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Anomalous solubility parameter and probe dependency of polymer–polymer interaction parameter in inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) has been widely used to measure the Flory–Huggins interaction parameters, χ, between two polymers. For over two decades studies have shown the polymer–polymer interaction parameter to be probe dependent. This study found that the solubility parameters of miscible polymer blends measured by IGC were lower than the volume average values of the components. This led to the conclusion that when specific interactions occur between two polymers the probes have less probability to contact the functional groups of the polymers, leading to a lower apparent solubility parameter. Using the solubility parameter model this deviation was shown to cause the probe dependency. Two methods were proposed to test the miscibility. One was to examine the deviation of the specific retention volume from the weight average rule. The other was to plot $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs. the solubility parameters of probes. For miscible blends a linear trend with negative slope was observed. The slope was proportional to the deviation of solubility parameter of the polymer mixtures from the volume average, which could be used as a measurement for miscibility.

Keywords: Inverse gas chromatography; Thermodynamic interaction parameter; Solubility parameter; Polymer blends

1. Introduction

The knowledge of the interaction parameters between two 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 studying the thermodynamic properties of polymers [1–4]. When a liquid probe is injected into the column the probe vaporizes and flows with the carrier gas, and a characteristic specific retention volume can be measured. Using Flory–Huggins theory [5], the Flory–Huggins interaction parameter between a polymer and probe, χ, can be related to the specific retention volume of the probe, V_g^0, by the following equation [1–4]:

$$\chi = \ln\left(\frac{273.16Rv_2}{V_g^0P_1^0V_1}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (1)$$

where R is the gas constant, T is the column temperature, v_2 is the specific volume of the stationary

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phase, and P_1^0, V_1, and B_{11} are the vapor pressure, liquid molar volume, and the second virial coefficient of the probe, respectively. When a polymer blend 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 of polymer solutions [5] to a ternary system with two polymers and one probe, the interaction parameter $\chi_{1(23)}$ can be related to the difference between pair interaction of probe–polymers, χ_{12} and χ_{13}, and polymer–polymer 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. Since molar volumes of polymers may not be accurately known it is a practice in IGC study to define a probe normalized interaction parameter [3,4]:

$$\chi'_{23} = \chi_{23}(V_1/V_2) \quad (3)$$

The advantage of this parameter is that it can be calculated through the specific retention volume by the following formula without calculating the individual interaction parameters [6]:

$$\ln\left(\frac{V^0_{\mathrm{g,blend}}}{w_2v_2 + w_3v_3}\right) = \phi_2 \ln\left(\frac{V^0_{\mathrm{g},2}}{v_2}\right) + \phi_3 \times \ln\left(\frac{V^0_{\mathrm{g},3}}{v_3}\right) + \phi_2\phi_3\chi'_{23} \quad (4)$$

Here v is the specific volume and w is the weight fraction. Eqs. (2) and (4) were frequently used to study the interaction of two stationary phases using the IGC method.

Deshpande et al. [7] were among the first to apply the IGC technique for the determination of the interaction between a polymer and a non-polymeric compound. Su et al. [8] measured the interaction parameter of PVC and di-octyl phthalate as plasticizer to study their compatibility. Later, this method was also utilized to measure the compatibility of polymer blends. However, many studies showed that the polymer–polymer interaction parameter determined by this technique depended on the probes used and blend compositions. Hsu and Prausnitz [9] and Patterson and coworkers [8] suggested that the compatibility of polymeric components should reflect not only the interaction between the components themselves, i.e., χ'_{23}, but also the difference in strength of the polymer–probes interactions, i.e., $\Delta\chi = |\chi_{12} - \chi_{13}|$. They called it the $\Delta\chi$ effect, and a large $\Delta\chi$ in addition to a high χ'_{23} value leads to incompatibility. Su and Patterson [10] suggested that the probe dependency of χ'_{23} arises from the difference between χ_{12} and χ_{13}. Accordingly, one must select probes that give $\chi_{12} = \chi_{13}$ for studying the blend. Later, Farooque and Deshpande [11] proposed to rearrange Eq. (2) to the following form:

$$(\chi_{1(23)} - \chi_{13})/V_1 = \phi_2(\chi_{12} - \chi_{13})/V_1 - \phi_2\phi_3\chi_{23}/V_2 \quad (5)$$

