Macromolecules **1991,** *24,* 2391–2396

Flory's Equation of State for Nonrandom Polymer–Solvent Solutions. Application of Local Compositions and the Two-Fluid Theory of Mixtures

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Received July 26, 1990; Revised Manuscript Received October 29, 1990

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. As in previous publications, the original random-mixing assumption is rejected; to take nonrandomness into account, a two-fluid theory is used coupled with the local-composition concept. However, with the new form of the partition function, Flory's equation of state for binary mixtures is obtained, without any correction term as found in previous publications. Theoretical expressions are then derived for free energy, enthalpy, entropy, chemical potential, and other partial molar quantities. The expression for the osmotic pressure is also given, using the Flory–Stavermann expression for the combinatorial contribution. The properties of five polymer–solvent systems are interpreted according to the new theory. For three systems, with only two adjustable parameters, the new model represents both activity and enthalpies of mixing data. For all the systems, with the same binary parameters, it is also possible to describe volumetric properties at low pressures.

Introduction

Renuncio and Prausnitz[1] first suggested that a limitation of Flory's equation of state when extended to mixtures can be ascribed, in part, to the random-mixing assumption, and they proposed a phenomenological equation that takes into account nonrandomness.

Using a partition function similar to that of Renuncio and Prausnitz,[1] Brandani[2,3] pointed out that the general form of Flory's equation of state is significantly modified by the introduction of the correction term $-A/\tilde{T}^2\tilde{v}^2$. Obviously, this modification affects the residual thermodynamic functions, which are calculated from an equation of state.

Successively, Rubio and Renuncio[4] and Canovas et al.[5] proposed empirical modifications for the combinatorial entropy and for the parameters of the model, which do not significantly change the conclusions attained by Brandani.[3]

The aim of this work is to show that when the expression for the partition function is correctly formulated, the derived equation of state for binary mixtures has the same general form as Flory's equation of state for pure components.

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.

Using the two-fluid theory,[6-9] and the concept of local compositions, first proposed by Wilson[10] and extended by Maurer and Prausnitz[9] to mixtures of molecules of arbitrary size and shape, we define

$$\langle \omega^{(1)} \rangle = \frac{1}{2}s_1(\Theta_{11}\eta_{11} + \Theta_{21}\eta_{21}) \tag{1}$$

$$\langle \omega^{(2)} \rangle = \frac{1}{2}s_2(\Theta_{22}\eta_{22} + \Theta_{12}\eta_{12}) \tag{2}$$

where, following Flory,[11] the potential energy per contact of sites i and j is

$$\eta_{ij} = -\eta_{ij}{}^0/(v^*\tilde{v}) \tag{3}$$

$\langle \omega^{(i)} \rangle$ is the average intermolecular energy of the hypothetical cell of type i. Here $\langle \omega^{(i)} \rangle$ is the energy released by the condensation process of a vaporized segment of a molecule of type i into a hypothetical fluid, where it is surrounded by $s_i\Theta_{ii}$ neighbors of species i and $s_i\Theta_{ji}$ neighbors of species j. Θ_{ii} and Θ_{ji} are the average local area fractions defined by

$$\Theta_{ii} = 1 - \Theta_{ji} = \frac{\Theta_i}{\Theta_i + \Theta_j\tau_{ji}} \quad (i, j = 1, 2) \tag{4}$$

Equation 4 gives the relation between the average local area fractions and the overall area fraction Θ_i and parameters τ_{ji}. The overall area fractions are defined by

$$\Theta_i = \frac{s_ir_ix_i}{\sum s_kr_kx_k} = \frac{s_i\Phi_i}{\sum s_k\Phi_k} \quad (i = 1, 2) \tag{5}$$

and

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

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

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

Following Brandani and Prausnitz,[12-14] we assume that the partition function for binary mixtures takes the form

$$Z = \text{constant} \times Z_{\text{comb}}(\tilde{v}^{1/3} - 1)^{3(r_1N_1c_1 + r_2N_2c_2)} \times \exp\left\{-\frac{N_1r_1\langle\langle \omega^{(1)} \rangle\rangle}{kT}\right\} \exp\left\{-\frac{N_2r_2\langle\langle \omega^{(2)} \rangle\rangle}{kT}\right\} \tag{8}$$

where Z_{comb} is the combinatorial factor;[15] $3c_i$ is the number of external degrees of freedom per segment of type i; $\langle\langle \omega^{(i)} \rangle\rangle$ is the average free energy in a cell of type i.

