Probing Polymer–Polymer Interaction Parameters in Miscible Blends by Inverse Gas Chromatography: Solvent Effects

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ABSTRACT: The problem of the solvent influence on the determination of polymer–polymer interaction parameters by inverse gas chromatography (IGC) has been reexamined in the light of a phenomenological approach recently proposed. Experimental data previously reported by different authors have been analyzed with this new alternative. Two main conclusions can be inferred. First, there is not a significant difference between the results of such an analysis and those obtained with the aid of more sophisticated and time-consuming procedures. Second, a correct selection of the probes can reduce the confidence intervals of the obtained polymer–polymer interaction parameters.

Introduction

The usefulness of inverse gas chromatography (IGC) for determining polymer–small molecule interactions is well established.[1,2] This method provides a fast and convenient way of obtaining thermodynamic data for concentrated polymer systems. This technique can also be used to measure polymer–polymer interaction parameters via a ternary solution approach.[3] However, earlier attempts at using IGC to characterize polymer blends were unsuccessful. The polymer–polymer interaction parameters evaluated were found to vary with the probe used.[4–6] For this reason, the use of IGC for the study of polymer blends has been severely questioned. Conceptually, such a variation should not be entirely surprising. Unless the volatile phase molecule partitions randomly between the components of the stationary phase, some perturbation in the energies at polymer/polymer contacts should be expected.

Munk and co-workers[7,8] have been concerned with the above-stated problem for some time. After rigorous and systematic experimental work, they have demonstrated that, to a considerable degree, the probe variations can be mitigated by scrupulous attention to experimental details in the IGC methodology. These details are centered on modifications of the polymer coating during column preparation, on improving the measurements of the carrier gas flow, and on corrections of the effects of the marker and the support retentions on the final probe retention volume. Even after this systematic checking of error sources, the interaction parameters continued to depend on the chemical nature of the injected probe. The same group developed a method in which a "true" polymer–polymer interaction parameter can be obtained through a data analysis in which solubility parameters both of the components alone and the mixture are used.

Prolongo et al.[9] have emphasized the weakness of the approximation which implies the assumption that the Gibbs mixing function for the ternary solvent–polymer–polymer system is additive with respect to the binary contributions. A resolution of this problem is possible by using a nonclassical model such as the Flory–Orwoll–Vrij–Eichinger equation of state model. The authors have proposed an equation, specifically derived for IGC analysis, in which a true polymer–polymer interaction parameter χ_{23}^{T}, can be obtained,

$$\chi_{23}^{A} = \chi_{23}^{T}\frac{s_1}{s_3} + (\chi_{12} - \chi_{13})\frac{(s_3 - s_2)V_2^*}{(\phi_2 s_2 + \phi_3 s_3)V_1^*} - \kappa \quad (1)$$

χ_{23}^{A} is the apparent polymer–polymer interaction parameter from the classical Scott–Tompa equation. χ_{1i} are the binary polymer–solvent interaction parameters and the rest of the magnitudes are related to equation of state parameters of the probe, pure polymers, and the blend. In addition, eq 1 illustrates the role played by the different interactions between the probes and the components of the blend in the form of the term $\Delta\chi = \chi_{12} - \chi_{13}$.

Other recent approaches[10,11] to the problem of the solvent influence in the polymer–polymer interaction parameters have a more phenomenological nature and try to calculate the "effective" concentration each solvent is probing in the column. In this work we have focused our attention on a recent paper published by Farooque and Deshpande,[11] in which the authors proposed to use the classical Flory–Huggins type expression for the ternary polymer–polymer–solvent system,

$$\chi_{123} = \chi_{12}\phi_2 + \chi_{13}\phi_3 - \frac{\chi_{23}V_1}{V_2}\phi_2\phi_3 = \chi_{12}\phi_2 + \chi_{13}\phi_3 - \chi'_{23}\phi_2\phi_3 \quad (2)$$

in a different way. From (2) it is possible to write,

$$\left[\frac{\chi_{123} - \chi_{13}}{V_1}\right] = \left[\frac{\chi_{12} - \chi_{13}}{V_1}\right]\phi_2 - \left[\frac{\chi_{23}}{V_2}\right]\phi_2\phi_3 \quad (3)$$

where 1–3 refer to solvent and the two polymers and V_i are molar volumes.

