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Interaction energies in polymer/polymer mixtures

A. Etxeberria*, A. Unanue, C. Uriarte and J. J. Iruin
Departamento de Ciencia y Tecnologia de Polimeros, Universidad del Pais Vasco,
PO Box 1072, 20080 San Sebastian, Spain
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In the application of the lattice fluid theory to explain and simulate thermodynamic functions and phase diagrams of polymeric mixtures involving both homo- and copolymers, the only adjustable parameter is the so-called characteristic interaction energy density ΔP^*. In this paper, we present a test of consistency between the ΔP^* values obtained from phase diagrams and from retention specific volumes determined by inverse gas chromatography. Measurements have been done on a blend of poly(vinyl methyl ether) and poly(hydroxy ether of bisphenol A), which exhibits an LCST-type phase diagram. The previously reported ΔP^* temperature dependence seems to be verified. Another interesting conclusion is the dominant role played by ΔP^* in the thermodynamic functions describing the miscibility of the mixture. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Some years ago, Paul and Barlow[1] introduced the so-called binary interaction model, an intuitive and highly efficient approach to the observed phase behaviour of polymer/copolymer blends. The most relevant result was its capacity to explain experimental evidence of miscibility between a homopolymer A and a copolymer BC even though neither homopolymer B nor C was miscible separately with A. The repulsive intramolecular interactions between B and C units in the copolymer chain, 'diluted' by the presence of A units, were, according to the model, mainly responsible for the phase behaviour. A logical extension of the model is to consider every member of a homologous series of polymers, such as the polymethacrylate family, as a 'copolymer' of methacrylate-containing moieties and methylene units.

After the introduction of the model, a lot of work was done by different and important research groups in order to verify the feasibility of this approach[2–16]. Using the experimental phase diagrams described above and fitting them with the help of the binary interaction model, the final goal was to develop a database so that the interaction energies between any unlike chemical moieties could be tabulated and used in the simulation of phase diagrams of new polymer mixtures.

In its most simple version[1], the binary interaction model is used in the framework of the well-known Flory–Huggins theory. In doing so, the model has to predict or explain phase diagrams, which in most of the cases are of the LCST type, a kind of behaviour the FH theory is unable to predict unless adequate empirical corrections have been introduced.

Kim and Paul[4,5] have demonstrated that the use of the binary interaction model together with an appropriate equation-of-state theory that does predict LCST behaviour can provide an adequate framework to use the information which can be extracted from experimental phase diagrams. In most of the recent papers[4–10] the equation-of-state theory which has been used in combination with the binary interaction model is the Sanchez and Lacombe[17,18] lattice fluid (LF) theory. From the experimental point of view, the use of phase diagrams determined according to the so-called critical molecular weight method has allowed the independent evaluation of the interaction energies in a vast number of moiety pairs[9]. In this context, the interaction between every pair of unlike moieties is represented by the characteristic interaction energy density, ΔP^*, defined as a 'bare' interaction energy density in which the free volume effects have been stripped away.

Temperature may affect the interaction energy between a given polymer segment pair. The LF theory accounts for at least part of this variation by considering the effect of this variable on the specific volume, even when ΔP^* is usually assumed to be temperature-independent. This approach, which greatly simplifies the calculations, has been successfully tested in reproducing phase diagrams of a number of systems, as previously mentioned, and seems reasonable in the absence of strong specific interactions[19]. More consistent doubts appear when ΔP^* is used to calculate different thermodynamic functions along extended ranges of temperature.

From an apparently different point of view, our own research programme has been focused on a systematic study of the real possibilities of a chromatographic technique, the so-called inverse gas chromatography (i.g.c.), as an appropriate alternative to study thermodynamic properties of polymer solutions and blends[20]. The major i.g.c. inconvenience in polymer/polymer studies is that thermodynamic functions representing

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* To whom correspondence should be addressed

the blend (for instance, the polymer/polymer interaction energy density, B, related to the excess free energy of mixing, see later) have shown a well-documented dependence on the nature of the injected probe[21–23]. In a recent paper[24] we decided to follow a suggestion of Sanchez[25], who claimed that the above-mentioned problems could be solved if IGC data are not used to extract a B value as representative of a given polymer/polymer pair but ΔP^*, which can be considered as a B without compressibility or free volume effects. An analysis of this kind requires use of the LF framework.

