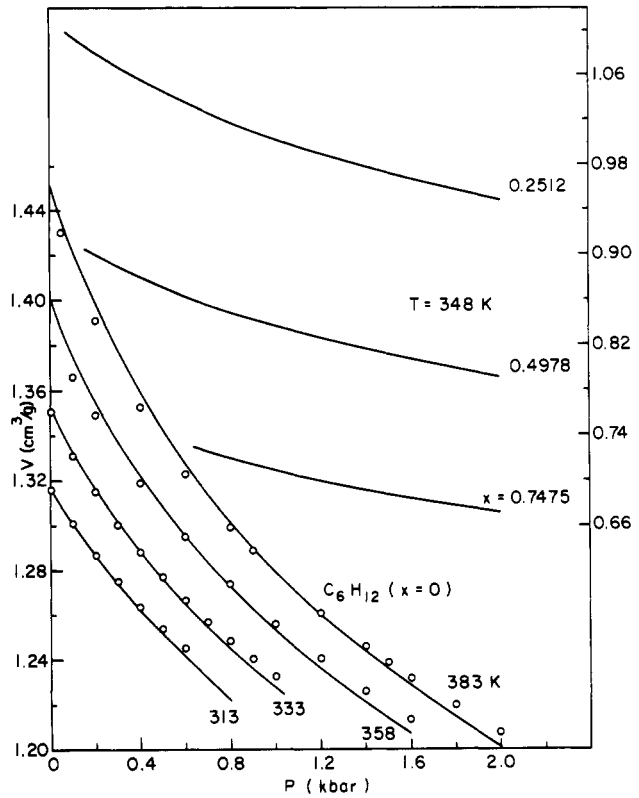

Figure 6. Theoretical and experimental isotherms of C_6H_{12} between 313 and 383 K and predictions for its mixtures with CCl_4 at 348 K. Circles from ref 13.

Conclusion

The theory is successful in accounting for the equation of state of the mixture based on information for the pure components and a minimum of data for the mixture. Specifically, predictions for elevated pressures can be derived from atmospheric isobars. However, refined numerical procedures are required for the simultaneous determination of all parameters, when atmospheric-pressure data for the liquid phase are not available. It remains to be seen what refinements must be introduced for more dissimilar pairs than those studied so far (see also earlier comments).

Acknowledgment. This work was supported by the National Science Foundation through Grants DMR 78-10889 and 80-12232, Polymers Program. R.K.J. is on leave from Rajdhani College, University of Delhi, New Delhi—110015, India.

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Nonrandomness Binary Parameters for Polymer Solutions

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ABSTRACT: Thermodynamic functions of polymer solutions are studied with the assumption of nonrandom mixing. This nonrandomness approximation is based on the intuitive concept of local composition. Temperature dependence of local composition is studied, with the result that its quantitative influence on thermodynamic excess functions is small. An approximate expression for the combinatorial entropy is introduced in the model. Since this expression is also based on the concept of local composition, it is phenomenological. Two binary parameters are adjusted for each of the polymer solutions studied. These parameters, obtained by means of the nonrandomness approximation, represent simultaneously activity and heat-of-mixing data.

An approximation for nonrandomness in polymer–solution thermodynamics was proposed a few years ago.[1] This approximation was not rigorous but intuitive and phenomenological. It introduced very few modifications in the partition function given by Flory's one-fluid theory[2] in order to retain the theory's simplicity. The results obtained showed the interest of such an assumption and suggested new approaches treating the problem of nonrandomness. We study in this paper the influence of local site fractions and their temperature dependence on the thermodynamic excess functions. We also examine the expression for the combinatorial entropy used in ref 1 and propose an alternative expression for this function.

Following the usual notation, each of the N molecules of the system is considered to be divided into r segments with $3c$ external degrees of freedom[3] per segment. The hard-core volume of a segment, or characteristic volume, is denoted by v^*. The reduced volume is given by $\tilde{v} = v/v^*$, where v is the volume of a segment, which may be calculated from the volume of a molecule V by $v = V/r$.

Flory[2] introduced the partition function Z as

$$Z = Z_{comb}(rv^*)^{rNc}(\tilde{v}^{1/3} - 1)^{3rNc} \exp\{-E_0/kT\} \quad (1)$$

where E_0 is the intermolecular energy and Z_{comb} is the combinatorial factor which takes into account the number

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0024-9297/80/2213-1508$01.00/0

of ways of interspersing the $\bar{r}N$ segments among one another, regardless of the nature of their neighbors in the case of a pure substance (randomness) and considering their nature in the case of a mixture (nonrandomness). Z_{comb} will be introduced later in this paper.