As shown by Brandani and Prausnitz,[12-14] the relationship between $\langle\langle \omega^{(i)} \rangle\rangle$ and $\langle \omega^{(i)} \rangle$ is given by

$$\langle\langle \omega^{(i)} \rangle\rangle = \frac{1}{\beta}\int_0^\beta \langle \omega^{(i)} \rangle \, \mathrm{d}\beta \tag{9}$$

where

$$\beta = 1/kT \tag{10}$$

0024-9297/91/2224-2391$02.50/0

Therefore, as shown in Appendix A, we have

$$\langle\langle \omega^{(i)} \rangle\rangle = -\frac{1}{2}s_i\frac{\eta_i{}^{0}}{v^*\tilde{v}} + kT\ln\frac{\Theta_{ii}}{\Theta_i} \tag{11}$$

and for the logarithm of the partition function

$$\ln Z = \text{constant} + \ln Z_{\text{comb}} + 3rcN\ln(\tilde{v}^{1/3} - 1) + \frac{1}{2}N_1r_1s_1\frac{\eta_{11}{}^{0}}{v^*\tilde{v}kT} + \frac{1}{2}N_2r_2s_2\frac{\eta_{22}{}^{0}}{v^*\tilde{v}kT} - N_1r_1\ln\frac{\Theta_{11}}{\Theta_1} - N_2r_2\ln\frac{\Theta_{22}}{\Theta_2} \tag{12}$$

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

$$P = \frac{RT}{Nrv^*}\left(\frac{\partial\ln Z}{\partial\tilde{v}}\right)_{T,N_1,N_2} \tag{13}$$

is then

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} \tag{14}$$

as shown in Appendix B.

Equation 14 has the same general form of Flory's equation of state for binary mixtures as well as for pure components.

The nonrandomness modifies only the expressions for the characteristic parameters and does not change the form of the equation of state for binary mixtures as in the case of previous publications.[1-5]

For the binary mixtures the characteristic parameters are given by

$$P^* = \Phi_1P_1^* + \Phi_2P_2^* + \Phi_1\Theta_{21}\nu_{21} + \Phi_2\Theta_{12}\nu_{12} \tag{15}$$

$$1/T^* = \left(\Phi_1\frac{P_1^*}{T_1^*} + \Phi_2\frac{P_2^*}{T_2^*}\right)/P^* \tag{16}$$

$$c = P^*v^*/RT^* \tag{17}$$

The characteristic pressures for pure components are

$$P_1^* = \frac{1}{2}s_1\frac{\eta_{11}{}^{0}}{v^{*2}} \qquad P_2^* = \frac{1}{2}s_2\frac{\eta_{22}{}^{0}}{v^{*2}} \tag{18}$$

The characteristic temperatures for pure components are

$$T_1^* = \frac{1}{2}s_1\frac{\eta_{11}{}^{0}}{Rc_1v^*} \qquad T_2^* = \frac{1}{2}s_2\frac{\eta_{22}{}^{0}}{Rc_2v^*} \tag{19}$$

Enthalpy of Mixing

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

$$\Delta H^{\text{M}} = Nrv^*\left(\Phi_1\frac{P_1^*}{\tilde{v}_1} + \Phi_2\frac{P_2^*}{\tilde{v}_2} - \frac{P^*}{\tilde{v}}\right) \tag{20}$$

or the alternative form

$$\Delta H^{\text{M}} = Nrv^*\left\{\Phi_1P_1^*\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \Phi_2P_2^*\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) - \frac{1}{\tilde{v}}(\Phi_1\Theta_{21}\nu_{21} + \Phi_2\Theta_{12}\nu_{12})\right\} \tag{21}$$

where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of pure components 1 and 2, respectively. Equations 20 and 21 are analogous to those reported by Brandani.[3]

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

$$B = \lim_{\Phi_2\to 0}\left(\frac{\Delta H^{\text{M}}}{N_1\Phi_2}\right) = \frac{V_1^*}{V_2^*}\lim_{\Phi_2\to 0}\left(\frac{\Delta H^{\text{M}}}{N_2}\right) \tag{22}$$

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

$$B = \frac{V_1^*}{V_2^*}\bar{H}_2^{\text{R}}(\infty) \tag{23}$$

where $\bar{H}_2^{\text{R}}(\infty)$ is the partial molar residual enthalpy of component 2 at infinite dilution. From series expansion of eq 20 in the power of Φ_2 and applying eq 22, we obtain

$$B = \frac{V_1^*}{\tilde{v}_1}\left\{P_2^*\left[\frac{\tilde{v}_1}{\tilde{v}_2} - 1 - \alpha_1T\left(1 - \frac{\tilde{T}_2}{\tilde{T}_1}\right)\right] - (1 - \alpha_1T)\left[\nu_{12} + \frac{s_2}{s_1}\nu_{21}\tau_{21}\right]\right\} \tag{24}$$

where

$$\alpha_1T = 3(\tilde{v}_1{}^{1/3} - 1)/(4 - 3\tilde{v}^{1/3}) \tag{25}$$

Residual Free Energy and Entropy

We make the assumption discussed by Hildebrand and Scott[16] that at low pressures $\Delta A^{\text{M}} = \Delta G^{\text{M}}$. Therefore, the residual free energy

$$G^{\text{R}} = \Delta G^{\text{M}} - \Delta G^{\text{M}}_{\text{comb}} \tag{26}$$

can be obtained from eq 12. It is

$$G^{\text{R}}\,Nrv^*\left\{3\Phi_1P_1^*\tilde{T}_1\ln\frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + 3\Phi_2P_2^*\tilde{T}_2\ln\frac{\tilde{v}_2{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \Phi_1P_1^*\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \Phi_2P_2^*\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}}\right) + \Phi_1P_1^*\frac{\tilde{T}_1}{c_1}\ln\frac{\Theta_{11}}{\Theta_1} + \Phi_2P_2^*\frac{\tilde{T}_2}{c_2}\ln\frac{\Theta_{22}}{\Theta_2}\right\} \tag{27}$$

