



ELSEVIER

Journal of Chromatography A, 969 (2002) 245–254

JOURNAL OF  
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

# Polymer–solvent interaction parameters in polymer solutions at high polymer concentrations

C. Etxabarren, M. Iriarte, C. Uriarte, A. Etxeberría, J.J. Iruin\*

*Polymer Science and Technology Department and Institute for Polymer Materials (POLYMAT), University of the Basque Country, P.O. Box 1072, San Sebastian, Spain*

## Abstract

Molecular mass and temperature dependences of the polymer–solvent interaction parameter have been investigated in the extreme interval of high polymer concentration using inverse gas chromatography (IGC). The observed molecular mass dependence has been compared with the predictions of a theoretical model, which emphasises the role of intramolecular contacts in the polymer chain. The model reproduces reasonably well the molecular mass dependence. However, enthalpic and entropic contributions of the interaction parameter, obtained from IGC measurements at different temperatures, exhibit behaviours difficult to explain in the framework of the current models.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer–solvent interactions; Inverse gas chromatography; Flory–Huggins parameter; Polymers

## 1. Introduction

Most of the papers devoted to polymer solutions have studied these mixtures in the dilute concentration regime. The success of the Flory–Huggins theory in explaining the shape and the location of the phase diagrams in this concentration range has been claimed as one of the reasons for the important number of papers devoted both to experimental and theoretical studies of very diluted polymer solutions. Moreover, the characterisation of the molecular mass and its distribution of the polymeric materials, as well as their conformational properties, can be also in the origin of the interest for this concentration regime.

However, the opposite concentration range is also very interesting in some polymer applications. For

instance, the transport of a non-polymeric molecule through a polymer is a complex mechanism involving solubility and diffusion of the penetrant in the polymer matrix. These transport properties are relevant in applications such as barrier polymers [1], polymeric membranes for different types of separations [2], in the kinetics of heterogeneous polymerisations [3] in which the monomer or a solvent can penetrate the polymer being generated or, finally, in eliminating traces of volatile organic compounds (VOCs) in polymeric raw materials.

The Flory–Huggins interaction parameter is the key parameter in modelling the solubility of a liquid or vapour in a rubbery polymer. In order to calculate interaction parameters, the easiest alternative is the Van Laar–Hildebrand equation:

$$\chi = \left( \frac{V_M}{RT} \right) \cdot (\delta_m - \delta_p)^2 + \beta \quad (1)$$

where  $V_M$  is the molar volume of the penetrant,  $\delta$  is

\*Corresponding author. Fax: +34-943-212-236.

E-mail address: [popirsaj@sq.ehu.es](mailto:popirsaj@sq.ehu.es) (J.J. Iruin).

the solubility parameter and  $\beta$  is a constant, which accounts for entropic effects (it is often approximated by 0.34). Solubility parameters can be obtained from the vapourisation enthalpy in the case of monomeric liquids and by different group contribution methods or swelling experiments in the case of the polymers. In general, this provides a single and characteristic  $\chi$  parameter for a polymer–solvent pair. More refined approximations have introduced other temperature dependences of the  $\chi$  parameter using temperature dependent equations for the solubility parameters of monomer and polymer. But different semi empirical parameters are required for every component.

Different experimental results have shown that the interaction parameter depends on the temperature [4], the concentration [5] and, perhaps, on the molecular mass of the polymer [6]. The concentration dependence has been reasonably explained after the consideration of the different compressibilities (or free volumes) of the components. Different models have used equation-of-state data of the components and introduced mixing rules that provide concentration dependences. In most cases, the models reproduce the experimental behaviour from dilute to high concentrated solutions. In any case, such concentration dependence is not relevant in applications such as those above mentioned, where the polymer concentration tends to a weight or volume fraction close to unity.

A parabolic dependence of  $\chi$  with temperature is necessary in order to explain the lower and upper critical solution temperatures characteristic of most of the polymer solutions. In fact, there are experimental evidences of such type of dependence [4,7] although because of the limitations imposed by the degradation of the polymer and the freezing point of the solvent, a limited temperature range can be studied and only a part of this parabolic curve is usually evidenced. In principle, this dependence could be possible in considering free volume effects [8], although in other approaches to the interaction parameter, a  $1/T$  dependence, similar to that originally introduced in the Flory–Huggins treatment, has been used.

Molecular mass dependence of the interaction parameter has been a recurrent subject in the polymer literature, and more recently Petri et al. [9] have

reported new experimental results which seem to indicate that there is a real molecular mass dependence of  $\chi$ , especially in the range of moderately concentrations [10].

This molecular mass dependence has been considered in a recently reported new model for non-dilute polymer solutions. Coleman and Painter have systematically studied the number of hydrogen bonds found in mixtures of low-molecular-mass molecules, homopolymer blends, polymer solutions, random copolymers and random copolymer–homopolymer blends [11]. From their experimental results, mainly obtained by Fourier transform infrared spectroscopy (FT-IR), significant deviations from the random contacts in these mixtures were encountered and attributed to chain connectivity effects, which are the result of both local and long-range effects. In a later paper, Painter et al. [12] extended the idea of the connectivity effects to polymer solutions without hydrogen bonding.

