

Thermodynamic Properties of Atactic Polypropylene Solutions

Hiroshi OCHIAI,* Toshihiko OHASHI,* Yuji TADOKORO,**
and Ichiro MURAKAMI*

*Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730, Japan.

**Chemistry Laboratory, Faculty of Integrated Arts and Sciences,
Hiroshima University, Higashisenda-machi,
Naka-ku, Hiroshima 730, Japan.

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ABSTRACT: The heats of mixing of atactic polypropylene at infinite dilution were measured at 25°C in linear alkanes, aromatic hydrocarbons, cyclohexane, chloroform, and carbon tetrachloride. For some solvent systems excess volume and chemical potential measurements were also performed at 25°C. The results were treated by the new Flory theory for polymer solutions. The exchange interaction parameter X_{12} increases with an increase in the chain length of *n*-alkanes and decreases with the introduction of aliphatic groups into benzene. These changes can be interpreted well in terms of the difference in force field between methyl–methylene contacts or aliphatic–aromatic contacts. The observed excess volumes are negative for *n*-alkanes and positive for rather globular cyclohexane, chloroform, carbon tetrachloride, and benzene, which is consistent with the prediction by the theory. However, the calculated excess volumes are less than those observed for all systems studied. Agreement between experimental and theoretical χ -parameters can be achieved by the introduction of the exchange entropy parameter Q_{12} and adjusting the contact surface ratio (s_2/s_1).

KEY WORDS Thermodynamics / Polypropylene / Exchange Interaction
Parameter / Heats of Mixing / Excess Volume / χ -Parameter /

The concentration dependence of the χ -parameter, lower critical solution temperature (LCST), volume change and exothermic heat of mixing of polymer solutions were beyond the scope of conventional polymer solution theories. Thermodynamic theories based on the free volume concept have enabled us to explain these interesting and unsolved problems. Patterson *et al.*^{1,2} succeeded in explaining the LCST phenomenon by applying the cell model to polymer solutions. Flory *et al.*^{3,4} also proposed a new theory applicable to various non-polar polymer solutions, and explained the concentration dependence of the χ -parameter and volume change on mixing. Both theories emphasize the importance of the effects of the pure component properties on the solution properties, *e.g.*, the differences in “free volume” and “force field” between polymer and solvent. The former difference gives an exothermic effect to the heat of mixing and the latter gives an endothermic effect.

Atactic polypropylene (APP) is a non-polar amorphous polymer and is of interest from the stand point of polymer solution property analysis, similar to polyisobutylene (PIB). However, the thermodynamic properties of APP solution have so far received little attention.^{5,6} In the present study, the heats of mixing, excess volume and vapor pressure measurements were carried out at 25°C for the APP–various solvent systems, and the results are discussed on the basis of the new Flory theory.

EXPERIMENTAL

Materials

Atactic polypropylene (APP) was obtained as an ether soluble material of conventional polypropylene and provided by Sumitomo Chemicals Industries Ltd. The polymer was made into three crude fractions using benzene–methanol solutions. The middle fraction was repeatedly purified by

precipitation and recovered by freeze-drying from a benzene solution. The molecular weight estimated from intrinsic viscosity was about 1.8×10^4 .

The solvents used here were six linear alkanes (n -C₅- n -C₁₀), six aromatic hydrocarbons (benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylenes), cyclohexane, chloroform, and carbon tetrachloride. All the solvents were purified by ordinary methods prior to use.

Measurements

Solvent activity was measured by vapor sorption using apparatus similar to that of Tait.⁷ Accuracy was within ± 0.1 mmHg for vapor pressure and ± 0.5 mg for solvent uptake.

Heats of mixing at infinite dilution were determined by a twin-type conduction microcalorimeter (Tokyo-Riko), which is well suited for the measurement of slow thermal effects such as polymer dissolution. Five to ten runs were made, and the experimental values of h_∞^E expressed in J g^{-1} were averaged. Average deviations were $\pm 5\%$ for the largest heats and $\pm 10\%$ for the smallest heats.

Excess volume was estimated from the density values of mixtures measured with a glass pycnometer, consisting of a bulb of sufficient volume (about 10 ml) and a calibrated capillary (20 cm long and 0.8 mm in diameter). Accuracy was about 2×10^{-4} g ml^{-1} .

