

Entropy–Enthalpy Compensation in Solution Properties of Solutes at Infinite Dilution in Nonpolar Polymers

Jan-Chan Huang

Plastics Engineering Department, University of Massachusetts Lowell, Lowell, Massachusetts 01854

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ABSTRACT: The knowledge of the Flory–Huggins interaction parameter, χ , between organic liquids and polymers is very important in the study of their miscibility. From the temperature dependency of χ the enthalpy and residual entropy of solution can be determined. In this study literature data of thirty-two solutes, ranging from alkanes to alcohols, at infinite dilution in isotactic polypropylene, poly(ethyl ethylene), and poly(dimethylsiloxane), were tested and linear entropy–enthalpy compensation was observed. The plot of residual free energy versus enthalpy of solution was also linear, with a lower correlation coefficient than the entropy–enthalpy plot. The range of enthalpy of solution was wider

than those of the size corrected free energy of solution. In nonpolar solvents the enthalpy of solution reflected largely the interaction within the solute liquid state, and showed a linear trend with respect to solute cohesive energy density for *n*-alcohols. The wide range of enthalpy of solution suggests the use of a two-dimensional solubility parameter model to correlate the enthalpy of solution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1241–1247, 2007

Key words: thermodynamics; solution properties; polysiloxane; entropy–enthalpy compensation; interaction parameter

INTRODUCTION

Many techniques have been developed to measure the interaction parameters of polymers and organic liquids.^{1,2} Among them inverse gas chromatography (IGC) is an effective tool for measuring the thermodynamic properties of solute (probe) vapors in high molecular weight polymers, particularly at the infinite dilution state.^{3–8} From sorption data of low molecular weight solutes in polymers at several temperatures one can obtain the enthalpy and entropy of the solution process. In a recent study Huang et al.⁹ showed that linear entropy–enthalpy relationship was observed in IGC study of solutes in a nonpolar hydrocarbon solvent and a polar polyethylene oxide solvent. For some moderately polar solvents the correlation was less noticeable. This was because both solvents and solutes contained functional groups and there were many possible combinations in interaction within pure components and in solutions. Since solution properties represent the property difference between the pure components and solution state, the study can be simplified when a nonpolar solvent is considered. The interaction within a nonpolar solvent is dominated by the dispersion interaction. Better entropy–enthalpy correlation for solution properties could be obtained when nonpolar solvents were used. Furthermore,

the variation in solution properties among solutes reflects the difference in interaction within pure solute liquids.⁹ Thus, one might see a good correlation between heat of vaporization and enthalpy of solution for solutes in nonpolar solvents. This is explored in the present study.

ENTROPY–ENTHALPY COMPENSATION IN THE SOLUTION PROCESS

In the original Flory–Huggins treatment, the interaction parameter, χ , was a constant that represented the contact energy difference between solute–solvent interaction and those of the pure components.^{1,10} However, experience has shown that χ usually depends on temperature.^{10,11} Guggenheim¹¹ suggested that χ , the size corrected reduced free energy of solution, be separated so that:

$$\chi = \chi_H + \chi_S \quad (1)$$

where the reduced excess enthalpy of solution, χ_H , and reduced residual entropy of solution, χ_S , are defined as:²

$$\chi_H = -T \left(\frac{\partial \chi}{\partial T} \right) = \Delta \bar{H}_{re}^{\infty} / RT \quad (2)$$

$$\chi_S = \frac{\partial (T\chi)}{\partial T} = -\Delta \bar{S}_{re}^{\infty} / R \quad (3)$$

Here $\Delta \bar{S}_{re}^{\infty}$ is the residual entropy of solution or the noncombinatorial part of the entropy of solution. It

Correspondence to: J.-C. Huang (Jan_Huang@uml.edu).

is associated with the solute–solvent interaction. The residual enthalpy of solution is generally considered to be the excess enthalpy of solution. In many IGC studies, plots of entropy versus enthalpy were used in discussions of solution thermodynamics.^{12–15} It was noted by Huang and coworkers¹⁵ that the size correction gives a contribution to the entropy of solution, but there is no counterpart in the enthalpy of solution. Therefore, in making an entropy–enthalpy plot of solution properties, the size corrected result should be used. The plot of χ_S versus χ_H is equivalent to the plot of $\Delta\bar{H}_{re}^\infty$ versus $\Delta\bar{S}_{re}^\infty$. The slope reaches minus unity when the entropy term has a near complete compensation effect on the enthalpy of solution.

