Comparison between Static (Sorption) and Dynamic (IGC) Methods in the Determination of Interaction Parameters in Polymer/Polymer Blends

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ABSTRACT: Polymer−polymer interaction energy densities have been measured by two different techniques: inverse gas chromatography (IGC) and gas sorption experiments in a Cahn electrobalance. Both use a third component as a molecular probe to investigate the interactions between the two polymers. The poly(epichlorohydrin)/poly(methyl acrylate) (PECH/PMA) blend has been selected as a system that ensures the liquid state of the polymeric phase in all the experiments. It also stresses the convenience of a previously proposed procedure that selects the most adequate solvents to obtain a reliable polymer−polymer interaction energy density by IGC. A permanent gas, CO_2, has been used as molecular probe in sorption measurements, after verifying the inconvenience of using organic solvents as probes, due to the overshoot phenomena observed in their sorption kinetics. Both techniques give similar polymer−polymer interaction values.

Introduction

Inverse gas chromatography (IGC) has been widely used to obtain the polymer(2)−polymer(3) interaction energy densities (B_{23}), a magnitude related with the Flory−Huggins interaction parameter (χ_{23}). Both parameters have been used to characterize the true thermodynamic miscibility of two polymers.[1−3] Other IGC studies have been devoted to immiscible polymer blends[4,5] or to determine the interactions in copolymer blends.[6] However, the most important problem that could be found in IGC determinations is the dependence of these parameters on the solvent used as a probe. This has been related to the nonrandom partitioning of the probe, the so-called $\Delta\chi$ effect.[7−9] It has been recently proposed that this effect could be used to study the microstructure of polymer blends.[10]

However, due to the advantages that IGC presents over other techniques (light scattering, small-angle X-ray scattering, solvent vapor sorption, etc.), numerous attempts have been made to solve this problem.[11−14] Among them, the purely phenomenological method proposed by Farooque and Deshpande[15] has been found to be one of the easiest to use. It does not need the large number of parameters required by other more sophisticated methods,[11−13] giving results that are comparable to those obtained by these other methods.[15−20] In fact, it can be considered as a simplification of a thermodynamically more rigorous treatment.[18]

But, from the first results in the application of this method to our systems,[16,17,21] it was noted that an adequate selection of the probes was necessary to reduce the large confidence intervals[22] in the values of B_{23}. In a previous work, it was suggested that the appropriate probes should have very different specific retention volumes with the pure components of the blend in order to reduce the confidence interval values.[17] Now, it seems that this criterion is not sufficient. In the Farooque−Deshpande plots, the points are often confined to a restricted interval, giving larger errors in the values of B_{23} so obtained. To avoid this problem, probes should be adequately chosen.

On the other side, B_{23} values (equilibrium parameters) obtained by IGC could be questionable due to the dynamic character of the technique. Although in the 1970s good agreement was reported between values of polymer/solvent interaction parameters obtained by IGC and those obtained by sorption equilibrium techniques, few comparisons of polymer/polymer interaction parameters obtained by these two methods can be found in the literature.[23−27] In one of them, Panayiotou and Vera[26] compared B_{23} values of poly(vinyl chloride)/poly(ϵ-caprolactone) (PVC/PCL) mixtures obtained by sorption experiments at 65 °C with those obtained by Olabisi[7] in the same system using IGC but at 120 °C. Both studied the blend using the same solvent, carbon tetrachloride, obtaining different positive values of B_{23}. The differences between the values could be a consequence of the different experimental conditions employed. In fact, at 65 °C, the blend could not be in the liquid state. (PCL has a melting temperature of 60 °C, and PVC has a glass transition temperature near to 87 °C.) In addition, sorption values at relatively low concentrations of polymer have been extrapolated to the IGC concentration regime (nearly pure polymer) with the corresponding uncertainties associated with such kind of extrapolation. Despite these complications, the trend of B_{23} with the PVC concentration is the same in both studies.

