

# Determination of the Diffusion Coefficients of Organic Solvents in Polyepichlorohydrin: A Comparative Study of Inverse Gas Chromatography and Sorption Methods

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**ABSTRACT:** The diffusivity of organic solvents in polyepichlorohydrin was studied with two different experimental setups: inverse gas chromatography (IGC) with packed columns and sorption measurements in gravimetric experiments monitored in a Cahn electrobalance. The aim of this work was to test the possibility of solving an inherent problem in the data reduction of IGC measurements, that is, the necessity of characterizing the morphology of the polymer coated on the support (usually given in the so-called geometric factor of the column). Temperatures between 35 and 65°C were used in the IGC experiments, whereas the sorption measurements were performed between 30 and 40°C. Glass beads were used as supports in IGC for obtaining data concerning the variation of the plate height with the average

gas velocity, with which the use of the Van Deemter equation allowed the determination of the diffusion coefficient if the geometric factor was known. In the sorption experiments, the diffusion coefficients at different penetrant activities were directly measured. For their extrapolation within the same concentration range used for IGC (infinite dilution of the penetrant), the theoretical model of Vrentas and Duda was used. By a combination of sorption and IGC experiments, the geometric factor of an IGC column could be adjusted, and this allowed the determination of the diffusion parameters of any other solvent in the same column. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2216–2223, 2003

**Key words:** diffusion; chromatography

## INTRODUCTION

The use of polymer materials for different applications, such as the packaging of foods and chemicals, medical drugs, and biosensors, implies the necessity of knowing the different mechanisms that govern the transport of small molecules through polymer films. According to the so-called solution-diffusion mechanism, gas permeation is a complex process controlled by both the diffusion (a kinetic process) and solution (an equilibrium process) of the penetrant gas or vapor molecules in the polymer. From a technological point of view, the transport properties are usually quantified by the permeability coefficient ( $P$ ), which is written as the product of the effective diffusion ( $D$ ) and solubility ( $S$ ) coefficients:

$$P = DS \quad (1)$$

The gas sorption or solubility in a polymer is a thermodynamic equilibrium process directly related to the change in the free energy associated with the mixing

process. The diffusion process is related to the rate of a penetrant going through a membrane. There are many experimental techniques for obtaining the parameters related to these transport processes. Among them, inverse gas chromatography (IGC) is very versatile and low-cost. The principle behind this technique is based on the partitioning of a volatile solvent between a mobile gas phase and a stationary polymer phase. The fundamental magnitude of this kind of measurement is the specific retention volume. It allows us<sup>1</sup> to calculate thermodynamic magnitudes related to the dissolution process, such as the partition or activity coefficients and the Flory–Huggins interaction parameters. In this kind of study, the polymer has to be above its thermal transitions to guarantee liquid–liquid equilibrium. Literature data seem to confirm the similarity between thermodynamic data obtained by IGC and other static methods such as gravimetric sorption techniques.<sup>2</sup> However, this is not the case for diffusion coefficient data.

Most reported diffusion coefficients have been measured by sorption experiments.<sup>3–8</sup> Although they allow the determination of diffusion coefficients over a relatively extended range of solvent concentration, they present some disadvantages, mainly because of the long times required for the experiments. Additional difficulties appear in the determination of the diffusion coefficient of trace amounts of a solvent in a

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polymer, a very important problem both for making and applying polymer membranes and films, or when the diffusion of the penetrant is slow. In all these cases, sorption methods become inadequate. IGC has been proposed<sup>9,10</sup> as an alternative technique for these problematic situations. IGC measurements are generally quicker and can be performed over more extended temperature ranges. Diffusion coefficients so obtained correspond to an infinite dilution regime.

The first IGC studies measuring diffusion coefficients of penetrants in polymers mainly used packed columns, in which a polymer was loaded into a column as solid particles or supported onto an inert material. In this way, Romdhane and Danner<sup>11</sup> proposed a new mathematical model for describing the chromatographic process in packed columns. A close review of different results shows some problems in getting reliable diffusion data, mainly because of the difficulties in knowing the stationary-phase morphology. This morphology can be different according to the polymer nature, the drying process, or the amount of polymer employed for preparing the column. This geometry should be known because the data reduction used to calculate diffusion coefficients by this method implies the previous assumption of a type of geometry coating.