Our results[24] showed that ΔP^* was also probe-dependent. Our nearly definitive conclusion is that every parameter related to polymer/polymer interaction energies and obtained by i.g.c. or alternative methods using a common solvent can be affected by similar dependencies. The main problem is that we are extracting information about polymer/polymer interaction from a combination of data coming from polymer/solvent and polymer/polymer/solvent mixtures. In general, polymer/polymer interaction energies are much more smaller than those associated with solutions. So, an inherent error is associated with these calculations. In the specific case of i.g.c., the polymer/polymer interaction is obtained from the combination of retention volumes of each solvent in columns of the pure polymers and their mixtures. The way to minimize the inherent error previously mentioned is the selection of the solvents with appropriate retention volumes. By appropriate we mean that the specific retention volumes of a solvent or probe with the pure components of the blends have to be sufficiently separate. If this is possible, the solvent dependence can be substantially reduced[26].

But, another very interesting result of our previous paper[24] is one concerning the temperature dependence of ΔP^*. Either using the data from a single solvent as a 'probe' or averaging the rather different values of a series of 15 different solvents, the characteristic interaction energy density ΔP^* was always temperature-dependent. This effect has been encountered in both poly(hydroxy ether of bisphenol A)/poly(vinyl methyl ether) (PH/PVME) and poly(epichlorohydrin)/poly(methyl acrylate) (PECH/PMA) blends, and has important effects on the calculation of the different thermodynamic functions controlling the blend miscibility. It is also true that these are two systems where relatively strong interactions are supposed to operate, although not as strong as in other blends where hydrogen bonding seems to be the more relevant factor affecting miscibility.

It can be argued that the values of ΔP^* and their temperature dependence could be an artifact of the technique mainly arising from the problems mentioned above concerning the probe effect. In the current work we are presenting new data for ΔP^*, now calculated using the phase diagrams of a PH/PVME mixture. With this strategy we propose to demonstrate the consistency of our previous i.g.c. data on the same mixture. After checking this consistency, we will illustrate the importance of the ΔP^*–T dependence on the calculation of thermodynamic functions. We also want to analyse the relative importance of the interactional and free volume effects on the same functions.

THEORETICAL BACKGROUND

Irrespective of the theoretical assumptions used in describing the free energy of mixing of two polymers, it can be written as

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

where ϕ_i and V_i are, respectively, the volume fraction and the molar volume of the i component. Polymers are denoted by the subscripts 2 and 3 (subscript 1 is reserved for the probe, as is usually the case in i.g.c. measurements). In this equation, we separate the combinatorial or ideal entropy from the rest of the possible effects, and use an excess term which contains the interaction energy density B. Both Δg_{mix} and B are expressed in calories per cubic centimetre. The spinodal condition describing the phase diagram can be determined from the second derivative of equation (1),

$$\frac{\mathrm{d}^2\Delta g}{\mathrm{d}\phi_2^2} = RT\left(\frac{1}{\phi_2 V_2} + \frac{1}{\phi_3 V_3}\right) - 2B_{\text{sc}} = 0 \qquad (2)$$

B_{sc} being the interaction energy density at the spinodal condition, which only coincides with B if this is concentration-independent.

As previously mentioned, one of the theories describing polymer/polymer mixtures is the LF theory of Sanchez and Lacombe[17,18], in which the introduction of the compressibility of the mixture allows the prediction of an LCST-type phase diagram. We will give a summary of the LF theory, starting with the configurational Gibbs free energy per hard core volume of mixture, $G/(rNv^*)$, which can be written as

$$\frac{G}{rNv^*} = \left[\frac{RT}{v^*}\sum_i \frac{\phi_i}{r_i}\ln\phi_i\right] - \tilde{\rho}P^* + P\tilde{v} + \frac{RT}{v^*} \times \left[\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho}\right] \qquad (3)$$

where N is the number of polymer chains, v^* the average mer hard core volume, ϕ_i the hard core volume fractions and r (or chain length) is a dimensionless size parameter proportional to the molecular weight,

$$r_i = \frac{M_i P_i^*}{RT_i^*\rho_i^*} = \frac{M_i}{\rho_i^* v_i^*} \qquad (4)$$

