Polymer-Solute Diffusion and Equilibrium Parameters by Inverse Gas Chromatography

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Inverse gas chromatography (IGC) was used to measure diffusion and thermodynamic parameters of volatile compounds in polymers. A comprehensive model for IGC is proposed, and a numerical solution for it is developed. Four capillary columns were prepared using PDMS and EPDM as the stationary phase. Toluene, ethanol, water, and some chlorinated compounds were the probes for the chromatographic experiments. Limitations of the IGC technique, although not reported in the literature, are explained. Nevertheless, the results for the systems chosen were satisfactory and agreed with the literature. The effect of adsorption on the column wall is important when water is used as a solute. The adsorption effect was incorporated into the model. The parameters obtained for water using the modified model became more reliable. The parameters obtained with IGC were used to get further understanding of the pervaporation process.

Introduction

The use of inverse gas chromatography (IGC) to obtain thermodynamic parameters is widespread in the literature (Nobrega and D'Ávila, 1984; Vilcu and Leca, 1990; Constantino et al., 1991; Wohfarth, 1994). The technique involves the use of a solid or liquid material of interest as a stationary phase in the column. This stationary phase can be a thin polymeric coating on an inert substrate (packed columns) or on the column wall (capillary columns). A volatile probe is eluted by an inert gas through the column and the output is monitored. The residence time of the probe and the shape of its elution curve rely on the interactions between the probe and the stationary phase. In essence, the technique is the same as that of the usual gas chromatography. The term "inverse" is only used to indicate that the aim of the study is to measure properties of the stationary phase rather than the chromatographic separation process itself. Nevertheless, this technique has the advantages of simplicity, accuracy, precision, and fast data collection.

More recently, IGC has also been used to study molecular diffusion of low molecular-weight molecules in polymers (Pawlisch et al., 1987, 1988; Arnould and Laurence, 1992; Bonifaci et al., 1992, 1994; Danner and Romdhane, 1993; Danner et al., 1995; Munk et al., 1987; Bemgard and Blomberg, 1989; Scheiber and Qin, 1994; Faridi et al., 1996). Diffusion plays an important role in many processes that involve polymers as, for example, solvent devolatilization, residual monomer stripping, drying of paints and coatings, and membrane separation. Conventional methods for estimation of diffusion coefficients depend on bulk equilibrium and gravimetric vapor sorption/desorption experiments. However, these methods become very difficult when the probe is present in vanishing concentrations. Under these conditions, IGC is an appropriate method for determining diffusion coefficients.

There has been an increasing interest in pervaporation within the membrane separation processes (Brüschke, 1991; Huang, 1991; Rautenbach et al., 1992; Futselaar et al., 1995). This process consists of the partial vaporization of liquid mixtures through dense polymeric films (membrane). The separation mechanisms rely on two phenomena, the sorption of the mixture compounds in the membrane and their diffusion through it (Mulder and Smolders, 1984). According to Rautenbach et al. (1992), two applications of this process have obtained technical and economical success: the dehydration of polar organic compounds, and the removal of traces of volatile organic solvents from water. The latter application has some interesting characteristics, as it shows neither plastisizing nor fluxes coupling due to the low concentration of both water and organic compound in the membrane (Brun and Larchet, 1985). Under these conditions, the value of the

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diffusion coefficients obtained by IGC should be close to those occurring in the pervaporation process. Since the process of obtaining pervaporation data is time-consuming (Borges et al., 1992), especially when working with the removal of traces of organic solvents from water, it would be interesting to get an earlier insight into the system using faster techniques. IGC is an option for obtaining the required parameters (thermodynamic and transport) due to its characteristic of fast data collection.

In order to obtain reliable information concerning diffusion in polymers with IGC, an accurate mathematical model is necessary. This model should describe the physical phenomena, which occur in an IGC run as precisely as possible because they affect the column output. Taking this fact into account, it is preferable to work with capillary columns rather than packed ones, as pointed out by Pawlisch et al. (1987). The former is an open channel and the latter is an irregular porous medium. Danner and Romdhane (1993), presented the drawbacks concerning the modeling of packed columns. The most difficult problem to overcome when working with packed columns is to determine the polymer coating thickness. Since the substrate has an irregular surface, the coating thickness varies widely along the column. This can be partially circumvented by using regular surfaces as a substrate such as glass beads. However, the experimental difficulty in obtaining regular film coatings still remains. A second serious disadvantage in using packed columns is to model the irregular path run by the gas phase. The drawbacks in using packed columns are thoroughly discussed by Pawlisch et al. (1987). Therefore, the difficulties involved in modeling packed columns lead to the choice of capillary columns.