Linear relationships between entropy and enthalpy frequently were found in thermodynamic and kinetic processes.^{16–20} They are also cited as enthalpy–entropy compensation effects, extrathermodynamic phenomena, or isokinetic relationships. The entropy–enthalpy compensation effect can be represented in the following form:

$$\Delta H = \beta \Delta S + \alpha \quad (4)$$

The parameter β is a positive parameter designated as the “compensation temperature.” A positive β indicates that when there is a positive variation for a series of solutes, there is a change in the entropy, which compensates for some of the change. The result is a smaller change in ΔG relative to ΔH . Experimental results of ΔH and ΔS obtained from free energies for a series of temperatures have been used frequently for the plots. However, Krug et al.¹⁹ demonstrated that when enthalpy is calculated using the temperature dependence of free energies, propagated errors often give a straight line with a slope equal to the average temperature of the experimental measurements. Therefore, statistical errors tend to bias the extra-thermodynamic relationship unless the slope of the entropy–enthalpy plot happens to be different from the average of the experimental temperatures.

Using a general statistical mechanical model, Sharp²⁰ also showed that a correlation could occur with a slope within 20% of the experimental temperature. This behavior is insensitive to the model details, thus revealing little extra-thermodynamic or causal information about the system. In a recent study, Huang et al.⁹ showed that the plot of χ_S versus χ_H was linear for solutes in nonpolar squalane and polar low molecular weight poly(ethylene oxide) (PEO). Squalane is a saturated natural hydrocarbon commonly used as a gas chromatography stationary phase. The slope was about -0.5 and was statistically different from unity. This suggests that entropy–enthalpy compensation could be established in an IGC study. In this study the same approach was tested in different polymers with more solutes.

RESULTS OF THREE POLYMERS

Tian and Munk²¹ determined the retention volume of a series of solutes in several polymers by the IGC method. In their study, specific retention volume and Flory–Huggins parameters were reported for several temperatures between 70 and 110°C. Three polymers, isotactic polypropylene (PP), poly(ethyl ethylene) (PEE), and poly(dimethylsiloxane) (PDMS), were selected for this study. PDMS has been studied by IGC methods.^{2,8,22–25} These three polymers were chosen because they were nonpolar and their interactions were dominated by the dispersion force. Without the influence of different types of interaction in polymers, the entropy–enthalpy compensation may be more readily observed.⁹ Thirty-two solutes ranging from nonpolar *n*-alkanes to strongly polar alcohols were used. This gave the opportunity to compare the polar effect of solutes. In this study the density and vapor pressure of solutes were calculated using correlation methods from standard sources.²⁶ The heat of vaporization was calculated using the Clausius–Clapeyron equation. The solubility parameters of solutes are listed in Table I. Also listed in Table I are components of solubility parameters,²⁷ which were used in later discussion.