Reduced properties are defined as $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$ and $\tilde{\rho} = 1/\tilde{v} = v^*/v$. Moreover, the equation of state according to the LF theory has the following form:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \qquad (5)$$

The characteristic parameters of a polymeric component in the pure state, P^*, T^* and ρ^* (or v^*), can be obtained from its density, and two of the three following coefficients: thermal pressure, thermal expansion and isothermal compressibility. Furthermore, mixing rules are required to describe the mixtures. Although they can be arbitrary, we will use the ones outlined by Sanchez[17], which have also been employed in the series of papers by Paul *et al.*[4–10] as well as in our previous work[24],

$$\frac{1}{v^*} = \sum_i \frac{\phi_i}{v_i^*} \qquad \frac{1}{\rho^*} = \sum_i \frac{w_i}{\rho_i^*} \qquad \frac{1}{r} = \sum_i \frac{\phi_i}{r_i} \qquad (6)$$

where w_i is the weight fraction of component i. Finally, the characteristic pressure of the mixture is

$$P^* = \sum_i \phi_i P_i^* - \sum_{i<j}\sum_i \phi_i\phi_j\,\Delta P^* \qquad (7)$$

where ΔP^* is the characteristic interaction energy density, previously mentioned and calculable from phase diagrams or i.g.c. data. Both the enthalpic and the entropic contributions to the excess free energy of mixing to polymers, the B term in equation (1), can be derived from the LF theory as shown by Kim and Paul[4,5]. The enthalpic part of B, associated with the heat of mixing, can be written as

$$B_{\mathrm{h}} = \tilde{\rho}\,\Delta P^* + \left[\frac{P_2^*}{\phi_3}(\tilde{\rho}_2 - \tilde{\rho}) + \frac{P_3^*}{\phi_2}(\tilde{\rho}_3 - \tilde{\rho})\right] + \frac{P^*}{\phi_2\,\phi_3}(\tilde{v} - \phi_2\tilde{v}_2 - \phi_3\tilde{v}_3) \qquad (8)$$

and, similarly, another relationship can be derived for the entropic part of B:

$$-TB_{\mathrm{s}} = \frac{RT}{\phi_2\,\phi_3}\left\{\frac{1}{v^*}\left[\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r}\right] - \frac{\phi_2}{v_2^*}\left[\frac{1-\tilde{\rho}_2}{\tilde{\rho}_2}\ln(1-\tilde{\rho}_2) + \frac{\ln\tilde{\rho}_2}{r_2^0}\right] - \frac{\phi_3}{v_3^*}\left[\frac{1-\tilde{\rho}_3}{\tilde{\rho}_3}\ln(1-\tilde{\rho}_3) + \frac{\ln\tilde{\rho}_3}{r_3^0}\right]\right\} \qquad (9)$$

where r_i^0 is the chain length of i polymer in the pure state, defined by equation (4). The interaction energy density B is the combination of both previous terms, $B = B_{\mathrm{h}} - TB_{\mathrm{s}}$. Finally, the spinodal condition for a compressible blend allows us to derive the value of B related to the second derivative of the excess free energy:

$$B_{\mathrm{sc}} = \tilde{\rho}\,\Delta P^* + \left\{P_3^* - P_2^* + (\phi_3 - \phi_2)\Delta P^* + \frac{RT}{\tilde{\rho}}\left[\frac{1}{r_2^0 v_2^*} - \frac{1}{r_3^0 v_3^*}\right] - RT\left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right] \times \left[\frac{1}{v_2^*} - \frac{1}{v_3^*}\right]\right\}^2 \left\{\frac{2RT}{v^*}\left[\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1-1/r}{\tilde{\rho}^2}\right]\right\}^{-1} \qquad (10)$$

As previously mentioned, B and B_{sc} are different if B is composition-dependent.

