

Linear Solvation Energy Relationship and Evaluation of Mutual Miscibility of Polymers Using Inverse Gas Chromatography Data

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ABSTRACT: Inverse gas chromatography (IGC) has been widely used to determine the Flory–Huggins parameters, χ , between solutes (probes) and polymers. In a previous study a multiparameter acid–base model, which included dispersion, polarity, acidity, and basicity components, was used to correlate the Flory–Huggins parameters of a series of probes obtained from IGC measurement. Using IGC data from two polymers the parameters of poly(ϵ -caprolactone) (PCL) and polyepichlorohydrin (PECH) were calculated and used to estimate the interaction parameter between them. In the present study a modified linear method was proposed to

obtain the parameter differences between the two polymers directly from their chromatographic retention data. This method offers a more convenient assessment on the mutual miscibility between the two polymers. This method is also related to the linear solvation energy relationship (LESR). Correlations between the descriptors of LESR and the parameters in this acid–base model are discussed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1295–1301, 2012

Key words: gas chromatography; PECH; PCL; LESR; thermodynamics; acid–base model; interaction parameter

INTRODUCTION

The knowledge of the interaction parameters between polymers and organic solvents is very important in the study of their miscibility and thermodynamic properties of solutions. Inverse gas chromatography (IGC) has been demonstrated to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in molten polymers.^{1–4} In IGC measurement a known amount of nonvolatile stationary phase is dissolved in a volatile solvent and coated on a porous inert support. In the operation of IGC a carrier gas is passing through the column continuously. When a volatile probe liquid is injected into the column the liquid vaporizes and flows with the carrier gas. The solubility of the solute in the stationary phase is measured as the specific retention volume, V_g^0 . Using Flory–Huggins theory⁵ the Flory–Huggins interaction parameter between a polymer and probe, χ , can be related to V_g^0 by the following equation^{1–4}:

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

where Subscript 1 indicates the solute and 2 indicates the polymer solvent, R is the gas constant, T is the column temperature, v_2 is the specific volume of the stationary 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 at column temperature, respectively. When $\chi < 0.5$, the probe liquid is generally characterized as a good solvent for the polymer, while a value higher than 0.5 means the probe is a poor solvent and may lead to phase separation.⁵ In the case of a polymer–polymer blend the ratio χ/V is a better parameter⁶ because molar volume of a polymer is not generally known. For a polymer blend the mutual miscibility generally requires $\chi/V < 0$ because the high molecular weight of both components diminishes the contribution of the combinatorial entropy.

MULTIPARAMETER SOLUTION MODEL

Hildebrand's regular solution theory and solubility parameter model⁷ were generally used in the discussion of solute–polymer interaction.^{1–4} But these models and three dimensional Hansen solubility parameter model predict a positive heat of mixing.⁸ For a miscible polymer blend, it generally requires a negative χ , and a different model is needed. In a recent study⁹ the following equation was used to correlate the Flory–Huggins parameter of solutes in polymers at infinite dilution:

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$$\chi RT/V_1 = (\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 + (\alpha_1 - \alpha_2)(\beta_1 - \beta_2) \quad (2)$$

where Subscript 1 indicates the solute and 2 indicates the polymer solvent, λ is the dispersion component, τ is the polar component, α is the acidity, and β is the basicity. The major difference between this model and the Hansen solubility parameter method is that the hydrogen bonding has direction, i.e., an acceptor (acid) and a donor (base). The strength of acid parameter indicates the ability of a molecule to accept electrons in solute-solvent interaction, and the basic parameter indicates the ability of a molecule to donate electrons. This is an equation commonly used for vapor-liquid equilibrium of low molecular weight solvents or polymer-solvent solutions.⁹⁻¹¹ Equation (2) is capable of producing negative χ if $(\alpha_1 - \alpha_2)$ and $(\beta_1 - \beta_2)$ have opposite signs. Using χ values of a series of solutes with different combination of components, the parameters of the polymer could be estimated. From the parameters of two polymers their interaction parameter can be estimated through the use of eq. (2) with the parameters of two polymers. This approach was demonstrated using IGC data of PCL and PECH in a previous study.⁹