As Al-Saigh and Munk[7] demonstrated some years ago, eq 2 can be written in terms of the specific retention volumes (V_g^0) experimentally measured in columns of the pure components and in that of a certain composition of the blend,

$$\ln\left[\frac{V_{g,\text{blend}}^{0}}{\omega_2 v_2 + \omega_3 v_3}\right] = \phi_2 \ln\left[\frac{V_{g,2}^{0}}{v_2}\right] + \phi_3 \ln\left[\frac{V_{g,3}^{0}}{v_3}\right] + \left[\frac{\chi_{23}V_1}{V_2}\right]\phi_2\phi_3 \quad (4)$$

In eq 4 ω_i and v_i refer to weight fractions of the polymers in the blend column and their specific volumes, respectively. Using this last equation, eq 3 can also be written

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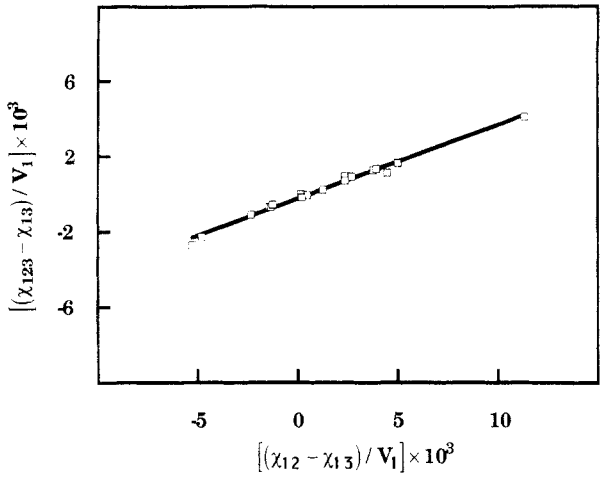

Figure 1. Plot of the Farooque–Deshpande method[11] corresponding to the PS/PVME 45/55 w/w blend at 40 °C.[17]

in terms of experimentally measurable magnitudes,

$$\left(\frac{1}{V_1}\right)\ln\left[\frac{v_{\text{blend}}V_{g,3}^{\,0}}{v_3 V_{g,\text{blend}}^{\,0}}\right]=\phi_2\left(\frac{1}{V_1}\right)\ln\left[\frac{v_2 V_{g,3}^{\,0}}{v_3 V_{g,2}^{\,0}}\right]-\left(\frac{\chi_{23}}{V_2}\right)\phi_2\phi_3 \quad (5)$$

Adequate plots of $(\chi_{123}-\chi_{13})/V_1$ against $(\chi_{12}-\chi_{13})/V_1$, or alternative terms written with the aid of specific retention volumes, can give us a volume fraction ϕ_2 from the slope and χ_{23}/V_2 from the intercept. The physical meaning of this volume fraction is certainly obscure, but it can be thought of in terms of an average effective column composition the solutes are probing.

From χ_{23}/V_2 another form of expressing the interaction between the components of the blend can be written,[12] the so-called interaction energy density (B, usually in cal/cm^3),

$$B = RT(\chi_{23}/V_2) \quad (6)$$

Methods and Procedures

Data are usually compiled in the literature in the form of tables of χ_{12}, χ_{13}, and χ'_{23} from which χ_{123} is also accessible. In other cases, specific retention volumes for pure components and blends of different compositions are available. In both cases the use of eq 3 or, alternatively, eq 5 allows us to obtain the average volume fraction and the true interaction parameter.

As far as the molar volumes are concerned, they have been taken from the original papers, if available. If this is not the case, they have been taken from various compilations, usually cited in IGC papers.[13-16]

Results and Discussion

Let us start with a well-known blend in thermodynamic studies which is composed of polystyrene (PS) and poly(vinyl methyl ether) (PVME). We have used the data of Su and Patterson,[17] who determined the interaction parameter by IGC at 40 °C in two blends of PS(2) and PVME(3) (molecular weights 600 and 10 000, respectively). The PS weight fractions were 0.45 and 0.625, and they used 20 different probes. These data have been previously employed by Prolongo et al.[9] in a paper in which the equation of state properties of the components are supposed to play a predominant role in the deviations of the ternary system from the additivity.

Molar volumes of the probes have been taken from the book of Reid, Prausnitz, and Sherwood.[13] Figures 1 and 2 show plots of experimental data according to equation 3. In order to compare our results with those provided by the application of the Prolongo et al. method,[9] we have also eliminated the data of chloroform and isopropyl alcohol.