In order to calculate ΔP^* from phase diagrams, we will recall that for a miscible blend the following condition must be fulfilled:

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}\phi_2} = r_2\phi_3\left\{\frac{RT}{2v^*}\left[\frac{1}{r_2\phi_2} + \frac{1}{r_3\phi_3}\right] - \tilde{\rho}\left[\Delta P^* + \frac{RT}{2v^*}(\Psi^2\tilde{T}P^*\beta\right]\right\} > 0 \qquad (11)$$

where β is the mixture isothermal compressibility, and

$$\Psi = \left\{\tilde{\rho}\left[\nu\left(\frac{1}{\tilde{T}_2} - \frac{1}{\tilde{T}_3}\right) + \frac{(\phi_2^2 - \nu\phi_3^2)\Delta P^* v_2}{RT}\right] - \nu\left(\frac{1}{r_2^0} - \frac{1}{r_3^0}\right) + \frac{\tilde{P}\tilde{v}}{\tilde{T}}(\nu - 1)(\phi_2 + \nu\phi_3)\right\}(\phi_2 + \nu\phi_3)^{-2} \qquad (12)$$

$$\tilde{T}P^*\beta = \frac{\tilde{v}}{1/(\tilde{v}-1) + 1/r - 2/\tilde{v}\tilde{T}} \qquad (13)$$

where $r_i = r_i^0 v_i^*/v^*$ and ν is the pure polymer hard core volume relation, so $\nu = v_2^*/v_3^*$. The only unknown parameter in equations (8)–(10) is ΔP^*, but since at any point of the spinodal separation curve equation (11) is equal to zero, phase diagrams will allow us to calculate ΔP^*.

The theoretical LF background under the data treatment of i.g.c. measurements which provides the characteristic interaction energy density ΔP^* has been previously reported[24].

EXPERIMENTAL

We used the same polymer samples of PVME and PH described in our previous paper[24].

Blends for the phase diagram determinations were prepared from 10% solutions of both polymers in dioxane. Dioxane evaporation was conducted at room temperature. The resulting films were dried in a vacuum oven at 40°C until they reached a constant weight, and then stored in a vacuum to avoid moisture adsorption.

Location of the phase separation temperatures of different blend compositions was first investigated by means of optical analysis. The films, which were directly cast onto glass microscope slides from solutions, in a similar manner to that described in the previous paragraph, were placed in a Mettler hot-stage device. They were heated at a heating rate of 4°C min^{-1} under a Leitz Aristomet microscope equipped with a photoelectric cell. The appearance of a cloud point was detected as the onset of a transmitted light jump.

The average thickness of the blend samples prepared for scattering experiments was 0.24 mm. The experimental scattering equipment has been previously and extensively described in the papers of Higgins *et al.*[27–29]. It consists of a 6832A laser, a sample block and a light-detecting system with 32 photodiodes mounted over 60°. The samples were preheated at a temperature below that observed in the transmitted light experiments. The temperature was then increased at a constant rate (between 0.4 and 1.5°C min^{-1}). The phase separation temperature was taken as the point where the scattered intensity suddenly increased. All the experiments were done under a slight flow of nitrogen in order to prevent PVME degradation.

Characteristic LF parameters for PH and PVME (see *Table 1*) were determined using temperature relationships of density, thermal expansion and thermal pressure coefficients reported previously[30]. Slightly different values have been reported by Rodgers[31] after fitting P–V–T data, although these differences do not have any significant influence on the absolute value of ΔP^* or on its evolution with temperature[24].

In calculating the different thermodynamic functions at different temperatures, reduced densities of the blends are needed and must be calculated. A similar procedure has been employed in order to determine both the pure polymer and the mixture reduced densities. The pure component reduced temperatures were calculated from

Table 1 LF equation-of-state parameters for polymers used in this work

	ρ^* (g cm^{-3})	P^* (cal cm^{-3})	T^* (K)
PH	1.215	152.4	761
PVME	1.089	75.4	697

the corresponding characteristic temperatures and, after that, reduced densities were calculated using a corresponding-state relationship between ($\tilde\rho$) and ($\tilde T$) (see Table II in Sanchez and Lacombe[32]). In the case of a polymer/polymer mixture its reduced temperature is given by[7]

$$\frac{1}{\tilde T} = \frac{\phi_2/\tilde T_2 + \nu\phi_2/\tilde T_3}{\phi_2 + \nu\phi_3} - \frac{\phi_2\phi_3\,\Delta P^* v^*}{RT} \qquad (14)$$

