by the Shultz-Flory method (eqs. (3) and (6): ---), by equation (8) (—) and by equations (18) and (19) (-·-·-). Light scattering data from Scholte et al. [5-9] (O) and from Gordon et al. [11-13] (●). System cyclohexane/polystyrene. Critical points: □

Table 1. Parameters values for equations (3) and (8)

g_s	=	-0.26
g_H/K	=	234
B_0	=	0.57
B_1/K	=	108
γ	=	0.22
C	=	-0.22

The binary binodals, calculated with the parameters so obtained, show a much better agreement with the measured coexistence curves (fig. 1). Both maximum separation temperature and concentration are now reproduced. Yet, the shape of the curves still deviates, the experimental curves being broader than the calculated ones. The improvement over equation (3) is most spectacular with the data in figure 2. The introduction of the surface area ratio shifts the calculated curves into the range of the measurements. It should be noted that the σ_2/σ_1 value following from the fitting of the critical points is 0.78 and compares favourably with the value calculated with Bondi's method, viz. 0.87.

The calculated spinodals show a quite comparable situation, as shows figure 4. The values of the parameters leading to this description and prediction are listed in table 1, together with those for the Shultz-Flory treatment. Figures 1, 2 and 4 present examples for one or a few chain lengths only, the other molar masses, ranging 50 to 520 kg/mole, show analogous behaviour.

The deviations between calculated and measured curves come out clearly in binodals and spinodals (figs. 1 and 4). Figure 2 (χ values) also clearly shows the deviations at high concentration but less convincingly at the dilute end. A different way of treating the data, and the issuing plots, does not only bring the differences out more clearly but also reveals that C must be a function of temperature. To this end we use the parameters B_0 , B_1 and γ of table 1 and let the χ data (fig. 2) determine a value of C for each molar mass separately. The contribution of C to χ is given by

$$C' = C - \phi_1 \partial C / \partial \phi_2. \quad (9)$$

Figure 5, showing a plot of C' vs. T for $M = 51$ kg/mole, reveals that, at concentrations above $\phi_2 \approx 0.15$, C' hardly depends on concentration and is, to a good approximation, linear in T . At $\phi_2 < 0.15$ and $T > 300$ K, C' is also independent of concentration and linear in T . This linearity extends to $T < 300$ K for $\phi_2 > 0.15$. At

$\phi_2 < 0.15$ and $T < 300$ K we see a dependence of C' on concentration which increases upon a decrease of ϕ_2 . Summarizing, one might write

$$C'(\phi_2 > 0.15) = A(T) = A_1 + A_2 T. \quad (10)$$

With those other molar masses for which a sufficient T range has been measured, one finds analogous results but different values for A_1 and A_2 , both of which seem to be expressible in a linear relation to reciprocal molar mass (see fig. 6).

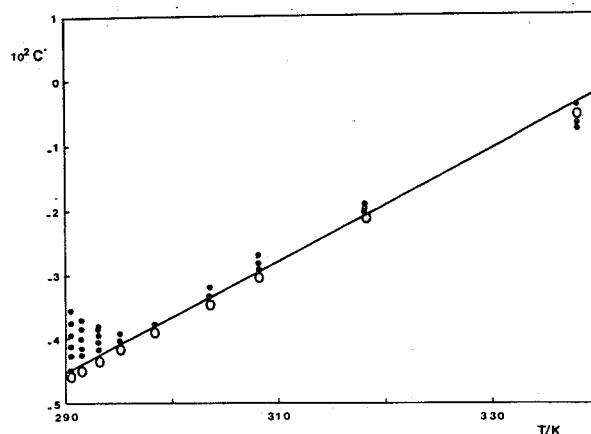


Fig. 5. The quantity C' (eqs. (8) and (9)) calculated from experimental values of the chemical potential of the solvent cyclohexane as a function of temperature, molar mass polystyrene 51 kg/mole. Polymer mass fraction $w_p \leq 0.15$: \bullet ; $0.15 \leq w_p \leq 0.4$: \circ . The drawn curve was calculated by regression analysis of C' data for $w_p \geq 0.15$ (see text)

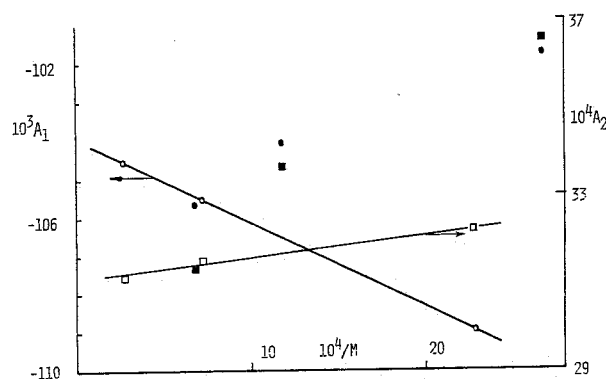


Fig. 6. Chain length dependence of the coefficients A_1 and A_2 in equation (10). The curves were fitted to the three data sets for molar masses 51, 166 and 520 kg/mole (\circ, \square) for which A_1 and A_2 could be estimated from a wide temperature range. For the other three molar masses (\bullet, \blacksquare) (45, 103 and 180 kg/mole) only a limited T -interval was available, which might explain the deviation of two of the points

From these findings we see that the free enthalpy expression still needs improvement on two points if a quantitative covering of the present sets of data is to be obtained. Corrections are necessary for the dilute solution regime as well as the range of higher concentrations. The next two sections deal with these aspects.

Before continuing we might reflect on a possible molecular origin of the obviously necessary contributions B_o and C . The term B_1 is well anchored in the molecular concept of the interchange energy associated with the breaking of contacts between like molecules and replacing them by unlike nearest neighbours (see e. g. ref. [27] or [28]).

