liquid and compare it with $(\partial\phi/\partial T)_p{}^{\mathrm{l}}$ observed for liquid in the normal manner; and (iii) evaluate $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}}$ for the liquid with volume expansion held the same as in the glass and compare it with the ordinary glass property $(\partial\phi/\partial T)_p{}^{\mathrm{g}}$. (The superscripts l and g are to denote properties pertaining to liquid and glass, respectively, and are used here in place of the subscripts $\boldsymbol{A} = 0$ and $\boldsymbol{z}'$ in Appendix A.)

$(\partial\phi/\partial T)_V$ can be related to $(\partial\phi/\partial T)_p$ through the standard relation effecting the change of variables:

$$(\partial\phi/\partial T)_V{}^{\mathrm{l}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial p)_T{}^{\mathrm{l}}\,(\partial p/\partial T)_V{}^{\mathrm{l}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial p)_T{}^{\mathrm{l}}(\alpha_{\mathrm{l}}/\beta_{\mathrm{l}}) \qquad \text{(B1)}$$

By taking the difference of (B1) from the similar expression pertaining to the glass we have:

$$\Delta(\partial\phi/\partial T)_V = \Delta(\partial\phi/\partial T)_p + \Delta[(\partial\phi/\partial p)_T(\alpha/\beta)] \qquad \text{(B2)}$$

$(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{l}}}$, which one would obtain by performing a fast measurement by changing both T and p simultaneously so as to maintain its thermal expansion to correspond to α_{l}, is given by:

$$(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{l}}} = (\partial\phi/\partial T)_{\mathrm{p}}{}^{\mathrm{g}} + (\partial\phi/\partial V)_T{}^{\mathrm{g}}\,[(\partial V/\partial T)_p{}^{\mathrm{l}} - (\partial V/\partial T)_p{}^{\mathrm{g}}] = (\partial\phi/\partial T)_p{}^{\mathrm{g}} - (\partial\phi/\partial p)_T{}^{\mathrm{g}}(\Delta\alpha/\beta_{\mathrm{g}}) \qquad \text{(B3)}$$

By substracting (B3) from $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{l}}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}}$, we obtain:

$$\Delta(\partial\phi/\partial T)_{\alpha=\alpha_{\mathrm{l}}} = \Delta(\partial\phi/\partial T)_p + (\partial\phi/\partial p)_T{}^{\mathrm{g}}(\Delta\alpha/\beta_{\mathrm{g}}) \qquad \text{(B4)}$$

One may also perform a slow measurement in which T and p are altered to maintain the volume expansion equal to α_{g}. $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}}$ thus determined would be related to $(\partial\phi/\partial T)_p{}^{\mathrm{l}}$ by:

$$(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} - (\partial\phi/\partial V)_T{}^{\mathrm{l}}\,[(\partial V/\partial T)_p{}^{\mathrm{l}} - (\partial V/\partial T)_p{}^{\mathrm{g}}] = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial V)_T{}^{\mathrm{l}}(\Delta\alpha/\beta_{\mathrm{l}}) \qquad \text{(B5)}$$

Subtraction of $(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{g}}} = (\partial\phi/\partial T)_{\mathrm{p}}{}^{\mathrm{g}}$ from (B5) leads to:

$$\Delta(\partial\phi/\partial T)_{\alpha=\alpha_{\mathrm{g}}} = \Delta(\partial\phi/\partial T)_p + (\partial\phi/\partial p)_T{}^{\mathrm{l}}(\Delta\alpha/\beta_{\mathrm{l}}) \qquad \text{(B6)}$$

The expressions B2, B4, and B6 give the methods of correcting the observed difference in the temperature coefficients of ϕ in the liquid and the glass to allow for their different volume expansions. To utilize these, one has to have additional data on the pressure coefficient of ϕ for the liquid, for the glass, or for both.

The correction term, or the last term on the right of each of expressions B2, B4, and B6, becomes the same if:

$$(\partial\phi/\partial p)_T{}^{\mathrm{g}}/\beta_{\mathrm{g}} = (\partial\phi/\partial p)_T{}^{\mathrm{l}}/\beta_{\mathrm{l}} \qquad \text{(B7)}$$

or

$$(\partial\phi/\partial V)_T{}^{\mathrm{g}} = (\partial\phi/\partial V)_T{}^{\mathrm{l}} \qquad \text{(B8)}$$

Thus, to the approximation that the dependence of the property ϕ on the volume can be considered the same for glass and for liquid, the three expressions B2, B4, and B6 can be used interchangeably.

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Effect of Nonrandomness in Polymer-Solution Thermodynamics

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ABSTRACT: Polymer solutions are described by a modified form of Flory's partition function which provides an approximate, but satisfactory, representation of liquid binary mixtures at low pressures. The random-mixing assumption is rejected; to take nonrandomness into account, a two-fluid theory is used, coupled with the local composition concept. Theoretical expressions are derived for free energy, enthalpy, entropy, chemical potential, and other partial molar quantities. Characteristic parameters for pure components are evaluated according to usual methods, because Flory's model remains unchanged when applied to pure liquids. The properties of four polymer–solvent systems are interpreted according to the new nonrandom theory. Using only two adjustable parameters, the nonrandom model represents both activity and enthalpies-of-mixing data. For two systems with the same binary parameters, it is also possible to describe volumetric properties at low pressures.

Recently Renuncio and Prausnitz[1] suggested that a limitation of Flory's equation of state extended to mixtures can be ascribed, in part, to the random-mixing assumption. Therefore, they have proposed a phenomenological

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equation which takes into account nonrandomness.

As pointed out by us,[2] nonrandomness modifies the general form of Flory's equation of state and this modification affects the residual thermodynamic functions which are calculated from an equation of state.