RESULTS AND DISCUSSION

PH and PVME form an adequate mixture for the type of study proposed here. They are miscible at low temperatures but phase separate at temperatures above 160°C[30]. Although specific interactions have been proposed to be the origin of the miscibility of such a system, *FT* i.r. studies[33] have shown a very small shift to higher frequencies in the phenoxy hydrogen-bonded hydroxyl peak. In fact, after comparing *FT* i.r. spectra of this blend and that of the immiscible polyvinyletherether (PVEE)/PH mixture, the authors[33] confess that the shift would not have been considered significant without prior knowledge of the compatibility of the system. In conclusion, we propose that PH/PVME can be studied in the framework of a model where the geometric mean rule can accept small deviations.

Figure 1 shows the experimental separation temperatures for the PH/PVME mixture by light scattering and transmitted light microscopy at several compositions. Even though in other systems temperatures measured by these two techniques differ to some degree[28], in the PH/PVME case they are practically identical.

At the spinodal separation temperature, equation (11) is equal to zero, and ΔP^*, the only unknown term, can be calculated. As would be expected after the small differences in *Figure 1*, ΔP^* takes nearly the same value at each composition irrespective of the experimental technique used in determining the phase diagrams. In *Figure 2* the average values of ΔP^* from both experimental phase diagrams against blend composition are presented. The flat shape of the phase diagram is reflected in the slight dependence of ΔP^* on blend composition.

Figure 3 presents previously reported[24] ΔP^* average values obtained by i.g.c. with 15 different solvents in the 110–210°C range. At low temperatures ΔP^* is positive and tends towards negative values when the temperature increases. In the same figure we also present the single ΔP^* value obtained from the experimental phase diagram (see *Figure 1*) at the phase separation temperature which corresponds to a PH/PVME 60:40 w/w mixture (the composition studied by i.g.c.). A reasonable agreement is evident from *Figure 3*, confirming that i.g.c. is a valid alternative with which to determine ΔP^* and, moreover, the consistency of the LF theory for ΔP^* calculated in two very different ways.

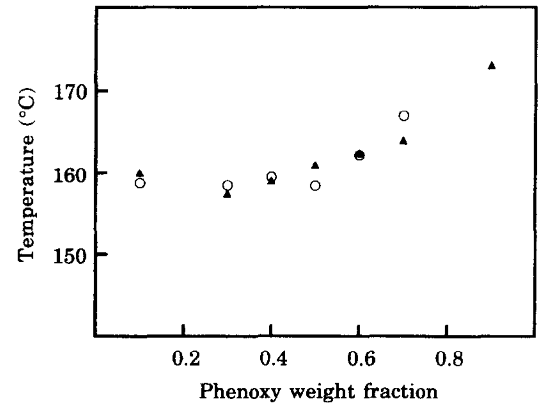

Figure 1 Experimental separation temperatures for the PH/PVME blend. ○, light scattering; ▲, cloud point

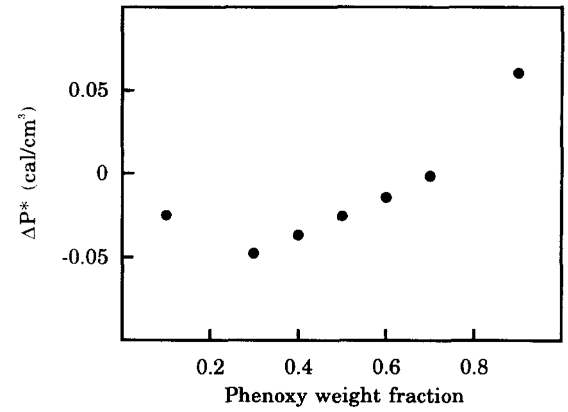

Figure 2 Characteristic interaction energy density ΔP^* for PH/PVME blends from experimental separation temperatures