Many years ago it was already pointed out by Staverman [41] that it does not suffice to consider only the energy of mixing on the basis of numbers of contacts between molecules. The entropy of mixing should then also be calculated for the numbers of contacts rather than the numbers of molecules, as is usually done. Today this is still very much the normal practice, it involves the assumption of a constant coordination number z on the lattice.

We relax that condition and allow the various species to differ in coordination number z_{ij} . If the two component molecules or repeat units differ in size but not much in shape, we have three coordination numbers, setting $z_{11} \approx z_{22}$. If all z_{ij} are equal the number of arrangements on the lattice is well known [20–25, 27, 28, 36]. We denote this number by Ω_o . If $z_{11} = z_{22} \neq z_{12} \neq z_{21}$ we need to correct Ω_o for the over- and underestimations referring to z_{12} and z_{21} . Following a procedure suggested by Huggins [36] and Silberberg [42] we can write [43]

$$\Omega = \Omega_o (z_{12}/\bar{z})^{P_{12}} (z_{21}/\bar{z})^{P_{21}} \quad (11)$$

where $P_{12} \equiv P_{21}$ is the number of unequal contact pairs, and \bar{z} is an average number depending on concentration.

Arbitrarily writing

$$\bar{z} \propto \sigma_1 \phi_1 + \sigma_2 \phi_2 \quad (12)$$

and using the regular solution approximation for P_{12} , one obtains

$$C = 2z_{22} (\ln Q)/Q; \quad B_o = -z_{22} \ln (z_{12} z_{21}/z_{11}^2) \quad (13)$$

where $Q = 1 - \gamma\phi_2$.

It is seen that equation (13) thus supplies an after the fact explanation for the empirical parameters B_o and C , though in a qualitative sense. We ignore a possible

ϕ_2 dependence of C (by the term Q). It should be noted that Staverman has recently developed a rigorous treatment of contact statistics [44].

Non-uniform segment density

The concentration range covered by the experimental data employed here contains two essentially different regimes. As was pointed out by Flory as early as 1949, polymer solutions cannot, at high dilution, be looked upon as systems with uniformly distributed segments [45]. They consist of isolated coils separated by regions of pure solvent. The other regime ranges upward from concentrations where the coils overlap effectively, and the segment density can be considered approximately uniform.

Theoretical treatments of dilute solutions [45, 46] on the one hand, and concentrated systems on the other [1, 47, 48], are abundant, but a ΔG expression continuously covering both concentration regimes has had very little attention so far. However, it is needed for the description of liquid-liquid phase equilibria in polymer solutions where one of the phases is normally very dilute, and the other so concentrated that the coils overlap extensively.

To remedy the situation, Stockmayer et al. [49] wrote the interaction function as a sum of two terms, one for each concentration range:

$$g = g^*(T, m_2) P + g^c \quad (14)$$

where g^c , governing the concentrated regime, can be expressed by equation (8). The term $g^*(T, m_2)$ quantifies the differences relevant for the dilute regime compared with the uniform density state. The first term in equation (14) is attenuated by the probability factor P

$$P = \exp(-\lambda_o m_2^{1/2} \phi_2) \quad (15)$$

where λ_o can be expressed in molecular parameters, independently determinable [49]. P stands for the probability that a given volume element in the solutions does not fall within any of the coil domains.

The function g^* was originally 'calibrated' versus the osmotic second virial coefficient, expressions for which are in ample supply [46]. However, it has become clear that a fully theoretical treatment of equation (14) leads to qualitative agreement with experiment only [2, 50]. It is therefore not surprising that we had to drop the theoretical definition of g^* in order to obtain the quantitative agreement aimed at.

A detailed analysis of the upward curvature in C' at small ϕ_2 confirms, within experimental accuracy, the

theoretical probability factor P in its general exponential form, whereas we found g^* to be well represent by

$$g^* = \{g_1 + g_2 (T - \theta)\} (T - \theta)/m_2 \quad (16)$$

where g_1 and g_2 are adaptable parameters and θ is the Flory temperature. It is to be noted that equation (16) does not obey the theoretical boundary condition that the dilute solution effect should disappear for a mixture of small molecules:

$$\lim_{m_2 \rightarrow 1} g^*(T, m_2) = 0. \quad (17)$$

This boundary condition can be included if, rather arbitrarily, we introduce a further chain length dependence:

$$g^* = \{g_1 + g_2 (T - \theta)\} (T - \theta) (1 - 1/m_2)/m_2. \quad (18)$$

All these considerations finally result in a semi-empirical expression for the interaction function g [4]:

$$g = (B_0 + B_1/T)/(1 - \gamma\phi_2) + A(T, m_2) + g^*(T, m_2)P \quad (19)$$

where

$$A(T, m_2) = A_{10} + A_{11}/m_2 + (A_{20} + A_{21}/m_2) (T - \theta). \quad (19a)$$

Expressing the temperature variable as $(T - \theta)$ proved advantageous in the fitting. We also noted that the additional factor $(1 - 1/m_2)$ improved the overall agreement between semi-empirical theory and experiment.

The adjustable parameters in equation (19) were determined in a simultaneous optimisation of the complete data-set consisting of χ values, spinodal points, coexisting phase compositions and critical points, each with the relevant equation. A representative selection of the resulting descriptions is shown in figures 1, 2, 4 and 7-9. Full details and a comprehensive report on the procedure, including the step-wise approximations eventually leading to equation (19), can be found in [4]. Table 2 lists the values of the various parameters found to give the best fit to the complete data set.