Model Development

The first attempt to give a formal theory for gas chromatography was developed by van Deemter et al. (1956). This procedure has been used to estimate diffusion coefficients of low molecular-weight molecules in polymers (Guillet and Gray, 1973; Kong and Hawkes, 1975; Munk et al., 1987; Bemgard and Blomberg, 1989; Scheiber and Qin, 1994; Jackson and Higlin, 1995). Nevertheless, this approach has many drawbacks as pointed out by (Pawlisch et al., 1987). Other models for gas chromatography have been proposed in the literature (Wicar et al., 1971; Grushka, 1972; Munk and Hattam, 1988; Danner and Romdhane, 1993). These models were developed for packed columns and, as mentioned earlier, modeling this kind of column has serious limitations.

Pawlisch et al. (1987, 1988) developed a model for capillary columns and proposed an approach to obtain diffusion and equilibrium parameters of low molecular-weight molecules in polymers, a method that has been used for other authors (Arnould and Laurence, 1992; Bonifaci et al., 1992, 1994; Xie, 1993; Baltus et al., 1993; Danner et al., 1995; Faridi et al., 1996). The model proposed by Pawlisch et al. (1987) consists of a system of partial differential equations, which the authors solved by using the Laplace transform. In order to carry out the solution procedure, the authors assumed the following simplifications: plug flow in the mobile phase and rectangular coordinates for the stationary phase. Besides these assumptions, they had to restrict the solution to the end of the column ($z = L$) due to the solution method. Despite these simplifications, the authors could not obtain an analytical inversion of the result within the time domain. Therefore, they used a moment-generating property of the Laplace transform in order to obtain the parameters of interest as well as a numerical procedure to invert the transform in order to carry out simulations. Nevertheless, the moments method is not generic as the same authors pointed out in a subsequent article (Pawlisch et al., 1988). In this latter article, they proposed to fit the numerical inversion to the experimental data in order to obtain the parameters.

In this work we chose to carry out a numerical solution for our model. So, the assumptions proposed by Pawlisch et al. (1987) (plug flow in the mobile phase and rectangular coordinates for the stationary phase) are not necessary. Moreover, the numerical solution allows us to get the axial concentration profile in the whole column and to propose a more flexible model, which can easily incorporate other mass-transfer phenomena, as will be shown in this article.

In order to develop a model for gas chromatography using capillary columns, the following assumptions are made:

- The column is a straight, open tube.
- The sample is at infinite dilution in both phases (mobile and stationary).
- The system is isothermal.
- The mobile phase is incompressible due to the low-pressure drop along the column.
- Laminar flow with parabolic profile.
- The thickness of the stationary phase is constant.
- The axial diffusion in the stationary phase is neglected.
- The sweeping gas does not dissolve in the stationary phase.
- The absorption isotherm is linear.
- The thermodynamic equilibrium in the gas–polymer interface is instantaneous.
- The adsorption in the polymer surface and in the column wall are neglected.
- The diffusion coefficients in both phases are not concentration-dependent.
- The admission chamber is represented by a first-order dynamic delay.

Further assumptions are not necessary unlike the former works (Pawlisch et al., 1987, 1988), which needed additional simplifications. The preceding assumptions were applied to the continuity equation for both phases, thereby deriving the following equations:

Mobile phase

$$\frac{\partial c}{\partial t} + 2 \cdot V \cdot \left[1 - \left(\frac{r}{R}\right)^2\right] \cdot \frac{\partial c}{\partial z} = D_g \cdot \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial c}{\partial r}\right) + D_g \cdot \frac{\partial^2 c}{\partial z^2}. \tag{1}$$

Stationary phase

$$\frac{\partial q}{\partial t} = D_p \cdot \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial q}{\partial r}\right). \tag{2}$$