The nonlinear regression method to determine the parameters of a polymer using eq. (2) is a tedious process. However, it can be greatly simplified when solubility data of two polymers of interest are compared directly. Taking the difference of the Flory-Huggins parameters of two polymers A and B, the following relation is obtained from eq. (2):

$$\begin{aligned} (\chi_A - \chi_B)RT/V_1 &= [(\lambda_1 - \lambda_A)^2 \\ &+ (\tau_1 - \tau_A)^2 + (\alpha_1 - \alpha_A)(\beta_1 - \beta_A)] - [(\lambda_1 - \lambda_B)^2 \\ &+ (\tau_1 - \tau_B)^2 + (\alpha_1 - \alpha_B)(\beta_1 - \beta_B)] \\ &= -2\lambda_1(\lambda_A - \lambda_B) - 2\tau_1(\tau_A - \tau_B) - \beta_1(\alpha_A - \alpha_B) \\ &- \alpha_1(\beta_A - \beta_B) + [\lambda_{A^2} - \lambda_{B^2} + \tau_{A^2} - \tau_{B^2} + \alpha_A\beta_A - \alpha_B\beta_B] \end{aligned} \quad (3)$$

Note that the last term is a constant when two polymers are compared. This expression is a multiple linear form with four independent variables of probes: λ_1 , τ_1 , β_1 , and α_1 . The differences of the four parameters between the two polymers, $(\lambda_A - \lambda_B)$, $(\tau_A - \tau_B)$, $(\alpha_A - \alpha_B)$, and $(\beta_A - \beta_B)$, are unknown coefficients. The difference of the Flory-Huggins parameters turned out to be a linear combination of the difference of parameters of two polymers. When sufficient amount of probes with linearly independent values of λ_1 , τ_1 , β_1 , and α_1 are used, the four unknown coefficients, $\lambda_A - \lambda_B$, $\tau_A - \tau_B$, $\alpha_A - \alpha_B$, and $\beta_A - \beta_B$, can be obtained using a linear regression method. After the determination of these four

parameter differences the interaction parameter of two polymers can be estimated by eq. (2). By this approach the screening of miscibility of any pairs of polymers can be made before attempting to study the mixtures of the two polymers. eq. (3) can be simplified further. A combination of eqs. (1) and (3) gives:

$$\begin{aligned} (RT/V_1)\ln(V_{g,A}/V_{g,B}) &= 2\lambda_1(\lambda_A - \lambda_B) + 2\tau_1(\tau_A - \tau_B) \\ &+ \beta_1(\alpha_A - \alpha_B) + \alpha_1(\beta_A - \beta_B) + \text{constant} \end{aligned} \quad (4)$$

The ratio of specific volume between two polymers, v_A/v_B , is included in the constant term. The constant term involves only the properties of the two polymers. This equation is also a multiple linear form, which can be used to determine the parameter differences between two polymers. Equation (4) has an advantage that only the specific retention volume of solutes is needed. There is no need to calculate χ using eq. (1). The information about the specific volume of polymers and the second virial coefficient of solutes at column temperature are not required. These quantities are frequently inaccurate or unknown. In fact when the accurate amount of the polymer in the IGC column is unavailable the net retention volume can also be used, as long as the same column is used for all solutes.

