Probe Dependency of Flory–Huggins Interaction Parameters Between Solvents: Cases of Hydrocarbons and Isosteric Derivatives

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ABSTRACT: Inverse gas chromatography has been widely used to determine the Flory–Huggins parameter, χ, between two solvents. Many studies showed that interaction parameters were probe dependent. In recent studies, it was proposed that the interaction between two solvents may lead to different contact probability between solutes and solvent mixtures and create an apparent solubility parameter different from volume average rule. An equation was previously derived to relate the probe dependency to the deviation of solubility parameter from the volume average rule. By plotting $\phi_2\phi_3RT(\chi_{23}/V_2)$ versus the solubility parameter of solutes, a linear trend could be observed with a negative slope for miscible mixtures. When there was an unfavorable interaction between two solvents, an opposite situation would be observed. In this study, mixtures of 19,24-dioctadecyldotetracontane (C78) and its derivatives were tested. The solubility parameters of mixtures showed negative deviation from the volume average. The plots of $\phi_2\phi_3RT(\chi_{23}/V_2)$ versus solubility parameter of solutes had positive slopes. For two derivatives the best estimated values of $RT(\chi_{23}/V_2)$ were negative in certain temperatures. Enthalpy–entropy compensation plot showed that these two derivatives have higher entropy of mixing. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The knowledge of the interaction parameters between two high molecular weight solvents such as polymers is very important in the study of their miscibility and thermodynamic properties of solutions. Inverse gas chromatography (IGC) has been demonstrated to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in nonvolatile solvents.[1–4] In IGC measurement a known amount of high molecular weight stationary phase is dissolved in a volatile solvent and coated on a porous inert support to act as a chromatography solvent. In the operation of IGC a carrier gas is passing through the column packed with the coated support. When a volatile probe liquid is injected into the column the probe vaporizes and flows with the carrier gas. The dissolution of the probe vapor in the chromatography solvent delays the travelling speed of the probe. This delay is measured as the retention volume of the solute. Using Flory–Huggins theory,[5] the Flory–Huggins interaction parameter between a polymer and a probe, χ, can be related to the specific retention volume of the probe, V_g^0, by the following equation:[1–4]

$$\chi = \ln\left(\frac{273.2Rv_2}{V_g^0 P_1^o V_1}\right) - 1 + 1/m - \frac{P_1^o}{RT}(B_{11} - V_1) \quad (1)$$

where R is the gas constant, T is the column temperature, v_2 is the specific volume of the stationary phase, m is the molar volume ratio between the solute and solvent, and P_1^0, V_1, and B_{11} are the vapor pressure, the liquid molar volume, and the second virial coefficient of the probe, respectively. When a solvent mixture is used in an IGC study, the corresponding specific retention volume and density data of blends can be used in eq. (1). The interaction parameter obtained is called $\chi_{1(23)}$. Applying the Flory–Huggins equation[5] to a ternary system with two solvents and one probe, the interaction parameter $\chi_{1(23)}$ can be related to the difference between pair interactions of probe–solvents, χ_{12} and χ_{13}, and solvent–solvent χ_{23}:[3,4]

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}(V_1/V_2) \quad (2)$$

Here ϕ is the volume fraction of the two stationary phases. As molar volumes of polymeric solvents may not be accurately

known, it is a practice in IGC study to define a probe normalized interaction parameter, $\chi'_{23} = \chi_{23}(V_1/V_2)$. Equation (2) then becomes:[3,4]

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi'_{23} \qquad (3)$$

Equation (3) was frequently used to study the interaction between two solvents using the IGC method. But many studies have shown that the value of χ'_{23} depends on the probe used.[6–11] In examining literature data it was found that in many systems, when probe dependency occurred, the values of χ'_{23} were positive when χ_{12} and χ_{13} were positive, and decreased toward negative values when χ_{12} and χ_{13} decreased. In many miscible systems some negative χ'_{23} values were generally observed for probes with low χ_{12} and χ_{13}. This trend caused the slope of the $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ plot to be slightly lower than unity.[12–14] It has been pointed out that χ'_{23} contains V_1, which makes χ'_{23} probe dependent even with a constant χ_{23}. The comparison of χ_{23} or χ_{23}/V_2 measured from different probes will be more appropriate for studying probe dependency[12–14] because no V_1 involved.

