Comparison with experiment is not possible at present because all measurements of normal stresses have been made in concentrated or moderately concentrated solutions rather than in dilute solutions. Those measurements that have been made have generated much controversy concerning the sign of $\sigma_2$,[12,13] and there have been many reports on errors in pressure determinations.[14-16] Tanner[12] has surveyed measurements of $\sigma_1$ and $\sigma_2$ on solutions of polyisobutylene and concludes that $\sigma_2 \cong -0.15\sigma_1$ throughout a wide range of shear rates. Recent experiments on other systems also have found $\sigma_2/\sigma_1$ to be negative.[13,16]

Clearly, measurement of $\sigma_1$ and $\sigma_2$ would be extremely difficult in dilute solution. Even for a polymer of molecular weight $10^9$, such as a bacterial chromosome, $\sigma_1$ would be of the order of $10^{-6}$ atm. Nonetheless, an interesting manifestation of normal stress effects in dilute solutions of large DNA-radial migration of molecules in concentric cylinder flow toward the inner cylinder has been observed and studied theoretically.[17,18]

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# An Approximation for Nonrandomness in Polymer-Solution Thermodynamics

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ABSTRACT: In concentrated polymer solutions, residual thermodynamic functions arise from the variation of free volume with composition. These functions are traditionally calculated from an equation of state using a one-fluid theory, coupled with the assumption of random mixing. This article suggests that one limitation of Flory's equation for liquid mixtures may, in part, be due to the random-mixing assumption. To account for nonrandomness, a phenomenological equation is used to relate the potential energy of a mixture to its composition. This equation, while not rigorous, is based on the intuitive notion of a "local composition" which, in concept, is related to Guggenheim's quasichemical theory. Since the local compositions are temperature dependent, the residual entropy is also affected by nonrandomness. When applied to experimental data for a few binary polymer-solvent systems, the local-composition equation can represent both enthalpy-of-mixing and activity data using only two adjustable parameters.

It is now well known that the lattice model for polymer solutions is inadequate and that free-volume (or equation-of-state) contributions cannot be neglected when calculating thermodynamic excess functions.[1]

For the last ten years it has become common practice to use for this purpose an equation of state proposed by Flory;[2] this equation follows from a partition function that is fundamentally of the van der Waals type (hard spheres located in a uniform field of attractive energy), modified to take into account all external degrees of freedom through the parameter $3c$, as suggested by Prigogine.[3] When this partition function is extended to binary mixtures, it is necessary to make some assumption concerning the effect of composition on potential energy. The common assumption made by Flory and all subsequent workers assumes complete randomness: the polymer segments and the solvent molecules arrange themselves in a state of maximum disorder, that is, a state where a polymer segment (or a solvent molecule) chooses its closest neighbors blindly, without preference for one or the other. This assumption is attractive because it is simple and because no rigorous method is known for introducing nonrandomness, even in solutions of equisized molecules. In this work we propose an approximation for introducing nonrandomness. The approximation is not based on any clearly defined statistical-mechanical procedure but is fundamentally intuitive or phenomenological. It retains simplicity and, judging from a preliminary comparison, appears to be consistent with experimental data.

The limitations of Flory's equation of state have been pointed out previously[4-6] but in these earlier papers, primary attention was given to the failure of this equation at very low densities and to its inadequacy at very high pressures. Here we are concerned with the extension of Flory's equation of state to mixtures. For a binary mixture containing $N_1$ molecules of component 1 and $N_2$ molecules of component 2, the key relation used by Flory for the energy $E_0$ is

$$-E_0 = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v \qquad (1)$$

where

$$2A_{11} + A_{12} = s_1r_1N_1$$

$$2A_{22} + A_{12} = s_2r_2N_2$$

where $s_2$ is the external area of interaction of a polymer segment and $s_1$ is the external area of interaction of a solvent molecule. As indicated by the single subscript, these are properties of the pure components, independent of the nature of the other component.

