# Lattice Fluid Theory and Inverse Gas Chromatography in the Analysis of Polymer–Polymer Interactions

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ABSTRACT: In this work, inverse gas chromatography has been used to calculate interaction energy densities of two polymer blends: poly(epichlorohydrin) (PECH)/poly(methyl acrylate) (PMA) and poly(hydroxy ether of Bisphenol A) (phenoxy, PH)/poly(vinyl methyl ether) (PVME) at different temperatures. An approach based on the lattice fluid theory has been used in an attempt to eliminate the well-known probe dependence of the thermodynamic parameters calculated by IGC. In the two polymer blends under study, the above mentioned data analysis seems to be unable to remove the probe dependence. However, it allows the calculation of an average characteristic interaction energy density $\Delta P^*$ which can be used in the calculation of the interaction energy density $B$, its enthalpic and entropic components, and the interaction energy density related to the second derivative of the free energy, $B_{sc}$. The thermodynamic properties so calculated are in good agreement with those obtained from a phenomenological and simpler data analysis.

## Introduction

In the last 20 years, inverse gas chromatography (IGC) has been used to characterize different features of polymer systems.[1-4] Among them, polymer–polymer interaction parameters can be determined using the Scott–Flory–Huggins formalism for ternary polymer–polymer–solvent systems.[5] However, polymer–polymer interaction parameters calculated in such a way have shown a clear and unremovable dependence on the solvent used as a probe.[6-8] Some authors have pointed out that this variation arises from the different interaction of the probe with the blend components, which can be expressed in terms of the binary polymer–probe interaction parameter difference, $\Delta\chi = \chi_{12} - \chi_{13}$ ($\Delta\chi$ effect).[6,9]

This probe dependence must be removed if the IGC technique is used as a way to study polymer–polymer blends from a thermodynamic point of view. Different methods of data analysis have been proposed with the aim of eliminating this probe dependence. Previously, Munk et al.[10] undertook a rigorous procedure to reduce the possible sources of experimental errors, showing that even with a careful control of these sources, the dependence of the interaction parameter on the probe was real. Among the proposed techniques of data analysis, El-Hibri et al.[11] and Chee[12] have used approaches based on the solubility parameter. A more phenomenological solution has been given by Shi and Schreiber[13] for immiscible blends, later extended to miscible blends by our own group.[14] In these works, the fact that nonrandom partitioning of the probe in the polymer mixed stationary phases could mask the true polymer–polymer interaction is the basis of the proposed procedures.

Using a different approach and starting from the inadequate description of the probe–polymer–polymer system via the Scott–Flory–Huggins theory, Prolongo et al.[9] have proposed a data analysis based on the Flory–Orwell–Vrij equation-of-state theory as an alternative way to consider all the perculiarities of such a ternary system. Finally, in a recent paper, Farooque and Deshpande[15] have proposed a simple data treatment based on a modification of the usual equation in IGC studies. This method provides a single interaction parameter for the whole set of probes.

From a different point of view, Sanchez[16] pointed out that the experimentally observed probe dependence of the polymer–polymer interaction parameter is due to the use, in the classical theory, of composition independent interaction parameters, an assumption not always fulfilled. He clearly showed that the experimental polymer–polymer interaction parameters depend on whether the experimental method probes the mixture's free energy, its first derivative, or its second derivative. In general, four different interaction parameters are required to describe a binary polymer mixture, although if any one is experimentally determined, the others can be calculated.

From this observation, the author proposed a possible resolution of the probe dependence of the polymer–polymer interaction parameter resorting to the lattice fluid theory (LF). Using this theory, he showed that it is possible to determine a "bare" interaction parameter, i.e., an interaction parameter in which all the free volume effects have been removed. This interaction parameter must be independent of the composition and of the chemical nature of the probe.[16]

As far as we know, there is only one paper in the literature where polymer–polymer interaction parameters have been determined by IGC following Sanchez's procedure.[15] However, the authors compared the interaction parameters so calculated with those obtained according to other methods previously cited. A correct comparison of the different results must imply, however, the inclusion of the free-volume effects in the "bare" interaction parameters.

Recent papers of Paul et al.[17-22] have extensively used the lattice fluid theory in an attempt to explain phase diagrams in polymer–polymer and polymer–copolymer blends. They prefer to define the polymer–polymer interactions in terms of the so-called interaction energy density $B$, a parameter closely related to the interaction parameter but defined as an energy per volume unit. They have derived different equations defining the temperature dependent interaction energy density $B^{(T)}$,

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its enthalpic and entropic components, $B_h$ and $B_s$, and the so-called $B_{sc}$ energy density related with the second derivative of the free energy.[17] In general, $B^{(T)}$ and $B_{sc}$ are different, but they are related, as has been shown by Sanchez[16] and previously mentioned. In all these equations the only unknown parameter is the characteristic interaction energy density $\Delta P^*$, easily related to the "bare" interaction parameter, determined by IGC.

In this paper, we will analyze the polymer–polymer interaction energy density $B$, calculated according to the LF theory, after determining the bare interaction parameters (or $\Delta P^*$) by IGC. The potential advantage of this technique is the possibility of measuring $\Delta P^*$ over a wide range of temperatures. In papers where $\Delta P^*$ is determined from phase boundary experiments, a single and temperature independent $\Delta P^*$ value is usually obtained.[17-22]

We have applied the method to two polymer blends studied in our laboratory by IGC, i.e. poly(epichlorohydrin) (PECH)/poly(methyl acrylate) (PMA) and poly(hydroxy ether of Bisphenol A) (phenoxy, PH)/poly(vinyl methyl ether) (PVME). The first one has been already studied by IGC at two temperatures by Munk et al.[10] Here, we have obtained more extensive data in a wider temperature range. Experimental data of our group for the second polymer–polymer system have been previously used to test other alternatives to solve the interaction parameter dependence on the probe.[23] In this paper, both polymer mixtures will allow us to test the ability of Sanchez's method to obtain a true polymer–polymer interaction parameter.