In the same work, Panayiotou and Vera also studied the poly(styrene)/poly(vinyl methyl ether) (PS/PVME) mixture following sorption at 25 °C. They used two different solvents (chloroform and benzene), obtaining different values of B_{23} for the two solvents, a result which can be considered as a consequence of the mentioned probe influence in the determination of polymer−polymer interaction parameters. The values with chloroform were higher than those with benzene. On the other hand, the trend with the blend composition is the same for the two solvents but different from that

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obtained by Kwei et al.[27] in PS/PVME/benzene at 30 and 50 °C. In this case, the values of B_{23} were negative and decreased when the PS fraction increased. The same system, PS/PVME, was studied by IGC with several solvents by Su and Patterson.[39] Although the B_{23} values were positive when benzene and chloroform were used as penetrants and similar to those reported by Panayiotou and Vera, the trend with the blend composition was similar to that in the Kwei et al. paper.

As in the IGC case, B_{23} could not be reliable in sorption experiments because of its dependence on the probe. With the aim of removing this probe dependence, Prolongo et al.[11] used the above-mentioned data to test a new method for obtaining independent polymer–polymer parameters. The B_{23} values obtained from sorption experiments at different composition were extrapolated to a zero solvent fraction and compared with those obtained using IGC. The values were similar, but the variation with the blend composition continued being different.

Consequently, experimental data reveal some discrepancies in the comparisons between the two techniques. Such differences could arise from two sources: First, we have to consider the solvent dependence of the polymer–polymer interaction parameter, an influence that can be minimized in IGC measurements where it is customary to use a set of selected solvents and average the values so obtained. And, second, differences in the solvent concentration, temperature, the polymer phase presentation, etc., can introduce reasonable differences in the experimental results. In this sense, it would be necessary to have the polymer blend in the liquid state in both types of measurements, a condition not always fulfilled in some comparative studies.

It is known that static methods such as vapor sorption experiments are long and tedious. Moreover, some complications arising from the fact that sorption curves exhibited an overshoot in the weight pickup have been reported in the literature.[28–30] Because of this and after some experiments with organic vapors, CO_2 was selected as a less interacting penetrant. This gas has already been used in papers where its sorption kinetics in polymer blends have been used to extract information about the thermodynamics controlling the state of the blend.[31–34]

Thus, the aim of this work is to demonstrate that with a previous selection of the probes the error in the B_{23} values obtained by IGC can be minimized. On the other hand, we will compare these values with those obtained using sorption experiments. To have the best conditions for such a type of comparison, we have selected the poly(epichlorohydrin)/poly(methyl acrylate) (PECH/PMA)[16,21,35] blend. This system has been previously studied by IGC, giving us the opportunity to check the validity of the methodology we are going to use. In addition, both polymers and their miscible blends are amorphous and behave as rubbers at temperatures at which both experimental setups can run, a condition required for a correct comparison of true equilibrium data coming from the two techniques.

Experimental Section

Polymers and IGC Procedures. The polymers and the IGC equipment have been the same as in our previous work.[21] The chromatographic measurements were carried out following the procedure well-described elsewhere.[21,35] Characteristics of the used columns are presented in Table 1.

Table 1. Characteristics of the PECH/PMA Columns

column	support (g)	PECH (g)	PMA (g)
PECH	5.5755	0.4831	
25/75	5.4614	0.1374	0.3983
50/50	5.4811	0.2725	0.2707
75/25	5.4489	0.3973	0.1388
PMA	5.5439		0.4971

Sorption Experiments. Films of PMA, PECH, and their blends having weight ratios of 75/25, 50/50, and 25/75 were prepared by casting from THF solutions onto a flat PTFE surface. After solvent evaporation at room temperature, the films were further dried on a vacuum oven. The thickness of these films was measured with an induction magnetic-type meter (Duo-Check St-10) with an accuracy of 1 μm.

The measurements of vapor and CO_2 sorption were accomplished using a Cahn D-200 electrobalance with a sensitivity of 0.1 μg. The weighting unit was enclosed in a thermostated chamber at 30 °C. The membranes were loaded onto the sample pan of the balance. Then, the system was degassed by a vacuum pump for 2 days minimum.

a. Solvent Sorption. Solvents were of purity higher than 99%. The organic solvent was in a reservoir inside the chamber, but it was thermostated at lower temperatures than the balance by means of a thermostatic bath. This avoids possible condensation of the vapor in the balance chamber. When the adequate temperatures were achieved, the solvent vapor was allowed to flow from the reservoir to the balance.

b. CO_2 Sorption. CO_2 used in this study was of 99.995% purity. Experiments were performed at pressures of approximately 250, 500, and 760 mmHg. The procedure with gases has been described in a previous paper.[36]

Results and Discussion

IGC Results. It has been previously[16,17,21] pointed out that B_{23} data obtained from IGC measurements are affected by a considerable error due to the weak contribution of the B_{23} term in the equation from which it is calculated (see for instance eq 1). In other words, we are determining a parameter (B_{23}) which is several orders of magnitude smaller than the measured experimental magnitudes (specific retention volumes or V_g^0). This conclusion is general for all the methods proposed in the literature in order to remove the probe dependence of B_{23}.

