

Determination of Polymer–Polymer Interaction Parameters Using Inverse Gas Chromatography

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ABSTRACT: A modified method is discussed that is based on Farooque and Deshpande's method to obtain polymer–polymer interaction parameters using inverse gas chromatography (IGC) data. In the Farooque and Deshpande method, the ratio of the difference of probe–polymer interaction parameters between two polymers and the probe volume $[(\chi_{12} - \chi_{13})/V_1]$ is used as the abscissa. In the modified method, the ratio $[(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1]$ is used as the abscissa. Experimental data previously reported for a poly(ϵ -caprolactone)-polyepichlorohydrin (PCL/PECH) blend and a poly(ethyl acrylate)-poly(vinyl propionate) (PEA/PVPr) blend are analyzed. It is found that the slopes obtained by the new method had smaller deviations from the theoretical values than the Farooque and Deshpande method. The standard deviations of both slopes and inter-

cepts obtained from the new method are also smaller. Using the new method, the polymer–polymer interaction parameters obtained from the intercept are negative numbers for the PCL/PECH system and very small positive numbers for PEA/PVPr. Explanations are given for the probe and concentration dependency of the polymer–polymer interaction parameters that are generally observed in IGC studies. A new method for selecting the best probe for calculating the interaction parameter is discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 671–680, 2003

Key words: inverse gas chromatography; thermodynamic interaction parameter; polymer blend; poly(ϵ -caprolactone); polyepichlorohydrin; poly(ethyl acrylate)

INTRODUCTION

In the classical theory of Flory and Huggins the Flory–Huggins interaction parameter (χ), which takes into account the enthalpic and noncombinatorial entropy of mixing contributions, was commonly used to describe the interaction between two components. Because of the extremely low values of the combinatorial entropy of mixing, miscible polymer blends generally require the existence of a specific interaction between the polymers. In the absence of a specific interaction the Flory–Huggins interaction parameter of polymer blends is usually positive, leading to an immiscible blend. Experimental determination of the interaction parameter between two polymers is very important in the study of their miscibility. Many techniques have been used to study the miscibility of different polymers.^{1,2} Among them, inverse gas chromatography (IGC) is a widely recognized tool for measuring the thermodynamic properties of solute (probe) vapors in high molecular weight polymers.^{1–6}

In IGC measurements a known amount of a non-volatile stationary phase is dissolved in a volatile solvent and coated on a porous inert support. In the operation of an IGC apparatus a carrier gas is contin-

uously passed through the column. When a volatile probe liquid is injected into the column, the probe vaporizes and flows with the carrier gas. If the molecular weight of the stationary phase is known, the retention volume of the probe is related to the Flory–Huggins interaction parameter (χ_{12}) between the probe (component 1) and the stationary phase (component 2) by the following equation^{1–10}:

$$\chi_{12} = \ln\left(\frac{273.16Rv_2}{V_s^0 P_1^0 V_1}\right) - 1 + \frac{V_1}{M_2 v_2} - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (1)$$

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 second virial coefficient of the probe, respectively. In the IGC study of polymers the M_2 value is large; the $V_1/M_2 v_2$ term is usually small and can be neglected. When χ_{12} is less than 0.5, the probe liquid is generally characterized as a good solvent for the polymer whereas a value higher than 0.5 makes a poor solvent and may lead to phase separation.¹¹

THEORY

Interaction parameters of polymer blends by IGC

When a polymer blend is used in an IGC study, eq. (1) can be applied to the blend using the retention volume

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data and density of the blend. The interaction parameter obtained from the blend is expressed as $\chi_{1(23)}$. 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–polymer interaction parameters (χ_{12} and χ_{13}) and the polymer–polymer interaction parameter (χ_{23}) by the following equation:

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

where ϕ_2 and ϕ_3 are the volume fractions of the polymers and V_2 is the molar volume of component 2. Because the molar volumes of polymers may not be accurately known, it is a common practice in IGC studies to define a probe normalized interaction parameter [$\chi_{23}' = \chi_{23}(V_1/V_2)$] and eq. (2) becomes:

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

The advantage of using χ_{23}' is that it can be directly related to the retention volume by the following formula without calculating the individual interaction parameters^{3–5,10–17}:

$$\chi_{23}' = \frac{1}{\phi_2\phi_3} \left[\ln \left(\frac{V_{g,\text{blend}}^0}{w_2v_2 + w_3v_3} \right) - \phi_2 \ln \left(\frac{V_{g,2}^0}{v_2} \right) - \phi_3 \ln \left(\frac{V_{g,3}^0}{v_3} \right) \right] \quad (4)$$

Equation (4) has frequently been used to study the interaction of two stationary phases using the IGC method. Su et al.¹⁰ used this technique to measure the interaction parameter of poly(vinyl chloride) (PVC) and a plasticizer, dioctyl phthalate, 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 that were used. Hsu and Prausnitz¹² and Patterson and coworkers^{13,14} 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 termed it the $\Delta\chi$ effect, and a large $\Delta\chi$ in addition to a high χ_{23}' value leads to incompatibility. Su and Patterson¹⁵ suggested that the probe dependency of χ_{23}' arose from the difference between χ_{12} and χ_{13} . Accordingly, one must select probes that give $\chi_{12} = \chi_{13}$ for studying the blend. El-Hibri et al.¹⁷ measured the polymer–polymer interaction parameter of poly(ϵ -caprolactone)–polyepichlorohydrin (PCL/PECH) using 25 probes in three blend compositions, and they found a correlation between the average value of an interaction den-

sity parameter ($B_{23} = RT\chi_{23}/V_2$) and the solubility parameter of the probe.