SOLUBILITY PARAMETERS OF SOLVENTS AND SOLVENT MIXTURES

Because of the probe dependency in the IGC method, Huang[15,16] proposed to study the variation of solubility parameter of the mixture as a means to measure the interaction between two solvents. If the heats of vaporization of a mixture and its components are known, the heat of mixing can be calculated. The heat of vaporization is related to the solubility parameter, δ, of the liquid by the relation:[17]

$$\delta = \left(\frac{\Delta E_{vap}}{V}\right)^{1/2} \qquad (4)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the solvent. The ratio $\Delta E_{vap}/V$ is the cohesive energy density; it represents the energy required to separate the liquid molecules into the ideal gas state. Experimental values of χ have been used to estimate the solubility parameters of high molecular weight solvents such as polymers using the method of DiPaola-Baranyi and Guillet.[18,19] In their studies, the Flory–Huggins parameter between a solute and a polymer was assumed to have the following expression:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_S \qquad (5)$$

Here χ_S is the entropy term. Equation (5) can be changed into the following expression:[18,19]

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right) \qquad (6)$$

where η is the average value of χ_S/V_1. From a linear regression method, δ_2 can be determined. When a mixture is used as the stationary phase, the solubility parameter of the mixture, δ_m, can be compared with the prediction of the regular solution

method, which predicts the solubility parameter to be the volume average of the two components, $\delta_{m,r}$ defined as:[17]

$$\delta_{m,r} = \phi_2\delta_2 + \phi_3\delta_3 \qquad (7)$$

If there were a specific interaction between two solvents that produced negative enthalpy of solution, the value of δ_m would be higher than the prediction of eq. (7), to account for the separation of the additional specific interaction between the mixtures and pure components in the vaporization process. A comparison of the solubility parameter of polymer mixtures would be a good indicator to predict their miscibility. In the previous study,[15] this concept was tested using the data of the poly(ε-caprolactone) (PCL)/poly(epichlorohydrin) (PECH) system at 80°C. It was found that the solubility parameter of the mixture was lower than the prediction of eq. (7). This was opposite to the above argument, even though there were some specific interactions between PCL and PECH and the system was miscible. When a deviation from eq. (7) occurs, a deviation parameter, Δ, for the solubility parameter of the mixture can be defined as:

$$\delta_m = \phi_2\delta_2 + \phi_3\delta_3 - \Delta = \delta_{m,r} - \Delta \qquad (8)$$

A mechanism was then proposed to explain this observation.[15] When two solvents with specific interactions are brought together, some functional groups interact with each other and are less available to the probes. Compared with the average values based on nominal composition, the probes will have less specific interaction with the mixture. As a consequence, polar probes show a decrease in retention volume compared with the weight average value of the specific retention volume of the components, and for n-alkane probes the percentage of decrease may be smaller. This difference between probes is exhibited as the probe dependency. The solubility parameter of mixtures measured by the IGC method also decreases, reflecting the change in the interaction between the probe and the solvent mixtures. It can no longer be related entirely to the cohesive energy density. The extent of such solubility parameter change, as measured by the parameter, Δ, could be used as an indicator of the interaction between the two solvents.

Based on the above arguments a method was proposed to test the miscibility.[15] From eqs. (3), (5), (7), and (8) the following equation was obtained in the previous study:[15]

$$\phi_2\phi_3RT(\chi_{23}/V_2) = \phi_2\phi_3(\delta_2 - \delta_3)^2 - 2\Delta(\delta_1 - \delta_{m,r}) - \Delta^2 \\ + RT(\phi_2\chi_{s,2} + \phi_3\chi_{s,3} - \chi_{s,m})/V_1 \qquad (9)$$