PREDICTION OF MISCIBILITY OF PCL-PECH BLEND

Tian and Munk¹³ reported an extensive measurement of specific retention volumes and interaction parameters of more than forty solutes in several polymers over a wide temperature range. In that study the specific retention volumes of the polymers were measured by the IGC method for temperatures between 70 and 110°C and interaction parameters were calculated using eq. (1). The χ values of solutes in PCL and PECH were correlated by eq. (2) to obtain the parameters of each polymer in a previous study.⁹ A table of polarity, acidity, and basicity components of solutes was available from Eckert and co-workers,¹⁰ which enabled the use of eqs. (2) and (4). The dispersion component was calculated by the correlation methods given by Thomas and Eckert.¹¹ The solutes whose parameters were available are listed in Table I. The molar volumes of solutes were calculated using the method of Spencer and Danner described by Reid et al.¹²

In this study the specific retention volume data of Tian and Munk¹³ were used to calculate the difference of parameters between PECH and PCL through eq. (4). The results of parameter differences and the value of $\chi RT/V$ between PCL and PECH are shown in Table II. Also shown in Table II are the parameter

TABLE I
Parameters of Solutes Used in Eq. (2)

Solutes	λ	τ	α	β
Heptane	7.81	0.072	0	0
Octane	7.91	0.048	0	0
Nonane	8	0.04	0	0
Decane	8.07	0.032	0	0
Benzene	8.49	1.965	0	0.458
Toluene	8.45	1.593	0	0.425
Ethylbenzene	8.49	1.446	0	0.401
Methylene chloride	8.2	2.748	2.77	0
Chloroform	8.43	2.04	2.861	0
Carbon tetrachloride	8.58	1.117	0	0
Butyl chloride	7.96	1.47	0	0.199
Chlorobenzene	8.71	1.928	0	0.444
Acetone	7.49	2.952	0.594	1.86
Methyl ethyl ketone	7.71	2.624	0.488	1.695
Tetrahydrofuran	8.02	2.063	0	1.902
1,4-dioxane	8.08	3.006	0	1.749
Methyl acetate	7.52	3.134	0	1.331
Ethyl acetate	7.64	2.58	0	1.216
<i>n</i> -butyl acetate	7.96	1.846	0	1.047
Ethanol	7.51	0.435	5.882	1.912
<i>n</i> -propanol	7.79	0.321	5.216	1.689
<i>n</i> -butanol	7.93	0.146	4.716	1.527

Units = $\text{cal}^{0.5}/\text{cm}^{1.5}$.

differences calculated using the results of the previous study.⁹ Figure 1 shows the plot of predicted values of $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ versus the IGC values. It can be seen that the linear relation held well with a slope near unity. The correlation in Figure 1 was higher than the similar plot to compare the results of $\chi RT/V_1$ of PCL and PECH using eq. (2) for the same solutes in the previous study.⁹ It is also noted that ethanol and *n*-butanol now have relatively less deviation in Figure 1 compared to the previous study.⁹ This was because in Figure 1 the plot was made using $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$. This quantity is proportional to the transfer free energy for solutes to move from one polymer to another polymer. It was pointed out by Huang et al.¹⁴ that in calculating transfer properties of a solute between two solvents the solute liquid state interaction of all probes can be eliminated. Therefore, the large contribution of hydrogen bonding interaction in the solute liquid state in alcohols is removed when transfer properties are used.

TABLE II
Parameter Differences and the $\chi RT/V$ Between PECH and PCL at 90°C

	Results of this study	From Previous study (Ref. 9)
$\lambda_{PECH} - \lambda_{PCL}$ ($\text{cal}^{0.5}/\text{cm}^{1.5}$)	0.4	0.4
$\tau_{PECH} - \tau_{PCL}$ ($\text{cal}^{0.5}/\text{cm}^{1.5}$)	0.0	0.3
$\alpha_{PECH} - \alpha_{PCL}$ ($\text{cal}^{0.5}/\text{cm}^{1.5}$)	1.8	1.6
$\beta_{PECH} - \beta_{PCL}$ ($\text{cal}^{0.5}/\text{cm}^{1.5}$)	-1.3	-0.8
$\chi RT/V$ (cal/cm^3)	-2.1	-1.0

