

Role of Free Volume Change on Polymer Solutions; Osmotic Pressure of Moderately Concentrated Polyisobutene—Normal Alkane Systems

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ABSTRACT: An attempt was made to verify the effect of free volume dissimilarity, which is predicted by the cell (or free volume) theory, upon the χ parameter. Osmotic pressures of moderately concentrated polyisobutene solutions in *n*-pentane, *n*-hexane, and *n*-heptane were measured at various temperatures, and values of the χ_1 parameter were obtained. It was found that χ_1 increases with increasing temperature in each system, and decreases with the increasing chain length of *n*-alkanes used as solvents at fixed temperature. This effect is in agreement with the cell theory. Lower critical solution temperatures (L.C.S.T.) of various polyisobutene—*n*-alkane systems were calculated from experimental χ_1 values by using the theoretical relationship. These predicted L.C.S.T. values are compared with values experimentally obtained by Patterson, *et al.*

KEY WORDS Free Volume / Cell Theory / χ Parameter / High-Pressure Osmometry / Polyisobutene / Normal Alkane /

It has been considered that the statistical-mechanical approximation for the thermodynamical nature of polymer solutions achieved an essentially satisfactory form through the Flory—Huggins theory¹ which is based on a strictly regular solution theory for the mixtures of spherical molecules of equal size. It appears, however, that the qualitative physical picture of solutions has to be changed in view of many experimental results for the thermodynamical nature of polymer solutions, *e.g.*, the behaviour of polymer—solvent interactions and the χ parameter, the temperature dependence of polymer solubility, and the phase separation which takes place in all polymer solutions at an elevated temperature (called the lower critical solution temperature). Although the traditional ideas, such as the Flory—Huggins theory, have been refined, they can not explain these results even qualitatively. Apparently a new factor is needed. In the traditional treatment, the factor which lowers the mutual solubility of solute and solvent concentrates on the dissimilarity of contact energies or cohesive energies between segments of polymer and solvent molecules of different chemical nature. In the early 1950's Prigogine,

et al.,²⁻⁴ introduced into solution theory a new factor which was due to the dissimilarity between the free volumes of the polymer and solvent molecules. This free volume dissimilarity exists, even between a polymer and a chemically identical homologous solvent of low molecular weight, due to the inescapable difference of size or chain length. The free volume theory gives a picture much different from the Flory—Huggins theory for the solution properties. Nevertheless many recent investigations by Patterson, *et al.*,⁵⁻¹⁵ and by Flory, *et al.*,¹⁶⁻²⁸ are based on the free volume theory.

The residual chemical potential parameter χ presented by Flory¹⁸ for a polymer solution depends on the dissimilarity of either the cohesive energies or the free volumes between segments of polymer and solvent molecules. Hence it is expected that measurement of χ for various polymer—solvent systems gives significant information for understanding the solution thermodynamics. In this work, measurements of osmotic pressures were made, in order to obtain the χ value directly at various temperatures in a concentration range of more than 10% where the segments of the polymer chain are supposed

to be distributed homogeneously in solution.

The purpose of this study was restricted to the verification of the contribution of the free volume change to thermodynamic mixing functions. Polyisobutene-*n*-alkane systems were employed because of the smallness of cohesive energy dissimilarities between segments of the polymer and solvent molecules. Other investigators usually controlled the free volumes of the chemically homologous solvents only by using various solvents of different chain length. It must be emphasized that in this study they were controlled not only by using various solvents but also by changing temperature.

SURVEY OF THE THEORY

The distinctive feature of the cell theory is that the movements of the elements around their respective sites are taken into account. According to Prigogine's corresponding states principle,⁴ the molar configurational quantities (apart from the combinatorial entropy) of pure *r*-mer liquids are related to dimensionless reduced quantities (with tilde) through characteristic values (with asterisk);

$$\begin{aligned} V(T, r) &= \tilde{V}(T) \cdot V^*(r); & V^*(r) &= NrR^* \\ U(T, r) &= \tilde{U}(T) \cdot U^*(r); & U^*(r) &= Nq(r)\epsilon^* \\ S(T, r) &= \tilde{S}(T) \cdot S^*(r); & S^*(r) &= Nc(r)k \\ T &= \tilde{T} \cdot T^*(r); & T^*(r) &= U^*(r)/S^*(r) \\ P &= \tilde{P} \cdot P^*(r); & P^*(r) &= U^*(r)/V^*(r) \end{aligned} \quad (1)$$

where *V*, *U*, and *S* are molar volume, configurational energy and entropy, respectively, *N* is Avogadro's number, *T* is temperature, *P* is pressure, and *k* is Boltzmann's constant. The coefficient *c* is one-third of the degrees of freedom per one molecule consisting of *r* elements, *q* is the effective number of elements per chain-molecule with the consideration of coordination number, and *R*^{*} is the distance between two elements at which intermolecular potential has its minimum value, ϵ^* .