The last term represents the correspondent difference between the entropy of solution between pure solvents and the solvent mixtures. The left-hand side can be plotted versus the solubility parameter of the probe, δ_1. In the plot, a linear trend with a negative slope is predicted for miscible blends. The slope is proportional to Δ, the deviation of the solubility parameters of the solvent mixtures from the volume average, which could be used as a measurement of miscibility. In a later study,[16] this approach was applied to plasticized poly(vinyl chloride) (PVC) and a
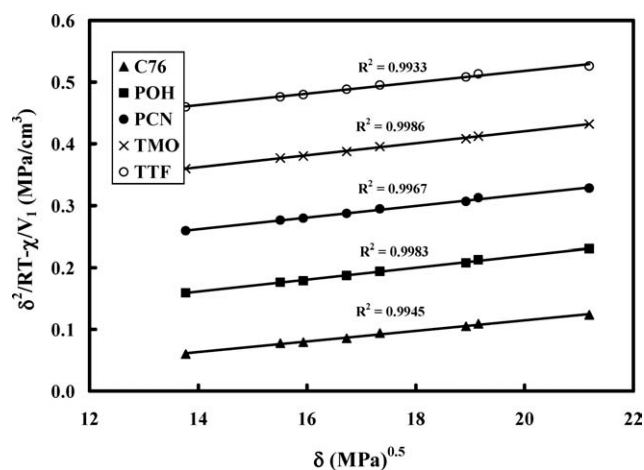
Figure 1. The plot of LHS of eq. (6) versus the solubility parameter of probes for five solvents at 363.15 K. From bottom to top the vertical axis were shifted upward by 0, 0.1, 0.2, 0.3, and 0.4, respectively.

PVC copolymer, and to poly(vinylidene fluoride)−poly(ethyl methacrylate) blends. It was shown that the data could be correlated by straight lines with negative slopes. Thus the technique was demonstrated in the above two miscible systems.

For a polymer–polymer mixture the entropic contribution to the free energy of mixing is diminished because of high molecular weight. The enthalpic term dominates the free energy of mixing and a small positive χ_{23} could lead to an immiscible system. The use of IGC technique and eq. (3) in immiscible systems led to an apparent positive interaction parameters.[20] However, in a more recent study, Huang[21] showed that random copolymers with different ratio of two monomers can be treated as a mixture of two homopolymers and eq. (9) still applicable treated in the same way. The results are positive interaction parameters, and the deviation parameter, Δ, in eq. (8) became negative. This is opposite to a miscible system with specific interaction and the results of that study[21] confirmed that eq. (9) can also be applied to a thermodynamically unfavorable system too.

PROBE DEPENDENCY OF χ_{23} OF MIXTURES OF C78 AND DERIVATIVES

For low molecular weight solvents, a miscible system can be formed with a moderate positive χ_{23}. In this study, the IGC results from Sreekanth and Reddy[22] on mixtures of 19,24-dioctadecyldotetracontane (C78) and its derivatives were analyzed. In the study of Sreekanth and Reddy four derivatives of C78 were studied. Two of the derivatives were formed by replacing one of the —CH$_3$ groups of C78 by —OH 18,23-dioctadecylhentetracontan-1-ol (POH) group and —CN 1-cyano-18,23-dioctadecylhentetracontane (PCN) group, and the other two solvents were formed by replacing all the four —CH$_3$ groups of C78 by four —CF$_3$ 19,24-bis(18,18,18-trifluorooctadecyl)-1,1,1,42,42,42-hexafluorodotetracontane (TTF) groups and four —OCH$_3$ 17,22-bis-(16-methoxyhexadecyl)-1,38-dimethoxyoctatriacontane (TMO) groups. Chemical procedures to prepare these derivatives were reported in the literature.[23] Because of the dominating size of the hydrocarbon backbone, the five solvents have similar structures, and nearly the same density, molar volume, and thermal expansion coefficient.

