

Concentration Dependency of Interaction Parameter Between PVC and Plasticizers Using Inverse Gas Chromatography

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ABSTRACT: The inverse gas chromatography method was extended to study the concentration dependent Flory–Huggins interaction parameter between poly(vinyl chloride) (PVC) and plasticizers using literature data. For both PVC/polyadipate and PVC/epoxidized soybean oil (ESO) systems, the miscibility was better at the high PVC end. The specific interaction between PVC and plasticizers was estimated from the difference between the experimental results and the enthalpies of mixing predicted by the solubility

parameter model. The interaction was negative and skewed toward the high PVC end, and rendered the overall interaction parameter negative at high PVC compositions. Chemical potential was used to determine the phase composition of PVC/plasticizer mixtures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 146–156, 2004

Key words: chromatography; thermodynamics; poly(vinyl chloride) (PVC)

INTRODUCTION

Poly(vinyl chloride) (PVC) is a commercially important polymer. It is difficult to process, so plasticizers are used in many applications. Plasticizers are low melting point solids or high boiling point organic liquids added to plastics to increase their workability, flexibility or distensibility. Plasticization occurs when plasticizer molecules interact with the polar groups of the polymer and replace polymer–polymer interactions with polymer–plasticizer interactions, thus shielding polymer chains from interacting with each other. Thus, plasticizers require molecular interaction with a portion of the polymer molecule, and the plasticizer molecule possesses another nonpolar portion in order to reduce interaction.^{1–3} The most common plasticizers are the alkyl esters of phthalic acid, which contain an aromatic ring and ester groups to interact with PVC, and aliphatic acid chains to maintain nonpolar contact with other molecules. Commercial plasticizers are usually liquids of moderately high molecular weight. The plasticizer can also be a polymeric material, which is nonvolatile and is generally called a “permanent plasticizer.” A common polymeric plasticizer is poly(adipate ester). The glycol used can be 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol or neopentyl glycol.³

The plasticizer is usually a marginal solvent for the polymer.¹ General purpose plasticizers such as dioctyl phthalate will dissolve PVC on heating, and remain dispersed in the plasticized gel on cooling. Less polar plasticizers such as dioctyl adipate are less bonded to the polymer, giving it more freedom and softer properties. More polar plasticizers such as tricresyl phosphate and butyl benzyl phthalate will dissolve PVC rapidly, but are so firmly bonded to the polymer that they immobilize it and give it harder properties. If polarity is too low, then the plasticizer exudes and is called a secondary plasticizer. The solubility parameter and Flory–Huggins interaction parameter were proposed to screen plasticizers.¹ The thermodynamic interaction between a solvent (probe) and a polymer or a mixture of plasticizer and polymer can be studied by gas liquid chromatography (GLC).^{4–11} The molecular probe technique of GLC, generally known as inverse gas chromatography (IGC), reveals information about the interaction between probes and polymeric stationary phases as well as the interaction between polymer and plasticizers. The specific retention volume of probes, V_g^0 , is related to the Flory–Huggins interaction parameter between the solvents and polymer, χ , by the following equation:^{4–11}

$$\chi = \ln\left(\frac{273.16Rv_2}{V_g^0 P_1^0 V_1}\right) - 1 + \frac{V_1}{M_2 v_2} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (1)$$

where R is the gas constant, T is the column temperature, v_2 is the specific volume, M_2 is the molecular weight of the stationary phase, and P_1^0 , V_1 , and B_{11} are the vapor pressure, molar volume and the second virial

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coefficient of the probe, respectively. Knowledge of the interaction parameter between a solvent and polymer is very useful in the selection of solvents for the polymer. When χ is less than 0.5, the probe liquid is generally characterized as a good solvent for the polymer, while a value higher than 0.5 is a poor solvent and may lead to phase separation.¹² In the absence of specific interaction between a probe and polymer, the interaction parameter is generally positive and can be estimated from the solubility parameter model. The solubility parameter model has been successful in describing thermodynamic properties of solutions, especially when the component liquids are nonpolar. Group calculation methods have been proposed for calculating the solubility parameters.^{13–15} The Flory–Huggins interaction parameter can be related to the solubility parameters of two components by the following equation:¹²

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \quad (2)$$

where δ_1 and δ_2 are the solubility parameters of the probe and polymer, respectively, and V_1 is the volume of the probe. The above equation implies that χ is always positive. A negative experimental value of χ can occur in systems with a specific interaction. When a specific interaction exists between solvent and polymer, the interaction parameter can have a negative value.

Interaction parameters of polymer blends by IGC method

When a polymer blend is used in an IGC study, the corresponding retention volume data and density of the blends can be used in eq. (1). The interaction parameter obtained is called $\chi_{1(23)}$. Applying the Flory–Huggins equation of polymer solutions to a ternary system with two polymers and one probe, the interaction parameter $\chi_{1(23)}$ can be related to the probe–polymers interactions, χ_{12} and χ_{13} , and to polymer–polymer interaction, χ_{23} , by the following equation:

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}(V_1/V_2) \quad (3)$$

In the derivation of the above equation, it was assumed that all χ values are constant. Since molar volumes of polymers, V_2 , may not be accurately known, it is a practice in IGC study to define a probe normalized interaction parameter:^{7,9,11,16}

$$\chi'_{23} = \chi_{23}(V_1/V_2) \quad (4)$$

The advantage of this parameter is that it can be related to the specific retention volumes directly by

the following formula without calculating the individual interaction parameters:^{7,9,11,16}

$$\chi'_{23} = \frac{1}{\phi_2\phi_3} \left[\ln\left(\frac{V_{g,\text{blend}}^0}{w_2v_2 + w_3v_3}\right) - \phi_2\ln\left(\frac{V_{g,2}^0}{v_2}\right) - \phi_3\ln\left(\frac{V_{g,3}^0}{v_3}\right) \right] \quad (5)$$

Eq. (5) is frequently used to study the interaction of two stationary phases using the inverse gas chromatography method. Deshpande and coworkers⁶ applied this technique to determine the thermodynamic interaction between the components of a mixture of polymeric and non-polymeric compound. Su et al.¹¹ used this technique to measure the interaction parameter of PVC and dioctyl phthalate plasticizer to study their compatibility. Later, this method was also utilized to measure the compatibility of polymer blends. However, many studies have shown that the polymer–polymer interaction parameter determined by this technique depends on the probes used and the blend compositions. Hsu and Prausnitz¹⁷ and Patterson and coworkers¹⁸ suggested that the compatibility of polymeric components in solution should reflect not only the interaction between the components themselves, i.e. χ_{23}' , but also the difference in strength of the polymer–probe 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 Patterson¹⁹ suggested that probe dependency of χ_{23}' arises from the difference between χ_{12} and χ_{13} . Accordingly, one must select probes that make χ_{12} equal to χ_{13} to study the blend.