## Theoretical Background

The simpliest model for describing polymer mixtures is the Flory–Huggins theory.[24] This theory assumes that the only entropic contribution is the combinatorial entropy, the enthalpic term being summarized in a van Laar type parameter. Consequently, the free energy of mixing of two polymers denoted as 2 and 3 (in IGC papers subindex 1 is reserved for the probe) is given by

$$\Delta g_{\mathrm{mix}} = RT\left(\frac{\phi_2 \ln \phi_2}{V_2} + \frac{\phi_3 \ln \phi_3}{V_3}\right) + B\phi_2\phi_3 \qquad (1)$$

where $\phi_i$ and $V_i$ are the volume fraction and molar volume of component $i$, respectively, and $\Delta g_{\mathrm{mix}}$ and $B$ are expressed in cal cm$^{-3}$. From eq 1 the spinodal condition can be determined,

$$\frac{\mathrm{d}^2\Delta g}{\mathrm{d}\phi_2{}^2} = RT\left(\frac{1}{\phi_2 V_2} + \frac{1}{\phi_3 V_3}\right) - 2B_{\mathrm{sc}} \qquad (2)$$

$B_{sc}$ being the interaction energy density at the spinodal condition. As has been mentionated by Sanchez,[16] $B$ and $B_{sc}$ are only equal if the former is independent of the composition. Equation 2 provides an expression for $B_{sc}$,

$$B_{\mathrm{sc}} = -\frac{1}{2}\frac{\mathrm{d}^2\Delta g_{\mathrm{nc}}}{\mathrm{d}\phi_2{}^2} \qquad (3)$$

where $\Delta g_{nc}$ is the noncombinatorial free energy.

However, equation-of-state theories, such as the lattice fluid theory of Sanchez and Lacombe,[25-27] are more useful for polymer mixtures than the Flory–Huggins theory. The latter ignores the fact that the polymeric mixtures are compressible, a fact which is responsible for the LCST behavior of many polymer blends and solutions. In this sense, theories which employ the free volume concept are able to predict such a boundary phase. The equation of state of a system according to the lattice fluid theory has the following form:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \qquad (4)$$

where the reduced properties are defined as $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$ and $\tilde{\rho} = v^*/v$ and $r$ is a dimensionless size parameter proportional to the molecular weight,

$$r_i = \frac{M_i P_i^*}{RT_i^* \rho_i^*} = \frac{M_i}{\rho_i^* v_i^*} \qquad (5)$$

For any polymer, the characteristic parameters, $P^*$, $T^*$, and $\rho^*$ (or $v^*$), can be obtained from its density, thermal expansion coefficient, and isothermal compressibility. In all the statistical theories, some mixing rules are required for describing the mixtures. We will assume the ones outlined by Sanchez.[28] For instance, each pure component has its own mer volume $v_i^*$ but in the mixture all the mers require the same average volume $v^*$. Thus, a molecule $i$ that will occupy $r_i^{\mathrm{o}}$ sites, defined by eq 5, has a volume of $r_i^{\mathrm{o}}v_i^*$ in the pure close-packed state, but it will need $r_i$ sites in the mixture, so, $r_i^{\mathrm{o}}v_i^* = r_i v^*$. The rest of the mixing rules are compiled in the following expressions:

$$\phi_2 = \frac{\dfrac{w_2}{\rho_2^*}}{\dfrac{w_2}{\rho_2^*} + \dfrac{w_3}{\rho_3^*}} \qquad \frac{1}{\rho^*} = \frac{w_2}{\rho_2^*} + \frac{w_3}{\rho_3^*}$$

$$\frac{1}{v^*} = \frac{\phi_2}{v_2^*} + \frac{\phi_3}{v_3^*} \qquad P^* = \phi_2 P_2^* + \phi_3 P_3^* - \phi_2\phi_3\Delta P^* \qquad (6)$$

$$\nu = \frac{v_2^*}{v_3^*} \qquad \frac{1}{\tilde{T}} = \frac{\dfrac{\phi_2}{\tilde{T}_2} + \dfrac{\nu\phi_3}{\tilde{T}_3}}{\phi_2 + \nu\phi_3} - \frac{\phi_2\phi_3\Delta P^* v^*}{RT}$$

where $w_i$ is the weight fraction of component $i$ and $\Delta P^*$ is defined as the binary characteristic interaction energy density. Both enthalpic and entropic contributions to the free energy can be derived from the lattice fluid theory along with the mixing rules, as shown by Kim and Paul.[17] Consequently, the enthalpic contribution to $B$ can be also derived as

$$B_h = \tilde{\rho}\Delta P^* + \left[\frac{P_2^*}{\phi_3}(\tilde{\rho}_2 - \tilde{\rho}) + \frac{P_3^*}{\phi_2}(\tilde{\rho}_3 - \tilde{\rho})\right] + \frac{P}{\phi_2\,\phi_3}(\tilde{v} - \phi_2\tilde{v}_2 - \phi_3\tilde{v}_3) \qquad (7)$$

and, similarly, the entropic contribution

$$-TB_s = \frac{RT}{\phi_2\phi_3}\left\{\frac{1}{v^*}\left[\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r}\right] - \frac{\phi_2}{v_2^*}\left[\frac{1-\tilde{\rho}_2}{\tilde{\rho}_2}\ln(1-\tilde{\rho}_2) + \frac{\ln\tilde{\rho}_2}{r_2^{\mathrm{o}}}\right] - \frac{\phi_3}{v_3^*}\left[\frac{1-\tilde{\rho}_3}{\tilde{\rho}_3}\ln(1-\tilde{\rho}_3) + \frac{\ln\tilde{\rho}_3}{r_3^{\mathrm{o}}}\right]\right\} \qquad (8)$$

The interaction energy density $B^{(T)} = B_h - TB_s$ and, finally, the spinodal condition for a compressible blend allow us to derive the interaction energy density related to the second derivative of the free energy,

$$B_{\mathrm{sc}} = \tilde{\rho}\Delta P^* + \left\{P_3^* - P_2^* + (\phi_3 - \phi_2)\Delta P^* + \frac{RT}{\tilde{\rho}}\left[\frac{1}{r_2^{\mathrm{o}}v_2^*} - \frac{1}{r_3^{\mathrm{o}}v_3^*}\right] - RT\left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right]\left[\frac{1}{v_2^*} - \frac{1}{v_3^*}\right]\right\}^2 \Big/ \left\{\frac{2RT}{v^*}\left[\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1-1/r}{\tilde{\rho}^2}\right]\right\} \qquad (9)$$