Chain length dependence of the entropy of mixing

In most theoretical treatments of concentrated solutions the chain length dependence of the entropy of

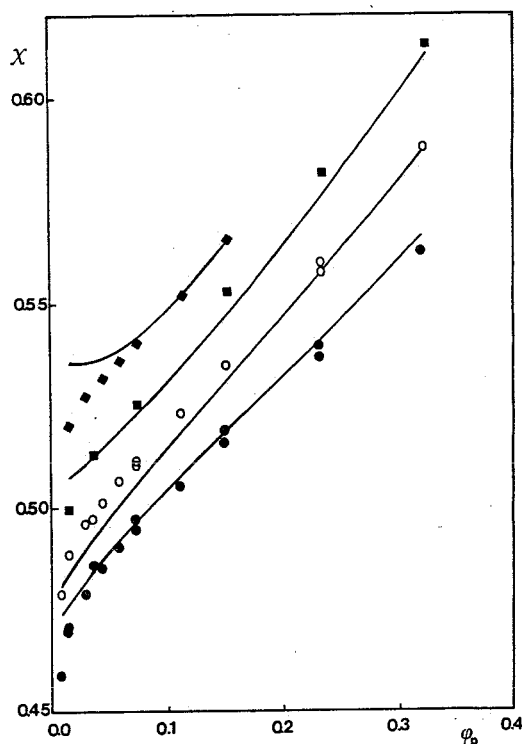


Fig. 7. Experimental χ data for polystyrene ($M = 51$ kg/mole) in cyclohexane as a function of concentration and temperature, and their description by equations (18) and (19). Data from Scholte et al. [5-9]

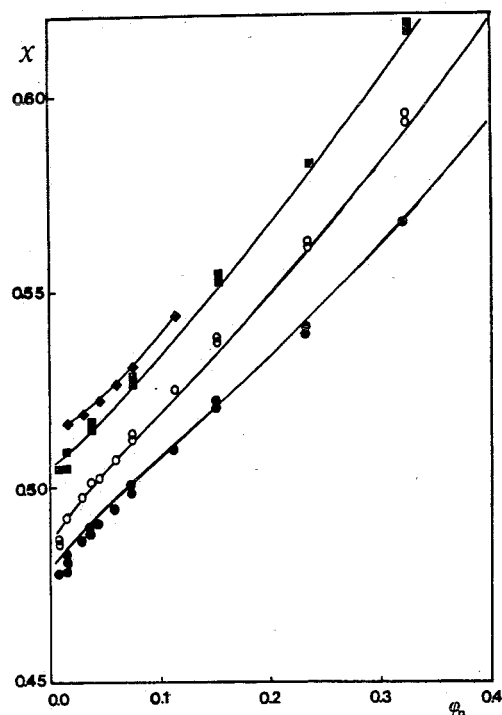


Fig. 8. As figure 7, $M = 166$ kg/mole

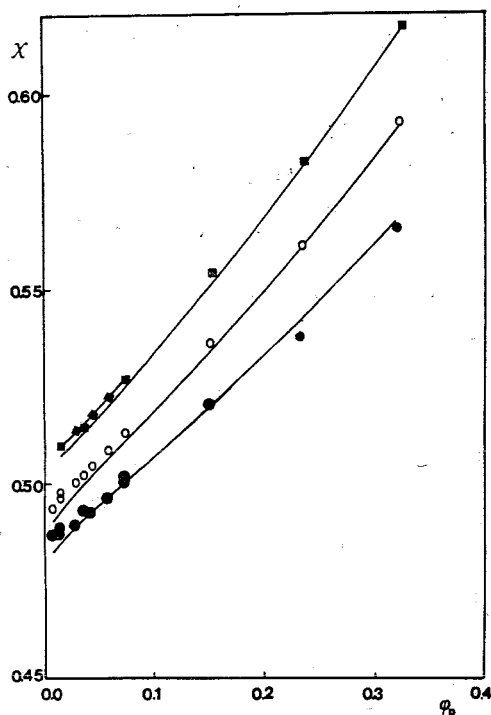


Fig. 9. As figure 7, $M = 520$ kg/mole

Table 2. Parameter values for equations (18) and (19)

B_0	=	-0.89
B_1/K	=	490
γ	=	0.29
A_{10}	=	-0.003
A_{11}	=	-2.10
A_{20}	=	0.00282
A_{21}	=	0.032
g_1	=	-0.0281
g_2	=	0.00069
λ_0	=	0.885

mixing is considered to be adequately accounted for by the second, combinatorial, term in equation (1). Writing ΔG per mole of lattice sites in equation (20) we see the reciprocal dependence on m_2 , and the second term diminishes with increasing m_2 , vanishing at $m_2 \rightarrow \infty$. For this reason it is sometimes neglected altogether

$$Z = \Delta G/NRT = \phi_1 \ln \phi_1 + (\phi_2/m_2) \ln \phi_2 + \Gamma/N. \quad (20)$$

Such simplifications are not commendable because, even if the second term is very small compared to the

first, it may still be too large to be negligible. The sum total of the many contributions to Z is itself, most of the time, relatively small. Minor contributions may thus influence the value of the sum. Since details in $Z(\phi_2)$ determine phase relationships sensitively, it is evident that none of the contributions should be ignored without checking. Also, both small and large terms should be assessed with the maximum possible precision.

The original ΔG expression (1) with g function (3) has the osmotic second virial coefficient α_2 independent of molar mass:

$$\alpha_2 \propto \left(\frac{1}{2} - \chi_1 \right) \quad (21)$$

where

$$\chi_1 \equiv g. \quad (21a)$$

Equation (21) is appropriate also if g depends on ϕ_2 , then we have

$$\chi_1 = (g - \phi_1 \partial g / \partial \phi_2)_{\phi_2=0}. \quad (21b)$$

The molar mass dependence of α_2 has been observed in early measurements already and has been successfully attributed to the non uniform segment density in dilute polymer solutions [45, 46]. The dilute solution theory can be summarized as

$$\alpha_2 \propto \left(\frac{1}{2} - \chi_1 \right) h(z) \quad (21c)$$

where $h(z)$ is the excluded volume function [46] which introduces the chain length dependence in a qualitatively correct manner.

Recently, Tong et al. [51] have questioned the validity of equation (21c) and, thereby, dilute solution theory in general. The basis of their criticism was formed by extensive measurements of α_2 by light scattering at $T < \theta$ for a wide range of molar masses in the system cyclohexane/polystyrene.