Farooque and Deshpande²⁰ studied several methods to overcome probe dependency. They tested these methods on polystyrene–polybutadiene blends and found that the interaction parameters were still probe-dependent. They proposed rearranging eq. (3) to the following form:

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

By plotting the left hand side of eq. (6) versus $\phi_2(\chi_{12} - \chi_{13})/V_1$, the interaction parameter can be obtained from the intercept. This method was used by Etxeberria et al.^{21,22} and Lezcano et al.²³, and very good linear lines were obtained. However, the slopes deviated from their theoretical values. Recently, this author (J.-C. Huang) proposed the rearrangement of eq. (6) into the following form:^{24,25}

$$\chi_{1(23)}/V_1 = (\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - \phi_2\phi_3\chi_{23}/V_2 \quad (7)$$

A linear plot can be obtained from the left hand side versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The polymer-polymer interaction term can be determined from the intercept at $\phi_2\chi_{12} + \phi_3\chi_{13} = 0$. This equation was used in blends of PVC and nitrile rubbers reported by Sen and Mukherjee²⁶, and lines with high correlation coefficients were obtained.²⁴ However, the slopes were slightly lower than unity. In another study,²⁵ the author compared eqs. (7) and (8) using poly(ϵ -caprolactone)/polyepichlorohydrin systems reported by Munk et al.²⁷ and poly(ethyl acrylate)/poly(vinyl propionate) systems reported by Mandal et al.²⁸ It was concluded that eq. (7) gave smaller standard deviation for slopes and intercepts than eq. (6).

The deviation of the slopes from unity was important in explaining the probe dependence of the polymer-polymer interaction parameters that have been reported in many studies. Because the slopes were not exactly a unity, a systematic deviation existed when the last term in eq. (7), $\phi_2\phi_3\chi_{23}/V_2$, was calculated from the difference between $\chi_{1(23)}/V_1$ and $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The difference increased when $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ was increased from zero. This systematic difference was combined into the calculation of χ_{23} and had a tendency to distort its value. To illustrate this point, let us assume that in the linear regression line of eq. (7), the slope was $(1 - \kappa)$ where κ was a small positive number and the intercept was a constant λ . Eq. (7) yields the following expression for χ_{23} :

$$\begin{aligned} \phi_2\phi_3\chi_{23}/V_2 &= (\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - \chi_{1(23)}/V_1 \\ &= \kappa(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - \lambda \quad (8) \end{aligned}$$

The value of χ_{23} therefore has a small probe dependency through χ_{12} and χ_{13} . The values of χ_{12} and χ_{13} usually increase or decrease at the same time for miscible blends with components that have similar properties. The value of χ_{23} also changes when the values of χ_{12} and χ_{13} change. This trend has been observed in many studies.¹⁶⁻²³ According to eq. (8), only when $(\phi_2\chi_{12} + \phi_3\chi_{13})$ has a value of zero is the value of $\phi_2\phi_3\chi_{23}/V_2$ the true probe independent value.

The use of eq. (7) is not just a simple mathematical manipulation. In eq. (7), the quantity $\phi_2\chi_{12} + \phi_3\chi_{13}$ represents the size-corrected free energy of solution for a probe molecule moving from pure probe liquid to the mixture in the stationary phase. When $\phi_2\chi_{12} + \phi_3\chi_{13}$ is equal to zero, the probe has zero enthalpy and non-combinatorial entropy of solution, which would be close to an "ideal solution" condition. In eq. (6), the variable is proportional to the $\Delta\chi$ effect. When extrapolating to zero, it was implied that χ_{12} and χ_{13} reach an equal value. The probe has the same affinity for the two polymers and experiences a true random distribution in the polymer mixture, as discussed by several authors.¹⁷⁻¹⁹ Since such an ideal probe may not

physically exist, an interpolation or extrapolation method can be used to obtain a zero point. Furthermore, when $\phi_2\chi_{12} + \phi_3\chi_{13}$ is small, the individual values of χ_{12} and χ_{13} are generally small, which also implies the $\Delta\chi = 0$ condition. Thus, the plot of eq. (7) can be used to satisfy both conditions.

The concentration dependency of χ_{23} can also be explained through eq. (7). In the Flory-Huggins equation, as well as the solubility parameter model, it was assumed that the enthalpy and non-combinatorial entropy of mixing was symmetric to the volume fractions of the polymers. This assumption might not be correct when a specific interaction exists, because the specific interaction tends to be stoichiometric and depends on the concentrations of functional groups. In the event that the interaction term is not symmetric to the volume fraction, an attempt to use a symmetric expression will lead to a concentration dependency on χ_{23} . The possibility of using a composition dependent χ_{23} to explain IGC data was also discussed by Sanchez²⁹ and Chee.³⁰ Sanchez pointed out that, when an interaction parameter depended on compositions, there were four different types of polymer-polymer interaction functions that could be defined based on the technique of measurement. However, when one of the four parameters is known, the other three could be derived from it. When χ_{23} is composition-dependent, the last term of eq. (7) is different and the equation can be written as:^{29,30}

$$\chi_{1(23)}/V_1 = (\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - (\phi_2\phi_3/V_2) \frac{\partial(\phi_3\chi_{23})}{\partial\phi_3} \quad (9)$$

The last term as a whole can still be determined from the intercept of the linear regression line using a series of probes. With enough data from different blend compositions, the expression of χ_{23} versus volume fraction can be determined from IGC study. The purpose of this study is to extend the use of eqs. (7) and (9) to obtain information about the concentration dependent interaction parameters of PVC/plasticizer systems where specific interactions are known to exist.