Binary Mixtures and Equation of State

According to Wilson's[4] concept of local composition, the fractions of sites in the vicinity of an external site j are θ_{ij} and θ_{jj}, belonging to neighbors of type i and j, respectively. Similarly, for a molecule i, there are θ_{ji} and θ_{ii} fractions of sites of type j and i, respectively. These fractions of sites are subject to conditions $\theta_{ij} + \theta_{jj} = \theta_{ji} + \theta_{ii} = 1$. Note that $\theta_{ij} \neq \theta_{ji}$.

For a mixture of two components, the energy E_0 may be written in terms of local site fractions as

$$-E_0 = (z/2v)[q_1N_1(\theta_{11}\eta_{11} + \theta_{21}\eta_{21}) + q_2N_2(\theta_{22}\eta_{22} + \theta_{12}\eta_{12})] \quad (2)$$

where z is the coordination number, q_1 and q_2 are the external-site parameters, zq_i is the number of external interaction sites of the molecule i, and η_{ii}/v is the interaction energy of contact i–i. The characteristic pressure of the mixture, p^*, is given by[1]

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* + \phi_1\theta_{21}\nu_{21} + \phi_2\theta_{12}\nu_{12} \quad (3)$$

where ϕ_i are the segment fractions, and ν_{21} and ν_{12} are two adjustable binary parameters of the mixture, related to the interaction energy differences $\eta_{21} - \eta_{11}$ and $\eta_{12} - \eta_{22}$. The local site fractions θ_{21} and θ_{12} can be written in terms of the binary parameters as

$$\theta_{ii} = 1 - \theta_{ji} = \theta_i/(\theta_i + \theta_j\tau_{ji}) \quad (4)$$

where

$$\theta_i = 1 - \theta_j = q_iN_i/(q_iN_i + q_jN_j)$$

$$\tau_{ji} = \exp\{-\nu_{ji}v^*/RT\tilde{v}\}$$

$$i, j = 1, 2 \ (i \neq j)$$

Terms $q_1N_1\theta_{21}\eta_{21}$ and $q_2N_2\theta_{12}\eta_{12}$ of eq 2 express the potential energy of i–j contacts. We must consider the energy of unlike contacts separated into two contributions, one corresponding to N_1 molecules and the other to N_2.

Recently, Brandani[5b] suggested that η_{ij}/v is the potential energy per contact i–j in a two-fluid theory. He has considered the specific volumes of both hypothetical fluids to be identical. It is obvious that both fluids have different compositions and therefore different specific volumes too. On the other hand, it is easy to show that local site fractions of both hypothetical fluids are different from those of the overall fluid (mixture).

Since the intermolecular energy given by Brandani[5b] is essentially identical with eq 2, we maintain that η_{21} and η_{12} have no physical meaning by themselves but that the two together allow us to calculate the potential energy of unlike contacts, E_{12}

$$-E_{12} = (z/2v)(q_1N_1\theta_{21}\eta_{21} + q_2N_2\theta_{12}\eta_{12}) \quad (5)$$

Equation 5 expresses the empirical meaning of η_{ij}. Taking into account this consideration, eq 15 in ref 5b is not meaningful because the η_{ij} contribution to the potential energy, E_{12}, can be higher or lower without the significance given in ref 5b.

The equation of state derived from eq 1 is

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{T}\tilde{v}} + \frac{A}{\tilde{T}^2\tilde{v}^2} \quad (6)$$

$$A = \frac{p^*v^*}{RT^*}\left[\phi_1\theta_{11}\theta_{21}\left(\frac{\nu_{21}}{p^*}\right)^2 + \phi_2\theta_{22}\theta_{12}\left(\frac{\nu_{12}}{p^*}\right)^2\right]$$

For calculations at low pressure (1 atm), the left-hand term of eq 6 vanishes. The last term on the right modifies Flory's equation of state. However, values of $\tilde{v}$ obtained from eq 6 for the polymer systems which we have studied differ not more than 0.5% from those calculated with Flory's equation of state. If τ_{ij} is defined with the opposite sign in its exponent, as Brandani[5b] did, the derived equation of state is also eq 6 but with the opposite sign for A.

