Thermodynamics of Mixing of *n*-Alkanes with Polyisobutylene

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ABSTRACT: The volume changes on mixing polyisobutylene (PIB) with *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and *n*-hexadecane have been determined by direct measurements at 25°, and for *n*-heptane at 0 and 50° as well. They are negative in every case; the magnitude of the excess volume decreases with chain length, and increases with temperature. These results on volume changes, which are beyond the scope of conventional theories of polymer solutions, are rationally taken into account by the recent statistical mechanical theory of solutions which relates properties of the mixture to characteristics of the pure liquids manifested in their equation-of-state parameters. The negative enthalpies of mixing found by Delmas, Patterson, and Somcynsky for all of these systems with the exception of PIB–*n*-hexadecane are similarly shown to arise from negative equation-of-state contributions to the enthalpy which reflect differences between the liquid characteristics of *n*-alkane and PIB. The energy contributed by interchange of neighbor species in contact is shown to be small but *positive*, as should be expected for the nonpolar molecules involved. It diminishes with chain length of the alkane, becoming little greater than zero in the limit of an infinite alkane chain (polymethylene). Osmotic pressures of concentrated solutions (*ca.* 15–50%) of PIB in *n*-octane at 25° yield values of the residual chemical potential, expressed in terms of the conventional parameter χ, which are well reproduced by the theory without arbitrary parameters. The partial molar enthalpy and entropy of dilution are dominated by equation-of-state contributions rendering both of them negative, despite the large positive combinatory entropy. The appearance of critical miscibility at higher temperatures is thus prediced by the theory without resort to special explanations.

Inadequacies of conventional solution theories as applied to mixtures of polymers with low molecular diluents have long been apparent. These theories,[1,2] in common with their analogs for mixtures of small molecules, are formulated from a combinatorial entropy of mixing and an energy of mixing determined explicitly by the energies of interaction between neighbor pairs in the solution. The parameter χ introduced to characterize these interactions usually is found to vary with concentration, contrary to its formal definition and the theory it represents. Entropies are characteristically less than the calculated combinatorial entropy, *i.e.*, the entropy parameter ψ_1 (see ref 1) is substantially smaller than its combinatorial value of one-half. Excess volumes of mixing and other volumetric properties of the solution are beyond the scope of conventional theories, which in effect take the volume of the solution to be the sum of the volumes of the two components.

These various deficiencies are traceable to the failure of such theories to take account of the divergent characteristics of the respective liquid components. These characteristics are reflected in their equations of state, *i.e.*, in the relationships of volume to temperature and pressure. Just as the volume of the mixture usually may depart from simple additivity, the intermolecular entropy and energy will not in general interpolate linearly with composition. Hence, the changes experienced by various thermodynamic functions upon mixing will depend in general on properties peculiar to the components comprising the mixture. Such effects are especially large for many polymer solutions owing to the drastic differences between the liquid-state characteristics of the pure components, one of them a low molecular liquid and the other a polymer.

The need for a proper account of the characteristics of the components of liquid mixtures has long been recognized.[3,4] Theories propounded on the basis of a law of corresponding states represent an attempt in this direction. In essence, the intermolecular force law is assumed to be of universal functional form and hence of the same form for both kinds of molecules. Two parameters, an energy and a length, are assumed to be required to fit the universal law to a given liquid. Adaptation to pairs of unlike species involves arbitrary postulates, with the result that the prescription to be followed in treating mixtures is subject to a wide latitude of choice. Moreover, compliance with a law of corresponding states by two such dissimilar liquids as a low molecular diluent and a polymer is highly questionable.

A theory introduced several years ago,[5,6] and until recently applied principally to binary mixtures of monomeric liquids[7] and to mixtures of various pairs of *n*-alkanes,[5,8] offers the prospect of accounting for the intrinsic properties of the components without resort to special assumptions on the correspondence of the intermolecular force laws for the several pairs of molecular neighbors in the mixture. In brief, a simple partition function is formulated which lends itself to adaptation, without ambiguities, to mixtures of molecules which may be nonspherical and may differ in size.[6] The partition function is reducible to parametric form and it prescribes an equation of state which, like the parent partition function, involves three parameters. These can be represented by a

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(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XII.

(2) H. Morawetz, "Macromolecules in Solution," Interscience Publishers, Inc., New York, N. Y., 1965.

(3) I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N. Y., 1959.

(4) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworth and Co., Ltd., London, 1959.