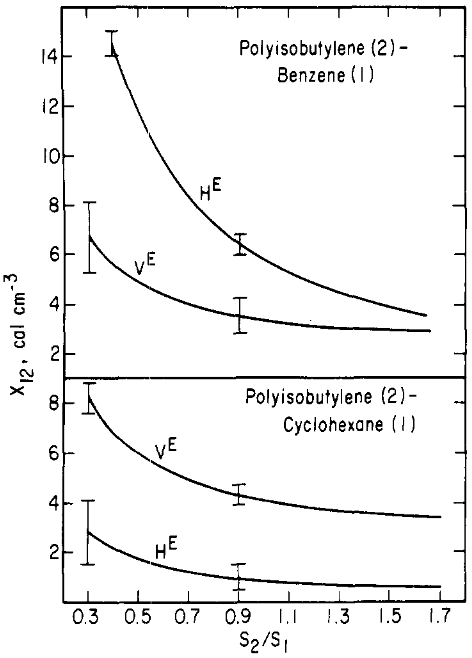

**Figure 1.** Excess enthalpy data and excess volume data cannot give a unique set of Flory parameters $X_{12}$ and $s_2/s_1$ for two polymer–solvent systems at 25 °C.

In eq 1, $\eta_{ij}/v$ reflects the interaction energy for an $i$–$j$ pair. In Flory's theory, eq 1, these interaction energies are weighted by composition factors $A_{ij}$ which depend only on the stoichiometry of the system; it is this weighting which is the essence of the random-mixing approximation.

Following Flory's notation, the binary parameter $X_{12}$ is given by

$$X_{12} = s_1 \Delta\eta / 2v^{*2} \tag{2}$$

where

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \tag{2a}$$

In eq 1, the only adjustable binary parameter is $X_{12}$ which is determined by the potential energy of a 1–2 contact. However, since there is no unambiguous way to fix independently the ratio $s_2/s_1$, that ratio, in effect, is also treated as a semiadjustable binary parameter. In view of the physical significance of this ratio, its numerical value is not freely arbitrary but must be of the order of unity.

To eliminate possible uncertainties introduced by calculated combinatorial contributions, we have examined binary excess-volume and excess-enthalpy data; these excess functions contain no combinatorial contributions but follow exclusively from the equation of state. Assuming several physically reasonable values of $s_2/s_1$, we then computed the corresponding values of $X_{12}$, using the equations given by Flory and co-workers.[1,7-10] Figure 1 shows results for polyisobutylene (PIB) and benzene and for PIB and cyclohexane. The vertical bars indicate possible variations due to experimental uncertainties. A similar plot is given in Figure 2 for the system carbon tetrachloride–neopentane. These figures show that, within experimental error, it is not possible to fix one set of parameters ($X_{12}$ and $s_2/s_1$) which simultaneously fits $H^E$ and $V^E$ data. While other explanations may be possible, these negative results suggest to us that the random-mixing equation [eq 1] is erroneous.

## A Phenomenological Equation for Nonrandomness

Since a rigorous correction to eq 1 is not available, we propose to replace eq 1 by introducing the concept of local composition which has been remarkably successful in the empirical representation of excess functions for solutions of ordinary (low-molecular-weight) liquids.[11] The local-composition concept first proposed by Wilson[12] follows from the intuitive notion that, when viewed microscopically, the composition in the immediate vicinity of any one point in the solution is not the same as that in the immediate vicinity of some other point. In polymer solutions this notion has been verified by the observation of domains in mixtures containing block copolymers.[13,14]

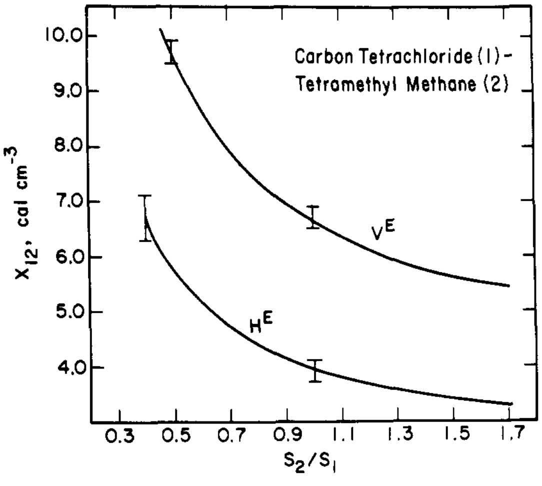

**Figure 2.** Excess enthalpy data and excess volume data cannot give a unique set of Flory parameters $X_{12}$ and $s_2/s_1$ for the system carbon tetrachloride–neopentane at 0 °C.

Following conventional notation, let $r_i$ be the number of segments per molecule $i$, let $zq_i$ be the number of external interaction sites of that molecule and, following Flory, let $\eta_{ij}/v$ stand for the potential energy per contact of sites $i$ and $j$. As usual, $z$ is the coordination number and $v$ is the macroscopic volume (per segment) as given by the equation of state.