In the study of Sreekanth and Reddy,[22] the interaction parameter χ_{12} and $\chi_{1(23)}$ were reported for eight probes in solvents and C78-solvent mixtures for temperatures in range from 363.15 to 443.15 K. The probes used were n-hexane, cyclohexane, benzene, 1-chlorobutane, hexanal, 1-butanol, 1,4-dioxane, and cyclohexanone. Figure 1 showed the plot of eq. (6) for five solutes at 363.15 K. Because at 443.15 K the reduce temperature of hexane reaches 0.87, the vapor phase imperfection correction for the solubility parameter[24] is applied in the calculation of solute parameters of solutes. The solubility parameters of five solvents and solvent mixtures were determined by eq. (6) and are listed in Table I. The solubility parameters of each solvent and mixture decreased when the temperature increased, but the rate of decrease is small compared with the results without the vapor phase correction. This is because when the vapor phase imperfection is included, the solubility parameters of solutes tend to be higher than those obtained without vapor phase correction. This trend also affects the results of the solvents. But the rate of decrease in the solvents is not as much as in solutes because a high molecular weight solvent tends to have a lower

Table I. The Solubility Parameters of Solvents and Solvent Mixtures Determined by eq. (6)

Solvents	363.15 K	383.15 K	403.15 K	423.15 K	443.15 K
C78	13.00	12.96	12.91	12.82	12.74
TMO	14.68	14.46	14.23	14.04	13.86
PCN	14.18	14.00	13.86	13.69	13.59
TTF	13.92	13.83	13.72	13.62	13.53
POH	14.59	14.25	13.97	13.71	13.52
TMO (1/2)	14.07	13.89	13.72	13.56	13.42
PCN (1/2)	13.73	13.57	13.46	13.33	13.21
TTF (1/2)	13.56	13.48	13.39	13.27	13.20
POH (1/3)	13.58	13.44	13.28	13.16	13.05
POH (2/3)	14.14	13.86	13.63	13.42	13.30

Solvents with parenthesis indicate the volume fraction in the C78-solvent mixture. Units = (MPa)$^{0.5}$.

Table II. The Values of Δ Determined by eq. (8)

| Solvents	363.15 K	383.15 K	403.15 K	423.15 K	443.15 K
TMO (1/2)	−0.23	−0.19	−0.16	−0.13	−0.12
PCN (1/2)	−0.14	−0.09	−0.07	−0.08	−0.04
TTF (1/2)	−0.10	−0.08	−0.07	−0.05	−0.06
POH (1/3)	−0.05	−0.06	−0.02	−0.04	−0.05
POH (2/3)	−0.08	−0.04	−0.02	−0.01	−0.04

Parenthesis indicates the volume fraction in the C78-solvent mixture. Units = $(MPa)^{0.5}$.

thermal expansion coefficient, and the rate of decrease of cohesive energy density and the solubility parameter is smaller than with the probe liquids.

From the solubility parameters of solvents and solvent mixtures the deviation parameter can be determined from eq. (8) and are listed in Table II. In all cases, the deviation parameter is negative because mixtures have a higher apparent solubility parameter than the volume average. The magnitude of the deviation parameter decreased when the temperature increased. The plot of eq. (9) is shown in Figures 2 and 3 for TMO and PCN, respectively. The slope at each temperature was positive and decreased when the temperature increased. For the C78-TMO system the slopes had lower values, indicating that the deviation parameter is smaller in C78-PCN. The correlation coefficients for TMO are better than PCN. This happens in part because TMO results have higher slopes than PCN results at the same temperature. The correlation coefficients also decreased for both systems when temperature increased. The values of deviation parameters determined from slopes match the values in Table II, and are not shown separately.

For TMO, TTF, and PCN the deviation parameters were measured at equal volume composition. There were two compositions reported for C78-POH mixtures. The deviation parameters of C78-POH were smaller in magnitude compared with the previous three solvents. This occurs in part because they were determined at 1/3 and 2/3 volume fraction of POH as opposite to 1/2 volume fraction. The deviation of solubility parameter from the volume average rule usually follows a second order polynomial.[21] Using a second order function to estimate the deviation at 50 vol % for POH and compared with other derivatives, TMO turns out to have the highest deviation at 50 vol % among four derivative-solvent mixtures. This may be because TMO has four functional groups, while TTF also with four functional groups, has a slightly polar —CF_3 group which have not much impact on the interaction. The other two solvents have only one functional group.