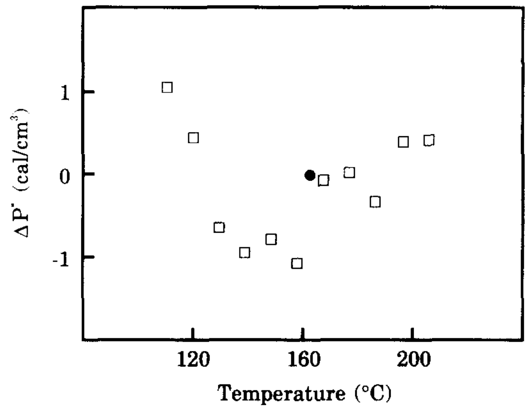

Figure 3 Variation of ΔP^* with temperature as determined by i.g.c. in a PH/PVME 60:40 w/w blend. The value determined by light scattering for this composition is also shown for comparison. □, i.g.c.; ●, scattering

The additional aim of this paper was to test the differences in simulating thermodynamic functions when ΔP^* is introduced as temperature-dependent or not. In order to select a representative temperature-independent ΔP^* value, we have used the spinodal curve data. Callaghan and Paul[6] have proposed that the most adequate value of ΔP^* is that calculated with spinodal data near to the critical point. In the PH/PVME system (see *Figure 1*) this point is located near the PH/PVME 30:70 weight fraction composition. Another possibility is to select a ΔP^* averaged over the values of the different investigated compositions. Preliminary calculations showed us that both ΔP^* values provide similar results for the different thermodynamic functions under study. Given that the flat phase diagram makes correct location of the critical point difficult, we have preferred to use the average ΔP^* value ($-0.025\,\mathrm{cal\,cm^{-3}}$).

Considering ΔP^* as a temperature-independent parameter, as usually done by Paul *et al.*[4–9], and the adequate equations previously introduced, we have calculated the interaction energy density B, its enthalpic and entropic

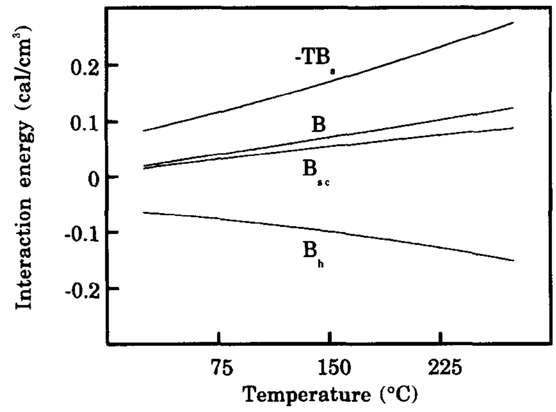

Figure 4 Temperature dependences of the interaction energy density, its entropic and enthalpic components and its value related to the second derivative of the free energy for the PH/PVME 60:40 w/w blend, using the average ΔP^* calculated by light scattering

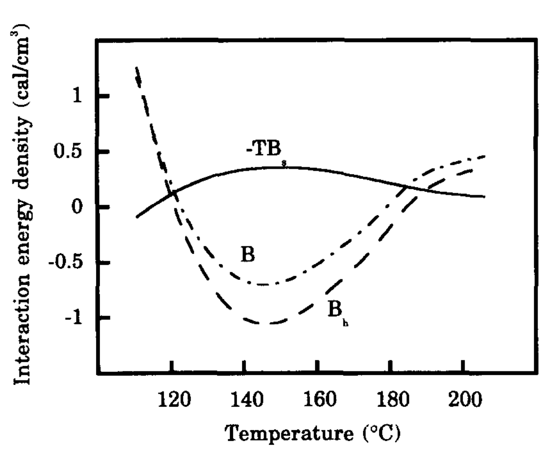

Figure 5 Temperature dependences of the interaction energy density B and its enthalpic and entropic terms for the PH/PVME 60:40 w/w blend using the ΔP^*–T relationship calculated by i.g.c.

components B_h, B_s and its value related to the second derivative of the free energy B_{sc} for a PH/PVME 60:40 w/w blend (the one used in i.g.c. experiments) over a wide temperature range. The results are presented in *Figure 4*. In this figure, it is interesting to note that phase separation is driven by the entropic term, $-TB_s$. This term becomes more positive when the temperature increases, and at high temperatures overcomes B_h. Finally, B and B_{sc} are not identical, but their dependence on temperature must be similar, as occurs here.