The scope of this work is to derive an equation of state for liquid mixtures and the corresponding residual thermodynamic functions, taking into account nonrandomness and using the two-fluid theory.[3-6]

Partition Function and Equation of State

Following conventional notation, we imagine molecule i to be subdivided into r_i segments, each having a "hard-core" volume v^* and an external area of interaction s_i.

Following Flory[7] and the two-fluid theory, we assume that the partition function for a binary mixture takes the form

$$Z = Z_{\mathrm{comb}}(\gamma v^*)^{rcN}(\tilde{v}^{1/3} - 1)^{3(r_1c_1N_1+r_2c_2N_2)} \exp\left(-\frac{N_1r_1\omega_{(1)} + N_2r_2\omega_{(2)}}{kT}\right) \quad (1)$$

where Z_{comb} is a combinatorial factor which takes into account "the number of ways of interspersing $rN = r_1N_1 + r_2N_2$ segments among one another"; γ is a geometric factor; $3c_i$ is the number of external degrees of freedom per segment of type i; $\omega_{(i)}$ is the mean intermolecular energy of cell type i. Here $\omega_{(i)}$ is the energy released by the condensation process of a vaporized segment of molecule type i into a hypothetical fluid, denoted by subscript (i), where it is surrounded by $s_i\Theta_{ii}$ neighbors of species i and $s_i\Theta_{ji}$ neighbors of species j.

Introducing the concept of local composition, first proposed by Wilson[8] and extended by Maurer and Prausnitz[6] to mixtures of molecules of arbitrary size and shape, we define

$$\omega_{(1)} = \tfrac{1}{2}s_1(\Theta_{11}\eta_{11} + \Theta_{21}\eta_{21})$$
$$\omega_{(2)} = \tfrac{1}{2}s_2(\Theta_{22}\eta_{22} + \Theta_{12}\eta_{12}) \quad (2)$$

where η_{ij}/v is the potential energy per contact of sites i and j. Θ_{ii} and Θ_{ji} are the average local area fractions defined by

$$\Theta_{ii} = \frac{\Theta_i}{\Theta_i + \Theta_j\tau_{ji}} \qquad \Theta_{ji} = \frac{\Theta_j\tau_{ji}}{\Theta_i + \Theta_j\tau_{ji}} \quad (3)$$
$$(i, j = 1, 2)$$

and subject to conditions

$$\Theta_{ii} + \Theta_{ji} = 1 \qquad (i, j = 1, 2) \quad (4)$$

Equation 3 gives the relation between the average local area fractions and the overall area fractions Θ_i and the parameters τ_{ji}. The overall area fractions are defined by

$$\Theta_i = \frac{s_ir_ix_i}{\sum_{k=1}^{2} s_kr_kx_k} = \frac{s_i\phi_i}{\sum_{k=1}^{2} s_k\phi_k} \qquad (i = 1, 2) \quad (5)$$

and

$$\tau_{ji} = \exp\{\tfrac{1}{2}s_i(\eta_{ji}{}^0 - \eta_{ii}{}^0)/vRT\} = \exp\{v^*\nu_{ji}|\tilde{v}RT\} \quad (6)$$
$$(i, j = 1, 2)$$

where ϕ_i is the segment fraction and ν_{ji} is defined by

$$\nu_{ji} = \tfrac{1}{2}s_i\left(\frac{\eta_{ji}{}^0 - \eta_{ii}{}^0}{v^{*2}}\right) \qquad (i, j = 1, 2) \quad (7)$$

The reduced equation of state which follows from the previous equations and from the thermodynamic relationship

$$P = \frac{RT}{Nrv^*}\left(\frac{\partial \ln Z}{\partial \tilde{v}}\right)_{T,N_1,N_2}$$

is then

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} - \frac{A}{\tilde{T}^2\tilde{v}^2} \quad (8)$$

Equation 8 differs from Flory's equation of state in the third term on the right side, in which

$$A = c\left\{\phi_1\Theta_{11}\Theta_{21}\left(\frac{\nu_{21}}{P^*}\right)^2 + \phi_2\Theta_{22}\Theta_{12}\left(\frac{\nu_{12}}{P^*}\right)^2\right\} \quad (9)$$

where

$$P^* = \phi_1P_1^* + \phi_2P_2^* + \phi_1\Theta_{21}\nu_{21} + \phi_2\Theta_{12}\nu_{12} \quad (10)$$

and

$$c = \frac{P^*v^*}{RT^*} = \phi_1c_1 + \phi_2c_2 \quad (11)$$

The characteristic pressures for the pure components are

$$P_1^* = \tfrac{1}{2}s_1\frac{\eta_{11}{}^0}{v^{*2}} \qquad P_2^* = \tfrac{1}{2}s_2\frac{\eta_{22}{}^0}{v^{*2}} \quad (12)$$

From eq 10 and 11, the characteristic temperature T^* for the mixture is given by

$$1/T^* = (\phi_1P_1^*/T_1^* + \phi_2P_2^*/T_2^*)/P^* \quad (13)$$

where the characteristic temperatures T_1^* and T_2^* are defined by

$$T_1^* = \tfrac{1}{2}s_1\frac{\eta_{11}{}^0}{Rc_1v^*} \qquad T_2^* = \tfrac{1}{2}s_2\frac{\eta_{22}{}^0}{Rc_2v^*} \quad (14)$$

Equation 8 differs also from the equation of state derived from the approximation proposed by Renuncio and Prausnitz and reported elsewhere.[2] The difference is in the sign of the third term on the right. It depends on the definition of the average local area fractions. If we consider, for example, the ratio Θ_{21}/Θ_{11}, we have the result

$$\frac{\Theta_{21}}{\Theta_{11}} = \frac{\Theta_2}{\Theta_1}\exp\left\{\frac{v^*\nu_{21}}{\tilde{v}RT}\right\} \quad (15)$$

For $\Theta_1 = \Theta_2$ and $\nu_{21} > 0$, we have $\Theta_{21} > \Theta_{11}$; i.e., around a segment of molecule 1, the contacts 2–1 are more numerous when the intensity of interactions 2–1 is higher than that of interactions 1–1. This result is consistent with the essence of the local composition concept.