RESULTS AND DISCUSSION

Probe-polymer interactions

Demertzis et al.³¹ determined the retention volume of a series of solutes using PVC with a polyadipate ester, Santicizer 409 A. The polyadipate ester is called polyester in this study. The PVC had a molecular weight (MW) of about 100,000, and the polyester had a MW of 1800. These authors also measured the specific retention volumes of solutes in several mixtures of PVC and polyester at weight ratios of 92/8, 85/15, 75/25, 60/40, 45/55, and 25/75. The probes used included

TABLE I
Molar Volume, Solubility Parameter, and Entropy of Vaporization of Probes at 100°C

Probes	Molar volume (cm ³ /mole)	Solubility parameter (cal/cm ³) ^{0.5}	ΔS_{vap} (cal/K/mole)
Tetrahydrofuran	91.0	8.42	17.6
Chloroform	91.3	8.30	17.6
Carbon tetrachloride	109.9	7.68	16.2
Benzene	100.2	8.21	16.7
Toluene	116.7	8.10	17.4
Cyclohexane	122.9	7.33	19.7
n-Hexane	147.1	6.57	17.0
n-Heptane	160.3	6.75	18.8
n-Octane	174.6	6.88	21.4
n-Nonane	189.5	6.99	24.0
n-Decane	203.6	7.10	26.5

tetrahydrofuran, chloroform, carbon tetrachloride, benzene, toluene, cyclohexane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane. Specific retention volumes at 100°C were reported together with probe-polymer interaction parameters at 90, 100, 110, and 120°C. In another study,³² the same authors determined the retention volume using a PVC with molecular weight of about 90,000 and an epoxidized soybean oil (ESO). The ESO contained approximately 4.5 oxirane rings in its structure. The molecular weight was about 960. For this system, the specific retention volumes at 90°C were reported. The χ values of probes in PVC were reported for all temperatures studied and showed no significant variation associated with the glass transition. In both studies, the authors presented the results of χ_{23}' which showed probe dependence as well as concentration dependence. At the high PVC end of composition, the values of χ_{23}' decreased from positive values to negative. A similar dependency on χ_{23}' in the PVC/dioctyl phthalate system was reported by Su et al.¹¹ The values of χ_{23}' at a PVC/plasticizer ratio of 92/8 were also reported for different temperatures by Demertzis et al.^{31,32} The values of χ_{23}' increased as temperature increased, suggesting that the system became less thermodynamically compatible. A similar temperature dependency was also observed in the results of a study by Su et al.¹¹

The values of retention volumes and interaction parameters between probes and PVC, χ_{12}' , and probes and plasticizer, χ_{13}' , reported by Demertzis et al.^{31,32} were used to calculate solubility parameters of PVC and plasticizers. In the present study, the specific volumes of PVC at 90 and 100°C were taken from Zoller and Walsh.³³ For polyadipate, the specific volume was 1.082 g/cm³ at 25°C, and the thermal expansion coefficient was 0.00071°C⁻¹. For ESO, the density was 0.995 cm³/g, and the thermal expansion coefficient was 0.00072°C⁻¹.¹ The molar volumes of the probes were estimated using the density at 25°C, according to the methods of Spencer and Danner described by Reid et al.³⁴ The solubility parameters of the probes were

calculated from internal energy change of vaporization, ΔE_{vap} , and molar volume V_1 based on the definition $\delta^2 = \Delta E_{\text{vap}}/V_1$. The Clausius-Clapeyron equation was used to calculate the enthalpy change of vaporization ΔH_{vap} :

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_{\text{vap}}}{R} \quad (10)$$

The vapor pressure, P , and molar volume V_1 of the probes were estimated using the methods described by Reid et al.³⁴ The molar volumes, solubility parameters, and entropies of vaporization for the probes are listed in Table I. Since polymers have no appreciable vapor pressure and their molar volume may not be known accurately, the experimental values of χ have been used in the determination of the solubility parameters of polymers. The following equation was used to calculate solubility parameters of stationary phases using the experimental values of Flory-Huggins interaction parameters:^{24,35,36}

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

where χ_s contains the enthalpy from specific interaction and non-combinatorial entropy terms. Using a series of probes with different solubility parameters, the solubility parameter of the polymer, δ_2 , can be calculated from the slope. The Flory-Huggins interaction parameter represents the size-corrected free energy of solution and is calculated as $RT\chi$.¹⁰ The enthalpy of solution is calculated based on eq. (2) as $RT\chi_H = (\delta_1 - \delta_2)^2 V_1$. The difference, $RT\chi_s$, can have either a positive or a negative value and represents the deviation from the solubility parameter model. Guillet et al.^{35,36} demonstrated the use of IGC in the determination of χ and the solubility parameters of polymers. The values of χ_s for hydrocarbon probes in ethylene-propylene rubber, *cis*-polyisoprene and amorphous

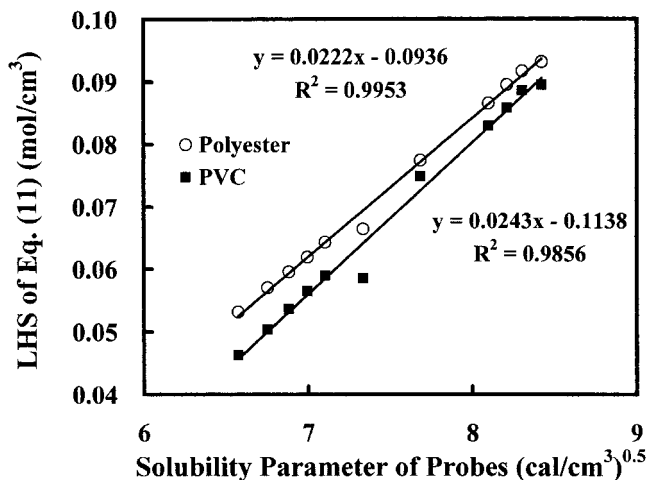


Figure 1 Left side of eq. (11) versus the solubility parameters of probes for PVC and Polyester at 100°C.