According to Pawlisch,<sup>12</sup> these problems can be solved with capillary columns with a uniform distribution of the polymeric stationary phase on the wall. In the past, there have been many articles<sup>10-13</sup> reporting diffusion data obtained in capillary columns. However, the preparation of such a uniform morphology in capillary columns also requires a careful methodology, and in this sense, elastomeric polymers, such as the stationary phase studied in this article, or polymers with low glass-transition temperatures ( $T_g$ 's) could present more difficulties.<sup>14</sup> More recently,<sup>15</sup> a novel type of column has been proposed (rectangular, thin-channel column IGC) as an alternative to the widely used capillary columns.

In this study, we reconsidered the possibility of obtaining reliable diffusion coefficients with packed columns with glass beads. Gray and Guillet<sup>16</sup> were the first to use glass beads as supports to get uniform coatings for adequate diffusion coefficient measurements with packed columns. To solve the problem of the influence of the geometry of the coating in the calculation of these coefficients, we used sorption measurements as a way of obtaining diffusion coefficients in an independent experiment. The comparison of both types of measurements allowed us to calculate the so-called geometric factor for the IGC column, an empirical parameter giving the characteristics of the morphology of the column, and allowed its subsequent use with a variety of solvents or penetrants.

For reliable diffusion coefficients to be obtained by IGC, the polymer coating in the column must be above

**TABLE I**  
**Description of the Gas Chromatographic Column**

Length (m)	Packing	Weight of packing (g)	Polymer (%)
1.2	Glass beads 60/80 mesh	42.659	0.362

$T_g$ . This is the case for polyepichlorohydrin (PECH) in the rubbery state at ambient temperatures.

## EXPERIMENTAL

### Materials

PECH was supplied by Aldrich (Alcobendas, Spain) and used without further purification. Its number-average and weight-average molecular weights were 170,000 and 976,000, respectively, as determined by gel permeation chromatography in tetrahydrofuran (THF) at 25°C and with polystyrene (PS) standards.  $T_g$  was -23.6°C. The solutes were reagent-grade.

### IGC procedure

Chromatographic measurements were carried out in a modified Sigma 300 PerkinElmer gas chromatograph equipped with a flame ionization detector. For the preparation of a column, a weighted quantity of the polymer was completely dissolved in THF, and glass beads were added in a known quantity to provide a suitable range of support particles. The solvent was evacuated with a rotary evaporator and finally dried in a vacuum oven at 30°C for 1 week. The coated support was then packed into a stainless steel column with a 1/4-in. outside diameter by the application of a vacuum to the end. Glass wool was used to block the ends of the column. The column characteristics are shown in Table I. Nitrogen and methane were used as the carrier gas and marker, respectively. The retention times were determined by monitoring with a Hewlett-Packard model 56 integrator. The pressures at the inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention times through the James-Martin factor ( $j$ ).

A molecular probe, including a small amount of a methane marker (<0.01  $\mu$ L), was injected into the column with the aid of a Hamilton 10- $\mu$ L syringe. At least three injections were made for each probe and temperature.

Sorption measurements were performed in a Cahn D-200 electrobalance enclosed in a thermostatic chamber at the desired temperature. After the polymer films were put into the balance sorption chamber, the system was evacuated for 48 h, and after that, the solvent vapor was allowed to enter into the system at the desired activity and temperature. The sample weight changes were recorded.

PECH films for sorption measurements were prepared by the casting of chloroform solutions onto a Teflon plate. The films were dried at 40°C in a vacuum oven for 4 days. The thickness was measured with a Duo Check gauge ( $\pm 1 \mu\text{m}$ ).

### THEORETICAL BACKGROUND

Ideally, when an infinitesimal amount of a solvent is injected into a gas chromatograph, a very narrow peak should be obtained after a time that depends on the interactions between the vapor and stationary phase. However, the normal behavior is to obtain a broad asymmetrical peak. The reasons for that behavior can be directly connected to the operator (experimental conditions), to the nonlinearity of the thermodynamic process (the isothermal partition is not linear), and to the nonideality of the chromatographic process (because of the different transport processes happening in the column, such as axial diffusion in the gas phase, eddy diffusion, or probe diffusion in the liquid phase). From the shape of the chromatographic peak, it is possible to obtain information related to transport phenomena occurring in the column.