The Residual Thermodynamic Functions

The residual free energy defined as $G^R = \Delta G^M - \Delta G_{comb}$ is derived from eq 1, giving

$$G^R = 3\bar{r}Nv^*\left[\phi_1 p_1^*\tilde{T}_1 \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \phi_2 p_2^*\tilde{T}_2 \ln\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right] + \bar{r}Nv^*\left[\frac{\phi_1 p_1^*}{\tilde{v}_1} + \frac{\phi_2 p_2^*}{\tilde{v}_2} - \frac{p^*}{\tilde{v}}\right] \quad (7)$$

where $\bar{r}N = r_1N_1 + r_2N_2$ is the total number of segments in the mixture.

The residual entropy, S^R, is obtained by differentiating eq 7 with respect to the temperature at constant pressure

$$S^R = -3\bar{r}Nv^*\left[\frac{\phi_1 p_1^*}{T_1^*} \ln\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{\phi_2 p_2^*}{T_2^*} \ln\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right] + \frac{\bar{r}Nv^*p^*}{T}\frac{A}{\tilde{T}\tilde{v}^2} \quad (8)$$

The last term on the right side of this equation is a consequence of the temperature dependence of local site fractions. As with the $A/(\tilde{v}^2\tilde{T}^2)$ term of eq 6, this term is a correction for residual entropy and is of little numerical significance, less than 0.3% for the polymer systems studied in this paper. For activity coefficient data reduction it is necessary to derive the expression of the residual chemical potential of solvent

$$(\mu_1 - \mu_1^\circ)^R = (\partial G^R/\partial N_1)_{T,p,N_2} = p_1^*V_1^* \times [3\tilde{T}_1 \ln\{(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)\} + (\tilde{v}_1^{-1} - \tilde{v}^{-1})] - (V_1^*/\tilde{v})[\theta_{21}^2\nu_{21} + (\phi_2/\phi_1)\theta_{22}\theta_{12}\nu_{12}] \quad (9)$$

It is important to note that temperature dependence of local site fractions does not affect the residual chemical potential and the residual free energy. Equation 9 is the same as that in ref 1.

Taking into account the temperature dependence of local site fractions, the enthalpy of mixing may be obtained from eq 1

$$\Delta H^M = \bar{r}Nv^*\left[\frac{\phi_1 p_1^*}{\tilde{v}_1} + \frac{\phi_2 p_2^*}{\tilde{v}_2} - \frac{p^*}{\tilde{v}} + \frac{Ap^*}{\tilde{T}\tilde{v}^2}\right] \quad (10)$$

The difference between energy and enthalpy has been ignored in eq 10. The last term on the right side is equivalent to the corrective term of eq 8. It is obvious that eq 10, 8, and 7 satisfy the relation $G^R = \Delta H^M - TS^R$.

Equation 10 represents an inconsistency with the interaction energy defined by eq 2. To be consistent with eq 2 we will not make use of eq 10, which is equivalent to ignoring the temperature dependence of local site fractions. On the other hand, it would not be correct to consider local

site fraction dependence on temperature when all the interaction energies have been taken as not dependent on temperature (isothermal process). Therefore we will adopt the usual heat-of-mixing expression

$$\Delta H^{M} = \bar{r}Nv^{*}\left[\frac{\phi_1 p_1^{*}}{\tilde{v}_1} + \frac{\phi_2 p_2^{*}}{\tilde{v}_2} - \frac{p^{*}}{\tilde{v}}\right] \tag{11}$$

According to this, eq 8 must be rewritten as

$$S^{R} = -3\bar{r}Nv^{*}\left[\frac{\phi_1 p_1^{*}}{T_1^{*}} \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \frac{\phi_2 p_2^{*}}{T_2^{*}} \ln \frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right] \tag{12}$$

The integral heat of mixing, B, is defined by Eichinger and Flory[7] as $\Delta H^{M} = BN_1\phi_2$. At low polymer concentrations, B is a constant independent of concentration. Its value at infinite dilution is

$$B = \lim_{\phi_2 \to 0}\left[\frac{\Delta H^{M}}{N_1\phi_2}\right] = \frac{V_1^{*}}{V_2^{*}} \lim_{N_2 \to 0}\left[\frac{\Delta H^{M}}{N_2}\right] \tag{13}$$

