

Estimation of Solubility Parameter Components of Solutes and Polymers Using Heat of Vaporization and Heat of Sorption of Solutes

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ABSTRACT: In a recent study, a two-dimensional solubility parameter model was used to correlate the heat of solution for solutes ranging from *n*-alkanes to alcohols, dissolved in isotactic polypropylene (PP), poly(ethyl ethylene) (PEE), and poly(dimethylsiloxane) (PDMS). When literature data of solubility parameter components of solutes were used, the correlation had some scattering for solutes with low values of cohesive energy density. In this study, the components of solubility parameters of solutes and polymers were estimated from cohesive energy and heat

of sorption of solutes. Good correlation was obtained for the specific heat of sorption ($\Delta U_{\text{sorp}}/V$) for solutes ranging from *n*-alkanes to alcohols, and PDMS had a polar component as previously estimated. Free volume effect in solution process may be the source of a small systematic deviation from the model. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2027–2032, 2009

Key words: thermodynamics; solution properties; polypropylene; solubility parameter; free volume

INTRODUCTION

Inverse gas chromatography (IGC) is an effective tool for measuring the thermodynamic properties of solute (probe) vapors in high-molecular weight polymers, particularly at infinite dilution.^{1–3} In IGC measurement, a known amount of nonvolatile stationary phase is dissolved in a volatile solvent and coated on a porous inert support. In the operation of IGC, a carrier gas is passing through the column continuously. When a volatile probe liquid is injected into the column the probe vaporizes and flows with the carrier gas. The specific retention volume at the column temperature of a probe, V_g^T , is calculated from the following equation:

$$V_g^T = j(t_p - t_m)F/w \quad (1)$$

where, w is the mass of the polymer in the column, and F is the volumetric flow rate of the carrier gas measured at the column temperature and at the column outlet. t_p and t_m are the retention times of the probe and marker, respectively. j is the correction factor to account for the compressibility of the carrier and is given by the following:

$$j = (3/2)[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1] \quad (2)$$

where, P_i/P_o is the ratio between the inlet and outlet pressures. V_g^T is a measurement of solubility of the probe at the column temperature. It is related to the partition coefficient of the solute between the carrier gas and polymer.⁴ From the temperature dependence of $\ln(V_g^T)$, one can obtain the sorption enthalpy of the solute in the polymer by the following^{1–3}:

$$d[\ln(V_g^T/T)]/d(1/T) = -\Delta H_{\text{sorp}}/R \quad (3)$$

where, R is the gas constant, and T is the column temperature. This equation provides experimental values for sorption enthalpies of solutes in polymers, which can be determined even without the information of solute vapor pressure and accurate quantity of the stationary phase. When the vapor of solutes is near an ideal gas state, the heat of sorption can be estimated as follows: $\Delta U_{\text{sorp}} = \Delta H_{\text{sorp}} - RT$. The sorption process can be viewed as a combination of two thermodynamic steps. The first is the condensation of the solute vapor to the liquid state. This is the reverse of the vaporization process and involves the heat of vaporization, which is usually a large quantity. The second step is the dissolution of the liquid solute into the polymer. This step involves a heat of solution. Thus, heat of sorption contains heat of vaporization, ΔU_{vap} , and heat of solution, ΔU_s as follows⁵:

$$\Delta U_{\text{sorp}} = -\Delta U_{\text{vap}} + \Delta U_s \quad (4)$$

The intermolecular interaction of organic compounds contains three mechanisms: dispersion,

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polar, and hydrogen bonding.^{6,7} For solutes of a given molar volume, the heat of vaporization is the smallest when the solute is nonpolar, and increases when there are additional interaction mechanisms such as polar interaction and hydrogen bonding. When the solutes are dissolved into a nonpolar polymer, the interaction between solutes and polymer is dominated by the dispersion interaction. On the volume basis, the interaction energy, or the heat of sorption of solutes, will be similar in strength. Therefore, for polar solutes, an increase in ΔU_{vap} is accompanied by a more positive ΔU_s . This was demonstrated in a recent study by Huang.⁸ A proportional trend between cohesive energy density and specific enthalpy of solution was observed for solutes ranging from *n*-alkanes to alcohols when poly(ethyl ethylene) (PEE), polypropylene (PP), and poly(dimethylsiloxane) (PDMS) were used as the solvents. However, the data of nonpolar and slightly polar solutes were scattered. Strictly speaking, the dispersion components of different solutes and that of polymers might not be identical, but vary within a range. A different assignment of the solubility parameter components might be able to give a better correlation for $\Delta U_{\text{sorp}}/V$ of solutes. In this study, a method is present to evaluate the two-dimensional solubility parameter components of solutes and polymers from heat of vaporization and heat of sorption of various solutes in polymers.