According to Van Deemter's model,<sup>17</sup> the height equivalent to one theoretical plate ( $H$ ) of a column can be calculated as follows:

$$H = A + \frac{B}{u} + Cu \quad (2)$$

where  $u$  is the flow rate;  $A$  is a constant related to eddy diffusion;  $B$  depends on the axial diffusion in the gas phase; and  $C$  depends on, among other things, probe diffusion in the liquid phase. In principle, experimental values of  $C$  obtained through an adequate treatment of  $H$  and  $u$  data can be used in the determination of the diffusion coefficient of a penetrant through a polymer. For instance, in the most favorable case, when elevated flow rates are used, the second term of eq. (2),  $B/u$ , tends to be negligible, and a plot of experimental values of  $H$  versus  $u$  should be linear with  $C$  as the slope.

$H$  is calculated from the experimental eluted peak as follows:

$$H = \left( \frac{l}{5.54} \right) \left( \frac{d}{t_r} \right)^2 \quad (3)$$

where  $l$  is the column length,  $d$  is the measured peak width at half the maximum height (in the same units as  $t_r$ ), and  $t_r$  is the retention time for the eluted solvent.

The average linear flow is given as follows:

$$u = \frac{j l}{t_m} \quad (4)$$

where  $t_m$  is the retention time of the marker.

The Van Deemter model relates  $C$  to  $D$ :

$$C = \frac{8}{\pi^2} \frac{k}{(1+k)^2} \frac{d_f^2}{D} \quad (5)$$

where  $k$  is a constant proportional to the partition coefficient and  $d_f$  is the thickness of the polymer coating. However, this equation is not valid if the coating on the support is not homogeneous and if the thickness of the film is not constant. Giddins<sup>18</sup> proposed several expressions for relating  $C$  and  $D$  that depended on parameters related to the structure of the columns and the process across the column (adsorption-desorption, etc.).

When glass beads are used as supports of the polymer coating, Giddins<sup>18</sup> proposed two types of distribution for the liquid polymer: the liquid uniformly coats the bead surface or it concentrates on the contact points between the glass beads. In the first case, Giddins obtained an expression similar to that of Van Deemter, only changing the  $8/\pi^2$  term by  $2/3$ . If the liquid is accumulated on the contact points, the following expression is obtained:

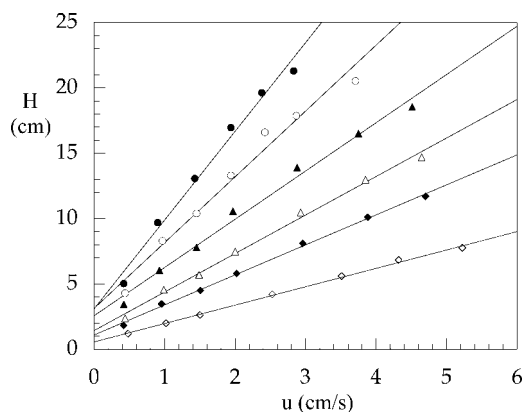
$$C = \frac{1}{120} \frac{k}{(1+k)^2} \frac{d_p^2}{D} \left( \frac{\% \rho_g}{3m\rho_l} \right)^{1/2} \quad (6)$$

where  $d_p$  is the diameter of the glass beads, % is the weight percentage of the polymer in the support,  $\rho_g$  is the density of the beads,  $m$  is the number of contact points per ball (estimated to be 6.25), and  $\rho_l$  is the density of the liquid phase coated on the glass beads.

Several other approximations have been proposed in the literature.<sup>16,19-26</sup> In all cases, the discussion concerns the supposed disposition of the coating on the beads. This implies the inclusion of a combination of different numerical factors in the final equations, which can be summarized<sup>27</sup> in a generic expression in which  $q$ , the geometric factor, can take different values depending on the morphology in the column:

$$C = q \frac{k}{(1+k)^2} \frac{d_f^2}{D} \quad (7)$$

For the calculation of  $D$  from IGC measurements and eq. (2), this geometric factor should be known previously. Articles have been published<sup>28,29</sup> in which  $q$  has been obtained from diffusivity measurements that combine IGC with other techniques, such as sorption or permeability measurements. In this way, the value of  $q$  would be an average measure of the different kinds of morphologies existing in the column. By adjusting  $q$ , we also consider the differences in the morphology between coated beads and the films used in gravimetric experiments. However, in comparing dif-



**Figure 1** Van Deemter's plot of the PECH/toluene system at different temperatures: (●) 37.7, (○) 41.5, (▲) 46.1, (△) 51.5, (◆) 56.3, and (◇) 66°C.

fusion coefficients obtained by IGC with those obtained by other techniques, we must take into account that they have been determined in different concentration ranges. Consequently, it is necessary to extrapolate the data to the zero penetrant concentration, the usual value in IGC. There are different published data<sup>12,16</sup> showing acceptable agreement between diffusion coefficient data obtained by different techniques.