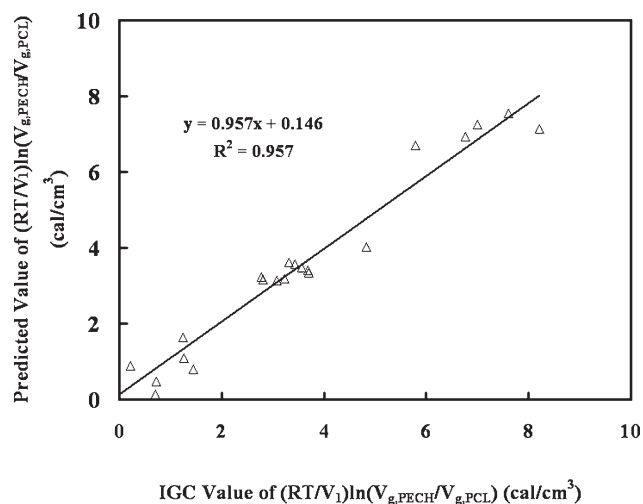


Figure 1 Plot of IGC values of $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ versus predicted values at 90°C using eq. (4).

The use of alcohols is important because this class of molecules contains both acidity and basicity. The inclusion of alcohols introduces probes with high values of α and can reduce the covariance between parameters of probes. In Table I many so-called polar probes have only acidic or basic components. To properly estimate all components it is necessary to include alcohol as probes. The data points that have high values of $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ in Figure 1 are alcohols, methylene chloride, and chloroform. It can be seen from Table I that these solutes have large difference between acidity and basicity. They are expected to have good interaction in basic PCL and dislike acidic PECH. They also have relatively small molecular volumes. These make them the probes with the largest difference in $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ values.

In Table II the value of $\chi RT/V$ calculated in this study is -2.1 cal cm^{-3} , which is higher magnitude than the previous result based on nonlinear model which fit parameters of each polymer using eq. (2). But this value is close to the conclusion of IGC study using polymer blends.¹⁵ The magnitudes of both $\alpha_{PECH} - \alpha_{PCL}$ and $\beta_{PECH} - \beta_{PCL}$ in this study are higher than the previous study, but remain the same signs. The reason for the change in the magnitudes of acid and base parameters is because when the regression method is applied to eq. (2), more weight is put on the solutes with large $\chi RT/V$. These solutes include *n*-alkanes and alcohols. Alkanes are nonpolar with little specific interactions toward polymers and may not be good probes. In contrast, in eq. (4) more weight is put on solutes that have a large transfer free energy, e.g., methylene chloride, chloroform, and alcohols. These solutes have large acid and base parameters to interact with polymers. Because a miscible polymer blend requires acid-base

interaction, the use of eq. (4) is probably better when miscibility is investigated.

LINEAR SOLVATION ENERGY RELATIONSHIP AND TRANSFER PROPERTIES

Equation (4) resembles the linear solvation energy relationship commonly used in gas chromatography study. To facilitate separation of samples in analytical gas chromatography studies, many solvents with different modes of interactions to solutes have been developed. However, retention data of solutes in many of these solvents can still be correlated using a multiple variable solution model. These models are called linear solvation energy relationship (LESR) models. These models assume solute-solvent interactions can be separated into linear combination of cavity formation, dipole/dipole and dipole/induced dipole interaction, hydrogen bond donor (acid), and hydrogen bond acceptor (base) terms. The strength of dipolar term, hydrogen bond acid, and hydrogen bond base of an organic compound are called as the descriptors of the compound. They are determined by solvatochromism, where spectrum changes were measured using standard solvents. The simple form of LESR proposed by Kamlet and Taft^{16,17} uses three descriptors, and has the following form:

$$xyz = zyz_0 + s\pi_{KT,1}^* + a\alpha_{KT,1} + b\beta_{KT,1} \quad (5)$$

Here xyz is the property studied, xyz_0 is the reference value, $\pi_{KT,1}^*$ is the dipole-dipole interaction, $\alpha_{KT,1}$ is the overall hydrogen-bond acidity, $\beta_{KT,1}$ is the overall hydrogen-bond basicity of a solute. The parameters, $\pi_{KT,1}^*$, $\alpha_{KT,1}$, and $\beta_{KT,1}$ are the descriptor of solute. The dimensionless parameters s , a , and b represent the solvent's ability to interact with a solute via dipolar processes, donate a proton to solutes, and the ability to accept a proton from solutes, respectively. To be consistent with eq. (1) the Subscript 1 denotes the solute, and Subscript 2 is used to indicate polymer solvents; this is different from LESR literature which uses 2 for solutes.