TABLE I
Parameters of Selected Organic Compounds

Probe	δ (J/cm ³) ^{0.5}	δ_d (J/cm ³) ^{0.5}	λ (J/cm ³) ^{0.5}
Hexane	13.11	13.11	0
Heptane	13.68	13.68	0
Octane	14.01	14.01	0
Nonane	14.30	14.30	0
Decane	14.38	14.38	0
Undecane	14.60	14.60	0
Cyclopentane	15.41	15.41	0
Cyclohexane	15.10	15.10	0.17
Cycloheptane	15.84	15.84	0
Cyclooctane	16.14	16.14	0
Benzene	16.72	16.63	1.75
Toluene	16.55	16.40	2.24
Ethylbenzene	16.36	16.30	1.36
Methylene chloride	17.92	16.06	7.96
Chloroform	16.89	15.90	5.69
Carbon tetrachloride	16.06	16.05	0.52
<i>n</i> -Butyl chloride	15.68	14.66	5.57
1,1-Dichloroethane	16.82	15.06	7.48
Methylchloroform	18.79	17.06	7.87
Trichloroethylene	15.87	15.23	4.46
Chlorobenzene	18.09	17.52	4.52
Acetone	17.86	13.65	11.51
Methyl ethyl ketone	17.18	14.22	9.64
Tetrahydrofuran	17.36	15.01	8.73
Dioxane	18.50	17.30	6.55
Methyl acetate	16.96	14.17	9.32
Ethyl acetate	16.01	13.92	7.90
<i>n</i> -Butyl acetate	15.64	14.24	6.47
Ethanol	22.96	13.75	18.39
<i>n</i> -Propanol	21.37	14.09	16.07
<i>n</i> -Butanol	20.34	14.27	14.49

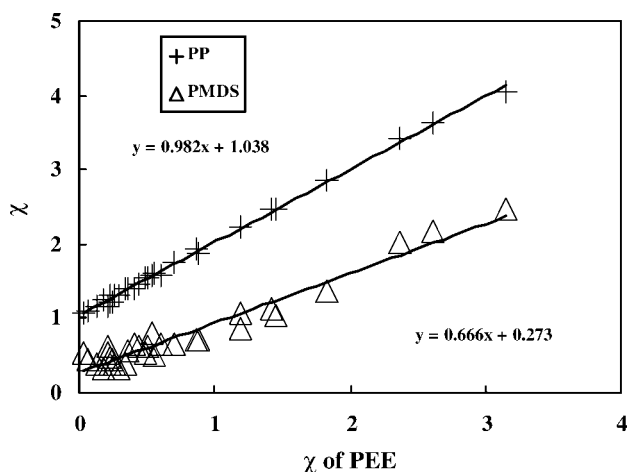


Figure 1 Plot of Flory–Huggins interaction parameters of solutes in PP (+) and PDMS (Δ) versus PEE at 90°C. The result of PP was shifted upward by 1.0.

Figure 1 shows the plot of Flory–Huggins interaction parameters for PP versus PEE and PDMS versus PEE at 90°C. This is similar to the plot of $\log V_g$ for a pair of stationary phases.^{12,13,15} This is a convenient method for comparing and scanning interactions between solutes and solvents, particularly in the presence of a specific interaction and when the solvent molecular weights are unknown. The use of the plot of χ requires the knowledge of vapor pressure, but it has a benefit that the effect of vapor pressure, which is affected by the solute liquid state interaction, was removed. It can be seen that the plot between PP and PEE was very close to a straight line, with a slope near unity. This was because both polymers were hydrocarbons with similar structural units. They provided a similar environment for interaction with probes. The plot of PDMS versus PEE had a smaller slope and was more scattered. The intercept was a positive number,

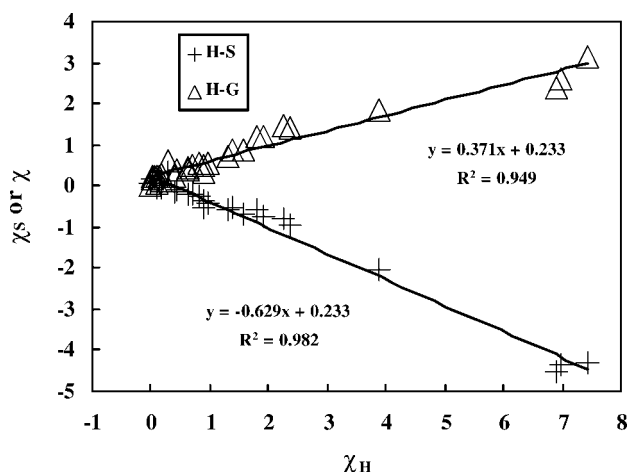


Figure 2 Reduced residual entropy (χ_s) and reduced size corrected free energy (χ) versus reduced excess enthalpy (χ_H) of solutes in PEE at 90°C.