In this work, we attempt to check the validity of this procedure, that is, obtaining the geometric factor of an IGC column from diffusion coefficients measured by sorption data experiments with one or several solvents and the subsequent application of that factor for the calculation of diffusion coefficients of any other solvent with the same IGC column.

In rubbery polymers, it is expected that the diffusion of organic solvents will follow a Fickian behavior. The sorption of a film of thickness  $l$  (when the amount of the penetrant solvent is between 50–90% of the final possible sorbed mass) can be expressed with the following equation (long-time approximation):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D t}{l^2}\right) \quad (8)$$

where  $M_t$  and  $M_\infty$  refer to the mass sorbed at time  $t$  and the sorption equilibrium is finally attempted. With a plot of  $\ln(1 - M_t/M_\infty)$  versus  $t$ ,  $D$  can be obtained from the corresponding slope. As previously mentioned, correlating sorption and IGC data requires extrapolating sorption data to the IGC infinite dilution regime. We made an attempt to correlate our data at different concentrations with a mathematical expression proposed in the literature,<sup>30</sup> but the correlation was not good enough. As an alternative, the Vrentas–Duda model was used to extrapolate our sorption data to the IGC interval.

Vrentas and Duda<sup>31,32</sup> proposed that the diffusion process occurs because of the existence of free volume. The diffusion of a penetrant depends on the probability of creating a hole big enough near the penetrant molecule and on the probability that this molecule gets enough energy to jump into the hole. The basic assumptions made in that model are as follows:

- The thermal expansion coefficients necessary to calculate different volumes are considered not to change in the studied temperature range.
- The solvent and polymer partial specific volumes are considered to remain constant at different concentrations.
- The chemical potential of the solvent is calculated by the Flory–Huggins equation, in which the polymer/solvent interaction parameter is constant at different concentrations and temperatures.

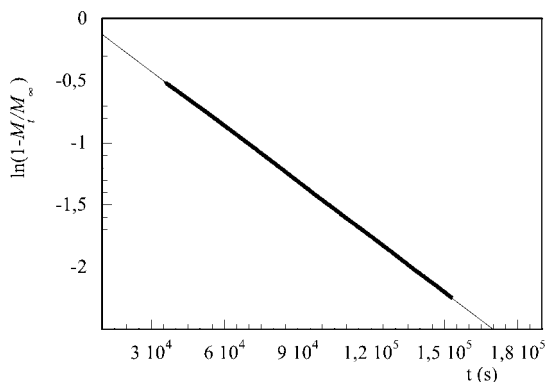
The original formulation has suffered several modifications to be adapted to different systems.<sup>33–36</sup> It includes different parameters that need to be adjusted, and this renders the model not totally predictive. More recently, some authors proposed a strategy for calculating all these parameters without the necessity of fitting the experimental data of diffusion coefficients.<sup>37</sup> Although this alternative gives acceptable results in some polymer/solvent systems such as PS/benzene or PS/THF, in other cases, its predictions do not agree reasonably well with experimental data. In a later article,<sup>10</sup> they reconsidered the problem and proposed a semipredictive version in which most of the parameters can be independently known and only two need to be adjusted with experimental data. Once these parameters are known, it is possible to calculate diffusion coefficients when the solvent concentration tends to zero (the IGC regime).

According to the model, the self-diffusion coefficient for the solvent ( $D_1$ ) can be expressed as follows:

$$D_1 = D_0 \exp\left(\frac{-E^*}{RT}\right) \exp\left(\frac{-(w_1 \hat{V}_1^* + \xi w_2 \hat{V}_2^*)}{\hat{V}_{FH}/\gamma}\right) \quad (9)$$

**TABLE II**  
**C' Values in the PECH/Toluene System at Different Temperatures with IGC Glass-Bead-Packed Columns**

Temperature (°C)	C'
37.7	53.79
41.5	42.44
46.1	26.49
51.5	18.36
56.3	11.06
66.0	6.647