Theory

According to the new Flory theory, the equation-of-state for a pure liquid and mixture, expressed in its reduced form, is given by,

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

The heat of mixing per gram of polymer at infinite dilution is,

$$h_\infty^E = P_2^* v_2^* [(\tilde{v}_2^{-1} - \tilde{v}_1^{-1}) - \alpha_1 T/\tilde{v}_1(1 - T_1^*/T_2^*)] + (s_2/s_1)(v_2^*/\tilde{v}_1)X_{12}(1 + \alpha_1 T) \quad (2)$$

The χ -parameter and excess volume of mixing are given as follows:

$$\begin{aligned} (\mu_1 - \mu_1^0)^R &= RT\varphi_2^2\chi \\ &= P_1^* V_1^* \{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \\ &\quad + (\tilde{v}_1^{-1} + \tilde{v}^{-1})\} + V_1^* X_{12} \theta_2^2/\tilde{v} \end{aligned} \quad (3)$$

$$\tilde{v}^E = \tilde{v} - \tilde{v}^0, \quad \tilde{v}^E/\tilde{v}^0 = \Delta v/v^0 \quad (4)$$

where

$$\tilde{v}^0 = \varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2 \quad (5)$$

The reduced volume \tilde{v} at a given composition is obtained as the solution of eq 1 for $p=0$, using the reduced temperature \tilde{T} for the mixture:

$$\tilde{T} = (\varphi_1 P_1^* \tilde{T}_1 + \varphi_2 P_2^* \tilde{T}_2) / (\varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12}) \quad (6)$$

In these equations, the subscripts 1 and 2 express the solvent and polymer components, respectively. The tiled variables \tilde{v} , \tilde{P} , and \tilde{T} are defined as $\tilde{v} = v/v^*$, $\tilde{P} = P/P^*$, and $\tilde{T} = T/T^*$ where v^* , P^* , and T^* are the respective reduction parameters. The symbol s is the number of contact sites per segment (proportional to the surface area per segment), α is the thermal expansion coefficient, X_{12} is the exchange interaction parameter related to the difference in force field between solvent and polymer. φ and θ are the segment fraction and the surface fraction, respectively.

The reduction parameters v^* , P^* , and T^* for APP and solvents were evaluated from the density, thermal expansion coefficient and thermal pressure coefficient in their pure state (Table I). The necessary data were obtained from ref 5 and 8 for APP, and in ref 9, 10, and 11 for solvents. The values of s was estimated from the ratio of surface area-to-

Table I. Equation-of-state parameters for pure components at 25°C

Component	v^*	T^*	P^*	S
	$\text{cm}^3 \text{g}^{-1}$	K	J cm^{-3}	A^{-1}
Polypropylene	0.9661	5930	468.8	0.64
<i>n</i> -Pentane	1.1829	4158	406.4	1.08
<i>n</i> -Hexane	1.1559	4445	423.6	1.04
<i>n</i> -Heptane	1.1346	4654	429.0	1.01
<i>n</i> -Octane	1.1180	4826	433.2	0.99
<i>n</i> -Nonane	1.1072	4993	435.3	0.98
<i>n</i> -Decane	1.0944	5095	445.8	0.95
Cyclohexane	1.0012	4720	531.6	0.93
Benzene	0.8860	4709	627.8	0.99
Toluene	0.9784	5025	560.9	0.91
Ethylbenzene	0.9806	5202	540.0	0.87
<i>o</i> -Xylene	0.9731	5342	540.0	0.87
<i>m</i> -Xylene	0.9872	5267	540.0	0.87
<i>p</i> -Xylene	0.9872	5194	531.6	0.87
CHCl ₃	0.5197	4625	565.0	0.97
CCl ₄	0.4890	4720	564.0	1.03

volume, assuming right cylinders for *n*-alkanes and spheres for other solvents. The APP chain was similarly treated as a cylinder having a crystallographic repeating length of 6.5×10^{-8} cm for three monomer units¹² and a radius of 3.15×10^{-8} cm, as required by the characteristic molar volume V_2^* .