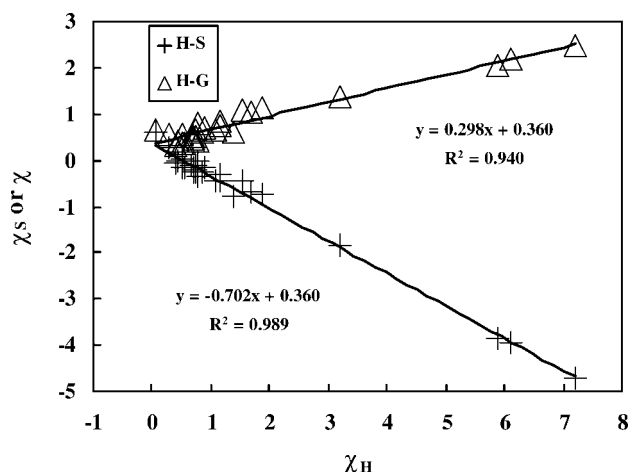


Figure 3 Reduced residual entropy (χ_s) and reduced size corrected free energy (χ) versus reduced excess enthalpy (χ_H) of solutes in PDMS at 90°C.

which indicated that nonpolar solutes were less favorable to dissolve into PDMS than into PEE. However, for solutes with high χ values, e.g., alcohols, the interaction parameters were lower for PDMS. Both trends happened because PDMS has oxygen, which had interactions with the polar hydroxyl group of alcohols and gave smaller χ than in PEE.

Figures 2 and 3 show the plots of χ_s and χ versus χ_H for PEE and PDMS, respectively. It can be seen that for both plots, χ_H of most solutes was positive, while χ_s was negative, and amounted to about two-thirds of χ_H . These slopes were near the values obtained previously with different polymeric stationary phases.⁵ This made χ only about one-third of χ_H . The correlation was higher for the H-S plot than the H-G plot. Krug et al.²⁸ concluded that the plot of free energy versus enthalpy is more rigorous than the plot of entropy versus enthalpy. Therefore, the true compensation was not as strong as implied by the correlation coefficient of the H-S plot. However, the correlations of the H-G plot were still high enough as an evidence for some types of compensation. The results of PP were similar to PEE and are not shown here. The slope and correlation coefficients of the three polymers are summarized in Table II. Note that the standard deviations of slopes were about 0.02. Therefore, the slope was statistically different from unity and represents a compensation effect. However, the corre-

TABLE II
Slopes and Correlation Coefficients (R)
of χ_s vs. χ_H and χ vs. χ_H Plots at 90°C

	χ_s vs. χ_H		χ vs. χ_H	
	Slope	R	Slope	R
PEE	-0.629	0.982	0.371	0.949
PP	-0.652	0.969	0.348	0.901
PDMS	-0.702	0.989	0.298	0.940

lation itself alone did not uniquely define a model. A solution model would have to be developed and confirmed separately.

ENTHALPY OF SOLUTION AND COHESIVE ENERGY DENSITY

The results of the previous study⁹ and this one suggest that the enthalpy of solution has a wider range than residual entropy or free energy of solution. This seems to be a common situation and makes the enthalpy of solution an important solution property to be investigated. The polymers studied here are nonpolar. For a nonpolar solvent the solution is dominated by the dispersion interaction, which may have a similar magnitude for different types of probes. The enthalpy of solution of a probe represents the difference in interaction between the solute liquid state and solution state. When the interaction strength in the solution state has a similar magnitude, the enthalpy of solution reflects the strength in solute liquid state interaction.⁹ This concept was also suggested by Golovnya et al.²⁹ In their IGC study a nonpolar solvent was used to characterize liquid state interaction of a series of solutes. The solute state interaction was measured as the difference between the normal boiling points of the probe liquids and the boiling points of *n*-alkanes with a similar retention volume. This approach assumed that the dispersion interaction of polar probes in IGC stationary phases was similar to that of an *n*-alkane, and the additional interaction of probe molecules in liquid state was measured by the increment of the boiling point. The additional interaction can also be measured from the components of the cohesive energy density, which is explained in the following paragraphs.