In eqs 7−9 the only unknown parameter is $\Delta P^*$, which has been calculated in different papers of Paul et al. from experimental spinodal curves.[17−22] The characteristic interaction energy density $\Delta P^*$ can be expressed in terms of the bare interaction parameter,

$$\Delta P^* = RT\chi_{23}^{\mathrm{S}} \qquad (10)$$

This interaction parameter is also available from IGC experiments according to the data analysis method proposed by Sanchez.[16] With Henry's law constant defined as

$$H = w_i/\mathrm{P} \qquad (11)$$

$H$ can be calculated from the specific retention volume ($V_g^{\mathrm{o}}$), which is the measured value by IGC, as

$$H = \frac{V_g^{\mathrm{o}}M_1}{273.16R} \qquad (12)$$

Using the LF theory, the Henry's law constant for a gas (probe)−homopolymer system is given by

$$H = \left(\frac{M_1}{RT\rho_2}\right)\exp\left\{\tilde{\rho}_2(M_1/\rho_1^*)\left(\frac{P_1^*}{RT} - \chi_{12}^{\mathrm{S}}\right) - r_1\left[1 + \left(\frac{1-\tilde{\rho}_2}{\tilde{\rho}_2}\right)\ln(1-\tilde{\rho}_2)\right]\right\} \qquad (13)$$

$\chi_{12}^{\mathrm{S}}$ being the binary polymer−probe "bare" interaction parameter. For a polymer−polymer blend the corresponding Henry's law constant, in the same IGC experimental conditions and for high molecular weight polymers, is given by

$$H = \left(\frac{M_1}{RT\rho}\right)\exp\left\{\tilde{\rho}(M_1/\rho_1^*)\left(\frac{P_1^*}{RT} - (\phi_2\chi_{12}^{\mathrm{S}} + \phi_3\chi_{13}^{\mathrm{S}} - \phi_2\phi_3\chi_{23}^{\mathrm{S}})\right) - r_1\left(1 + \left(\frac{1-\tilde{\rho}}{\tilde{\rho}}\right)\ln(1-\tilde{\rho})\right)\right\} \qquad (14)$$

where $\rho$ and $\tilde{\rho}$ are the density and the reduced density of the polymer blend. Assuming that the polymer components of the blend have large molecular weights, the equation of state, given by eq 4, becomes

$$\tilde{\rho} = 1 - \exp\left(-\frac{\rho^2T^*}{T} - \tilde{\rho}\right) \qquad (15)$$

$T^*$ is the characteristic temperature of the blend which, using eqs 6 and 10, can be written as

$$T^* = \frac{\phi_2P_2^* + \phi_3P_3^* - \phi_2\phi_3RT\chi_{23}^{\mathrm{S}}}{\phi_2P_2^*/T_2^* + \phi_3P_3^*/T_3^*} \qquad (16)$$

Equation 15 can be solved by iteration, but it has to be noticed that, through eqs 15 and 16, $\tilde{\rho}$ is a function of $\chi_{23}^{\mathrm{S}}$. Consequently, both $\chi_{23}^{\mathrm{S}}$ and $\tilde{\rho}$ must be calculated by an iteration method. The polymer−polymer interaction parameter so calculated is also "bare", all the contributions of free volume having been removed. Moreover, it should be independent of composition and probe nature.

## Experimental Section

**Materials.** Poly(epichlorohydrin) (PECH) and poly(methyl acrylate) (PMA) were supplied by Aldrich and used without further purification. PECH average molecular weights were $M_n$ = 170 000 and $M_w$ = 976 000, and the glass transition temperature was $T_g$ = −23.6 °C, the values for PMA being 27 700, 44 000, and 22.5 °C, respectively. Molecular weights were measured in THF at 25 °C by GPC and polystyrene standards. Values for PH and PVME have been previously given.[29]

**IGC Procedures.** Chromatographic measurements were carried out in a modified Sigma 300 Perkin-Elmer chromatograph equipped with a flame ionization detector. For the study of the PECH/PMA blend, six chromatographic columns were prepared from THF solutions in the usual manner. Chromosorb W-AW (80−100 mesh) was used as support and the column characteristics are shown in Table 1. Nitrogen and methane were used as the carrier gas and marker, respectively. Retention times were determined by using a CROM+ card and the adequate software in an Olivetti M24 microcomputer. Probes and a small amount of the marker were injected into columns with the aid of a 10 μL Hamilton syringe. At least three injections were made for each probe, column, and temperature and, in cases where the retention time depended on the injected volume, extrapolations to zero height were made. Nineteen probes of different chemical natures and polarities were chosen. The required probe values for the data analysis have been taken from the usual compilations.[30,31]

**Data Corrections.** Some explanations about data corrections are required. As can be seen in Table 1, column 6 has been filled with unloaded support. Card et al.[32] have demonstrated that unloaded support can interact with the probe, giving an extra contribution to the measured retention time. Results obtained with this colunn 6 allow us to correct experimental retention times.

Nearly all the probes were retained, but while alkanes and toluene had Gaussian elution peaks, other probes such as THF, dioxane, 2-butanone, ethyl acetate, *n*-propanol, and acetonitrile showed asymmetric elution peaks with a large tail, a characteristic of Langmuir isotherms. This shape reflects surface adsorption processes due to the presence of a small number of strong polar sites in the support.[33] However, the support retention disappeared above 76 °C for all the probes except acetonitrile in which we needed temperatures above 85 °C. The largest correction in specific retention volume (3%) was obtained for alkanes at low temperatures, being less than 1% for the rest of the probes.

On other hand, El-Hibri and Munk[34] have pointed out that the retention time of the marker (usually methane) also makes a contribution to the specific retention volume due to its interaction with the stationary phase. It must be remembered that the role of the marker is to determine the time the probe needs to go through the column, without any interaction. They proposed a method to correct this retention volume which has been applied in our work. However, results obtained with the five columns showed that the marker specific retention volume, $V_g^{\mathrm{o(M)}}$, calculated by such a method, had an erratic variation with temperature and composition. If methane had the same behavior as the rest of the probes, $V_g^{\mathrm{o(M)}}$ must decrease with increasing temperature. The observed behavior for methane could be due to difficulties in measuring such a small value of

**Table 1. Chromatographic Column Characteristics for the PECH/PMA System**

| column | amt of PECH (g) | amt of PMA (g) | amt of support (g) |
|---|---|---|---|
| PECH | 0.460 | | 4.338 |
| PMA | | 0.493 | 4.435 |
| PECH/PMA 80:20 | 0.418 | 0.103 | 5.218 |
| PECH/PMA 50:50 | 0.250 | 0.245 | 4.541 |
| PECH/PMA 75:25 | 0.124 | 0.373 | 4.476 |
| support | | | 4.991 |