(5) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Amer. Chem. Soc* **86**, 3507, 3515 (1964).

(6) P. J. Flory, *ibid.*, **87**, 1833 (1965).

(7) A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).

(8) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6814 (1967).

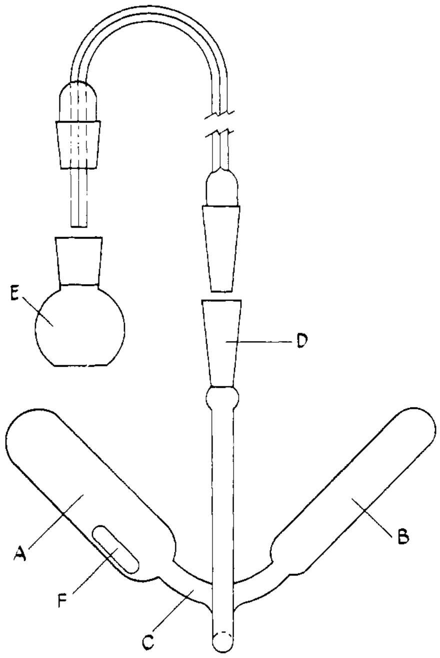

Figure 1. Apparatus for measuring volume changes on mixing.

characteristic molar volume V^* (or specific volume v_{sp}^*), a characteristic temperature T^*, and a characteristic pressure p^*. They may be evaluated from properties of the liquid; a suitable choice for this purpose consists of the molar volume V, the thermal expansion coefficient $\alpha = V^{-1}(\partial V/\partial T)_p$, and the thermal pressure coefficient $\gamma = (\partial p/\partial T)_V$. Application to a binary mixture requires the parameters V_1^*, T_1^*, p_1^* and V_2^*, T_2^*, p_2^* for the respective components, indexed 1 and 2. In addition thereto, an intermolecular interaction parameter X_{12} for the liquid pair must be specified. In general the latter parameter eludes evaluation from independent information. It must therefore be evaluated from an observed property of the mixture. The enthalpy of mixing may serve this purpose; alternatively, the excess chemical potential may be used. For accurate reproduction of the properties of mixtures over a wide range of conditions, separation of X_{12} into enthalpic and entropic parts may sometimes be required.[8,9]

Application of the theory cited requires a considerable fund of information on the equation-of-state properties of the pure liquid components, which often is not available in its entirety with the accuracy that is required. Recent investigations of Orwoll[10] provide reliable data for the n-alkanes from n-hexane to higher members of the series. As reported in the following paper,[11] we have determined the specific volume v_{sp}, α, and γ for polyisobutylene (PIB) over a wide range of temperature. The required background of data has thus been made available for an examination of solutions of PIB in n-alkanes. Enthalpies of mixing for these systems have been determined with extraordinary accuracy by Delmas, Patterson, and Somcynsky,[12] and the availability of their results enhanced interest in the present investigation. These systems present a number of interesting features. Although they are nonpolar, both enthalpies of mixing and volume changes on mixing are negative, and at elevated temperatures they exhibit lower critical miscibility; the latter feature is indicative of a *negative* entropy of dilution.

In this paper we report measurements of excess volumes for mixtures of PIB with several n-alkanes from C_5 to C_{16}. In addition, chemical potentials for the system n-octane-PIB have been determined for polymer concentrations from about 15 to 50% by weight, high pressure osmometry being used for this purpose. Both sets of results are interpreted on the basis of intermolecular interaction parameters X_{12} evaluated from the enthalpies of mixing determined by Delmas, *et al.*[12] No arbitrary parameters are employed.

Experimental Section

Materials. A broad fraction of PIB prepared as described in the following paper[11] was used in all experiments reported below. Its viscosity average molecular weight was *ca.* 40,000. Chromatoquality (Matheson Coleman and Bell) n-alkanes were used without further purification.