In many solution models it was assumed that the entropy of solution could be described by the Flory–Huggins model. Most of the development of solution models focused on the enthalpy portion of the free energy expression. One of the early models for the enthalpy of solution, or the heat of mixing, was the Hildebrand regular solution theory.³⁰ In the theory it was assumed that there was no entropy of mixing, and the heat of mixing could be estimated from the solubility parameters of the components. The solubility parameter is defined as:

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V} \right)^{1/2} \quad (5)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the solvent. The ratio $\Delta E_{\text{vap}}/V$ is the cohesive energy density; it represents the energy required to separate liquid molecules into the ideal gas state. The heat of mixing can be related to the sol-

ubility parameters of two components by:³⁰

$$\Delta U = V_1(\delta_1 - \delta_2)^2 \quad (6)$$

where δ_1 and δ_2 are the solubility parameters of the solvent and the polymer, respectively, and V_1 is the volume of the solvent. The cohesive energy of organic compounds may be divided into three parts, corresponding with three types of interaction forces: dispersion, polar, and hydrogen bonding.³¹ Blanks and Prausnitz³² considered the cohesive energy as the sum of a polar part and a nonpolar part, and proposed a two-dimensional solubility parameter model. The nonpolar part of cohesive energy is estimated from the heat of vaporization of a straight-chain hydrocarbon compound with the same molar volume and the same reduced temperature. The remainder of the cohesive energy is considered to be the polar component. The concept of three-dimensional solubility was proposed by Hansen³³ and the expression for the cohesive energy density and overall solubility parameter, δ , is:

$$\left(\frac{\Delta E_{\text{vap}}}{V} \right) = \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 = \delta_d^2 + \lambda^2 \quad (7)$$

where δ_d is the dispersion component of δ , δ_p is the polar component of δ , δ_h is the hydrogen bonding component of δ , and $\lambda (= \sqrt{\delta_p^2 + \delta_h^2})$ is the polar component in the two-dimensional model. A table of three-dimensional solubility parameters components was published by Hansen and Beerbower,²⁷ and a newer collection was made by Hansen.³⁴ The dispersion component was estimated from the method of Blanks and Prausnitz.³² The polar and hydrogen bonding components were then made on an empirical basis. Methods to estimate temperature dependency of each component were also given.

In this study the effect of polar interaction on the enthalpy of solution of probes in nonpolar polymers was illustrated using a two-dimensional model. The value of $RT\chi_{H,1}/V_1$ in a solvent is proposed to be:

$$RT\chi_{H,1}/V_1 = (\delta_{d,1} - \delta_{d,2})^2 + (\lambda_1 - \lambda_2)^2 \quad (8)$$

In this study the values of δ_d was taken from Hansen and Beerbower,²⁷ adjusted to temperature 90°C. Polar components were calculated as the remainder of the cohesive energy. The results of solubility parameter components are shown in Table I. For saturated acyclic hydrocarbon probes not listed by Hansen and Beerbower, the total solubility parameter calculated from the Clausius–Clapeyron equation was used as the dispersion component, and the polar component was assumed to be zero. Solutes with low boiling point were not included, because their solubility parameters might require the vapor phase correction.³⁵

From Table I it can be seen that for most probes the value of δ_d was around 15 J^{0.5}/cm^{1.5} with a range of

about $2 \text{ J}^{0.5}/\text{cm}^{1.5}$. But for polar probes the value of λ could range up to $18 \text{ J}^{0.5}/\text{cm}^{1.5}$. When the polymer is nonpolar the last term of eq. (8) simplifies to λ_1^2 . Since the dispersion component of the probes was similar to that of the polymers, the first term of the right-hand side was small. For strongly polar probes the value of $RT\chi_{H,1}/V_1$ was dominated by the last term of eq. (8). This suggested that, for strongly polar probes in nonpolar polymers, the plot of $RT\chi_{H,1}/V_1$ versus the cohesive energy density was linear with a slope equal to unity. This is shown in Figure 4 for PEE and PDMS. It can be seen that the slopes were near unity for probes with high cohesive energy density, and agreed with the above argument. For PDMS the values of $RT\chi_{H,1}/V_1$ were lower, indicating that there might be some polar interactions in PDMS which caused lower $\chi_{H,1}$. For probes with low values of cohesive energy density, the scattering occurred because the difference between dispersion components becomes important when polar effect is small.