Enthalpy of Mixing

The mean intermolecular energy $E°$ for a binary mixture, according to eq 1 and 2, is given by

$$E° = -\tfrac{1}{2}s_1\frac{r_1N_1}{v^*\tilde{v}}\{\eta_{11}{}^0 + \Theta_{21}(\eta_{21}{}^0 - \eta_{11}{}^0)\} - \tfrac{1}{2}s_2\frac{r_2N_2}{v^*\tilde{v}}\{\eta_{22}{}^0 + \Theta_{12}(\eta_{12}{}^0 - \eta_{22}{}^0)\} \quad (16)$$

Taking into account eq 7, 10, and 12, we have

$$E^0 = -Nrv^*\frac{P^*}{\tilde{v}} \quad (17)$$

Therefore, ignoring the difference between the energy and enthalpy of a condensed system at low pressure, we have for the enthalpy of mixing

$$\Delta H^{\mathrm{M}} = Nrv^*\left\{\phi_1\frac{P_1^*}{\tilde{v}_1} + \phi_2\frac{P_2^*}{\tilde{v}_2} - \frac{P^*}{\tilde{v}}\right\} \qquad (18)$$

which is equivalent in form to the corresponding expressions derived by Flory[7] and by Renuncio and Prausnitz.[1] Taking into account previous equations, we have an alternative form for the enthalpy of mixing

$$\Delta H^{\mathrm{M}} = Nrv^*\left\{\phi_1 P_1^*\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \phi_2 P_2^*\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) - \frac{1}{\tilde{v}}(\phi_1\Theta_{21}\nu_{21} + \phi_2\Theta_{12}\nu_{12})\right\} \qquad (19)$$

which differs from Flory's corresponding equation in the last term, defined by Flory as the "contact-interaction term", while the terms preceding it, the "equation-of-state terms", are formally identical with those of Flory's equation. The contact-interaction term is different from that of Flory's equation because we have used the two-fluid theory coupled with the nonrandomness assumption, in contrast to the one-fluid theory and the random-mixing hypothesis employed by Flory. In the equation-of-state terms, even if formally identical, there are substantial differences due to the effect of nonrandomness on the equation of state of binary mixtures. Only in the case of athermal mixtures, when $A = 0$, is our equation identical with that of Flory.

The Residual Free Energy and Entropy.

We make the assumption discussed by Hildebrand and Scott[9] that at low pressures $\Delta A^{\mathrm{M}} = \Delta G^{\mathrm{M}}$. Therefore, according to eq 1 and 19, the free energy of mixing is constituted by a combinatorial term $\Delta G_{\mathrm{comb}} = kT \ln Z_{\mathrm{comb}}$, a contact-interaction term and an equation-of-state term.

Following Flory, we define the residual free energy G^{R} as

$$G^{\mathrm{R}} = \Delta G^{\mathrm{M}} - \Delta G_{\mathrm{comb}} \qquad (20)$$

which is given according to eq 1 by

$$G^{\mathrm{R}} = 3Nrv^* \times \left\{\phi_1 P_1^*\tilde{T}_1 \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \phi_2 P_2^*\tilde{T}_2 \ln\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right\} + \Delta H^{\mathrm{M}} \qquad (21)$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of pure components 1 and 2, respectively. They are related to the values $\tilde{T}_1$ and $\tilde{T}_2$ by Flory's equation of state, which at low pressures gives

$$\tilde{T}_1 = \frac{\tilde{v}_1^{4/3}}{\tilde{v}_1^{1/3} - 1} \qquad \tilde{T}_2 = \frac{\tilde{v}_2^{4/3}}{\tilde{v}_2^{1/3} - 1} \qquad (22)$$

From eq 21, we have for the residual entropy

$$S^{\mathrm{R}} = -3Nrv^*\left\{\phi_1\frac{P_1^*}{T_1^*} \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \phi_2\frac{P_2^*}{T_2^*} \ln\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right\} \qquad (23)$$

Formally, eq 21 and 23 are identical with those quoted by Flory. We must, however, repeat that the equation-of-state terms are substantially different from the corresponding terms in Flory's equations because of the difference in the structure of the equation of state for a binary mixture.

The Residual Chemical Potential and Related Partial Molar Quantities

The residual chemical potential of component 1 is given by

$$(\mu_1 - \mu_1^0)^{\mathrm{R}} = \left(\frac{\partial G^{\mathrm{R}}}{\partial N_1}\right)_{T,P,N_2} \qquad (24)$$

Taking into account eq 21, we have

$$(\mu_1 - \mu_1^0)^{\mathrm{R}} = \left(\frac{\partial G^{\mathrm{R}}}{\partial N_1}\right)_{T,P,N_2} = \left(\frac{\partial G^{\mathrm{R}}}{\partial N_1}\right)_{T,\tilde{v},N_2} + \left(\frac{\partial G^{\mathrm{R}}}{\partial \tilde{v}}\right)_{T,N_1,N_2}\left(\frac{\partial \tilde{v}}{\partial N_1}\right)_{T,P,N_2} \qquad (25)$$

At low pressures, it can be demonstrated (see Appendix) that

$$(\partial G^{\mathrm{R}}/\partial \tilde{v})_{T,N_1,N_2} \simeq 0 \qquad (26)$$