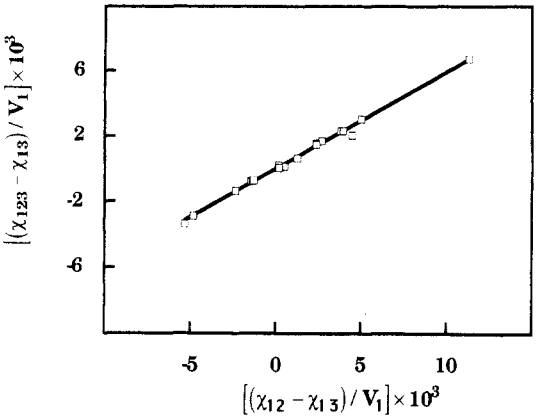

Figure 2. Plot of the Farooque–Deshpande method[11] corresponding to the PS/PVME 62.5/37.5 w/w blend at 40 °C.[17]

Both plots show excellent correlations. However, a strict analysis[18] of the intercept confidence interval gives a large percentage of uncertainty. This uncertainty is not surprising given the extremely low value of the intercept. We explain the good linearity of the Farooque and Deshpande[11] plots as arising from the fact that the term containing χ_{23} has a small weight in the equation we are using.

The most relevant result is that the intercept gives a B_{23} value of 0.6 (±0.24) cal/cm^3 for the 45/55 blend whereas the application of the Horta method gives a B_{23} value of 0.3 cal/cm^3). The Horta method provides a very small value, B_{23} = 0.03 cal/cm^3, for the 62.5/37.5 blend. The application of the Farooque and Deshpande method gives a very small and negative value of B_{23} = −0.001 (±0.32) cal/cm^3. Beaucage and Stein[19] have recently studied PS/PVME blends by neutron scattering. They have taken into account a fact previously clarified by Sanchez[20] that the interaction parameters obtained by this type of measurement (B_{sc}) are different from those obtained by IGC if the interaction density B is composition dependent. After a rigorous analysis of the dependence of B_{sc} with composition and temperature, it is possible to obtain a similar relationship for the interaction energy B, related to IGC measurements. For a 50/50 blend at 40 °C, the interaction energy density is −0.43 cal/cm^3, in reasonable agreement with the IGC results, given the low molecular weights employed by Su and Patterson[17] and the extremely low value of the interaction energy involved in this blend.

Similar results have been obtained with our own previous data of the blend composed of poly(ethylene oxide) (PEO) and the so-called phenoxy resin (PH).[21] Figure 3 shows the Farooque–Deshpande plot, according to eq 3, for our data of a 50/50 blend at 140 °C. This plot gives a B_{23} value of −1.3 (±1.4) cal/cm^3, practically identical to the −1.1 (±1.3) cal/cm^3 value we obtained after the strict application of the Prolongo et al. method.[9]

A similar situation has been found in the blend poly(vinyl acetate)/poly(vinylphenol) (PVA/PVPh), studied by Lezcano et al.[22] In Table 1 we have summarized the results of the graphical representations of these data according to eq 3. As in the previous PH/PEO blend large confidence intervals in the domain of ±1.8 cal/cm^3 are obtained. Given that the term containing χ_{23} is a minor contribution to χ_{123} (or to the specific retention volume of the blend column), it is plausible to argue that the use of eq 4 to calculate χ_{23} can imply large errors in those cases in which the specific retention volumes in the pure

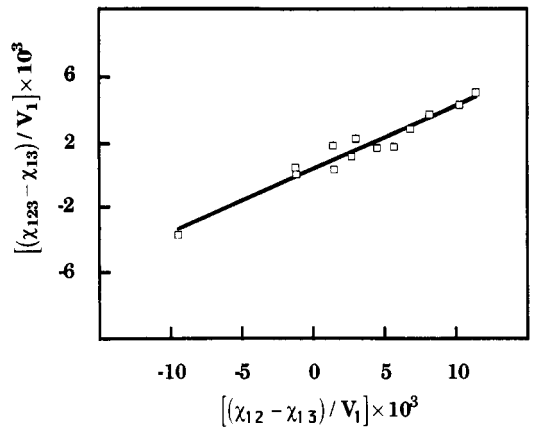

Figure 3. Plot of the Farooque–Deshpande method[11] of the PH/POE 50/50 w/w blend at 140 °C.[21]