Note that the use of the three-dimensional model in eqs. (7) and (8) gave the same conclusion for Figure 4. Therefore, the plot of Figure 4 is relatively model free. This result suggested that the dispersion interaction of cohesive energy could be separated from the polar and hydrogen bonding interactions with a form similar to eq. (7), and the dispersion interactions of probes and polymers were similar in strength. The result of PP was similar to PEE and is not shown here. An interesting comparison is that the use of $RT\chi_1/V_1$ in Figure 4 would produce a much smaller slope because the value of $RT\chi_1/V_1$ was only about one-third of $RT\chi_{H,1}/V_1$. The model in eq. (8) was more appropriate for the enthalpy of solution than for the free energy of solution. This finding is discussed further in the next section.

MODELS FOR ENTHALPY OF SOLUTION

It has been known that the use of the multi-dimensional solubility parameter model such as eq. (8) to

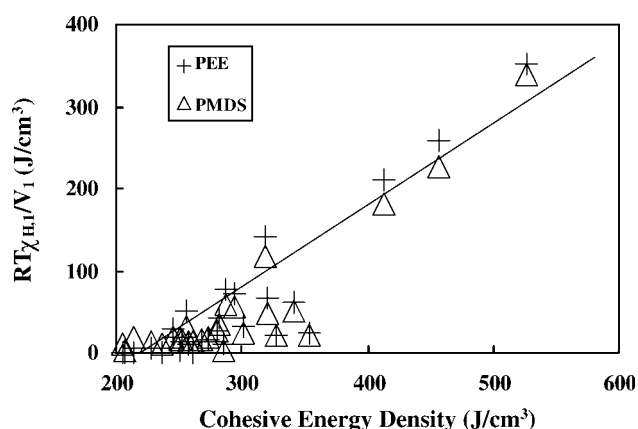


Figure 4 Plot of $RT\chi_{H,1}/V_1$ versus the cohesive energy density $\Delta E_{\text{vap}}/V_1$ ($= \delta^2$) for solutes in PEE and PDMS at 90°C . Solid line is drawn to show the trend of unit slope.

correlate residual free energy of solution led to an interaction parameter range wider than experimental results.^{36–39} This was because the polar components had a wider range than the dispersion components. Weimer and Prausnitz³⁶ proposed to reduce the polar component by a factor less than unity, based on the results of hydrocarbon solutes in polar solvents. In their study the heat of mixing had the following form:

$$\Delta U/V_1 = (\delta_{d,1} - \delta_{d,2})^2 + \lambda_2^2 - 2\psi_{12} \quad (9)$$

where $\psi_{12} = 0.396 \lambda_2^2$ for 7 hydrocarbons in 25 polar solvents. The first two terms on the right-hand side were the expression of a two-dimensional solubility model for systems with nonpolar solutes and polar solvents. The third term was used to correct the difference between the model and experimental results. This term was explained as an induction term between polar and nonpolar species. Helpinstill and Van Winkle³⁷ also proposed to use a similar factor in polar–polar systems. In their expression the heat of mixing had the following form:

$$\Delta U/V_1 = (\delta_{d,1} - \delta_{d,2})^2 + (\lambda_1 - \lambda_2)^2 - 2\psi_{12} \quad (10)$$

where $\psi_{12} = k(\lambda_1 - \lambda_2)^2$ with k varying from 0.399 to 0.447. Because the value of k was near 0.5, the last term in eqs. (9) and (10) significantly reduced the contribution of the polar term. In recent studies of Huang et al.^{38,39} a similar situation was also observed for IGC data of poly(vinyl chloride) (PVC), poly(tetramethylene glycol) (PTHF), and polycaprolactone (PCL), and the following three-dimensional expression was suggested for the Flory–Huggins interaction parameter of solutes:

$$RT\chi_1/V_1 = (\delta_{d,1} - \delta_{d,2})^2 + b[(\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2] + RT\eta \quad (11)$$

