Estimation of interaction parameters of a poly(hydroxy ether of bisphenol A)/poly(vinyl methyl ether) blend by inverse gas chromatography

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A blend of poly(hydroxy ether of bisphenol A) (phenoxy) and poly(vinyl methyl ether) (PVME) was investigated by inverse gas chromatography (i.g.c.) over a wide temperature range. Specific retention volumes were measured for a variety of probes in pure and mixed stationary phases and interaction parameters were calculated. It was found that the polymer–polymer interaction parameter was probe-dependent. Two methods of data analysis recently proposed were applied in an attempt to eliminate this dependence. In both cases similar results were obtained with similar and large confidence intervals. I.g.c. experimental results were compared with theoretical calculations of an association model for polymer mixtures with specific interactions. A reasonable agreement was found.

(Keywords: phenoxy/PVME blend; inverse gas chromatography; interaction parameters)

INTRODUCTION

Soon after inverse gas chromatography (i.g.c.) was introduced[1], Deshpande *et al.*[2] suggested the use of this technique for studying polymer blends. Extending to ternary systems the Flory–Huggins expression for the change in free energy of mixing, they proposed an i.g.c. method of analysis of the polymer–polymer interaction parameter. In general, the polymer–polymer interaction parameter obtained in this way exhibits a significant dependence on the chemical nature of the probe. It was suggested that such a variation arises from the differences between the binary interaction parameters of the pure components with the different probes. This has usually been described as the $\Delta\chi$ effect. Some authors[3,4] have stressed the fact that the Scott–Flory–Huggins treatment has been inappropriately applied to ternary mixtures, the weakness arising from the assumption that the Gibbs mixing function for ternary polymer–polymer–solvent systems is additive with respect to the binary contributions.

El-Hibri *et al.*[5] and Chee[6] have developed different approaches to a probe-independent interaction parameter. Both approaches are based on the use of solubility parameters. Other authors[7] have also noted the possibility that non-random partitioning of probe molecules could affect the forces acting between molecules of the mixed stationary phases, so that i.g.c. could be viewed as a unique source for information on interactions on a molecular rather than on a bulk scale. Finally, Farooque and Deshpande[8] have revised some of the above-mentioned methods. In the same paper, they proposed a different route for chromatographic data analysis, which, in a very simple way, gives a single interaction parameter for the whole set of probes.

The mixture of poly(vinyl methyl ether) (PVME) and poly(hydroxy ether of bisphenol A) (phenoxy) has been stated to be miscible at low temperatures and to exhibit a lower critical solution temperature (*LCST*) type of phase diagram[9,10]. In a previous paper[11], we studied this blend by means of inverse gas chromatography (i.g.c.) in the vicinity of the lower critical solution temperature. The comparison of the specific retention volume of the mixed stationary phase with the average value of the specific retention volumes of the pure components allowed detection of a phase separation diagram in good agreement with that obtained by optical microscopy. Interaction parameters at the cloud-point temperature were probe-dependent, negative and far from the critical value.

In this paper, we re-examine the problem by using recently proposed expressions for eliminating the so-called 'solvent effect'. We will also compare our experimental results with the simulations of an association model proposed by Coleman, Painter and coworkers[12]. In spite of its limited applicability to mixtures where specific interactions are capable of inducing changes in the characteristic *FT*i.r. bands of the components, the model only uses experimentally accessible parameters, a feature not fulfilled for other more general thermodynamic models, such as those derived from the equation-of-state or lattice fluid theories.

EXPERIMENTAL

Materials

Poly(hydroxy ether of bisphenol A) (phenoxy, PH) was obtained from Quimidroga (Barcelona, Spain) and

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corresponds to the PKHH product of Union Carbide. The commercial sample, after purification by dissolution in dioxane and precipitation in methanol, had a glass transition temperature of 368 K. Its average molecular weights, measured by g.p.c. in tetrahydrofuran (THF) (waters ALC 150 Gel Permeation Chromatograph) at 303 K, were $\bar{M}_n = 18\,000$ and $\bar{M}_w = 50\,400\,\mathrm{g\,mol^{-1}}$.

Poly(vinyl methyl ether) (PVME) was obtained from Polysciences (catalogue no. 3032). It was purified in a benzene/isooctane mixture. The average molecular weights were $\bar{M}_n = 29\,000$ and $\bar{M}_w = 61\,000\,\mathrm{g\,mol^{-1}}$ (g.p.c., THF, 303 K).