By plotting the left-hand side of Eq. (5) vs. $\phi_2(\chi_{12} - \chi_{13})/V_1$ the interaction parameter can be obtained from the intercept. This method was used by Etxeberria et al. [12,13] and Lezcano et al. [14], and straight lines were obtained. However, the slopes deviated from their theoretical values. In recent papers Huang proposed to rearrange Eq. (5) into the following form [15,16]:

$$\chi_{1(23)}/V_1 = (\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - \phi_2\phi_3\chi_{23}/V_2 \quad (6)$$

A linear plot can be obtained from the left-hand side vs. $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The polymer–polymer interaction term can be determined from the intercept at $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 = 0$. A physical meaning of this procedure is that when $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 = 0$ the probe is experiencing a similar environment in the blend as compared to the probe liquid. The disturbance of liquid polymer structure is expected to be the minimum. This approach was tested in several systems [15,16] but the plot of $\chi_{1(23)}/V_1$ vs. $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ was found to have a slope less than unity. Since χ is proportional to $\ln(V_g)$ this result also suggested that the probe had less specific retention volume in the mixture compared to the average of the components. It should be noted at this point that the so-called probe dependency of χ'_{23} is a certainty under the definition of Eq. (3) because it is proportional to the molar volume of the probe. What the literature referred to is actually the probe dependency of the polymer–polymer interaction parameter, χ_{23}. In this respect Eqs. (5) and (6) are better in obtaining χ_{23}/V_2, although one would have to use the ratio χ_{23}/V_2 as a single variable when the molar volume of the polymer is unknown [17,18]. An alternative is to define another interaction parameter $B = RT\chi_{23}/V_2$, which is the interaction energy per unit volume [19,20].

2. Apparent solubility parameters of polymer mixtures

Because polymer–polymer mixtures have little entropy of mixing, the miscibility is largely decided by the sign of the heat of mixing. The determination of the heat of mixing becomes the key factor. 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 [21]:

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V}\right)^{1/2} \tag{7}$$

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 the liquid molecules into the ideal gas state. An unambiguous value of solubility parameter can be determined if the material can be vaporized. The Flory–Huggins interaction parameter can be related to the solubility parameters of the two components by [21]:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{8}$$

where δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively, and V_1 is the volume of the solvent. Since polymers have no appreciable vapor pressure and their molar volumes are not accurately known, the definition in Eq. (7) cannot be used for polymers. Experimental values of χ have been used in the determination of the solubility parameters of polymers. The method of DiPaola-Baranyi and Guillet [22,23] has been used to determine the solubility parameters of polymers from χ obtained from IGC measurement. In their studies, Eq. (8) was modified as:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT}\right) \tag{9}$$

Using a series of probes with different solubility parameters the solubility parameter of the polymer, δ_2, can be estimated from the slope or the intercept. However, the solubility parameters determined from the slope and intercept terms of Eq. (9) are frequently different. One way to overcome this problem is by adding an entropy term into the Flory–Huggins interaction parameter so that $\chi = \chi_{\text{H}} + \chi_{\text{S}}$ [1–5,22–25], where the dimensionless χ_{S} is an entropy or specific interaction term which can be used to accommodate deviation from the original solubility parameter model in Eq. (8). When χ_{S} is added into the equation the following modified form of the solubility model is obtained:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_{\text{S}} \tag{10}$$

The Flory–Huggins interaction parameter represents the size-corrected free energy of solution which is calculated as $RT\chi$ [15,21]. The enthalpy of solution is calculated as $RT\chi_{\text{H}} = V_1(\delta_1 - \delta_2)^2$ based on Eq. (8). The entropy term can have either a positive or a negative value and represents the deviation from the solubility parameter model. Adding this new term Eq. (10) is changed into the following expression [15,16,22,23]:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right) \tag{11}$$

where η is the average value of χ_{S}/V_1. A linear regression method is generally used to determine δ_2. From δ_2 and χ the value of χ_{S} for each probe can be obtained from Eq. (10). The results of χ_{S} for hydrocarbon probes in ethylene–propylene rubber, *cis*-polyisoprene and amorphous polypropylene were around 0.3 and showed small probe dependence [22,23]. It was higher for linear alkanes and smaller for aromatic probes. Recent work of Huang [15] on PVC and two nitrile rubbers using polar probes showed that the χ_{S} term was negative for polar probes.