$\tilde{T}_1$ and $\tilde{T}_2$ are related to the reduced volumes of pure components by Flory's equation of state, which at low pressures gives

$$\tilde{T}_1 = \frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}_1{}^{4/3}} \qquad \tilde{T}_2 = \frac{\tilde{v}_2{}^{1/3} - 1}{\tilde{v}_2{}^{4/3}} \tag{28}$$

From eq 27 and 21, we have for the residual entropy

$$S^{\text{R}} = -Nrv^*\left\{3\Phi_1\frac{P_1^*}{T_1^*}\ln\frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + 3\Phi_2\frac{P_2^*}{T_2^*}\ln\frac{\tilde{v}_2{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\Phi_1\frac{P_1^*}{T_1^*} + \Phi_2\frac{P_2^*}{T_2^*}\right)\left(\Phi_1\Theta_{21}\frac{\nu_{21}}{P^*} + \Phi_2\Theta_{12}\frac{\nu_{12}}{P^*}\right)\frac{1}{\tilde{T}\tilde{v}} + \Phi_1\frac{P_1^*}{T_1^*}\frac{1}{c_1}\ln\frac{\Theta_{11}}{\Theta_1} + \Phi_2\frac{P_2^*}{T_2^*}\frac{1}{c_2}\ln\frac{\Theta_{22}}{\Theta_2}\right\} \tag{29}$$

Equations 27 and 29 are different from those obtained by Brandani,[3] because of the different form of the partition function.

Residual Chemical Potential and Related Partial Molar Quantities

As shown by Brandani,[3] the residual chemical potential of component 1 is given by

$$(\mu_1 - \mu_1{}^0)^{\mathrm{R}} = \left(\frac{\partial G^{\mathrm{R}}}{\partial N_1}\right)_{T,\tilde{v},N_2} \tag{30}$$

Applying eq 30 to eq 27, we obtain

$$\begin{aligned}(\mu_1 - \mu_1{}^0)^{\mathrm{R}} = P_1^* V_1^* \biggl\{ & 3\tilde{T}_1 \ln \frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) + \\ & \frac{\tilde{T}_1}{c_1} \ln \frac{\Theta_{11}}{\Theta_1} + \frac{\tilde{T}_1}{c_1}(\Theta_{21} - \Theta_2) - \frac{\Phi_2}{\Phi_1} \frac{P_2^*}{P_1^*} \frac{\tilde{T}_2}{c_2}(\Theta_{12} - \Theta_1) \biggr\}\end{aligned} \tag{31}$$

The partial residual enthalpy of component 1 is

$$\begin{aligned}\bar{H}_1^{\mathrm{R}} = \left(\frac{\partial \Delta H^{\mathrm{M}}}{\partial N_1}\right)_{T,P,N_2} = P_1^* V_1^* \biggl\{ & \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}}\right) - \biggl(\Theta_{21}{}^2 \frac{\nu_{21}}{P_1^*} + \\ & \Phi_2 \Theta_{22} \frac{\Theta_{12}}{\Phi_1} \frac{\nu_{12}}{P_1^*} \biggr) \frac{1}{\tilde{v}} - \biggl[\left(\Phi_1 \Theta_{11} \Theta_{21} \frac{v^* \nu_{21}{}^2}{RTP_1^*} + \Phi_2 \Theta_{22} \Theta_{12} \frac{v^* \nu_{12}{}^2}{RTP_1^*} \right) \frac{1}{\tilde{v}} + \\ & \Phi_1 + \Phi_2 \frac{P_2^*}{P_1^*} + \Phi_1 \Theta_{21} \frac{\nu_{21}}{P_1^*} + \Phi_2 \Theta_{12} \frac{\nu_{12}}{P_1^*} \biggr] \frac{\alpha T}{\tilde{v}} \biggl[\Phi_2 \left(\frac{P_1^* - P_2^*}{P^*} \right) + \\ & \Phi_2 \left(\Theta_{21} \frac{\nu_{21}}{P^*} - \Theta_{12} \frac{\nu_{12}}{P^*} \right) - \Theta_{11} \Theta_{21} \frac{\nu_{21}}{P^*} + \Phi_2 \Theta_{22} \frac{\Theta_{12}}{\Phi_1} \frac{\nu_{12}}{P^*} - \\ & \frac{T^*}{P^*} \Phi_2 \left(\frac{P_1^*}{T_1^*} - \frac{P_2^*}{T_2^*} \right) \biggr] \biggl[1 - \alpha T \tilde{v} \biggl(\Phi_1 \Theta_{11} \Theta_{21} \frac{v^* \nu_{21}{}^2}{RTP^*} + \\ & \Phi_2 \Theta_{22} \Theta_{12} \frac{v^* \nu_{12}{}^2}{RTP^*} \biggr) \biggr]^{-1} \biggr\}\end{aligned} \tag{32}$$