MODELS FOR HEAT OF SORPTION

In many polymer solution studies, it was assumed that the entropy of solution could be described by the Flory-Huggins method⁹ and the enthalpy of interaction was represented by the Flory-Huggins parameter, χ . Most of the development of solution models focused on the enthalpy portion of the free energy expression. In the condensed phases, the enthalpy of solution is usually identified as the heat of solution because the contribution of PV term is very small. One of the early models for the heat of mixing was the Hildebrand regular solution theory.⁶ In this 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 follows⁵:

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

where, ΔU_{vap} is the energy of vaporization, ΔH_{vap} is the enthalpy of vaporization, and V is the molar volume of the solvent. The ratio $\Delta U_{\text{vap}}/V$ is the cohesive energy density; it represents the heat required to separate liquid molecules into the ideal gas state.

The heat of mixing can be related to the solubility parameters of two components by the following^{5,6}:

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

where, δ_1 and δ_2 are the solubility parameters of the solutes and the polymer, respectively, and V_1 is the volume of the solute. There were several studies extending eq. (6) to a multidimensional form. Blanks and Prausnitz¹⁰ 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 was 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 was considered to be the polar component. The concept of three-dimensional solubility was proposed by Hansen,^{11,12} and the expression for the cohesive energy density and overall solubility parameter, δ , was as follows:

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

where, δ_d = the dispersion component of δ , δ_p = the polar component of δ , δ_h = the hydrogen bonding component of δ , and λ ($= \sqrt{\delta_p^2 + \delta_h^2}$) was the polar component in the two-dimensional model.

In the literature, eq. (6) has been extended to the following two-dimensional model with a polar component term¹⁰⁻¹⁶:

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

When eq. (8) was used in the free energy of solution with the Flory-Huggins expression, a negative correction term proportional to the polar term was necessary.¹³⁻¹⁶ In the previous study, it was suggested that the correction might be related to the entropy-enthalpy compensation effect, which reduced a portion of the polar component term in the free energy of solution.⁸ However, eq. (8) was shown to be able to correlate the heat of solution of a range of solutes in PP, PEE, and PDMS.⁸ But, the correlation had some scattering for solutes with low values of $\Delta U_s/V$ of solution. In this study, the dispersion and polar components of solutes and polymers are estimated from heat of vaporization of solutes and heat of sorption of solutes in the polymers.

With the assumption of an ideal gas phase and no excess volume in the liquid mixture, the corresponding expression for the specific heat of sorption for a polar solute (Component 1) in a polar polymer (Component 2) can be obtained from eqs. (4), (7), and (8):

$$-\Delta U_{\text{sorp}}/V_1 = 2\delta_{d,1}\delta_{d,2} - \delta_{d,2}^2 + 2\lambda_1\lambda_2 - \lambda_2^2 \quad (9)$$

When the polymer is nonpolar and solutes are polar eq. (9) simplifies to the following:

$$-\Delta U_{\text{sorp}}/V_1 = 2\delta_{d,1}\delta_{d,2} - \delta_{d,2}^2 \quad (10)$$

Note that the polar component of solutes was eliminated in eq. (10). This is true as long as the polymer is nonpolar and the dispersion interaction can be separated from polar and hydrogen bonding by eq. (7). This applies even if eq. (8) contains the hydrogen bonding component of the three-dimensional model or an acid-base interaction term. Therefore, eq. (10) is relatively model free. Equation (10) can be used to estimate the dispersion component of a polymer, $\delta_{d,2}$, through a linear plot versus $\delta_{d,1}$. In later sections, it will be shown that eq. (10) contains a free volume term with similar magnitude for different solutes, which makes the slope of $\Delta U_{\text{sorp}}/V_1$ versus $\delta_{d,1}$ a better approach to obtain $\delta_{d,2}$. From a nonpolar polymer with known $\delta_{d,2}$, one can also estimate the dispersion and polar component of polar solutes. This procedure is also shown in the later sections.