Applying the smoothed potential to cell partition function which was used for liquids by Prigogine, *et al.*,^{4,5} and assuming constant zero pressure, the expression for \tilde{T} can be given by

$$\tilde{T} = \frac{mn}{3(n-m)} \tilde{V}^{-m/3} (1 - \tilde{V}^{-(n-m)/3}) (1 - b\tilde{V}^{-1/3}) \quad (2)$$

where $b = R^*/\sigma = (m/n)^{1/(n-m)}$, σ is the intermolecular distance at which the intermolecular potential becomes zero, and *m* and *n* are the exponents of the Lennard-Jones intermolecular potential. The expressions for the coefficient of thermal expansion α become

$$3(\alpha T)^{-1} = -m + \frac{n-m}{\tilde{V}^{(n-m)/3} - 1} + \frac{b\tilde{V}^{-1/3}}{1 - b\tilde{V}^{-1/3}} \quad (3)$$

If $3-\infty$ are chosen as *m-n*, eq 2 and 3 become identical to Flory's expressions. As suggested and executed by Flory, *et al.*, experimental values of α at temperature *T* can give the characteristic volume from eq 3.^{16,18-20,24} Figure 2 shows the $\alpha T - \tilde{V}$ curves at the choices of $3-\infty$ and $6-12$ for *m-n*.

It is predicted by Prigogine, *et al.*, that the mixtures will also obey the corresponding states principle with certain average characteristic parameters for the mixtures.⁴ The noncombinatorial Gibbs free energy of mixing is given by

$$\begin{aligned} \Delta\tilde{G}_1 &= \chi RT\phi^2 = U_1^* \left[-\tilde{U}(\langle\tilde{T}\rangle) \nu^2 X_2^2 \right. \\ &\quad \left. + \tilde{G}(\langle\tilde{T}\rangle) - \tilde{G}(\tilde{T}_1) + (\tilde{T}_1 - \langle\tilde{T}\rangle) \frac{\partial\tilde{G}}{\partial\tilde{T}} \right] \quad (4) \end{aligned}$$

where $\langle\tilde{T}\rangle$ is the reduced temperature of solution, ϕ and *X* are the segment fraction and surface fraction, subscripts 1 and 2 correspond to solvent and solute, respectively, and ν^2 reflects differences in cohesive energy and size between segments of polymer and the solvent molecule (see eq 8 in ref 11 and Chapter 16 in ref 4).

Here it must be noticed that \tilde{G} is the universal function of \tilde{T} , and that the difference of \tilde{G} between pure components and mixture is due only to the difference of \tilde{T} . Then expanding eq 4 around \tilde{T}_1 , the residual chemical potential parameter of infinite dilution χ_1 can be expressed by

$$\chi_1 = U_1^* \left[\frac{-\tilde{U}_1}{RT} \nu^2 + \frac{\tilde{C}_{p1}}{2R} \tau^2 \right] \quad (5)$$

where C_p is the configurational heat capacity, and the coefficient $\tau = 1 - \tilde{T}_2/\tilde{T}_1$. In the expression of eq 5 the first term on the right corresponds to the traditional expression of interaction term which is proportional to T^{-1} . The second term which depends on \tilde{T} is related to free volume dissimilarity through eq 3.

For the special case that the cohesive energy

dissimilarity between the segments of polymer and the solvent molecule is small, *e.g.*, PIB—*n*-alkane systems, eq 5 can be reformed approximately to a simple particular form,^{6,9}

$$R\chi_1 = A(T/r_1)^{-1} + B(T/r_1) \quad (6)$$

where *A* and *B* are molecular parameters characterizing the whole series of polymer and homologous solvent systems, and *r*₁ is the chain length of solvents.