$V_g^{o(M)}$. In fact, the absolute values of $V_g^{o(M)}$ are within the assumed experimental error for the specific retention volume measurements. In our opinion, the marker correction is negligible, at least for our polymers in the studied temperature range.[35]

When the IGC method is applied to polymer blends, it is usual to calculate polymer–polymer interaction parameters by a phenomenological expression given by Al-Saigh and Munk.[10] We will rather employ a modification of the original expression in terms of interaction energy densities, which allow us to calculate the polymer–polymer interaction energy density,

$$B_{23} = RT\frac{\ln\dfrac{V^o_{gb}}{w_2 v_{sp,2} + w_3 v_{sp,3}} - \phi_2 \ln\dfrac{V^o_{g_2}}{v_{sp,2}} - \phi_3 \ln\dfrac{V^o_{g_3}}{v_{sp,3}}}{\phi_2\phi_3 V_1} \tag{17}$$

using only polymer specific volumes ($v_{spi}$) and experimental specific retention volumes ($V^o_{gi}$). Subindexes 2 and 3 refer to homopolymers, and b refers to the polymer blend. $V_1$ is the molar volume of the probe, which is taken as a reference volume. $w_i$ refers to the weight fraction of the $i$ component in the blend.

This equation requires that all the measurements have been carried out under the same conditions. Given the technical problems in the experimental control of the chromatographic oven temperature, specially at low temperatures, experimental measurements are not carried out at identical conditions of temperature. Consequently, assumptions made in eq 17 are not exactly fulfilled. In order to solve this problem, a linear regression analysis of $\ln[V^o_{g(exp)}]$ versus $1/T$ can be used. Linear regression coefficients are excellent for all the probes (above 0.99 except for acetonitrile, which was 0.98). The linear regression parameters permit calculations of specific retention volumes at the desired temperature.

Chromatographic data of PH, PVME, and a 60:40 blend were taken from previous papers of our group.[23,29]

***PVT* Procedures.** Pressure–volume–temperature (*PVT*) measurements were carried out in a GÖTTFERT Rheograph 2002 rheomether with an appropriate *PVT* accessory. The polymeric material was loaded in a small quantity and manually pressurized until the nozzle was filled (approximately 9–10 g), the exact weight being determined after extruding the nozzle when the measurements were finished. Volume measurements were performed in the 100–2000 bars pressure range and the 60–125 °C temperature range.

## Results and Discussion

***PVT* Section.** In order to apply the lattice fluid formalism the equation-of-state characteristic parameters for all the probes and polymers have to be known. Data for most of the used probes were available in the literature.[25] When it was not the case, they were calculated by using the method proposed by Sanchez and Lacombe,[28] taking the necessary values from the usual compilations.[30,31] In the case of polymers, these parameters can be calculated if we know their thermal expansion, isothermal compressibility, and thermal pressure coefficients (α, β, and γ, respectively) and with the aid of Table II in ref 27. The PH and PVME physical properties have been previously reported.[29]

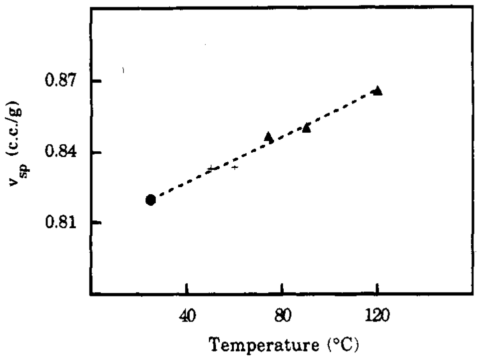

**Figure 1.** Dependence of the PMA specific volume on the temperature: (●) from Aldrich Chemical Co.; (+) *PVT*; (▲) dilatometer.

**Table 2. Temperature Dependence of the Specific Volume and Thermal Expansion, Isothermal Compressibility, and Thermal Pressure Coefficients for PECH and PMA Homopolymers**

| | | |
|---|---|---|
| PECH | $v_{sp} = 0.731 + 3.72 \times 10^{-4}T$ | $v_{sp}$ in cm$^3$/g, $T$ in °C |
| | $\alpha = 3.67 \times 10^{-4} + 1.87 \times 10^{-7}T$ | α in K$^{-1}$, $T$ in K |
| | $\gamma = 0.747 - 1.43 \times 10^{-3}T$ | γ in cal/(cm$^3$ K), $T$ in K |
| | $\beta = 2.39 \times 10^{-3} - 4.35 \times 10^{-7}T$ | β in bar/K, $T$ in K |
| PMA | $v_{sp} = 0.803 + 5.28 \times 10^{-4}T$ | $v_{sp}$ in cm$^3$/g, $T$ in °C |
| | $\alpha = 4.052 \times 10^{-4} + 2.38 \times 10^{-7}T$ | α in K$^{-1}$, $T$ in K |
| | $\gamma = 0.96 - 1.99 \times 10^{-3}T$ | γ in cal/(cm$^3$ K), $T$ in K |
| | $\beta = 1.456 \times 10^{-3} - 3.17 \times 10^{-7}T$ | β in bar/K, $T$ in K |

*PVT* experiments for PECH and PMA have been carried out by following previous works on this methodology.[36,37]

Measurements were carried out isothermally, the volume occupied by a known weight of the pure polymer at different pressures being determined. The extrapolation to atmospheric pressure ($P \to 0$) permits one to calculate the specific volume or the density at every temperature for these pressure conditions. In order to characterize the PMA density–temperature dependence and due to the small number of data, we have completed our experimental data with dilatometric determinations. Furthermore, data from literature[38] at room temperature have also been used, as can be seen in Figure 1.

From this density–temperature dependence we can calculate thermal expansion coefficients using the equation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{18}$$

The isothermal compressibility coefficient at every temperature can be obtained from *PVT* measurements, in a similar way. Finally, the thermal pressure coefficient is given by

$$\gamma = \frac{\partial P}{\partial T} = \frac{\partial P}{\partial V}\frac{\partial V}{\partial T} = \frac{1}{\beta}\alpha \tag{19}$$

The temperature dependence of these quantities is shown in Table 2. To test the accuracy of these relationships, we have compared the density and the thermal expansion coefficient of PECH calculated at 25 °C with data at this temperature reported in the literature.[39] The results are in good agreement, with an error in ρ less than 1.5% and 5% for α. Deviations might be due to the small experimental number of data used to obtain the relationships.