We analysed Tong et al.'s data with our empirical g^* function and found it to provide a quite satisfactory description, although the molar mass and temperature dependencies had to be extended to include quadratic and higher terms:

$$g^*(T, m_2) = g_0(m_2) + g_1(m_2)(T - \theta) + g_2(m_2)(T - \theta)^2 \quad (22)$$

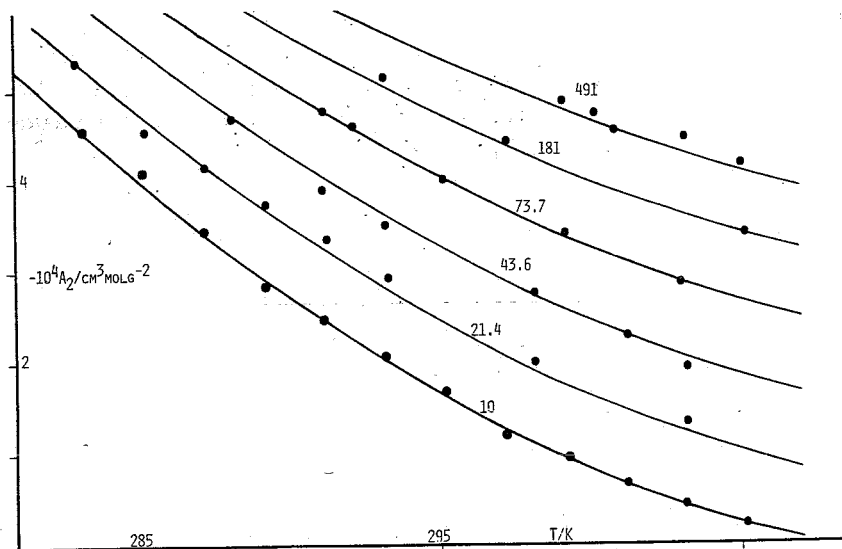


Fig. 10. Experimental second virial coefficients as a function of temperature. Molar masses in kg/mole indicated. Data from Tong et al. [51], curves fitted to the data with equation (22). All curves (except for $M = 10$ kg/mole) successively shifted vertically by $0.8 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-2}$.

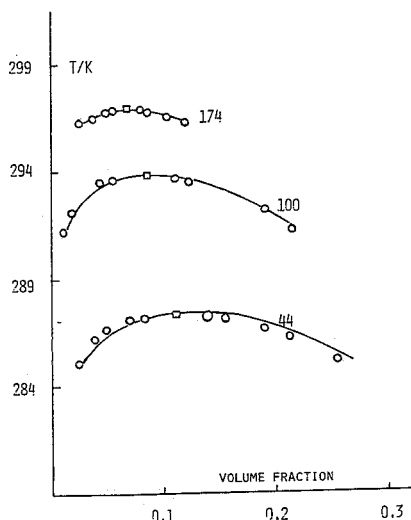


Fig. 11. As figure 1. Curves calculated with equations (19) and (22)

with

$$\begin{aligned} g_0(m_2) &= (g_{01} + g_{02}/m_2)/m_2 \\ g_1(m_2) &= (g_{11} + g_{12}/m_2)/m_2 \\ g_2(m_2) &= (g_{21} + g_{22}/m_2 + g_{23}/m_2^2)/m_2. \end{aligned}$$

Figure 10 shows the representation of the experimental second virial coefficients so obtained. Using the values of the A and B coefficients in table 2 in combination with g^* function (22) we calculated binodals for molar masses of 44, 100 and 174 kg/mole, and obtained a de-

scription comparable in quality to that in figure 1 (see fig. 11). We conclude therefore that Tong et al.'s virial coefficient data do not contradict the ΔG function developed in this paper.

Nevertheless, Tong et al.'s criticism of the dilute solution theory is justified, albeit for a slightly different reason. The chain length dependence we established for the contribution $A(T, m_2)$ to ΔG necessitates a further amendment to the dilute solution expression (21 c). The term χ_1 contains a contribution from $A(T, m_2)$ and consequently becomes chain length dependent, an effect not accounted for in the theory. Hence, we should write

$$\alpha_2 \propto \left\{ \frac{1}{2} - \chi_1(m_2) \right\} h(z) \quad (21 d)$$

and it is seen that the excluded volume function $h(z)$ should be tested with equation (21 d) rather than with equation (21 c). Whether this situation prevails at temperatures further removed from θ , where the solvent quality increases, is an open question at this moment. In view of remarks in the following paragraph one might expect any near θ situation to be representative of equation (21 d) rather than equation (21 c).

For a molecular explanation of the molar mass dependence of the term A in g^c we turn to a calculation by Staverman [52]. He considered the effect of the chains bending back on themselves on the entropy of mixing for the athermal case. Summarizing his equations one could write

$$g^c = g^c(\nu, \delta, T); \quad \delta = \delta(m_2, T) \quad (23)$$

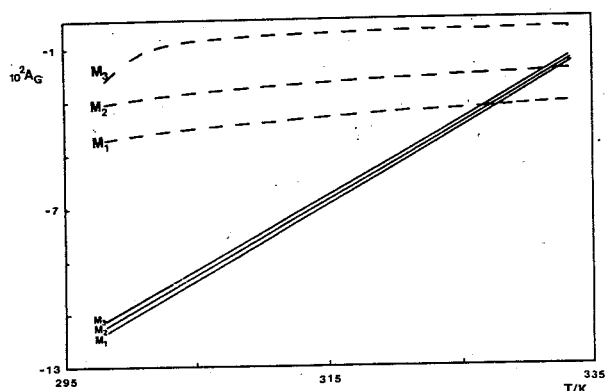


Fig. 12. Temperature dependence of the empirical free enthalpy contribution $A(T, m_2)$ (eqs. (10) and (19 a)) (—) and the same contribution as predicted by Staverman's model [4, 52] (---), calculated for molar masses M_1 , M_2 and M_3 of 50, 100 and 1000 kg/mole, respectively

where δ is the fraction of external contacts on the chain lost to intramolecular contacts by back-bending. According to Staverman, δ must be expected to depend on the size of the polymer coil and this, in turn, depends on molar mass and temperature.