As suggested by Patterson, *et al.*,¹² the free volume theory of Flory, *et al.*,¹⁸ should be a particular case of the Prigogine theory with the choice of exponents *m*—*n* as 3—∞. According to this theory, χ_1 is expressed as

$$RT\chi_1 = (A^2\alpha_1 T/2 + Y_{12})(P_1^* V_1^* / \bar{V}_1) \quad (7)$$

where

$$A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (s_2/s_1)(X_{12}/P_1^*)$$

and

$$Y_{12} = (s_2/s_1)^2 (X_{12}/P_1^*)$$

*X*₁₂ is the coefficient related to cohesive energy dissimilarity between the segments of polymer and solvent molecules, and *s*'s are the contact surface areas of the segments.

EXPERIMENTAL

Materials

The fractions of polyisobutene (PIB) were obtained from commercial Vistanex LM-MH by means of precipitation fractionation. Benzene and acetone were used as a solvent and a precipitant, respectively. For a PIB fraction selected for this measurement, the fractionation procedure was repeated three or more times to eliminate fractions of low molecular weight which would be able to permeate the semipermeable membrane in osmometry. Number-average molecular weight of the PIB fraction was determined as $\bar{M}_n = 99400$ by dilute solution osmometry.

Solvents used in this work were *n*-pentane, *n*-hexane, and *n*-heptane of spectro grade. They were dried and fractionally distilled before use.

Apparatuses and Measurements

A Zimm—Meyerson-type osmometer was used for the measurement in dilute solution which determined the molecular weight of the PIB fraction.

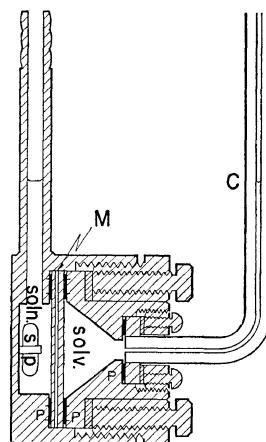


Figure 1. Schematic diagram of high-pressure osmotic cell: soln., solution room; Solv., solvent room; C, capillary; M, semipermeable membrane; lead or poly(tetrafluoroethylene) packing.

The osmotic pressure at the concentrated region became higher than 1 atm. Hence an osmotic cell was newly designed (Figure 1). The cell consisted of a solution room (soln) and a solvent room (solv) divided by a semipermeable membrane (M) which was held between two perforated brass plates. In the solution room a stirring piece (SP) was inserted in order to avoid the heterogeneity of concentration within the cell. The solvent room was connected to the glass capillary (C) in order to measure the permeation rate of the solvent. The connecting parts of the cell were sealed by poly(tetrafluoroethylene) or lead and bolted up. An ultracellafilter was used as the semipermeable membrane.

After the solution was put into the cell through a pipe standing on the upper part of the cell, the pipe was connected to a mercury monometer. Then the cell was steeped in a water bath of which the temperature was regulated to $\pm 0.01^\circ\text{C}$. A pressure as high as the expected value of the osmotic pressure was applied to the solution. The stirring piece in the solution room was rotated by a magnetic stirrer located outside the cell. In order to obtain homogeneity in temperature and concentration, the cell was kept in this condition for two or three hours before measurements. The osmotic pressure of the solution was determined by interpolation of applied pressure to the vanishing meniscus movement in

Table I. V^* and \tilde{V} of the pure components

Materials		0°C	20°C	40°C	60°C
<i>n</i> -Pentane	$V^*(\text{ml/mol})$	85.14	85.46		
	\tilde{V}	1.313	1.348		
<i>n</i> -Hexane	V^*	99.62	99.52	99.63	
	\tilde{V}	1.278	1.313	1.349	
<i>n</i> -Heptane	V^*	112.7	113.5	114.2	114.8
	\tilde{V}	1.270	1.292	1.318	1.347
PIB	$V^* \times 10^{-4}$	94.06	94.48	94.72	94.73
	\tilde{V}	1.137	1.147	1.154	1.167

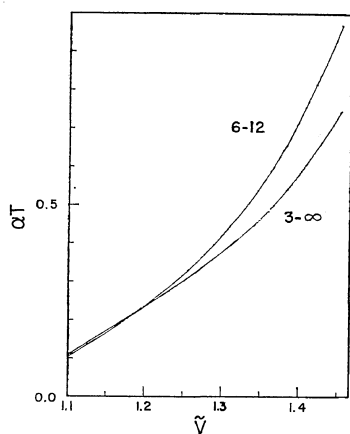


Figure 2. The curves of αT vs. \tilde{V} . The curves 3— ∞ and 6—12 were calculated by substituting 3— ∞ and 6—12, respectively, for m — n in eq 3.

the capillary (C).