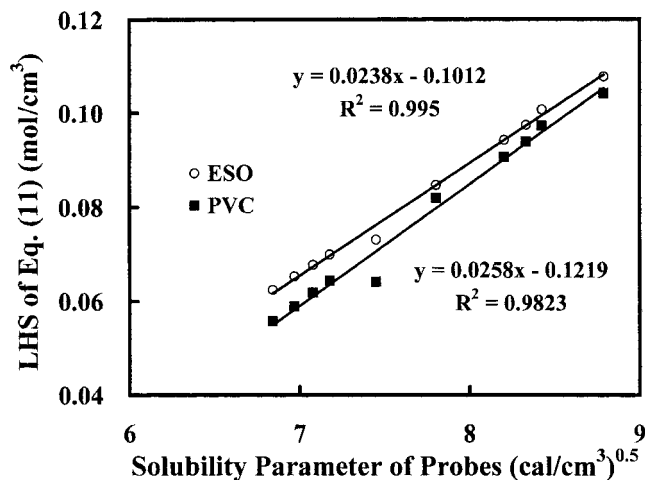


Figure 2 Left side of eq. (11) versus the solubility parameters of probes for PVC and ESO at 90°C.

polypropylene were around 0.3 and showed small probe dependence. The value of χ_S was higher for linear alkanes and smaller for aromatic probes.³⁶ A recent work by the author on PVC blends with two nitrile rubbers using polar probes showed that the χ_S term is negative for polar probes.²⁴

Plots for the determination of the solubility parameters of PVC and polyester at 100°C are shown in Figure 1. It can be seen that each line has a linear trend with a different slope. The slope was higher for PVC, and the correlation coefficient was higher for polyester. The solubility parameters were 9.01 and 8.23 $\text{cal}^{0.5}/\text{cm}^{1.5}$ for PVC and polyester, respectively. Cyclohexane showed a deviation from the linear trend for PVC, and there was also a smaller deviation in the plot of polyester. From Table I, it can be seen that cyclohexane had a higher solubility parameter than *n*-alkanes. This is because of its higher heat of vaporization and smaller molar volume. This difference makes cyclohexane deviate toward the right side of the regression line. Figure 2 shows the similar plots of PVC and ESO at 90°C. PVC again had a higher slope, and the correlation was better for ESO. Cyclohexane again deviated from the linear trend. The solubility parameters were 9.05 and 8.35 $\text{cal}^{0.5}/\text{cm}^{1.5}$ for PVC and ESO, respectively. The value of the solubility parameter of PVC was in agreement with the value of 8.94 at 130°C, calculated in a previous article²⁴ using data from PVC/nitrile rubbers.²⁶ Solubility parameter decreases when temperature increases. The solubility parameter of PVC at 25°C reported in the literature ranges from 9.53 to 10.9 $\text{cal}^{0.5}/\text{cm}^{1.5}$.³⁷

To observe any trend of deviation from the solubility parameter model, the χ_S terms of the probes in plasticizers are plotted against the same quantity of PVC in Figure 3. It can be seen that the χ_S terms were positive. The probe with the highest χ_S value was

cyclohexane. Its solubility parameter was closer to that of PVC and plasticizers than those of the *n*-alkanes and led to a small χ_H . With a similar value to the χ value of *n*-hexane, a small χ_H made χ_S large. The difference in $\Delta S_{100^\circ\text{C}}/R$ between cyclohexane and *n*-hexane is about 1.36. The entropy of vaporization, which indicates the organization of liquids, showed a higher value for cyclohexane than *n*-hexane and *n*-heptane. This indicates that there may be a higher order of organization in liquid cyclohexane than in *n*-alkanes with a similar molecular weight. This difference showed up during vaporization and solution processes. The difference of χ_S between cyclohexane and *n*-hexane in PVC was 0.82 and 0.85 at 90 and 100°C, respectively. Thus, for cyclohexane and *n*-hexane, a large portion of the difference in χ_S can be attributed to the difference in entropy of the pure liquids.

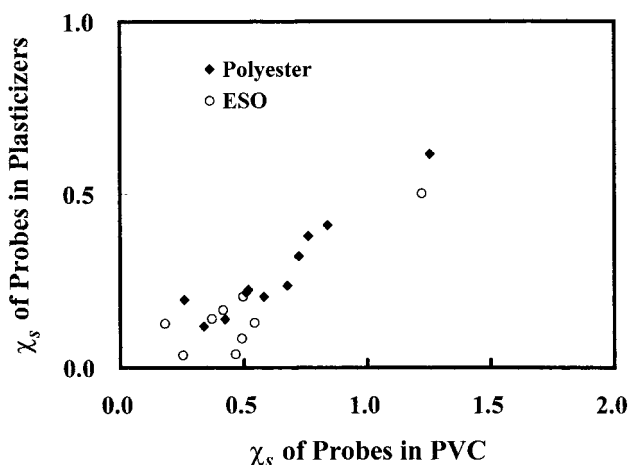


Figure 3 The plot of χ_S values of the probes in plasticizers versus the χ_S values in PVC.

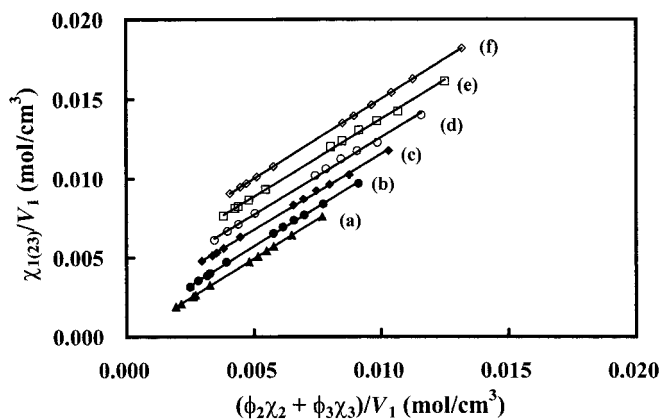


Figure 4 Linear regression plot of the quantity $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} - \phi_3\chi_{13})/V_1$ for PVC/polyester systems: (a) 25/75 wt %, (b) 45/55 wt % shifted upward by 0.001, (c) 60/40 wt % shifted upward by 0.002, (d) 75/25 wt % shifted upward by 0.003, (e) 85/15 wt % shifted upward by 0.004, (f) 92/8 wt % shifted upward by 0.005.

There was a correlation between the χ_S data of PVC and plasticizers given in Figure 3. The slope was close to 0.5, with that of PVC higher than that of plasticizers. Many of these differences originated from the higher χ values of the probes in PVC compared to plasticizers. A higher χ value tends to produce a higher value of χ_S and caused the correlation in Figure 3. The free volume effect can give a partial explanation of why the χ and χ_S values of PVC were higher than those of plasticizers. According to the Flory–Orwoll–Vrij theory,^{38,39} the free volume effect increases when the difference in reduced volumes between probes and polymer widens. PVC has a molecular weight of 100,000 and is more condensed than plasticizers, which have molecular weights on the order of 1000. The free volume effect gave a positive contribution to the excess free energy of solution⁴⁰ and would be higher in PVC than in plasticizers. This made the χ value of PVC higher than that of plasticizers. Another reason might be the partial crystalline feature of PVC,^{41,42} which made a portion of the polymer inaccessible to the probe molecules and reduced retention volume, causing a high χ value.