Extending his treatment to the non-athermal case we find the resulting equation for $A(T, m_2)$ to show the correct trend; magnitude and slope, however, are too small. Figure 12 illustrates the situation. Since the theory is in the process of further development at the moment [44] we let a further discussion of the $A(T, m_2)$ term rest. We only note that back bending is more likely to occur in near θ states than in good solvents.

Temperature dependence of the interaction function g

The ΔG function developed so far includes a semi-empirical expression for g with a rather complex temperature dependence. The original model, on the other hand, only allows for a linear dependence on $1/T$. This temperature function has often been and still is the ground for objections against the Flory-Huggins model, represented by equations (1) and (3), because of its alleged incapability to describe lower critical miscibility, in particular if it occurs together with upper critical miscibility in the same system. Such criticism is not justified [30].

In the first place there is no reason why g_H in equation (3) could not assume negative values, the interchange energy determining its sign. Lower critical miscibility goes with a negative g_H . Further, if the criticism

has no objections against the empirical transformation of g into an free enthalpy function by the addition of g_S , one can hardly refuse to accept the outcome of an application of some fundamental thermodynamic relations to g , viz:

$$\Delta H = \int \Delta c_p dT; \quad \Delta S = \int (\Delta c_p/T) dT \quad (24)$$

where ΔH , ΔS and Δc_p are the enthalpy, entropy and specific heat changes upon mixing.

The specific heat at constant pressure, c_p , of a liquid is known to depend on temperature. In addition, Δc_p must be expected to vary with concentration, e. g.

$$\Delta c_p = (c_0 + c_1 T) \phi_1 \phi_2. \quad (25)$$

Equations (24) and (25), together with equation (1), can now be understood to define the interaction function $g(T)$. One finds

$$g = g_a + g_b/T + g_c T + g_d \ln T \quad (26)$$

where g_a and g_b arise from integration constants (eq. (24)) and $g_c = -c_1/2NR$; $g_d = -c_0/NR$. Use of the Flory-Huggins equation in the form of equations (1) and (3) unrealistically ignores the temperature dependence of Δc_p . The latter was formulated theoretically by Delmas et al. [53] who found Prigogine's model [1] to supply expressions for g_b and g_c , sufficient to deal with the occurrence of both upper and lower critical miscibility.

We thus see that the Flory-Huggins equation, properly used, is not to be criticised in this respect. We see also that a complex $g(T)$ function, like our equations (18) and (19), is to be expected. Whether the various coefficients in equation (26) are consistent with those in equation (19) could not be checked and may probably not be expected. The main point, however, is that the form found experimentally for $g(T)$ is conceivable and qualitatively consistent.

Predictive calculations

During the development of an appropriate free enthalpy function for the present set of data, the treatment has changed character from a model to a curve-fitting procedure. The number of parameters is large and, though the general form of the equations can be supported by molecular considerations, the procedure needs justification. This can be found in the predictive power of the equations used and parameter values obtained.

Krigbaum's extensive osmotic pressure data, covering molar masses ranging from 51 to 566 kg/mole [19], offer a suitable example. We calculated the reduced osmotic pressure by standard methods, using the values of the parameters in table 2. It is seen in figure 13 that the 'predicted' curves pass through the experimental points within the accuracy specified by Krigbaum.

Other examples can be drawn from the work of Kuwahara et al. [16–18] who reported near binary coexistence curves (binodals). It is seen in figure 14 that the calculated binodals agree in shape with the experimental ones, but the temperatures are about 0.5 °C off. A small shift of the predicted curves makes them coincide fairly well.

As a final test we introduce polydispersity and try to calculate ternary binodals, assuming that the ternary system can be treated as a simple superposition of three binary ones without any cross terms. Figure 15 demonstrates that Hashizume et al.'s data [10] are well

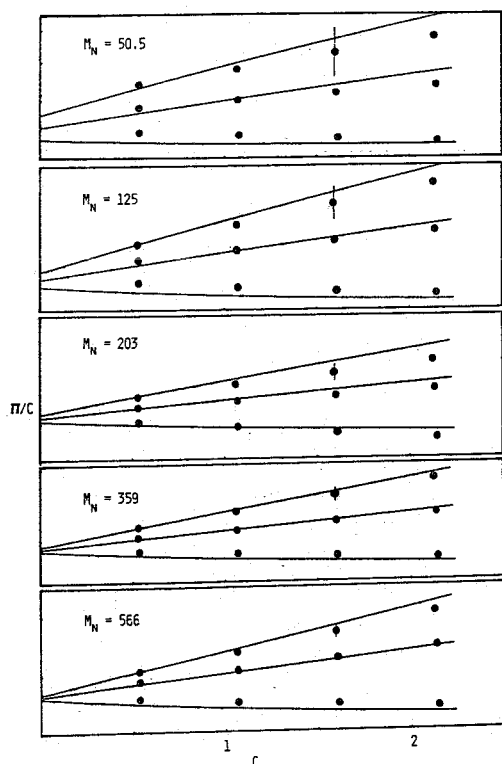


Fig. 13. Reduced osmotic pressures for various indicated molar masses (kg/mole) as a function of concentration and temperature (bottom, middle and top curves: 30, 40 and 50 °C, respectively) cyclohexane/polystyrene; data from Krigbaum [19]. Curves calculated with equations (18) and (19)

reproduced by the free enthalpy equation presented in this paper.