We then have

$$(\mu_1 - \mu_1^0)^{\mathrm{R}} = (\partial G^{\mathrm{R}}/\partial N_1)_{T,\tilde{v},N_2} \qquad (27)$$

Applying eq 27 to eq 21, we obtain

$$(\mu_1 - \mu_1^0)^{\mathrm{R}} = P_1^*V_1^*\left\{3\tilde{T}_1 \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right)\right\} - \frac{V_1^*}{\tilde{v}}\left\{\upsilon_{21}\Theta_{21}^2 + \frac{\phi_2}{\phi_1}\upsilon_{12}\Theta_{22}\Theta_{12}\right\} \qquad (28)$$

The partial residual enthalpy of component 1 is

$$\bar{H}_1^{\mathrm{R}} = \left(\frac{\partial \Delta \mathrm{H}^{\mathrm{M}}}{\partial N_1}\right)_{T,P,N_2} = P_1^*V_1^*\left\{\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) - \frac{\alpha T}{\tilde{v}}\left[1 + \frac{A}{\tilde{T}\tilde{v}}\right]\left[1 - \frac{\tilde{T}_1}{\tilde{T}}\right]\left[1 - \frac{\alpha T^*A}{\tilde{v}}\right]^{-1}\right\} - \frac{V_1^*}{\tilde{v}}\left[\upsilon_{21}\Theta_{21}^2 + \frac{\phi_2}{\phi_1}\Theta_{22}\Theta_{12}\upsilon_{12}\right]\left\{1 + \alpha T\left[1 + \frac{A}{\tilde{T}\tilde{v}}\right]\left[1 - \frac{\alpha T^*A}{\tilde{v}}\right]^{-1}\right\} \qquad (29)$$

The partial residual entropy of component 1 is

$$\bar{S}_1^{\mathrm{R}} = -P_1^*V_1^*\left\{3\frac{\tilde{T}_1}{\tilde{T}} \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{\alpha}{\tilde{v}}\left[1 + \frac{A}{\tilde{T}\tilde{v}}\right] \times \left[1 - \frac{\tilde{T}_1}{\tilde{T}}\right]\left[1 - \frac{\alpha\tilde{T}^*A}{\tilde{v}}\right]^{-1}\right\} - \alpha\frac{V_1^*}{\tilde{v}}\left[\upsilon_{21}\Theta_{21}^2 + \frac{\phi_2}{\phi_1}\Theta_{22}\Theta_{12}\upsilon_{12}\right]\left[1 + \frac{A}{\tilde{T}\tilde{v}}\right]\left[1 - \frac{\alpha T^*A}{\tilde{v}}\right]^{-1} \qquad (30)$$

The thermal expansion coefficient appearing in the above equations is given according to the equation of state for binary mixtures by

$$\alpha = \frac{1}{T}\left(\frac{1}{\tilde{T}\tilde{v}} + 2\frac{A}{\tilde{T}\tilde{v}^2}\right)\left(1/3\frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3}-1)^2} - \frac{1}{\tilde{T}\tilde{v}} - 2\frac{A}{\tilde{T}^2\tilde{v}^2}\right)^{-1} \qquad (31)$$

The integral heat of mixing, B, at infinite dilution is conventionally defined by

$$B = \lim_{\phi_2\to 0}\left(\frac{\Delta H^{\mathrm{M}}}{N_1\phi_2}\right) = \frac{V_1^*}{V_2^*}\lim_{N_2\to 0}\left(\frac{\Delta H^{\mathrm{M}}}{N_2}\right) \qquad (32)$$

or, as we have pointed out,[2] by the equivalent equation

$$B = \frac{V_1^*}{V_2^*}\bar{H}_2^{\mathrm{R}}(\infty) \qquad (33)$$

where $\bar{H}_2^{\mathrm{R}}(\infty)$ is the partial molar residual enthalpy of

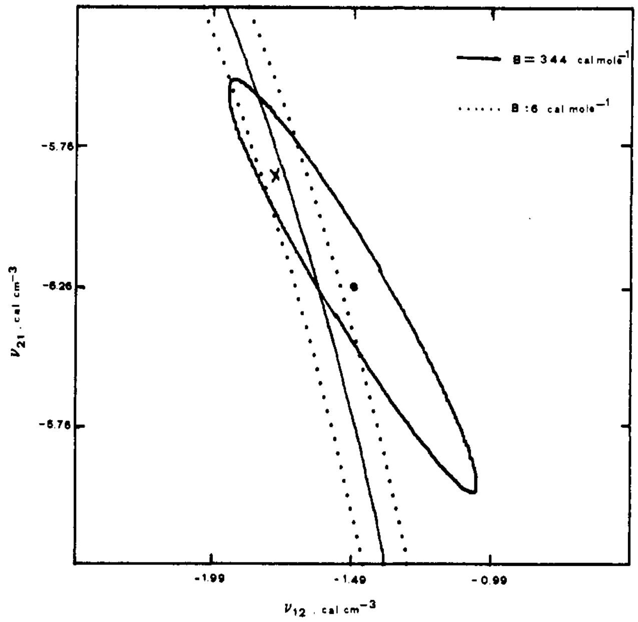

Figure 1. Approximate 99% confidence ellipse for ν_{21} and ν_{12} parameters. Benzene (1)–PIB (2) system at 25 °C; (●) best estimates of parameters.