RESULTS AND DISCUSSION

Heats of Mixing and the X_{12} -Parameter

The heats of mixing of APP at infinite dilution, h_{∞}^E , in various solvents are listed in Table II. All the heats are positive except for *n*-pentane and *n*-hexane. These results can be visualized by plotting the observed h_{∞}^E -values against the carbon atom number of each solvent, as in Figure 1, where the values for CHCl_3 and CCl_4 have been inserted in the empty space of the figure. For the linear alkanes, the h_{∞}^E -values are very small, as expected in view of the similarity of solute and solvent. A regular increase in heat is observed as the solvent chain length increases. The heats which are initially exothermic become endothermic for longer alkanes. Similar trends have been observed for various bulk polymers including APP in linear alkanes.^{1,5,13-15} However, for the aromatic solvents, the h_{∞}^E -values are very large and decrease with the introduction of

aliphatic groups into benzene, suggesting that the interactions with APP are appreciably different in linear alkanes and aromatics. For cyclohexane, CHCl_3 and CCl_4 , the heats exhibit the intermediate values of the above homologs.

According to the free volume theory, the experimental h_{∞}^E arises from two contributions: the equation-of-state contribution, the first term on the right-hand side of eq 2, originating from the difference in free volume or thermal expansibility between polymer and solvent, and the interaction contribution including the X_{12} -parameter, the second term, arising from the difference in force field. The X_{12} -parameter can be obtained by fitting the experimental h_{∞}^E to eq 2. Table II lists the values of h_{∞}^E , the equation-of-state term $f(\alpha, \bar{v})$, the interaction term $g(X_{12})$ and the X_{12} -parameter. The equation-of-state term is negative for all solvents. Especially for the linear alkane systems, the observed change in the h_{∞}^E -value with increasing the chain

Table II. Heats of mixing at infinite dilution of atactic polypropylene at 25°C

Solvent	h_{∞}^E	$f(\alpha, \bar{v})^a$	$g(X_{12})^a$	X_{12}
	J g ⁻¹	J g ⁻¹	J g ⁻¹	J cm ⁻³
<i>n</i> -Pentane	-4.7	-5.2	0.5	0.8
<i>n</i> -Hexane	-1.4	-2.8	1.4	2.3
<i>n</i> -Heptane	0.5	-1.8	2.3	3.5
<i>n</i> -Octane	1.0	-1.2	2.2	3.3
<i>n</i> -Nonane	2.4	-0.8	3.3	5.0
<i>n</i> -Decane	3.1	-0.6	3.7	5.5
Cyclohexane	3.9	-1.6	5.4	7.8
Benzene	30.8	-1.6	32.4	49.9
Toluene	16.5	-0.7	17.2	24.4
Ethylbenzene	14.2	-0.4	14.7	20.0
<i>o</i> -Xylene	13.4	-0.3	13.7	18.7
<i>m</i> -Xylene	12.3	-0.3	12.6	17.3
<i>p</i> -Xylene	10.3	-0.4	10.7	13.9
CHCl_3	17.2	-1.9	19.1	28.5
CCl_4	6.6	-1.5	8.1	12.8

^a $f(\alpha, \bar{v})$ and $g(X_{12})$ show the first and second terms of the right-handed side of eq 2. $h_{\infty}^E = f(\alpha, \bar{v}) + g(X_{12})$.

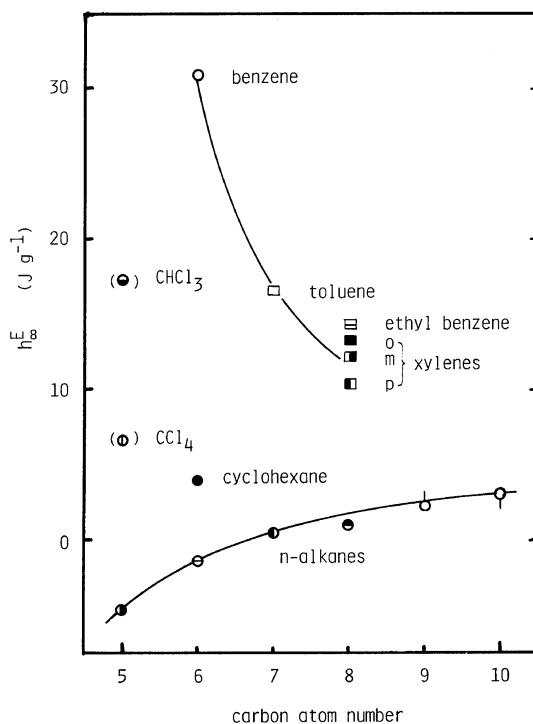


Figure 1. Heats of solution of APP at infinite dilution as a function of the carbon atom number of the solvent. The abscissa scale for CHCl_3 and CCl_4 is arbitrary. Symbols for solvents are the same as those appearing in Figures 1 to 5.