When it comes to wide molar mass distributions and to the description of distribution coefficients as a function of chain length, the present model and correlation function have not yet been analysed in depth [3, 4]. It is conceivable that the simple superposition method would be inadequate for such cases. This problem is a matter of current study.

Limiting critical concentration

We now drop the precise representation of data striven after in the preceding sections, and focus on a peculiar phenomenon indicated several years ago by Flory and Daoust [54]. These authors pointed out that the critical concentration at infinite chain length does not necessarily have to be zero. Later, Dušek [55] analysed the situation and found that in such a case, if existing at all, the θ temperature, taken to be the temperature at which the osmotic second virial coefficient vanishes, is not identical to the critical temperature at infinite chain length. Kennedy [56] suggested making a

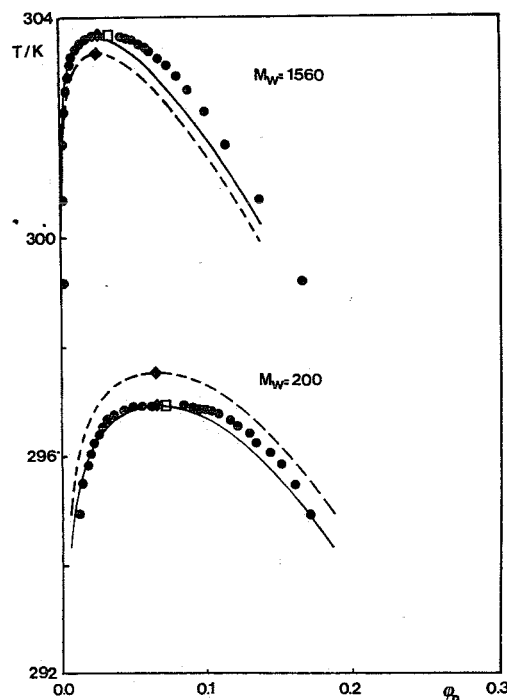


Fig. 14. Experimental binodals and their representation by equations (18) and (19) (—). System cyclohexane/polystyrene, data from Kuwahara et al. [16–18] (●). Critical points: □: experimental; ◆: calculated. Shifted calculated curves: ---

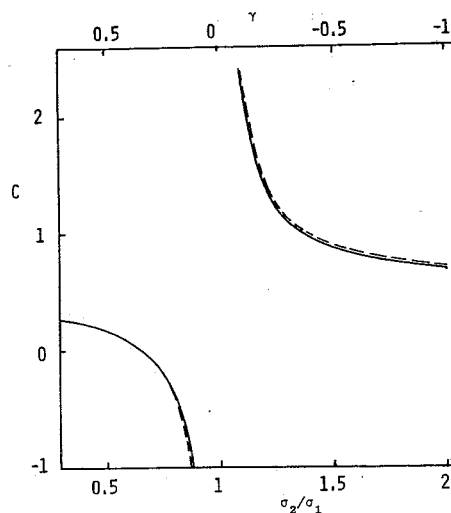
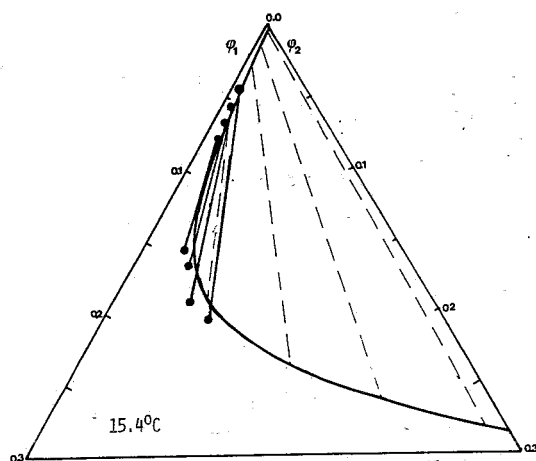
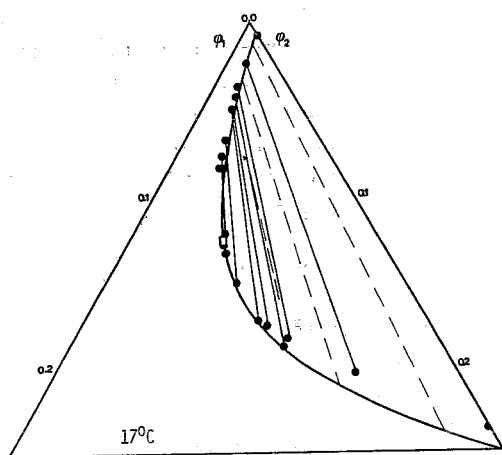


Fig. 16. Relation between C and γ for a non-zero limiting critical concentration at infinite chain length. $\phi_{2c} = 0.02$: —; $\phi_{2c} = 0.04$: ----



clear distinction between the θ state and the critical state for infinite m_2 , denoting the latter by the term 'limiting critical state'. Experimental evidence of the existence of a limiting critical concentration, ϕ_{2L} , has been reported [57].

Since we are now interested in properties at $m_2 \rightarrow \infty$, much of the intricacies discussed above can be dropped. Equation (19) reduces to equation (8) in which we shall ignore a possible temperature dependence of C . Combining equations (1), (4), (5) and (8) we can write the critical condition as

$$1/m_2 = (\phi_2/\phi_1)^2 (Q_1 - 3\gamma + 6C\gamma\phi_1^2)/Q_1 \quad (27)$$

where $Q_1 = 1 + 2\gamma\phi_2$.

Equation (2) shows that, at $m_2 = \infty$, $\phi_{2c} = 0$ always represents a possible root. Another root (ϕ_{2L}) might arise from the second expression between brackets, if the values of the parameters allowed it to be between 0 and 1. Figure 16 demonstrates that the parameters C and γ would have to be related in a special way. Since C values are often found to be close to zero the ratio σ_2/σ_1 of surface areas should be smaller than 1. The model thus predicts that experimental examples had best be sought in systems where the solvent molecule is bigger than the repeat units in the polymer.