The probes—diethylene glycol diethyl ether (DEGDEE), dimethylformamide (DMF), tetradecane, dioxane, toluene, 2-butanone, decane, benzene, ethyl acetate, n-propanol, 1,2-dichloroethane, acetonitrile and chlorobenzene—were selected in such a way that they cover different chemical natures and strengths of interactions with the polymers. They were of chromatographic quality or reagent grade, and were used without further purification.

Densities, thermal expansion coefficients, isothermal compressibilities and critical parameters for the solvents were taken from different sources and internal data[13–17]. Data used for polymers have been given previously[11].

Apparatus and procedures

The gas chromatographic measurements were carried out on a Perkin–Elmer Sigma 300 Gas Chromatograph equipped with a flame ionization detector and connected to an Olivetti M-24 personal computer with appropriate software in order to yield high-precision retention data. Nitrogen was used as the carrier gas and methane as a non-interacting marker. Pressures at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention times by the usual procedures.

The columns were prepared in the usual manner[13] using Chromosorb G (AW-DMCS treated, 80/100 mesh) as the packing support. The pure polymers and the polymer blend were coated from a solvent solution onto the packing support. After drying in a vacuum oven for ca. 48 h at 323 K, the coated support was packed into a 1/4 inch (~6 mm) o.d. stainless-steel column by applying a vacuum to the end. Glass wool was used to block one end of the column. The relative concentration of the polymer in the blend was assumed to be identical to that in the original solution prior to the deposition on the inert support. A description of the columns is given in *Table 1*.

The oven temperature was measured within ±0.1°C in the whole temperature range. The molecular probe, including a small amount of methane marker ($<0.01\,\mu$l), was injected manually with a 10 μl Hamilton syringe. The columns were conditioned at temperatures above T_g for ca. 48 h prior to use, while N_2 was flushed through the column in order that it should come to equilibrium.

Specific retention volumes, V_g, were calculated from the expression:

$$V_g = t_n \frac{F}{\omega} \frac{3}{2} \frac{273.15}{T_r} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad (1)$$

where t_n is the net retention time of each probe, ω is the mass of the polymer in the column, P_i and P_o are the inlet and outlet pressures, and F is the carrier gas flow at room temperature T_r. The values of V_g are usually extrapolated to zero flow rate to obtain V_g^0. In this work, V_g values were independent of the gas flow rate over the investigated range.

Table 1

Polymer	Loading (% w/w)	Wt polymer (g)	Column length (cm)
PH	10.06	0.5028	100
PVME	10.02	0.4415	100
PH/PVME (60/40 w/w)	10.04	0.4941	100

Table 2 Polymer–polymer interaction energy density in PH/PVME (60/40) blend at 421.8 K, calculated according to equation (3)

Probe	B (cal cm^{-3})
DEGDEE	−3.13
DMF	−2.49
Ethyl acetate	−1.26
Butanone	−2.65
Benzene	−1.00
n-Decane	−0.11
n-Propanol	0.28
Toluene	−0.80
n-Tetradecane	−0.40
1,2-Dichloroethane	−0.42
Dioxane	−0.62
Chlorobenzene	−4.54
Acetonitrile	−0.19
Average B_{23}	−1.33 (±1.43)

RESULTS AND DISCUSSION

Specific retention volumes of the 13 probes at 11 temperatures above any thermal solid–liquid transition were obtained for pure components (PH and PVME) and a PH/PVME (60/40 w/w) blend.

For expressing the interactions between two components, we have adopted the so-called interaction energy density B, which can be related to the polymer–polymer interaction parameter by means of:

$$B = RT(\chi_{23}/V_2) \qquad (2)$$

where 2 refers to phenoxy and 3 to PVME. B can be calculated from experimental specific retention volumes as:

$$B = \frac{RT}{V_1}\left[\ln\left(\frac{V_{g,b}^0}{v_{sp,b}}\right) - \phi_2 \ln\left(\frac{V_{g,2}^0}{v_{sp,2}}\right) - \phi_3 \ln\left(\frac{V_{g,3}^0}{v_{sp,3}}\right)\right]\frac{1}{\phi_2\phi_3} \qquad (3)$$

where V_1 is the molar volume of the probe, $v_{sp,i}$ are the specific volumes of the pure polymers (2 and 3) and the blend (b) assuming additivity and ϕ_i are the volume fractions of the polymers in the mixture. If we calculate B with this expression, large variations of B from probe to probe are obtained, as usual. *Table 2* gives the results of such calculations at an intermediate temperature of the investigated range (421.8 K).