Excess Volume. Volume changes on mixing were determined directly using the apparatus shown in Figure 1. The procedure described in detail elsewhere[9] was followed with minor modifications. The weighed sample of polymer was placed in bulb A, which was then sealed to the apparatus at C. After thoroughly degassing the polymer under high vacuum, the cell, including bulb B, was filled with clean, degassed mercury. A measured quantity of solvent was introduced from a syringe into bulb B by inserting the Teflon needle of a syringe through ground joint D; mercury displaced by the solvent overflowed from D. The solute and solvent components were retained in bulbs A and B, respectively, separated by mercury at C. The capillary and weighing bottle E were assembled at the ground glass connections shown in Figure 1, and contact between the mercury in the capillary and mercury in bottle E was established by warming bulbs A and B. The apparatus was placed in a water thermostat regulated at 25.00 ± 0.01° until thermal equilibrium was established. The bottle E and contents were then removed and weighed. After reconnecting bottle E, solvent and polymer were brought together by tilting the cell. Dissolution and thorough mixing were accomplished with the aid of the stirrer magnet F. The apparatus was again brought to constant temperature in the thermostat, after which E and its contents were reweighed. The difference in weight gave the volume change on mixing directly.

High-Pressure Osmometry. Osmotic pressures were measured using the apparatus and procedure described elsewhere.[9,13]

Characteristic Properties of the Pure Components. Equation-of-state data for the n-alkanes which served as solvent components of the binary mixtures with PIB are assembled in Table I. The data refer to the temperatures, given in the second column, at which the alkane–PIB system was investigated in each case. Specific volumes v_{sp}, thermal expansion coefficients α, and thermal pressure coefficients γ for n-hexane, n-octane, and n-hexadecane were determined by Orwoll.[10] The corresponding data for other n-alkanes are

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(9) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, in press.

(10) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967); R. A. Orwoll, Ph.D. Thesis, Stanford University, 1966.

(11) B. E. Eichinger and P. J. Flory, *Macromolecules*, **1**, 285 (1968).

(12) G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **57**, 79 (1962).

(13) P. J. Flory and H. Daoust, *ibid.*, **25**, 429 (1957).

TABLE I

PROPERTIES OF *n*-ALKANES USED AS SOLVENTS[a]

Liquid	t, °C	v_{sp}, cc g^{-1}	$\alpha \times 10^3$, deg^{-1}	γ, cal cc^{-1} deg^{-1}	$\tilde{v}$	v_{sp}^*, cc g^{-1}	T^*, °K	p^*, cal cc^{-1}
C_5H_{12}	25	1.6094	1.610[b]		1.3607	1.1828	4158	$97._1$[b]
C_6H_{14}	25	1.5268	1.385	0.194_5	1.3215	1.1554	4437	$101._2$
C_7H_{16}	0	1.4275	1.210		1.2694	1.1245	4534	$104._2$[c]
	25	1.4721	1.253		1.2973	1.1347	4652	$102._5$[c]
	50	1.5200	1.321		1.3299	1.1429	4739	$100._3$[c]
C_8H_{18}	25	1.4320	1.159	0.212	1.2793	1.1194	4836	$103._5$
$C_{10}H_{22}$	25	1.3769	1.050		1.2578	1.0947	5093	$106._5$[c]
$C_{16}H_{34}$	25	1.2992	0.901	0.246_5	1.2270	1.0503	5548	$110._7$

[a] See ref 8. [b] Values of α and p^* for *n*-pentane were obtained by extrapolation of empirical relations based on results for *n*-hexane and higher alkanes (see ref 8). [c] These values of p^* were obtained by interpolation from data for other homologs given in ref 8.

taken from this critical resumé of previously published results. The thermal expansion coefficient given for *n*-pentane was obtained by extrapolation of results for higher alkanes.[10] Densities of *n*-pentane tabulated as a function of temperatures by Timmermans[14] yield a value of α within about 1% of the value given in Table I. The characteristic properties of PIB are given in Table I of the following paper.

The reduced equation of state takes the form[5,6,15]

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

where $\tilde{v}$, $\tilde{T}$, $\tilde{p}$ are reduced variables defined by

$$\tilde{v} = V/V^* \qquad (2)$$

$$\tilde{T} = T/T^* \qquad (3)$$

$$\tilde{p} = p/p^* \qquad (4)$$

The symbols bearing asterisks have been cited as the characteristic parameters. Their relation to the primary parameters entering the partition function is given elsewhere.[5,6] We note however that the characteristic volume V^* has the significance of a hard core volume per mole (or other specified quantity) of the component. Subscripts identifying the component are omitted.