Let us now focus attention on an external interaction site of molecule $j$. In the immediate vicinity of this site there are other external sites available for interaction; some of these belong to molecules of species $i$ and others belong to molecules of species $j$. Since we are concerned only with *external* interaction sites, we exclude those nearest-neighbor segments that are chemically bonded to the site $j$ on which we are focussing attention.

The local composition in the immediate vicinity of external site $j$ is given by $\theta_{ij}$ and $\theta_{jj}$ where $\theta_{ij}$ is the fraction of sites (in the immediate neighborhood of site $j$) which belong to a molecule of species $i$. Similarly, $\theta_{jj}$ is the fraction of sites (in the immediate neighborhood of site $j$) which belong to a molecule of species $j$, excluding those to which site $j$ is directly bonded chemically. These two local site fractions are not dependent since

$$\theta_{ij} + \theta_{jj} = 1 \tag{3}$$

Similarly, we can focus attention on an external interaction site belonging to molecule $i$. We then define local site fractions $\theta_{ji}$ and $\theta_{ii}$ in an analogous fashion, again subject to the condition

$$\theta_{ji} + \theta_{ii} = 1 \tag{4}$$

It is important to note that $\theta_{ij} \neq \theta_{ji}$.

We now propose to relax Flory's random-mixing assumption by expressing the energy in Flory's partition function for a binary mixture in terms of local site fractions

$$-E_0 = \frac{z}{2v}\,[q_1N_1(\theta_{11}\eta_{11} + \theta_{21}\eta_{21}) + q_2N_2(\theta_{22}\eta_{22} + \theta_{12}\eta_{12})] \tag{5}$$

To use eq 5, it is necessary to relate the local site fractions to the overall site fractions as determined by the overall composition and the external-site parameters $q_1$ and $q_2$. The overall site fractions are defined in the usual manner:

$$\theta_1 = N_1q_1/(N_1q_1 + N_2q_2)$$

$$\theta_2 = N_2q_2/(N_1q_1 + N_2q_2) \qquad (6)$$

There is no rigorous way to relate local site fractions to overall site fractions. However, following procedures suggested by Guggenheim[15] leading to his quasichemical theory, it is possible to obtain a reasonable approximation, as shown by Abrams.[11] We propose to relate local site fractions to overall site fractions by essentially heuristic arguments:

$$\theta_{11} = \frac{\theta_1}{\theta_1 + \theta_2 \exp\left[-\frac{zq_1}{2r_1}\left(\frac{\eta_{21} - \eta_{11}}{RTv}\right)\right]}$$

$$\theta_{22} = \frac{\theta_2}{\theta_2 + \theta_1 \exp\left[-\frac{zq_2}{2r_2}\left(\frac{\eta_{12} - \eta_{22}}{RTv}\right)\right]} \qquad (7)$$

These modifications do not affect the general form of Flory's equation of state which is

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \qquad (8)$$

where $\tilde{v} = v/v^*$, $\tilde{T} = T/T^*$, and $\tilde{P} = P/P^*$; as in Flory's work, $v^*$ is a hard-core volume per segment, $T^*$ is proportional to a characteristic potential energy, and $P^*$ is a characteristic potential energy density. In our notation

$$P_i^* = \frac{zq_i\eta_{ii}}{2r_iv^{*2}} \qquad (9)$$

Since local site fractions (eq 7) are temperature dependent, it follows that the residual entropy calculated from the model suggested here is different from that of Flory.

Following Flory, we use a one-fluid theory for the mixture. However, since we are using a nonrandom expression for the potential energy, eq 5, instead of the random expression, eq 1, our mixing rule for $P^*$ has changed. For a mixture the total number of segments is

$$N\bar{r} = r_1N_1 + r_2N_2 \qquad (10)$$

where $N = N_1 + N_2$.