There were several attempts to explain probe or concentration dependent interaction parameters through the equation of state and free volume approach.^{18–27} Farooque and Deshpande²⁷ tested these methods on polystyrene–polybutadiene blends and found that the interaction parameters were still probe dependent, and they proposed a simpler method to obtain the interaction parameter. They rearranged eq. (2) into 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) versus $(\chi_{12} - \chi_{13})/V_1$, the interaction parameter could be obtained from the intercept. This method was used by Etxeberria et al.^{28,29} and Lezcano et al.³⁰ and good linear lines were obtained, but the slopes were different from those predicted by eq. (5).

New approach to obtain χ_{23}

Zhao and Choi³¹ recently suggested the use of an ethylene segment as a reference volume in an IGC study on the polymer–polymer interaction parameter of high-density polyethylene and low-density polyethylene blends. Their definition of χ differed from the traditional definition by a ratio of the reference volume to the probe volume (V_0/V_1). In terms of the nomenclature of common definitions, their equation had the following form:

$$[(V_0/V_1)\chi_{1(23)}] = \phi_2[(V_0/V_1)\chi_{12}] + \phi_3[(V_0/V_1)\chi_{13}] - \phi_2\phi_3[(V_0/V_2)\chi_{23}] \quad (6)$$

The quantities in brackets represent the new interaction parameters defined by Zhao and Choi.³¹ From the equation a linear plot was obtained from the left-hand side versus $\phi_2[(V_0/V_1)\chi_{12}] + \phi_3[(V_0/V_1)\chi_{13}]$. Equation (6) was similar to eq. (2) with a difference in the ratio V_0/V_1 . A previous article proposed the use of the following equation to derive a linear regression line³²:

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

In this study the method of Farooque and Deshpande and the proposed new method are applied to literature data to examine the advantage of each method. Miscible PCL/PECH and poly(ethyl acrylate)–poly(vinyl propionate) (PEA/PVPr) blends are selected for this study. The validity of applying the IGC technique to immiscible polymer systems was questioned in a recent article by Du et al.³³ In their study a mathematical analysis was applied to a system

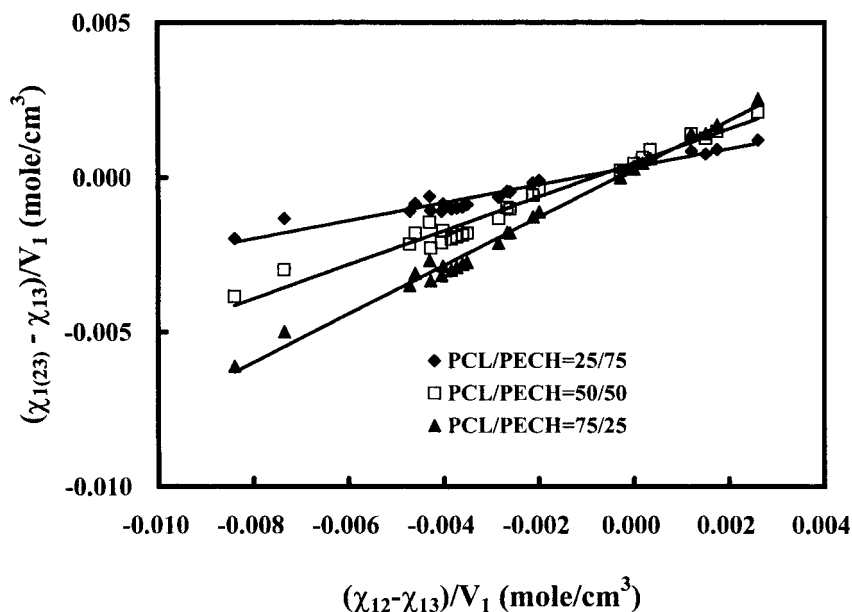


Figure 1 The linear regression plot of the quantity $(\chi_{1(23)} - \chi_{13})/V_1$ versus $(\chi_{12} - \chi_{13})/V_1$ for the PCL/PECH system.

containing two immiscible polymers using eq. (1) for single polymer stationary phases and eq. (4) for the blend. They derived an apparent dependency between the probe-polymer interaction parameters (χ_{12} and χ_{13}) and the probe normalized polymer-polymer interaction parameter [$\chi_{23}' = (\chi_{12} - \chi_{13})^2/2$]. This equation was confirmed by the IGC results of a PVC and poly(tetramethylene glycol) blend. Light scattering measurements revealed that the system was phase separated. Therefore, the IGC results on polymer-polymer interaction parameters from known immiscible systems should be treated with caution.