Summarising their main results [12], the Flory–Huggins interaction parameter can be expressed as:

$$\chi_{\text{FH}} = \frac{(1-\gamma)^2}{(1-\gamma\phi_2)^2} \cdot (\chi_0/T) - \frac{1}{\phi_2^2} \cdot \left[ \left( \frac{1}{\gamma} \right) \ln(1-\gamma\phi_2) + \phi_2 \right] \quad (2)$$

where the first term is the enthalpic part of the interaction parameter and the second is the entropic one. In inverse gas chromatographic (IGC) measurements, where the volume fraction of the polymer tends to unity, the above equation is simplified to:

$$\chi_{\text{FH}} = \left( \frac{\chi_0}{T} \right) - \left[ \left( \frac{1}{\gamma} \right) \ln(1-\gamma) + 1 \right] \quad (3)$$

where the first term introduces the enthalpic part as a function of  $1/T$ ,  $\chi_0$  being a constant and  $\gamma$  is expressed by the equation:

$$\gamma = \gamma_i + (1-\gamma_i)\gamma_s \quad (4)$$

where  $\gamma_s$  is the fraction of the intrachain contacts and:

$$\gamma_i = \left( \frac{2}{z} \right) \cdot \left( 1 - \frac{1}{m} \right) \quad (5)$$

where  $z$  is the coordination number and  $m$  the

number of segments of the polymer having the solvent molar volume.

Computer simulations [13] have shown that the fraction of intrachain contacts is a function of this number of segments:

$$\gamma_s = a - \frac{b}{m^{0.5}} \quad (6)$$

where  $a$  and  $b$  are constants.

In the following pages we will compare these equations with the experimental results obtained by IGC using different polystyrene (PS) standards, which cover the low molecular mass range.

The problem of the temperature dependence of the interaction parameter will be considered in this set of PS standards as well as other polymeric materials. For example, polyisobutylene (PIB)–benzene solutions have been repeatedly studied along the last 40 years because of their particular phase diagrams, enthalpies of mixing, etc. They are interesting mixtures for a detailed discussion about the entropic and the enthalpic contributions to the Flory–Huggins interaction parameter, directly derived from its temperature dependence.

## 2. Experimental

Standard PS samples of different molecular mass were purchased from Scientific Polymer Products (Ontario, New York, USA). Molecular mass and polydispersity are detailed in Table 1. For every molecular mass, a packed column was prepared according to a method previously described [7]. Chloroform was used as casting solvent and Chromosorb W, 80–100 mesh, as support, both provided by Sigma–Aldrich (Alcobendas, Spain). Table 1 also includes the main features of the PS packed columns used in this work.

Three different solvents, representative of different types of interactions, have been used: *n*-decane, toluene and chlorobenzene. The purity was higher than 99% and they were used without further purification (Aldrich, Alcobendas, Spain).

A sample of polyisobutylene (Aldrich) with a mass-average molecular mass of 450 000 was used to prepare an IGC column, using Fluoropack 80

Table 1  
Characteristics of the packed columns containing different PS samples

$M_n$	$M_w/M_n$	Coating (%)	Stationary phase mass (g)
680	1.12	10.42	0.4933
1180	1.10	10.01	0.4772
2145	1.10	10.19	0.4660
3400	1.09	10.10	0.4888
6100	1.05	10.32	0.4610
8000	1.05	9.72	0.4791
12 400	1.06	9.43	0.4561
15 800	1.05	9.96	0.4847
18 100	1.07	10.87	0.5369
28 900	1.01	9.88	0.4844
33 000	1.06	9.67	0.4697

$M_n$  = number-average molecular mass;  $M_w$  = mass-average molecular mass.

(Varian, Basel, Switzerland) as support. Due to the rubbery condition of the sample, the preparation of the column was slightly different to that described above. After eliminating the solvent (benzene, Aldrich) used to mix polymer and support, the resulting sticky sample was mixed with solid carbon dioxide in order to get the adequate particle size for compacting the column. The percentage of the polymer coating in the stationary phase was 10.94%. The quality of the solvent, benzene, used both in preparing the column and in the IGC measurements, was similar to that of the solvents used in the PS columns.

Measurements were carried out in a modified Sigma 300 Perkin-Elmer (Norwalk, CT, USA) gas chromatograph equipped with a flame ionisation detector. Nitrogen was used as carrier gas. Methane gas was used as a non-interacting marker to correct the dead volume in the column. The chromatograms were monitored in a Perkin-Elmer integrator, Model 59. A minimum of four measurements were taken for every molecular probe and for each temperature in all columns. Pressures at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures [14]. Flow-rates, measured at the end of the column with the aid of a bubble flowmeter were between 5 and 10  $\mu\text{l}/\text{min}$ , depending on the column.

Columns were conditioned at temperatures above  $T_g$  for ca. 48 h prior the use, while nitrogen was

flushed through the column in order to achieve an adequate equilibrium. Small amounts of the solvents (less than 0.01 ml), including a small amount of the marker (methane) were injected manually with a 10-ml Hamilton syringe.