When eq 5 is divided by eq 10 we obtain

$$-\frac{E_0}{\bar{r}N} = \Phi_1\frac{zq_1\eta_{11}}{2r_1v} + \Phi_2\frac{zq_2\eta_{22}}{2r_2v} + \Phi_1\theta_{21}\frac{zq_1(\eta_{21} - \eta_{11})}{2r_1v} + \Phi_2\theta_{12}\frac{zq_2(\eta_{12} - \eta_{22})}{2r_2v} \qquad (11)$$

where the segment fraction $\Phi$ is defined in the usual way

$$\Phi_1 = \frac{r_1N_1}{r_1N_1 + r_2N_2} \quad \text{and} \quad \Phi_2 = \frac{\mathrm{r}_2\mathrm{N}_2}{\mathrm{r}_1\mathrm{N}_1 + \mathrm{r}_2\mathrm{N}_2} \qquad (12)$$

By analogy to a pure component, we define

$$-\frac{E_0}{\bar{r}N} = P^*v^*/\tilde{v} \qquad (13)$$

Substitution of eq 11 into eq 13 gives $P^*$ for the mixture

$$P^* = \Phi_1P_1^* + \Phi_2P_2^* + \Phi_1\theta_{21}\nu_{21} + \Phi_2\theta_{12}\nu_{12} \qquad (14)$$

where, to simplify notation,

$$\nu_{21} = \frac{zq_1(\eta_{21} - \eta_{11})}{2r_1v^{*2}} \quad \text{and} \quad \nu_{12} = \frac{zq_2(\eta_{12} - \eta_{22})}{2r_2v^{*2}} \qquad (15)$$

For convenience, we also rewrite the local site fractions in terms of $\nu$; these are

$$\theta_{11} = \frac{\theta_1}{\theta_1 + \theta_2\exp(-\nu_{21}v^*/RT\tilde{v})} \qquad (16a)$$

and

$$\theta_{22} = \frac{\theta_2}{\theta_2 + \theta_1\exp(-\nu_{12}v^*/RT\tilde{v})} \qquad (16b)$$

As shown in Appendix A, when eq 5 is expanded in powers of $1/T$, the first term is identical with Flory's equation [eq 1].

Following Flory, we set $v^*$ (per segment) equal for all components. This, in effect, defines the number of segments because

$$V_1^*(\text{per molecule}) = r_1v_1^*$$

and

$$V_2^*(\text{per molecule}) = r_2v_2^* \qquad (17)$$

We arbitrarily select a value for $r_1$ where subscript 1 denotes the smaller molecule. We then *fix* $r_2$ by

$$r_2 = r_1(V_2^*/V_1^*) \qquad (18)$$

It follows that $v_1^* = v_2^* = v^*$. In our calculations below we always set $r_1 = 1$ but this choice is arbitrary.

As discussed elsewhere, pure-component parameters $V^*$, $P^*$, and $T^*$ are obtained from volumetric data.[6] Arbitarily setting $r_1 = 1$, we then find $r_2$ from eq 18. To find values of $q$, we use Bondi's work[16] for fixing the $q/r$ ratio. (For benzene $q/r = 0.753$, for cyclohexane it is 0.758, and for PIB it is 0.883.) For the mixture, $\tilde{T}$ is found as in ref 8.

Like Flory's theory, that presented here contains two adjustable parameters; they are $\nu_{21}$ and $\nu_{12}$. By contrast, Flory's two adjustable parameters are $X_{12}$ and $s_2/s_1$. However, there is an important conceptual difference between the two sets of adjustable parameters. The ones presented here ($\nu_{21}$ and $\nu_{12}$) are truly *binary* parameters. Flory's $X_{12}$ is also a binary parameter but $s_2/s_1$ is not; rather it is the ratio of two pure-component parameters. Allowing the ratio $s_2/s_1$ to be an adjustable binary parameter leads to an intolerable difficulty whenever one considers a mixture of three (or more) components because necessarily

$$s_2/s_3 = (s_2/s_1)(s_1/s_3) \qquad (19)$$

If all three of these ratios are adjusted independently from binary experimental data, there is no assurance that eq 19 is obeyed. In the thermodynamics of mixtures containing low-molecular-weight liquids, a similar well-known difficulty arises with the van Laar equation for activity coefficients.

The heuristic framework described here can be readily and consistently extended to multicomponent systems using only binary and pure-component parameters.

For binary systems we present in Appendix B equations for the chemical potential and for the enthalpy of mixing. We also indicate there that the attractive simplifying assumption $\eta_{12} = \eta_{21}$ is *not* permissible because it leads to an internal inconsistency in the model whenever $\theta_{11} \neq \theta_1$ and $\theta_{22} \neq \theta_2$.