At $p = 0$ we have from eq 1 that

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (5)$$

$$\tilde{v}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \qquad (6)$$

$$\tilde{p} = p/\gamma T\tilde{v}^2 \qquad (7)$$

These equations in conjunction with eq 2-4 relate the characteristic parameters to measurable quantities. Thus, the thermal expansion coefficient yields the reduced volume $\tilde{v}$ according to eq 6; eq 5 then gives $\tilde{T}$; the reduced pressure $\tilde{p}$ follows from γ according to eq 7. In those instances where accurate experimental values of γ are unavailable, values of p^* given in Table I have been interpolated from results for other alkanes using empirical formuls derived by Orwoll.[10]

Thermodynamic Properties of Mixtures

The Enthalpy of Mixing. The adaptation of the theory to mixtures is straightforward.[5,6] Volume fractions φ_1 and φ_2 of the solvent and solute, respectively, are defined in terms of the characteristic, or core, volumes. Thus

$$\varphi_2 = 1 - \varphi_1 = w_2v_{sp;2}^*/(w_1v_{sp;1}^* + w_2v_{sp;2}^*) \qquad (8)$$

where w_1 and w_2 are the weight fractions.[16] Also required is the surface fraction $\theta_2 = 1 - \theta_1$ which may be defined in terms of the numbers of surface sites, s_1 and s_2, per unit core volume as

$$\theta_2 = \varphi_2s_2/(\varphi_1s_1 + \varphi_2s_2) \qquad (9)$$

Only the ratio s_2/s_1 is required, and this ratio can be estimated with sufficient accuracy from molecular dimensions. The characteristic temperature and pressure for the mixture are then given by[6]

$$T^* = (\varphi_1p_1^* + \varphi_2p_2^* - \varphi_1\theta_2X_{12})/(\varphi_1p_1^*/T_1^* + \varphi_2p_2^*/T_2^*) \qquad (10)$$

where X_{12} is the interaction parameter denoting the energy change for formation of contacts between species 1 and 2 in exchange for contacts between like species.

The enthalpy of mixing N_1 moles of solvent with N_2 moles of solute is expressed according to the theory[6] as

$$\Delta H_M = N_1p_1^*V_1^*[(1/\tilde{v}_1) - (1/\tilde{v})] + N_2p_2^*V_2^*[(1/\tilde{v}_2) - (1/\tilde{v})] + [N_1V_1^*\theta_2/\tilde{v}]X_{12} \qquad (11)$$

where V_1^* and V_2^* are the molar characteristic volumes, and $\tilde{v}$ is the reduced volume of the mixture. The latter quantity may be calculated according to eq 5 from $\tilde{T} = T/T^*$ for the mixture, T^* being obtained from eq 10. In the limit of a very large excess of the solvent eq 11 gives for the enthalpy of mixing[9]

$$\Delta H_M(\infty) = (N_2V_2^*/\tilde{v}_1)\{p_2^*(\tilde{v}_1/\tilde{v}_2) - 1 - \alpha_1T(1 - \tilde{T}_2/\tilde{T}_1)] + (1 + \alpha_1T)(s_2/s_1)X_{12}\} \qquad (12)$$

Analysis of the precise calorimetric results of Delmas, Patterson, and Somcynsky[12] is presented in Table II. Their heats of mixing, expressed as calories per mole of repeating unit (56 g) dissolved in a very large excess of the solvent, are given in the second column. The values of $X_{12}s_2/s_1$ calculated from these heats through use of eq 12 are presented in the third column of Table II. Characteristic parameters required for these calculations were taken from Table I and from the

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(14) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950, p 33.

(15) H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

(16) The derivation of this equation and those to follow is conveniently carried out in terms of segments, arbitrarily defined in relation to the characteristic volume of one of the components.[5,6] The segment is an artifice which can be eliminated from the resulting equations. Hence, we have chosen to avoid introducing it here. The core volume and surface fraction, φ_2 and θ_2, may appear to be defined differently than heretofore.[6] The definitions are equivalent, however.

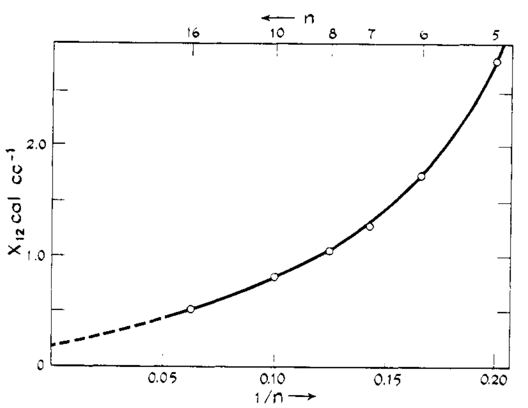

Figure 2. Contact interaction parameter X_{12} for normal alkane mixtures with PIB plotted against the reciprocal of the length n of the alkane $H(CH_2)_nH$.