Here the constant b modifies the weighting of the polar and hydrogen bonding interactions and η is the average of χ_s/V_i . The value of b was in the range 0.2–0.5. Again the weighting of polar and hydrogen bonding components was smaller than the dispersion component, similar to the conclusions of low molecular weight liquid mixtures. A value of b less than unity suggests that there is a factor reducing the positive ΔU , and the factor is proportional to the polar and hydrogen bonding interactions. The physical meaning of b becomes clear when entropy–enthalpy correlation is considered. The reduction of polar interaction using ψ_{12} or b represents the entropy effect, which is in addition to the size correction of the Flory–Huggins method.

On the basis of the results of Figure 4 it is proposed here that the formula in eq. (8) could represent the enthalpy of solution, while eqs. (9)–(11) are a result of residual entropy which reduced the enthalpy of solution. To verify this proposal the model of eq. (9) was

TABLE III
Solubility Parameter Components of Polymers at 90°C

	δ_d (J/cm ³) ^{0.5}		λ (J/cm ³) ^{0.5}	
	Method 1	Method 2	Method 1	Method 2
PP	14.2	12.5	0	0
PEE	14.3	14.3	0	0.4
PDMS	14.5	13.8	1.1	1.1

Method 1 is the averaging results of the lowest five probes and method 2 is the results of minimization of error square.

tested for the three polymers. Two methods were used to estimate the parameters of the polymers. The first was an averaging method proposed by Choi et al.⁴⁰ This method estimates the solubility parameter components by averaging the parameters of five probes with the lowest $RT\chi_{H,1}/V_1$. The second method was the minimization of the sum of error square in the prediction of $RT\chi_{H,1}/V_1$ using eq. (8). The first method relied entirely on the probes with low $RT\chi_{H,1}/V_1$ while the second method weighted more heavily on the probes with high values of $RT\chi_{H,1}/V_1$.^{38,39} The results of components of the solubility parameters are listed in Table III.

It can be seen that using the first method PP and PEE had zero λ because the five probes with good solubility were hydrocarbons devoid of polar interactions, but PDMS had a small polar component. In the second method the λ of PDMS was the same as the first method. This agreement indicated that the component would be valid for the entire spectrum of probes. The λ of PDMS was lower than the value estimated using interaction parameter based on free energy,⁷ which was about 4–5 (J/cm³)^{0.5}. But in this study χ_H was used. A smaller polar interaction agrees better with the nonpolar properties of PDMS, such as low surface tension. The overall solubility parameter of PDMS based on the second method is 13.8 (J/

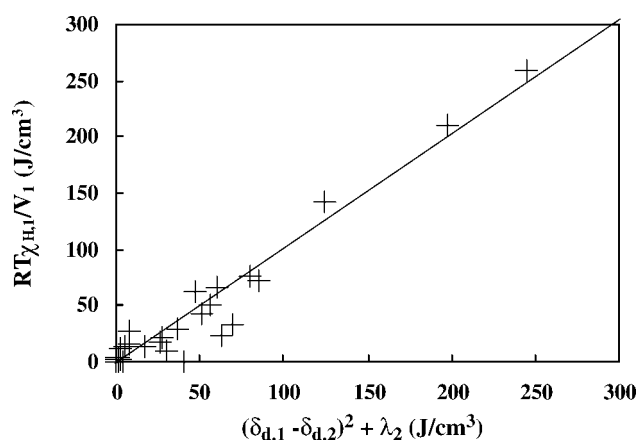


Figure 5 Plot of $RT\chi_{H,1}/V_1$ versus the predicted value for solutes in PEE at 90°C.