Experiments on diphenylether/polyethylene [58], cyclohexane/polystyrene [15], and benzene/polyisobutylene [57] show that such a trend can indeed be observed. Recent measurements on diphenylether/polyisobutylene also indicate $\phi_{2L} > 0$ (see fig. 17). The

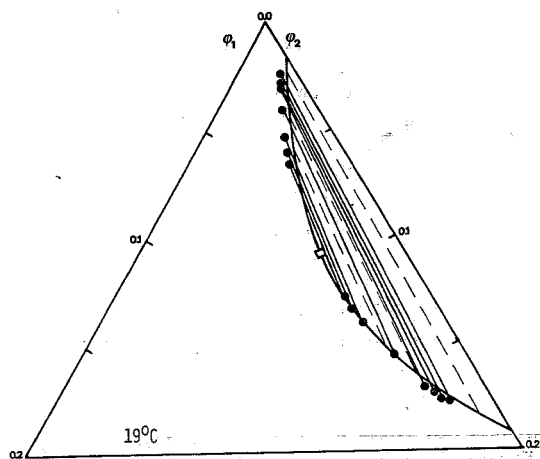


Fig. 15. Ternary phase relations for the system cyclohexane/polystyrene. Molar masses polymer constituents: 45 and 103 kg/mole. Data from Hashizume et al. [10]. Binodals (—) and tie lines (----) calculated with equations (18) and (19)

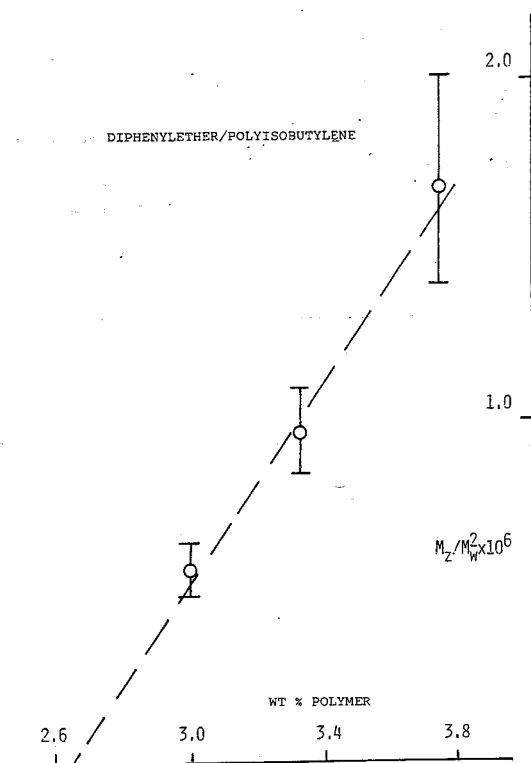


Fig. 17. Experimental indication for non-zero critical concentration ϕ_{2L} at infinite chain length. The abscissa represents value of M_z/M_w^2 to correct for differences in polydispersity. The experimental error in the critical concentration (determined with the phase-volume-ratio method [30]) is indicated by the horizontal lines on the error bars

Bondi ratios σ_2/σ_1 are 0.28, 0.87, 0.93 and 0.57, respectively. Most samples had wide molar mass distributions and we should therefore have used the multi-component versions of equations (4) and (5) to derive equation (27). This can be shown to lead to replacement of m_2 by m_w^2/m_z , where m_w and m_z are the mass- and z-average chain lengths [59]. Hence, this quantity, or M_z/M_w^2 , has been plotted in figure 17 and the ratio M_z/M_w^2 is assumed to remain finite when $M_w \rightarrow \infty$. We do not want to stretch the present argument too far, but feel justified in concluding that these examples further exemplify the importance of accounting for differences in size and shape between the constituent molecules and repeat units.

Discussion

In this paper we have tried to carry the description of thermodynamic properties of polymer solutions as

far as the rigid lattice model would permit. In the course of the development we relaxed the constancy of the coordination number, giving up the model in its strict, literal sense, but obviously greatly adding to its applicability. A further improvement includes the chain length dependence at a high degree of dilution. Finally, we saw that the back bending of chains onto themselves affects the free enthalpy of mixing, particularly in the concentrated regime where the coils overlap extensively. However, we are still left with a sizeable correction term to which the present model cannot assign a molecular basis.

It should be noted that the data sets used come from different sources and yet allow a comprehensive treatment. It must be admitted that the number of adaptable parameters seems excessive (table 2), but dropping one or more immediately worsens both description and predictions [4]. Therefore we feel that, at the moment, the presented procedure is the optimum treatment within the lattice model.

In spite of the multitude of parameters the molecular background behind most of the necessary correction terms is clear. We know that molecules and repeat units differ in size and shape, and will differ considerably in the number of nearest neighbour contacts they can make. Further, we have the well known phenomenon that dilute and concentrated polymer solutions differ essentially in segment density. Finally, we acknowledge the effect back bending of chains may have, in particular in poor solvents like the system with which we are dealing.

That the theoretical treatments are still too rough to come up with quantitative answers is hardly surprising. The various contributions to ΔG , arising from these physically evident effects, are not seldom larger than ΔG itself. Even minute inaccuracies, unavoidable with approximate theories and negligible in each term separately, may seriously distort the resulting ΔG value. Large errors, in particular in phase relations, may easily ensue. The prediction of such properties requires a high precision on ΔG which, at present, can only be had at the cost of a relatively large number of parameters.

In the end we retained a correction for the concentrated regime that so far seems to escape obvious molecular interpretation within the model. Free volume, left out of consideration here, must certainly be held responsible for part of the concentration dependence of g [60–63]. Inclusion will doubtless change the values of the parameters obtained so far, but allow excess volumes and the influence of pressure to be treated. This point is the subject of current research.