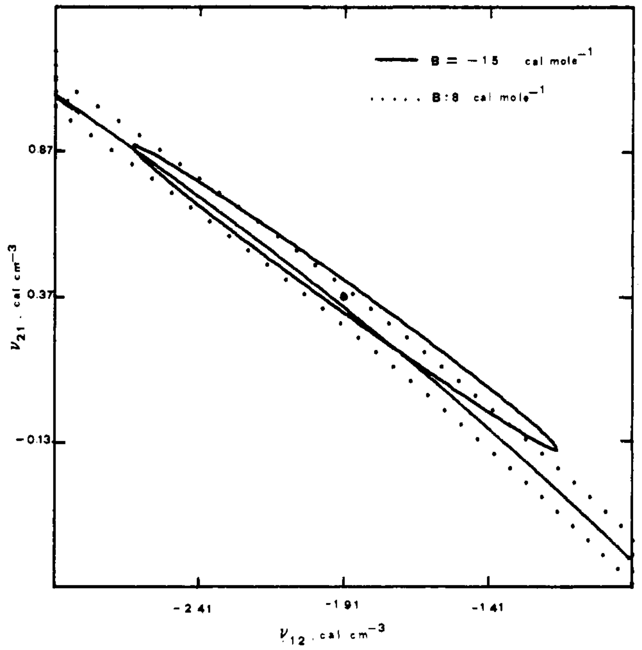

Figure 2. Approximate 99% confidence ellipse for ν_{21} and ν_{12} parameters. Cyclohexane (1)–PIB (2) system at 25 °C; (●) best estimates of parameters.

component 2 at infinite dilution. From eq 29, written for component 2, eq 33 gives

$$B = \frac{V_1^*}{\tilde{v}_1}\left\{P_2^*\left[\frac{\tilde{v}_1}{\tilde{v}_2} - 1 - \alpha_1 T\left(1 - \frac{\tilde{T}_2}{\tilde{T}_1}\right)\right] - (1 + \alpha_1 T) \times \left[v_{12} + \frac{s_2}{s_1}v_{21}\tau_{21}\right]\right\} \qquad (34)$$

The same result is obtained from series expansion of eq 18 in powers of ϕ_2 and applying eq 32.

Data Reduction for Binary Systems

We have examined four binary systems, of which two (polyisobutylene–benzene and polystyrene–acetone) present a positive value for the integral heat of mixing at infinite dilution and two (polyisobutylene–cyclohexane and polyisobutylene–*n*-pentane) have a negative value of B. As discussed elsewhere,[7] pure-component parameters are obtained from volumetric data. These characteristic parameters are reported in Table I. For fixing the s values

Table I
Characteristic Parameters for Two Polymers and Four Solvents at 25 °C

system	T^*, K	v^*, cm^3/g	p^*, cal/cm^3	ref
PIB	7580	0.9493	107	Eichinger and Flory[13]
polystyrene	7420	0.8098	131	Flory and Höker[10]
benzene	4708	0.886	150	Francis[11]
cyclohexane	4720	1.0012	127	Francis[11]
n-pentane	4158	1.1827	97.1	Francis[11]
acetone	4319	0.956	149.8	Francis[11]

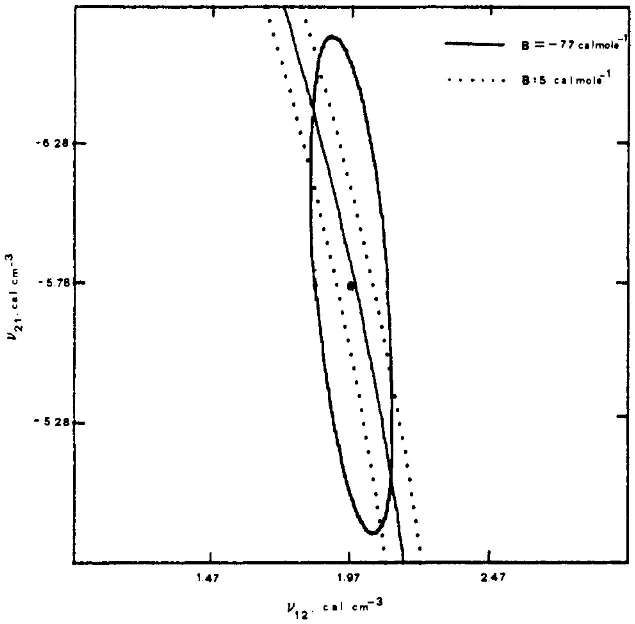

Figure 3. Approximate 99% confidence ellipse for ν_{21} and ν_{12} parameters. *n*-Pentane (1)–PIB (2) system at 25 °C; (●) best estimates of parameters.

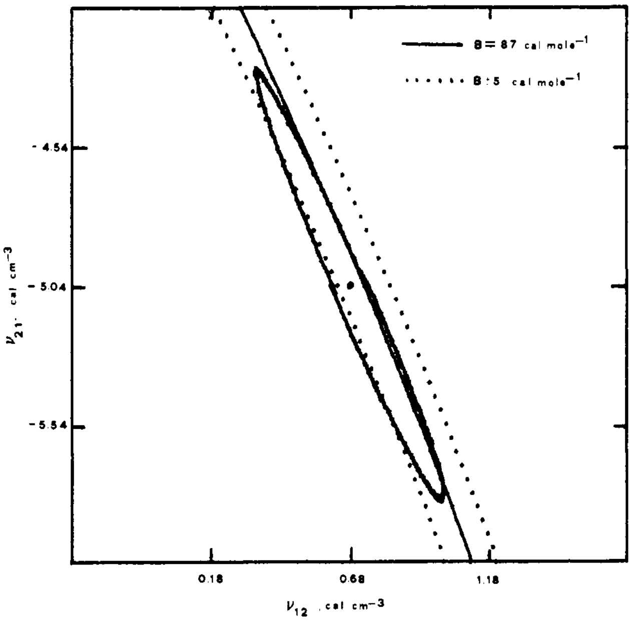

Figure 4. Approximate 99% confidence ellipse for ν_{21} and ν_{12} parameters. Acetone (1)–Polystyrene (2) system at 25 °C; (●) best estimates of parameters.