Table II
Interpretation of Enthalpies of Mixing of Polyisobutylene with Various n-Alkanes at 25°

Solvent	$\Delta H_M(\infty)$, cal mol^{-1} of C_4H_8[a]	$(s_2/s_1)X_{12}$, cal cc^{-1}	s_2/s_1[b]	X_{12}, cal cc^{-1}
C_5	−48	1.48	0.53	2.8
C_6	−34	0.96	0.55	1.75
C_7	−24	0.73	0.57	1.28
C_8	−16	0.61	0.58	1.05
C_{10}	−7.3	0.49	0.60	0.82
C_{16}	+0.6	0.33	0.64	0.52

[a] Enthalpies of mixing PIB with a large excess of diluent determined calorimetrically by Delmas, Patterson, and Somcynsky.[12] [b] Estimated as described in text.

following paper.[11] The ratios s_2/s_1 listed in the fourth column were calculated from molecular dimensions as follows. The n-alkanes were treated[8] as right cylinders of mean radius 2.49 Å and length $l^* = 1.19n + 1.32$, also in angstrom units; these dimensions correspond to the mean crystallographic radii and the core volumes V^* of the n-alkanes. The PIB chain was similarly treated as a cylinder having a crystallographic repeat length of 18.6 Å for eight units, or 2.325 Å per unit, and a radius of 3.48 Å, as required by the characteristic molar volume V_u^* for a repeating unit. The ratio of the surface area per repeating unit of PIB to the molecular surface area of the n-alkane is divided by the ratio of the corresponding core volumes (*i.e.*, by V_u^*/V_1^* where V_u^* is the characteristic molar volume of the repeating unit of PIB) to obtain s_2/s_1, the ratio for segments of equal characteristic volumes.

Values of the neighbor interchange interaction parameter X_{12} given in the last column are plotted in Figure 2 against the reciprocal of the number n of carbon atoms in the alkane chain. This choice of coordinate scales is essentially arbitrary. First to be noted is the smoothness of the plot, which bears testimony to the consistency and precision of the results of Delmas, *et al.*[12] Second, it will be observed that X_{12} extrapolates to a value of only about 0.2 for $n = \infty$, *i.e.*, contact interactions between the CH_2 groups of a very long polymethylene chain and the exposed groups of the sterically hindered PIB chain (with its methyl groups compressed by mutual crowding) are almost indistinguishable from the mean of the interactions between species of the same kind.

The increase in X_{12} with decrease in chain length n of the alkane may reasonably be ascribed to the lower van der Waals interactions of terminal groups. The properties of n-alkanes and their binary mixtures denote reduced interactions for terminal compared with midchain groups.[8,10] In effect, the mixing of end groups with midchain members of the n-alkanes entails an increase in energy, *i.e.*, the parameter which is the analog of X_{12} is appreciably positive for this mixing process. Since in the limit $n \rightarrow \infty$ the contact interaction for mixing polymethylene segments with PIB is very nearly zero, we may assume that contact interchanges for terminal groups of n-alkanes with PIB will make an appreciable positive contribution to X_{12}. This contribution and its dependence on the length of the alkane chain are difficult to formulate in quantitative terms. The magnitude of the effect on X_{12} and its dependence on n shown in Figure 2 are qualitatively consistent with this hypothesis, however.[17] For all of the systems studied, with the partial exception of n-pentane–PIB, the values of X_{12} are relatively small. Neighbor interactions make only minor contributions to the properties considered below; hence the precise value of X_{12} is not critical.

Of foremost significance is the success of the theory in accounting for negative enthalpies of mixing, which for the lower n-alkanes are fairly large, without invoking a contribution from neighbor interactions of the same sign. In fact, the theory finds this latter contribution to be positive, as should be expected for contact interactions between nonpolar molecules. The observed negative enthalpies of mixing in these systems are to be attributed to "equation-of-state" contributions which dominate the positive contributions of smaller magnitude from contact interactions.[18] Both contributions are treated quantitatively and unambiguously by the theory. The opposite trends of $\Delta H_M(\infty)$ and of X_{12} with n are thus explained. The negative equation-of-state contribution, whose magnitude increases with decrease in n, is directly traceable to the disparity between the properties of the liquid components. This will be apparent from scrutiny of eq 11 and 12 and the values of quantities entering therein, as given in Table I.