RESULTS AND DISCUSSION

PCL/PECH system

El-Hibri et al.¹⁷ studied the interaction parameter between PCL and PECH using 25 probes. The weight-average molecular weight of PCL was 37,000 and that of PECH was 700,000. These authors measured the retention volumes of probes in PCL and PECH and blends at volume ratios of 25/75, 50/50, and 75/25. The retention volume data were used in this study to calculate the value of $\chi_{1(23)}$. The specific volumes of

PCL and PECH at 80°C were reported to be 0.9463 and 0.7607 cm³/g, respectively.

Figure 1 shows the Farooque–Deshpande plot of three blends for PCL/PECH (component 2/component 3). It can be seen that the data fell on linear trends. The systematic error of different probes tended to be similar in all three lines. The corresponding parameters of the three regression lines are reported in Table I. It can be seen that the slope of each line was higher than its respective theoretical value, which should be the volume fraction of component 2. The difference was statistically significant compared to the standard deviation of each line. From the intercept the value of χ_{23}/V_2 was calculated for three compositions. The values were negative with statistical significance, indicating that there was an exothermic interaction between the two polymers and that the polymer blend was miscible.

Figure 2 shows the plot of the new method for the three compositions. The theoretical value for the slope of each plot was unity, which made the lines very close to each other. Therefore, lines corresponding to different volume fractions were shifted in the vertical coordinate by different magnitudes to separate them.

TABLE I
Parameters of Linear Regression Using Farooque–Deshpande Method for PCL/PECH System

Compositions	Slope ^a	Intercept ^a (mol/cm ³)	R ²	χ_{23}/V_2 (mol/cm ³)
25/75	0.2908 ± 0.0136	0.00034 ± 0.000050	0.9519	-0.00183
50/50	0.5501 ± 0.0204	0.00047 ± 0.000075	0.9693	-0.00189
75/25	0.7828 ± 0.0162	0.00028 ± 0.000060	0.9902	-0.00148

^a The values are means ± standard deviations

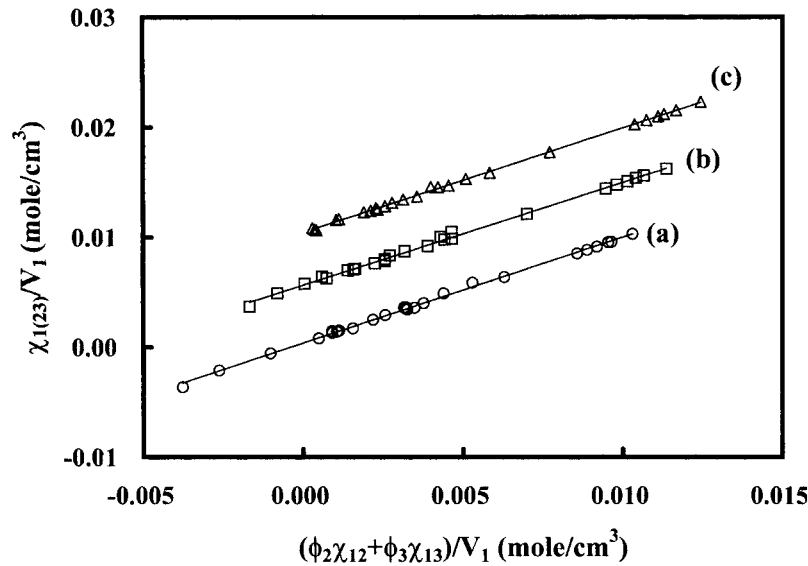


Figure 2 The linear regression plot of the quantity $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for the PCL/PECH system. (a) 25/75 PCL/PECH, (b) 50/50 PCL/PECH shifted upward by 0.005, and (c) 75/25 PCL/PECH shifted upward by 0.01.

It can be seen that the data again fell on very good linear trends. The corresponding parameters are reported in Table II. A close comparison between Tables I and II indicates that the new method produced linear lines with higher correlation coefficients (R^2) and smaller standard deviations for both the slope and intercept. The slopes of the new method were lower than the theoretical value, which was unity. The intercepts were also negative with statistical significance. Using the average value of χ_{23}/V_2 , the value of B_{23} was estimated to be -1.6 cal/cm^3 .

The deviation of the slopes from unity was important in explaining the probe and concentration dependence of polymer–polymer interaction parameters that are reported in many studies. Because the slopes were not exactly 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 changed 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 positive λ as in the

case of PCL/PECH in Figure 2. Equation (7) yielded the following expression for χ_{23} :

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

Therefore, χ_{23} has a probe dependency through changing values of χ_{12} and χ_{13} . The probe dependency of χ_{23} can also be explained using the solubility parameter model. In this model the Flory–Huggins interaction parameter can be related to the solubility parameters δ_1 and δ_2 by the following expression^{32,34,35}:

$$\chi_{12} = V_1(\delta_1 - \delta_2)^2/RT + \gamma \quad (9)$$

where γ represents the specific interaction and non-combinatorial entropy in the free energy of mixing. Combining eqs. (8) and (9), the following equation was derived:

$$\begin{aligned} \phi_2\phi_3\chi_{23}/V_2 &= \kappa[\phi_2(\delta_1 - \delta_2)^2 + \phi_3(\delta_1 - \delta_3)^2]/RT \\ &\quad + \kappa(\phi_2\gamma_{12} + \phi_3\gamma_{13})/V_1 - \lambda \quad (10) \end{aligned}$$

TABLE II
Parameters of Linear Regression Using New Method for PCL/PECH System

Compositions	Slope ^a	Intercept ^a (mol/cm ³)	R^2	χ_{23}/V_2 (mol/cm ³)
25/75	0.9491 ± 0.0058	0.00048 ± 0.000037	0.9991	-0.00254
50/50	0.9358 ± 0.0092	0.00063 ± 0.000053	0.9978	-0.00212
75/25	0.9633 ± 0.0084	0.00038 ± 0.000045	0.9983	-0.00203

^a The values are means ± standard deviations.