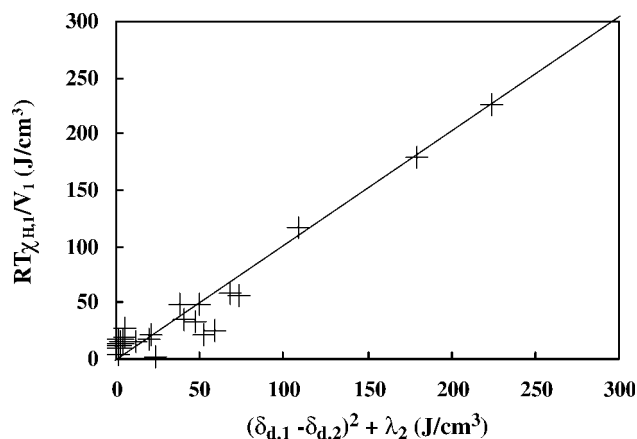


Figure 6 Plot of $RT\chi_{H,1}/V_1$ versus the predicted value for solutes in PDMS at 90°C.

cm³)^{0.5} at 90°C, which is near the result of Humpa et al.²⁴ at the same temperature, 13.4 (J/cm³)^{0.5}. In the second method PEE had a small polar component. The PEE used in the study of Tian and Munk was a sample prepared from hydrogenation of poly(1,2-butadiene). There was a possibility that the sample still had some double bonds left and interacted more favorably with alcohols. Since the second method weighted more heavily on alcohols, the interaction between the double bonds and alcohols might produce a small polar component for PEE. Aromatics, such as benzene and toluene, also had a small polar component, as shown in Table I.

There were differences in dispersion components estimated by the two methods. The dispersion components of PP and PMDS were lower in the second method. A variation of solubility parameter components depending on the solvents used was also experienced in different techniques.⁹ The variation in this study was smaller. The difference between the results of two methods probably represented the accuracy limit in estimating polymer solubility parameter by a probing method. A better approach probably would be to take δ_d estimated by the averaging method and λ estimated by the second method, because the first method weighted more on low polarity probes while the second method weighted more on the polar probes. Using this combination of components a plot was made to compare $RT\chi_{H,1}/V_1$ versus $(\delta_{d,1} - \delta_{d,2})^2 + (\lambda_1 - \lambda_2)^2$ in Figures 5 and 6 for PEE and PDMS, respectively. It can be seen that the data fell on a linear trend and the magnitude of deviation was smaller when compared with Figure 4. The slope was near unity in both figures. The use of λ of method one brought the data of alcohols close to the line in Figure 5, but with an increase in the sum of error square. No visible change was seen for PDMS in Figure 6 with the same change. The deviations in Figures 5 and 6 were much smaller than those plots using $RT\chi_1/V_1$ in

different systems.^{38,39} Therefore, eq. (8) successfully correlated the enthalpy of solution for the systems considered here.

From these results, two important conclusions can be drawn. One is that the two-dimensional model successfully described the enthalpy of solution without the need of a reduction or correction of an induction effect. The second conclusion is that all three polymers had residual entropy of solution in addition to the combinatorial entropy using the Flory–Huggins model. This may be the source of the correction terms suggested in previous studies. The source of this residual entropy of solution deserves future study. The systems studied here deviated from the regular solution concept because they had residual entropy of solution, but the heat of mixing could be estimated by the solubility parameter components, which could be considered as an extension of the regular solution model.

CONCLUSIONS

From Flory–Huggins interaction parameters, χ , obtained through the IGC measurement, the reduced excess enthalpy of solution, χ_H , and reduced residual entropy of solution, χ_S , of a variety of solutes in three nonpolar polymers were examined. Entropy–enthalpy compensation was observed for all three polymers. The correlation for free energy–enthalpy was lower than the entropy–enthalpy plots. The enthalpy of solution showed a linear relation to the cohesive energy density of strongly polar probes. On the basis of these results it was concluded that the two-dimensional model could correlate the enthalpy of solution for solutes in nonpolar solvents.

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