**Figure 2** Plot of the gravimetric sorption data of the PECH/toluene system at 30°C and at a toluene activity of 0.33 used to obtain  $D$ , with eq. (8) taken into account.

where  $D_0$  is a pre-exponential factor,  $E^*$  is the activation energy required for a molecule to overcome the attractive forces holding it to its neighbors,  $\hat{V}_i^*$  is the critical local hole free volume required for a  $i$  unit to jump,  $w_i$  is the weight fraction of the  $i$  component, and  $\gamma$  is an overlap factor (between 1/2 and 1) introduced to correct for overlapping free volume. The  $\xi$  parameter is the ratio of the polymer and solvent molar jumping units:

$$\xi = \frac{M_{j1} \hat{V}_1^*}{M_{j2} \hat{V}_2^*} \quad (10)$$

where  $M_{ji}$  is the molecular weight of a jumping unit of component  $i$ .  $\hat{V}_{FH}$  is the critical free volume of the system:

$$\frac{\hat{V}_{FH}}{\gamma} = w_1 \frac{k_{11}}{\gamma_1} (k_{21} - T_{g1} + T) + w_2 \frac{k_{12}}{\gamma_2} (k_{22} - T_{g2} + T) \quad (11)$$

where  $k_{11}$  and  $k_{21}$  are free-volume parameters. With the Flory–Huggins theory,  $D_1$  can be related to the reciprocal diffusion coefficient ( $D$ ) as follows:

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \quad (12)$$

**TABLE III**

**$D$  Values for the PECH/Toluene System Obtained from Sorption Data at Different Values of Solvent Activity**

Activity	$W_{\text{toluene}}$	$D$ (cm <sup>2</sup> /s)
0.13	0.0180	$8.5 \times 10^{-10}$
0.20	0.0340	$2.8 \times 10^{-10}$
0.33	0.0540	$3.7 \times 10^{-9}$
0.48	0.1139	$1.8 \times 10^{-8}$

**TABLE IV**  
 **$D_1$  Values for the PECH/Toluene System at 30°C Calculated with eq. (12)**

$\phi_1$	$D_1$ (cm <sup>2</sup> /s)
0.0271	$9.1 \times 10^{-10}$
0.0512	$3.2 \times 10^{-9}$
0.0785	$4.5 \times 10^{-9}$
0.1518	$2.7 \times 10^{-8}$

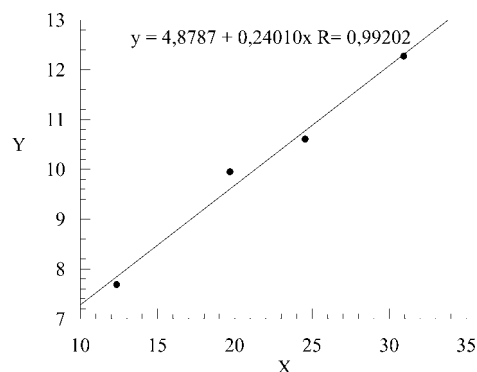
where  $\chi$  is the Flory–Huggins interaction parameter and  $\phi_1$  is the penetrant volume fraction. In IGC, both coefficients are the same as long as  $\phi_1 \rightarrow 0$ .

Consequently, the parameters that we need are  $D_0$ ,  $E$ ,  $\hat{V}_i$ ,  $\xi$ ,  $k_{11}/\gamma$ ,  $k_{21}$ ,  $T_{g1}$ ,  $k_{21}/\gamma$ , and  $T_{g2}$ . All of them, except  $E^*$  and  $\xi$ , can be known, as we explain later. These two remaining parameters must be adjusted with, at least, two experimental data of diffusion coefficients.

## RESULTS AND DISCUSSION

For  $D$  to be obtained from IGC measurements,  $H$  has to be plotted versus  $u$ . Figure 1 shows the behavior in the case of toluene. Parallel to the results shown here, IGC data were obtained for other polymer/solvent systems. Unfortunately, in most of them, the Van Deemter plots deviate from the expected behavior, becoming nonlinear even at high values of  $u$ . Although the value of  $C$  can be calculated by the adjustment of the experimental data to the three parameters involved, we have preferred to limit our study to solvents for which Van Deemter behavior is expected. For instance, in Figure 1, it is clear that in the PECH/toluene system, the Van Deemter equation in the studied temperature range can be simplified to a linear relationship.