In this sense, we have already mentioned the advantages of a phenomenological method proposed by Farooque and Deshpande.[15] This method is based on a simple rearrangement of the well-known classical Flory–Huggins expression for a ternary solvent–polymer–polymer system. When all the IGC measurements are carried out in the same experimental conditions,[35] the rearranged equation can be written directly in terms of the experimental measured magnitudes,

$$Y = X\phi_2 - B_{23}\phi_2\phi_3/RT \tag{1}$$

where

$$Y = [\ln(v_{sp,b}V^0_{g,3}/v_{sp,3}V^0_{g,b})]/V_1 \quad \text{and}$$
$$X = [\ln(v_{sp,2}V^0_{g,3}/v_{sp,3}V^0_{g,2})]/V_1$$

V_1 is the solvent molar volume; $v_{sp,i}$ and $V^0_{g,i}$ are the specific volume and the specific retention volumes of the pure polymers (2 and 3) and the blend (b), respectively; ϕ_i is the volume fraction of the polymers in the blend, and B_{23} is the interaction energy density of the polymer blend. In this method, a simple plot of Y vs X will yield ϕ_2 from the slope and $-B_{23}\phi_2\phi_3/RT$ from the intercept.

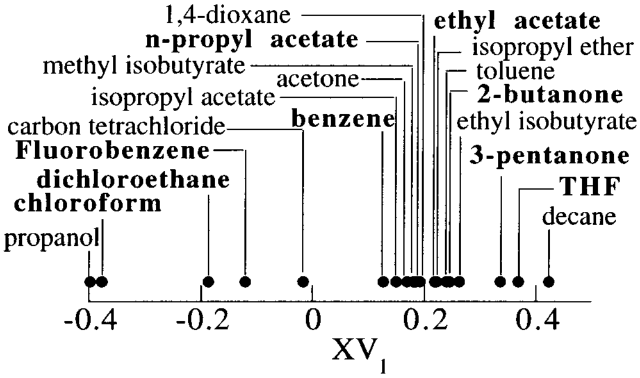

Figure 1. Values of XV_1 for all the injected probes in order to select the more adequate ones. The selected solvents finally used are indicated in bold.

ϕ_2 so obtained could be slightly different from the bulk composition originally prepared and has been interpreted as the effective polymer composition the probes observe across the chromatographic column.[17]

Although this method gives reliable B_{23} values, they are affected by large errors, as we have previously mentioned. To reduce the uncertainty in the B_{23} values, a possible alternative is an adequate selection of the probes to use. In a previous work,[17] the principal features of the selection procedure were established: First, rejection of the probes that have similar interaction parameters with both pure polymers. Although they would be the ideal probes (no $\Delta\chi$ effect), this implies similar specific retention volumes (V_g^0) values. Any small error in the values of V_g^0 is magnified when the B_{23} is determined. Second, the probes were selected trying to cover all possible chemical structures and polarities.

So, 19 probes have been injected in order to select the most adequate ones. Their behavior with both PECH and PMA is reflected in Figure 1, where the X values of eq 1 are represented. Despite the fact we have used solvents of very different nature, X values of most of them are disposed in a small interval. Thus, although according to their X values they would be appropriate for such kinds of experiments, only some of them were selected in this interval in order to simplify the number of experiments. The rest of the probes were selected trying to cover a more extended X range. This allows us to estimate the parameters of the fitted straight line with a minor error. On the other side, even though the *n*-decane and the 1-propanol are in the extremes of the range, they have been rejected. It is a generalized experience in IGC that *n*-alkanes and alcohols often behave anomalously in the determination of polymer–polymer interaction parameters.[5,12,14,20,21,35,37,38] The precipitant character of such penetrants with the majority of the polymers and the possible dominant character of surface adsorption phenomena against bulk sorption could be in the origin of such types of behavior. Furthermore, in our case, we have the possibility of using other solvents with similar X values to those of *n*-decane and 1-propanol (tetrahydrofuran and chloroform, respectively).