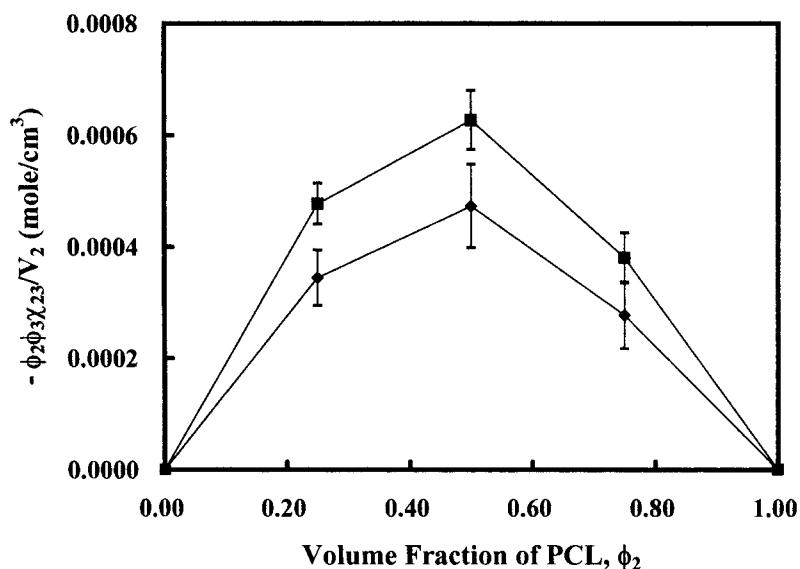


Figure 3 The enthalpy and combinatorial entropy term, as determined from the last term of eq. (2), versus the volume fraction of PCL. The upper curve is the result of the new method and the lower curve is from the Farooque–Deshpande method.

This equation indicated that, when the solubility parameter of the probes was varied from the average of the solubility parameters of the two polymers (δ_2 and δ_3), the values of χ_{23} and B_{23} varied as a parabolic function. It could also be concluded that the probe dependency of χ_{23} arose from the difference between the solubility parameters of the probes and the polymer when the slopes deviated from their theoretical values. A line with a slope smaller than unity causes χ_{23} and B_{23} to gradually increase from a minimum to a more positive value when the solubility parameter of the probe decreases from the average of the two polymers. This explained the correlation of B_{23} versus the solubility parameter of probes reported by El-Hibri et al.¹⁷ A probe with a solubility parameter close to the polymer would be a good selection for estimating B_{23} . However, even at the minimum point of eq. (10) versus δ_1 , the value of the left-hand side might still be different from the true intercept term (λ) because the bracket contains two nonnegative terms whereas the γ term was shown to be positive for nonpolar hydrocarbons in nonpolar polymers^{34,35} and negative for PVC and nitrile rubbers.³² Negative values of γ could account for the more negative value of B_{23} (-2.0 cal/cm³) that were estimated by El-Hibri et al.¹⁷

The above problem can be avoided using the method proposed in this study. In the use of eq. (7) in the PCL/PECH system, as well as the PEA/PVPr system to be discussed later, it was observed that the volume average of probe–polymer interactions ($\phi_2\chi_{12} + \phi_3\chi_{13}$) varied from a negative to a positive value. Near the zero point of $\phi_2\chi_{12} + \phi_3\chi_{13}$, one of the χ terms was a small negative number whereas the other was a small positive number. The occurrence of neg-

ative χ terms implied some degree of specific interactions between the probe and polymer, which was necessary for good miscibility between the probe and polymer. At $\phi_2\chi_{12} + \phi_3\chi_{13} = 0$ the probe had zero excess free energy of solution between the pure probe liquid state and the polymer matrix. If both χ_{12} and χ_{13} were also small (i.e., the $\Delta\chi$ effect was small), the probe also experienced a random distribution in the polymer mixture as discussed by other authors.^{12–14} This would represent the most ideal condition for probing the polymer–polymer interaction with a minimum disturbance to the structure of the polymer mixture. A zero point could be located in the linear regression line, and the χ_{23} determined from the zero point could be free from the limitation of using the solubility parameter model. The new method proposed here is better than a plot of the left-hand side of eq. (10) versus δ_1 .

The concentration dependency of the interaction parameter can also be explained through eq. (2). In the Flory–Huggins equation, as well as the solubility parameter model, it was assumed that the enthalpy and noncombinatorial entropy of mixing were symmetric to the volume fractions of the polymers. To examine this assumption the last term of eq. (2) ($\phi_2\phi_3\chi_{23}/V_2$), as determined from the intercepts of Figures 1 and 2, was plotted versus the volume fraction of PCL in Figure 3, together with the standard deviation. It can be seen that both methods gave positive values and the new method had higher values. Both results showed slight skewness toward the left-hand side. When eq. (2), which contained an interaction term symmetric to the volume fraction, was used to calculate χ_{23} , this skewness created the concentration de-

pendency of the polymer–polymer interaction parameter.