A table of polarity, acidity, and basicity components of solutes was available from Carr and coworkers,¹⁸ which enabled the use of eq. (2). The values of descriptors of solutes are shown in Table III. Because the acid and base are multiplied together in eq. (2), an increase in " α "; can be compensated by a decrease in " β "; in eq. (4). Similarly in eq. (5), an increase in $\alpha_{KT,1}$ and $\beta_{KT,1}$ can also be compensated by a decrease of " a " and " b ," respectively. The values of parameters can be compared among different probes within the same method, but not between different methods. In Tables I and III the ranking of magnitude of acid and base components of solutes are similar even though their magnitudes

TABLE III
Descriptors of Linear Solvation Relationship
in Kamlet-Taft Method

Solutes	π^*	α_{KT}	β_{KT}
Heptane	-0.02	0	0
Octane	0.01	0	0
Nonane	0.02	0	0
Decane	0.03	0	0
Benzene	0.59	0	0.1
Toluene	0.54	0	0.11
Ethylbenzene	0.53	0	0.12
Methylene chloride	0.82	0.3	0
Chloroform	0.58	0.44	0
Carbon tetrachloride	0.28	0	0
Butyl chloride	0.39	0	0.1
Chlorobenzene	0.71	0	0.07
Acetone	0.71	0.08	0.48
Methyl ethyl ketone	0.67	0.06	0.48
Tetrahydrofuran	0.58	0	0.55
1,4-dioxane	0.55	0	0.37
Methyl acetate	0.6	0	0.42
Ethyl acetate	0.55	0	0.45
<i>n</i> -butyl acetate	0.46	0	0.45
Ethanol	0.54	0.83	0.45
<i>n</i> -propanol	0.52	0.78	0.45
<i>n</i> -butanol	0.47	0.78	0.45

Parameters were taken from Ref. 18.

are different. This suggests that there may be some relationships existing between the parameters. This will be discussed later.

There are two main approaches being used in conjunction with gas liquid chromatography studies. One of them was proposed by Abraham and coworkers^{20,21} the other was proposed by Carr and coworkers.^{18,22} Both approaches use five descriptors for solutes and a set of six system constants for each solvent. In the present study the transfer properties of solutes between two solvents can be considered as the partition coefficient of the solute between two solvents. IGC data has been used as a tool to measure the partition coefficient of solutes between two solvents.¹⁹ The LESR used in liquid-liquid transfer of a solute between two solvents has the form^{17,18}:

$$xyz = zyz_0 + mV_1 + s\pi_{KT,1}^* + a\alpha_{KT,1} + b\beta_{KT,1} \quad (6)$$

The coefficient m is the susceptibility of a solute to a change in the cohesive energy of the solvent, and V_1 is the molar volume of solute. This product mV_1 takes into account of the cavity formation energy in a solvent. When the transfer property of a solute between two solvents, A and B , are considered, eq. (6) gives:

$$\Delta xyz = V_1 \Delta m + \pi_1^* \Delta s + \alpha_{KT,1} \Delta a + \beta_{KT,1} \Delta b \quad (7)$$

When $\ln(V_g)$ is used as the property, eq. (7) can be written as:

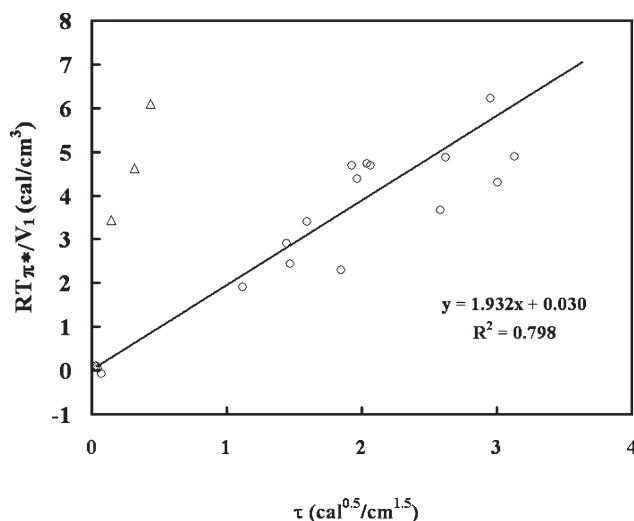


Figure 2 Correlation between τ and $RT\pi_{KT,1}^*/V_1$ for solutes in this study. Triangles symbols are alcohols. The correlation line was made using the remainder of solutes.

$$(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH}) = RT\Delta m + \Delta s(RT\pi_{KT,1}^*/V_1) + \Delta a(RT\alpha_{KT,1}/V_1) + \Delta b(RT\beta_{KT,1}/V_1) \quad (8)$$

The left-hand side of eq. (8) represents the transfer free energy per unit volume. $RT\Delta m$ is the difference of the cohesive energy density between PCL and PECH, Δs is the difference in dipole-dipole interaction between the two polymers, Δa is the difference in overall hydrogen-bond acidity between the two polymers, and Δb is the difference in overall hydrogen-bond basicity between two polymers. In eq. (8), $(RT\pi_{KT,1}^*/V_1)$, $(RT\alpha_{KT,1}/V_1)$, and $(RT\beta_{KT,1}/V_1)$ are the descriptors of solutes. Using a series of solutes with different combination of descriptors as probes, the system constants [$RT\Delta m$, Δs , Δa , Δb] of two polymers was obtained.

CORRELATIONS BETWEEN PARAMETERS

The similarity between eqs. (4) and (8) is remarkable. Through a comparison between eqs. (4) and (8) it can be seen that the cavity formation term, $RT\Delta m$, in eq. (8) represents the average value of the first term in eq. (4), $2\lambda_1(\lambda_A - \lambda_B)$. Because λ_1 is relatively constant, $RT\Delta m$ is also proportional to the difference in dispersion component of two polymers, $(\lambda_A - \lambda_B)$. The parameter Δs in eq. (8) represents the difference of polar components of polymers, which is $2(\tau_A - \tau_B)$ in eq. (4). The parameter $RT\pi_{KT,1}^*/V_1$ in eq. (8) represents the polar component of the probes, which is τ_1 in eq. (4). The next two terms in eq. (8) contain crossed products. The acid and base components of solutes are multiplied by their complement components of polymers. The parameter $RT\alpha_{KT,1}/V_1$ in eq. (8) is the acidity of the probe, which represents α_1 in

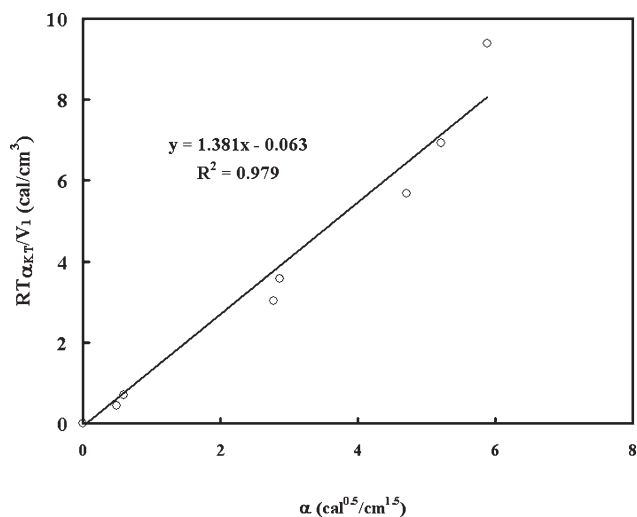


Figure 3 Correlation between α and $RT\alpha_{KT,1}/V_1$ for solutes in this study.