The partial residual entropy of component 1 is

$$\begin{aligned}\bar{S}_1^{\mathrm{R}} = -\frac{P_1^* V_1^*}{T} \biggl\{ & \left(\Theta_{21}{}^2 \frac{\nu_{21}}{P_1^*} + \Phi_2 \Theta_{22} \frac{\Theta_{12}}{\Phi_1} \frac{\nu_{12}}{P_1^*} \right) \frac{1}{\tilde{v}} + \\ & \biggl[\left(\Phi_1 \Theta_{11} \Theta_{21} \frac{v^* \nu_{21}{}^2}{RTP_1^*} + \Phi_2 \Theta_{22} \Theta_{12} \frac{v^* \nu_{12}{}^2}{RTP_1^*} \right) \frac{1}{\tilde{v}} + \Phi_1 + \Phi_2 \frac{P_2^*}{P_1^*} + \\ & \Phi_1 \Theta_{21} \frac{\nu_{21}}{P_1^*} + \Phi_2 \Theta_{12} \frac{\nu_{12}}{P_1^*} \biggr] \left(-\frac{\alpha T}{\tilde{v}} \right) \biggl[\Phi_2 \left(\frac{P_1^* - P_2^*}{P^*} \right) + \\ & \Phi_2 \left(\Theta_{21} \frac{\nu_{21}}{P^*} - \Theta_{12} \frac{\nu_{12}}{P^*} \right) - \Theta_{11} \Theta_{21} \frac{\nu_{21}}{P^*} + \Phi_2 \Theta_{22} \frac{\Theta_{12}}{\Phi_1} \frac{\nu_{12}}{P^*} - \\ & \frac{T^*}{P^*} \Phi_2 \left(\frac{P_1^*}{T_1^*} - \frac{P_2^*}{T_2^*} \right) \biggr] \biggl[1 - \alpha T \tilde{v} \biggl(\Phi_1 \Theta_{11} \Theta_{21} \frac{v^* \nu_{21}{}^2}{RTP^*} + \\ & \Phi_2 \Theta_{22} \Theta_{12} \frac{v^* \nu_{12}{}^2}{RTP^*} \biggr) \biggr]^{-1} + 3\tilde{T}_1 \ln \frac{\tilde{v}_1{}^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \\ & \frac{\tilde{T}_1}{c_1} \ln \frac{\Theta_{11}}{\Theta_1} + \frac{\tilde{T}_1}{c_1}(\Theta_{21} - \Theta_2) - \frac{\Phi_2}{\Phi_1} \frac{P_2^*}{P_1^*} \frac{\tilde{T}_2}{c_2}(\Theta_{12} - \Theta_1) \biggr\}\end{aligned} \tag{33}$$

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

$$\alpha T = \frac{3(\tilde{v}^{1/3} - 1)}{4 - 3\tilde{v}^{1/3}} \tag{34}$$

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

system	T^*, K	V^*, cm^3/g	P^*, atm	ref
PIB	7580	0.949	4420	18
polystyrene	7420	0.810	5410	19
natural rubber	6780	0.934	5140	24
benzene	4710	0.886	6200	21
cyclohexane	4720	1.001	5230	21
n-pentane	4160	1.183	4010	21
acetone	4320	0.956	6190	21

Osmotic Pressure

For the osmotic pressure[17]

$$\pi v_1 = -(\mu_1 - \mu_1{}^0) \tag{35}$$

where v_1 is the molar volume of the solvent and

$$(\mu_1 - \mu_1{}^0) = (\mu_1 - \mu_1{}^0)_{\mathrm{comb}} + (\mu_1 - \mu_1{}^0)^{\mathrm{R}} \tag{36}$$

To express the combinatorial contribution to the chemical potential of the solvent, we use the equation of Guggenheim[15]

$$\begin{aligned}(\mu_1 - \mu_1{}^0)_{\mathrm{comb}} = RT \biggl\{ & \ln \Phi_1 + \Phi_2 \left(1 - \frac{r_1}{r_2} \right) + \frac{1}{2} r_1 s_1 \biggl(\ln \frac{\Theta_1}{\Phi_1} + \\ & \frac{\Phi_1}{\Theta_1} - 1 \biggr) \biggr\}\end{aligned} \tag{37}$$