Initial conditions

$$c(z,r,0)=0 \tag{3}$$

$$q(z,r,0)=0. \tag{4}$$

Boundary conditions

$$2\cdot V\cdot\left[1-\left(\frac{r}{R}\right)^2\right]\cdot F(t)\cdot c_0=2\cdot V\cdot\left[1-\left(\frac{r}{R}\right)^2\right]\cdot c(r,0,t)-D_g\cdot\left.\frac{\partial c}{\partial z}\right|_{z=0} \tag{5}$$

$$\begin{cases} F(t)=\left[1-\exp\left(-\dfrac{t\cdot P}{V_{\text{inj}}}\right)\right]\cdot\dfrac{p}{P} & 0\le t\le t_{\text{inj}} \\ F(t)=\left[1-\exp\left(-\dfrac{t_{\text{inj}}\cdot P}{V_{\text{inj}}}\right)\right]\cdot\exp\left[\dfrac{P}{V_{\text{inj}}}\cdot(t_{\text{inj}}-t)\right]\cdot\dfrac{p}{P} & t>t_{\text{inj}} \end{cases}$$

$$-D_g\left.\frac{\partial c(z,r,t)}{\partial z}\right|_{z=L}=0 \tag{6}$$

$$\left.\frac{\partial c(z,r,t)}{\partial r}\right|_{r=0}=0 \tag{7}$$

$$D_g\cdot\left.\frac{\partial c(z,r,t)}{\partial r}\right|_{r=R}=D_p\cdot\left.\frac{\partial q(z,r,t)}{\partial r}\right|_{r=R} \tag{8}$$

$$q(z,R,t)=K\cdot c(z,R,t) \tag{9}$$

$$\left.\frac{\partial q(z,r,t)}{\partial r}\right|_{r=R+\epsilon}=0. \tag{10}$$

Using the following dimensionless variables:

$$\tau=t\cdot V/L;\quad C=c/c_0,\ Q=q/c_o;\quad \zeta=z/L;\quad \rho=(r/R)^2;$$
$$\eta=(r-R)/\epsilon;\ \alpha=4\cdot D_g\cdot L/R^2\cdot V;\quad \beta=D_g\cdot/L\cdot V;$$
$$\gamma=D_p\cdot L/\epsilon^2\cdot V;\quad \tau_{\text{inj}}=t_{\text{inj}}\cdot V/L;\ \nu=R\cdot D_p/2\cdot\epsilon\cdot D_g,$$

the system can be rewritten as follows:

$$\frac{\partial C}{\partial\tau}+2\cdot(1-\rho)\cdot\frac{\partial C}{\partial\zeta}=\alpha\cdot\left(\frac{\partial C}{\partial\rho}+\rho\cdot\frac{\partial^2 C}{\partial\rho^2}\right)+\beta\cdot\frac{\partial^2 C}{\partial\zeta^2} \tag{11}$$

$$\frac{\partial Q}{\partial\tau}=\gamma\cdot\left(\frac{1}{\eta+R/\epsilon}\cdot\frac{\partial Q}{\partial\eta}+\frac{\partial^2 Q}{\partial\eta^2}\right) \tag{12}$$

$$C(\zeta,\rho,0)=0 \tag{13}$$

$$Q(\zeta,\eta,0)=0 \tag{14}$$

$$2\cdot(1-\rho)\cdot F(\tau)=2\cdot(1-\rho)\cdot C(0,\rho,\tau)-\beta\cdot\left.\frac{\partial C}{\partial\zeta}\right|_{\zeta=0} \tag{15}$$

$$\begin{cases} F(\tau)=\left[1-\exp\left(-\dfrac{\tau\cdot L\cdot P}{V\cdot V_{\text{inj}}}\right)\right]\cdot\dfrac{p}{P} & 0\le\tau\le\tau_{\text{inj}} \\ F(\tau)=\left[1-\exp\left(-\dfrac{\tau_{\text{inj}}\cdot L\cdot P}{V\cdot V_{\text{inj}}}\right)\right] & \\ \qquad\cdot\exp\left[\dfrac{L\cdot P}{V\cdot V_{\text{inj}}}\cdot(\tau_{\text{inj}}-\tau)\right]\cdot\dfrac{p}{P} & \tau>\tau_{\text{inj}} \end{cases}$$

$$\left.\frac{\partial C(\zeta,\rho,\tau)}{\partial\zeta}\right|_{\zeta=1}=0 \tag{16}$$

$$\left.\frac{\partial C(\zeta,\rho,\tau)}{\partial\rho}\right|_{\rho=1}=\nu\cdot\left.\frac{\partial Q(\zeta,\eta,\tau)}{\partial\eta}\right|_{\eta=0} \tag{17}$$

$$Q(\zeta,0,\tau)=K\cdot C(\zeta,1,\tau) \tag{18}$$

$$\left.\frac{\partial Q(\zeta,\eta,\tau)}{\partial\eta}\right|_{\eta=1}=0. \tag{19}$$