There were several reasons that could be the cause of the skewness in Figure 3. The first was the relative concentration of functional groups. There were two modes of specific interactions possible between PCL and PECH. One was a direct dipolar interaction between the chlorine atom in PECH with the carbonyl group in PCL, and the other was the polarization of hydrogen α to the chlorine and subsequent hydrogen bonding with the carbonyl group.³⁶ Using the density information it was calculated that, for each cubic centimeter of melt, PCL contained 0.0093 mol of carbonyl groups and PECH contained 0.015 mol of chlorine functional groups. If the functional groups were freely accessible and fully interacted, it would take about 60 vol % PCL to reach the maximum interaction with PECH under the first mode. For the second mode there was twice the α -hydrogen concentration in PECH and the maximum volume fraction of PCL was reduced but might not have been exactly halved because not all hydrogen atoms could participate in the interaction simultaneously because of chain configuration restrictions. Additional factors to be considered are that because the polymers were not equally flexible and there might be a difference in hindrance in accessing the two functional groups, the maximum may not occur at a stoichiometric ratio of functional groups and it would not generally be at 50 vol % as suggested by the Flory–Huggins theory. Any deviation from 50 vol % could lead to a concentration dependency in the polymer–polymer interaction parameter when eq. (2) was used. The possibility of using a composition dependent χ_{23} value to explain IGC data was also discussed by Sanchez²⁴ and Chee.³⁷ Sanchez pointed out that, when an interaction parameter depended on compositions, there were four different types of polymer–polymer interaction parameters that could be defined based on the technique of measurement.²⁴ However, when one of the four parameters was known, the other three could be derived from it.

It should be pointed out that the composition dependence of χ_{23} was only one method for explaining the probe dependence of polymer–polymer interaction parameters. Sanchez²⁴ proposed that inclusion of the free volume effect between probes and polymers could eliminate probe dependence. The work of Etxeberria et al.,²⁶ however, showed that the characteristic interaction energy density (ΔP^*) was still probe dependent. In a different approach, Lezcano et al.³⁰ showed that Horta's equation²² could be simplified to a form similar to eq. (5) but the slope was the core volume fraction multiplied by a factor that contained the difference of the molecular surface to volume ratio of the two polymers. The core volume and molecular surface to volume ratio were parameters used in the

Flory–Orwoll–Vrij model.^{18–21} This expression would yield a slope close to but slightly different from the volume fraction used in eq. (5). It opened the possibility of assigning a different physical meaning to the slope.

PEA/PVPr system

As another comparison, the PEA/PVPr system studied by Bhattacharya et al.³⁸ was also analyzed. In their study the number-average molecular weight of PEA was 197,600 and that of PVPr was 49,000. These authors reported the χ_{12} and χ_{13} values of individual polymers and the χ_{23}' value of a 50/50 (w/w) blend at temperatures of 60, 80, 100, and 120°C. The densities of PEA and PVPr at 32°C were 1.112 and 1.106 g/cm³, respectively. The thermal expansion coefficients used by these authors were (7.2 and 7.4) $\times 10^{-4}/^\circ\text{C}$, respectively.

Figure 4 shows the Farooque–Deshpande plot of the blend for four temperatures of PEA/PVPr. It can be seen that the data are rather scattered with a low correlation coefficient. The range of data on the abscissa gradually increased when the temperature increased, indicating that the difference between the probe–polymer interaction parameters of each probe gradually increased when the temperature was increased. It was also noted that the abscissa range of data at 60, 80, and 100°C did not extend down to zero, which indicated the probes still had some $\Delta\chi$ effect. The linear trend of the data became better at higher temperatures. At 100 and 120°C only ethanol deviated from the linear trend. At 80°C ethanol and *n*-heptane (C7) deviated from the linear trend. Both *n*-heptane and ethanol had higher values of probe–polymer interaction parameters than other probes. At 60°C more data deviated from the linear trend. It was noted that the location of ethanol moved substantially between 60 and 80°C. This was because it had a large value of χ_{23}' at 60°C. The corresponding parameters of four regression lines are reported in Table III. Note that the slopes deviate from their theoretical value of 0.5 by a large magnitude and the intercepts of these lines are positive, which would predict immiscible blends and contradict the experimental results. If ethanol was removed from Figure 4(c,d), the correlation coefficient and the agreement between the slope and volume fraction improved but the intercepts predicted an even higher positive polymer–polymer interaction parameter, which also disagreed with the miscibility results.