Specific retention volumes were calculated using:

$$V_g^0 = \Delta t \cdot \left( \frac{F}{\omega_L} \right) \cdot \left( \frac{273.16}{T_r} \right) \cdot \left( \frac{3}{2} \right) \cdot \left[ \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \right] \quad (7)$$

where  $\Delta t$  is the difference between the experimental retention times of the probe and of the marker,  $F$  is the flow-rate of the carrier gas at the temperature  $T_r$  and atmospheric pressure;  $\omega_L$  is the mass of the stationary phase and  $P_i$  and  $P_o$  are the inlet and outlet pressures, respectively.

Flory–Huggins interaction parameters can be calculated from specific retention volumes  $V_g^0$  as:

$$\chi_{FH} = \ln \left( \frac{273.16 R v_2}{V_g^0 V_1 P_1^0} \right) - 1 + \left( \frac{V_1}{M_2 v_2} \right) - \left[ \frac{(B_{11} - V_1)}{RT} \cdot P_1^0 \right] \quad (8)$$

where  $R$  is the gas constant,  $M_2$  and  $v_2$  the molecular mass and the specific volume of the polymer and  $V_1$ ,  $B_{11}$  and  $P_1^0$  the molar volume, second virial coefficient and vapour pressure of the solvent at the experimental temperature, respectively. It is important to remark that the term containing the molecular mass of the polymer (which has been neglected in some IGC studies) is very important here, given the very low molecular masses used in some columns. This is also the case of the term containing the second virial coefficient  $B_{11}$ . If neglected, it would affect the calculations of the enthalpic and entropic components of the interaction parameter described below.

In order to have interaction parameters at the exact temperatures sometimes used in the text (140, 150, etc.), specific retention volumes ( $V_g$ ) at the experimental conditions were fitted to linear plots of  $\ln V_g$  vs.  $1/T$ . For instance, in the PS columns, measurements were performed at 137.6, 142.5, 147.4 and 152.2 °C. Data at other temperatures between 120

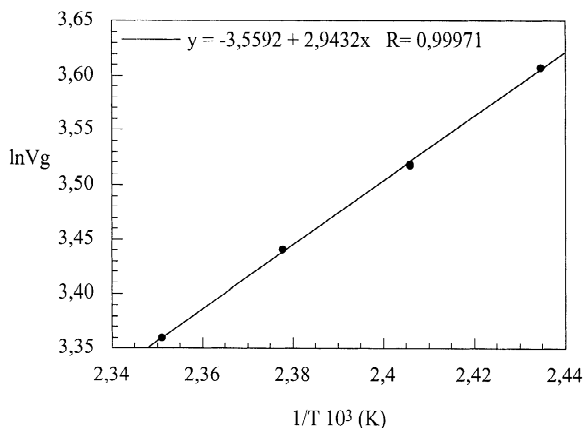


Fig. 1.  $\ln V_g$  against  $1/T$  for the PS 18 700–chlorobenzene column.

and 160 °C were obtained from plots such as those presented in Fig. 1.

### 3. Results and discussion

Fig. 2 illustrates the observed behaviour of the Flory–Huggins interaction parameter measured by IGC (i.e., at infinite dilution of the solvent) with the

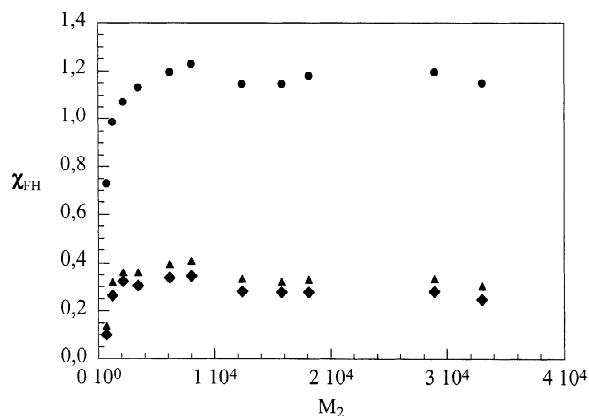


Fig. 2. Molecular mass dependence of the interaction parameter at 137.6 °C in mixtures of PS and *n*-decane (●), toluene (▲) and chlorobenzene (◆).

molecular mass of the polymer at one of the investigated temperatures (137.6 °C).

As can be observed, values for *n*-decane are higher than those of the other two solvents, indicating the low solubility capacity of this alkane. The observed tendency with the polymer molecular mass is identical for the three solvents. The same behaviour was observed in the rest of the investigated temperatures. It can be concluded that above a molecular mass of about 5000, the molecular mass does not alter the polymer–solvent interaction parameter. This result supports the previous conclusions of Petri et al. [9] and Schuld and Wolf [10] using a new experimental procedure to measure activities of the solvent, based on conventional gas chromatography and a headspace accessory (HS-GC). Using higher molecular masses and different concentrations, they deduced that the molecular mass dependence is more pronounced in the moderately concentrated solutions, tending to diminish at higher polymer concentrations such as those of IGC experiments. As is shown in Fig. 2, our IGC results indicate that only at very low molecular masses the interaction parameters decrease in a significant manner.