According to these criteria, the chosen solvents were chloroform, 1,2-dichloroethane, fluorobenzene, benzene, *n*-propyl acetate, ethyl acetate, ethyl methyl ketone, 3-pentanone, and tetrahydrofuran. To confirm the validity of our selection, we have also injected carbon tetrachloride (a penetrant with similar interaction parameter with both pure polymers) and *n*-decane, a representative member of the above-described precipitant families.

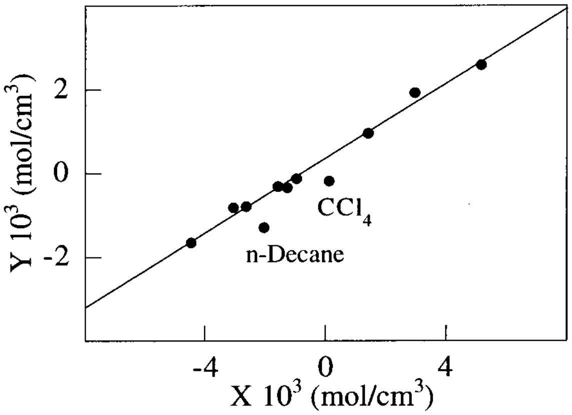

Figure 2. Farooque–Deshpande plot for the 50/50 PECH/PMA blend at 95 °C.

In Figure 2, a plot of eq 1 is presented for the PECH/PMA 50:50 blend at 95 °C for the mentioned nine solvents plus *n*-decane and carbon tetrachloride. As can be seen, data of the selected solvents are perfectly along a straight line with an excellent correlation (superior to 0.99), but the points corresponding to the *n*-decane and carbon tetrachloride clearly deviate from it. Thus, the used criteria should be appropriate (we will confirm later this result).

As we have already mentioned in some previous works and above,[16,17,21] excellent correlations in such types of plots do not imply small errors in the B_{23} values. In fact, an adequate analysis[22] gives large confidence intervals, as a consequence of the small contribution of B_{23} to eq 1. Thus, plots with correlations close to 1 would have errors of 100%. In this point of the discussion, two comments about this method are necessary. First, since in the blend here studied B_{23} has values close to zero, any little change in the fitted data or in the number of them could change strongly the final value of B_{23}. For instance, when all our previous data[21] were used, the determined B_{23} was 0.22 cal/cm^3. Removing some probes (alkanes, alcohols, and acrylonitrile), its value changed to 0.04 cal/cm^3, and putting together this series and the data of Al-Saigh and Munk,[35] we obtained −0.5 cal/cm^3. The new data presented in this work give a value of −1.01 cal/cm^3. This result is in good agreement with the value given in a previous paper of Munk et al.[2] where C'_{23}, which has a similar meaning of B_{23}, was −1.11 cal/cm^3 for the 50/50 blend at 100 °C.

The precedent paragraph illustrates, in our opinion, the extremely low weight of B_{23} in eq 1. Consequently, small confidence intervals are the only alternative we have in order to certify the validity of our experimental determinations.

The second comment is about the confidence interval itself. Up to now, we have generally given relative error values of B_{23}. Then, the higher is the absolute value of B_{23}, the lower relative error is determined. But, we think that the goodness of the selection procedure must be reflected in the absolute value of the confidence interval, independent of the intercept value. In addition, having two data series, one without probe selection[21,38] and another one using carefully chosen solvents, it would be a good chance to compare the confidence intervals. In this sense, the confidence intervals for both data series are presented in Table 2. Those calculated

Table 2. Confidence Intervals ($\times 10^3$) for the Intercept of Eq 1 in the PECH/PMA Blend Obtained Previously[38] (A) and in This Work (B)

	75:25[a]		50:50		25:75	
T (°C)	(A)	(B)	(A)	(B)	(A)	(B)
60	0.21		0.22		0.21	
65	0.20	0.10	0.20	0.11	0.21	0.11
70	0.18		0.19		0.20	
76	0.17	0.08	0.17	0.09	0.20	0.08
85	0.16	0.07	0.15	0.08	0.20	0.06
95	0.14	0.06	0.13	0.07	0.19	0.05
105	0.13	0.07	0.11	0.06	0.18	0.04
115	0.10	0.06	0.10	0.07	0.20	0.05
125	0.09	0.07	0.10	0.08	0.20	0.06

[a] In our previous work the composition was actually 80:20.