## Data Reduction for Binary Systems

Given a finite set of experimental data (for example, activities of a volatile component in a binary polymer solution), it is not possible to obtain by data reduction a *unique* set of binary parameters.[17] It is always possible to find several sets of binary parameters which can represent the data within experimental uncertainty. The binary parameters are strongly correlated with each other; if one is known, the other can often be fixed with high certainty. But if both binary parameters

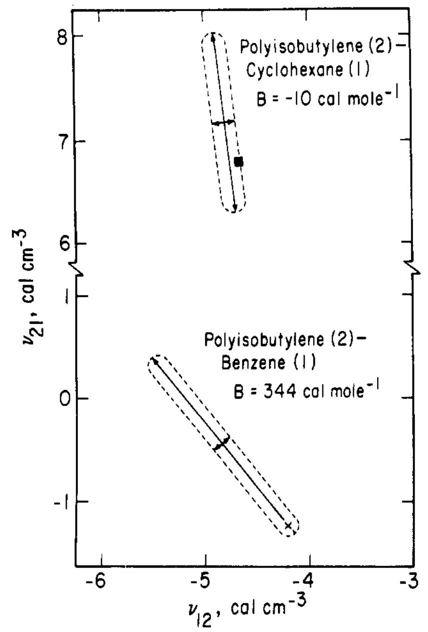

**Figure 3.** Ranges of acceptable binary parameters in nonrandom approximation as obtained from activity data for two binary systems. Points (■) and (X) correspond to indicated values of $B$; these were obtained from enthalpy-of-mixing data at high dilution. All data at 25 °C.

must be determined from a finite set of data, it is possible only to obtain a bounded two-dimensional surface; such a surface is typically an ellipse with one long axis and one short axis. Any point within that surface represents a particular set of binary parameters. But it is not possible, without additional information, to say which point within that surface is the best. [A similar situation exists when second-virial coefficient data are reduced with a two-parameter potential function, as shown long ago by Michels.[18] For example, if second-virial coefficient data for argon are reduced using the Lennar-Jones 6–12 potential, several sets of $\sigma$, $\epsilon$ parameters can equally well reproduce the experimental results.]

Figure 3 shows two-dimensional surfaces of $\nu_{21}$ and $\nu_{12}$ parameters for the systems benzene–polyisobutylene and cyclohexane–polyisobutylene. These surfaces were obtained by reducing the activity data of Eichinger et al.[9,10] In performing the data reduction it was necessary to assign reasonable experimental uncertainties as described by Britt and Luecke.[19] Further, it was necessary to use some theoretical expression for the combinatorial contribution; to be consistent with our use of $r$'s and $q$'s, we adopted the combinatorial formula of Tompa[2] and Lichtenthaler et al.[21] as reduced to practice by Donohue.[22] However, essentially the same results would have been obtained if we had used the conventional Flory combinatorial formula.

To locate the "best" point within each surface, additional experimental information is required. We used experimental enthalpy-of-mixing[9,10,23,24] to find the parameter $B$ (see Appendix B) which is found from caloric data at high dilution. Since $B$ also depends on the same two adjustable parameters ($\nu_{21}$ and $\nu_{12}$), many sets of these two parameters are possible. We choose that set which falls within the two-dimensional region that was found from activity data. For the system PIB–cyclohexane, $B$ is equal to $-10$ cal/mol, giving the (square) point shown in Figure 3; the parameters are $\nu_{12} = -4.63$ and $\nu_{21} = 6.80$ cal/cm$^3$. For the system PIB–benzene, $B$ is equal to 344 cal/mol, giving the (cross) point shown in Figure 3; the parameters are $\nu_{12} = -4.20$ and $\nu_{21} = -1.22$ cal/cm$^3$.

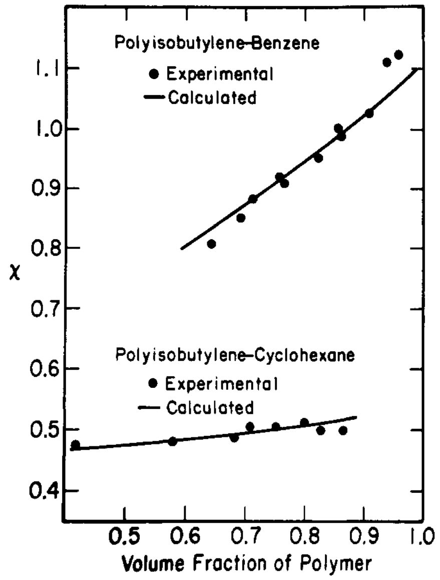

**Figure 4.** Flory $\chi$ parameter as a function of composition for two polymer–solvent systems. Calculations based on nonrandom approximation with parameters as indicated in the text. $T$ = 25 °C.