PVC–Plasticizer interaction

In the analysis of PVC/plasticizer systems, the subscripts 1, 2 and 3 were used to indicate the probe, PVC, and plasticizer, respectively. Figure 4 shows the plot for the PVC–polyester system. The same plot for PVC/ESO is shown in Figure 5. Because these lines are very close to each other, the lines corresponding to different blend compositions were shifted upward by a different amount in order to separate them. It can be seen that in both figures data show very good linear trends without unusual deviation. Despite the devia-

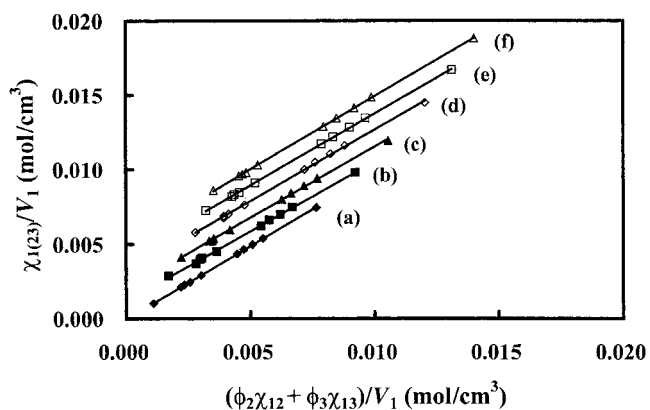


Figure 5 Linear regression plot of the quantity $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for PVC/ESO systems: (a) 25/75 wt %, (b) 45/55 wt % shifted upward by 0.001, (c) 60/40 wt % shifted upward by 0.002, (d) 75/25 wt % shifted upward by 0.003, (e) 85/15 wt % shifted upward by 0.004, (f) 92/8 wt % shifted upward by 0.005.

tion in Figures 1 and 2, cyclohexane also falls into the linear category. The range of data in abscissa gradually widens as the volume fraction of PVC increases. This is because the χ value in PVC is higher than that in the plasticizer. For PVC/ESO, the lines are closer to the y-axis. This is because the values of χ are smaller for this system. The values of the last term of eq. (7) were determined from the intercept term in the regression lines. The intercepts and other parameters of linear regression are listed in Tables II and III for PVC/polyester and PVC/ESO, respectively. The sign of the intercept term varied with composition and gave clear evidence of concentration dependency. For the PVC/polyester system, the values of the intercept term were positive for all compositions except at the highest PVC composition. For the PVC/ESO system, the situation was reversed. The interaction terms were all negative, with the exception of the composition with the lowest PVC content. A negative intercept term indicates that some degree of specific interaction existed in both systems. These specific interactions were higher in the PVC/ESO than in the PVC/polyester system.

TABLE II
Parameters of Linear Regression Using Eq. (9) for PVC/Polyester System

Composition	Slope	R^2	$(\phi_2\phi_3/V_2)(\delta\phi_3\chi_{23}/\delta\phi_3)$ (mole/cm ³)
25/75	0.9944 ± 0.0038	0.9999	0.000042 ± 0.000018
45/55	0.9898 ± 0.0091	0.9992	0.00023 ± 0.000052
60/40	0.9570 ± 0.0100	0.9990	0.000026 ± 0.000065
75/25	0.9731 ± 0.0143	0.9981	0.00015 ± 0.00011
85/15	0.9764 ± 0.0111	0.9988	0.000019 ± 0.000088
92/8	0.9822 ± 0.0037	0.9999	-0.000081 ± 0.000031

TABLE III
Parameters of Linear Regression Using Eq. (9) for PVC/ESO System

Composition	Slope	R^2	$(\phi_2\phi_3/V_2)(\delta\phi_3\chi_{23}/\delta\phi_3)$ (mole/cm ³)
25/75	0.9817 ± 0.0043	0.9998	0.000037 ± 0.000019
45/55	0.9327 ± 0.0099	0.9991	-0.000187 ± 0.000052
60/40	0.9490 ± 0.0097	0.9992	-0.000027 ± 0.000058
75/25	0.9564 ± 0.0089	0.9993	-0.000103 ± 0.000061
85/15	0.9622 ± 0.0049	0.9998	-0.000127 ± 0.000037
92/8	0.9816 ± 0.0038	0.9999	-0.000106 ± 0.000030

In Figures 6 and 7, the last term of eq. (7) is plotted against the volume fraction of PVC. The general trend was that it was not symmetric with respect to the volume fraction, and the interaction energy tended to become negative at the high PVC end of the composition. In the PVC/polyester system, the data in the middle compositions were higher than zero at a statistically significant level. In the PVC/ESO system, the data were lower than zero. At the high PVC end, there were three compositions showing negative values at a significant level. To find the general dependence of the interaction term on the volume fraction, the data were fitted to a function, $\phi_2\phi_3(k_1 - k_2\phi_2)$. This expression is equivalent to the first two terms of the polynomial expansion of χ as the function of volume fraction of polymer proposed by Tompa.⁴³ The constants k_1 and k_2 for PVC/polyester were determined to be 0.00101 and 0.00135 mol/cm³, respectively. The values for PVC/ESO were 0.000326 and 0.00145 mol/cm³, respectively. The value of k_1 indicates the extent of the interaction density between PVC and plasticizer, and k_2 indicates the extent of skew toward the high PVC end. The function $\phi_2\phi_3(k_1 - k_2\phi_2)$ was plotted in both figures.