Equation-of-state parameters for the polymers used in this work have been reported by Rodgers.[40] Table 3 shows the comparison of these parameters and those calculated from data summarized in Table 2. Similar

**Table 3. LF Equation-of-State Parameters for Polymers and Probes Used along This Work**

| | $\rho^*$ (g/cm$^3$) | $P^*$ (cal/cm$^3$) | $T^*$ (K) |
|---|---|---|---|
| PECH[a] | 1.382 | 91.5 | 809 |
| PECH[b] | 1.435 | 105.1 | 679 |
| PMA[a] | 1.251 | 116.2 | 713 |
| PMA[b] | 1.263 | 122.9 | 604 |
| PH[a] | 1.215 | 152.4 | 761 |
| PH[b] | 1.224 | 139.7 | 740 |
| PVME[a] | 1.089 | 75.4 | 697 |
| PVME[b] | 1.085 | 101.7 | 650 |
| *n*-heptane[c] | 0.800 | 73.8 | 487 |
| *n*-octane[c] | 0.815 | 73.6 | 502 |
| *n*-nonane[c] | 0.828 | 73.4 | 517 |
| *n*-decane[c] | 0.837 | 72.6 | 530 |
| THF[d] | 1.030 | 108.9 | 532 |
| dioxane[d] | 1.204 | 138.9 | 500 |
| 2-butanone[c] | 0.913 | 106.8 | 513 |
| ethyl acetate[c] | 1.052 | 109.4 | 468 |
| *n*-propanol[c] | 0.972 | 211.8 | 420 |
| *tert*-butanol[c] | 0.952 | 165.6 | 448 |
| benzene[c] | 0.994 | 106.0 | 523 |
| toluene[c] | 0.966 | 96.1 | 543 |
| chloroform[c] | 1.688 | 109.0 | 512 |
| 1,2-dichloroethane[d] | 1.422 | 120.5 | 541 |
| acetonitrile[d] | 0.822 | 91.9 | 368 |
| DEGDEE[d] | 0.947 | 94.6 | 486 |
| DMF[d] | 1.009 | 145.2 | 609 |
| *n*-tetradecane[c] | 0.864 | 70.7 | 570 |
| chlorobenzene[c] | 1.206 | 104.4 | 585 |

[a] Used in this work. Calculated from Table 2 and ref 29. [b] From ref 40. [c] From ref 25. [d] Calculated by the method proposed in ref 28.

**Table 4. Interaction Energy Densities, $B_{23}$ in cal/cm$^3$, by Eq 17 for the PECH/PMA System at 70 °C**

| | PECH/PMA (w/w) | | |
|---|---|---|---|
| probe | 80:20 | 50:50 | 25:75 |
| *n*-heptane | 2.06 | 1.76 | 1.70 |
| *n*-octane | 1.77 | 1.37 | 1.30 |
| *n*-nonane | 1.47 | 0.96 | 1.02 |
| *n*-decane | 1.80 | 0.83 | 0.77 |
| THF | 0.59 | 0.76 | 0.04 |
| dioxane | 0.48 | −0.55 | −0.63 |
| 2-Butanone | 0.21 | 0.26 | −0.38 |
| ethyl acetate | 0.12 | 0.00 | −0.16 |
| *n*-propanol | 0.39 | 1.00 | 1.33 |
| *tert*-butanol | 1.86 | 1.66 | 2.76 |
| benzene | 0.15 | 0.11 | 0.37 |
| toluene | 0.57 | 0.17 | 0.41 |
| chloroform | 1.47 | 0.57 | 1.05 |
| 1,2-dichloroethane | −0.33 | −0.55 | −0.75 |
| acetonitrile | −2.56 | −1.05 | −2.61 |
| av of $B_{23}$ | 0.67 | 0.49 | 0.39 |
| std dev | 1.14 | 0.80 | 1.19 |

data for PH and PVME were previously reported.[29] Parameters for PECH and PMA were calculated at 95 °C, and those for PH and PVME at 148.6 °C. Table 3 also contains the characteristic parameters of the probes. Although differences between the polymer data could be a consequence of our scanty experimental measurements, it is also true that different values of characteristic equation-of-state parameters can be obtained from data series at different temperatures, in spite of the fact that, according to the theory, they must be identical. The possible influence of the chosen data set in Sanchez's data analysis results will be discussed below.

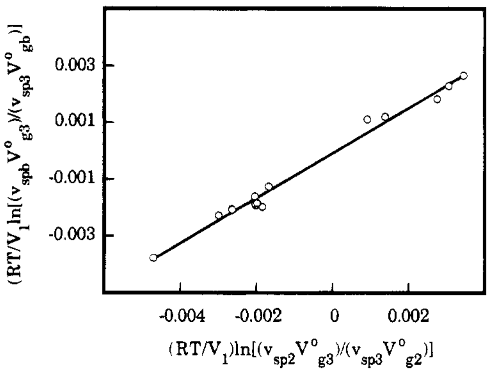

**Figure 2.** Farooque–Deshpande plot for an 80:20 PECH/PMA blend at 95 °C.

**Table 5. Interaction Energy Densities, $B_{23}$ in cal/cm$^3$, at Different Temperatures for PECH/PMA Blends, Determined According to the Farooque and Deshpande Data Analysis[15]**

| temp (°C) | PECH/PMA 80:20 | PECH/PMA 50:50 | PECH/PMA 25:75 |
|---|---|---|---|
| 60 | 0.755 | 0.606 | 0.748 |
| 65 | 0.701 | 0.550 | 0.648 |
| 70 | 0.647 | 0.493 | 0.549 |
| 76 | 0.583 | 0.428 | 0.437 |
| 85 | 0.491 | 0.331 | 0.276 |
| 95 | 0.392 | 0.224 | 0.112 |
| 105 | 0.339 | 0.146 | −0.008 |
| 115 | 0.096 | 0.047 | −0.186 |
| 125 | −0.135 | −0.086 | −0.305 |

**IGC Section.** The results of $B_{23}$ calculated from eq 17 for the three studied compositions of PECH/PMA blend are summarized in Table 4 at 70 °C as an example. Results at other temperatures have similar behaviors. At first sight it can be observed that $B_{23}$ values strongly depend on the probe. As previously mentioned in the Introduction of this work, different reasons have been given to justify this behavior. It is clear that the variation of $B_{23}$ from probe to probe is very unsatisfactory and should be reduced in order to optimize IGC experimental determinations of polymer–polymer miscibility.