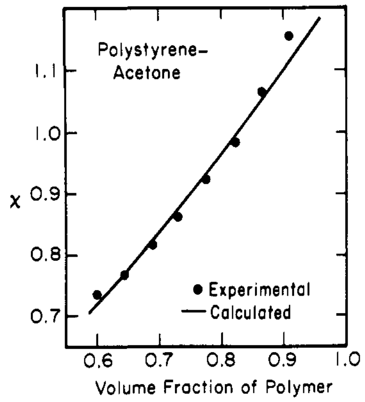

**Figure 5.** Flory $\chi$ parameter as a function of composition for the system polystyrene–acetone. Calculations based on nonrandom approximation with parameters as indicated in the text. $T$ = 25 °C.

The important conclusion that can be drawn from Figure 3 is this: Using experimental activity data and experimental enthalpy-of-mixing data, it is possible to find for each binary system one *unique* set of binary parameters which, within experimental error, can reproduce *both* experimental activity and enthalpy-of-mixing measurements. This conclusion contrasts with Flory's results because Flory requires three adjustable parameters ($X_{12}$, $s_1/s_2$, $Q_{12}$) to fit the measurements.

Figures 4 and 5 show calculated and experimental reduced residual chemical potential, $\chi$, for three polymer–solvent systems. For the two systems containing polyisobutylene, calculated results are based on the $\nu_{ij}$ parameters quoted above.

For the system acetone–polystyrene we used activity data of Bawn et al.[25] and enthalpy-of-mixing data reported by Schulz et al.[26] Using only the activity data, we obtain $\nu_{12} = -9.83 \pm 0.29$ and $\nu_{21} = 17.69 \pm 2.14$ cal/cm$^3$. Considering probable experimental errors, it is not possible to fix unique values of these parameters from activity data alone. All values of $\nu_{12}$ and $\nu_{21}$ within the indicated ranges can reproduce the activity data withn experimental uncertainty. However, from Schulz's data we obtain $B = 87.0 \pm 5$ cal/mol. If we adopt the values $\nu_{12} = -9.83$ and $\nu_{21} = 17.69$, we calculate $B = 87.5$ cal/mol. Within experimental error, therefore, these two $\nu_{ij}$ pa-

Table I
Specific Volumes of Two Binary Solutions Containing Polyisobutylene at 25 °C

| Solvent | Segment fraction of polymer | Exptl sp. vol, cm$^3$/g | % error *a* | % error *b* | % error *c* |
|---|---|---|---|---|---|
| Benzene | 0.2185 | 1.1297 | 0.8 | 0.7 | 0.7 |
| | 0.4648 | 1.1200 | 0.8 | 0.6 | 0.7 |
| | 0.6206 | 1.1136 | 0.6 | 0.4 | 0.5 |
| Cyclohexane | 0.2159 | 1.2268 | 1.5 | 1.5 | 1.5 |
| | 0.4003 | 1.1979 | 0.9 | 0.8 | 0.8 |
| | 0.5728 | 1.1700 | 0.3 | 0.3 | 0.2 |

[a] Flory's theory with $X_{12}$ from enthalpy of mixing and $s_2/s_1$ from pure-component data. [b] Flory's theory with $X_{12}$ and $s_2/s_1$, determined from activity and enthalpy-of-mixing data. [c] Nonrandom theory as discussed here with $\nu_{12}$ and $\nu_{21}$ from activity and enthalpy-of-mixing data.

rameters fit both the activity data and the enthalpy-of-mixing data for acetone–polystyrene.

While it was possible in each binary mixture considered here to obtain a unique set of binary parameters ($\nu_{21}$ and $\nu_{12}$) from activity data and from caloric measurements, unfortunately these parameters do not offer any improvement in the predicted volumes of the solutions; as shown in Table I, these predicted volumes are approximately the same as those obtained using Flory's parameters based on activity and enthalpy-of-mixing data.

## Conclusion

In this work we have proposed an alternative to the random-mixing approximation commonly used to calculate residual properties of solutions from Flory's equation of state. This alternative is based on intuitive arguments and has little claim to rigor. The intuitive alternative follows from the concept that, when viewed microscopically, the composition at any point of the solution is not the same as that at some other point. This alternative, then, attempts to account in an approximate manner for clustering (or short-range order) in liquid solutions.