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 gives δ_{m} to be the volume average of the two components [21]:

$$\delta_{\text{m}} = \phi_{\text{A}}\delta_{\text{A}} + \phi_{\text{B}}\delta_{\text{B}} \tag{12}$$

From this equation the formula of specific heat of mixing in the regular solution theory, $\Delta H/V = \phi_{\text{A}}\phi_{\text{B}}(\delta_{\text{A}} - \delta_{\text{B}})^2$, could be derived. If there was a specific interaction that produced negative enthalpy of solution the value of δ_{m} would be higher than the prediction of Eq. (12) to account for the separation of the additional specific interaction of the mixtures in the vaporization process. A measurement of the solubility parameter of the polymer mixtures would then be a good indicator to predict their miscibility. In this study this argument was tested using the data of Munk et al. on the poly(ε-caprolactone)(PCL)/polyepichlorohydrin (PECH) system [26]. In that study IGC measurement was made using 25 solutes in pure components and three mixture compositions

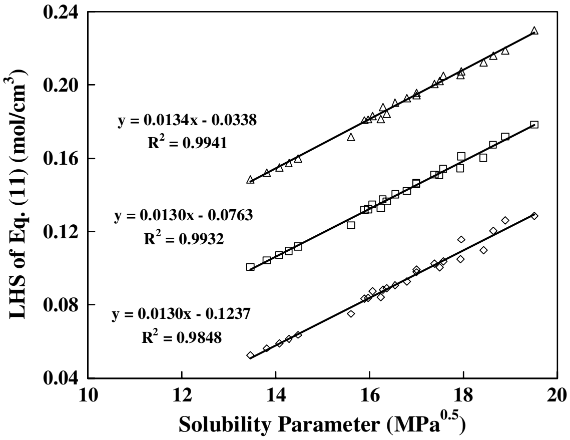

Fig. 1. Plot of LHS of Eq. (11) vs. solubility parameter of probe, δ_1 for PCL (◇), 50/50 volume blend (□), and PECH (△) at 80 °C. The last two lines were shifted upward by 0.05 and 0.1 mol/cm^3, respectively.

at 80 °C. Fig. 1 shows the plot of Eq. (11) vs. the solubility parameter of probes for PCL, PECH, and the 50/50 volume mixture. It can be seen that all three lines had good correlation. The slope of the 50/50 volume mixture lay between those of the two polymers. The parameters are shown in Table 1. The solubility parameters are plotted as a function of volume fraction of PCL in Fig. 2. It can be seen that the solubility parameter of mixtures was lower than the prediction of Eq. (12). This was opposite to the above argument even though there was some specific interaction between PCL and PECH and the system was miscible.

Using the above result a mechanism of probe dependency is proposed here. When two polymers with specific interactions are brought together some functional groups interact with each other and are no longer available to the probes. Relative to the volume average of the pure components the probes will feel the mixture becomes lower in polar or hydrogen bonding interaction and more in nonpolar dispersive force. In other words, the mixture becomes more "alkane-like". The polar probes will be squeezed from the stationary phase and the specific retention volume decreased, which increases $\chi_{1(23)}$ through Eq. (1) then decreases χ_{23} through Eq. (6). Therefore, polar probes have lower retention volume and χ_{23}, and for *n*-alkane probes the change is less. This difference between probes is exhibited as the probe dependency. The solubility parameter of the mixtures measured by the IGC method also reflects the change in the interaction between the probe and the polymer mixtures. It can no longer be related to the cohesive energy density by Eq. (2).

Table 1
Parameters of PCL/PECH blends at 80 °C

Composition	δ (MPa$^{0.5}$)	ηRT (MJ/m^3 = MPa)
PCL	19.04	0.25
PCL/PECH(75/25)	19.02	2.76
PCL/PECH(50/50)	19.15	4.48
PCL/PECH(25/75)	19.39	4.56
PECH	19.74	3.60

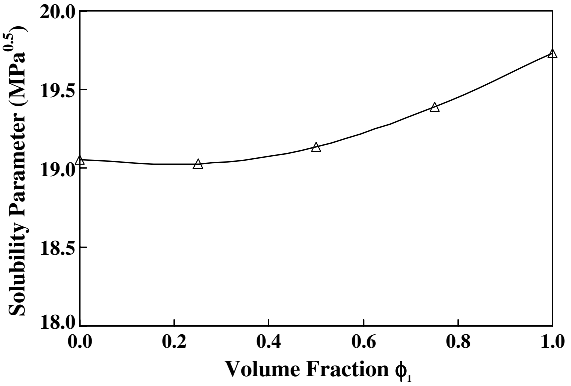

Fig. 2. Plot of solubility parameter of polymer mixtures vs. volume fraction of PCL for PCL(1)/PECH(2) at 80 °C.