length can be explained as the gradual disappearance of the exothermic contribution toward the heat, leaving only the positive contribution for longer alkanes. But for the aromatic systems, the free volume contribution is minor and the major contribution is the interaction term. For the cyclohexane, CCl_4 , and benzene systems, the equation-of-state terms are nearly equal to each other ($\sim -1.6 \text{ J g}^{-1}$), and therefore the difference in the heats may be ascribed mainly to the force field difference between APP and each solvent component.

As with the h_{∞}^E -value, the X_{12} -value increases with increasing chain length and decreases by introducing aliphatic groups into benzene. The dependence of the X_{12} -value on solvent properties has been examined by many authors. For alkane mixtures, although there are some difficulties, this dependence is generally ascribed to the small difference in the force field surrounding the methyl-end groups and the methylene interior groups of the components.¹⁶⁻¹⁸ In the present systems also; it seems relevant to discuss the dependence of X_{12} in terms of the methyl-methylene and aliphatic-aromatic contacts. Thus the present X_{12} -values are plotted against the methyl surface fraction of solvent for the alkane series (Figure 2a), and against the aromatic surface fraction for the aromatic series (Figure 2b). The methyl and aromatic surface fractions can be evaluated from the tabulation by Bondi.¹⁹ The present scale of the abscissa seems more reasonable than the carbon atom or segment numbers of solvent molecules, since the number of contacts on mixing will be in proportion to the surface area of each component.

As can be seen from Figure 2, the plots are smooth for both the alkane and aromatic series, which incur a gradual change in force field surrounding the polymer segments. For the aromatic series, the introduction of aliphatic substituents on benzene greatly reduces the X_{12} -value as well as the heat of mixing. This suggests that the contact interchange of an aromatic ring with APP is very large, and that the X_{12} -value for more highly substituted benzene will approach a value comparable to that for alkanes. In the case of the alkane series, the X_{12} -value increases with a decrease the methyl surface fraction (or increasing the chain length). A smoothed extrapolation to the same methyl surface fraction as that of APP (\downarrow APP) gives a value of X_{12}

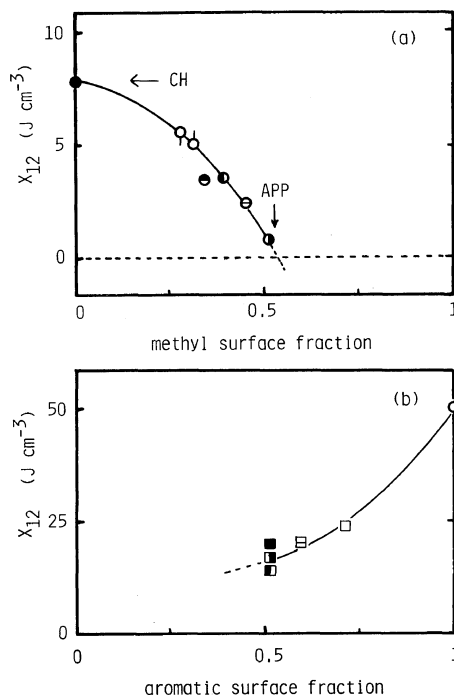


Figure 2. The dependence of X_{12} on (a) the methyl surface fraction and (b) the aromatic surface fraction of solvent. \leftarrow CH and \downarrow APP signify extrapolations to the same methyl surface fractions as cyclohexane and polypropylene, respectively.