Figure 5 shows the plot of the new method for the blend at four temperatures. The results of different temperatures are shifted by different values for clarity. In contrast to Figure 4, the range of data narrowed when the temperature was increased. This was because the values of the probe–polymer interaction parameters of different probes converged when the tem-

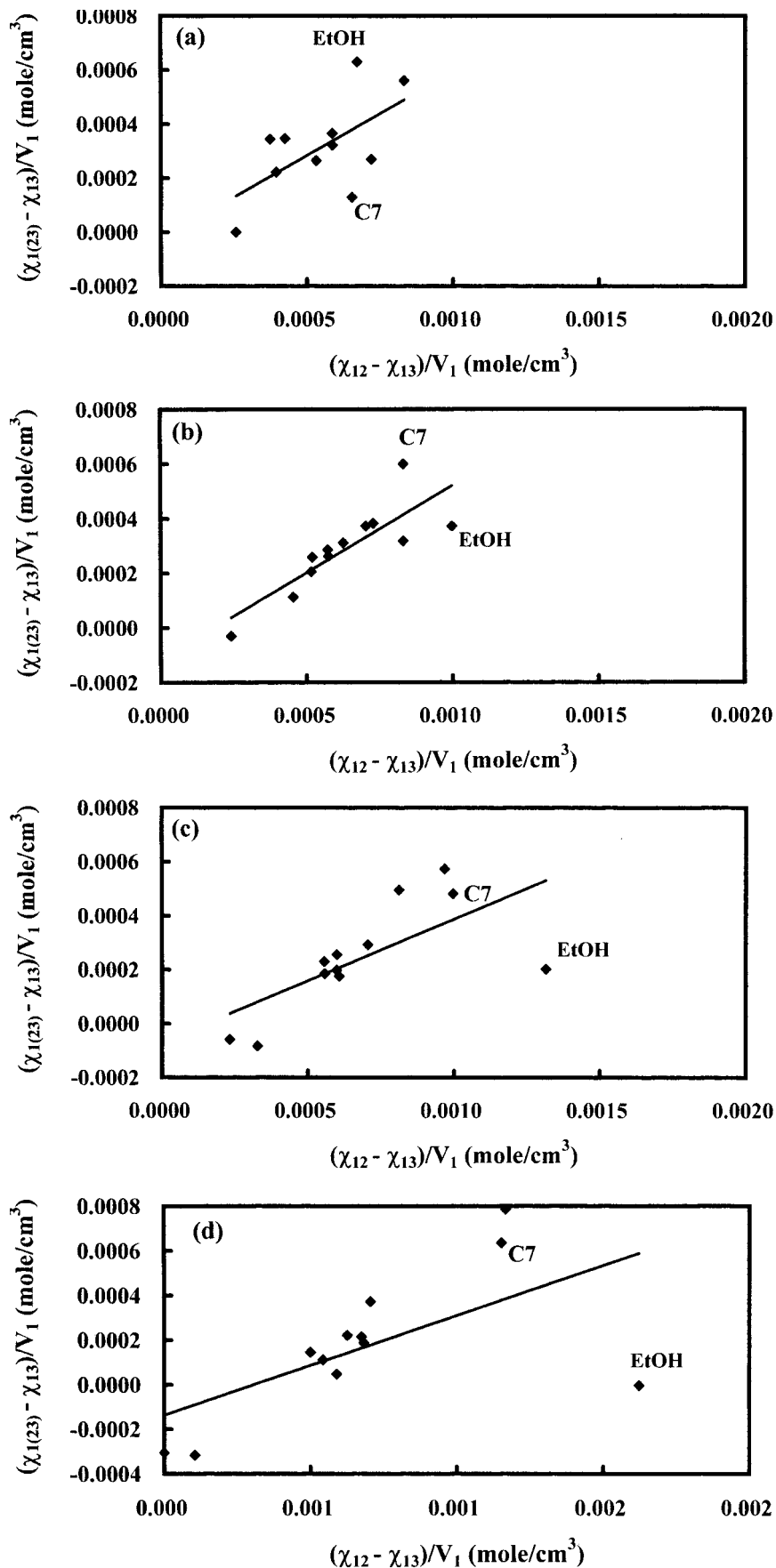


Figure 4 The linear regression plot of the quantity $(\chi_{1(23)} - \chi_{13})/V_1$ versus $(\chi_{12} - \chi_{13})/V_1$ for PEA/PVPr at a 50/50 (w/w) ratio at (a) 60, (b) 80, (c) 100, and (d) 120°C.

TABLE III
Parameters of Linear Regression Using Farooque–Deshpande Method for PEA-PVPr System at 50/50 (w/w)

Temp. (°C)	Slope ^a	Intercept ^a (mol/cm ³)	R ²	χ_{23}/V_2 (mol/cm ³)
60	0.3631 ± 0.2740	-0.00003 ± 0.00016	0.3631	0.0001
80	0.6389 ± 0.1347	-0.00112 ± 0.00009	0.6924	0.0045
100	0.4562 ± 0.1559	-0.00007 ± 0.00012	0.4614	0.0003
120	0.4417 ± 0.1799	-0.00014 ± 0.00015	0.3818	0.0006

^aThe values are means ± standard deviations.

perature was increased. The data varied gradually as the temperature changed. There was no deviation from the linear trend at all temperatures for ethanol and *n*-heptane. Because of the high value of the interaction parameters, they were located at the right end of the linear lines. This trend indicated the consistency of the experimental results under the analysis of the new method, despite some scattering in Figure 4, which had a smaller scale. The corresponding parameters are reported in Table IV. This table shows that the correlation coefficients were close to unity and much higher than the corresponding values in Table III. The slopes were higher than unity and increased gradually when the temperature increased. This was different from the PCL/PECH system in which the slopes were lower than unity. The intercepts showed an increasing trend, starting with a small negative number at 60°C, then turned into positive numbers when the temperature increased. This indicated that the system was miscible and gradually turned into a less favorable mixture at higher temperatures. If the trend continued, a lower critical solution temperature could occur.³⁹ This is common to many polymer sys-

tems, but the differential scanning calorimetry study by Mandal et al.³⁸ indicated that there was no phase separation below the decomposition temperature (about 300°C). This may be the result of the relatively low molecular weight of PVPr (49,000).