Table 1. Comparison between Farooque and Deshpande (FD) and Prolongo et al. (PMH) Methods with Data of Lezcano et al.[22] from Blends of PVA/PVPh

blend	B_{23} (cal/cm^3) (PMH)	B_{23} (cal/cm^3) (FD)	FD plot regression correlation
PVA/PVPH 74/26	−0.89	−0.32	0.996
PVA/PVPH 62/38	−1.95	−3.72	0.993
PVA/PVPH 49/51	−0.89	−0.86	0.989
PVA/PVPH 24/76	+0.89	+1.68	0.917

Table 2. Values of B_{23} (cal/cm^3) Obtained from the Application of the Farooque and Deshpande Method to Three Columns of PH/PCL at Different Temperatures[23]

T (°C)	25/75	50/50	75/25
129.6	−1.16	−1.78	−1.47
139.3	−1.37	−1.83	−1.66
149.0	−1.80	−1.57	−2.17
158.5	−2.68	−1.62	−2.31

component columns were small and similar. This seems to be the case in our PH/PEO study. The smaller confidence interval in the PS/PVME measurements could be a consequence of the low experimental temperature and the large number of probes. In the PVA/PVPh case, the high temperature (170 °C) and the use of various members of the same functional group family with similar $\Delta\chi$ could affect the final confidence interval.

A final comparison between the method of Farooque and Deshpande[11] and that of Prolongo et al.[9] has been recently undertaken in our laboratory with blends of phenoxy resin (PH) and poly(ϵ-caprolactone) (PCL).[23] In order to minimize the problems above described we have selected solvents fulfilling the following conditions: first, they should have very different specific retention volumes in the pure component columns, and secondly, the values of these retention volumes should not be excessively small.

Table 2 summarizes the polymer–polymer interaction parameters, expressed as B_{23}, for three different PH/PCL compositions at four different temperatures after the application of the Farooque and Deshpande method.

Figure 4 compares the results for a 50/50 blend at different temperatures with those obtained after using the Prolongo et al.[9] method. This figure also includes the confidence intervals. Three comments are relevant. First, the selection of the solvents has reduced the uncertainties in both methods to an average value of ±0.75 cal/cm^3. This reduction is significant if we compare these values with those of PH/PEO and PVA/PVPh, where similar temperatures and numbers of probes have been used. Second, there are not large differences between the interaction parameter values of the two methods, and

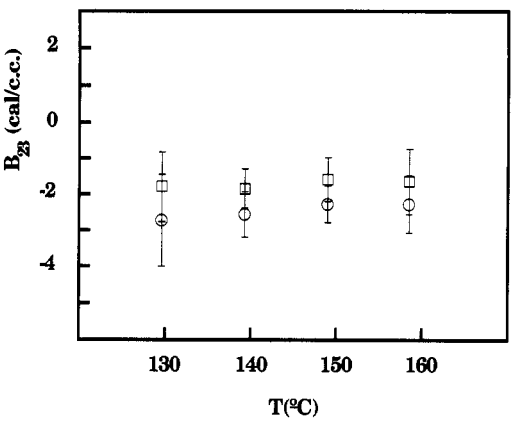

Figure 4. Comparison of the Farooque–Deshpande method,[11] □, and the Prolongo et al.[9] method, ○, in obtaining B and its confidence interval for a PCL/PH 50/50 w/w blend.

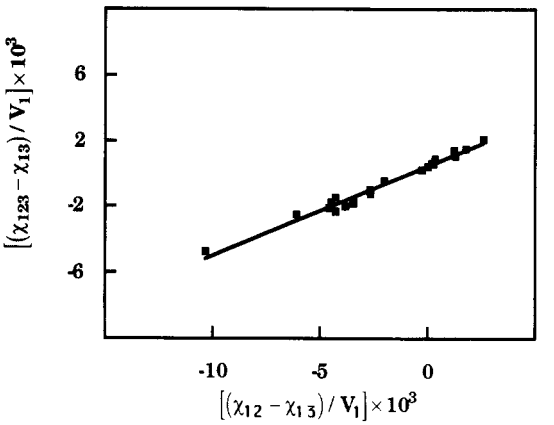

Figure 5. Plot of the Farooque–Deshpande method[11] for the PCL/PECH 50/50 w/w blend at 80 °C.[27]

finally, there is a good agreement between the interaction parameter so obtained and previous data of different laboratories using melting point depression analysis.[24,25] The interaction energy density so obtained was close to −2.4 cal/cm^3 at 63 °C whereas, in our IGC measurements, B values for a 50:50 blend range from −1.79 and −1.62 cal/cm^3 if the temperature varies from 130 to 158.5 °C.