3. Evaluation of miscibility

As mentioned above different types of probes act differently when polymer mixtures become more "alkane-like". For a completely immiscible mixture the specific retention volume in IGC measurement is the weight average of two components [27]. When the specific interaction occurs between two polymers, a probe-dependent deviation would occur. Therefore, a measurement of the deviation of the specific retention volume from the weight average rule, using a series of probes, could be a test for miscibility. Earlier, DiPaola-Baranyi et al. [28] also drew a similar conclusion. This deviation actually can be observed in several studies [14,29], although the results usually are present in graphic form as a plot of V_g vs. composition rather than as a percentage of deviation at a particular composition. Fig. 3 shows a plot of percentage deviation of specific retention volume for 50/50 volume PCL/PECH vs. $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. It can be seen that the deviation was higher for solutes with small $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$, which corresponded to polar probes. For

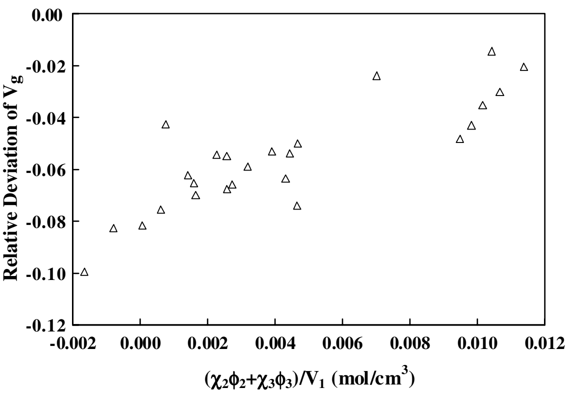

Fig. 3. Plot of relative deviation of specific retention volume of polymer mixture from the weight average value vs. $(\phi_2\chi_{12}+\phi_3\chi_{13})/V_1$ of solutes for 50/50 volume PCL/PECH at 80 °C.

hydrocarbon probes located at the right-hand side the deviation was smaller.

Accompanied by the change in the solubility parameter of the mixture is the variation of the specific interaction term, ηRT, vs. the volume fraction, which is shown in Fig. 4. It can be seen that there was a maximum near the center of the composition. An interpretation of this positive deviation is that when functional groups of the two polymers interact with each other the polymer mixture is similar to an "interpenetrating network" and there is a decrease in chain flexibility and accessibility of the space around the functional groups by the probes. The probe molecules are squeezed into a smaller space, which leads to a smaller entropy of solution for the mixture and a more positive η_m. In previous works the values of ηRT for poly(vinyl chloride) [30], poly(tetramethylene glycol) [30], nitrile rubber [15], PECH [31], and PCL [31] were in the range of 0–3 cal/cm^3 (0–12 MJ/m^3) but for poly(hydroxyl ether of bisphenol A) (PH) [32] the value of ηRT was a much higher value of about 10 cal/cm^3 (40 MJ/m^3). Since PH has hydrogen bonding, this agrees with the mechanism that a stationary phase with a higher intermolecular interaction tends to produce a higher ηRT for probes.

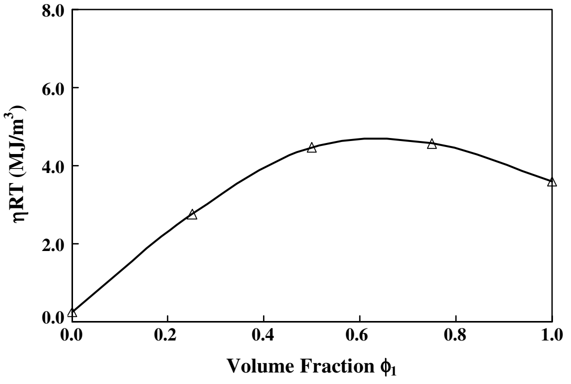

Fig. 4. Plot of ηRT vs. volume fraction of PCL for PCL(1)/PECH(2) at 80 °C. Unit: MJ/m^3 = MPa.