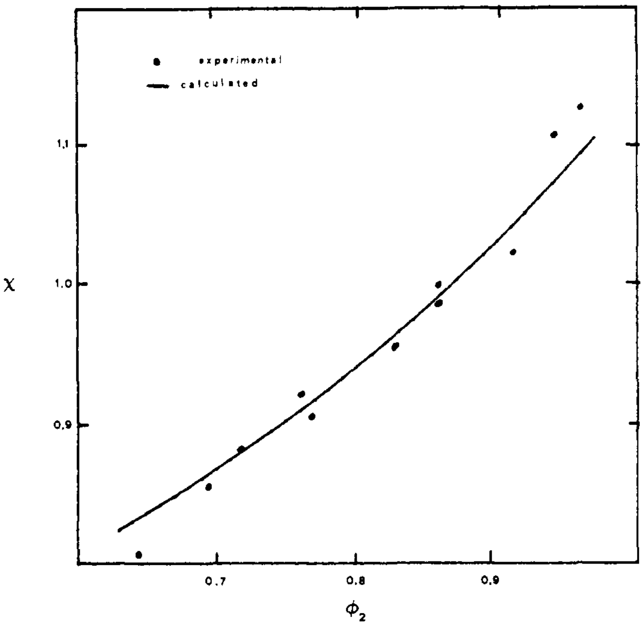

Figure 5. Flory χ parameter as a function of composition for the benzene (1)–PIB (2) system at 25 °C. Calculations based on nonrandom approximation with parameters reported in Table II.

Table II
Parameters for the Nonrandom-Mixing Approximation

system	ν_{21}, cal/cm^3	ν_{12}, cal/cm^3
benzene-PIB	−5.86	−1.77
cyclohexane-PIB	0.37	−1.91
n-pentane-PIB	−5.78	1.97
acetone-polystyrene	−5.04	0.68

Table III
Specific Volumes of Two Binary Solutions at 25 °C

system	ϕ_2	exptl spec vol, cm^3/g	*a*	*b*
benzene-PIB	0.1989	1.1227	1.1292	1.1302
	0.4355	1.1202	1.1204	1.1220
	0.5923	1.1135	1.1139	1.1156
cyclohexane-PIB	0.1971	1.2267	1.2268	1.2268
	0.3731	1.1979	1.1969	1.1970
	0.5445	1.1700	1.1685	1.1686

[a] Calculated values with parameters reported in Table II (cm^3/g). [b] Flory's theory with parameters from enthalpy of mixing (cm^3/g).

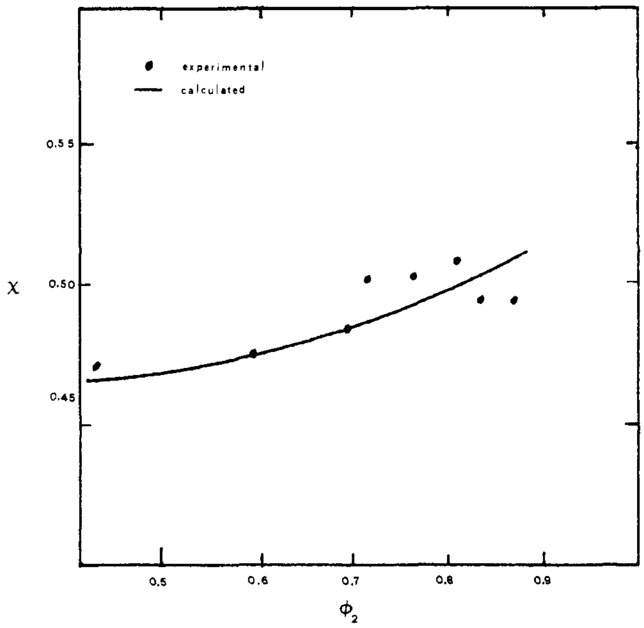

Figure 6. Flory χ parameter as a function of composition for the cyclohexane (1)–PIB (2) system at 25 °C. Calculations based on nonrandom approximation with parameters reported in Table II.

we use Bondi's work.[12] (For benzene s = 7.53; for cyclohexane s = 7.58; for *n*-pentane s = 8.67; for acetone s = 9.01; for PIB s = 8.83; and for polystyrene s = 6.98.)

Figures 1–4 show the approximate ellipses of parameters υ_{21} and υ_{12} for the systems benzene–PIB, cyclohexane–PIB, *n*-pentane–PIB, and acetone–polystyrene, respectively. These surfaces were obtained by reducing the activity data of Eichinger and Flory[13-15] and Bawn et al.[16] Data reduction was performed using a method based on the maximum-likelihood principle developed by Anderson et al.[17] to determinate model parameters from experimental data when all the measured variables are subject to error.

For the combinatorial contribution we have used Flory's combinatorial formula.

Nicolaides and Eckert[18] as well as Anderson and Prausnitz[19] have shown that a confidence ellipse results when experimental data for liquid mixtures of ordinary molecular weight are reduced to yield two binary parameters. The same occurs for polymer solutions; indeed, it is *not* possible to find one *unique* set of binary parameters which, within experimental error, can reproduce both experimental activity and enthalpy-of-mixing measurements. In fact, using the experimental enthalpy[1,13-15,20-22] we arrive at the parameter B which depends on the same two adjustable parameters, as we can see from eq 34. For the system benzene–PIB, B = 344±6 cal/mol; for the system cyclohexane–PIB, B = −15±8 cal/mol; for the system *n*-pentane–PIB, B = −77 ± 5; and for the system acetone–polystyrene, B = 87 ± 5 cal/mol. The continuous lines in Figures 1 to 4 represent the values of parameters υ_{21} and υ_{12} which give the value of B for each system, while the dotted lines characterize all values of υ_{21} and υ_{12} which can reproduce the parameter B within experimental uncertainty.