According to eq. (2), it is possible to calculate  $C$  from the slope of these plots and from  $C$  the diffusion coefficient if we know the value of  $q$  and the ratio  $k/(1+k)^2$ . Given that the last one remains almost con-



**Figure 3** Plot for calculating  $\xi$  and  $E^*$  with the Vrentas–Duda model and eqs. (17)–(19) for the PECH/toluene system at 30°C

TABLE V  
Vrentas and Duda's Model Parameters Used in the Text Calculations

Toluene <sup>a</sup>		PECH	
$V_1^*$ (cm <sup>3</sup> /g)	0.917	$V_2^*$ (cm <sup>3</sup> /g)	0.66
$k_{11}/\gamma$ (cm <sup>3</sup> /g K)	$1.57 \times 10^{-3}$	$k_{12}/\gamma$ (cm <sup>3</sup> /g K)	$1.47 \times 10^{-4}$
$k_{21}-T_{g1}$ (K)	-90.5	$k_{22}$ (K)	52
$D_0$ (cm <sup>2</sup> /s)	$4.17 \times 10^{-4}$	$T_{g2}$ (K)	250
	$E^*$ (kcal/mol)	2.93	
	$\xi$	0.240	
	$\chi$	0.238	

<sup>a</sup> Values collected from ref. 39.

stant in the employed flow range, we decided to plot  $H$  versus  $k/(1+k)^2u$ . The new slope is  $C'$ :

$$C' = q \frac{d_f^2}{D} \quad (13)$$

From this, the diffusion coefficient can be obtained if  $q$  is known. In Table II, we list data for  $C'$  at different temperatures for the investigated PECH/toluene pair. As can be seen, the value of  $C'$  diminishes when the temperature increases, implying a normal behavior for the corresponding diffusion coefficient, which becomes larger when the temperature rises. However, for quantitative values of  $D$  from  $C'$ , we need the value of  $q$ , and that is calculated from sorption data of toluene in PECH films.

From an adequate treatment<sup>38</sup> of sorption experiments [see Fig. 2 and eq. (8)], it is possible to calculate diffusion coefficients. The obtained values are reported in Table III for different activities of the solvent at 30°C.

For these data to be compared with those obtained by IGC,  $D$  must be known in the same range of concentration.  $D$  at infinite dilution can be calculated with the data in Table III and the Vrentas–Duda model. For this purpose, we need the list of parameters mentioned in the previous section. In our case, we only need to calculate the PECH data. The data for toluene ( $D_0$ ,  $\hat{V}_1^*$ ,  $k_{11}/\gamma$ , and  $k_{21}-T_{g1}$ ) have been taken from the literature.<sup>39</sup>

The value of  $\hat{V}_2^*$  has been calculated with two methods: a group contribution method proposed by Sudgen<sup>40</sup> and with the following equation:

$$\hat{V}_2^* = V_g - \alpha T_g V_g \quad (14)$$

where the polymer volume is related to its expansion coefficient and to its volume at  $T_g(V_g)$ . In the first case,  $\hat{V}_2^*$  is 0.67 cm<sup>3</sup>/g, and in the last one, it is 0.65 cm<sup>3</sup>/g. We have used an average value of 0.66 cm<sup>3</sup>/g. The  $k_{12}/\gamma$  and  $k_{22}$  values have been obtained with the Williams–Landel–Ferry constants  $C_{12}$  and  $C_{22}$  and the following expressions:

$$\frac{k_{12}}{\gamma_2} = \frac{\hat{V}_2^*}{2.303C_{12}C_{22}} \quad (15)$$

$$k_{22} = C_{22} \quad (16)$$

The values for  $C_{12}$  and  $C_{22}$  are 40 and 52, respectively.<sup>41</sup>

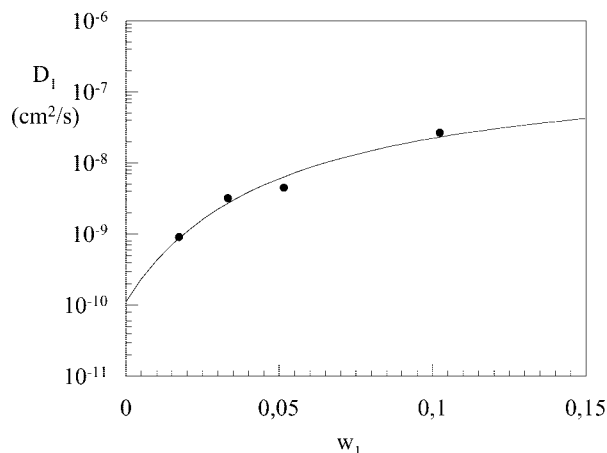
Finally, we also need  $E^*$  and  $\xi$ . They can be calculated with only theoretical expressions, but in the semipredictive version of the model, they are adjusted with diffusion coefficient data measured by the sorption method.