RESULTS FOR THREE POLYMERS

Tian and Munk¹⁷ determined the retention volume of a series of solutes in several polymers by the IGC method. In their study, specific retention volumes and Flory-Huggins parameters were reported for several temperatures between 70 and 110°C. These authors also calculated the heat of sorption for solutes in the polymers. Sorption enthalpy was not available for some solutes. Only those reported were used in this study. Three polymers, isotactic polypropylene (PP), poly(ethyl ethylene) (PEE), and poly(dimethylsiloxane) (PDMS), were selected for this study. PP and PEE contain only saturated hydrocarbon units and are considered nonpolar. PDMS may contain a small degree of polarity. Solute 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 molar volume of solutes at 90°C was calculated using correlation methods from standard sources.¹⁸ The heat of vaporization was calculated using the Clausius-Clapeyron equation. The overall solubility parameters of solutes at 90°C were calculated using eq. (5) and are listed in Table I. Also listed in Table I are components of solubility parameters, which were determined in later paragraphs.

The first step in estimating parameter components is to assign the overall solubility parameters of nonpolar solutes to their dispersion components. These solutes include all saturated linear and acyclic hydrocarbons. The dispersion components of nonpolar polymers can be estimated from eq. (10) using

TABLE I
Parameters of Selected Organic Compounds at 90°C

Probe	δ (J/cm ³) ^{0.5}	δ_d (J/cm ³) ^{0.5}	λ (J/cm ³) ^{0.5}
Hexane	13.77	13.77	0
Heptane	14.00	14.00	0
Octane	14.23	14.23	0
Nonane	14.34	14.34	0
Decane	14.47	14.47	0
Undecane	14.61	14.61	0
Cyclohexane	15.51	15.51	0
Cycloheptane	15.91	15.91	0
Cyclooctane	16.19	16.19	0
Cyclohexene	16.16	16.14	0.71
Benzene	17.35	16.79	4.38
Toluene	16.90	16.49	3.70
Ethylbenzene	16.62	16.29	3.32
Methylene chloride	19.00	17.32	7.81
Chloroform	17.90	16.67	6.51
Carbon tetrachloride	16.32	15.98	3.31
Butyl chloride	15.89	15.38	4.00
Pentyl chloride	15.60	15.50	1.72
Chlorohexane	15.80	15.41	3.48
Chlorooctane	15.59	15.49	1.79
1,1-Dichloroethane	16.96	15.97	5.71
Methylchloroform	16.03	15.46	4.25
Trichloroethylene	17.70	17.30	3.75
Chlorobenzene	18.26	17.54	5.09
Acetone	18.67	14.69	11.52
Methyl ethyl ketone	17.46	15.52	8.00
Tetrahydrofuran	18.19	17.07	6.29
Dioxane	18.92	17.48	7.25
Methyl acetate	18.04	15.76	8.78
Ethyl acetate	16.90	15.37	7.02
Propyl acetate	16.41	15.18	6.23
Butyl acetate	16.36	15.29	5.82
1-Propanol	22.56	16.51	15.37
1-Butanol	21.19	16.29	13.55
1-Pentanol	20.15	16.18	12.02

these nonpolar solutes. Figures 1 and 2 show the plots of eq. (10) for PEE and PP, respectively. The saturated solutes are shown as filled symbols. It can be seen that linear plots were obtained for both polymers. From the slope, the dispersion components at 90°C were determined to be 14.45 and 14.57 J^{0.5}/cm^{1.5}, respectively, for PEE and PP. The result of PP is in the lower end of literature values of PP (16–19 J^{0.5}/cm^{1.5} at 20°C) after taking into account the temperature difference. These numbers were also in agreement with the solubility parameters of higher members of *n*-alkanes at the same temperature, e.g., undecane, in Table I.