Sanchez²⁹ provides a procedure to relate the interaction parameter obtained from IGC to other interac-

tion parameters. The reduced heat of mixing per unit volume in the Flory-Huggins theory is calculated by $\Delta H/RTV_2 = \phi_2\phi_3\chi_{23}/V_2$, or $\phi_2\phi_3\chi$ in the nomenclature of Sanchez. Since χ_{23} is concentration dependent, two interaction parameter functions defined by Sanchez,²⁹ $\chi_{\mu 2}$ and $\chi_{\mu 3}$, were obtained by IGC measurement for components 2 and 3, respectively:

$$\chi_{\mu 2} = [\chi_{23} + \phi_2(d\chi_{23}/d\phi_2)]/V_2 \quad (12)$$

$$\chi_{\mu 3} = [\chi_{23} + \phi_3(d\chi_{23}/d\phi_3)]/V_2 \quad (13)$$

From these two interaction parameter functions, the following two relations can be obtained:²⁹

$$\chi_{\mu 2} - \chi_{\mu 3} = (d\chi_{23}/d\phi_2)/V_2 \quad (14)$$

and

$$\chi_{23}/V_2 = \phi_3\chi_{\mu 2} + \phi_2\chi_{\mu 3} \quad (15)$$

Thus, from the experimental value of one component, $\chi_{\mu 2}$ or $\chi_{\mu 3}$, the other function can be determined from eq. (14), and the true value of χ_{23}/V_2 can be determined from eq. (15). The function $\chi_{\mu 3}$ is related to the intercept term of eq. (9) by the following relation:

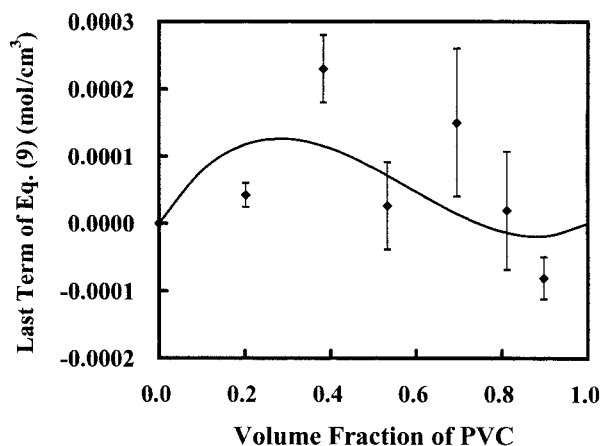


Figure 6 The last term of eq. (9) as function of PVC/polyester blend composition. Solid line is curve fitting using the equation: $\phi_2\phi_3(k_1 + k_2\phi_2)$.

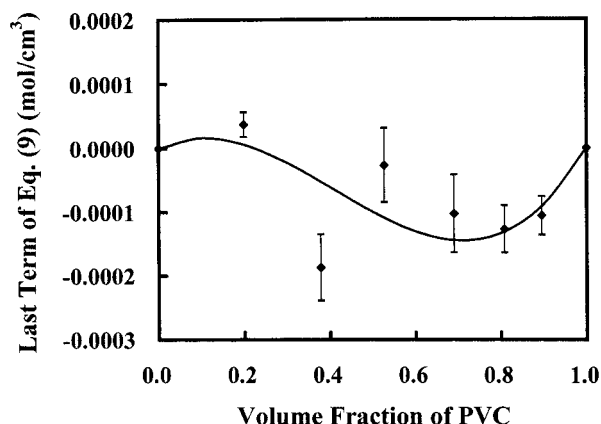


Figure 7 The last term of eq. (9) as function of PVC/ESO blend composition. Solid line is curve fitting using the equation: $\phi_2\phi_3(k_1 + k_2\phi_2)$.

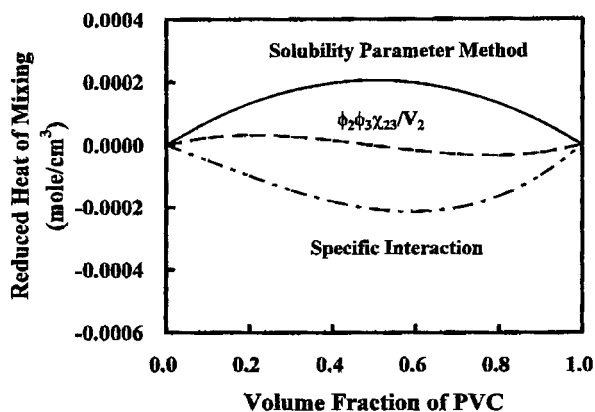


Figure 8 Comparison of reduced heat of mixing per unit volume calculated based on: the solubility parameter method (upper curve); the experimental value of $\Delta H/RTV_2 = \phi_2\phi_3\chi_{23}/V_2$ (middle curve); and the difference between the two, which indicates the specific interaction for the PVC/polyester system (bottom curve).

$$\begin{aligned} (\partial \phi_3 \chi_{23} / \partial \phi_3) / V_2 &= \chi_{23} / V_2 + (\phi_3 / V_2) \\ &\times (d\chi_{23} / d\phi_3) \equiv \chi_{\mu 3} = k_1 - k_2 \phi_2 \quad (16) \end{aligned}$$

Using eqs. (14) and (15), the corresponding expressions for $\chi_{\mu 2}$ and χ_{23} are derived:

$$\chi_{\mu 2} = k_1 - k_2/2 - k_2 \phi_2 \quad (17)$$

$$\chi_{23} / V_2 = k_1 - k_2/2 - k_2 \phi_2 / 2 \quad (18)$$

Eq. (18) can also be obtained by the integration of eq. (16). The expression in eq. (16) is first order with respect to the volume fraction. A higher order dependency is possible if the last term of eq. (9) is curve fitted into a higher order expression. But this would require more extensive data. From the above expression of χ_{23}/V_2 , the reduced heat of mixing of PVC and plasticizers can be calculated as $\Delta H/RTV_2 = \phi_2\phi_3\chi_{23}/V_2 = \phi_2\phi_3(k_1 - k_2/2 - k_2\phi_2/2)$. The curves of $\phi_2\phi_3\chi_{23}/V_2$ are plotted in Figures 8 and 9 for PVC/polyester and PVC/ESO, respectively. It can be seen that for PVC/polyester, the value is positive at the low PVC end and negative at the high PVC end. For PVC/ESO, the ΔH is negative for all compositions. The magnitude of heat of mixing can be compared using the parameter $B = \Delta H / \phi_2\phi_3V_2 = RT\chi_{23}/V_2$, calculated at a volume fraction of 0.5. The values were -0.25 and -0.81 cal/cm³ for PVC/polyester and PVC/ESO, respectively. The values of B for blends of PVC and several polyesters were determined by Woo et al.⁴⁴ using melting point depression method, differential scanning calorimetry, and dynamic mechanical measurement. A window of miscibility was observed when the CH₂/COO ratio was between 3 and 10, and the value of B reached a minimum value of -4 cal/

cm³ when the CH₂/COO ratio was 7. For the polyester plasticizer in this study, the CH₂/COO ratio was about 3 to 3.5, which was just at the edge of the boundary and accounted for a value near zero. For ESO, there is no direct comparison because it contains oxirane groups. The more negative value obtained by Woo et al. can be explained by the lower temperature ($<80^\circ\text{C}$) of measurement. As pointed out earlier, the χ_{23} values of PVC/plasticizers^{11,31,32} showed an increasing trend when temperature increased. In the study of Woo and coworkers,⁴³ cloud points and lower critical solution temperatures were also observed between 140 and 180°C for polyesters with a CH₂/COO ratio between 11 and 14, indicating that χ_{23} became more positive when temperature increased.