eq. (4), and the parameter Δa in eq. (8) represents the $(\beta_A - \beta_B)$ in eq. (4), the difference in basicity of the polymers. The parameter β_1 in eq. (4) is the basicity of the probe, which is represented by $RT\beta_{KT,1}/V_1$ in eq. (8), and the parameter Δb represents $(\alpha_A - \alpha_B)$ of the polymers in eq. (4).

Because descriptors in eq. (8), $(RT\pi_{KT,1}^*/V_1)$, $(RT\alpha_{KT,1}/V_1)$, and $(RT\beta_{KT,1}/V_1)$, represent τ , α , and β , respectively, they could be used to relate parameters in two approaches. The plots between these two sets of parameters are shown in Figures 2–4, respectively. The plot between τ and $(RT\pi_{KT,1}^*/V_1)$ is shown in Figure 2. It can be seen that alcohols deviated from the trend. The τ values assigned to alcohols were probably too low. This may explain the abnormal trend of the alcohols in the previous study.⁹ The correlation in Figure 2 was made using

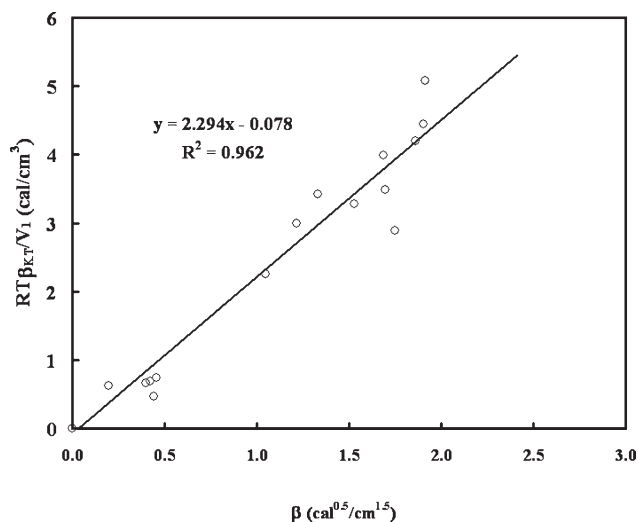


Figure 4 Correlation between β and $RT\beta_{KT,1}/V_1$ for solutes in this study.

the remainder of the solutes. If the correlation equation of other solutes and π^*_{KT} values of the alcohols are used the values of τ are estimated to be 3.14, 2.37, and 1.71 $\text{cal}^{0.5}/\text{cm}^{1.5}$ for ethanol, *n*-propanol, and *n*-butanol, respectively. With the exception of alcohols in Figure 2 the remainder of solutes and all the solutes in Figures 3 and 4 show good linear relationships. The small value of intercept in each plot indicates that there is a proportional relation between the two types of parameters.

Other relationships between these parameters have been proposed in the literature. The following relationships for the same parameters were proposed by Eckert and coworkers.²³ in a study on space predictor for infinite dilution activity coefficients (SPACE) model:

$$\alpha = \frac{A\alpha_{KT} + B}{V_1^{1/2}} \quad (9)$$

The equations for τ and β have similar forms but with different constants *A* and *B*. Although not shown here the plot of $\alpha V_1^{1/2}$ versus α_{KT} has a similar correlation of determination (R^2) as this study. With these correlations one can relate the parameters used in the different methods and widen the parameters available for the calculation.