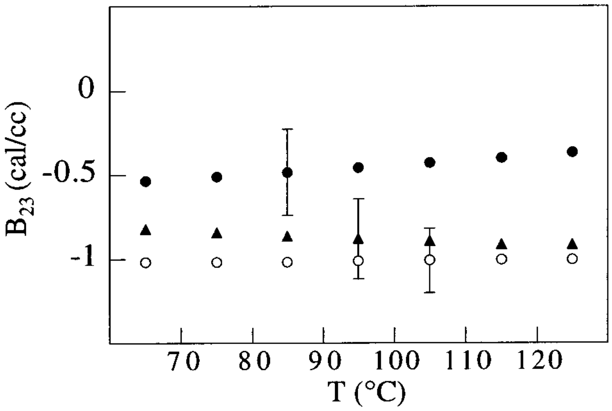

Figure 3. Values of B_{23} determined by IGC and the Farooque–Deshpande plot for the PECH/PMA blends: (●) 25/75; (○) 50/50; (▲) 75/25. (The average confidence intervals are shown as error bars.)

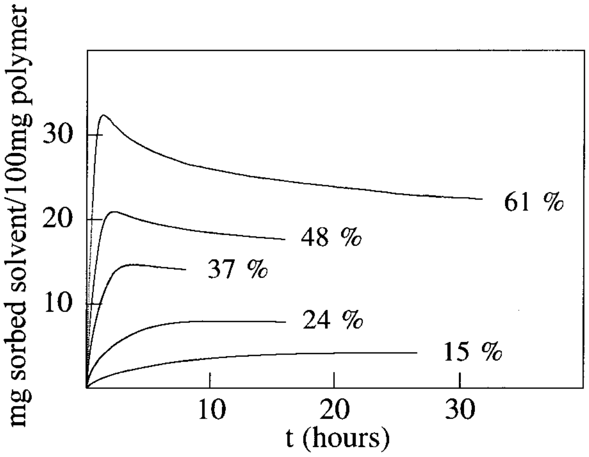

Figure 4. Sorption kinetics for 1,2-dichloroethane, at different activities, in PECH membranes at 30 °C.

for the PECH/PMA with the selected nine solvents are smaller than those without the selection rules in the whole temperature range. They are also smaller than those obtained in a previous work with the poly(hydroxy ether of bisphenol A)/poly(ϵ-caprolactone) (PH/PCL) blend.[17] This is important because in this blend stronger interactions and higher B_{23} values are expected, giving a larger B_{23} weight in eq 1 and a reduction of the confidence intervals. These confidence interval values suppose, in average, an absolute error bar in B_{23} of 0.5 cal/cm^3, which, in our opinion, is the minimum error that can be achieved using the Scott–Tompa assumption in IGC measurements.

The definitive result confirming the goodness of the followed criteria is that the confidence interval increases more than a 100% when both *n*-decane and carbon tetrachloride are included. In this sense, we have to point out that increasing the fitted data number the confidence interval would be reduced if the data were appropriate. The correlation is also considerably poorer: 0.996 in the case of the nine chosen solvents and 0.974 when *n*-decane and carbon tetrachloride are included. In conclusion, this selection procedure is an adequate way to minimize the error involved in the determination of a unique and reliable B_{23} by IGC, applying the method of Farooque and Deshpande, even though, as is the case in our blend, its value was small.

In this work, we were also interested in corroborate the behavior of the B_{23} values with the temperature. Previously,[21] a decrease of the B_{23} values in the temperature range studied was reported. This is not the expected behavior in blends with LCST phase diagrams.[39] The energy density parameters obtained in this work for the three compositions are shown in Figure 3. They have been calculated using volume fractions ϕ_2 obtained from the slopes of the Farooque–Deshpande plots. These volume fractions are slightly different to the compositions originally prepared but both give similar B_{23} values. For instance, at 95 °C and the 50/50 (w/w) the bulk PECH volume fraction was 0.475, and the volume fraction from the slope was 0.436. When these values are used to calculate B_{23}, the results were -0.996 and -1.01, respectively. Similar differences have been found in other temperatures and compositions.