This limit can be calculated by series expansion[1,7] of ΔH^{M} in powers of ϕ_2. This method gives the result of eq B-2 in ref 1. Brandani[5a] applied L'Hôpital's theorem to the second limit of eq 13 and obtained a different result because he substituted into eq 13 the approximate expression for residual partial molar enthalpy given by eq B-3 in ref 1. Using L'Hôpital's theorem and taking into account that

$$\lim_{N_2 \to 0} \tau_{21} = \tau_{21}^{\circ} = \exp\{-\nu_{21}v^{*}/RT\tilde{v}_1\} \tag{14}$$

$$\lim_{N_2 \to 0}\left[\frac{\partial \tilde{v}}{\partial N_2}\right]_{T,p,N_1} = \frac{r_2}{r_1 N_1} \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_1^{1/3} - 4/3} \frac{\tilde{v}_1}{p_1^{*}}\left[p_2^{*}\left(1 - \frac{T_1^{*}}{T_2^{*}}\right) + \nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\left(1 - \frac{v^{*}\nu_{21}}{RT\tilde{v}_1}\right)\tau_{21}^{\circ}\right] \tag{15}$$

we obtain for B

$$B = \frac{V_1^{*}}{\tilde{v}_1}\left[p_2^{*}\left(\frac{\tilde{v}_1}{\tilde{v}_2} - 1 - \alpha_1 T\left(1 - \frac{T_1^{*}}{T_2^{*}}\right)\right) - (1 + \alpha_1 T)\nu_{12} - \nu_{21}\frac{q_2/r_2}{q_1/r_1}\left(1 + \alpha_1 T\left(1 - \frac{v^{*}\nu_{21}}{RT\tilde{v}_1}\right)\right)\tau_{21}^{\circ}\right] \tag{16}$$

where α_1 is the thermal expansion coefficient of component 1. Since for pure substances eq 6 becomes Flory's equation of state, α_1 is given by[2]

$$\alpha_1 T = (1 - \tilde{v}_1^{1/3})/(\tilde{v}_1^{1/3} - 4/3) \tag{17}$$

equation 16 differs from eq B-2 in ref 1 only in the last term because the factor $1 - v^{*}\nu_{21}/RT\tilde{v}_1$ is lost during the series expansion of powers of ϕ_2. This modifies the values of B less than 0.3% for the polymer systems studied in this paper. It could be neglected since experimental values of B usually have an accuracy of only a few percent.

Combinatorial Partition Function

Nonrandomness is a restrictive assumption for the combinatorial partition function. In order to estimate the number of possible configurations (microstates), Ω, we make use of the quasi-chemical hypothesis of Abrams and Prausnitz,[6] which takes into account local site fractions. Ω may be written as

$$\Omega = \prod_{\substack{i=1,2 \\ j \neq i}} \frac{(q_iN_i\theta_{ii} + q_jN_j\theta_{ij})!}{(q_iN_i\theta_{ii})!(q_jN_j\theta_{ji})!} \frac{(q_iN_i\theta_i)!(q_iN_i\theta_j)!}{(\theta_i(q_1N_1 + q_2N_2))!}\omega^{0} \tag{18}$$

where ω^{0} is the random limit which can be identified with Flory's value. The combinatorial entropy of mixing is

$$\Delta S_{comb} = \Delta S^{\circ}_{comb} + k \sum_{\substack{i=1,2 \\ j \neq i}} q_iN_i \times \left[\ln \theta_i + \theta_{ii} \ln\left(1 + \frac{\theta_j\theta_{ji}}{\theta_i\theta_{ii}}\right) + \theta_{ji} \ln\left(1 + \frac{\theta_j\theta_{jj}}{\theta_i\theta_{ji}}\right)\right] \tag{19}$$

where

$$\Delta S^{\circ}_{comb} = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \tag{20}$$

The combinatorial partial molar entropy is

$$\frac{S_{1,comb}}{R} = \frac{S^{\circ}_{1,comb}}{R} + q_1\left[\ln \theta_1 + \sum_{i=1,2}\left(\theta_{ii} \ln\left(1 + \frac{\theta_2\theta_{i2}}{\theta_1\theta_{i1}}\right) + \frac{\theta_i\theta_{1i}\theta_{2i}}{\theta_1} \ln \frac{\theta_{2i}(\theta_1\theta_{11} + \theta_2\theta_{12})}{\theta_{1i}(\theta_1\theta_{21} + \theta_2\theta_{22})}\right)\right] \tag{21}$$

where

$$S^{\circ}_{1,comb} = -R[\ln (1 - \phi_2) - (1 - r_1/r_2)\phi_2] \tag{22}$$

Data Reduction for Binary Systems

As has been discussed previously,[1] it is not possible to obtain a unique set of binary parameters to fit a finite set of experimental data. We can only determine a bounded two-dimensional surface of ν_{21} and ν_{12} whose points correspond to sets of parameters which reproduce data within experimental error. We use activity data to bound this surface, which is typically an ellipse with one long axis and one short axis. To locate the best set of parameters, we use the experimental heat of mixing at infinite dilution.