Expanding eq 36 in series with the retention only of terms in lower powers of Φ_2, we obtain the limiting law

$$\begin{aligned}\frac{\pi}{C} = \frac{RT}{M} + \frac{1}{2} \biggl[& RT \bigl\{ 1 - \tfrac{1}{2} r_1 s_1 (1 - s_2/s_1)^2 \bigr\} - P_1^* V_1^* \biggl\{ \frac{\alpha_1 T}{\tilde{v}_1} \biggl(\frac{P_2^*}{P_1^*}(1 - \\ & T_1^*/T_2^*) + \frac{\nu_{12}}{P_1^*} + \frac{s_2}{s_1} \tau_{21}^* \frac{\nu_{21}}{P_1^*} \biggr)^2 + \frac{\tilde{T}_1}{c_1} \left(\frac{s_2}{s_1} \right)^2 (1 - \tau_{21}^*{}^2) - \\ & 2 \frac{P_2^*}{P_1^*} \frac{\tilde{T}_2}{c_2} \frac{s_2}{s_1} \left(1 - \frac{1}{\tau_{12}^*} \right) \biggr\} \frac{\bar{v}_2{}^2}{v_1} C\end{aligned} \tag{38}$$

where C is the concentration in grams per cubic centimeter, $\bar{v}_2$ is the specific volume of the polymer, and

$$\tau_{12}^* = \exp\{v^* \nu_{12}/\tilde{v}_1 RT\} \qquad \tau_{21}^* = \exp\{v^* \nu_{21}/\tilde{v}_1 RT\} \tag{39}$$

Following Flory,[17] we have assumed

$$\frac{\Phi_2 r_1}{r_2 v_1} = \frac{C \bar{v}_2 r_1}{r_2 v_1} = \frac{C}{M} \tag{40}$$

Data Reduction for Binary Systems

We have examined five binary systems, of which three (polystyrene–acetone, natural rubber–benzene, and polyisobutylene–benzene) 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,[11] pure-component parameters are obtained from volumetric data. These characteristic parameters are reported in Table I. For fixing the s values we use Bondi's work.[22] (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; for polystyrene s = 6.98; and for natural rubber s = 8.30).

Figure 1 shows calculated and experimentally reduced residual chemical potential, χ, for the five polymer–solvent systems. The parameters ν_{12} and ν_{21} obtained from the fitting are reported in Table II, together with their standard deviations. Taking into account standard deviations, only for the acetone–polystyrene and the benzene–natural

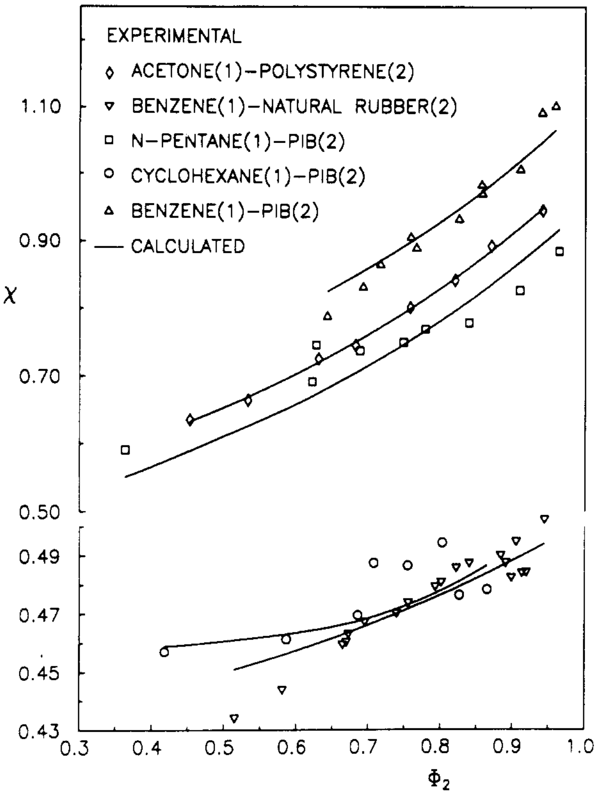

Figure 1. Flory χ parameter as a function of composition for five systems at 25 °C.

Table II
Parameters of the Model and Their Standard Deviations Obtained by Fitting Activity of Solvents

system	ν_{12}, atm	ν_{21}, atm	ref
acetone–polystyrene	-158 ∓ 3	-168 ∓ 5	23
benzene–natural rubber	-76 ∓ 19	-38 ∓ 16	24
benzene–PIB	-3 ∓ 22	-278 ∓ 28	18
cyclohexane–PIB	-228 ∓ 13	130 ∓ 7	25
n-pentane–PIB	50 ∓ 13	-175 ∓ 20	26

Table III
Experimental and Calculated Integral Heat of Mixing at Infinite Dilution

system	*B*, cal/mol exptl	this work	Rubio & Renuncio	ref
acetone–polystyrene	195	289		23
benzene–natural rubber	182	141	155	20
benzene–PIB	344	222	302	18
cyclohexane–PIB	-10	-10	79	28
n-pentane–PIB	-77	-67	-72	25

rubber systems are the two parameters both negative, and therefore there is a tendency for the two components to segregate.