The second step is to estimate the dispersion and polar components of polar solutes. In both Figures 1 and 2, the deviation of polar solutes from the trend of saturated solutes occurs because polar solutes have polar interactions in the overall solubility parameter but the polar components do not have the contribution to the heat of sorption. The dispersion component of a polar solute is estimated from saturated solutes with the same $-\Delta U_{\text{sorp}}/V_1$ using the

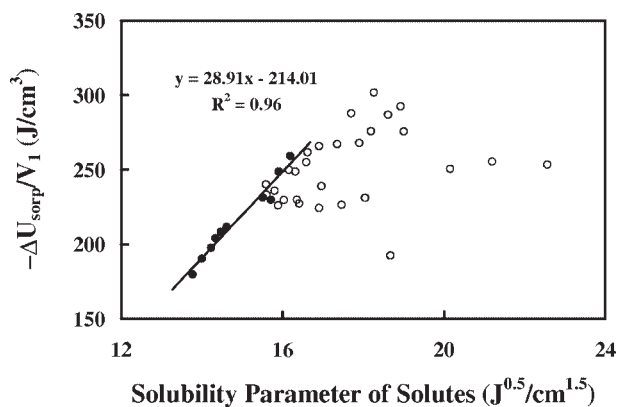


Figure 1 Plot of $-\Delta U_{\text{sorp}}/V_1$ versus the solubility parameter of nonpolar solutes for PEE at 90°C. Symbols: (●) Saturated hydrocarbons and (○) Polar solutes.

least square equations in Figures 1 and 2. In this approach, it is assumed that the dispersion interaction of a polar probe in a nonpolar IGC stationary phases is similar to that of saturated hydrocarbons with the same $-\Delta U_{\text{sorp}}/V_1$. This concept was suggested by Golovnya et al.¹⁹ and Huang⁸ and is similar to the method of Blanks and Prausnitz.¹⁰

Note that one would obtain one set of $\delta_{d,1}$ for polar solutes for each nonpolar polymer. If the model is perfect, the results would be identical for different nonpolar polymers. The results of $\delta_{d,1}$ of polar solutes from PEE and PP were similar, with an average difference of $0.07 \text{ J}^{0.5}/\text{cm}^{1.5}$ for 21 polar solutes with available sorption enthalpy data. The results were very close, which supports the model underlying eq. (8). The average of two values is listed in Table I as the dispersion components for polar solutes. From $\delta_{d,1}$ of polar solutes, the rest of the cohesive energy was assigned as the polar component based on eq. (7) and is listed in Table I. It is noted that acetone has a large polar component as was assigned

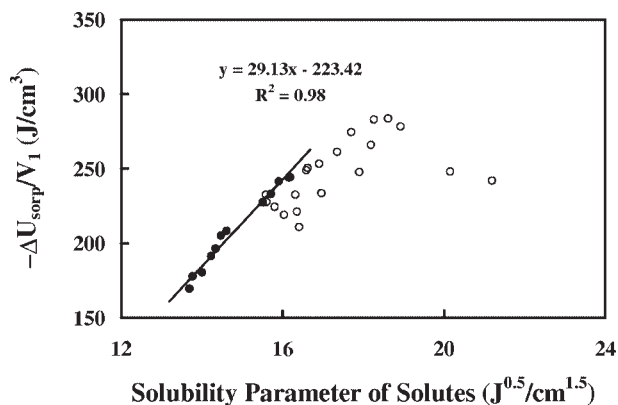


Figure 2 Plot of $-\Delta U_{\text{sorp}}/V_1$ versus the solubility parameter of nonpolar solutes for PP at 90°C. Symbols: (●) Saturated hydrocarbons and (○) Polar solutes.

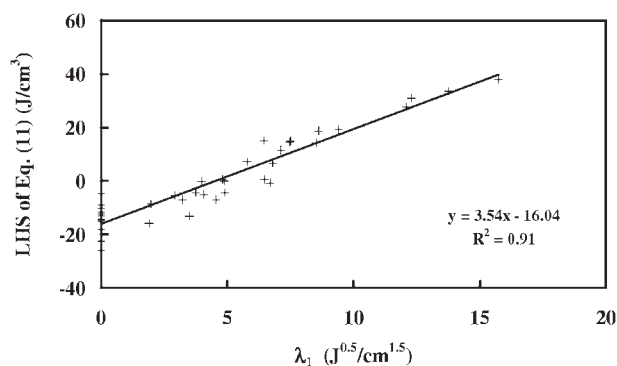


Figure 3 LHS of eq. (11) versus λ_2 for polar solutes in PDMS at 90°C.

by other methods.^{8,11,12,20} Alcohols also have a large polar component, but not as large as literature values.