After the measurement of osmotic pressure, the solution was removed to a weighing bottle. The weight fraction of the solute was determined by a drying method. The segment fraction of solute ϕ was calculated from the weight fraction using the following equation,

$$\phi = x_2 V_2^* / (x_1 V_1^* + x_2 V_2^*) \quad (8)$$

where x_s are molar fractions. The values V^* of pure components were determined from density data^{21,24} through Figure 2 and eq 1 with the assumption $m=3$, $n=\infty$, and are listed in Table I with \tilde{V} which is the most direct measure of the free volume.

ANALYSIS OF EXPERIMENTAL RESULTS

Because of high osmotic pressure, to discuss

these data as an example of the solution theory it is necessary to ascertain that the values of osmotic pressure in this concentration region are also the measures of the chemical potential of mixing. In terms of the thermodynamics, the condition for equilibrium which was realized between pure solvent and solution with a difference of external pressure is, in general,

$$\mu_1^0(T, P) = \mu_1(T, P + \pi, x)$$

where μ_1^0 and μ_1 are the chemical potentials of the solvent, P and $P + \pi$ are the external pressure in pure solvent and solution, respectively; T is the temperature, and x is the molar fraction of the solute. Carrying out a series expansion of μ_1 in powers of π around P , the condition for equilibrium becomes

$$\Delta\mu_1(T, P, x) = -\pi \bar{V}_1 + \frac{1}{2} \bar{\beta}_1 \bar{V}_1 \pi^2 + \dots$$

where $\Delta\mu_1$ is a difference of chemical potential between solution and solvent under the same external pressure, \bar{V}_1 is the partial molar volume of the solvent, and $\bar{\beta}_1$ is the partial compressibility of the solvent. The compressibility of ordinary pure organic solvents is less than 10^{-4} atm⁻¹, and $\bar{\beta}_1$ must be very similar to them, so that the second term is negligible as compared with the first term. As a consequence, $\pi \bar{V}_1$ in this concentration region is also regarded as a chemical potential of mixing.

According to the Flory—Huggins equation the chemical potential of mixing in a moderately concentrated polymer solution is expressed as,^{1,25}

$$\Delta\mu_1 = RT[\ln(1-\phi) + (1-1/r)\phi + \chi\phi^2] \quad (9)$$

where r is the ratio of molar characteristic volume of polymer to that of solvent and χ is the residual chemical potential parameter. Here, $-\pi \bar{V}_1$ being

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 Table II. Osmotic pressure and χ parameter