We arbitrarily choose $r_1 = 1$ for the smaller molecule. Since we are taking the hard-core volume per segment, v^{*}, to be the same for both components, r_2 is given by

$$r_2 = r_1(V_2^{*}/V_1^{*}) \tag{23}$$

To find values of q_i we use Bondi's[8] values for q and r for fixing the q/r ratio. Table I gives the ratio q/r and the characteristic parameters of the pure components considered in this paper.

Binary polymer systems of polyisobutylene (PIB), natural rubber, and polystyrene (PS) with hydrocarbons have been studied. Table II gives the binary parameters obtained for the system PIB + n-pentane from activity data.[9] It also includes the values of the reduced volume and combinatorial chemical potential for one of the experimental datum (the nearest to segment fraction 0.5) and the predicted integral heat of mixing, eq 16. Four different models are used in this calculation. Model 1 uses Flory's equation of state and combinatorial entropy; the latter is modified by using Donohue's[10] parameters. Model 1 is the one used in ref 1. Model 2 uses eq 6 as the equation of state and the same expression for the combinatorial entropy in model 1. Model 3 uses eq 6 and Flory's combinatorial entropy, eq 20. Model 4 uses eq 6 and eq 19 and 20 for the combinatorial entropy. The parameters listed in Table II are those of the center of the ellipse of solutions (middle-point parameters). Since these calculations are carried out for the same set of experimental data, it is easy to understand that there are no differences in the size, shape, and orientation of the ellipses. The residual chemical potential is not included in Table II because its value is the same for the four models; eq 6 is used in all of them.

Table I
Characteristic Parameters of Pure Components

subs	T/°C	q/r	p^{*} [a]	T^{*}/K	v^{*} [b]	v [b]	ref
benzene	25	0.752	150	4709	0.8860	1.1444	7
cyclohexane	25	0.758	127	4720	1.0012	1.2921	13, 14
	34		126	4740	1.0030	1.3067	13, 14 [c]
	44		125	4765	1.0051	1.3234	13, 14 [c]
pentane	25	0.867	97	4158	1.1828	1.6094	15, 16
hexane	20	0.858	104	4447	1.1562	1.5162	17, 18 [c]
	40		101	4467	1.1387	1.4971	17, 18
heptane	20	0.851	103	4621	1.1352	1.4627	17
octane	25	0.844	104	4836	1.1994	1.4320	16, 17, 18
PIB	20	0.830	107	7545	0.9486	1.0875	19
	25		107	7580	0.9493	1.0906	19
	40		106	7660	0.9511	1.1000	19
PS	34	0.701	130	7482	0.8110	0.9385	20
	44		128	7551	0.8124	0.9439	20
rubber	25	0.740	124	6775	0.9342	1.0951	7

[a] In cal/cm³. [b] In cm³/g. [c] Estimated from.

Table II
Middle-Point Binary Parameters for PIB + n-Pentane at 25 °C

model	ν_{21} [a]	ν_{12} [a]	$\tilde{v}$ [b]	$(\mu_1 - \mu_1^{\circ})_{comb}$ [b]	B [c]
1	−1.49	4.05	1.2079	−134.7	−437
2	−1.43	3.89	1.2083	−134.7	−422
3	−4.83	7.42	1.2120	−217.7	−72
4	−4.77	7.41	1.2119	−214.5	−88

[a] In cal/cm³. [b] For $\Phi_2 = 0.62$; chemical potential in cal/mol. [c] In cal/mol.

Table III
Middle-Point Binary Parameters for Binary Systems

system	T/°C	ν_{21} [a]	ν_{12} [a]	B [b]	B_{expt} [b]	ref for act	ref for B
PIB + n-hexane	20	−2.94	3.76	−60	−64 [c]	23	22
	40	−3.48	4.60	−54		23	
PIB + n-heptane	20	−2.44	2.98	−51	−36	23	22
PIB + n-octane	25	−2.48	3.01	−25	−30	16	22
PIB + benzene	25	−0.24	−4.94	302	344	10	10
PIB + cyclohexane	25	−2.60	2.13	79	−10	9	22
rubber + benzene	25	−1.73	−0.89	155	182	12	12

[a] In cal/cm³. [b] In cal/mol. [c] At 25 °C.