The Volume Change on Mixing. Results of experiments on volume changes accompanying mixing of PIB with various n-alkanes are recorded in the penultimate column of Table III. The value for n-pentane agrees with the results Baker, *et al.*[19] In every case the excess volume, expressed in Table III as the percentage of

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(17) The values of X_{12} in Table II are comparable to those for the same hydrocarbon in admixture with polymethylene.[8] For example, X_{12} for n-hexane–polymethylene calculated from empirical relations given in ref 8 is *ca.* 3.0 cal cc^{-1} compared with 1.75 cal cc^{-1} for n-hexane–PIB (Table II). Interactions involving terminal groups are obviously responsible for X_{12} in n-alkane mixtures. The similarity of value of X_{12} therefore supports the explanation given in the text.

(18) For example, in the case of the PIB solution in n-hexane, the equation-of-state terms contribute −89 cal mol^{-1} to $\Delta H_M(\infty)$ compared with 54 cal mol^{-1} from contact interactions. For solutions in n-decane the respective contributions are −34 and 27 cal mol^{-1}.

(19) C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, 3, 215 (1962).

TABLE III

EXCESS VOLUMES OF PIB-*n*-ALKANE MIXTURES

Solvent	t, °C	w_2, weight fraction solute	φ_2	$\tilde{v}^0$	$-(V^E/V^0) \times 10^2$	
					Obsd	Calcd
C_5	25	0.593	0.539	1.2465	1.270	1.54
C_6	25	0.530	0.481	1.2384	0.842	0.98
	25	0.588	0.540	1.2282	0.857	0.97
	25	0.684	0.640	1.2110	0.822	0.88
C_7	0	0.576	0.533	1.1986	0.474	0.57
	25	0.576	0.532	1.2183	0.615	0.74
	50	0.576	0.531	1.2402	0.804	0.97
C_8	25	0.466	0.425	1.2238	0.472	0.54
	25	0.573	0.532	1.2099	0.481	0.54
	25	0.642	0.603	1.2006	0.470	0.52
C_{10}	25	0.487	0.452	1.2085	0.283	0.33
	25	0.568	0.533	1.1997	0.291	0.33
	25	0.656	0.623	1.1899	0.277	0.36
C_{16}	25	0.462	0.437	1.1928	0.077	0.11
	25	0.540	0.515	1.1867	0.080	0.11
	25	0.640	0.616	1.1788	0.078	0.10

the volume, is negative. The magnitude of the excess volume decreases with increase in the alkane chain length n.

The reduced volume $\tilde{v}$ of the mixture may be calculated from T^* as obtained from eq 10. Substitution of $\tilde{T} = T/T^*$ in eq 5 and solution by trial gives $\tilde{v}$. The reduced volume which would be obtained if the volume of the mixture were additive in the volumes of the components (*i.e.*, if the excess volume V^E were zero) is

$$\tilde{v}^0 = \varphi_1\tilde{v}_1 + \varphi_2\tilde{v}_2 \qquad (13)$$

These "ideal" reduced volumes are recorded in the fifth column of Table III. The excess reduced volume is the difference

$$\tilde{v}^E = \tilde{v} - \tilde{v}^0 \qquad (14)$$

and of course $V^E/V^0 = \tilde{v}^E/\tilde{v}^0$. Values of this ratio are given in the final column of Table III.

Calculated excess volumes throughout the full range of composition are shown by the solid curves in Figure 3. Experimental data from Table III are included for comparison. The calculated values of V^E/V^0 are consistently negative in agreement with experiment. Although about 15–20% larger than those observed, the calculated values exhibit a dependence on chain length of the solvent that parallels observation. The dependence of V^E/V^0 on composition was not investigated in detail. The locations of the minima in V^E/V^0 appear to be represented satisfactorily by the calculations, however. The effect of temperature, examined experimentally for a solution in *n*-heptane, is also well reproduced by theory (see Table III).

The effect of the term in X_{12} in eq 10 on T^*, and hence on $\tilde{v}$ and $\tilde{v}^E$, is quite small for these mixtures. If X_{12} were set equal to zero for the mixture with *n*-heptane, for example, the magnitude of $\tilde{v}^E$ would be increased by only 6%. Differences in equation-of-state parameters account for the preponderance of the volume decrease on mixing. Of foremost significance in this regard is the difference between the thermal expansion coefficients for the two components, a difference which is reflected in the values of T^* for the *n*-alkane solvent and for PIB. The fewer number of intermolecular degrees of freedom per unit volume for the polymer gives rise to a denser packing in the liquid state. In qualitative terms, it is this rather marked difference between the two components which is responsible for the decrease in volume on mixing, and for the large equation-of-state contributions to other thermodynamic properties.