Solvents	Temp, °C	w_2^a	ϕ	π , g cm ⁻²	χ
<i>n</i> -Pentane	0	0.1031	0.08449	53.7	0.5042
		0.1323	0.1091	89.3	0.5116
		0.1713	0.1424	151.5	0.5232
		0.1965	0.1642	219.8	0.5285
		0.2284	0.1922	334.7	0.5359
		0.2534	0.2144	432.9	0.5440
		0.09976	0.08152	49.9	0.5028
	20	0.1411	0.1163	96.9	0.5169
		0.1681	0.1393	143.3	0.5240
		0.1861	0.1548	183.1	0.5286
		0.2142	0.1792	239.7	0.5395
		0.2304	0.1934	299.6	0.5431
		0.2584	0.2182	406.7	0.5516
		0.08490	0.07059	72.4	0.4599
<i>n</i> -Hexane	0	0.1211	0.1014	148.5	0.4673
		0.1394	0.1171	204.6	0.4696
		0.1612	0.1361	282.3	0.4744
		0.1951	0.1656	446.7	0.4798
		0.2130	0.1814	553.9	0.4832
		0.08579	0.07157	70.8	0.4671
		0.1194	0.1002	142.7	0.4719
	20	0.1468	0.1239	226.8	0.4761
		0.1696	0.1437	314.7	0.4808
		0.1982	0.1688	453.0	0.4869
		0.2251	0.1926	585.2	0.4976
		0.08670	0.07245	77.9	0.4647
		0.1254	0.1055	153.5	0.4782
		0.1495	0.1263	222.9	0.4840
<i>n</i> -Heptane	0	0.1722	0.1461	312.3	0.4878
		0.2023	0.1727	451.2	0.4955
		0.2299	0.1972	615.6	0.4978
		0.09972	0.08527	98.1	0.4608
		0.1365	0.1174	171.2	0.4742
		0.1682	0.1454	295.4	0.4761
		0.2020	0.1756	445.5	0.4850
	20	0.2287	0.1997	584.0	0.4941
		0.09735	0.08284	90.0	0.4663
		0.1318	0.1128	171.4	0.4722
		0.1625	0.1398	277.3	0.4769
		0.1972	0.1706	418.5	0.4873
		0.2192	0.1904	550.3	0.4908
		0.2282	0.1985	586.6	0.4960
40	0.2534	0.2213	776.9	0.5004	
	0.2880	0.2530	1075	0.5093	
	0.1128	0.09589	112	0.4777	
	0.1347	0.1150	177.0	0.4763	
	0.1653	0.1418	276.6	0.4833	
	0.1928	0.1663	398.8	0.4887	
	0.2203	0.1908	550.7	0.4980	
	0.2494	0.2171	757.7	0.5010	
	60	0.09113	0.07704	79.6	0.4693
		0.1205	0.1024	112	0.4904
		0.1270	0.1080	155.7	0.4772
		0.1587	0.1357	255.2	0.4833
		0.1853	0.1592	359.8	0.4899
		0.2167	0.1872	520.9	0.4976
0.2430		0.2109	698.1	0.5033	
0.2799	0.2445	986.9	0.5140		

^a w_2 is the weight fraction of solute.

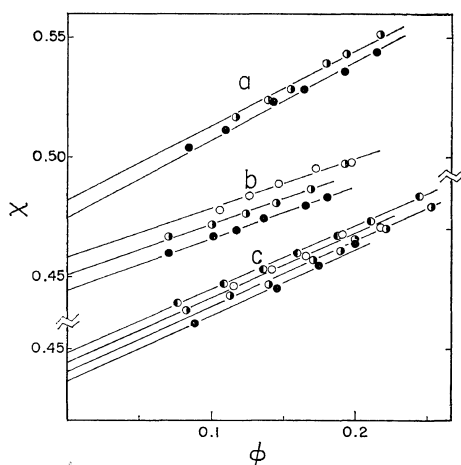


Figure 3. Plots of χ vs. ϕ : a, PIB-*n*-pentane; b, PIB-*n*-hexane; c, PIB-*n*-heptane; ●, 0°C; ○, 20°C; ◐, 40°C; ◑, 60°C.

taken as $\Delta\mu_1$, parameter χ can be calculated from measured values of π and ϕ as

$$\chi = \phi^{-2} [-\pi \bar{V}_1 / RT - \ln(1-\phi) - (1-1/r)\phi] \quad (10)$$

The χ values of PIB-*n*-alkanes at various temperatures and various concentrations are listed in Table II. Figure 3 shows the plots of χ vs. ϕ ; PIB solutions in *n*-hexane at 0 and 20°C (a), in *n*-hexane at 0, 20, and 40°C (b), and in *n*-heptane at 0, 20, 40, and 60°C (c). Previously we verified that the extrapolation to infinite dilution of the plots of χ at θ temperature falls to 0.50 for the poly(dimethylsiloxane) solution of methyl ethyl ketone at 20°C. This is consistent with the prediction that the second virial coefficient vanishes at θ temperature. This was also shown by Flory, *et al.*²⁹ It suggests that an extensively significant value of χ_1 which contri-

butes to the second virial coefficient can be obtained by the linear extrapolation of the χ value from this concentration region to infinite dilution; *i.e.*, χ can be approximately expressed as

$$\chi = \chi_1 + \chi_2 \phi$$

The residual chemical potential parameter at infinite dilution χ_1 may be divided into enthalpy terms and entropy terms; then

$$\chi_1 = \chi_{H1} + \chi_{S1}$$

According to the Flory terminology¹ χ_{H1} and χ_{S1} are called κ_1 and $1/2 - \phi_1$, respectively. By obtaining the χ_1 value at a different temperature for a polymer-solvent system, parameters χ_{H1} and χ_{S1} of this system can be estimated from Flory's relation. Table III shows χ_1 values of PIB in each solvent and at each temperature, and χ_{H1} and χ_{S1} values of each system at 20°C.