LINEAR SOLVATION ENERGY RELATIONSHIP RESULTS OF POLYMERS

A linear regression was made using eq. (8) and the descriptors $(RT\pi^*_{KT,1}/V_1)$, $(RT\alpha_{KT,1}/V_1)$, and $(RT\beta_{KT,1}/V_1)$ of solutes. The corresponding system constants for the transfer between PCL and PECH are shown in Table IV. The comparison between calculated values and IGC values of $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ are shown in Figure 5. It can be seen that the correlation of determination (R^2) is about the same value as in Figure 1. Most of the solutes fell in the same relative position except those with small values of transfer property. They are solutes with small acid or base parameters. From Table IV it can be seen that Δm is 3.65 cal cm^{-3} . Using an average values of $\lambda_1 = 8.0 \text{ cal}^{0.5}/\text{cm}^{1.5}$ the value of $(\lambda_{PCL} - \lambda_{PECH})$ is estimated to be 0.23 $\text{cal}^{0.5}/\text{cm}^{1.5}$ which is

TABLE IV
System Constants of Linear Solvation Model for
 $RT/V_1\ln(V_{g,PCL}/V_{g,PECH})$ at 90°C

Parameters	Values
$RT\Delta m$ (cal/cm^3)	3.65
Δs	0.10
Δa	-6.20
Δb	10.42

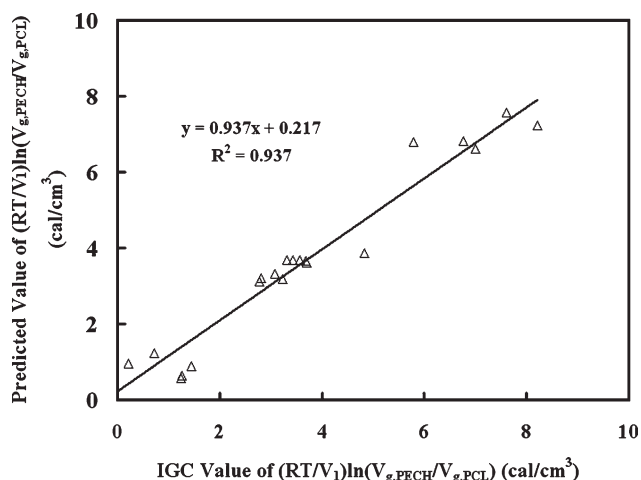


Figure 5 Plot of experimental values of $(RT/V_1)\ln(V_{g,PCL}/V_{g,PECH})$ versus predicted values at 90°C using eq. (8).

near the value in Table II. From Table IV it can be seen that Δa is positive and Δb is negative. Keep in mind that the parameter Δa now represents the difference in basicity component and Δb is the difference in acidity component of the polymers. These results are in agreement with Table II, i.e., PCL was more basic and PECH was more acidic. The corresponding product of $(a_{PCL} - a_{PECH})(b_{PCL} - b_{PECH})$ is a negative number, suggesting that acid-base interaction is indeed the source of miscibility according to eq. (2). As noted earlier the magnitude of "*a*" and "*b*" are affected by the magnitude of α_{KT} and β_{KT} . Their difference and the sign of product $(a_{PCL} - a_{PECH})(b_{PCL} - b_{PECH})$ are the key factor in the evaluation of miscibility. Because the parameters *a* and *b* are dimensionless, estimating the value of $\chi RT/V$ between the two polymers using LESR needs to go through the conversion of parameters by the use eq. (4).

CONCLUSIONS

The interaction between solutes and a polymer is usually represented by the values of the Flory-Huggins interaction parameter, χ , and analyzed through the solubility parameters of the polymer and solutes. This study continues the study of correlation the Flory-Huggins parameter using a multiparameter acid-base model, which includes dispersion, polar, acidity, and basicity components. A method is suggested to estimate the difference of parameters of two polymers from IGC data using a series of probes. The difference in the parameters of the polymers can then be used to evaluate miscibility. The parameters of LESR were shown to have linear relationship with the parameter in the multiparameter model for the Flory-Huggins parameter.

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