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References

1. See eg: Prigogine I (1957) *The Molecular Theory of Solutions*, North-Holland Publ Co, Amsterdam
2. Kleintjens LA, Koningsveld R, Stockmayer WH (1976) *Br Polym J* 8:144
3. Onclin MH (1980) PhD Thesis, University of Antwerp, Belgium
4. Nies E (1983) PhD Thesis, University of Antwerp, Belgium
5. Scholte ThG (1970) *Eur Polym J* 6:1063
6. Scholte ThG (1971) *J Polym Sci, Part A2*, 9:1553
7. Scholte ThG (1972) *J Polym Sci, Series C* 39:281
8. Scholte ThG (1970) *J Polym Sci, Part A2*, 8:841
9. Rietveld BJ, Scholte ThG, Pijpers J (1972) *Br Polym J* 4:109
10. Hashizume I, Teramoto A, Fujita H (1981) *J Polym Sci, Polym Phys Ed* 19:1405
11. Derham KW, Goldsbrough J, Gordon M (1974) *Pure Appl Chem* 38:97
12. Irvine P, Gordon M (1980) *Macromol* 13:761
13. Irvine P, Kennedy JW (1982) *Macromol* 15:473
14. Koningsveld R (1970) *Disc Farad Soc*, No 49:144
15. Koningsveld R, Kleintjens LA, Shultz AR (1970) *J Polym Sci, Part A2*, 8:1261
16. Kuwahara N, Nakata M, Kaneko M (1973) *Polymer* 14:415
17. Nakata M, Kuwahara N, Kaneko M (1975) *J Chem Phys* 62:4278
18. Nakata M, Dobashi N, Kuwahara N, Kaneko M, Chu B (1978) *Phys Rev, A* 18:2683
19. Krigbaum WR (1954) *J Am Chem Soc* 76:3758
20. Flory PJ (1941) *J Chem Phys* 9:660
21. Flory PJ (1942) *J Chem Phys* 10:51
22. Huggins ML (1941) *J Chem Phys* 9:440
23. Huggins ML (1942) *Ann NY Acad Sci* 43:1
24. Staverman AJ, van Santen JH (1941) *Rec Trav Chim* 60:76
25. Staverman AJ (1941) *Rec Trav Chim* 60:640
26. Koningsveld R, Staverman AJ (1968) *J Polym Sci, A2*, 6:325
27. Flory PJ (1953) *Principles of Polymer Chemistry*, Cornell Univ Press
28. Guggenheim EA (1952) *Mixtures*, Clarendon Press, Oxford
29. Rehage G (1963) *Kunststoffe* 53:605
30. Koningsveld R (1968) *Adv Interf Coll Sci* 2:151
31. Shultz AR, Flory PJ (1952) *J Am Chem Soc* 74:4760
32. Derham KW, Goldsbrough J, Gordon M, Koningsveld R, Kleintjens LA (1975) *Makromol Chem Suppl* 1:401
33. Staverman AJ (1937) *Rec Trav Chim* 56:885
34. Langmuir I (1925) *Coll Symp Monogr* 3:48
35. Butler JAV (1933) *J Chem Soc* 19:681
36. See eg: Huggins ML (1948) *J Phys Coll Chem* 52:248
37. See eg: Kanig G (1963) *Kolloid Z u Z Polym* 190:1
38. Bondi A (1968) *J Phys Chem* 68:441
39. Rowlinson JS (1959) *Liquids and Liquid Mixtures*, Butterworth, London
40. Koningsveld R, Kleintjens LA (1971) *Macromol* 4:637
41. Staverman AJ (1938) PhD Thesis, University of Leiden
42. Silberberg A (1968) *J Chem Phys* 48:2835
43. Koningsveld R (1985) *Proc Intern Disc Meeting Polym Sci Technol*, Rolduc, Netherlands, April
44. Staverman AJ (1985) *Proc Intern Disc Meeting Polym Sci Technol*, Rolduc, Netherlands, April
45. Flory PJ (1949) *J Chem Phys* 17:1347
46. Yamakawa H, (1971) *Modern Theory of Polymer Solutions*, Harper & Row, New York
47. See eg: Olabisi O, Robeson LM, Shaw MT (1979) *Polymer-Polymer Miscibility*, Academic Press
48. See eg: Kurata M (1982) *Thermodynamics of Polymer Solutions*, Harwood Acad Publ
49. Koningsveld R, Stockmayer WH, Kennedy JW, Kleintjens LA (1974) *Macromol* 7:73
50. Chu SG, Munk P (1977) *J Polym Sci, Polym Phys Ed* 15:1163
51. Tong Z, Ohashi S, Einaga Y, Fujita H (1983) *Polymer J* 15:835
52. Staverman AJ (1950) *Rec Trav Chim* 69:163
53. Delmas G, Patterson D, Somcynski T (1962) *J Polym Sci* 57:79
54. Flory PJ, Daoust H (1957) *J Polym Sci* 25:429
55. Dušek K (1969) *Coll Czechoslov Chem Comm* 34:3309
56. Kennedy JW (1970) *J Polym Sci, Part C*, No 39:71
57. Koningsveld R, Kleintjens LA (1973) *Pure Appl Chem, Macromol Chem* 8:197
58. Kleintjens LA, Koningsveld R, Gordon M (1980) *Macromol* 13:303
59. Stockmayer WH (1949) *J Chem Phys* 17:588
60. Flory PJ (1965) *J Am Chem Soc* 87:1833
61. Orwoll RA, Flory PJ (1967) *J Am Chem Soc* 89:6814, 6822
62. Kleintjens LA, Koningsveld R (1980) *Coll & Polym Sci* 258:711
63. Koningsveld R, Kleintjens LA, Leblans-Vinck AM, Ber Bunsenges, in press
64. Lal M, Swinton FL (1968) *Physica* 40:446
65. Singh J, Pflug HD, Benson GC (1968) *J Phys Chem* 72:1939

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