Table IV
Middle-Point Binary Parameters for PS + Cyclohexane

model	ν_{21} [a]	ν_{12} [a]	$(\mu_1 - \mu_1^{\circ})_{comb}$ [b]	B [c]
Molecular Weight M_n = 440 000 at 34 °C				
2	2.02	1.75	−25.5	−415
4	9.71	−6.81	−176.0	268
Molecular Weight M_n = 440 000 at 44 °C				
2	1.11	2.86	−24.5	−471
4	7.52	−6.81	−171.0	376
Molecular Weight M_n = 25 000 at 44 °C				
2	−2.14	5.12	−175.0	−358
4	8.38	−6.79	−433.0	378

[a] In cal/cm³. [b] In cal/mol; referred to experimental datum closest to $\Phi_2 = 0.5$. [c] In cal/mol.

Models 1 and 2 give similar values for the binary parameters and very similar values for the reduced volume. Model 3 gives values different from those of models 1 and 2 for the binary parameters and for the combinatorial chemical potential. The binary parameters of model 4 are similar to those of model 3 and the combinatorial chemical potential is slightly smaller.

The combinatorial chemical potential calculated with Donohue's parameters[10] is much smaller (absolute value) than the one obtained when eq 21 is used. Analogous conclusions about the combinatorial entropy are found for all systems studied in this paper. The combinatorial entropy of model 4 is never more than 3.5% smaller than Flory's combinatorial entropy given by eq 20.

Since there is no direct procedure to select the best expression for the combinatorial chemical potential (models 2 or 4), we have made use of the experimental integral heat of mixing at infinite dilution. We consider that the most realistic model (ideal) should predict as many thermodynamic properties as possible with only one set of binary parameters. The middle-point parameters reproduce the experimental values as if data were accurate; therefore the best model should predict other thermodynamic properties besides activity data, such as the integral heat of mixing, B. The experimental value of B for the system PIB + n-pentane is −77 cal mol^{-1} given by Eichinger.[9]

Models 3 and 4 predict values of B close to the experimental value while the value of model 2 is very different from the experimental one. Although this is not a rigorous selection method, it can be pointed out that models 3 and 4 are more realistic. We consider model 4 slightly superior to model 3 becuase it includes somehow the nonrandomness effect in the combinatorial entropy. We have observed a similar behavior for the other systems studied. Therefore we propose eq 21 and 22 for calculating the combinatorial chemical potential (model 4). Tables III and IV give the binary parameters for the other systems. For the sake of brevity, Table III shows only results of model 4.

Table IV gives information analogous to that in Table II for the system PS + cyclohexane at different temperatures and molecular weights. Activity data for this system are taken from Krigbaum.[11] Table III also includes results for the system PIB + n-hexane at two temperatures in order to show how the binary parameters change with respect to temperature.

Although there is no theoretical support for the temperature dependence of binary parameters, calculations of both systems show such dependence. It is important to note that this effect is much smaller for model 4 than for model 2. For the PS + cyclohexane system, only one of the parameters changes in this case. The improvement is not so notorious for the PIB + n-hexane system.

Donohue's model for combinatorial entropy substitutes r_2 for $r_2^{p_2}$ ($p_2 \leq 1$) into eq 22. Therefore, this moddel diminishes the combinatorial entropy as the polymer's molecular weight increases (r_1 is not considered since it is taken to be equal to unity). This effect is shown in Table

Table V
Recommended Values for the Binary Parameters

system	T/°C	ν_{21}[a]	ν_{12}[a]	$\sigma(\chi)$
PIB + *n*-pentane	25	−4.65	6.95	0.04
PIB + *n*-hexane	20	−2.71	3.30	0.01
	40	−3.60	4.80	0.01
PIB + *n*-heptane	20	−2.65	3.36	0.02
PIB + *n*-octane	25	−2.50	3.01	0.08
PIB + benzene	25	−1.05	−4.28	0.03
PIB + cyclohexane	25	−2.20	−2.30	0.08
rubber + benzene	25	−2.32	−0.33	0.01

[a] In cal/cm^3.