An alternative method of data analysis is that proposed by Farooque and Deshpande and previously used by our group.[23,41,42] Writing eq 17 in the form

$$\frac{(RT)}{(V_1)}\ln\left[\frac{(w_2 v_{\mathrm{sp},2} + w_3 v_{\mathrm{sp},3})V^{\circ}_{\mathrm{g}3}}{v_{\mathrm{sp},3}V^{\circ}_{\mathrm{gb}}}\right] = \phi_2\left(\frac{RT}{V_1}\right)\ln\left[\frac{v_{\mathrm{sp},2}V^{\circ}_{\mathrm{g}3}}{v_{\mathrm{sp},3}V^{\circ}_{\mathrm{g}2}}\right] - B_{23}\phi_2\phi_3 \quad (20)$$

a plot of the left-hand term of the equation against the term which multiplies $\phi_2$ in the other side allows us to calculate the interaction energy density from the intercept. Although good plots are usually obtained (see Figure 2), we have previously noticed that this good linearity must be taken with caution when the interaction energy density is calculated.[23,35] In fact, a large confidence interval is obtained for $B_{23}$ after an adequate analysis, probably as a consequence of the small contribution of the term containing $B_{23}$ to the equation which magnifies possible experimental errors. Results obtained by this method for the three investigated compositions along the investigated temperature range are summarized in Table 5. We have previously reported[41] that our data and those reported by Al-Saigh and Munk[10] can be successfully fitted by eq 20. Moreover, the $B_{23}$ value so obtained is in good agreement with that determined by Munk et al.[43] using an alternative IGC data treatment.

Sanchez's method[16] is another proposed way to remove such probe dependence. After his formalism was

**Table 6. Characteristic Interaction Energy Densities, $\Delta P^*$ in cal/cm$^3$, and Polymer–Polymer System Reduced Densities, $\tilde{\rho}$, Calculated by Sanchez's Method for the Three PECH/PMA Blend Compositions, in Weight Fraction, at 70 °C**

| | 80:20 | | 50:50 | | 25:75 | |
|---|---|---|---|---|---|---|
| probe | $\Delta P^*$ | $\tilde{\rho}$ | $\Delta P^*$ | $\tilde{\rho}$ | $\Delta P^*$ | $\tilde{\rho}$ |
| *n*-heptane | 2.40 | 0.9523 | 2.06 | 0.9498 | 1.99 | 0.9482 |
| *n*-octane | 2.13 | 0.9524 | 1.66 | 0.9500 | 1.57 | 0.9483 |
| *n*-nonane | 1.76 | 0.9525 | 1.16 | 0.9502 | 1.23 | 0.9484 |
| *n*-decane | 2.14 | 0.9524 | 1.00 | 0.9502 | 0.93 | 0.9485 |
| THF | 0.37 | 0.9527 | 0.93 | 0.9503 | 0.10 | 0.9487 |
| dioxane | 0.57 | 0.9528 | −0.59 | 0.9508 | −0.67 | 0.9489 |
| 2-butanone | 0.27 | 0.9529 | 0.33 | 0.8505 | −0.36 | 0.9489 |
| ethyl acetate | 0.17 | 0.9529 | 0.04 | 0.9506 | −0.15 | 0.9488 |
| *n*-propanol | 0.39 | 0.9528 | 1.02 | 0.9502 | 1.37 | 0.9484 |
| *tert*-butanol | 2.51 | 0.9523 | 2.25 | 0.9548 | 3.72 | 0.9477 |
| benzene | 0.23 | 0.9529 | 0.18 | 0.9505 | 0.51 | 0.9486 |
| toluene | 0.68 | 0.9527 | 0.23 | 0.9505 | 0.51 | 0.9486 |
| chloroform | 1.73 | 0.9525 | 0.71 | 0.9503 | 1.27 | 0.9484 |
| 1,2-dichloroethane | −0.33 | 0.9530 | −0.57 | 0.9508 | −0.79 | 0.9490 |
| acetonitrile | −2.69 | 0.9536 | −1.05 | 0.9510 | −2.73 | 0.9494 |
| av of $\Delta P^*$ | 0.85 | | 0.62 | | 0.57 | |
| std dev | 1.30 | | 0.93 | | 1.43 | |

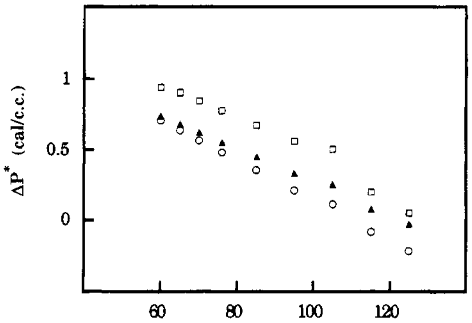

**Figure 3.** Dependence of $\Delta P^*$ on temperature for the three studied compositions of the PECH/PMA system (w/w): (□) 80:20; (▲) 50:50; (○) 25:75.

applied to PECH/PMA data, bare interaction parameters were calculated and from them (see eq 10), characteristic interaction energy densities, $\Delta P^*$, which are presented in Table 6. From this table it is clear that, in general, Sanchez's procedure has not been able to provide a unique or probe independent $\Delta P^*$. A slight improvement is found for alcohols, which have been traditionally recognized in IGC as inadequate probes due to their strong self-association character.[43,44] The values of $\Delta P^*$ are subject to an error bar similar to that of $B_{23}$ values, but given its higher absolute values, they have deviations of about 150%, whereas in the case of $B_{23}$, a similar error bar supposes a 200% deviation. Figure 3 shows that $\Delta P^*$ averaged over all the investigated probes has a tendency to more negative values when temperature increases, irrespective of the considered composition. This behavior is a general rule for all the probes.

The temperature dependence of the averaged $\Delta P^*$ value was an unexpected result. As previously mentioned $\Delta P^*$ does not contain any free volume contribution. In this sense, Sanchez's definition for $\Delta P^*$ is analogous to the exchange interaction parameter, $X_{ij}$, defined in the Flory–Patterson theory and according to the Patterson analysis for blends containing specific interactions the purely interactional term in $\Delta P^*$ should increase when temperature increases.[5] Moreover, it should be mentioned that experimental results of $B_{23}$ obtained using the Farooque and Deshpande data analysis[15] have similar trends, as we show later.