In order to perform similar calculations but using a temperature-dependent ΔP^*, we have used ΔP^* values belonging to the best fit to the experimental ΔP^*–T relationship obtained from the i.g.c. determinations. *Figure 5* shows the dependence of B, B_h and $-TB_s$ on temperature. We have not included B_{sc} for the sake of clarity in the figure, but its behaviour is quite similar to that of B. Important changes are observed when *Figures 4* and *5* are compared. Using the temperature dependence of ΔP^*, the entropic term, $-TB_s$, does not depend significantly upon temperature. More specifically, $-TB_s$ does not increase constantly with temperature as it did when a constant ΔP^* was used (see *Figure 4*). However, the enthalpic term B_h shows a strong dependence on ΔP^*. In fact, it follows a parallel behaviour to that of ΔP^* (see *Figure 3*). Below 160°C (a temperature near the experimental LCST) B_h takes negative values, while above this temperature B_h tends towards positive values. When B is computed using these two contributions, and as expected given the slight temperature dependence of $-TB_s$, it exhibits a quite similar behaviour to that of B_h and ΔP^*.

In looking for an explanation of the similar behaviour of B, B_h and ΔP^*, calculations have been performed using equations (8) and (9) with different, and totally arbitrary, ΔP^* values between -2 and $2\,\mathrm{cal\,cm^{-3}}$. It has been evident that for high values of ΔP^*, irrespective of the sign, the first term in equation (8) dominates the values of B_h and B. However, this occurs not because the rest of the terms (mainly related to free volume effects) are negligible but because they cancel each other. For instance, at 125°C, in a PH/PVME 50:50 w/w mixture and using a value of $\Delta P^* = -2\,\mathrm{cal\,cm^{-3}}$, the term containing ΔP^* amounts to -1.83, whereas the other term in equation (8) is equal to -0.48, and $-TB_s = -0.56$. When ΔP^* is $-0.5\,\mathrm{cal\,cm^{-3}}$, the term containing ΔP^* amounts to -0.46, the other term contributing to B_h is -0.11, and $-TB_s = -0.13$. Similar trends are observed at other temperatures. Only when ΔP^* is sufficiently low (i.e. -0.01) is the term containing ΔP^* lower than the algebraic addition of the other terms contributing to B. But, in this case B is also very low. Similar qualitative trends are obtained with positive values of ΔP^*. It is important to remark that in the previous papers of Paul *et al.* (see, for instance, refs 6 and 7), ΔP^* for moieties pairs pertaining to miscible blends are found to be as negative as -0.5 (this is the value, for instance, for a styrene-2,6-dimethyl-1,4-phenylene oxide pair) whereas a positive value, as high as 8, is reported for the α-methylstyrene/acrylonitrile pair.

We have performed similar calculations with the mixture PECH/PMA, previously studied in our previous paper[24]. The results were exactly the same, mainly because the equation-of-state parameters of the components in the two mixtures under consideration are not different enough to provoke important changes in the thermodynamic functions.

The important question we are not able to answer here refers to what we are measuring in ΔP^*. Is it purely interactional or are we including in it (as Flory did in his interaction parameter) other contributions not specified in the model we are using? By contrast, it is clear that except in those cases where ΔP^* is very small (near the phase separation of the corresponding homopolymers) the free volume contribution does not seem to play an important role in the final value of B. In fact, Table 4 of Gan *et al.*[7] leads to the same conclusion, given the close similarity between ΔP^*, calculated from polymer/copolymer phase diagrams and the LF theory, and B calculated with the same diagrams and the Flory–Huggins framework.

It can be concluded that phenomenological values of B tabulated in a database can be enough to simulate properties of other polymer mixtures. These B values can be obtained from phase diagrams or, as demonstrated previously by our own group[26,34], it is also possible to obtain them using i.g.c and a very simple data treatment introduced by Farooque and Deshpande[35]. In relation to this, it would be interesting to check the real possibilities of i.g.c. in obtaining interaction energies for segment pairs representative of immiscible polymers. Some of the pairs evaluated by Paul *et al.* in the papers repeatedly mentioned above will be good candidates for such a test.

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