The equations previously introduced and derived from the interchain contacts model [12] can reproduce reasonably well the exhibited behaviour. As previously mentioned, the fraction of intrachain contacts is a function of the number of polymer segments (see Eq. (6)). Previous simulations [13] have shown that  $\gamma_s$  tends to 0.38 in a cubic lattice when the molecular mass (or the number of segments) tends to infinite. Consequently, this fraction can be written as:

$$\gamma_s = 0.38 + \frac{b}{m^{0.5}} \quad (9)$$

The molecular mass dependence of  $\gamma_i$  is comparatively less important because it contains the term  $1/m$ . So, in a first approximation we will rewrite the previous definition of this parameter, Eq. (5), as:

$$\gamma_i = \frac{2}{z} \cdot \left(1 - \frac{1}{m}\right) \approx \frac{2}{z} \quad (10)$$

If, as usual in this type of calculations [12], we use

a value of  $z=9$ , then  $\gamma_i=0.222$  and the  $\gamma$  term becomes:

$$\gamma = \gamma_i + (1 - \gamma_i)\gamma_s = 0.222 + 0.778\gamma_s \quad (11)$$

or:

$$\gamma = 0.222 + 0.778\gamma_s = 0.222 + 0.778 \cdot \left[0.38 + \frac{b}{m^{0.5}}\right] = 0.52 + \frac{0.778b}{m^{0.5}} \quad (12)$$

If we introduce this expression in the equation of the interaction parameter, Eq. (3), the molecular mass dependence of the interaction parameter depends on two adjustable parameters  $\chi_0$  and  $b$ , which can be determined by fitting experimental results to this equation. Fig. 3 shows such type of fitting in PS–*n*-decane solutions at 137.6 °C. The resulting adjustable parameters were:

$$b = -1.86 \quad \text{and} \quad \chi_0 = 372$$

Similar fittings can be performed with data of PS–toluene and PS–chlorobenzene solutions. At 137.6 °C the resulting parameters were (–0.428, –9.01) for toluene and (–0.389, –32.4) for chlorobenzene. It is important to remark that this implies that whereas the enthalpic part in PS–*n*-decane solutions is positive (0.905), it results –0.022 and –0.079 in toluene and chlorobenzene, respectively, indicating better interactions, as expected.

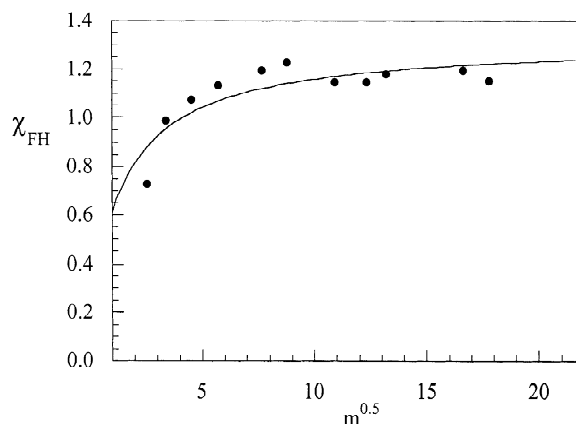


Fig. 3. Fitting the model to the experimental dependence of the interaction parameter on the molecular mass. See text.

It is also remarkable the fact that very similar values of  $b$  and  $\chi_0$  to those of PS- $n$ -decane were obtained by Painter et al. [12] in adjusting phase diagrams of PS-cyclohexane solutions. These values were used to simulate the concentration dependence of the interaction parameter of these mixtures [12], in excellent agreement with experimental results. So, it seems that the model is consistent in reproducing such type of dependencies.

### 3.1. Temperature dependence of the Flory–Huggins interaction parameter at high polymer concentrations

According to Eq. (3), extrapolated to the IGC limit, the model we are using predicts that the enthalpic and entropic components of the Flory–Huggins interaction parameter can be expressed as:

$$\chi_H = \frac{\chi_0}{T} \quad \chi_S = - \left[ \left( \frac{1}{\gamma} \right) \ln(1 - \gamma) + 1 \right] \quad (13)$$

In previous pages, we have fitted experimental results of  $\chi_{FH}$  vs. molecular mass in order to have the two adjustable parameters implied in these equations. The  $1/T$  dependence of the enthalpic part is similar to that introduced in the original Flory–Huggins formulation.