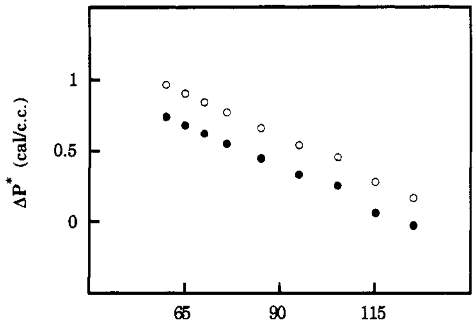

**Figure 4.** Influence of the equation-of-state parameters on the determined $\Delta P^*$ for the PECH/PMA 50:50 w/w blend: (○) taken from Rodgers;[40] (●) calculated from Table 2.

Another interesting result refers to the fact that $\tilde{\rho}$, the mixture reduced density, decreases when $\Delta P^*$ increases. This is in good agreement with the expected behavior because higher values of $\Delta P^*$ imply more unfavorable interactions, the free volume increasing as a way to minimize the unfavorable interactions.

In the *PVT* section two data series of equation-of-state parameters for the four polymers here employed have been compared. Although their absolute values are quite different, the results of Sanchez's data analysis method for both data series are similar not only in absolute value but also in the temperature dependence, as can be seen in Figure 4 for the PECH/PMA 50:50 blend. We have decided to employ the equation-of-state parameters determined in this work due to the fact that the expressions in Table 2 have been employed in a previous paper[41] where a different IGC data treatment[15] was used. This earlier data analysis will be compared later with that here considered.

Experimental data of $\Delta P^*$ and $\tilde{\rho}$ for the different probes at different temperatures and blend compositions, obtained using Sanchez's IGC data analysis, have been used to calculate various thermodynamic functions of the blend. The entropic and enthalpic terms of the free energy of mixing, the interaction energy density associated with the spinodal condition, $B_{sc}$, and finally, $B^{(T)}$, as the sum of $-TB_s$ and $B_h$ terms, can be calculated according to eqs 7–9. This type of analysis is different from that recently used by Paul et al. in a series of papers.[17–22] They calculated the evolution of $B$ with temperature using a constant value for $\Delta P^*$ obtained from experimental spinodal curves. In this work, however, $\Delta P^*$ values have been determined by IGC experiments over a wide temperature range.

Averaged $\Delta P^*$ and $\tilde{\rho}$ data for every temperature have been used to calculate the four interaction energy density terms cited above. Before turning to the results, a comment about the reduced density calculation procedure is pertinent. Characteristic parameters of pure polymers and their reduced densities ($\tilde{\rho}_i$) are available from the corresponding density–temperature relationships (Tables 2 and 3). However, the reduced density of the mixture ($\tilde{\rho}$) depends on the actual interactions in the blend, as can be seen through eqs 14–16.

Given that any slight difference in $\tilde{\rho}$ could imply a large variation on $B_s$, $B_h$, and $B_{sc}$. For instance, a $\Delta\rho$ of 0.0002 g/cm$^3$ supposes, in some cases, variations of the order of 0.1–0.3 cal/cm$^3$ in the $B$ terms. In order to simplify our calculations, reduced densities for both the pure polymers and the mixture have been cal-

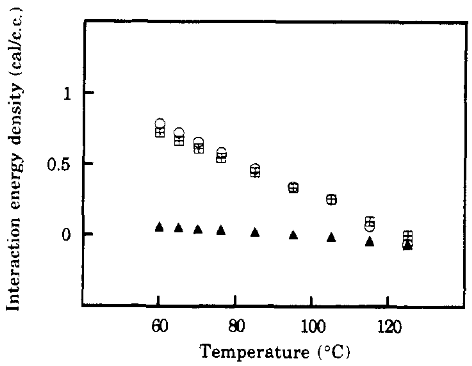

**Figure 5.** Temperature dependence of different interaction energy terms in PECH/PMA 50:50 blends: (▲) $-TB_s$; (○) $B_h$; (□) $B^{(T)}$; (+) $B_{sc}$.

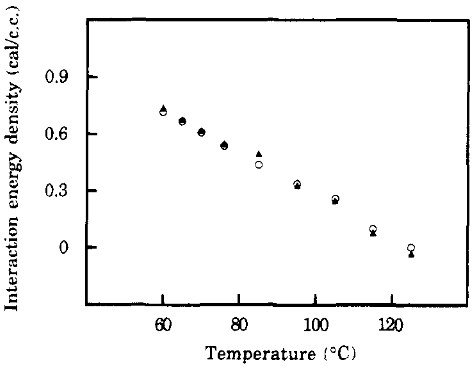

**Figure 6.** Dependence of $B_{23}$, eq 20, and $B^{(T)}$ on temperature for the PECH/PMA 50:50 w/w blend: (▲) $B_{23}$, eq 20; (○) $B^{(T)}$.

culated by the same procedure. The reduced temperature was first calculated from the corresponding characteristic temperature and, after that, reduced densities were calculated using a corresponding-state relationship between $\tilde{\rho}$ and $\tilde{T}$ (see Table II in ref 27).

Figure 5 shows the evolution of $B_h$, $B_s$, $B^{(T)}$, and $B_{sc}$ with temperature. The strong variation of $B_h$ toward more negative values when $T$ increases cannot be easily explained in a blend in which specific interactions are postulated as the origin of the blend stability. Furthermore, the value of $B_h$ at 80 °C is in disagreement with the heat of mixing determined by a group contribution method.[45] In terms of eq 7 this behavior is a consequence of the variation of $\Delta P^*$ with temperature (Figure 3) since free volume effects in the enthalpic term (second and third term in eq 7) cannot balance the contribution of $\Delta P^*$ to $B_h$.