A more quantitative criterion can be made with the help of the solubility parameter model. Here it will show that the deviation of solubility parameters of mixtures from their value in Eq. (12) is the source of probe dependency. When Eq. (10) is applied to the interaction parameters between solute–polymer and the polymer–polymer mixture, χ is replaced by the solubility parameter term and the entropy/specific interaction term:

$$\begin{aligned}(\delta_1-\delta_m)^2+\chi_{s,m}RT/V_1 &= \phi_2(\delta_1-\delta_2)^2+\phi_2\chi_{s,2}RT/V_1+\phi_3(\delta_1-\delta_3)^2\\ &\quad+\phi_3\chi_{s,3}RT/V_1-\phi_2\phi_3RT(\chi_{23}/V_2)\end{aligned}\tag{13}$$

In this equation $\chi_{s,2}$, $\chi_{s,3}$, and $\chi_{s,m}$ are the entropy terms between probes and polymer 2, 3, and the mixture, respectively. Eq. (13) can be simplified further using the relation:

$$\delta_1-\delta_m=\delta_1-\delta_{m,r}+\Delta\tag{14}$$

Here Δ is the deviation of the solubility parameter of the polymer mixture from the regular solution value, $\delta_{m,r}$, which is calculated from Eq. (12). Combining the above two equations the following equation is obtained:

$$\begin{aligned}\phi_2\phi_3RT(\chi_{23}/V_2) &= \phi_2\phi_3(\delta_2-\delta_3)^2-2\Delta(\delta_1-\delta_{m,r})\\ &\quad-\Delta^2+RT(\phi_2\chi_{s,2}+\phi_3\chi_{s,3}-\chi_{s,m})/V_1\end{aligned}\tag{15}$$

The left-hand side can be plotted vs. the solubility parameter of the probe, δ_1. The advantage of plotting $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs. δ_1 is that data can be determined from the specific retention volume without additional calculation. The former can be calculated from Eq. (4) using the specific retention volume data. This plot is demonstrated for PCL/PECH in Fig. 5. There was a general decreasing trend when δ_1 increased. From Eq. (15) it can be seen that χ_{23}/V_2 was probe dependent through two terms, $2\Delta(\delta_1-\delta_{m,r})$ and $RT(\phi_2\chi_{s,2}+\phi_3\chi_{s,3}-\chi_{s,m})/V_1$. From the first term the plot of $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs.

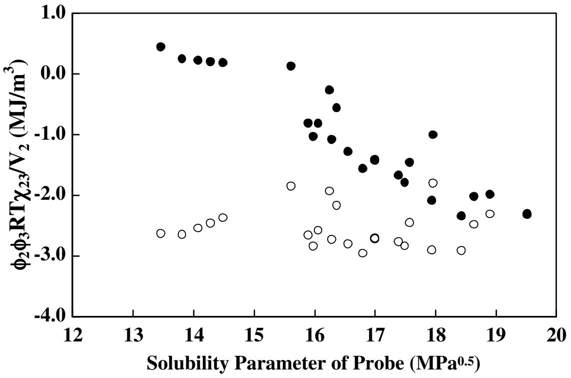

Fig. 5. Plot of $\phi_2\phi_3RT(\chi_{23}/V_2)$ (●) and $RT(\phi_2\chi_{s,2}+\phi_3\chi_{s,3}-\chi_{s,m})/V_1$ (○) vs. solubility parameter of probes, δ_1, for 50/50 volume PCL/PECH at 80 °C. Unit: MJ/m^3 = MPa.

δ_1 had a slope equal to -2Δ. Only when $\Delta = 0$ could the value of χ_{23} be a constant. The value of Δ is a function of blend composition. It is generally a maximum near the equal volume composition. The deviation term is an indicator of the miscibility of the system. It can be seen that the slope was about -0.4 MPa$^{0.5}$. This gave the value of Δ about 0.2 MPa$^{0.5}$, which agreed with the deviation in Fig. 2.

The last term of Eq. (15) produced scattering of data along the general trend. The value of this term for each probe is also plotted in Fig. 5. It can be seen that the last term was negative and its scattering was reflected in the overall results. The scattering occurred because some probes were polar with similar types of functional groups as PCL and PECH. These probes could compete with the polymers in interacting with each other. When this happened the specific retention volume would be different from the trend of other probes without similar interactions. In this respect the best probes for the IGC study of polymer miscibility would be those that interact similarly and only weakly with the polymer components so that the specific interaction between the polymers would not be disturbed.