In the mixtures of C78 and derivatives the value of χ_{23} is expected to be positive, because hydrocarbon is nonpolar and the derivatives contain polar groups. In addition, there may be some self association interaction between the polar groups in the liquid derivatives. This association would shield functional
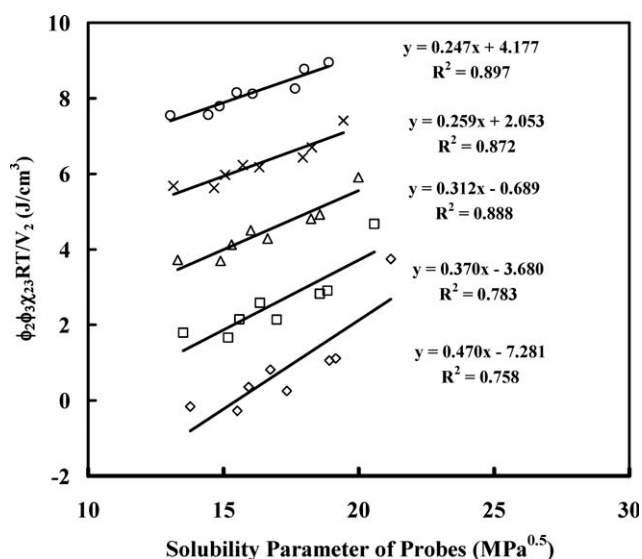
Figure 2. The plot of $\phi_2\phi_3 RT\chi_{23}/V_2$ versus the solubility parameter of probes at five temperatures for C78-TMO systems. Temperatures from bottom to top are 363.15, 383.15, 400.15, 423.15, 443.15 K, respectively. From bottom to top the vertical axis were shifted upward by 0, 2, 4, 6, and 8, respectively.
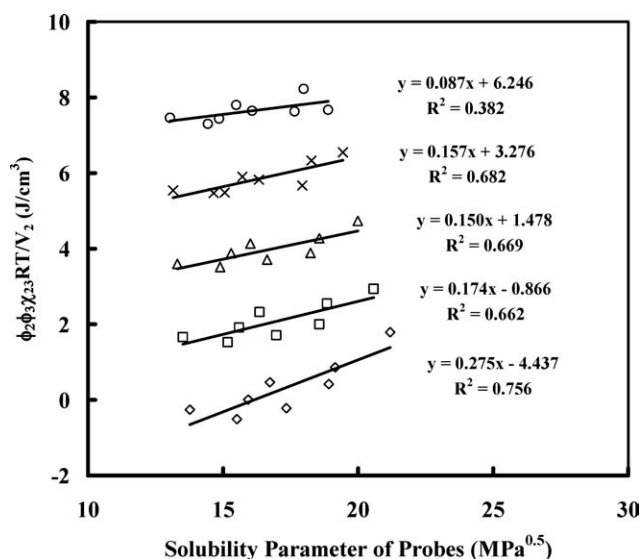
Figure 3. The plot of $\phi_2\phi_3 RT\chi_{23}/V_2$ versus the solubility parameter of probes at five temperatures for C78-PCN systems. Temperatures from bottom to top are 363.15, 383.15, 400.15, 423.15, 443.15 K, respectively. From bottom to top the vertical axis were shifted upward by 0, 2, 4, 6, and 8, respectively.

groups from interaction with the solutes. In the mixture of C78 and the derivatives, some of these groups dissociated and were available to interact with solutes. The result of this dilution process was that probe molecules in the mixture had more polar interaction than the volume average estimation based on components. This apparently higher polar interaction of solvent mixtures when probed by solutes was opposite to the situation of the miscible polymer blends, where there was a specific interaction between the two solvents, and lead to a higher apparent solubility parameter and a negative Δ. Therefore, when the interaction parameter χ_{23} of a solvent mixture was positive, there was a tendency that slope would also be positive, and χ_{23} would increase when the solutes became more polar.