The important conclusion that can be drawn from Figures 1 to 4 is that by using experimental activity data and experimental enthalpy-of-mixing data, it is possible to find many sets of binary parameters (within the confidence ellipse which falls between the dotted lines), which, within experimental error, can reproduce the activity and enthalpy-of-mixing measurements. This conclusion contrasts with Flory's results because Flory requires three adjustable parameters to fit the experimental data.

While for the systems PIB–cyclohexane, PIB–*n*-pentane, and polystyrene–acetone the best estimates of the parameters come between the dotted lines, for the system PIB–benzene, from among the possible values, we have chosen the cross point shown in Figure 1, because the best estimates of the parameters from activity data are out of the region in which the parameters reproduce both experimental measurements.

Using the parameters reported in Table II, we have drawn Figures 5, 6, 7 and 8, which show calculated and experimentally reduced residual chemical potential, χ, for the four polymer–solvent systems. We see that only for the PIB–benzene system are the two parameters both negative, and therefore there is a tendency for the two components to segregate.

The set of binary parameters chosen for the PIB–benzene system describes very well the behavior of the solution volumes, as can be seen from data shown in Table

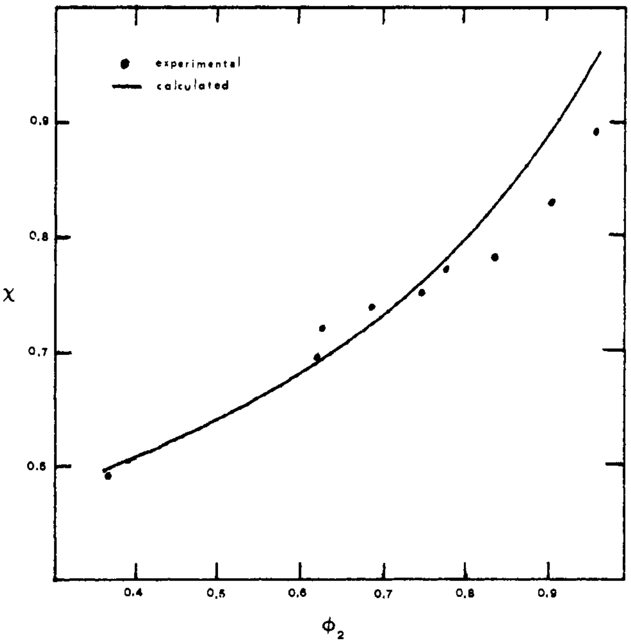

Figure 7. Flory χ parameter as a function of composition for the *n*-pentane (1)–PIB (2) system at 25 °C. Calculations based on nonrandom approximation with parameters reported in Table II.

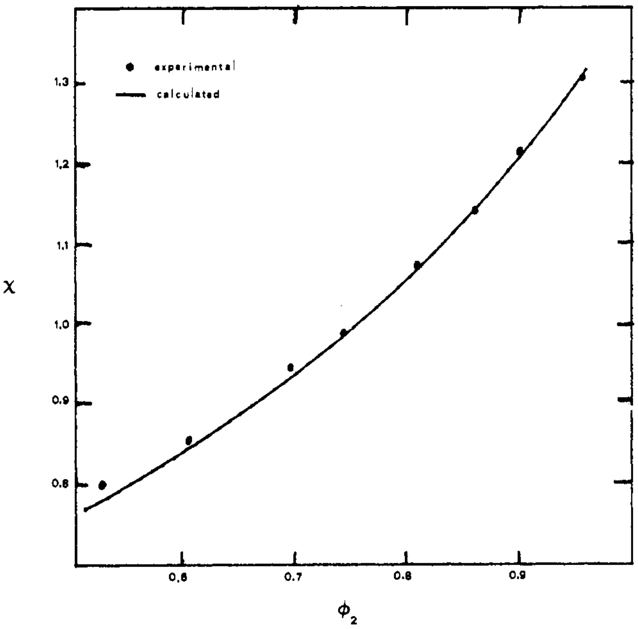

Figure 8. Flory χ parameter as a function of composition for the acetone (1)–polystyrene (2) system at 25 °C. Calculations based on nonrandom approximation with parameters reported in Table II.

III, where the experimental specific volumes[23] for two polymer–solvent systems are reported. The predicted volumes are approximately the same as those obtained using Flory's parameters based on the enthalpy-of-mixing data, for the PIB–cyclohexane system, but there is an improvement for PIB–benzene.

Table IV reports the differences between calculated and experimental values of the ratio v/v^0 at 1000 bars for the PIB–benzene and PIB–cyclohexane systems. There is only slight improvement when we use the nonrandom model in place of Flory's equation.

Conclusion

In this work, we have presented an improved version of the nonrandom-mixing approximation first proposed by Renuncio and Prausnitz to calculate residual properties of solutions. This improved approximation modifies the form of Flory's equation of state for binary solutions, and, therefore, it consequently alters the expressions of residual properties.

Table IV

Differences between Calculated and Experimental Values of v/v^0 at 1000 bars and 25 °C

system	ϕ_2	difference × 10^4		
		a	*b*	*c*
benzene-PIB	0.1989	35	36	36
	0.4355	41	35	38
	0.5923	41	27	33
cyclohexane-PIB	0.1971[d]	21	15	−313
	0.3731	31	35	−547
	0.5445	43	43	−488

[a] Calculated with Flory's equation. [b] Calculated from nonrandom approximation by using parameters from fitting experimental volumes at 1 bar. [c] Calculated from nonrandom approximation by using parameters reported in Table II. [d] At 400 bars.