To make a comparison with the regular solution theory, the prediction of reduced heat of mixing per unit volume based on the solubility parameter, $\phi_2\phi_3(\delta_2 - \delta_3)^2$, was plotted in the same figures. The result of the solubility parameter model was symmetric to the volume fraction and was higher than the experimental values of $\phi_2\phi_3\chi_{23}/V_2$ in both cases. The difference between the experimental heat of mixing and that predicted by the regular solution theory gave the estimation of the specific interaction between PVC and plasticizers. The results were also plotted in both figures. It can be seen that both systems had some degree of specific interaction and the PVC/ESO system had higher interaction. The PVC/ESO system also had a smaller contribution from the solubility parameter difference because of the proximity of δ_2 and δ_3 . These two factors made its overall heat of mixing more negative than that of PVC/polyester.

The interaction between PVC and plasticizers is generally believed to be the interaction between the ester groups of polyester and PVC. For the PVC/ESO

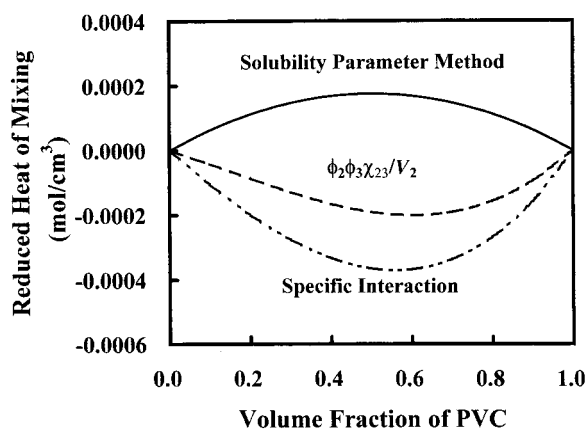


Figure 9 Comparison of reduced heat of mixing per unit volume calculated based on: the solubility parameter method (upper curve); the experimental value of $\Delta H/RTV_2 = \phi_2\phi_3\chi_{23}/V_2$ (middle curve); and the difference between the two, which indicates the specific interaction for the PVC/ESO system (bottom curve).

blend, similar interaction can also occur, and interaction between oxirane rings and PVC may also occur. There are several possible explanations for the skew in Figures 8 and 9. The first is the relative concentration of functional groups. There were two modes of specific interaction possible between PVC and esters. One was a dipolar interaction between the chlorine atom in PVC and the carbonyl group of the ester, while the other was the polarization of the hydrogen α to the chlorine and subsequent hydrogen bonding with the carbonyl group.⁴⁵ Using the density information, it was calculated that, for each cubic centimeter of melt, PVC contained 0.0093 moles of α -hydrogen, polyester contained 0.0105 moles of carbonyl group, and ESO contained 0.0033 moles of carbonyl group and 0.005 moles of oxirane group. If the functional groups were freely accessible and fully interacted, it would take about 53 vol % of PVC to reach the maximum interaction. For ESO, the maximum interaction would occur at 47 vol % if oxirane groups participate in the interaction. A comparison between Figures 8 and 9 indicates that the maximum of PVC/ESO indeed occurred at a lower PVC concentration than PVC/polyester but both maxima occurred at a higher PVC concentration than the above prediction. Partial crystallinity of PVC can cause a portion of the PVC molecule to be inaccessible to interaction. It would require more PVC to reach the maximum number of interactions per unit volume. This indicates the importance of considering chain flexibility and accessibility of functional groups in comparing the specific interaction. Again, it can be expected that it will be very rare for a specific interaction to be symmetric to volume fraction, as suggested by the Flory-Huggins theory. Any deviation from 50 vol % leads to a concentration dependency in the polymer-polymer interaction parameter when the last term of eq. (3) is used. One more factor is that ESO had a higher value of specific interaction on the volume basis, although its density of functional groups was lower than that of polyester. This was because it contained oxirane groups, which have a different interaction strength compared to ester groups.

Determination of miscibility

The pattern of ΔH curves indicates that the dissolution of PVC in the plasticizers was less favorable than dissolution of the plasticizers into PVC. This made the interaction parameters more positive at the high plasticizer end than at the high PVC end. The interaction parameters function of PVC, $\chi_{\mu 2}$, and plasticizers, $\chi_{\mu 3}$, and the mixture, χ_{23}/V_2 , are plotted against the volume fraction of PVC in Figure 10. It can be seen that for the same system, the interaction parameters, $\chi_{\mu 2}$ and $\chi_{\mu 3}$, differed by a constant. This is a result of the linear dependency of χ_{23} on ϕ_2 . Since the slopes of

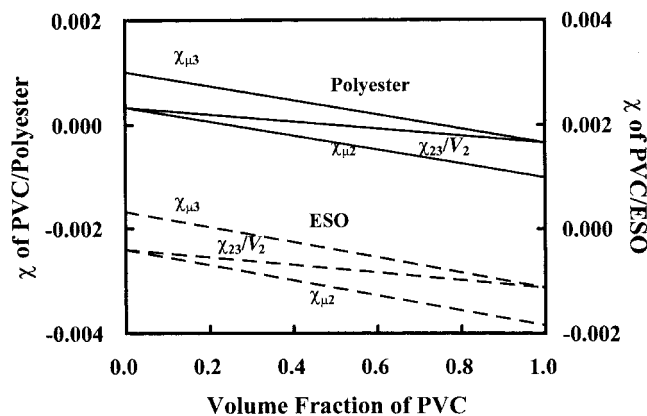


Figure 10 Interaction parameters of PVC, $\chi_{\mu 2}$; plasticizer, $\chi_{\mu 3}$; and the overall value χ_{23}/V_2 (cm^3/mol).