For a polar polymer, the estimation of solubility parameter components can still be made. Similar to nonpolar polymers the dispersion component of a polar polymer, $\delta_{d,2}$, was estimated by eq. (10) using nonpolar solutes. After the determination of $\delta_{d,2}$, eq. (9) can be changed as follows:

$$-\Delta U_{\text{sorp}}/V_1 - 2\delta_{d,1}\delta_{d,2} + \delta_{d,2}^2 = 2\lambda_1\lambda_2 - \lambda_2^2 \quad (11)$$

From the plot of the left hand side versus λ_1 of the solutes, the polar component of the polymer, λ_2 , can be obtained from the slope. This is demonstrated using the data of PDMS in Figure 3. It can be seen that a single line correlated all the solutes. From the slope, λ_2 of PDMS was estimated to be $1.77 \text{ J}^{0.5}/\text{cm}^{1.5}$. The resulting parameters of PDMS are listed in Table II. In a previous study, PEE had a small polar component.⁸ In this study, λ_2 of PEE was assigned to be zero because a plot similar to Figure 3 did not yield a trend. The λ_2 of PDMS was similar to the previous study,⁸ but lower than the value estimated using the interaction parameter based on free energy of solution,²¹ which gave about 4–5 $(\text{J}/\text{cm}^3)^{0.5}$. The comparison between experimental values of $-\Delta U_{\text{sorp}}/V_1$ and eq. (9) is shown in Figures 4 and 5 for PEE and PDMS, respectively. The plots gave near unit slope for the entire range of solutes and the deviation from linearity was smaller than in the previous study. But the IGC value of $-\Delta U_{\text{sorp}}/V_1$

TABLE II
Solubility Parameter Components of Polymers at 90°C, Mean Deviation, and Standard Deviation in Fitting eq. (9)

POLYMER	PP	PEE	PDMS
$\delta \text{ (J/cm}^3\text{)}^{0.5}$	14.57	14.45	14.97
$\delta_d \text{ (J/cm}^3\text{)}^{0.5}$	14.57	14.45	14.87
$\lambda \text{ (J/cm}^3\text{)}^{0.5}$	0	0	1.77
Mean deviation $\text{(J/cm}^3\text{)}$	13.5	6.79	17.4
SD of deviation $\text{(J/cm}^3\text{)}$	4.49	2.61	7.7

was lower than the right-hand-side of eq. (9) for each plot. The average values of deviation are listed in Table II.

FREE VOLUME EFFECT IN ENTHALPY OF SORPTION

A negative deviation of IGC values for all three polymers in Figures 4 and 5 is an interesting result. The standard deviation for the error of the model for each polymer is also shown in Table II. The averages of the deviation terms were higher than zero by two standard deviations. This suggested that there is another mechanism in heat of sorption besides the solubility parameter. A possible explanation for this result is the free volume effect. According to Flory-Orwoll-Vrij theory,²² the interaction parameter χ^* has following form:

$$\chi^* = (P_1^* V_1^*/RT) \left[1/\tilde{V}_1 - 1/\tilde{V} + 3\tilde{T}_1 \ln \left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] + X_{12}/\tilde{V} \quad (12)$$

Here, two reduced variables are defined as follows:

$$\tilde{V} = V/V^* \quad (13)$$

$$\tilde{T} = T/T^* \quad (14)$$

Here, P^* , V^* , and T^* are characteristic pressure, volume, and temperature of solutes. X_{12} is the exchange energy parameter between the solute and polymer. V^* and T^* can be estimated from density and thermal expansion coefficient of liquids, but estimation of P^* requires isothermal compressibility data. In IGC conditions, the sorption enthalpy arising from free volume can be given by the following equation²³:

$$\chi_h = (P_1^* V_1^*/RT) [1/\tilde{V}_1 - 1/\tilde{V}_2 + \alpha T (\tilde{T}_1/\tilde{T}_2 - 1) + V_1^* (1 + \alpha T) X_{12}/\tilde{V}_2 RT] \quad (15)$$