The first point that we must consider is that our values correspond to reciprocal coefficients and we have to transform them into self-diffusion coefficients (to compare them with data obtained by IGC). To do this, we need a value for the PECH/toluene interaction parameter ( $\chi_{\text{PECH/toluene}}$ ). Although the model assumes a concentration-independent interaction parameter, we have minimized the possible influence of the concentration, taking a value obtained by our group<sup>42</sup> with IGC measurements. Experimental data from 60 to 125°C have been extrapolated to 30°C, and the obtained value is 0.238. With this value, we could calculate self-diffusion coefficients ( $D_1$ ) with eq. (12), and the values are reported in Table IV. Rewriting eq. (9), we obtain

$$Y = \xi X + \frac{E^*}{RT} \quad (17)$$

TABLE VI  
 $D_1$  Values Corresponding to Toluene Concentration Zero Calculated by Vrentas and Duda's Model and Calculated  $q$  Values for the PECH Column

Temperature (°C)	$D_1$ (cm <sup>2</sup> /s)	$q$
37.7	$2.6 \times 10^{-10}$	20.0
41.5	$3.9 \times 10^{-10}$	23.0
46.1	$5.6 \times 10^{-10}$	21.0
51.5	$9.2 \times 10^{-10}$	23.8
56.3	$1.3 \times 10^{-9}$	20.2
66.0	$2.6 \times 10^{-9}$	24.0



**Figure 4** Fitting of the experimental diffusion coefficient data according to the Vrentas–Duda model for the PECH/toluene system.

where  $X$  and  $Y$  are related to different parameters previously defined:

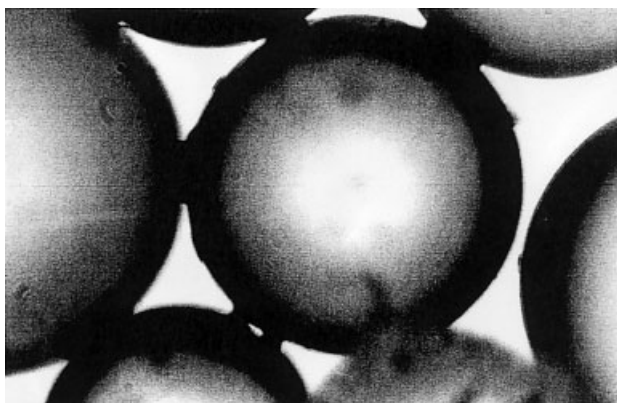
$$X = \frac{w_2 \hat{V}_2^*}{\hat{V}_{FH}/\gamma} \quad (18)$$

$$Y = \ln D_0 - \ln D_1 - \frac{w_1 \hat{V}_1^*}{\hat{V}_{FH}/\gamma} \quad (19)$$

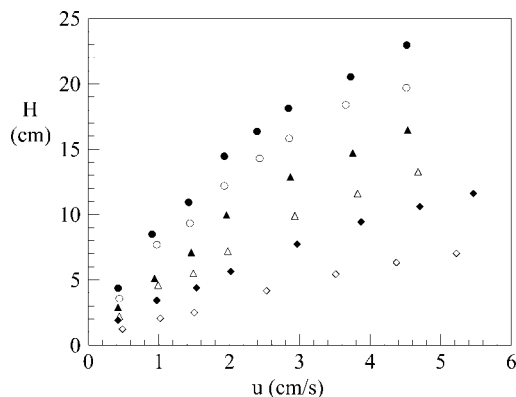
Plotting  $Y$  versus  $X$ , we could calculate  $\xi$  and  $E^*$  from the slope and the ordinate in the origin, respectively.

Figure 3 shows a plot of this type. The values obtained are  $E^* = 2.93$  kcal/mol and  $\xi = 0.240$ . Table V summarizes the Vrentas–Duda parameters we use in the following paragraphs to calculate the infinite dilution diffusion coefficient for the PECH/toluene mixture.