Munk and co-workers[26–29] have proposed different levels of a data analysis method in which a model based on the solubility parameters of the pure components and the blend is used. In the simplest approximation[26] a correlation was found to exist between the apparent B_{23} values and the Hildebrand solubility parameter of the probe. On the basis of this correlation, the authors have hypothesized that the true B_{23} value for the blend is that corresponding to a probe which possesses the same solubility parameter as that of the blend. This needs a good estimation of the blend solubility parameter which the authors obtained by using the method established by Guillet and co-workers.[30] This analysis was applied to a mixture of poly(ϵ-caprolactone) (PCL) and poly(epichlorohydrin) (PECH). The average value of B for all the investigated blends was in the region of −2.0 cal/cm^3.

Figure 5 shows the plot of the data of a 50/50 blend according to the Farooque and Deshpande method. Again, an apparent good correlation was obtained with a B_{23} value of −1.3 cal/cm^3.

In a more recent and sophisticated version[28] of this approximation a term which accounts for the different molecular surfaces the components offer to the interaction is also introduced. The model ascribes to each element of a molecular surface four types of interactive properties: van der Waals, polar, electron donor, and electron acceptor.

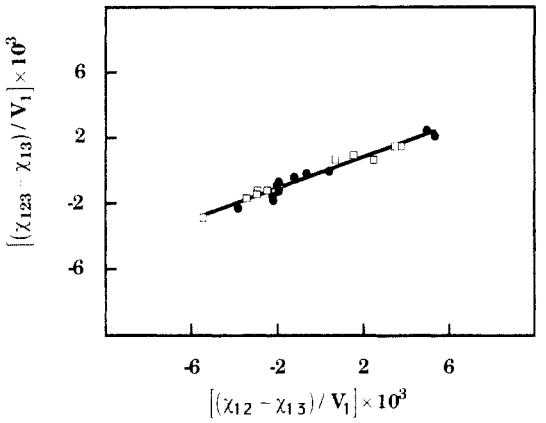

Figure 6. Application of the Farooque–Deshpande method[11] using data of PECH/PMA 50/50 w/w at 76 °C from different works: (●) Al-Saigh and Munk;[7] (□) Etxeberria.[31]

These properties may be averaged over the whole surface of each molecular species as long as the statistics of molecular arrangements conform to the concept of a regular solution. Their averaged values are temperature dependent as a result of changes of intermolecular distances with temperature. The probe surface parameters can be obtained from IGC experimental data of solvent–polymer systems. The extension of the method to polymer–polymer systems[27,29] allows us to obtain an interaction parameter $C'_{23} = B_{23}/(\phi_2 S_2 + \phi_3 S_3)$, where S_i refer to the same surface parameter but in the polymer cases. Unfortunately, the model does not allow us to determine the polymer surface parameters from experimental data, as is the case of the probe surface parameters.

In Figure 6 we present data of Munk et al.[7] together with others measured in our laboratory[31] for a 50/50 blend of poly(epichlorohydrin) (PECH) and poly(methyl acrylate) (PMA), a blend which has been recently studied by this version of the Munk et al. approximation.[27]

A good agreement was found between the two series of data, giving a good correlation and a value of B around -0.5 cal/cm^3. The method of analysis proposed by Munk et al. gave a C'_{23} value of -1.11 cal/cm^3. Most of the surface parameters for the probes range between 1 (the reference value, ascribed to the alkane family) and 1.4 in the case of halogenated probes. The authors consider that in the case of polymers this surface parameter should be smaller than that in low molecular weight probes. They explain this reduction on the basis of the small portion of the molecular surface available for the interaction. Consequently, our B_{23} value would be in reasonable agreement with that obtained from the Munk et al.[27] treatment.

Conclusions

Along this work it has been demonstrated that a simple and phenomenological method of IGC data handling, which only needs experimental magnitudes, allows us to determine polymer–polymer interaction energy densities, B, with accuracies similar to those of other more elaborate methods, as those proposed by Prolongo et al.[9] or Munk et al.[27]

All these methods give similar large uncertainty intervals for the B values. In the case of the Farooque and Deshpande method this unsatisfatory accuracy can be masked by the remarkable linearity of the employed plots. In our opinion, this behavior is only a consequence of the small role played by the polymer–polymer interaction term in eq 3, through which the interaction is determined. As a consequence of this fact, an intrinsic large confidence interval should result. From our results in the PH/PCL blend it appears that an adequate selection of probes, avoiding those with very similar specific retention volumes, can reduce the inherent confidence intervals in such types of measurements.

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