Table III shows a comparison between the experimental values of *B* and those calculated by our model using the parameters reported in Table II and by Rubio and Renuncio.[4] Our model gives the correct sign of *B* for all the systems, but for the acetone–polystyrene and the benzene–PIB systems calculated values differ from experimental values by more than 100 cal/mol.

Table IV shows the comparison of experimental specific volumes with those calculated by using the model with the parameters of Table II. The parameters obtained by fitting the activity of solvents accurately describe the behavior of the solution volumes, as can be seen from data shown in Table IV.

Table IV
Specific Volumes of Five Binary Solutions at 25 °C

system	Φ_2	specific volumes, cm^3/g exptl	calcd	ref
acetone–polystyrene	0.0860	1.2345	1.2353	23
	0.1748	1.1970	1.1970	
	0.2663	1.1595	1.1568	
	0.3609	1.1220	1.1147	
	0.4586	1.0845	1.0704	
benzene–natural rubber	0.2160	1.1344	1.1350	24
	0.2610	1.1322	1.1330	
	0.3060	1.1302	1.1309	
	0.3510	1.1280	1.1288	
	0.4100	1.1251	1.1259	
	0.5820	1.1167	1.1173	
	0.7610	1.1074	1.1080	
benzene–PIB	0.4550	1.1238	1.1281	18
	0.5470	1.1188	1.1237	
	0.6510	1.1132	1.1182	
cyclohexane–PIB	0.3350	1.2229	1.2232	25
	0.5550	1.1786	1.1787	
	0.6400	1.1614	1.1617	
n-pentane–PIB	0.5000	1.3353	1.3301	26

Table V
Parameters of the Model and Their Standard Deviations Obtained by Fitting Osmotic Pressure at 25 °C

system	ν_{12}, atm	ν_{21}, atm	ref
benzene–natural rubber	-105 ∓ 22	4 ∓ 21	24
benzene–PIB	88 ∓ 22	-421 ∓ 28	27
cyclohexane–PIB	-29 ∓ 13	-14 ∓ 7	27

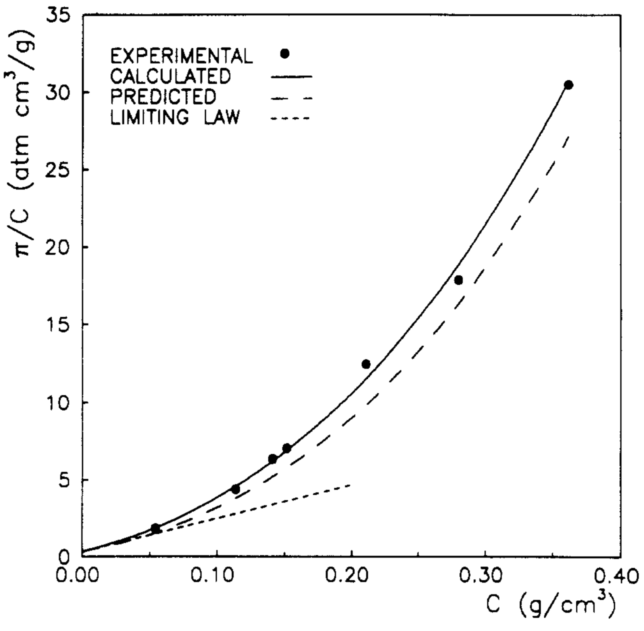

Figure 2. π/C plotted against C for natural rubber in benzene at 25 °C.

Table V shows the parameters ν_{12} and ν_{21} of three binary solutions obtained by fitting the experimental values of osmotic pressure. Except for the benzene–natural rubber system, the values of ν_{12} and ν_{21} for the other two systems are very different from those of Table II obtained by fitting the activity of the solvent. It is possible to conclude that the two series of experimental data (solvent activity and osmotic pressure) are not internally consistent.

Figures 2–4 show π/C plotted against the concentration for the three binary systems. Experimental values are compared with those calculated by using the parameters of Table V and those predicted by using the parameters of Table II. The limiting law, expressed by eq 38, is also represented. For the benzene–PIB system the predicted values are not reported, since they are negative. As

