This result reproduces that of Flory, Edwards, and others. It is not a self-consistent field calculation of $P(\mathbf{R})$. However, the dependence of R^2 on N is obtained directly, independent of the correctness or incorrectness of $P(\mathbf{R})$.

References and Notes

(1) A survey of much of the literature on this subject may be found in H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter III.
(2) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).
(3) S. F. Edwards, *Proc. Phys. Soc.*, **85**, 613 (1965).
(4) H. Reiss, *J. Chem. Phys.* **47**, 186 (1967).
(5) P. G. de Gennes, *Phys. Lett. A*, **38**, 339 (1972).
(6) J. des Cloizeaux, *Phys. Rev. A*, **10**, 1665 (1974).
(7) K. J. Freed, *Adv. Chem. Phys.*, **22**, 1 (1972).
(8) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).
(9) C. Domb, *Adv. Chem. Phys.*, **15**, 229 (1969).

Effect of Nonrandom Mixing on Flory's Equation of State

V. BRANDANI

Instituto di Chimica Applicata e Industriale, Università de' L'Aquila, 67100 L'Aquila, Italy. *Received May 25, 1978*

Renuncio and Prausnitz[1] have proposed a *one-fluid* theory, coupled with the assumption of nonrandom mixing, to obtain an equation of state from which to calculate residual thermodynamic functions. For a binary mixture, following Abrams,[2] they propose to relate local site fractions θ_{ij} to the overall site fractions θ_i and θ_j by

$$\theta_{11} = \frac{\theta_1}{\theta_1 + \theta_2\tau_{21}} \qquad \theta_{21} = \frac{\theta_2\tau_{21}}{\theta_1 + \theta_2\tau_{21}}$$
$$\theta_{22} = \frac{\theta_2}{\theta_2 + \theta_1\tau_{12}} \qquad \theta_{12} = \frac{\theta_1\tau_{12}}{\theta_2 + \theta_1\tau_{12}} \tag{1}$$

where, to simplify notation,

$$\tau_{21} = \exp(-\nu_{21}\mathbf{v}^*/RT\tilde{\mathbf{v}}) \tag{2}$$

and

$$\tau_{12} = \exp(-\nu_{12}\mathbf{v}^*/RT\tilde{\mathbf{v}}) \tag{3}$$

For the two adjustable parameters, ν_{21} and ν_{12}, the authors write

$$\nu_{21} = \frac{zq_1(\eta_{21} - \eta_{11})}{2r_1\mathbf{v}^{*2}} \qquad \nu_{12} = \frac{zq_2(\eta_{12} - \eta_{22})}{2r_2\mathbf{v}^{*2}} \tag{4}$$

As defined, the four *average* local site fractions are subjected only to the conditions

$$\theta_{11} + \theta_{21} = 1 \tag{5}$$

and

$$\theta_{22} + \theta_{12} = 1 \tag{6}$$

but, as clearly stated by Guggenheim[3] and by Hildebrand and Scott[4] in terms of distribution functions, another restraint, consistent with *one-fluid* theory, must be satisfied by local site fractions:

$$\theta_1\theta_{21} = \theta_2\theta_{12} \tag{7}$$

Equation 7 is merely a contact balance which is not verified, as Renuncio and Prausnitz have pointed out.

Therefore, Renuncio and Prausnitz have, in effect, used a *two-fluid* theory.

$$q_1N_1\theta_{21}\eta_{21} = q_2N_2\theta_{12}\eta_{12} \tag{8}$$

If they had used a *one-fluid* theory, the average energy balance of the 1–2 interactions for all values of N_1 and N_2 and for $\eta_{21} = \eta_{12}$ should have been satisfied, because of eq 7.

Further, Renuncio and Prausnitz state that the residual entropy is affected by nonrandomness, since the local compositions are temperature dependent. But why, one asks, do they use, in Appendix B, Flory's expression[5] of the residual entropy to calculate the residual chemical potential? Flory, in fact, has obtained his expression for a perfectly random mixture.