Numerical Analysis

In a first step, the solution of the system has been obtained by the following strategy:

- Polynomial approximation along variable ρ using the Jacobi polynomial ($P^{(\alpha,\beta)}$) zeros as interpolation points, with $\alpha=\beta=0$ (Villadsen and Michelsen, 1978; Biscaia, 1992):

$$C(\zeta,\rho,\tau)\cong\sum_{j=1}^{N+1} l_j(\rho)\cdot C_j(\zeta,\tau). \tag{20}$$

- Polynomial approximation along variable η using the Jacobi polynomial ($P^{(\alpha,\beta)}$) zeros as interpolation points, with $\alpha=\beta=1$ (Villadsen and Michelsen, 1978; Biscaia, 1992):

$$Q(\zeta,\eta,\tau)\cong\sum_{j=1}^{N+2} l_j(\eta)\cdot Q_j(\zeta,\tau). \tag{21}$$

- Along variable ζ the system was approximated by finite elements, each element being assumed to be the following polynomial:

$$C_j(\zeta,\tau)\cong L_1(\zeta)\cdot C_j(\tau)_{,i}+L_2(\zeta)\cdot C_j(\tau)_{,i+1/2}+L_3(\zeta)\cdot C_j(\tau)_{,i+1},\qquad \zeta_i\le\zeta\le\zeta_{i+1}, \tag{22}$$

where

$$L_1=\frac{\zeta-\zeta_{i+1/2}}{-\Delta\zeta/2}\cdot\frac{\zeta-\zeta_{i+1}}{-\Delta\zeta} \tag{23}$$

$$L_2=\frac{\zeta-\zeta_i}{\Delta\zeta/2}\cdot\frac{\zeta-\zeta_{i+1}}{-\Delta\zeta/2} \tag{24}$$

Table 1. First and Second Derivatives of the Element Coefficients

Point	i	$i+1/2$	$i+1$	Point	Any
dL_1/dx	$-3/\Delta x$	$-1/\Delta x$	$1/\Delta x$	d^2L_1/dx^2	$4/(\Delta x)^2$
dL_2/dx	$4/\Delta x$	0	$-4/\Delta x$	d^2L_2/dx^2	$-8/(\Delta x)^2$
dL_3/dx	$-1/\Delta x$	$1/\Delta x$	$3/\Delta x$	d^2L_3/dx^2	$4/(\Delta x)^2$

$$L_3 = \frac{\zeta - \zeta_{i+1/2}}{\Delta\zeta/2} \cdot \frac{\zeta - \zeta_i}{\Delta\zeta}. \tag{25}$$

The first and second derivatives of the element coefficients are given in Table 1. Once the element is a second-degree polynomial the second derivative is the same at any point.

These approximations change the original system of partial differential equations into a differential-algebraic one. This resulting system has been solved using the DASSL routine

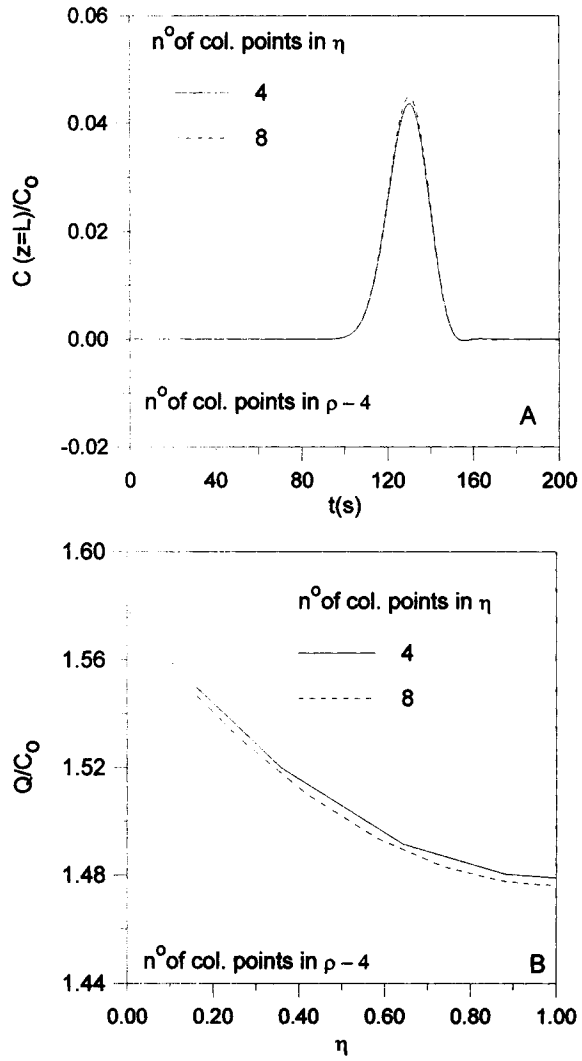

Figure 1. Variation of the number of collocation points along η on: (a) elution curve; (b) concentration profile in the stationary phase.