Similar error bars of about ±1.4 were obtained for the other investigated temperatures. Some authors have pointed out that, with an adequate precision in retention times, the scatter of the points cannot be due to experimental errors[18]. Nevertheless, there is a definite dependence of the polymer–polymer interaction parameter on the chemical nature of the probe. The origin of this dependence could arise from the shortcomings of rigid lattice models to describe thermodynamic properties of polymer solutions. Equation (3), derived from the classic Flory–Huggins rigid model, implies the frequent assumption that the interactional part of the Gibbs function of the ternary system is additive in the binary contributions. This can cause the i.g.c. data to be strongly probe-dependent.

In order to obtain a solution to this problem, different authors have proposed methods to get probe-independent interaction parameters. In the framework of the lattice fluid (LF) theory, Sanchez[19] proposed to eliminate free-volume effects from the polymer–polymer interaction parameter. The final result should be a 'bare' probe-independent interaction parameter. This is a similar solution to that proposed several years ago in the framework of the equation-of-state theory[2]. The modest results of this approach for determining polymer–polymer interaction parameters have been recognized by the authors[20].

Prolongo *et al.*[4] have developed a new treatment that permits calculation of a probe-independent interaction parameter. The formalism involves the use of the expression of the non-combinatorial part of the mixing free energy in a ternary polymer–polymer–solvent system, written in terms of the equation-of-state theory. This allows the authors to calculate the so-called true interaction parameter, which, besides the use of the free-volume concept, does not assume the additivity hypothesis. The final expression, specifically derived for i.g.c. calculations, can be written:

$$\chi_{23}^{\mathrm{app}} = \chi_{23}^{\mathrm{T}}\left(\frac{s_1}{s_3}\right) + (\chi_{12}-\chi_{13})\left(\frac{(s_3-s_2)V_2^*}{V_1^*(\phi_2 s_2+\phi_3 s_3)}\right) - \kappa \quad (4)$$

where κ can be calculated from equation-of-state parameters of the components such as characteristic and reduced volumes, molecular surface-to-volume ratios and reduced temperatures and pressures. Equation (4) predicts, among other effects, a dependence of the apparent interaction parameter on the difference between the binary polymer–probe interaction parameters. This concept was first introduced by Su and Patterson[21] and has been phenomenologically observed by Galin and Maslinko[22].

The true interaction parameters obtained from equation (4) can be immediately transformed to interaction energy densities by using equation (2). *Figure 1* shows such a type of plot for our system at the same temperature as used in *Table 2.*

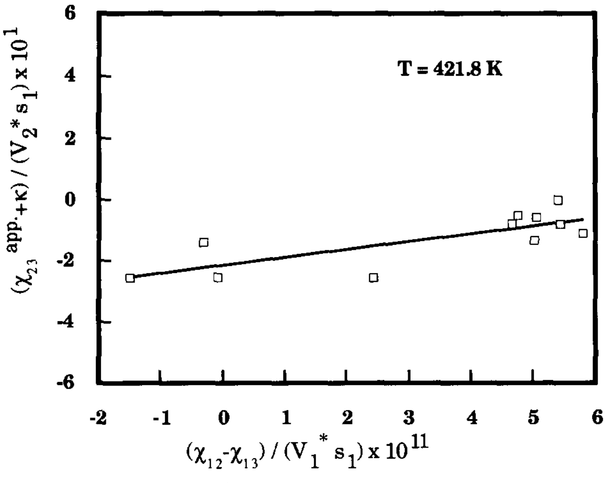

Figure 1 Prolongo *et al.*[4] plot, according to equation (4). Phenoxy/PVME (60/40 w/w) blend at 421.8 K

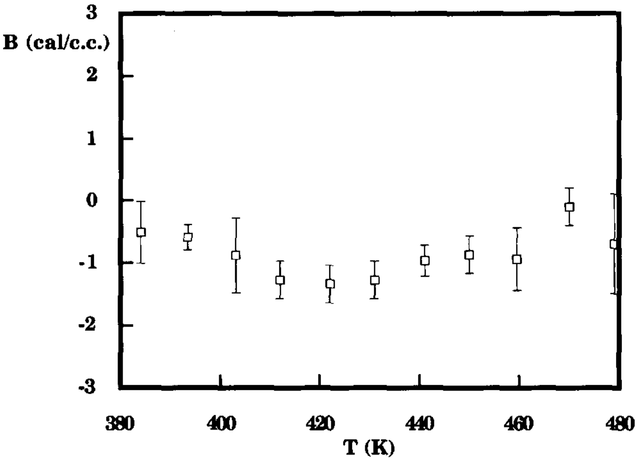

Figure 2 Temperature dependence of the interaction energy density as obtained from plots similar to *Figure 1*. Phenoxy/PVME (60/40 w/w) blend