Experimental values of these two contributions can be obtained from IGC data of the interaction parameter at different temperatures. From these data, the enthalpic component of the Flory–Huggins interaction parameter can be calculated as:

$$\chi_H = \frac{1}{T} \cdot \left[ \frac{\partial \chi_{FH}}{\partial \left( \frac{1}{T} \right)} \right] \quad (14)$$

and, corresponding:

$$\chi_S = \chi_{FH} - \chi_H \quad (15)$$

Fig. 4 shows the IGC experimental data of the interaction parameter as a function of the temperature for different PS molecular masses. Although, in a first approximation, the experimental data seem to follow a nearly linear dependence on  $1/T$ , as expressed in Eq. (3), a close inspection shows that, in all cases, data can be better fitted by a parabola. As previously mentioned, this is the general behaviour

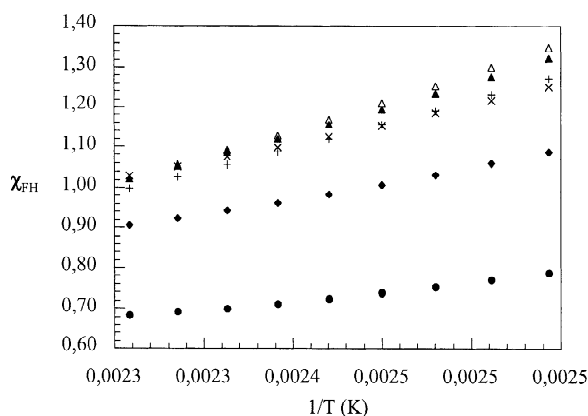


Fig. 4. Temperature dependence of the interaction parameter. PS- $n$ -decane mixtures at various PS molecular masses: 680 (●), 1180 (◆), 3400 (×), 18 100 (▲), 12 400 (+), 28 900 (△).

we expect in polymer–solvent solutions if the possibility of both lower (LCST) and upper (UCST) critical solution temperature phase separations is considered. Due to the restricted temperature range we are considering, only a part of this parabola is experimentally evidenced.

Moreover, in Fig. 5 we are comparing the experimental data of the interaction parameter at various temperatures for the PS sample having a molecular mass of 33 000 and those calculated using Eq. (3) and the fitting parameter  $\chi_0 = 372$  previously obtained. The figure clearly expressed the discrepancies between experimental and theoretical values.

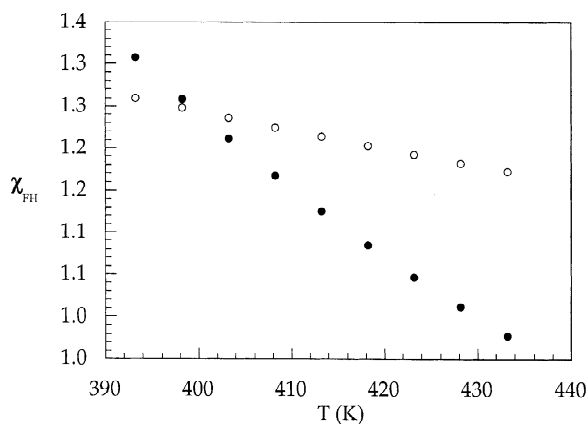


Fig. 5. A comparative between experimental (●) and theoretical (○) evolutions of the interaction parameter of a mixture PS (33 000)- $n$ -decane with the inverse of the temperature (K).

Using Eqs. (14) and (15) the enthalpic and entropic components of the interaction parameters of mixtures of PS–*n*-decane have been calculated for the different PS samples used as stationary phases of our chromatographic columns. Data are summarised in Fig. 6.

The figure clearly shows that these components have, in a qualitative sense, the same dependence on the molecular mass than the interaction parameter. Only at very low molecular masses the entropic and enthalpic components are sensitive to the molecular mass of the sample, although the tendency is just the opposite.

As previously mentioned, a value of 0.905 for the enthalpic contribution was obtained as a consequence of the fitting procedure we have used with the experimental dependence of the interaction parameter with the molecular mass. However, the experimental values of the enthalpic contribution rapidly increase up to values between 2.5 and 4.0, significantly higher than 0.90. Correspondingly (see Eq. (15)) the values of  $\chi_S$  are negative and between  $-1.5$  and  $-2.5$  when the model we are using predicts an entropic contribution between 0.2 and 0.3.

A comment is here pertinent about the accuracy of such type of experimental determinations. In the origins of the IGC technique, Hammers and DeLigny [15] pointed out the inherent difficulties in calculating the enthalpic and entropic contributions of the interaction parameter when the temperature depen-

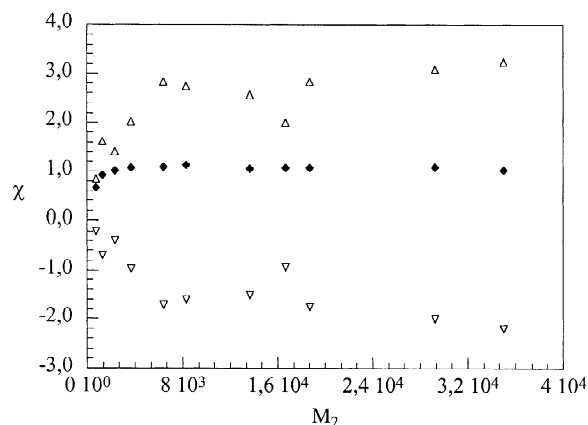


Fig. 6. Molecular mass dependence of  $\chi_{FH}$  ( $\blacklozenge$ ),  $\chi_H$  ( $\triangle$ ) and  $\chi_S$  ( $\nabla$ ). PS–*n*-decane at 120 °C.

dence of  $\chi_{FH}$  is low. This is the case of our results using toluene and chlorobenzene, where the variation of  $\chi_{FH}$  in the temperature interval here studied is less than 0.1. For this reason we have restricted our previous comparison between theory and experiments to the results for the PS–*n*-decane mixture.