Simulation conditions: $\phi = 0.56$ mm; $V = 50$ cm/s; $L = 2000$ cm; $k = 60$; $\epsilon = 5$ μm; $D_p = 20\times10^{-8}$ cm^2/s; $D_g = 0.7$ cm^2/s.

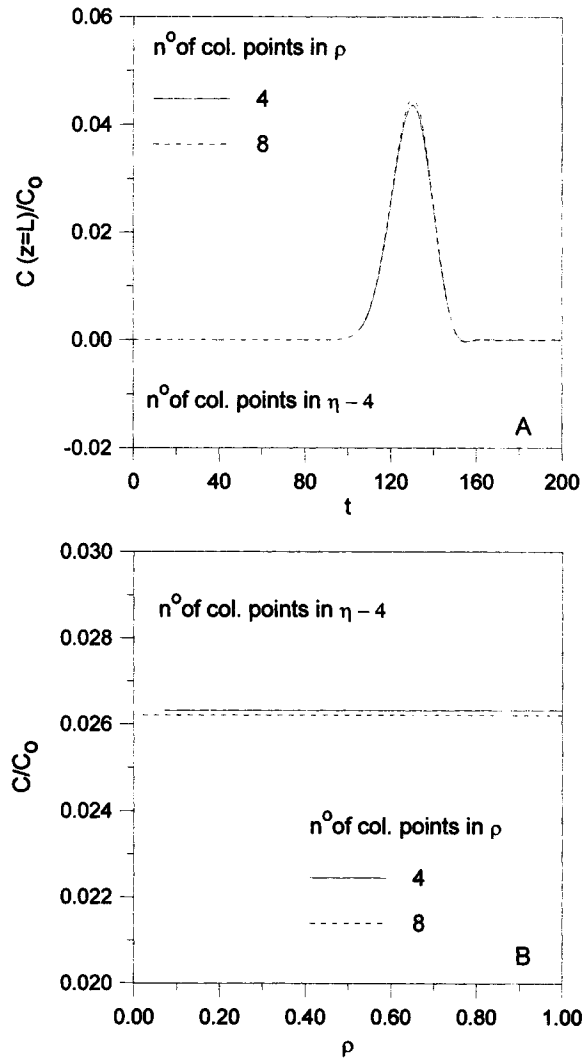

Figure 2. Variation of the number of collocation points along ρ on: (a) elution curve; (b) concentration profile in the mobile phase.

Simulation conditions: $\phi = 0.56$ mm; $V = 50$ cm/s; $L = 2000$ cm; $k = 60$; $\epsilon = 5$ μm; $D_p = 20\times10^{-8}$ cm^2/s; $D_g = 0.7$ cm^2/s.

(Brenan et al., 1989), which was specifically designed to solve this kind of system. One example of the system response as a function of the number of collocation points along the variable η is shown in Figure 1. For the range of the parameters used in our work, neither the elution curve nor the concentration profile in the stationary phase presents a significant variation. According to those results no more than four collocation points are necessary to obtain enough precision.

According to Figure 2 the same analysis can be made for the variable ρ. Concerning the number of collocation points, the conclusion is identical to that for the variable η. It can also be observed that the concentration profile along variable ρ is uniform. This fact leads to the simplification of Eq. 20 using a one-point collocation procedure, as follows:

$$C(\zeta,\rho,\tau) = l_1(\rho)\cdot C_{1/2}(\zeta,\tau) + l_2(\rho)\cdot C_1(\zeta,\tau). \tag{26}$$