Because the deviation of $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ from zero accounted for the probe dependency when a single probe was used to determine χ_{23} and B_{23} , it was better to use a probe whose $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ value was near zero. This also implied a probe with a solubility parameter close to the average of both polymers and a probe with a low $\Delta\chi$ effect, because both χ_{12} and χ_{13} were small. In practice it was better to make a plot similar to Figures 2 and 5 using a series of probes. Etxeberria et al.²⁹ reached the following two conditions in discussing the plotting method of Farooque and Deshpande²⁷: first, reject the probes that had similar interaction parameters with both pure polymers, because this implied similar specific retention volumes; second, the probes were selected in order to try to cover all possible chemical structures and polarities. The first condition was also suggested by Mandal et al.^{4,38} because a similar retention volume led to a

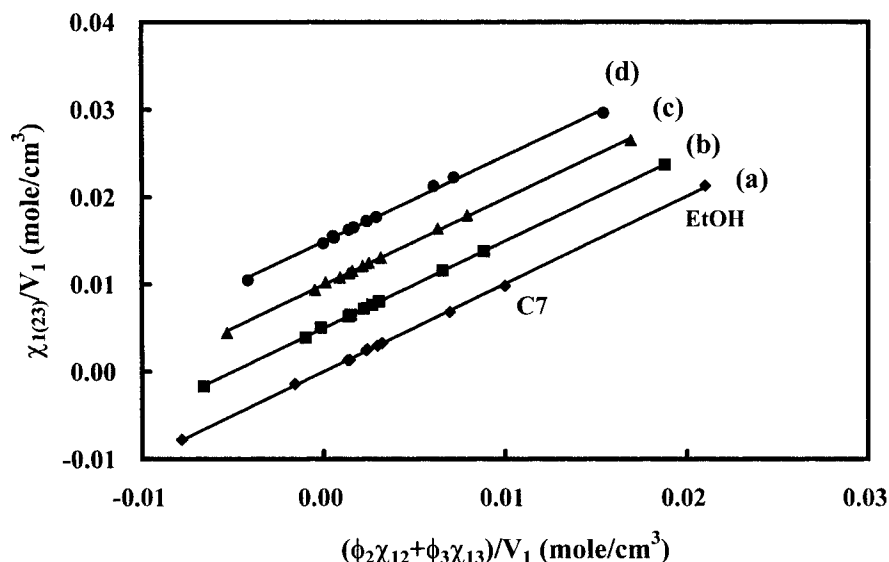


Figure 5 The linear regression plot of the quantity $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for the PEA/PVPr system at a 50/50 (w/w) ratio at (a) 60°C, (b) 80°C shifted upward by 0.005, (c) 100°C shifted upward by 0.01, and (d) 120°C shifted upward by 0.015.

TABLE IV
Parameters of Linear Regression under New Method for PEA/PVPr System

Temp. (°C)	Slope ^a	Intercept ^a (mol/cm ³)	R ²	χ_{23}/V_2 (mol/cm ³)
60	1.0038 ± 0.0064	0.000026 ± 0.000051	0.9996	-0.0001
80	1.0022 ± 0.0075	-0.000023 ± 0.000031	0.9995	0.0001
100	1.0194 ± 0.0073	-0.0001 ± 0.000028	0.9995	0.0004
120	1.0450 ± 0.0104	-0.0002 ± 0.000036	0.9991	0.0008

^a The values are means ± standard deviations.

higher error in the calculation. The second condition intended to find a probe with a large $|\chi_{12} - \chi_{13}|$ value to facilitate plotting of eq. (5). These suggestions were different from the conclusion reached in this study and those of Su and Patterson.¹⁵ This was because, in the plotting based on eq. (5), the variable was proportional to the difference between the two interaction

parameters whereas in the present study the variable was proportional to the volume average of the two interaction parameters. The present method imposed fewer requirements on the selection of probes.

Considering that the proposed plotting method gave a different selection method for probes, it would be best if one could find probes that satisfied both