Further, we have called attention to the difficulty in finding meaningful binary parameters from a finite set of experimental data which necessarily are subject to some experimental error. Using independently determined interaction surface parameters, obtained from pure-component data, we have shown that for some binary polymer mixtures where sufficient data are available it is possible to find *one set* of binary parameters which simultaneously represents the activity and the enthalpy of mixing. We cannot conclude from this work that the random-mixing approximation used by Flory, Patterson, and others is fundamentally in error; such a conclusion requires more convincing experimental evidence than that currently available. However, we can conclude that an intuitively attractive alternative to the random-mixing approximation is consistent with experiment and that by adopting this alternative we avoid the troublesome feature characteristic of previous work, where pure-component parameters ($s_1$ and $s_2$) depend on the particular binary mixture.

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## Appendix A

Series expansion of eq 5 in powers of $1/T$ gives:

$$-E_0 = \frac{z}{2v}(q_1N_1 + q_2N_2)[\theta_1\eta_{11} + \theta_2\eta_{22} - \theta_1\theta_2(\eta_{11} + \eta_{22} - (\eta_{12} + \eta_{21}))] - \frac{z^2\theta_1\theta_2}{4v^2RT}\left[q_1N_1\left(\frac{q_1}{r_1}\right)(\eta_{21} - \eta_{11})^2 + q_2N_2\frac{q_2}{r_2}(\eta_{12} - \eta_{22})\right] + \frac{z^3\theta_1\theta_2(\theta_1 - \theta_2)}{8v^3(RT)^2} \times \left[q_1N_1\left(\frac{q_1}{r_1}\right)^2(\eta_{21} - \eta_{11})^3 + q_2N_2\left(\frac{q_2}{r_2}\right)^2(\eta_{12} - \eta_{22})^3\right] + \ldots \quad \text{(A1)}$$

This equation shows that the leading term contains only one parameter $[(\eta_{11} + \eta_{22}) - (\eta_{12} + \eta_{21})]$; this leading term expresses the randomness assumption in Flory's theory. Equation A1 is consistent with van der Waals' energy of interaction[27] where the leading term represents rigorously the random interactions. The higher terms provide nonrandomness corrections.

The equivalence between the first term of eq A1 and the corresponding equation in Flory's theory [eq 32] in ref 8 can readily be shown.

As mentioned in the text, $zq_i$ is the number of external interaction sites per molecule; then $zq_i/r_i$ is the corresponding quantity per segment, which is $s_i$ in Flory's nomenclature. This means that site fractions defined by eq 6 have the same meaning as Flory's site fractions and also that $z(q_1N_1 + q_2N_2)$ is equivalent to $s\bar{r}N$ in Flory's theory.[8]

It is also clear that $[(\eta_{11} + \eta_{22}) - (\eta_{12} - \eta_{21})]$ is equivalent to Flory's $\Delta\eta$ in eq 2a.

Since $E_0$ is temperature-dependent, it contributes to the residual entropy.

## Appendix B

**Enthalpy of Mixing.** For low pressures, the enthalpy of mixing can be replaced by the energy of mixing. It is

$$\Delta H_{\mathrm{M}} = \tilde{v}Nv^*\left[\frac{\Phi_1P_1^*}{\tilde{v}_1} + \frac{\Phi_2P_2^*}{\tilde{v}_2} - \frac{P^*}{\tilde{v}}\right] \quad \text{(B1)}$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of each component while $\tilde{v}$ is that for the mixture.

The integral heat of mixing, $B$, is defined in ref 8 by $\Delta H_{\mathrm{M}} = BN_1\Phi_2$. At low polymer concentrations, $B$ is a constant independent of concentration.

Series expansion of eq B1 in powers of $\Phi_2$ gives in the limit at infinite dilution

$$B = \lim_{\Phi_2 \to 0} \left[\frac{\Delta H_M}{N_1 \Phi_2}\right] = \lim_{N_2 \to 0} \left[\frac{\Delta H_M}{N_2}\right]\left[\frac{V_1^*}{V_2^*}\right]$$
$$= \frac{V_1^*}{\tilde{v}_1}\left[P_2^* \left\{\frac{\tilde{v}_1}{\tilde{v}_2} - 1 - \alpha_1 T \left(1 - \frac{\tilde{T}_2}{\tilde{T}_1}\right)\right\}\right.$$
$$\left. - (1 + \alpha_1 T)\left\{\nu_{12} + \nu_{21} \frac{q_2/r_2}{q_1/r_1} \exp\left(-\frac{\nu_{21} v^*}{\mathrm{RT}\tilde{v}}\right)\right\}\right] \qquad \text{(B2)}$$

where $\alpha_1$ is the thermal expansion coefficient of the solvent and $\tilde{T}_2$ and $\tilde{T}_1$ are the reduced temperatures for polymer and solvent.