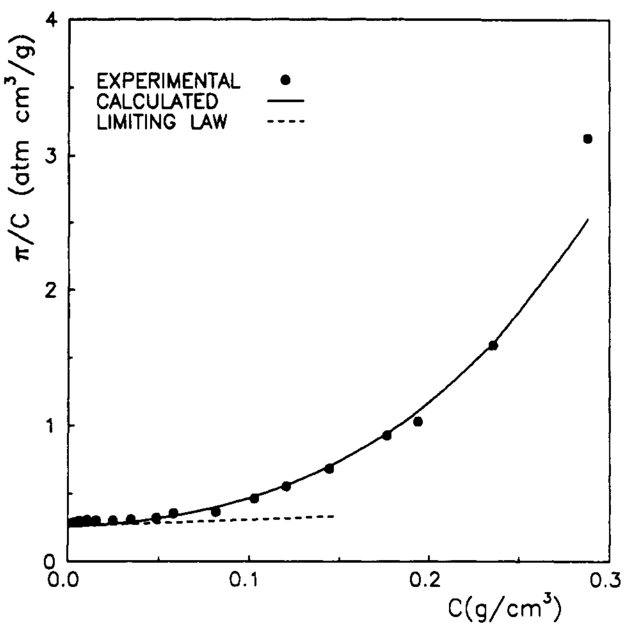

Figure 3. π/C plotted against C for PIB in benzene at 25 °C.

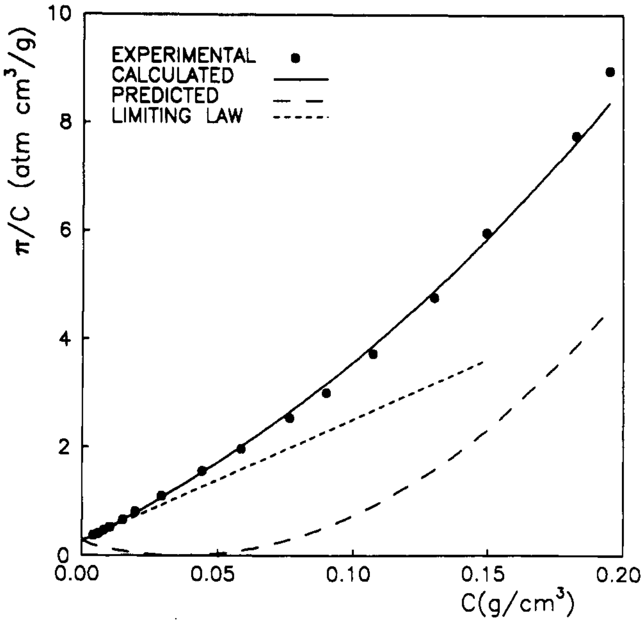

Figure 4. π/C plotted against C for PIB in cyclohexane at 25 °C.

expected, only for the benzene–natural rubber system are predicted values quite satisfactory.

Conclusions

In this work, we have presented a new expression for the partition function of binary solutions containing a polymer. This leads to an equation of state for polymer solutions of Flory's type. This equation does not require an additional corrective term as in the previous publications.[2-4]

The new model, like all local-composition models, presents two energy adjustable parameters, which are only weakly dependent on temperature.

With fixed parameters, it is not possible to predict accurately all the thermodynamic properties of polymer solutions. For example, we can predict accurately specific volumes of solutions using the parameters obtained by fitting solvent activities. However, whereas for B values the correct sign is predicted, for the acetone–polystyrene and the benzene–PIB systems predicted values are far apart from experiments.

Moreover, we should point out that the experimental values of solvent activities are not consistent with measurements of osmotic pressure for all the examined systems. Therefore, it is difficult to ascertain where the deficiencies of the model begin and how much is due to the inconsistencies of the experimental data of a different kind.

Nevertheless, the new model correctly introduces the two-fluid theory associated with the local-composition concept into the thermodynamics of polymer solutions.

Acknowledgment. We are indebted to the Italian Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica for financial support.

Appendix A

From eq 1–7, we have

$$\langle \omega^{(1)} \rangle = -\frac{1}{2} s_1 \frac{\eta_{11}^{\ 0}}{v^* \tilde{v}} - \frac{\nu_{21} v^*}{\tilde{v}} \Theta_{21} \tag{A-1}$$

Substituting eq A-1 into eq 9, we have

$$\langle\langle \omega^{(1)} \rangle\rangle = -\frac{1}{2} s_1 \frac{\eta_{11}^{\ 0}}{v^* \tilde{v}} - \frac{1}{\beta} \int_0^{\beta} \Theta_{21} \frac{\nu_{21} v^*}{\tilde{v}} \, \mathrm{d}\beta \tag{A-2}$$

Differentiating eq 6, we obtain

$$\frac{\nu_{21} v^*}{\tilde{v}} \, \mathrm{d}\beta = \frac{\mathrm{d}\tau_{21}}{\tau_{21}} \tag{A-3}$$

Multiplying both the left-hand side and the right-hand side of eq A-3 by Θ_{21}, we have

$$\Theta_{21} \frac{\nu_{21} v^*}{\tilde{v}} \, \mathrm{d}\beta = \Theta_{21} \frac{\mathrm{d}\tau_{21}}{\tau_{21}} \tag{A-4}$$