One can estimate the shielding effect of the mixture from the results of the solubility parameters of mixtures. This process was illustrated in a previous study.[21] For example, at 363.15 K in a mixture of 50 vol % TMO the measured solubility parameter was 14.07 MPa$^{0.5}$ rather than 13.84 MPa$^{0.5}$ from volume averaging. A value of 14.07 MPa$^{0.5}$ corresponds to an effective composition of 63.7 vol % TMO in the linear rule. Therefore, in a mixture of 50 vol % TMO, the equivalent of 13.7 vol % of functional groups may have been released from the association state during the dilution process and the solute would experience the mixtures as 63.7 vol % of TMO. A similar calculation yields 11.6% and 10.9% for PCN and TTF, respectively. These percentages do not differ much despite the wider variation of the values of Δ in Table II. This is probably because Δ also depends on the difference between the solubility parameter of the two pure components. When the difference between the solubility parameters of two solvents becomes wider, the Δ tends to be higher even with the same percentage of association. TMO has the highest deviation at 50 vol %. This may reflect that TMO has four functional groups. TTF also has four —CF$_3$ groups but may not have much impact on the interaction because the functional groups are only slightly polar. The other two solvents have only one functional group.

RELATION BETWEEN χ_{23} AND $\Delta\chi$ OF PURE COMPONENTS

The probe dependency made it difficult to evaluate the true value of χ_{23}. An additional analysis method was suggested previously[21] by examining the physical meaning of eq. (3). In the equation, $\chi_{1(23)}$ represents the specific free energy of a solute in the solvent mixture and $(\phi_2\chi_{12} + \phi_3\chi_{13})$ represents the volume average free energy of the solute in the components. The latter quantity also represents the free energy of the solution when no specific interaction occurs between the two components in the stationary phase. The quantity $\phi_2\phi_3\chi_{23}/V_2$ then represents the free energy of transfer for a solute to move from the interacted solvents mixture to the linear combination of the pure components. It also represents the difference that a solute molecule would experience in a mixture when the interaction between the two solvents is "charging up" from the ideal solution state. The free volume effect, which generally depends on the difference in the thermal expansion coefficients between the solvent and solute, is eliminated when a transfer property is considered and solvents and solvent mixture have similar thermal expansion, which is the case in this study.
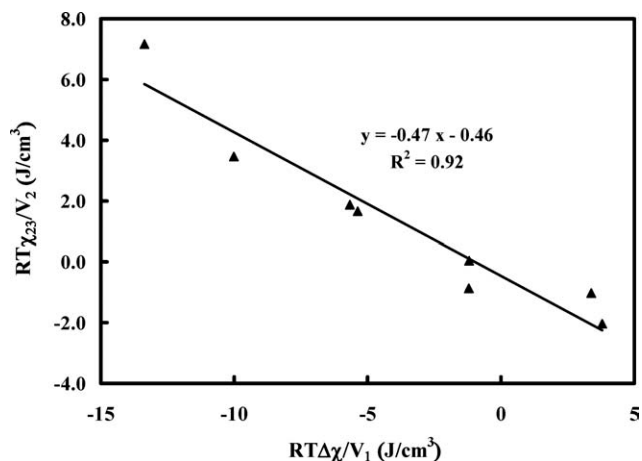
Figure 4. The plot of $RT\chi_{23}/V_2$ versus $RT\Delta\chi/V_1$ probes at 363.15 K for C78-PCN system.

For polar–nonpolar solvent mixtures this difference represented by eq. (3) is likely a function of the difference of the interaction parameters of the solutes between the two solvents, $\chi_{12}-\chi_{13}$. This phenomenon was called the $\Delta\chi$ effect in an earlier study.[9] Although $\Delta\chi$ effect was proposed for the study of favorable miscible mixtures, it is also applicable to an unfavorable, but miscible, mixture. The best solute that can be used to evaluate χ_{23} would be the one that has small or zero $\Delta\chi$. This conclusion is similar to miscible systems. Figure 4 shows the plot of $RT\chi_{23}/V_2$ versus $RT\Delta\chi/V_1$ of solutes in C78-PCN at 363.15 K. A linear relationship can be seen with a small negative intercept. PCN was assigned as Component 2. The plot was made with RT multiplied on both sides because in this study, both solvents are very similar and have high molar volumes, making χ_{23}/V_2 and $\Delta\chi/V_1$ both small. With a factor of RT the variables $RT\chi_{23}/V_2$ and $RT\Delta\chi/V_1$ represent energy per unit volume.