From similar plots for the other investigated temperatures, the temperature dependence of B is presented in *Figure 2*. If we compare the B values with those obtained from the direct application of equation (3), the error bars are certainly smaller. However, there is no substantial modification in the values or in their variation with temperature. Recent data[23] on the phenoxy/poly(ε-caprolactone) blend suggest that large errors are mainly caused by the use of probes with small and similar retention volumes. An adequate selection of probes can significantly reduce such deviations.

From a phenomenological point of view, a recent paper of Shi and Schreiber[7] has re-examined the problem from the point of view of differences between bulk and surface compositions of the stationary phase. A method has been proposed to estimate the effective composition that the solvent is 'seeing' in the column. With this convention, the probe dependence of the polymer–polymer interaction parameter for an immiscible blend has been significantly reduced. Recently[24] we have extended this method to miscible mixtures of poly(vinyl chloride) and poly(ethylene oxide).

In a similar phenomenological approach, Farooque and Deshpande[8] proposed another method of i.g.c. data handling. Reorganizing equation (3):

$$RTY/V_1 = (RTX/V_1)\phi_2 - B\phi_2\phi_3 \quad (5)$$

with

$$Y = \ln(v_{\mathrm{sp,b}} V_{\mathrm{g,3}}^0 / v_{\mathrm{sp,3}} V_{\mathrm{g,b}}^0) \quad (6)$$

and

$$X = \ln(v_{\mathrm{sp,2}} V_{\mathrm{g,3}}^0 / v_{\mathrm{sp,3}} V_{\mathrm{g,2}}^0) \quad (7)$$

A plot of RTY/V_1 *versus* RTX/V_1 can yield ϕ_2 from the slope and $-B\phi_2\phi_3$ from the intercept. Good plots are obtained from our data, as can be seen in *Figure 3* for the reference temperature we are using throughout this paper. The ϕ_2 value can be understood as an average value that the probes are actually seeing inside the column and the B value as the true interaction energy density. From the slope and intercept, a B value of $-1.74\,\mathrm{cal\,cm^{-3}}$ and a volume fraction of 0.530 can be obtained. The B value is within the range of the average B values obtained by means of equation (3) and the 'true' value obtained from the Prolongo *et al.*[4] analysis. The ϕ_2 value is slightly lower than that originally prepared

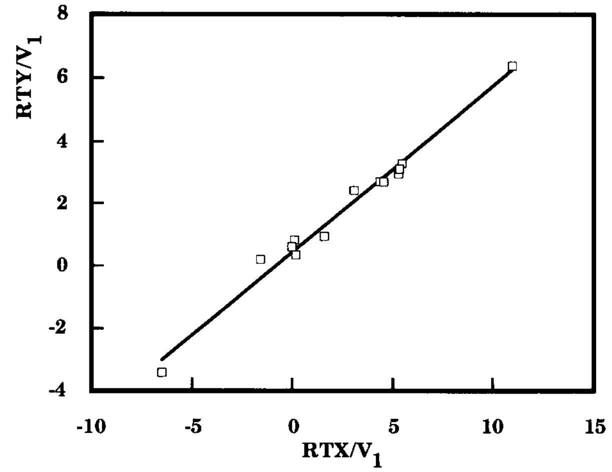

Figure 3 Farooque and Deshpande[8] plot, according to equation (5). Phenoxy/PVME (60/40 w/w) blend at 421.8 K

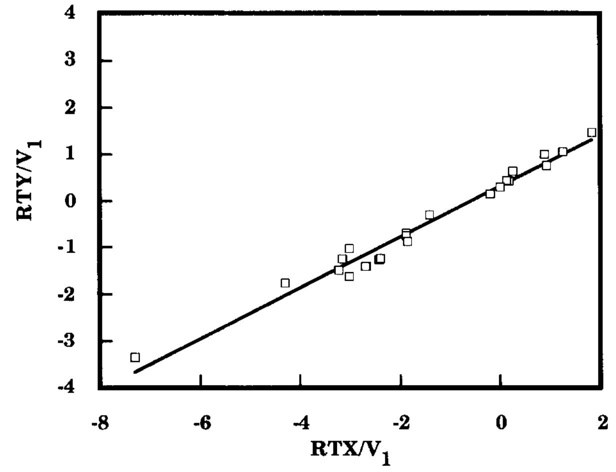

Figure 4 Farooque and Deshpande[8] plot, according to equation (5). PECH/PCL (50/50 w/w) blend at 353.2 K (data from El-Hibri *et al.*[18])