these lines were negative, the interaction parameter was lower at high PVC content and led to a more miscible system at high PVC content. The reason for this dependency was a decreasing trend of χ_{23} as the volume fraction of PVC increased. This phenomenon also explained the concentration dependency of χ_{23}' in the PVC/dioctyl phthalate system reported by Su et al.¹¹ Demertzis et al.⁴⁶ also studied the interaction parameters of polyester and triisononyl trimellitate with a copolymer of poly(vinylidene chloride) and PVC and found that χ_{23}' also decreased as PVC concentration increased. In other blends, such as polycarbonate-poly(ethylene terephthalate), it was also noted that the miscibility was better at the high poly(ethylene terephthalate) end.⁴⁷ Also for polycarbonate (PC) and styrene-acrylonitrile copolymer (SAN) it was noted that PC was more soluble in SAN than SAN in PC.^{14,48} The concentration dependent nature of the interaction parameter χ_{23} could be a common situation in many blends.

For polymer-polymer blends with high molecular weights, the entropy of mixing is small, and the sign of the enthalpy term decides the miscibility. A negative heat of mixing is necessary to create a miscible polymer-polymer blend. In the case of concentration dependent χ_{23} , the concentration that has heat of mixing of χ_{23} equal to zero determines the blend miscibility limit, but the interaction parameter function obtained from IGC measurement is $\chi_{\mu 3}$. This would result in different predictions of the miscibility range. Using the results of the PVC/polyester system, the lower limit of the miscible region for PVC calculated from χ_{23} would occur at a PVC concentration of 50 vol %, or 56 wt %. This is close to the result obtained by Woo et al.,⁴⁴ which gave phase separation at PVC below 60 wt %. Using $\chi_{\mu 3}$, the value would be 75 vol % or 79 wt %. This difference is a result of the concentration dependence of χ_{23} and could be an interesting subject for further study. To the best of our knowledge, this has

not been addressed in the past because IGC has not been able to offer accurate concentration dependency measurement of $\chi_{\mu 3}$ and χ_{23} for polymer-polymer blends.

Because the plasticizers used in this study had moderate molecular weights, the composition of a partially miscible blend was determined based on the chemical potential method. The volume fractions of PVC, ϕ_2 , and plasticizers, ϕ_3 , at equilibrium can be determined from the chemical potential of PVC, $\Delta\mu_2$, and plasticizers, $\Delta\mu_3$. In the case of concentration dependent χ_{23} , the expressions are written as:²⁹

$$\Delta\mu_2/RT = \ln \phi_2 + (1 - V_2/V_3)\phi_3 + V_2\chi_{\mu 2}\phi_3^2 = \ln \phi_2 + (1 - V_2/V_3)\phi_3 + V_2(k_1 - k_2/2 - k_2\phi_2)\phi_3^2 \quad (19)$$

$$\Delta\mu_3/RT = \ln \phi_3 + (1 - V_3/V_2)\phi_2 + V_3\chi_{\mu 3}\phi_2^2 = \ln \phi_3 + (1 - V_3/V_2)\phi_2 + V_3(k_1 - k_2\phi_2)\phi_2^2 \quad (20)$$

At equilibrium, the chemical potentials of each component in both phases are the same. Assume that the phases are called A and B; then at equilibrium the following relations can be used to calculate the composition of the two phases:

$$[\Delta\mu_2]_A = [\Delta\mu_2]_B \quad (21)$$

$$[\Delta\mu_3]_A = [\Delta\mu_3]_B \quad (22)$$

The composition of each phase can be calculated from eqs. (21) and (22). An iterative method was used in the calculation. Because of the large molar volume of PVC, eq. (21) predicts the plasticizer rich phase would have a volume fraction of plasticizer near unity and a volume fraction of PVC near zero. Let the plasticizer rich phase be phase A; then the calculation started with $(\phi_2)_A = 0$ and $(\phi_3)_A = 1$. This can be considered to be the solution of eq. (21) when V_2/V_3 is large. These values then were used in eq. (22) to solve for the value of $(\phi_2)_B$ and $(\phi_3)_B$. The values were in turn put back into eq. (21) to calculate $(\phi_2)_A$ and $(\phi_3)_A$ again. The process was repeated until convergence occurred. Using the values of V_3 , k_1 , and k_2 , the results of $(\phi_2)_A$ and $(\phi_2)_B$ for PVC/polyester were 0.0023 and 0.446, respectively. For PVC/ESO, the mixture is completely miscible, which is in agreement with the fact that ΔH is negative for all compositions. In comparison, for the PVC/polyester system, the zero point of $\chi_{\mu 3}$ occurs when the volume fraction of PVC is 0.75, and for the PVC/ESO system it occurs at 0.22. These are the same as the crossover points shown in Figures 6 and 7. Using eq. (18), the heat of mixing is zero for the PVC/polyester blend at a volume fraction of PVC of 0.50, which is slightly higher than the prediction of eqs. (22) and (23), of 0.446. This indicates that the

molecular weights of PVC and polyester were high enough that the entropy terms could not lower the miscibility limit from the prediction based on the enthalpy term alone. But these two results were much lower than the miscibility limit determined based on $\chi_{\mu 3}$. This difference occurs again because the concentration dependency of χ_{23} causes different interaction parameters in different measurements.²⁹

CONCLUSIONS

A previously proposed new plotting method to obtain interaction parameters between stationary phases of IGC was further tested in this study. From the intercept of the plot, the enthalpy of mixing term could be determined. The technique was used to examine literature data on PVC and two plasticizers, polyadipate and epoxidized soybean oil (ESO). It was found that for both systems the miscibility was better at the high PVC end. The concentration dependent interaction parameters between PVC and plasticizer were calculated. The specific interaction was on the same order of magnitude as the enthalpy of mixing predicted by the solubility parameter model. But the specific interaction was not symmetric to volume fraction and was higher at the high PVC end and rendered the overall interaction parameter negative at the high PVC end of composition. When the interaction parameter is concentration dependent, the heat of mixing is determined by χ_{23} , but the interaction parameter determined from IGC is $\chi_{\mu 3}$. Miscibility calculation using the former gave a lower value than the latter.

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