On the other side, B_{23} has not a similar variation with temperature for the three compositions: it increases as temperature increases for the blend richest in PMA, is practically constant for the 50:50 blend, and decreases slightly with the temperature for the 75:25 composition. These trends are not in agreement with our previous data, but they could be more consistent with the observed LCST behavior for this blend. On the other hand, it must be taken into account that the B_{23} changes are very small, and they could be within the experimental error.

Sorption Experiments. a. Solvent Sorption. The purpose of this work was to compare the B_{23} obtained in IGC experiments with those obtained by the sorption technique. As mentioned in the Introduction, few works have been found in the literature comparing the B_{23} values obtained by these two techniques.[23–27]

Therefore, our first aim was to obtain solvent-independent polymer–polymer interaction parameters by the sorption technique and then compare the results with those of IGC. Since we have already demonstrated that the Farooque–Deshpande method is a reliable way to determine a unique value of B_{23}, the same data treatment applied to the sorption results could give us also a B_{23} independent of the used solvent.

In this sense, sorption experiments were carried out in the Cahn balance. However, some difficulties were found when organic solvents were employed. Sorption overshoots were observed at all the solvent activities studied, as could be seen in Figure 4. The effect is more accused with high solvent activities. This phenomenon has been explained, in some circumstances, as a process of crystallization induced by the solvent.[28,40–42] In these cases, the crystallization starts only when a high degree of swelling is reached. The plasticization increases the mobility of the polymer chains, allowing the formation of ordered regions during the sorption process and

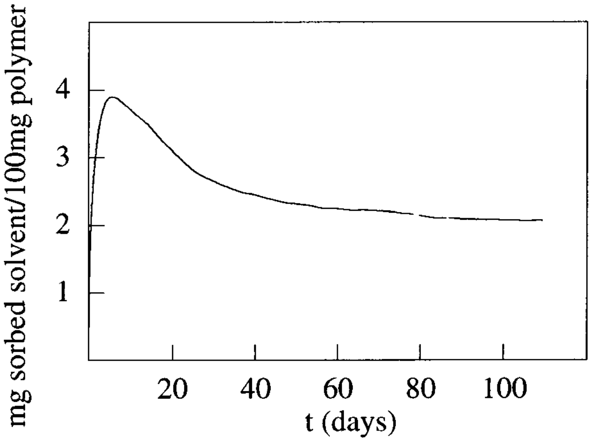

Figure 5. Overshoot phenomena in a sorption experiment using toluene and a 50/50 PECH/PMA membrane at 30 °C.

rejecting the solvent from these regions. However, our commercial PECH was atactic, and crystallization was not expected. To check the possibility of ordered regions after the sorption experiments, differential scanning calorimetry was employed, and no melting peaks were found.

Although most of these types of effects are usually described in glassy polymers, overshoots in rubbery polymers are also reported in the literature.[43-46] For instance, in the case of the poly(ethyl methacrylate)[43] the sorption overshoots were found in experiments at temperatures above the glass transition temperature of the polymer, and no crystallization was found. As in glassy polymers, the overshoot is related to the relaxation processes of the polymer chains. This is thought to be the cause of the overshoots reported in this work.

At high activities, the velocity of the solvent diffusion in the polymer is faster than the chain movements. This fast sorption stresses the polymeric chains, promoting relaxation processes facilitated by the plasticization effect of the sorbed solvent. The consequence of these structural rearrangements is a decrease in the solvent solubility and the appearance of the overshoots in the sorption kinetics. At lower activities, the solvent uptake is not very fast, so the effect is smaller.

However, the major limitations in these experiments in order to calculate B_{23} were not only the long times required to attain the equilibrium but also the difficulties to establish whether a true equilibrium has been achieved or not. This means that the determined B_{23} would be subjected to a large error. In fact, more than 10 days was needed in some runs, as is shown in Figure 4 for 1,2-dichloroethane. Moreover, this behavior is also present when a less interacting solvent is used, as is the case of toluene, which needs more than 100 days to reach the equilibrium (see Figure 5). Because of this, we tried to found another way to obtain the B_{23} value for the comparison with IGC experiments. The sorption anomalies were found when interacting solvents were used, so we have chosen carbon dioxide (CO_2) as a less interacting molecule.

b. Gas Sorption. CO_2 seems to be an adequate gas for studies with blends. Paul et al.[31] used this gas to determine the miscibility of the system constituted by polycarbonate and a copolyester. Kato et al.[32] studied the PS/PC blend. Spencer and Yavorsky[33] compared the B_{23} of the PS/PVME system obtained by CO_2 sorption with the benzene sorption data of Kwei et al. previously mentioned.[27] The agreement between both data is good so this method could be used to obtain the polymer–polymer interaction parameter.