(0.567). This change in the ϕ_2 value is consistent with the fact that, according to *Figure 1*, most of the probes have positive $(\chi_{12}-\chi_{13})$ differences, a consequence of the preferential solvation of the majority of the probes with PVME.

The method gives similar good correlations with previously published data. The data of El-Hibri *et al.*[18] for blends of poly(ε-caprolactone) (PCL) and poly(epichlorohydrin) (PECH), using 23 probes, are presented in *Figure 4*. A B value of $-1.29\ \mathrm{cal\,cm^{-3}}$ can be obtained from the intercept, not far from the value of $-2.1\ \mathrm{cal\,cm^{-3}}$ reported by the authors after a data handling involving the solubility parameters of the components of the ternary polymer–polymer–probe system[5].

However, the apparent success of this new method can be regarded with caution. The good linearity of such plots is only a consequence of the small contribution of the B term to the equation. In fact, a rigorous error estimation[25] provides a large confidence interval of the B values similar to that obtained using the method proposed by Prolongo *et al.*[4] and smaller than that obtained through the simple use of equation (3). At 421 K the confidence interval for B was ± 0.74 and ± 0.04 for ϕ_2, which extends the possible range of concentration beyond the bulk concentration originally prepared.

B values for PH/PVME blend at different temperatures obtained from linear extrapolations similar to those of *Figure 3* are summarized in *Figure 5* together with the confidence intervals. As can be seen, there is a reasonable agreement between these values and those obtained following the method of Prolongo *et al.*[4] through the investigated temperature range.

Given the apparent agreement between the very simple treatment of Farooque and Deshpande and other more sophisticated and time-consuming data handlings, the remaining question concerns the validity of the interaction parameters so determined. An interesting test of these data arises from the association model proposed by Coleman, Painter and coworkers[26] particularly applicable to this system, where specific interactions are supposed to be present and where a phase separation diagram is experimentally accessible.

The application of commercially available software of this model needs a previous determination of the association constants and enthalpies involved in the association equilibria between the interacting functional groups. This information can be obtained from *FT*i.r. studies of the blends or from analogous compounds. Data for the association equilibria between phenoxy and polyoxides and poly(vinyl ethers) have been determined previously by Espi[27]. The required data are collected in *Table 3*. In our calculation we have used a polymerization degree of 500 for PVME and 65 for phenoxy, in agreement with the experimental molecular weights of our components.

The association model provides a phase diagram that predicts a phase separation *LCST* type in good agreement with previous experimental evidence[9,10]. It should be taken into account that the method only uses association parameters obtained by independent experiments, without any adjustable parameters. *Figure 6* shows the simulated phase diagram. The *UCST* diagram has not been experimentally observed, but it is consistent

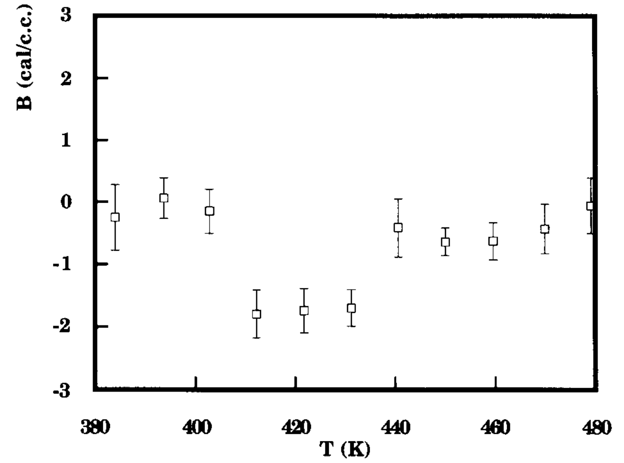

Figure 5 Temperature dependence of the interaction energy density as obtained from plots similar to *Figure 3*. Phenoxy/PVME (60/40 w/w) blend

Table 3 Equilibrium constants and enthalpy of hydrogen-bond formation for phenoxy–polyether blends[27]