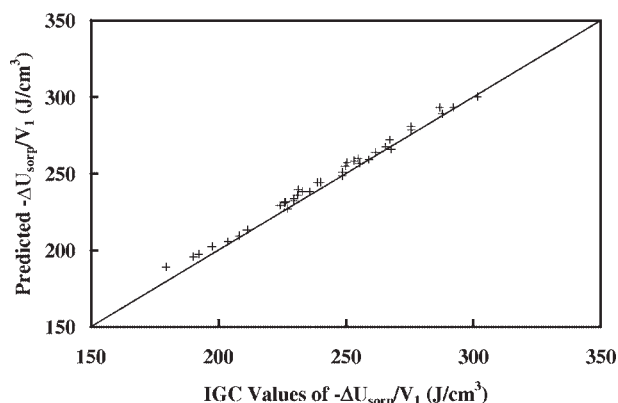


Figure 4 Plot of IGC values of $-\Delta U_{\text{sorp}}/V_1$ versus the predicted value using eq. (9) for solutes in PEE at 90°C.

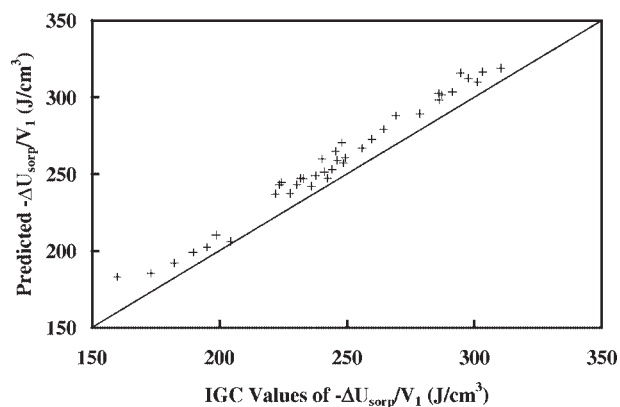


Figure 5 Plot of IGC values of $-\Delta U_{\text{sorp}}/V_1$ versus the predicted value using eq. (9) for solutes in PDMS at 90°C.

The χ_h values of cyclohexane and chlorobenzene in PDMS at 90°C were 0.3 and 0.6, respectively,²³ which represented 7 and 17 J/cm³, in the free volume effect, $\chi_h RT/V_1$. This was in the order of magnitude reported in Table II. In the IGC system, the solvent is usually nonvolatile and solutes are volatile with more free volume. The free volume effect is most noticeable in this type of system.^{24,25} When χ_h is considered, eq. (8) becomes the following:

$$\Delta U_s/V_1 = (\delta_{d,1} - \delta_{d,2})^2 + (\lambda_1 - \lambda_2)^2 + \chi_h RT/V_1 \quad (16)$$

Based on eq. (4), a positive χ_h can reduce the magnitude of ΔU_{sorp} , which is a negative number. The inclusion of $\chi_h RT/V_1$ term will bring predicted $-\Delta U_{\text{sorp}}/V_1$ value lower in Figures 4 and 5. The last term represents the deviation which is also required in eqs. (8)–(11). The mean value of deviation is given in Table II. This gives an indication of the average value of $\chi_h RT/V_1$. Note that in Table II, the mean value of the deviation increased when the overall solubility parameter of the polymer increased. This suggested that when the cohesive energy of the polymer increased, the characteristic temperature of the polymer also increased, and so did the free volume effect. Another important conclusion is that the slope term of eq. (10) was more appropriate in estimating the dispersion component of the polymer because the intercept term might contain the free volume effect. The same conclusion applies to eq. (11).

CONCLUSIONS

The two-dimensional solubility parameter and heat of solution model was tested using solutes ranging from *n*-alkanes to alcohols in PEE, PP, and PDMS. The solubility parameter components were estimated from heats of sorption measured by the IGC method. From these results, the two-dimensional model could be used to correlate cohesive energy and heat

of sorption. The method studied here could be considered as an extension of the regular solution model.

A small deviation from the solubility parameter model was explained as the free volume effect.

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