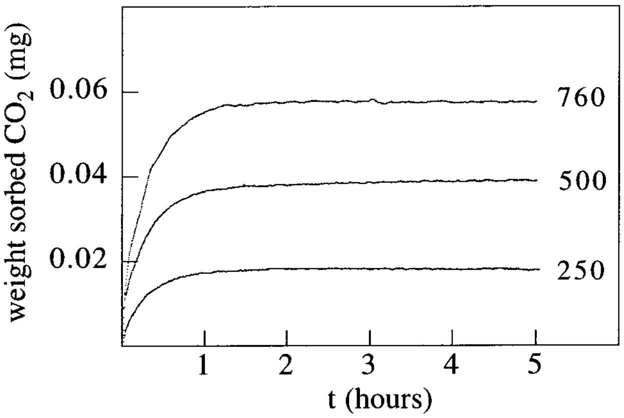

Figure 6. CO_2 sorption kinetics at different pressures in the 75/25 PECH/PMA membrane at 30 °C.

Furthermore, the blend of this work, PECH/PMA, has already been studied by CO_2 sorption at high pressures by Paul et al.[34] In their work, transport properties of several gases in the blend were reported. They used the mixing rules for miscible blends to obtain the permeabilities and diffusivities of blends of different composition.

Henry's law can describe the sorption of a simple gas in a rubbery and amorphous polymer:

$$C = k_D P \tag{2}$$

where C is gas concentration in the polymer phase, P is the pressure in the gas phase, and k_D is a solubility coefficient. The concentration, C, can be obtained from the following relation:

$$C\ (\text{cm}^3\ \text{STP}\ CO_2/\text{cm}^3\ \text{polymer}) = \frac{22.4 M_g}{44 V_p} \tag{3}$$

where M_g is the weight of the gas in the equilibrium and V_p is the volume of the membrane. Then, the values of k_D can be obtained from the slope of a C vs P plot.

For a ternary system, constituted by two polymers and the solvent, the solubility coefficient of a penetrant in a blend can be related to those in the constituent polymers by[27,31]

$$\ln k_D = \phi_2 \ln k_{D,2} + \phi_3 \ln k_{D,3} + (B_{23} V_1/RT)\phi_2\phi_3 \tag{4}$$

where B_{23} is the interaction energy density between the polymers and V_1 is the molar volume of the penetrant. As in the case of the IGC technique, this sorption procedure gives us a B_{23} value determined by means of a third component and consequently through a balance between magnitudes related to pure polymers and the polymer blend. Thus, the problems we have revised in the Introduction could be also present in these sorption measurements.

Using CO_2, both pure PECH and PMA and their blends have always achieved the equilibrium without the presence of any overshoot phenomena with experimental times substantially reduced over those of the organic solvents, as can be seen in Figure 6. The weight gain at the equilibrium was very small, and consequently, the polymer volume fraction was close to 1. Thus, the concentration conditions are approximately

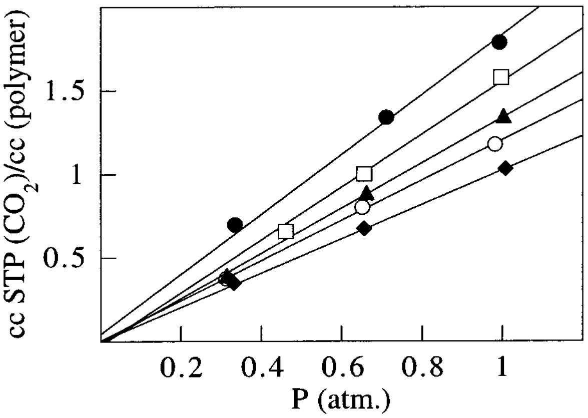

Figure 7. Sorption isotherms of CO_2 at 30 °C: (◆) pure PECH; (○) 75/25 PECH/PMA; (▲) 50/50 PECH/PMA; (□) 25/75 PECH/PMA; (●) pure PMA.