In Figure 4, polar solutes and nonpolar solutes gave different signs for $\Delta\chi$. Polar solutes had negative $\Delta\chi/V_1$ but higher values of χ_{23}/V_2. A higher value of χ_{23}/V_2 was observed because the polar solutes compete with the polar functional groups of the solvents even though they were associated. The interaction of polar solutes yielded a greater negative enthalpy of solution than the nonpolar solutes, and a more positive entropy of solution due to a decrease in molecular order in the self association of solvent in the solution, and therefore, resulted in a lower $\chi_{1(23)}$ and higher χ_{23} through eq. (3). The ability of a polar solute to interact with solvents can also be measured by the value of $RT\Delta\chi/V_1$ of the solute. A more polar solute resulted in a smaller χ value in the polar solvent (Component 2), and led to a more negative $RT\Delta\chi/V_1$. Thus, it was reasonable that $RT\chi_{23}/V_2$ and $RT\Delta\chi/V_1$ depended on the same mechanism and are mathematically related. From the plots, the best value of $RT\chi_{23}/V_2$ was -0.462 J/cm^3 for the PCN system at $RT\Delta\chi/V_1 = 0$.

Table III shows the values of $RT\chi_{23}/V_2$ for each mixture at five temperatures. It can be seen that for all mixtures the values of $RT\chi_{23}/V_2$ decreased quickly when temperature increased. At temperature higher than 403.15 K, the values turned into negative for TMO. For PCN the values were negative for the whole

Table III. The Values of $RT\chi_{23}/V_2$ Determined at $RT\Delta\chi/V_1 = 0$

Solvents	363.15 K	383.15 K	403.15 K	423.15 K	443.15 K
TMO (1/2)	1.004	0.495	0.447	−0.082	−0.557
PCN (1/2)	−0.462	−0.811	−1.009	−1.366	−1.810
TTF (1/2)	3.365	2.492	2.375	2.466	1.798
POH (1/3)	2.556	1.970	1.752	1.431	1.077
POH (2/3)	2.998	2.236	1.879	1.595	0.934

Parenthesis indicates the volume fraction of derivatives in the C78-derivative solvent mixture. Units = J/cm^3.

temperature of study. A rapidly decreasing trend of free energy when temperature increases indicates that there is a positive entropy change for the process. A solution process of two liquids usually leads to an entropy increase because of the mixing of different molecules. But in this case the size effect and combinatorial process were included in the Flory–Huggins formula. The more positive entropy of mixing indicates that in a pure liquid of derivatives there may have been a certain amount of structure organization which is destroyed in the mixing process and led to a more positive entropy of solution, and is represented by a more positive value in the last term in eq. (9). This increase in the entropy of mixing makes the overall value of free energy of mixing a negative number when the enthalpy of mixing is zero. The magnitude of structure organization differs in each derivative liquid because the type of functional groups and their layout in the molecule are different. The solubility parameter model assumes a regular solution, and molecules are treated as globular with all liquids having the same randomness. The results of this study show that for branched molecules with functional groups this assumption may not be the case.

ENTHALPY–ENTROPY RELATION OF $RT\chi_{23}/V_2$

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.[5,25] However, experience has shown that χ usually depends on temperature.[25,26] To further evaluate the entropy effect, the enthalpic and entropic portions of the Flory–Huggins interaction parameter need to be separated. Guggenheim[26] suggested that χ, the size corrected reduced free energy of solution, be separated so that:

$$\chi = \chi_H + \chi_S \qquad (10)$$

where the reduced excess enthalpy of solution, χ_H, and reduced residual entropy of solution, χ_S, are defined as:[26]

$$\chi_H = -T\left(\frac{\partial\chi}{\partial T}\right) = \Delta\bar{H}_{re}^{\infty}/RT \qquad (11)$$

$$\chi_S = \frac{\partial(T\chi)}{\partial T} = -\Delta\bar{S}_{re}^{\infty}/R \qquad (12)$$