Furthermore, it is possible to demonstrate that the expression (eq B3) given by the authors for the residual enthalpy is not consistent with the expression (eq B2) for the integral heat of mixing at infinite dilution. In fact, from the definition

$$B = \frac{V_1^*}{V_2^*}\lim_{N_2\to 0}\frac{\Delta H^{\mathrm{M}}}{N_2} \tag{9}$$

applying L'Hopital's theorem, one has

$$B = \frac{V_1^*}{V_2^*}\bar{H}_2^{\mathrm{R}}(\infty) \tag{10}$$

where, from the residual enthalpy equation quoted by Renuncio,

$$\bar{H}_2^{\mathrm{R}}(\infty) = \frac{V_2^*}{\tilde{\mathbf{v}}_1}\left\{P_2^*\left(\frac{\tilde{\mathbf{v}}_1}{\tilde{\mathbf{v}}_2} - 1\right) - \left(\nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\tau_{21}\right)\right\} \tag{11}$$

Substitution of eq 11 in eq 10 gives

$$B = \frac{V_1^*}{\tilde{\mathbf{v}}_1}\left\{P_2^*\left(\frac{\tilde{\mathbf{v}}_1}{\mathbf{v}_2} - 1\right) - \left(\nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\tau_{21}\right)\right\} \tag{12}$$

Equation 12 differs from eq B2 reported by the authors for B. I believe that this is due to the incorrect definition of the residual enthalpy given by Renuncio and Prausnitz, in fact

$$\bar{H}_1^{\mathrm{R}} = \{\partial\Delta H^{\mathrm{M}}/\partial N_1\}_{TN_2P}$$

while the authors assume (eq B3)

$$\bar{H}_1^{\mathrm{R}} = \{\partial\Delta H^{\mathrm{M}}/\partial N_1\}_{T,N_2,\tilde{\mathbf{v}}}$$

Finally, the assumption of nonrandomness also modifies the general form of Flory's equation of state for a binary mixture, that is

$$\frac{\tilde{P}\tilde{\mathbf{v}}}{\tilde{T}} = \frac{\tilde{\mathbf{v}}^{1/3}}{\tilde{\mathbf{v}}^{1/3} - 1} - \frac{1}{\tilde{\mathbf{v}}\tilde{T}} + \frac{A}{\tilde{\mathbf{v}}^2\tilde{T}^2} \tag{13}$$

where

$$A = \frac{P^*\mathbf{v}^*}{RT^*}\left\{\phi_1\theta_{11}\theta_{21}\left(\frac{\nu_{21}}{P^*}\right)^2 + \phi_2\theta_{22}\theta_{12}\left(\frac{\nu_{12}}{P^*}\right)^2\right\} \tag{14}$$

This result contrasts with Renuncio's statement that the modifications introduced to account for nonrandomness do not affect Flory's equation of state.

Equation 13 reduces to Flory's form only when the mixtures are athermal, i.e., when ν_{21} and ν_{12} are both equal to zero.

In Table I the reduced volumes, calculated by eq 13 and by eq 8 in ref 1, at two different temperatures are compared. A symmetric ($\nu_{21} = \nu_{12}$; $q_1/r_1 = q_2/r_2$) mixture, with $\phi_2 = 0.5$, is considered. Pure-component parameters employed in both equations were: $P_1^* = 150$ cal/cm^3, $T_1^* = 5000$ K, $V_1^* = 100$ cm^3/mol, $P_2^* = 100$ cal/cm^3, $T_2^* = 8000$ K. Table I shows that the contribution of the third term in the right side of eq 13 is not a negligible quantity.

0024-9297/78/2211-1293$01.00/0 © 1978 American Chemical Society

Table I
Effect of Temperature on the Reduced Volumes for Several Values of Energy Parameters

RT, cal	parameters $\upsilon_{21} = \upsilon_{12}$, cal/cm^3	$\tilde{V}$ calcd from eq 13	$\tilde{V}$ calcd from eq 8 in ref 1	deviation,[a] %
600	10	1.2131	1.2079	0.4
	20	1.2173	1.2098	0.6
	−10	1.2404	1.2338	0.5
	−20	1.2840	1.2702	1.1
	−30	1.3358	1.3209	1.1
800	10	1.3281	1.3199	0.6
	20	1.3399	1.3206	1.5
	−10	1.3797	1.3688	0.8
	−20	1.4767	1.4371	2.8
	−30	1.6452	1.5516	6.0

[a] Defined as $100(\tilde{V}_{13} - \tilde{V}_8)/\tilde{V}_8$.