But, in order to confirm results such as those of the PS–*n*-decane mixture, we have repeated IGC measurements previously reported [16] by our group. In that paper, we compared static (vapour pressure osmometry) and dynamic (IGC) methods as experimental techniques in obtaining polymer–solvent interaction parameter data. In that work we used a mixture that seemed to us particularly versatile: the one formed by PIB and benzene. This mixture has been repeatedly used as a testing system in basic studies of polymer–solvent thermodynamics [8]. It was also one of the mixtures Painter et al. [12] used in order to test the model we have previously mentioned. In a similar manner to that of PS–cyclohexane mixture, using phase separation diagrams with different PIB molecular masses, they adjusted the required parameters of the model. These parameters successfully reproduced the interaction parameter–concentration relationship experimentally reported by different authors.

Fig. 7 reports experimental (IGC) and theoretical values of a mixture of PIB (molecular mass 450 000) with benzene in an extended range of temperatures.

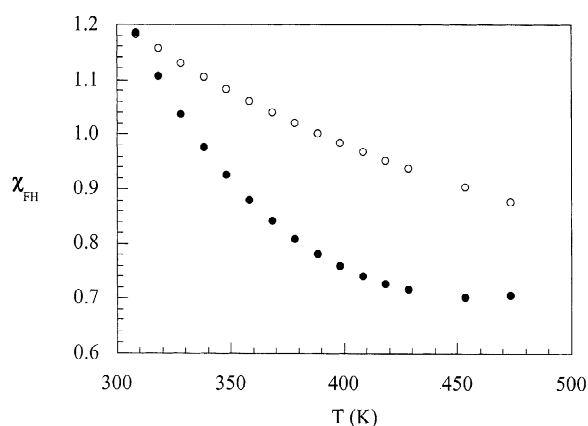


Fig. 7. Experimental ( $\bullet$ ) (IGC) and theoretical ( $\circ$ ) dependence of the PIB–benzene mixture with the temperature. The theoretical curve is calculated using fitting parameters of the Painter et al. model, taken from Ref. [12].

The theoretical line is a consequence of the  $1/T$  dependence implicit in the model.

However, it is important to note different characteristics of the experimental data. First, the value near 300 K (1.2) is similar to that obtained by extrapolating interaction parameters at different concentrations [5]. It is also important the well-defined parabolic tendency observed in the experimental data, tending to a minimum at the temperature of about 450 K, an indication of the nearly athermal character of this mixture at this temperature. Lidell and Swinton [17] obtained heats of mixing at very dilute polyisobutylene–benzene mixtures. At 298 K, the heat of mixing was clearly endothermic (1100 J/mol) but decreasing when temperature increased. A zero value was obtained in the vicinity of 440 K. Although in the opposite concentration regime, the coincidence is remarkable. On the other side, both UCST (298 K) and LCST (534 K) have been reported for polyisobutylene–benzene mixtures [8,18]. The curve of Fig. 7 is qualitatively consistent with this behaviour.

If the experimental data are conveniently managed using Eqs. (14) and (15) the enthalpic and entropic components of the interaction parameter can be calculated as a function of the temperature. Fig. 8 shows such kind of behaviour. In this case, it is interesting to note that according to the marked parabolic tendency of the precedent figure, the

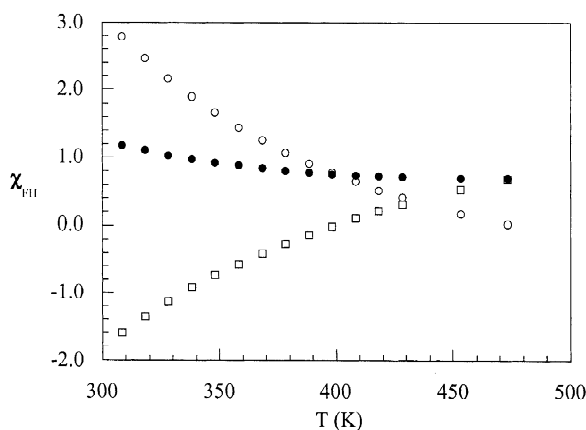


Fig. 8. Temperature dependence of the interaction parameter (●) and its entropic (□) and enthalpic (○) components. PIB–benzene, IGC experimental data.

entropic component changes from negative to positive values when the temperature increases. This change occurs in the vicinity of 400 K and, after that, the entropic component continues to increase up to 0.6 in the limit of the temperature interval studied.

Such high values, especially at low temperatures are clearly different of those determined in other concentration regimes. For instance in the seminal paper of Eichinger and Flory [5],  $\chi_H$  seems to vary between 0.3 and 1.0 when the volume fraction of the polymer goes from 0.3 to 0.75. The enthalpic component is less than the interaction parameter, so the entropic part is positive and small. However, the error bars in the determinations there included were very large and, in fact, at high polymer concentrations, the reduced partial molar entropy could be greater than the combinatorial partial molar entropy, thus giving negative  $\chi_S$  values. But this result is considered implausible by the authors [5] in the framework of its theory.