On the other hand, since both pure polymer reduced densities are similar in the investigated temperature range, temperature does not have a great influence on $B_s$ and its absolute value is near to zero. Although it could be expected after examination of both $B_s$ and $B_h$, the evolution of $B^{(T)}$ and $B_{sc}$ with temperature is not consistent with the experimentally observed LCST behavior of the PECH/PMA blend.[46]

When $B^{(T)}$ and $B_{23}$, determined by eq 20, are compared (see Figure 6), both have a clear tendency to negative values with increasing temperature. The observed trend is also similar to those obtained with other possible methods of data analysis.[35] This behavior is not consistent, as previously mentioned, with the reported LCST type phase diagram,[46] although the phase separation temperature is far above the experimental temperature range and the $B^{(T)}-T$ curve might change toward positive values at higher temperatures. It could be concluded that the observed behavior is a consequence of the IGC experimental data, although no reason has been found to question the validity of the measurements. In any case, values obtained from the LF data analysis are very similar to those obtained from the simple phenomenological analysis of Farooque and Deshpande. Our results reveal that Sanchez's method could be considered as an adequate IGC data treatment in order to obtain a unique interaction energy. They also confirm that the Farooque–Deshpande method is a simple and quick method to get interaction parameters without requiring a large number of parameters of the pure components, as was found in previous comparisons[23,41,42] of this method with other data analysis methods.[9,43]

**Table 7. Interaction Energy Densities, in cal/cm$^3$, Calculated by Eq 17, $B_{23}$, and Sanchez's Method, $\Delta P^*$, for PH/PVME, 60:40 in Weight Fraction, and Polymer–Polymer System Reduced Density, $\tilde{\rho}$, at 148.6 °C**

| probe | $B_{23}$ | $\Delta P^*$ | $\tilde{\rho}$ |
|---|---|---|---|
| DEGDEE | −3.13 | −0.79 | 0.9038 |
| DMF | −2.49 | −1.27 | 0.9040 |
| ethyl acetate | −1.26 | −1.91 | 0.9043 |
| 2-butanone | −2.65 | −1.95 | 0.9043 |
| benzene | −1.00 | 0.28 | 0.9033 |
| *n*-decane | −0.11 | 0.79 | 0.9031 |
| *n*-propanol | 0.28 | 0.68 | 0.9031 |
| toluene | −0.80 | 0.10 | 0.9034 |
| *n*-tetradecane | −0.40 | 0.08 | 0.9034 |
| 1,2-dichloroethane | −0.42 | −0.07 | 0.9035 |
| dioxane | −0.62 | −2.72 | 0.9047 |
| chlorobenzene | −4.54 | 0.29 | 0.9033 |
| acetonitrile | −0.19 | −3.79 | 0.9052 |
| av | −1.33 | −0.79 | |
| std dev | 1.37 | 1.37 | |

To clarify if the $\Delta P^*-T$ trend observed in the PECH/PMA system is a general rule in applying Sanchez's method, previous data of a PH/PVME blend have been reanalyzed.[23] For this blend, IGC data analysis according to the Prolongo et al.[9] or Farooque and Deshpande[15] methods have shown that $B_{23}$ has a parabolic variation going to positive values in a temperature range close to the reported phase separation temperature.[29] Moreover, measurements of FTIR spectroscopy have shown the weakening of the interactions when temperature is increased.[23]

With 148.6 °C as the reference temperature, as was the case in our previous work,[23] Table 7 presents the $B_{23}$ and $\Delta P^*$ results for PH/PVME at that temperature. At first sight, data are not good: both $B_{23}$ and $\Delta P^*$ have a great variation from probe to probe reflected in their standard deviations. Data of $\tilde{\rho}$, however, are in good agreement with the level of interactions in the mixture, as was the case of the PECH/PMA blend.

After the determination of $\Delta P^*$ at several temperatures, the LF theory has been applied in a way similar to that explained in the PECH/PMA data analysis. Figure 7 shows the variation of $\Delta P^*$ and $B^{(T)}$ with temperature. From this figure it is also clear that the $B^{(T)}$ value is clearly dominated by the $\Delta P^*$ behavior. In fact, both parameters have similar absolute values, showing that the free volume terms do not have a significant weight in the $B^{(T)}$ values of the PH/PVME blend. The $B^{(T)}$ behavior at low temperatures is also similar to that found in PECH/PMA: $B^{(T)}$ decreases strongly with temperature. But, at temperatures equal or superior to 160 °C the variation of $B^{(T)}$ is less clear. Besides its large error bar, it seems that $B^{(T)}$ shows a tendency to a constant value around to 0 cal/cm$^3$ in good agreement with the phase separation of this system.[29]

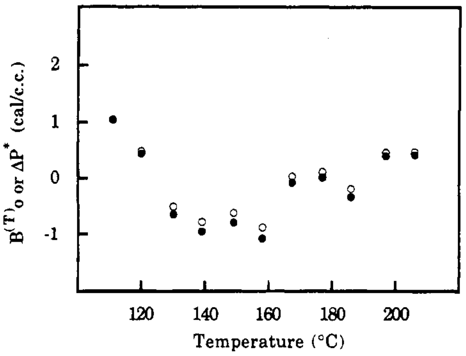

**Figure 7.** Interaction energy densities dependence on temperature for the PH/PVME 60:40 w/w system: (●) $\Delta P^*$; (○) $B^{(T)}$.

Furthermore, data of $B^{(T)}$ agree roughly with the parabolic variation of $B_{23}$ determined by eq 20 and other methods of IGC data analysis.[23]

## Summary and Conclusions

In this paper, we have attempted to use a method proposed by Sanchez in order to eliminate one of the main problems of the IGC method in characterizing polymer blends, that is, the probe dependence of the thermodynamic properties experimentally measured by this technique. *PVT* measurements have been performed in order to determine the required data for applying the lattice fluid theory which is the basis of Sanchez's method. At least in the blends investigated, the method does not provide probe independent interaction energy densities. Our opinion is that the best way to minimize such a dependence requires, if possible, an adequate selection of the probes, using only those having very different specific retention volumes with the pure components of the blend.[42]

However, without leaving the framework of the lattice fluid theory, IGC allows us to calculate an average characteristic interaction energy density $\Delta P^*$ from which $B^{(T)}$ and other related thermodynamic parameters can be calculated. Our calculations have shown that $\Delta P^*$ is crucial in the evolution of the interaction energy density and its enthalpic and entropic components with temperature and composition. These results can be compared with those contained in the papers of Paul,[17−22] where, in some cases, the entropic term has a more relevant role in the global interaction energy density. These differences could arise from the fact that Paul et al. used a constant $\Delta P^*$ determined from phase separation diagrams while here this parameter has been calculated by IGC at different temperatures.

It is also interesting to note that interaction energy densities here calculated are practically equal to those determined using the phenomenological Farooque−Deshpande data analysis method. However, the Farooque−Deshpande method, which had been previously compared with other data analysis methods,[23,41,42] is easier to use, its results are reasonably good, and in its application it does not need the large number of parameters required in methods based on free volume theories, as is the case of Sanchez's method. However, the application of such methods can give us new insights into the different factors contributing to the final polymer−polymer interaction energy density.

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