DISCUSSION

In all the systems examined in this work, χ_1 is increasing with temperature. The systems are exothermic, with negative values for χ_{H1} in contradiction to usual polymer-solvent systems. On the other hand, χ_1 decreases with increasing chain length of the solvent molecule in spite of the expectation that segments of each solvent have identical chemical natures. χ_{S1} is positive for all the systems as shown in Table III. Although positive values of χ_{S1} are very usual for many polymer-solvent systems,¹⁵ this means that the residual entropy of dilution is negative, *i.e.*, as the solution is diluted there is actually an ordering of the system.

Table III. Values of χ_1 at various temperatures, χ_{H1} and χ_{S1} at 20°C

Solvent	Temp, °C,	χ_1	χ_{H1}	χ_{S1}
<i>n</i> -Pentane	0	0.4750		
	20	0.4825	-0.103	0.585
<i>n</i> -Hexane	0	0.4445		
	20	0.4510	-0.104	0.555
	40	0.4585		
<i>n</i> -Heptane	0	0.4366		
	20	0.4405	-0.052	0.502
	40	0.4445		
	60	0.4485		

Table IV. Molecular parameters A and B for PIB- n -alkane systems obtained from this work in comparison with other experiments

Method	A , cal/mol	$B \times 10^3$, cal/mol deg ²
This work	26.4	7.05
ΔH_M	10.1	6.0
Swelling	20.2	10.1
Viscosity	22.0	8.9
Pure alkanes	—	8.4
L.C.S.T.	—	8.2

From Tables I and III it can be found that the χ_1 value increases with increasing \bar{V}_1 in each solvent and decreases with increasing chain length of the solvent at fixed temperatures. This behavior can be expected from eq 6 at the region where (T/r_1) is sufficiently large and the temperature dependence of the free volume dissimilarity term $B(T/r_1)$ is larger than that of the interaction term $A(T/r_1)^{-1}$. Applying eq 6 to our results observed from the variations of both T and r_1 , most appropriate values of A and B for PIB- n -alkane systems were obtained. Table IV shows the values of A and B estimated from this work in comparison with corresponding values obtained from other kinds of experiments by Patterson, *et al.*⁶ Values of r_1 were determined as $r_1 = (n_1 + 1)/2$, where n_1 is the number of carbon atoms of n -alkanes. For the B value, our result approximately agrees with those of other workers. However, our A value is larger than what we expected. We thought that it would be small because of the smallness of cohesive energy dissimilarity between the polymer segment and solvent molecules, and agrees with the A values obtained from swelling or viscosity rather than those from the heat of mixing. Although the radius of gyration is closely related to intersegmental interaction, the theories which are necessary to connect it with the actual χ_1 value are logically obscure.³⁰⁻³² The plot of experimental values for χ_1 vs. T/r_1 is shown in Figure 4. The curve was drawn by using $A=26.4$ cal/mol and $B=7.05 \times 10^{-3}$ cal/mol deg² from eq 6. In spite of including the rough approximation, eq 6 explains the experimental results. The critical condition for the polymer solution of infinite molecular weight can be ob-

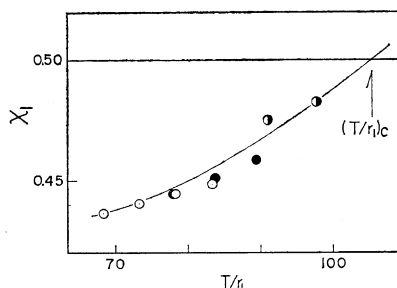


Figure 4. Plots of χ_1 vs. T/r_1 : \circ , PIB- n -heptane; \bullet , PIB- n -hexane; \ominus , PIB- n -pentane. The full curve was deduced from eq 6 by substituting $A=26.4$ cal/mol and $B=7.05 \times 10^{-3}$ cal/mol deg².