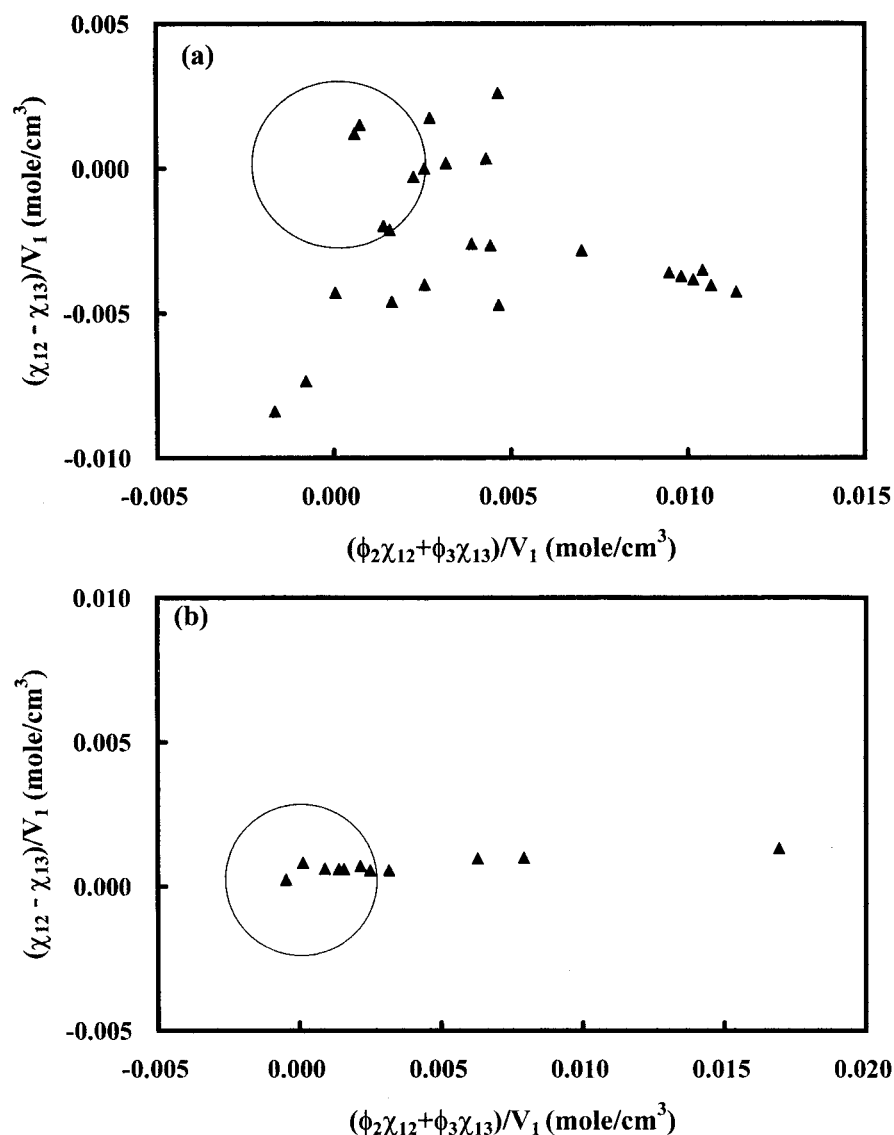


Figure 6 A plot of the quantity $(\chi_{12} - \chi_{13})/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for (a) PCL/PECH at 50/50 vol % at 80°C and (b) PEA/PVPr at 50/50 wt % at 100°C.

conditions at the same time. In Figure 6 the quantity $(\chi_{12} - \chi_{13})/V_1$ was plotted versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ using one condition from each system. The first quantity represented the magnitude of the $\Delta\chi$ effect and the second quantity represented the criteria of the new method. An ideal probe would be zero for both variables and would be located close to the origin. It can be seen that the data for PCL/PECH were scattered but the data with high $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ values showed a correlation between both variables. Other data were scattered with both positive and negative signs. The circle in Figure 6(a) shows that four probes were located within 0.0025 mol/cm^3 of the origin. These probes were tetrahydrofuran, dioxane, butyl acetate, and benzene. The first three probes contained oxygenate functional groups and benzene contained the aromatic ring, which could participate in a donor-acceptor interaction. Each of them had a specific interaction with the two polymers, but the overall interaction parameters were small and similar in both polymers. When these four probes were used, the average value of B_{23} was -1.44 cal/cm^3 , which was near the value of -1.6 cal/cm^3 determined from the intercept of Figure 2. It should also be pointed out that the location of probes in Figure 6 may change when the composition of the blends and temperature change. The selection of the best probes for calculating B_{23} could be affected by these factors. Using a scale similar to Figure 6(a), the data of PEA/PVPr in Figure 6(b) are almost horizontal. This is because the values of $(\chi_{12} - \chi_{13})/V_1$ were small for all probes, reflecting that the polymers were very similar to each other. However, using $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ as the variable, the data were spread and seven probes could be seen to lie within the similar circle of Figure 6(a). The new method provided a different guideline for selecting probes and a method of estimating polymer-polymer interaction parameters when polymers are very similar to each other.

CONCLUSIONS

A new method was used to analyze the polymer-polymer interaction parameter based on IGC data. By plotting $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$, the polymer-polymer interaction parameter χ_{23} could be determined from the intercept at $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 = 0$. Compared to the Farooque-Deshpande method, the new method provided smaller standard deviations for the slope and the polymer-polymer interaction parameter. It also gave slopes that agreed better with their theoretical values. The new method could be conveniently applied to IGC to obtain polymer-polymer interaction parameters and B_{23} parameters with few restrictions on the selection of probes. Based on the deviation of slopes from their theoretical value, an explanation was given for the source of the probe dependency of polymer-polymer interaction parameters that

was commonly observed in IGC studies. Concentration dependency occurred because the interaction term was not symmetric to the volume fraction of the polymers.

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