equal nearly zero. Another extrapolation to a very long polymethylene chain gives a value of X_{12} corresponding to that of cyclohexane (\leftarrow CH) which consists of all methylene segments, although cyclohexane is not linear. From these extrapolations of X_{12} for the methyl surface fraction, some interesting conclusions can be deduced: i) the X_{12} -value will be practically zero for mixtures in which the solvent has the same contact surface as that of the polymer, ii) the methyl contacts with APP make an appreciable negative contribution to the X_{12} -value, while the methylene contacts contribute positively. In fact, Delmas *et al.*⁵ found in their calorimetric studies for the APP-alkane systems that the X_{12} -value is rather negative for the branched alkanes having a methyl surface fraction higher than the corresponding linear alkanes and APP itself. For PIB-*n*-alkane systems similar to the present systems, however, the dependence of X_{12} on the chain length shows as opposite trend, the X_{12} -value is

larger for shorter alkanes, though the h_{∞}^E -value increases with increasing chain length, as in the case of the APP systems.^{5,13,14} This is considered due to an overestimation of the equation-of-state term, where the calculated value of $f(\bar{v}, \alpha)$ is appreciably negative due to a large difference in expansibility between shorter alkanes and PIB [$\alpha(\text{PIB}) = 5.55 \times 10^{-4} \text{ K}^{-1}$, while $\alpha(\text{APP}) = 8.06 \times 10^{-4} \text{ K}^{-1}$].⁵

Excess Volume of Mixing

Density measurements were carried out for mixtures of APP with various solvents which were three linear alkanes (*n*-pentane, *n*-hexane, *n*-heptane) and four rather globular solvents (cyclohexane, CCl_4 , CHCl_3 , benzene). The excess volumes $\Delta v/v^0$ are shown in Figure 3 as functions of composition. For the linear alkanes, the excess volumes are negative and the absolute values decrease with increasing chain length. Similar volume changes have been found for the PIB-linear alkane systems.¹³ For rather globular solvents, the excess volumes are positive and increase in order of cyclohexane < CCl_4 < CHCl_3 < benzene. The theoretical dependence of the excess volume on composition was

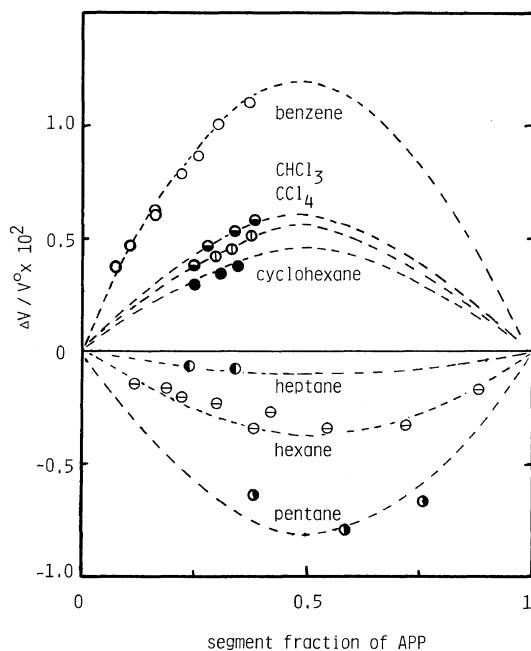


Figure 3. Excess volumes of mixing as functions of the segment fraction of APP. The dashed curves are drawn through the experimental points.

calculated for each system, using eq 4–6 and the corresponding X_{12} -value listed in Table II. The theory correctly predicts the sign of the excess volume, which is negative for the linear alkanes and positive for the globular solvents, in agreement with observation. However, the magnitude of the theoretical value was negatively overestimated for the linear alkanes, and positively underestimated for the globular solvents (see Figure 4). Since the excess volume is not sensitive to the X_{12} -value, improvement in the theoretical value is very difficult, using only a small change in X_{12} . For example, if we tried to fit the theoretical value to that observed, a very large value of X_{12} would be necessary: 17~25 J cm^{-3} for linear alkanes; 35 for cyclohexane; 30 for CCl_4 ; 80 for benzene. For various polymer solutions, it has been reported that the prediction of the excess volume by the X_{12} -value determined from the heat of mixing is poor.^{13,15,20–23}