Table VI contains infinite dilution diffusion coefficients at different temperatures that have been obtained from plots such as Figure 4. With these values,



**Figure 5** Photograph showing a PECH coating on glass beads.



**Figure 6** Van Deemter's plot of the PECH/butanol system at different temperatures: (●) 37.7, (○) 41.5, (▲) 46.1, (△) 51.5, (◆) 56.3, and (◇) 66°C.

experimental  $C'$  values obtained by IGC and eq. (13),  $q$  for our PECH column can be calculated at different temperatures. Table VI also contains the results of such  $q$  calculations.

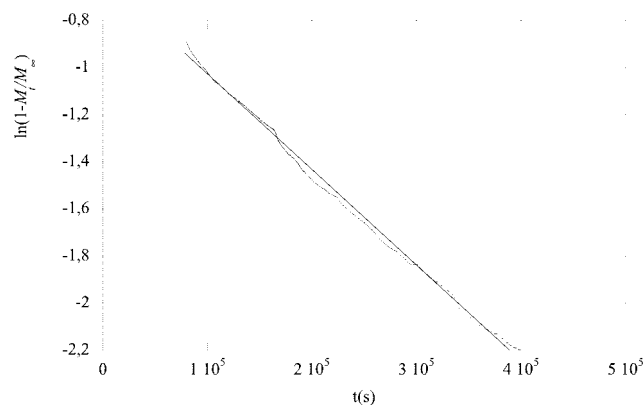
Apparently,  $q$  does not change with the temperature, at least in our temperature range, and this allows the use of an average value of  $q = 22$ . According to the literature,<sup>26,28</sup> low values of  $q$  correspond to a uniform coating of the glass beads, whereas high values of  $q$  indicate that the polymer accumulates at the contact points of the glass beads. In our case, the results correspond to an intermediate value that could be interpreted as an ambivalent situation in which part of the polymer is located at the contact points of the glass beads and another part coats them as a film, as discussed in the next photograph. (Fig. 5).

The  $q$  value so calculated characterizes the morphology of our column, allowing new determinations of  $D$  for every solvent injected into the column. To check the consistency of our procedure, we have selected the PECH/butanol system, for which plots of the solute plate heights from the eluted peaks ( $H$ ) as a function of  $u$  seem to follow the Van Deemter equation, especially at high temperatures (Fig. 6).

From the fitting of these plots with eq. (2), and having taken into account the value of  $q$  obtained before, we have calculated diffusion coefficients for

**TABLE VII**  
 $D_1$  Values for Butanol in PECH from the IGC Data ( $q = 22$ )

Temperature (°C)	$D_1$ (cm <sup>2</sup> /s)
37.7	$3.2 \times 10^{-10}$
41.5	$4.3 \times 10^{-10}$
46.1	$5.5 \times 10^{-10}$
51.5	$9.6 \times 10^{-10}$
56.3	$1.4 \times 10^{-9}$
66.0	$2.8 \times 10^{-9}$



**Figure 7** Plot according to eq. (8) for calculating PECH/butanol diffusion coefficient.

the PECH/butanol system at different temperatures (see Table VII).

These data have been compared with those obtained with sorption measurements. Figure 7 shows an appropriate plot of sorption data<sup>38</sup> used to calculate  $D$  from the slope at 40°C.

If we compare the value obtained by the sorption method ( $2.4 \times 10^{-10}$  cm<sup>2</sup>/s) with that calculated by IGC within an adequate temperature range, we can see that they reasonably agree, validating the procedure employed here.

## CONCLUSIONS

As pointed out in the introduction, IGC could be a rapid and low-cost alternative technique for measuring diffusion coefficients in cases in which the diffusion is slow or when the solvent is present in vanishing small amounts. However, the IGC packed columns used for this purpose require a previous characterization of their morphology in terms of the so-called geometric factor  $q$ . In this article, we have evaluated this factor with sorption experiments.

The  $q$  value so obtained is higher than other values proposed in the literature. However, it is constant with the temperature, and it is supposed to reflect a complex morphology of the polymer on the glass beads. Some of the polymer would accumulate at the contact points of the beads, and another part would coat the beads as a film.

More experimental work is necessary to check the conclusions of this article, mainly because the Van Deemter equation does not apply to some polymer/solvent data. This introduces new questions to be solved before the reliability of the method is concluded.

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