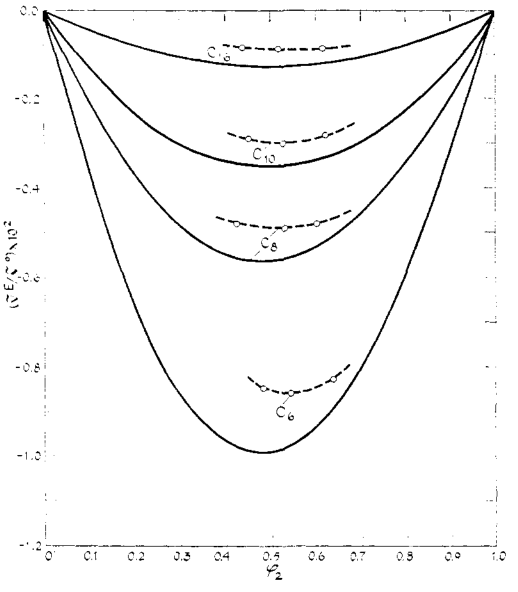

Figure 3. Calculated excess volume ratios V^E/V^0 at 25°, shown by solid curves, for the systems indicated. Points and dashed curves drawn through them represent experimental results from Table III.

Chemical Potentials. The chemical potential of the solvent is conveniently divided into two terms as follows[5,9]

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)_{\text{combn}} + (\mu_1 - \mu_1^0)^R \qquad (15)$$

The first term on the right represents the combinatorial contribution, and the last term the "residual," or noncombinatory part. The latter comprises equation-of-state and neighbor interaction contributions. For molecules of similar size, $(\mu_1 - \mu_1^0)_{\text{combn}}$ may be approximated by the ideal chemical potential $RT \ln x_1$ where x_1 is the mole fraction of the solvent. Then $(\mu_1 - \mu_1^0)^R$ may be identified with the excess chemical potential $(\mu_1 - \mu_1^0)^E$ as ordinarily defined. Inasmuch as a different expression for $(\mu_1 - \mu_1^0)_{\text{combn}}$ is required for polymer solutions, we have been obliged to introduce a different term, namely, *residual* chemical potential,[6] for the noncombinatory contribution.

We shall adopt the simple relationship[1,2]

$$(\mu_1 - \mu_1^0)_{\text{combn}} = RT[\ln(1 - \varphi_2) + (1 - 1/r)\varphi_2] \qquad (16)$$

for the combinatory chemical potential. Here r is the ratio of core volumes of solute and solvent. Equation 16 departs from the usual expression of polymer solution theory only through replacement of the nominal volume fraction by the segment, or core, volume fraction. According to the theory of noncombinatory contributions[6]

$$(\mu_1 - \mu_1^0)^R = p_1^* V_1^* \{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + (V_1^* X_{12}/\tilde{v})\theta_2^2 \qquad (17)$$

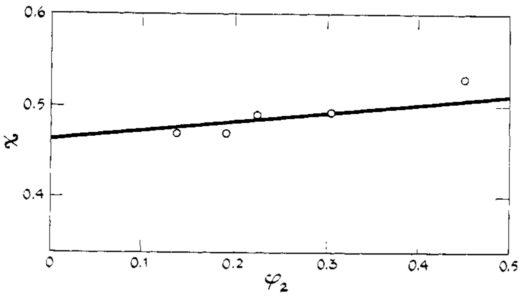

Figure 4. The reduced residual chemical potential χ (see eq 18 and 19) for *n*-octane–PIB mixtures plotted against composition expressed as the core volume fraction φ_2. The points represent results of high pressure osmometry at 25° (see Table IV). The line has been calculated according to eq 17 with $X_{12} = 1.05$ (see Table II).