Further, we have called attention to the *impossibility* of finding *one unique set* of binary parameters which simultaneously represents activity and enthalpy of mixing. In fact, it is possible to locate, for the systems examined here, an area characterized by many sets of binary parameters. These parameters reproduce, within experimental uncertainty, activity data, enthalpy-of-mixing data, and, with a satisfactory approximation, volumetric data at low pressures.

The theory of liquid mixtures, presented here, exhibits a few defects which are also present in Flory's theory. The main one is that the characteristic parameters change with temperature. This change affects the equation of state for pure components. As the effect of the equation of state for pure components has a remarkable influence on the properties of solutions, a more satisfactory representation of pure fluids can give a better description of the properties of mixtures.

Nevertheless, we can conclude that the nonrandom theory is satisfactory as it is consistent with experimental data at low pressures and it requires only two adjustable binary parameters. On the other hand, nonrandomness alone is not sufficient to explain the behavior of mixtures at higher pressures, and in this case an improvement in Flory's equation can probably be achieved by additionally modifying the hard-sphere contribution.

Appendix

From eq 21 we have

$$\left(\frac{\partial G^{\mathrm{R}}}{\partial \tilde{v}}\right)_{T,N_1,N_2} = -rNv^* \times \left\{[\phi_1 P_1{}^*\tilde{T}_1 + \phi_2 P_2{}^*\tilde{T}_2]\frac{\tilde{v}^{-2/3}}{\tilde{v}^{1/3}-1} + \frac{1}{\tilde{v}}\left(\frac{\partial P^*}{\partial \tilde{v}}\right)_{T,N_1,N_2} - \frac{P^*}{\tilde{v}^2}\right\} \tag{A1}$$

From eq 10 we obtain

$$\left(\frac{\partial P^*}{\partial \tilde{v}}\right)_{T,N_1,N_2} = -\frac{A}{\tilde{T}\tilde{v}^2}P^* \tag{A2}$$

Substitution of eq A2 into eq A1 gives

$$\left(\frac{\partial G^{\mathrm{R}}}{\partial \tilde{v}}\right)_{T,N_1,N_2} = -rNv^*\frac{\tilde{T}}{\tilde{v}}P^*\left[\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{T}\tilde{v}} - \frac{A}{\tilde{T}^2\tilde{v}^2}\right] \tag{A3}$$

At low pressures, the term in brackets is approximately equal to zero; we have therefore demonstrated the validity of eq 26.

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Kinetic Study of Polymerization of *trans*-2- and *trans*-3-Oxabicyclo[3.3.0]octane

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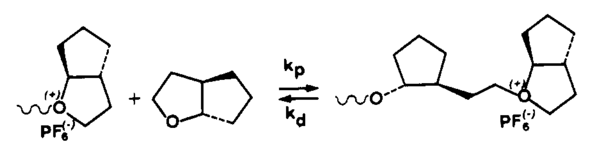
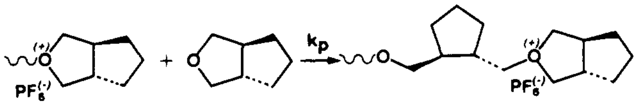
ABSTRACT: The kinetics of polymerization of the two bond-bridged bicyclic ethers, *trans*-2- and *trans*-3-oxabicyclo[3.3.0]octane, have been studied in methylene dichloride initiated by triethyloxonium hexafluorophosphate. The kinetics of both initiation and propagation were investigated by determination of the instantaneous concentration of propagating species at different temperatures in the interval −30 to 0 °C. The initiation reaction is more than three orders of magnitude slower than the propagation reaction. This difference in rate of the reaction of monomer with the triethyloxonium ion and the propagating oxonium ion, respectively, is attributed to the relief of strain in the case of the cyclic ion, and the activation enthalpies are quite different for these reactions ($\Delta H^{\ddagger}_{i}$ = 74 and 71 kJ·mol^{-1} and $\Delta H^{\ddagger}_{p}$ = 62 and 56 kJ·mol^{-1} for the two monomers). A mechanism is presented which includes the formation of two types of "dormant" tertiary oxonium ions involving the polymer chains. This mechanism is in accordance with the observed molecular weight distribution and the formation of oligomeric species.

Bond-bridged bicyclic ethers containing an oxacyclopentane ring fused in the trans position have previously been shown to undergo polymerization easily. In the case of compounds with the heterocyclic ring fused with a cyclohexane ring, the polymerization is either partially or completely reversible.[1,2] The fusion of two five-membered rings in trans positions yields a highly strained monomer, thus *trans*-3-oxabicyclo[3.3.0]octane (*trans*-3-OBCO) is very reactive and shows no sign of reversibility,[3] while the corresponding less-strained *cis*-3-oxabicyclo[3.3.0]octane (*cis*-3-OBCO) is completely inactive when contacted with phosphorus pentafluoride initiator.

In this paper, results are reported from a kinetic study of the polymerizations of the two bond-bridged bicyclic ethers, *trans*-2- and *trans*-3-OBCO. The polymerizations have been studied in CH_2Cl_2 in the temperature range −30 to 0 °C, using the salt triethyloxonium hexafluorophosphate (Et_3OPF_6) as the initiator. The mechanisms of chain propagation for the two monomers have also been investigated and already reported in preliminary form.[4] It was shown by ^{13}C NMR that the repeat units of the polymers correspond to ring opening exclusively by nucleophilic attack of monomer oxygen at the methylene carbon adjacent to the oxonium ion at the growing chain end:



trans-2-OBCO



trans-3-OBCO

The initiation and propagation steps are formulated as follows:

$$I + M \xrightarrow{k_i} M^* \quad (1)$$

$$M^* + M \xrightarrow{k_p} P^* \quad (2)$$

$$P^* + M \xrightarrow{k_p} P^* \quad (3)$$

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