Generally, the volume change on mixing has been interpreted in terms of the difference in free volume between polymer and solvent; this difference arises mainly from the difference in the respective reduced volumes or thermal expansion coefficients. In fact, in the present APP-linear alkane systems, a good correlation was observed between the observed excess volume and the difference in the reduced volumes of APP and solvent alkane, *i.e.*, the larger difference in the reduced volume leads to a more negative excess volume. It seems that in these systems, a closer fitting of solvent molecules to the polymer chain can be easily attained by an effective utilization of the large free volume difference. On the other hand, in rather globular solvent systems, in which the solvents have similar reduced volumes or thermal expansion coefficients, this interpretation is not suitable; the observed excess volume increases in order of cyclohexane < CCl_4 < CHCl_3 < benzene. This means that there is a contribution to the volume change other than that of the free volume difference. In this regard, it is of interest that both the theoretical and observed excess volumes have a rather good correlation with the h_{∞}^E - or X_{12} -values for all the solvent systems studied. In Figure 4, the excess volumes interpolated to $\phi_2 = 0.5$ are plotted against the logarithm of X_{12} . The plots exhibit nearly linear and parallel relations in both experiment and theory, though as mentioned before the discrepancy between them is large. We can easily see the change in the excess volume from negative to

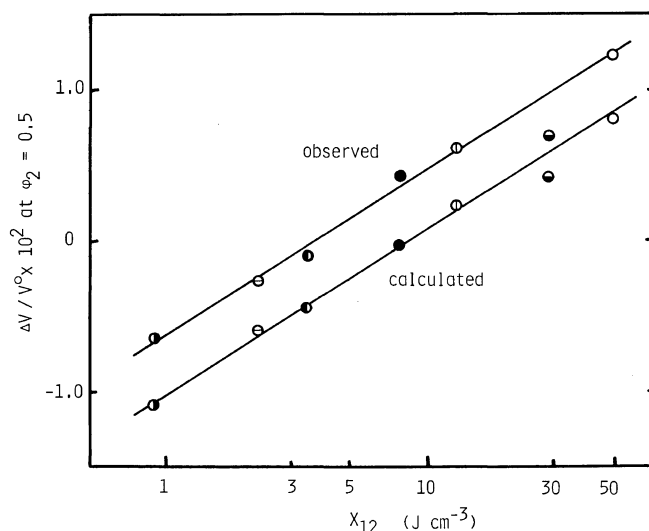


Figure 4. Relation between the excess volume interpolated at $\phi_2=0.5$ and the X_{12} -value determined from the heat of mixing.

positive on increasing the X_{12} -value. This means that, although the excess volume is not very sensitive to the X_{12} -values, the theory does to a certain extent reflect the effect of the force field difference on the excess volume through \tilde{T} including X_{12} (eq 6). However, at the present, we can give no reasonable interpretation for the large discrepancy between theoretical and experimental excess volumes.

The χ -Parameter

The χ -parameter was determined from the vapor sorption experiments for five solvent systems (*n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, and benzene), using the familiar Flory–Huggins equation. The segment fraction was used instead of the usual volume fraction. Figure 5 shows the results for the *n*-hexane, cyclohexane, and benzene systems. The results for *n*-pentane and *n*-heptane (not shown in the figure) are similar to those for *n*-hexane except that the χ -parameters are very slightly smaller for longer alkanes. The calculated χ -parameters were obtained using eq 3, the corresponding equation-of-state parameters and the X_{12} -value determined from the heats of mixing ($Q_{12}=0$ in Table III). The results are shown by the dotted lines in the figure. Agreement between calculation and experiment was not very good in any of the systems studied nor in cases of excess volume. For linear alkanes and

cyclohexane, the calculated values exhibit a somewhat smaller concentration dependence of the χ -

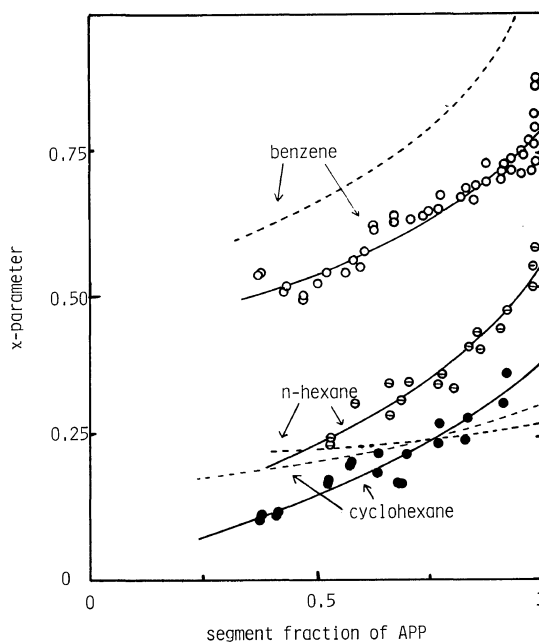


Figure 5. The χ -parameter as a function of segment fraction of APP. The solid curves are described by eq 3 with the values listed in Table III (see text). The dashed curves are calculated by theory with $Q_{12}=0$.