Table IV

Osmotic Pressures for Concentrated Solutions of PIB in *n*-Octane At 25°

Weight fraction solute	φ_2	π, atm	χ
0.159	0.138	0.319	0.47
0.217	0.190	0.672	0.47
0.253	0.223	0.852	0.490
0.342	0.306	2.125	0.493
0.493	0.452	6.25	0.535

It is customary to express the chemical potential for a polymer solution as follows

$$\mu_1 - \mu_1^0 = RT\{\ln(1-\varphi_2) + (1-1/r)\varphi_2 + \chi\varphi_2^2\} \quad (18)$$

Hence, the conventional parameter χ is identified in the present theory as the *reduced residual* chemical potential defined by

$$\chi = (\mu_1 - \mu_1^0)^R/RT\varphi_2^2 \quad (19)$$

We depart from custom in construing φ_2 to be the segment volume fraction instead of the nominal volume fraction, as already noted above.

Osmotic pressures determined for several solutions of PIB in *n*-octane covering the range up to about 50% by weight of polymer are presented in Table IV. Chemical potentials were calculated from the relation $\mu_1 - \mu_1^0 = -\pi V_1$, and values of χ were obtained according to eq 18 with $r = 300$, corresponding to a molecular weight of about 40,000 for the polymer. These experimental values are compared with the theoretical line in Figure 4. This line represents eq 17 with transcription to χ according to eq 19.[20]

In judging the agreement between calculations and observations, it is to be observed that the comparison places excessive burden on the reliability of eq 16 for the combinatory contribution. An error of as much as 0.1 in χ may be laid to the inaccuracy of any estimate of the combinatory entropy.[8,9] In the present instance the agreement is better than might have been expected. The theory predicts that χ should increase gradually with concentration, and this is confirmed by experiment (see Figure 4).

Neighbor interactions make only a small contribution to the residual chemical potential. The value of χ calculated according to theory would be decreased only about 10% if X_{12} were taken to be zero. The minor influence of X_{12} on the chemical potential recalls its small effect on the excess volume.

Experimental measurements by which to separate $(\mu_1 - \mu_1^0)^R$ for *n*-octane–PIB solutions into its partial molar enthalpic and entropic components have not been carried out, but it may be inferred from the integral heat of mixing $\Delta H_M(\infty)$ that the partial molar heat of dilution $\bar{H}_1^R = \bar{H}_1 - H_1^0$ is likewise negative at high dilutions. Calculations carried out on the basis of theory[5] yield

$$\lim_{\varphi_2\to 0} (\bar{H}_1^R/RT\varphi_2^2) \equiv \kappa_1 = -0.17$$

$$\lim_{\varphi_2\to 0} (\bar{S}_1^R/R\varphi_2^2) \equiv \psi_1 - {}^1/_2 = -0.64$$

for the reduced partial molar residual enthalpy and entropy, respectively, at $\varphi_2 = 0$. Here κ_1 and ψ_1 are the parameters of established usage in dilute polymer solution theory.[1] Hence

$$\kappa_1 - (\psi_1 - {}^1/_2) = \chi_1 = 0.47$$

where χ_1 is the limiting value of χ for $\varphi_2 = 0$ (see Figure 3); the subscripts on κ_1 and ψ_1 have the same significance. The reduced partial molar residual entropy (*i.e.*, $\psi_1 - {}^1/_2$) for this system is predicted to be strongly negative, its magnitude being sufficient to render $\psi_1 < 0$, and hence to dominate the positive combinatory entropy of dilution. Both the partial molar enthalpy and the partial molar entropy of dilution are negative. This circumstance presages the emergence of critical miscibility with increase in temperatures, as indeed has been observed by Freeman and Rowlinson.[21] Thus the theory unambiguously predicts a lower critical solution temperature (LCST); no special or arbitrary assumptions are involved. Quantitative prediction of the LCST is beyond the limits of reliability of the theory, however, and in particular would require accurate evaluation of the combinatory entropy.

The striking characteristics briefly cited above, namely, the large negative contributions of equation-of-state terms to both the partial molar enthalpy and the partial molar entropy of dilution and the increase of χ with concentration, are manifested to an even greater degree in the *n*-pentane–PIB system. This system has been investigated in detail with results which are reported elsewhere.[22] The theory gives a good account of the principal features of the excess thermodynamic functions for PIB–*n*-pentane.

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(20) Calculations according to eq 17 involve small differences between large quantities, and hence must be carried out with high precision. For the composition range covered here, the series expansion of eq 17 (see ref 6) offers a preferable means for calculating χ as a function of composition.

(21) P. I. Freeman and J. S. Rowlinson, *Polymer*, 1, 20 (1960).

(22) B. E. Eichinger and P. J. Flory, submitted for publication.