tained by substituting $\chi_1=1/2$ in eq 6, with the assumption that the coordination number closes to infinity as with Flory's temperature.⁸ $(T/r_1)_c$ value of our result was obtained as 100 deg per element. It is possible to predict theoretically the values of L.C.S.T. for any PIB- n -alkane system from this value of $(T/r_1)_c$ by substituting corresponding chain length r_1 . It is already known, however, that L.C.S.T. of homologous solvent systems are not proportional to the chain length of the solvent.⁹ Hence, we tried to predict the values of L.C.S.T. for the solvents which are near in chain length to the solvents used in the measurements. Table V shows the predicted values of L.C.S.T. for n -pentane to n -octane compared with the values observed by Patterson.⁹ They are in comparatively good agreement with each other for corresponding systems.

On the other hand, the temperature dependence of χ_1 was obtained for the PIB- n -heptane system using Flory's expression, eq 7. Whereas Flory, *et al.*, used the crystallographic method to determine s_2/s_1 value,²³ we chose a method to determine it from thermodynamic quantities only. In

Table V. Values of L.C.S.T. for PIB- n -alkane systems predicted from this work and observed by Patterson, *et al.*

Solvent	Predicted from A and B	Observed
n -Pentane	43.2°C	73
n -Hexane	95.9	129
n -Heptane	149	174
n -Octane	201	212

terms of Flory's theory,^{23,25} the enthalpy of mixing in the limit of an infinite dilution becomes

$$\begin{aligned} \Delta H_M^\infty = & (N_2 V_2^* / \tilde{V}_1) \{ P_1^* [(\tilde{V}_1 / \tilde{V}_2) \\ & - 1 - \alpha_1 T (1 - T_1^* / T_2^*)] \\ & + (1 + \alpha_1 T) (s_2 / s_1) X_{12} \} \end{aligned} \quad (11)$$

and

$$X_{12} = P_1^* [1 - (s_1 / s_2)^{1/2} (P_2^* / P_1^*)^{1/2}] \quad (12)$$

Using eq 11, the value of $(s_2 / s_1) X_{12}$ was calculated from the calorimetric results at 25°C reported by Delmas, *et al.*,⁶ (original of ΔH_M in Table IV), and s_2 / s_1 was determined from eq 12. By assuming that the s_2 / s_1 value is constant at various temperatures, the χ_1 value of the PIB-*n*-heptane system at various temperatures was calculated from eq 7. The behaviour of the χ_1 value against the varying temperature is shown in Figure 5 in comparison with our experimental results. Although the full curve calculated from eq 7 is too large and exceeds the critical value $\chi_1 = 1/2$, it agrees on temperature dependence with experimental results. The same discrepancy between experimental and calculated values of χ_1 had been found by Flory, *et al.*, for the PIB-*n*-pentane system at 25°C.²⁸ Even if the approximation in eq 7 is taken into account, eq 7 was deduced only from the configurational energy by neglecting the contribution from the cell partition function and the end effect of the chains. This discrepancy should not be ignored together with the disagreement between the values *A*, *B* from osmotic

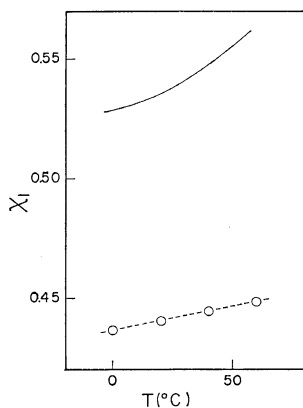


Figure 5. Temperature dependence of χ_1 for PIB-*n*-heptane system. Circles represent experimental results, and full curve was calculated from eq 7.

pressure, and those from heat of dilution in Table IV.

Although the quantitative consistency among thermodynamic quantities experimentally observed from different methods has not yet been accomplished, it is possible to explain many thermodynamical features of polymer solutions by the cell (or free volume) theory. Especially, the possibility of prediction for volume change on mixing (excess volume) and L.C.S.T. must be significant, since the traditional lattice theory is insufficient for them. Patterson, *et al.*, first applied the cell theory to L.C.S.T.^{6,9,10} and Flory, *et al.*, applied it to excess volume.^{17,19-23,25,26} It seems that the temperature dependence of χ_1 obtained from the present work for polymer solutions in different sized solvents supports the cell theory.

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