Here $\Delta\bar{S}_{re}^{\infty}$ is the residual entropy of solution or the noncombinatorial part of the entropy of solution. It 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 are used in discussions of solution thermodynamics.[27–31] It was noted by Huang et al.[27] that the size correction gives a contribution to the entropy of solution, but that 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 $\Delta\bar{S}_{re}^{\infty}$ versus $\Delta\bar{H}_{re}^{\infty}$. 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 are found in thermodynamic and kinetic processes.[32–36] They are also cited as enthalpy–entropy compensation effects, extra-thermodynamic phenomena, or isokinetic relationships. The entropy–enthalpy compensation effect can be represented in the following form:

$$\chi_S = -\beta\chi_H + \alpha \qquad (13)$$

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 χ relative to χ_H. When $\chi_H = 0$, the intercept term of eq. (13) gives the value of entropy. Therefore, when a system has a higher value of intercept it has a higher value of entropy for the process. The enthalpy–entropy plot of eight solutes in PCN was
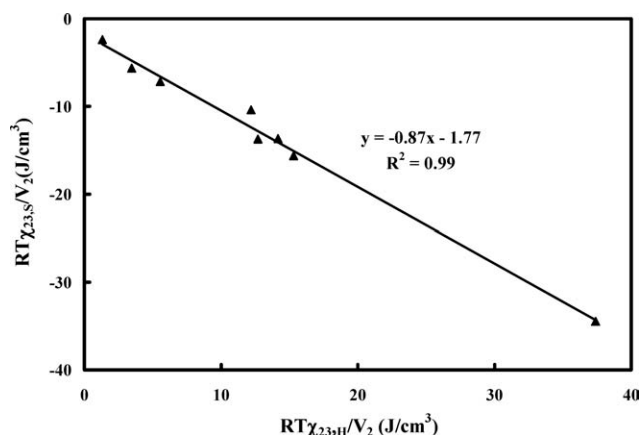
Figure 5. The plot of $RT\chi_{23,S}/V_2$ versus $RT\chi_{23,H}/V_2$ for solutes in C78-PCN system.

Table IV. Correlation Equations for Enthalpy–Entropy Relation for Solutes in Mixtures

Mixtures	Enthalpy–Entropy relation
TMO (1/2)	$RT\chi_{23,S}/V_2 = -0.84\ RT\chi_{23,H}/V_2 - 0.41$
PCN (1/2)	$RT\chi_{23,S}/V_2 = -0.87\ RT\chi_{23,H}/V_2 - 1.77$
TTF (1/2)	$RT\chi_{23,S}/V_2 = -0.90\ RT\chi_{23,H}/V_2 + 2.50$
POH (1/3)	$RT\chi_{23,S}/V_2 = -0.94\ RT\chi_{23,H}/V_2 + 1.67$
POH (2/3)	$RT\chi_{23,S}/V_2 = -0.92\ RT\chi_{23,H}/V_2 + 2.20$

calculated as $RT\chi_{23,S}/V_2$ versus $RT\chi_{23,H}/V_2$ and is shown in Figure 5. It can be seen that there is a linear pattern for the data. The slope of -0.83 is more compensated than those seen in the solution process of homopolymers or transfer between two polymers.[30,31] The correlation equations for the other systems are shown in Table IV. It can be seen that the intercept term is different for each mixture. PCN has a negatives intercept. At $\chi_{23,H} = 0$ this would give a negative overall χ. This explains why PCN has a negative χ in Table III. This effect is most pronounced in PCN. But TMO also had a negative intercept. As pointed out previously PCN and TMO may have some structure in their pure state. The mixing of C78 and these two solvents involved structure destruction and led to a more negative $\chi_{23,S}$ for all the solutes.

CONCLUSIONS

A mechanism previously proposed for the probe dependency of polymer–polymer interactions was tested using mixtures of C78 and its derivatives. The plot of $RT\chi_{23}/V_2$ versus δ_1 gave positive slopes for all mixtures, which is in agreement with the deviation of solubility parameters of the mixtures. But the intercept of $RT\chi_{23}/V_2$ versus $RT\Delta\chi/V_1$ plot at zero $\Delta\chi$ gave a negative values for TMO and PCN. Enthalpy–entropy plot revealed that these two systems have more negative $\chi_{23,S}$. In the mixtures of low or moderately high molecular weight mixtures the effect of entropy can bring the overall χ_{23} into a negative. However, the enthalpy portion still followed the physical interpretation proposed behind eq. (9).

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