Similar inconclusive comments can be done on the light of another free volume theory, the Lattice Fluid theory, developed by Sanchez and Lacombe. In their paper [8] they gave equations (B.14 and B.15 in Appendix B) for the enthalpic and the entropic part of the interaction parameter at the limit of the high polymer concentration. The model needs to adjust a dimensionless parameter,  $\zeta$ , which characterises the deviation of the characteristic pressure of the mixture from that calculated as the geometric mean of those of the components. In the above mentioned paper, the authors used the heats of mixing measured by Lidell and Swinton [17] in order to adjust the  $\zeta$  parameter, although they remarked the sensitivity of the calculated thermodynamic magnitudes on the value of this parameter.

We have calculated interaction parameters from their enthalpic and entropic components at different temperatures, using a value of  $\zeta=0.975$  that reasonably reproduced the interaction parameter at 298 K, a temperature at which our IGC data and those reported in the Eichinger and Flory paper [5] are very similar. Fig. 9 shows these calculations.

There are clear discrepancies between Figs. 8 and 9. Theoretical data of the two components seem to diverge in the vicinity of the LCST whereas in the UCST interval, the entropic part remains small and positive. Our experimental results, however, seem to



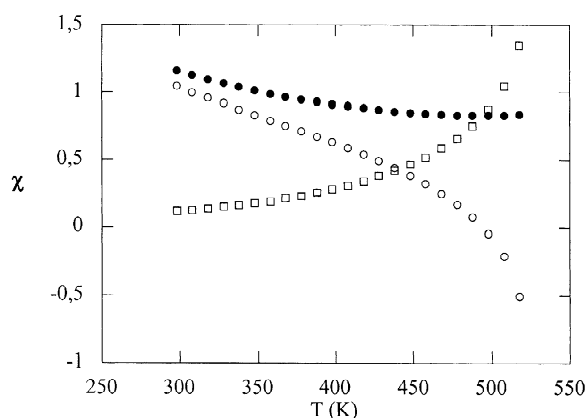


Fig. 9. Temperature dependence of the interaction parameter at the IGC concentration limit and its enthalpic and entropic components. Symbols as in Fig. 8.

indicate that both components of the interaction parameter diverge at low and very high temperatures. At low temperatures, the enthalpic component is positive (as the heats of dilution in Ref. [17]) and the entropic negative, whereas the opposite behaviour occurs at high temperatures. In conclusion, it seems that both components clearly and rapidly diverge at temperatures far above and below the athermal situation. In both situations, there is a clear mutual dependence of both components, giving reasonable low values of the interaction parameter in spite of

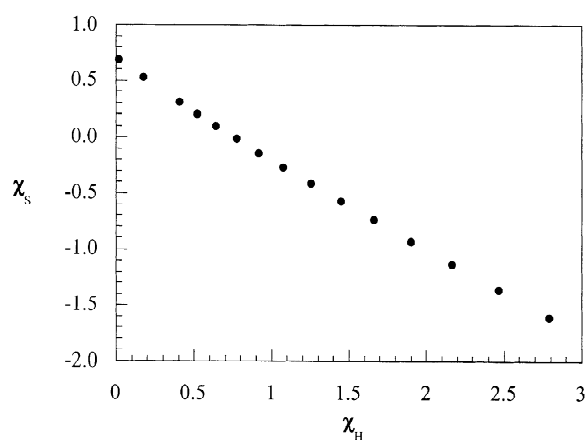


Fig. 10. Interdependence of the enthalpic and the entropic components of the interaction parameter. PIB–benzene, IGC experimental data.

their higher values. In fact, a linear dependence between both components was empirically found (see Fig. 10).

This behaviour has been repeatedly reported recently in literature [9,10], although in these papers the authors have obtained this dependence with values of  $\chi_S$  and  $\chi_H$  experimentally determined at different concentrations and the same temperature interval. It is also interesting to note that if their measurements are extrapolated at high polymer concentrations (IGC regime) both components take high absolute values, similar to those reported here, and positive or negative depending on the studied mixture.

#### 4. Conclusions

The experimental results here reported and other recently published [9,10] seem to indicate that a description of the behaviour of the interaction parameter of polymer–solvent systems at very high polymer concentration is still lacking. Part of the problem arises from the difficulty in having measurements from independent experimental techniques in such concentration interval. For instance, one of the possibilities to have interaction parameters at high polymer concentrations is to follow sorption kinetics by gravimetric experiments (spring or Cahn balances). But, in order to have liquid–liquid equilibrium data, the polymer should be in liquid state. For polymers with moderate or high glass transition temperatures, this implies experimental temperatures not accessible to the current sorption experimental setups. Experiments based on the combination of GC and a headspace accessory, recently introduced [9], are difficult to carry out at polymer volume fraction higher than 0.8, because of the difficulties in assuring a true thermodynamic equilibrium. IGC seems to be the only experimental possibility to have equilibrium data at such high concentrations. But the dynamic character of the technique has been repeatedly criticised.