Table II
Specific Volumes of Two Binary Mixtures Containing Polyisobutylene at 25 °C

solvent	segment fraction of polymer	exptl specific vol, cm^3/g	calcd specific vol,[a] cm^3/g	abs error, %[c]	calcd specific vol,[b] cm^3/g	abs error, %[c]
benzene	0.1989	1.1297	1.1312	0.13	1.1310	0.12
	0.4355	1.1202	1.1223	0.19	1.1219	0.15
	0.5923	1.1135	1.1156	0.19	1.1151	0.14
cyclohexane	0.1971	1.2267	1.2268	0.008	1.2253	0.11
	0.3731	1.1979	1.1981	0.017	1.1959	0.17
	0.5445	1.1700	1.1702	0.017	1.1679	0.18

[a] Values calculated from eq 13. [b] Values calculated from Renuncio's equation. [c] Defined as $100|V_e - V_c|/V_e$.

Moreover, the specific volumes of benzene–polyisobutylene and cyclohexane–polyisobutylene mixtures have been calculated with the ν_{21} and ν_{21} values quoted in ref 1. The results are shown in Table II together with the experimental data reported in the literature.[6] For the benzene–polyisobutylene system, eq 13 and Renuncio's equation give the same absolute errors, but for the cyclohexane–polyisobutylene system, eq 13 is far superior, because the deviation from experiment is about ten times smaller than that associated with Renuncio's equation.

References and Notes

(1) J. A. Renuncio and J. M. Prausnitz, *Macromolecules*, **9**, 898 (1976).
(2) D. S. Abrams and J. M. Prausnitz, *AIChE J.*, **21**, 116 (1975).
(3) E. A. Guggenheim, "Mixtures", Clarendon Press, Oxford, 1952, p 217.
(4) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Dover Publications, New York, N.Y., 1964, p 125.
(5) B. E. Eichinger and P. J. Flort, *Trans. Faraday Soc.*, **64**, 2035 (1968).
(6) J. A. Renuncio and J. M. Prausnitz, *Macromolecules*, **9**, 324 (19976).

Reply to the Note by V. Brandani

J. M. PRAUSNITZ* and J. A. R. RENUNCIO

Department of Chemical Engineering, University of California, Berkeley, California 94720.

Received August 21, 1978

We are most grateful to Vincenzo Brandani for having accepted the challenge with which we ended our admittedly speculative paper on nonrandomness: "These remarks. . .are intended. . .to stimulate reexamination of fundamental concepts in solution thermodynamics".

Regrettably, we erred in failing properly to take into account the consequences of the density dependence in our definitions of local site fractions [eq 7 of our paper]. As a result of this density dependence, "parameter" P^* [eq 14] is also density dependent. As a result, the equation of state for a mixture is not the same as that of Flory but contains an additional term, as shown correctly in Brandani's equation 14. Similarly, the residual entropy in the nonrandom treatment is different from that in Flory's random treatment.

Fortunately, our overall conclusions are not destroyed by Brandani's corrections. On the contrary, Brandani's calculations suggest that the effect of nonrandomness is perhaps more important than we claimed; with his corrected results, he obtains significantly better agreement with experiment than we did.

While we are thankful to Brandani for having found our mathematical error and having worked out the correct results, it is clear that the empirical flavor of our nonrandom "theory" remains. As before, it is our hope that the (now happily corrected) approximation which we have presented has called attention to the importance of partial order in liquid mixtures, and that it may stimulate research toward a more rigorous answer to the problem of nonrandomness in mixtures of dense fluids.

0024-9297/78/2211-1294$01.00/0 © 1978 American Chemical Society