K_2 (self-association, dimer formation)	14.40
K_B (self-association, polymer formation)	25.60
K_A ((A–B) association)	3.40
h_2 (kcal mol^{-1})	−2.5
h_B (kcal mol^{-1})	−3.4
h_A (kcal mol^{-1})	−3.0

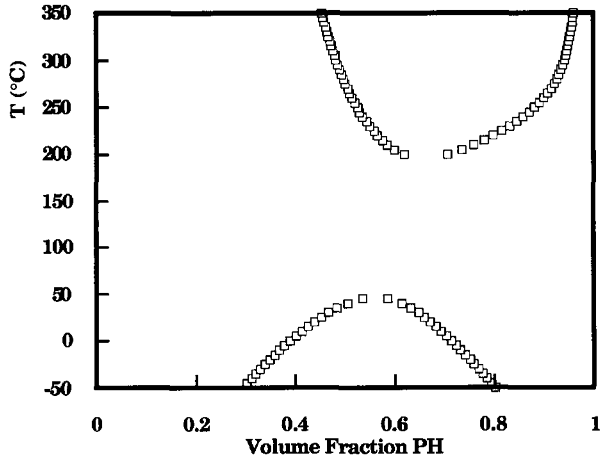

Figure 6 Phase diagram for a phenoxy/PVME (60/40 w/w) blend, simulated by an association model[26] and the association constants and enthalpies summarized in *Table 3*

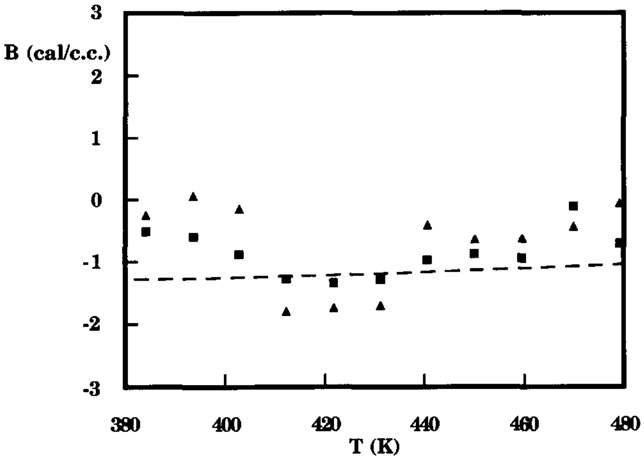

Figure 7 A comparison between experimental data following the Prolongo *et al.* and Farooque and Deshpande treatments and the theoretical calculations: (----) association model; (■) Prolongo *et al.*[4]; (▲) Farooque and Deshpande[8]

with the parabolic behaviour of the interaction parameter in *Figures 2* and *5*.

Mixing free energies can also be simulated by using this model. If we suppose that molecular weights are high enough to disregard the entropic contribution to the free energy of mixing, the theoretical value of this magnitude (in cal cm^{-3}) can be identified with the term $B\phi_2\phi_3$. *Figure 7* gives a comparison of the B parameter so obtained and those experimentally obtained using the Prolongo *et al.*[4] method and the simple plot of Farooque and Deshpande[8].

In conclusion, there are no big differences between the interaction energy densities calculated according to the method of Prolongo *et al.*[4] and that of Farooque and Deshpande[8]. Moreover, the experimental results so obtained are reasonably consistent with the theoretical predictions of an association model. The main difference between the classical use of equation (3) and that proposed by Farooque and Deshpande (equation (5)) rests in the obtention of a column concentration different to that originally prepared. Whether this average concentration has physical significance or not is an open question. Shi and Schreiber[7] have reviewed different experimental evidences that support the reality of a difference between surface and bulk compositions. This difference could arise from the fact that, in order to minimize the surface free energy of the solid blend inside the column, the system will drive to the surface the component with the lower surface energy. If this is true, the i.g.c. experiment is reporting accurately on the state of surface interaction in a binary stationary phase. The other possibility concerns the reality of a preferential sorption for each probe. In this case, the volume fraction obtained from linear plots according to equation (5) is only an average of the concentration that the probes are seeing inside the columns.

Our opinion is that, after a careful selection of solvents, avoiding those with similar or small specific retention volumes, the method of Farooque and Deshpande can provide a rapid estimation of the interaction parameter with a confidence interval not far from those inherent to other more sophisticated methods of i.g.c. data analysis. More i.g.c. data previously published are currently being analysed with the method of Farooque and Deshpande in order to confirm these previous ideas.

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