The large negative value of $\phi_2\phi_3RT(\chi_{23}/V_2)$ around $\delta_1 = \delta_{m,r}$ in Fig. 5 may be tempting to use to estimate the value of χ_{23}/V_2. In fact, this was done in the literature in the argument that it is the probe most compatible to the system. The right-hand side of Eq. (15) contains many terms. Note that for PCL/PECH the value of $\phi_2\phi_3(\delta_2-\delta_3)^2$ and Δ^2 were relatively small at around 0.08 and 0.02 MJ/m^3, respectively. A negative value of $\phi_2\phi_3RT(\chi_{23}/V_2)$ around $\delta_1 = \delta_{m,r}$ reflected the value of the last term in Eq. (15), which represented the change of the probe entropy terms between the polymer mixture and the pure components. Note that the average value of χ_s/V_1 was η, which could be determined from the plot of DiPaola-Baranyi and Guillet. From Fig. 4 the difference between η_mRT and the volume average value was estimated to be about -2.5 MJ/m^3, which was in agreement with the average value of the last term of Eq. (15) in Fig. 5. In the past the entropy term, χ_S, was usually considered to be a constant with the value ranging between 0.2 and 0.6 [33]. This study suggested that a careful study on the variation of χ_S as well as η between blends and pure components is important because the difference causes a negative value for $\phi_2\phi_3RT(\chi_{23}/V_2)$, which is generally being associated with the "true" polymer–polymer interaction. The mechanism of this difference is not clear, but may be related to the chain flexibility and accessibility of functional groups as pointed out earlier.

4. Failure of the random mixture assumption

Judging from Eq. (15) there is no suitable probe that can be used to estimate the value of χ_{23}/V_2 in the context of the solubility parameter model because of the dependency of δ_1 through non-zero Δ. The ultimate reason is because the regular solution model assumes a random mixture and functional groups have equal access to each other. This assumption is also implied in the Flory–Huggins treatment in the definition of χ. In the Flory–Huggins theory the segments of polymers were assumed to have $(z-2)$ number of coordinates and each coordinate had equal probability to contact solvent molecules [5]. From the difference of contact energy the Flory–Huggins interaction parameter, χ, was defined. In the Flory–Orwoll–Vrij equation-of-state approach the free volume effect was considered and the contact was proportional to the specific surface area of the segment but the contact probability was still assumed to be equal [34]. The free volume effect was also tried to explain the probe dependency [11]. However, the value of the free volume effect was very narrow at 50–150 cal/mol (200–600 J/mol) and did not vary much between non-polar and polar probes [35]. Furthermore, the effect of free volume was largely cancelled when the difference was taken between the mixture and the pure components. The free volume effect cannot be used to explain the wide range of χ_{23}/V_2 encountered in many studies.

The possibility of non-random distribution of probes in polymer mixtures in the IGC study was suggested by Galin and Rupprechi [36]. It was also mentioned by Demertzis et al. [37] as one possible source for probe dependency. In a study of surface adsorption of polymer mixtures by the IGC method, Shi and Schreiber [38] considered the possibility that surface and bulk compositions in polymer mixtures could be different. The results of specific retention volume of the mixtures were used to estimate the composition of the surface layer using the pure component data and a linear average rule. It was concluded that the polymer component with low surface energy was located preferentially in the surface.

From this concept the effective composition in the mixed stationary phase was proposed as an explanation for the deviation of the slope of Eq. (5) from its theoretical value [14,39,40]. For this approach to be valid for other systems the value of the specific retention volume and the interaction parameter of the mixtures should lie within the range of the two individual components in order to obtain a physically possible effective composition. However, this was not true in experimental results of many systems [14,26,29]. Also, one of the mixtures in Table 1 had a lower solubility parameter than either component. This cannot be accomplished by a linear combination of the two components using the effective composition method. Therefore, the reason for deviation of solubility parameters of the mixtures went beyond a simple segregation of the two components. It was related to the formation of the specific interactions between the two polymers in the mixture and the accompanied reduction in their intermolecular interactions with the probes. Since different functional pairs interact with different strengths it can be expected that the pair formation with a higher energy released would have higher probability. The probes would have less probability to contact with the functional groups of the polymer that participated in specific interactions. This would lead to a lower apparent solubility parameter. An unequal access between functional groups or segments also creates probe-dependent deviation from the volume average rule.

5. Conclusions

This study showed that there was negative deviation of solubility parameters of a miscible polymer mixture from the volume average rule, which is opposite to the physical mechanism that there was a specific interaction. This was accompanied by a positive deviation of the entropy term of the solubility parameter model. This deviation was the result of the failure of the assumption of equal access to the functional groups of the polymers in the solution. A mechanism was proposed to explain the probe dependency. Two methods were proposed to test the miscibility. One was to examine the deviation of specific retention volume. The other was to plot $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs. δ_1. The magnitude of the slope could be used as an indicator of miscibility.

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