Equation B2 is closely related to Flory's analogous expression, which is eq 42 in ref 8.

**Chemical Potential.** The residual chemical potential can be expressed in terms of the residual enthalpy and entropy. The residual enthalpy, calculated by the nonrandomness equation, is:

$$\overline{H}_1{}^{\mathrm{R}} = \overline{H}_1 - H_1{}^0 = (\partial \Delta H_M / \partial N_1)_{T,N_2,\tilde{v}} = V_1{}^* P_1{}^* (\tilde{v}_1{}^{-1} - \tilde{v}^{-1}) - (V_1{}^*/\tilde{v})[\theta_{21}{}^2 \nu_{21} + (\Phi_2/\Phi_1)\theta_{22}\theta_{12}\nu_{12}] \qquad \text{(B3)}$$

The residual entropy is the same as that given by Flory's expression 8. The residual chemical potential is

$$(\mu_1 - \mu_1{}^0)^R = \overline{H}_1{}^{\mathrm{R}} - T\overline{S}_1{}^{\mathrm{R}} = P_1{}^* V_1{}^* \{3\tilde{T}_1 \ln [(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1{}^{-1} - \tilde{v}^{-1})\} - (V_1{}^*/\tilde{v})[\theta_{21}{}^2 \nu_{21} + (\Phi_2/\Phi_1)\theta_{22}\theta_{12}\nu_{12}] \qquad \text{(B4)}$$

Equation B4 is also closely related to eq 48 in ref 8.

**Nonvalidity of Simplifying Assumption.** An energy balance of the 1–2 interactions requires that

$$q_1 N_1 \theta_{21} \eta_{21} = q_2 N_2 \theta_{12} \eta_{12} \qquad \text{(B5)}$$

It appears attractive to assume that $\eta_{21} = \eta_{12}$. However, except for the random-mixing case where local compositions are equal to overall compositions, eq B5 cannot be satisfied for all values of $N_1$ and $N_2$ when $\eta_{12} = \eta_{21}$.

The parameter $\eta_{ij}$ depends not only on the potential energy between segment *i* and segment *j* but also on the distribution function. In a simple liquid mixture, distribution function *i–j* is the same as distribution function *j–i* but in a mixture of polymer and solvent, local structure differences do not allow us to assume such symmetry. One may therefore say that any à priori insistence that $\eta_{ij}$ *must* equal $\eta_{ji}$ follows only from a narrow interpretation, erroneously conditioned either by strict lattice concepts or by considerations valid only for simple (argonlike) fluids. These remarks in no way "prove" the model proposed here which obviously has an empirical flavor. They are intended to support the plausibility of the model and, more important, to stimulate reexamination of fundamental concepts in solution thermodynamics.

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# ESR Studies of Polymer Transitions. 1[1]

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ABSTRACT: The ESR spin-probe technique, using a nitroxide radical as the paramagnetic probe, has been shown to be a general method for the study of molecular transitions, especially the glass transition, in a series of polymeric materials. The technique has been applied to 19 different polymers/copolymers and an empirical correlation between the glass temperature ($T_g$) and an experimental ESR parameter ($T_{50G}$) has been established; a theoretical basis for the observed correlation is also presented. Results of the application of this method to polymers for which the $T_g$ is a matter of controversy are also presented and discussed.

The use of electron spin resonance (ESR) techniques with nitroxide radicals to study motion in macromolecular systems was first applied to biological polymers.[3] The ESR technique is gaining increasing attention as an important tool for the study of synthetic polymers and copolymers following the pioneering work of Rabold[4] and of Stryukov and Rozantsev.[5] A recent review article by Buchachenko et al.[6] gives a good overview of the theory and scope of the technique, as well as a summary of prior experimental results.

The ESR work performed thus far falls into two different categories, "spin-probe" experiments or "spin-label" experiments. In the "spin-probe" experiment the paramagnetic molecule is present as a "free" or "guest" molecule in the polymer matrix at concentrations of 10–100 ppm;[6–11] in the