Table 3. Values of Henry's Solubility Coefficient, k_D, in the PECH/PMA System

	k_D (cm^3 STP/ cm$^3_{pol}$ at)	k_D (cm^3 STP/ cm$^3_{pol}$ at)[a]
PMA	1.791	1.981
25/75	1.433	1.708
50/50	1.350	1.374
75/25	1.206	1.153
PECH	1.026	0.946

[a] From ref 34.

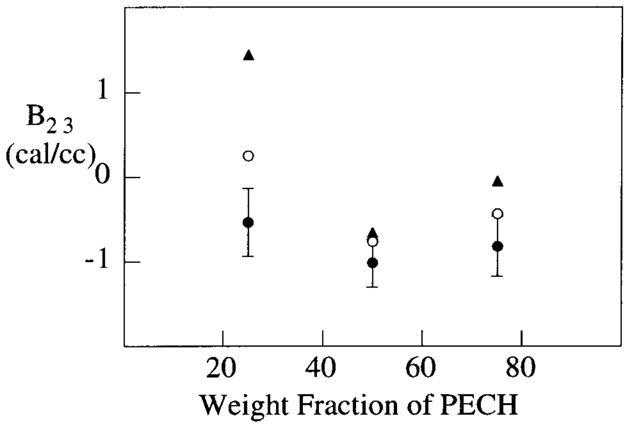

Figure 8. Comparison of the B_{23} values determined by (●) IGC and CO_2 sorption (○) in this work and from ref 34 (▲).

the same as those in IGC, and no extrapolations are needed. The sorption equilibrium data for CO_2 in the PECH/PMA system at the three used pressures are shown in Figure 7. The linearity indicates that the Henry law is followed, as was reported previously at higher pressures. The values of k_D are listed in Table 3, together with those values obtained by Paul et al.[34] The discrepancies between the values can be related to the different experimental setups and to the different molecular weight of the polymers.

Values of B_{23} obtained from eq 4 are shown in Figure 8 together with those obtained from IGC at 65 °C. In this case, as we have only used a solvent, we cannot take into account the possible influence of the solvent nature in the B_{23} value and, of course, we cannot apply a data treatment similar to the Farooque−Deshpande method. As can be seen, the trend with the PECH composition is the same in the three compositions. Except for the 25/75 blend, the differences between the other values are considered to be into the error.

Conclusions

In the past years, the optimization of the IGC technique in order to eliminate the solvent influence in the polymer−polymer interaction parameter value, as well as its confidence interval, has been one of our principal aims. In this sense, we have shown that a simple and phenomenological data treatment, the Farooque−Deshpande method,[21] gives a unique value of the polymer−polymer interaction parameter, or B_{23}. Besides, its value is in good agreement with those obtained from more sophisticated and thermodynamically rigorous methods.[11−13] In summary, we have considered the Farooque−Deshpande method as the more adequate one, and the results of the present work are in good agreement with this conclusion.

But, we have already shown that the error inherent in the IGC technique is large because the use of a third component implies that the usually small value of B_{23} is calculated by a balance of larger magnitudes (specific retention volumes). However, in this work, we have clearly demonstrated that an adequate selection of the solvents could reduce substantially the error with respect to the results obtained without any solvent selection. By an adequate selection we mean not only individual solvents with sufficiently different retention times but also a group of them covering an extended interval of the coordinates used in the Farooque−Deshpande plots. Furthermore, we consider that the calculated confidence errors are the minimum that can be achieved by the IGC technique. On the other hand, the variation of with temperature is more consistent with the LCST behavior of the PECH/PMA system than our previous ones.[21]

About the sorption measurements, the attempts with the organic solvents used in IGC have been useless due to the observed overshoot phenomena. This effect leads to the necessity of large times to attain the equilibrium with the corresponding uncertainty in having the correct B_{23} equilibrium value. However, a less interacting and smaller molecule such as CO_2 has allowed us to obtain reliable B_{23} values. We have shown that Henry's law is followed and that the calculated Henry's solubility coefficients are in a reasonable agreement with those previously reported. Moreover, both IGC and sorption techniques give similar B_{23} values. Thus, despite the dynamic nature of the IGC measurements, its results can be considered comparable with those obtained by a static technique that allows attaining a true equilibrium state.

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