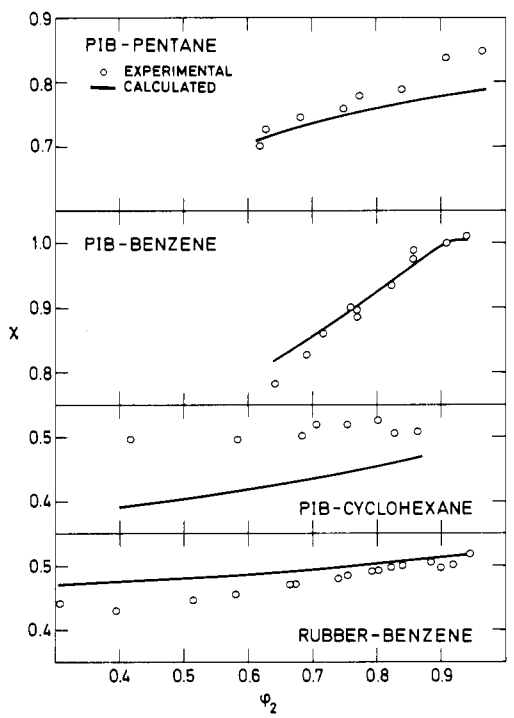

Figure 1. Flory χ parameter as a function of composition for concentrated systems. Experimental values are from eq 18. Calculations are made with parameters given in Table V.

IV when we compare the results of model 2 at constant temperature. There is a larger variation in the binary parameters with respect to molecular weight than with respect to temperature. However, model 4 shows a smaller variation in the parameters and combinatorial chemical potential with respect to both factors. The predicted values of B do not depend on molecular weight (B is a magnitude at infinite dilution) and they are in better agreement with the experimental value than values for B predicted by model 2. We have estimated a value of 423 cal mol^{-1} at 25 °C from the experimental heat-of-mixing data of Gee.[12]

Table V gives recommended values of parameters to fit both the experimental B and activity data. The reduced residual chemical potential, χ, defined by

$$\chi = (\mu_1 - \mu_1^\circ)^R/RT\phi_2^2 \qquad (24)$$

has been calculated from the experimental activity data as well as from the recommended binary parameters given in Table V. Both experimental and calculated values are shown in Figures 1 and 2. Table V also gives the standard deviations obtained when we compare the calculated and experimental χ. The system PS + cyclohexane has not been included in Table V because of the lack of heat-of-mixing data at the temperatures of 34 and 44 °C. Similarly, results for the system PIB + *n*-hexane are only estimates because of the difference between the temperatures for the activity and heat-of-mixing data.

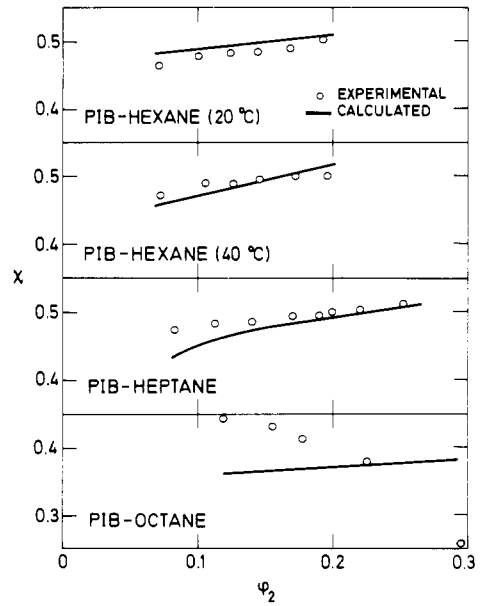

Figure 2. Flory χ parameter as a function of composition for diluted systems. The composition scale has been expanded. The experimental values and calculations are as in Figure 1.

Conclusion

We study in this paper the nonrandomness behavior of several polymer solutions. As was pointed out previously,[1] this approximation is based on intuitive arguments. We introduce in this paper an expression for the estimation of combinatorial entropy which is also intuitive.

Wilson's local site fractions introduce temperature and volume dependence into the exponential term of the partition function. This modifies the equation of state and some of the thermodynamic functions, adding new terms which are corrections of little numerical significance. These terms do not affect parameters calculated from activity data.

Combinatorial entropy is checked and we propose an expression which slightly modifies Flory's random entropy. Since we include local site fractions in the combinatorial factor of the partition function, we make this factor temperature and density dependent. Nevertheless, the physical meaning of the combinatorial factor allows us to consider eq 18 as the number of ways to organize segments in the nonrandom mixture. It is shown that the polymer molecular weight modifies the combinatorial entropy without important changes in the binary parameters and without changes in the predicted values of the integral heat of mixing at infinite dilution. Although we cannot make definitive conclusions, we can affirm that the nonrandomness approximation presented in this paper improves the one proposed previously[1] by making the theory more realistic and by providing a better simultaneous fitting of activity and heat-of-mixing data with only one set of binary parameters for each of the polymer systems studied.