Theoretical approaches have traditionally omitted the limit of the concentration regime where the IGC is operative. A close inspection of well-known Sanchez–Lacombe model (which includes calcula-

tions in this interval) does not match the tendency observed in this work.

From the results here discussed (using IGC and HS-GC as experimental techniques) it seems that two main conclusions need to be checked in other works. The interaction parameter seems to depend on the molecular mass at moderate concentration, this dependency vanishing at very high polymer concentration. In the other hand, a parabolic tendency of the interaction parameter with the temperature is clearly evidenced by IGC measurements and is consistent with the generic existence of both UCST and LCST for polymer solutions. Depending on the absolute values of the interaction parameter and their variations with temperature, the enthalpic and the entropic components could have different values and signs in the temperature interval experimentally available.

## 5. Nomenclature

$V_M$	Molar volume
$\delta$	Solubility parameter
$\beta$	A constant
$\chi$	Interaction parameter
$\chi_0$	A constant
$\gamma$	$\gamma = \gamma_t + (1 - \gamma_t)\gamma_s$
$\gamma_s$	Fraction of the intrachain contacts
$\gamma_t$	$\gamma_t = \left(\frac{2}{z}\right) \cdot \left(1 - \frac{1}{m}\right)$
$z$	Coordination number
$m$	Number of segments of the polymer having the solvent molar volume
$a$	A constant
$b$	A constant
$\Delta t$	Difference between the experimental retention times of the probe and of the marker
$F$	Flow-rate of the carrier gas
$T_r$	Temperature
$\omega_L$	Mass of the stationary phase
$P_i$	Inlet pressure
$P_o$	Outlet pressure
$T_g$	Glass transition temperature
$V_g^0$	Specific retention volume
$R$	The gas constant
$M_2$	Molecular mass of the polymer
$v_2$	Specific volume of the polymer
$V_1$	Molar volume of the probe
$B_{11}$	Second virial coefficient of the solvent

$P_1^0$	Vapour pressure of the solvent
$\chi_{FH}$	Flory–Huggins interaction parameter
$\chi_s$	Entropic contribution to the interaction parameter
$\chi_H$	Enthalpic contribution to the interaction parameter
$\zeta$	Dimensionless parameter

## Acknowledgements

This work has been supported by the CICYT (project No. MAT98-0530) and the University of the Basque Country (project No. 203215-13519/2001). C.E. also thanks the Gobierno de Navarra for a Ph.D. grant.

## References

- [1] W.J. Koros (Ed.), Barrier Polymers and Structures, ACS Symposium Series, No. 423, American Chemical Society, Washington, DC, 1990.
- [2] D.R. Paul, Y.P. Yampol'skii (Eds.), Polymeric Gas Separation Membranes, CRC Press, Boca Raton, FL, 1991.
- [3] J.J.C. Samson, G. Weickert, A.E. Heerze, K.R. Westerterp, AIChE J. 44 (1998) 1424.
- [4] N. Kuwahara, S. Saeki, T. Cuiba, M. Kaneko, Polymer 15 (1974) 777.
- [5] B. Eichinger, P.J. Flory, Trans. Faraday Soc. 64 (1968) 2053.
- [6] E. Nies, R. Koningsveld, L.A. Kleintjens, Prog. Colloid Polym. Sci. 71 (1985) 2.
- [7] C. Uriarte, M.J. Fernandez-Berridi, J.M. Elorza, J.J. Iruin, L.A. Kleintjens, Polymer 30 (1989) 1493.
- [8] I.C. Sanchez, R.H. Lacombe, Macromolecules 11 (1978) 1145.
- [9] H.M. Petri, N. Schuld, B.A. Wolf, Macromolecules 28 (1995) 4975.
- [10] N. Schuld, B.A. Wolf, J. Polym. Sci., Part B: Polym. Phys. 39 (2001) 651.
- [11] M.M. Coleman, P.C. Painter, Prog. Polym. Sci. 20 (1995) 1.
- [12] P.C. Painter, L.P. Berg, B. Veytsman, M.M. Coleman, Macromolecules 30 (1997) 7529.
- [13] P.C. Painter, B. Veytsman, S. Kumar, S. Shenoy, J.F. Graf, Y. Xu, M.M. Coleman, Macromolecules 30 (1997) 932.
- [14] A. Etxebarria, J. Alfageme, C. Uriarte, J.J. Iruin, J. Chromatogr. 607 (1992) 227.
- [15] W.E. Hammers, C.L. DeLigny, J. Polym. Sci. Polym. Phys. Ed. 12 (1974) 2065.
- [16] M.J. Fernandez-Berridi, I. Eguiazabal, J.M. Elorza, J.J. Iruin, J. Polym. Sci. Polym. Phys. Ed. 21 (1983) 859.
- [17] A.H. Lidell, F.L. Swinton, Discuss. Faraday Soc. 49 (1970) 115.
- [18] J.M. Bardin, D. Patterson, Polymer 10 (1969) 247.