Table III. Exchange interaction parameters

Solvent	$Q_{12}=0$		Best fit		
	X_{12}	s_2/s_1	X_{12}	Q_{12}	s_2/s_1
	J cm^{-3}		J cm^{-3}	$\text{J cm}^{-3} \text{K}^{-1}$	
<i>n</i> -Pentane	0.8	0.59	1.26	-0.021	0.40
<i>n</i> -Hexane	2.3	0.61	3.47	-0.021	0.40
<i>n</i> -Heptane	3.5	0.63	5.27	-0.025	0.42
Cyclohexane	7.8	0.68	11.3	-0.004	0.54
Benzene	49.9	0.65	43.5	+0.033	0.73

parameter than that observed. For benzene, the theory correctly predicts the concentration dependence of the χ -parameter, but overestimates the magnitude.

Following Flory^{4,13} we introduced a correction parameter Q_{12} into the X_{12} term of eq 3 as $(X_{12} - \bar{v}TQ_{12})$, where X_{12} represents the exchange enthalpy parameter and Q_{12} implies the corresponding entropy parameter. Calculations using only the Q_{12} parameter did not reproduce the observed concentration dependence of the χ -parameter. Thus, it was necessary to adjust the ratio (s_2/s_1) , since the dependence of χ on composition is very sensitive to (s_2/s_1) owing to the change in the site fraction $\theta_2 = \varphi_2(s_2/s_1)/[\varphi_1 + \varphi_2(s_2/s_1)]$. Therefore, in order to reproduce both the experimental χ and h_{∞}^E , calculations were performed by taking X_{12} , Q_{12} , and (s_2/s_1) as adjustable parameters, in which the product $X_{12}(s_2/s_1)$ was made to agree with that estimated from the observed h_{∞}^E . The values of X_{12} , Q_{12} , and (s_2/s_1) chosen for the best fit to the experimental χ and h_{∞}^E are given in Table III and the calculated values of χ are shown by the solid lines in Figure 4. For the linear alkanes the best fit required not only a large negative value of Q_{12} but also an appreciably smaller value of (s_2/s_1) than that estimated from the surface-to-volume ratio of the respective components. Here, the values of X_{12} larger than those for $Q_{12}=0$ in Table III correspond to the adjustment of (s_2/s_1) with somewhat smaller values. For benzene, a large positive value of Q_{12} is needed, though the values of X_{12} and (s_2/s_1) remain unchanged. The magnitude of Q_{12} for cyclohexane is very small and the experimental χ can be reproduced only by adjustment of the (s_2/s_1) or X_{12} values.

Thus, it may be concluded that the Flory theory requires the introduction of the exchange entropy parameter Q_{12} and/or the adjustment of the contact surface ratio (s_2/s_1) in order to reproduce both the experimental χ and h_{∞}^E values. The theoretical excess volume, however, is hardly affected by such parameter alternations. A nonzero value of Q_{12} is attributed mainly to refinement of the entropy contributions, such as inaccuracies in theoretical expressions for the combinatory entropy of the mixture and/or deviations from random mixing.^{4,23} Recently, Shiomi *et al.*²⁴ proposed a modified expression for excess thermodynamic quantities by assuming non-additivity of the external degree of freedom and adopting different core volumes of the segments for polymer and solvent. Delmas *et al.*^{5,25-27} and Patterson *et al.*^{18,28,29} also pointed out the importance of the molecular shape-specific effects, such as the orientation and steric hindrance in the polymer and solvent components. However, the Flory expressions for a simplified model have not directed any explicit consideration to such effects. The present Q_{12} -value may also contain contributions from these effects so far ignored. Unfortunately, it is difficult to choose reliable value of (s_2/s_1) , usually estimated from crystallographic data or molecular models or group surface contributions tabulated by Bondi. The present smaller values of (s_2/s_1) in alkanes suggest that the effective contact surface per polymer segment is much smaller than those of the solvent alkanes.

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