The introduction of eq 4 into the right-hand side of eq A-4 gives

$$\Theta_{21} \frac{\nu_{21} v^*}{\tilde{v}} \, \mathrm{d}\beta = \frac{\Theta_2}{\Theta_1 + \Theta_2 \tau_{21}} \, \mathrm{d}\tau_{21} \tag{A-5}$$

and therefore

$$\langle\langle \omega^{(1)} \rangle\rangle = -\frac{1}{2} s_1 \frac{\eta_{11}^{\ 0}}{v^* \tilde{v}} - \frac{1}{\beta} \int_1^{\tau_{21}} \frac{\Theta_2}{\Theta_1 + \Theta_2 \tau_{21}} \, \mathrm{d}\tau_{21} \tag{A-6}$$

Integration of eq A-6 gives

$$\langle\langle \omega^{(1)} \rangle\rangle = -\frac{1}{2} s_1 \frac{\eta_{11}^{\ 0}}{v^* \tilde{v}} - \frac{1}{\beta} \ln \left(\Theta_1 + \Theta_2 \tau_{21}\right) \tag{A-7}$$

But

$$\ln \left(\Theta_{11}/\Theta_1\right) = -\ln \left(\Theta_1 + \Theta_2 \tau_{21}\right) \tag{A-8}$$

and therefore

$$\langle\langle \omega^{(1)} \rangle\rangle = -\frac{1}{2} s_1 \frac{\eta_{11}^{\ 0}}{v^* \tilde{v}} + kT \ln \frac{\Theta_{11}}{\Theta_1} \tag{A-9}$$

and for the second hypothetical fluid, we have

$$\langle\langle \omega^{(2)} \rangle\rangle = -\frac{1}{2} s_2 \frac{\eta_{22}^{\ 0}}{v^* \tilde{v}} + kT \ln \frac{\Theta_{22}}{\Theta_2} \tag{A-10}$$

Equations A-9 and A-10 are the explicit forms of eq 11.

Appendix B

Differentiating eq 12, we have

$$\left(\frac{\partial \ln Z}{\partial \tilde{v}}\right)_{T,N_1,N_2} = rN\left\{c\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1}\frac{1}{\tilde{v}} - \frac{1}{2}\Phi_1 s_1\frac{\eta_{11}{}^0}{v^*kT}\left(-\frac{1}{\tilde{v}^2}\right) - \frac{1}{2}\Phi_2 s_2\frac{\eta_{22}{}^0}{v^*kT}\left(-\frac{1}{\tilde{v}^2}\right) - \Phi_1\Theta_{21}\frac{v^*\nu_{21}}{kT}\frac{1}{\tilde{v}^2} - \Phi_2\Theta_{12}\frac{v^*\nu_{12}}{kT}\frac{1}{\tilde{v}^2}\right\} \quad \text{(B-1)}$$

In fact

$$\left(\frac{\partial\Theta_{11}}{\partial\tilde{v}}\right)_{T,N_1,N_2} = \Theta_{11}\Theta_{21}\frac{v^*\nu_{21}}{kT}\frac{1}{\tilde{v}^2} \quad \text{(B-2)}$$

$$\left(\frac{\partial\Theta_{22}}{\partial\tilde{v}}\right)_{T,N_1,N_2} = \Theta_{22}\Theta_{12}\frac{v^*\nu_{12}}{kT}\frac{1}{\tilde{v}^2} \quad \text{(B-3)}$$

From eq 12 and eq B-1, we have

$$\frac{Pv^*}{RT}\tilde{v} = c\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \left\{\frac{1}{2}s_1\Phi_1\frac{\eta_{11}{}^0}{v^*} + \frac{1}{2}s_2\Phi_2\frac{\eta_{22}{}^0}{v^*} + \Phi_1\Theta_{21}v^*\nu_{21} + \Phi_2\Theta_{12\mathrm{v}}{}^*\nu_{12}\right\}\frac{1}{RT\tilde{v}} \quad \text{(B-4)}$$

Multiplying both the left-hand side and the right-hand side of eq B-4 by $1/c$ and taking into account eq 17, we have

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{P^*}\left\{\frac{1}{2}s_1\Phi_1\frac{\eta_{11}{}^0}{v^{*2}} + \frac{1}{2}s_2\Phi_2\frac{\eta_{22}{}^0}{v^{*2}} + \Phi_1\Theta_{21}\nu_{21} + \Phi_2\Theta_{12}\nu_{12}\right\}\frac{1}{\tilde{T}\tilde{v}} \quad \text{(B-5)}$$

Substituting eq 18 into eq B-5, we have

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{P^*}\{\Phi_1P_1^* + \Phi_2P_2^* + \Phi_1\Theta_{21}\nu_{21} + \Phi_2\Theta_{12}\nu_{12}\}\frac{1}{\tilde{T}\tilde{v}} \quad \text{(B-6)}$$

From eq B-6, taking into account eq 15, we obtain

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{T}\tilde{v}} \quad \text{(B-7)}$$

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