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Analysis of Lattice Chain Data and Test of the Theory of the Expansion Factor for Linear Polymers

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Received May 29, 1980

ABSTRACT: In order to test the theory of the expansion factor α of a linear polymer chain, the estimation of the excluded-volume parameter $z = (3/2\pi\langle R^2\rangle_0)^{3/2}n^2\beta$ and the unperturbed mean-square end-to-end length $\langle R^2\rangle_0 = C_n n a^2$ for lattice chains is reconsidered, where n, β, a, and C_n are the number of segments in the chain, the binary cluster integral for a pair of segments, the effective bond length, and the characteristic ratio, respectively. It is shown that Yamakawa's proposals that $C_n = 1$ and $\beta = \beta_0$, the volume per lattice point, are valid only for chains without short-range effects and that for those with short-range interactions the estimated values of z should be modified by a constant factor depending on the interactions. Approximate theories are compared with Monte Carlo and exact enumeration data. The Domb–Barrett equation for α, a 5(1,1) Padé approximant of α_R for the entire accessible range of z, and the original Flory equation of α_R for $z \gtrsim 5$ are all found to be very good, where the subscript R here refers to the end-to-end distance. The ratios $(\alpha^5 - \alpha^3)/z$ and $(\alpha^5 - 1)/z$ are each apparently constant for $z \gtrsim 5$ but with different proportionality constants, indicating that the asymptotic region is not yet reached for $z \sim 20$.

The excluded-volume effect of flexible polymers in dilute solutions has been well studied[2] but still continues to generate interest. Limiting exponents,[3] delineating the asymptotic behavior of very long chains in very good solvents, have received special attention. Experimentally, of course, only finite chains can be observed and a number of systems are known to deviate from the predicted exponents.[4] However, experimental evidence in general gives strong support to the so-called two-parameter principle.[2]

In the two-parameter scheme, excluded-volume effects on solution properties can be expressed by a single variable z, defined by

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{n^2\beta}{\langle R^2\rangle_0^{3/2}} \tag{1}$$

where n is the number of segments in a chain, $\langle R^2\rangle_0$ is the unperturbed mean-square end-to-end distance, and β is the binary cluster integral for a pair of segments, defined by

$$\beta = \int \left[1 - \exp\left(-\frac{w(\mathbf{R})}{kT}\right)\right] d\mathbf{R} \tag{2}$$

Here $w(\mathbf{R})$ is the potential of mean force of the segment–segment interaction as a function of the relative coordinates $\mathbf{R}$. Many mathematical difficulties are encountered in seeking functional forms of z for various properties. Rigorous results are limited to perturbation series,[2] which have a very limited range and indeed are asymptotic rather than convergent.[5–8] Furthermore, when an attempt is made to compare various approximate theories with experimental data, a fundamental difficulty arises from the fact that the parameter β (or z) is not observable in real solutions. However, a number of numerical studies of lattice chains have been performed,[9,10] and in such cases the above difficulty is eliminated, since β can be identified[11] as the volume β_0 per lattice point for self-avoiding chains.

Yamakawa,[2,12] among others[11–14] who attempted to compare lattice chain data with approximate theories, proposed that we should regard the overlap between bonds due to the reverse step as a part of the excluded-volume effect and take $\langle R^2\rangle_0 = na^2$, with a the bond length and $\beta = \beta_0$ for self-avoiding chains, and then observed that the relation between the expansion factor α and z may be approximated by a single composite curve independent of the type of lattice, as is consistent with the principle of the two-parameter theory. Later, Domb and Barrett[15] pursued this line further and proposed a closed formula for α, which takes account of the first three series coefficients but also of the estimated limiting values based on their lattice work. However, $\langle R^2\rangle_0 = na^2$ for 4-choice simple cubic lattice chains and for this case the data separate from the curve mentioned above.[12] This strongly suggests that the combination of $\langle R^2\rangle_0 = na^2$ and $\beta = \beta_0$ is not always valid for self-avoiding walks, and it thus appears necessary to reconsider the estimation of $\langle R^2\rangle_0$ and β. The main purpose of this paper is to correlate curves

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