Further improvement can be obtained using Eq. 18:

$$C(\zeta,\rho,\tau) = l_1(\rho)\cdot\bar{C}(\zeta,\tau) + l_2(\rho)\cdot\frac{Q(\zeta,0,\tau)}{K}, \quad (27)$$

with $l_1 = 2(1-\rho)$; $l_2 = 2\rho - 1$; $dl_1/d\rho = -2$; $dl_2/d\rho = 2$; $d^2l_1/d\rho^2 = 0$; $d^2l_2/d\rho^2 = 0$; therefore,

$$\frac{\partial C(\zeta,\rho,\tau)}{\partial\rho} = 2\cdot\left[\frac{Q(\zeta,0,\tau)}{K} - \bar{C}\right] \quad (28)$$

$$\frac{\partial^2 C(\zeta,\rho,\tau)}{\partial\rho^2} = 0. \quad (29)$$

In addition to the uniform concentration profile in the gas phase, the simulations also showed that the axial dispersion is negligible, as can be observed in Figure 3. In this example the diffusion coefficient in the gas phase was varied one order of magnitude and no significant variation in the peak profile was observed. Therefore, the axial diffusion term in Eq. 1 can be neglected. This simplification induces the use of the characteristics method.

In order to apply the characteristics method, the following modification was made:

$$\lambda = \tau - \zeta, \qquad \mu = \zeta \quad (30)$$

therefore,

$$\frac{\partial F}{\partial\lambda} = \frac{\partial F}{\partial\tau}$$
$$\frac{\partial F}{\partial\zeta} = \frac{\partial F}{\partial\mu} - \frac{\partial F}{\partial\tau}. \quad (31)$$

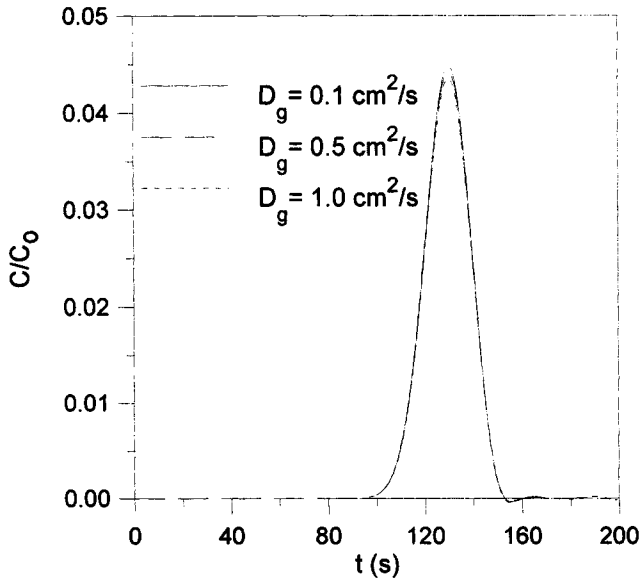

Figure 3. Influence of the axial dispersion in the gas phase.

Simulation conditions: $\phi = 0.56$ mm; $V = 50$ cm/s; $L = 2000$ cm; $k = 60$; $\epsilon = 5$ μm; $D_p = 20\times10^{-8}$ cm^2/s; $D_g = 0.7$ cm^2/s.

Taking into account the proposed simplifications, it is possible to improve the solution performance using a polynomial approximation in the μ variable instead of finite elements. This approximation uses the Jacobi polynomial ($P^{(\alpha,\beta)}$) zeros as interpolation points, with $\alpha = 0$ and $\beta = 1$ (Villadsen and Michelsen, 1978; Biscaia, 1992):

$$\bar{C}(\mu,\lambda) \cong \sum_{j=1}^{N+2} 1_j(\mu)\cdot\bar{C}_j(\lambda). \quad (32)$$

Experimental Studies

Column preparation

The capillaries were drawn from Duran 50 glass tubes with 5 mm ID and 8 mm OD using a Shimadzu drawing machine. The final capillaries had coil diameters of 11 cm, 0.56 mm ID and 0.89 mm OD. From these capillaries the columns were prepared according to the Grob's procedure (Grob, 1986), which consists of the following steps:

1. Acid lixiviation—filling the capillary with HCl (20%) and heating it at 170°C for 12 h.
2. Rinse and dehydration—washing the capillary with HCl (0.5%) and drying it at 300°C for 2 h.
3. Persilanization—treating the capillary with hexamethyldisilazane at 400°C for 12 h.

The stationary phase was applied to the glass surface by a static coating technique. The coating solution was prepared by dissolving the polymer in a mixture of pentane/dichloromethane (1:1 by volume). This solution was submitted to an ultrasonic treatment for degassing and homogenization. The capillary was filled with the solution and sealed by a flame at one of its ends. The other end was pressured with nitrogen in order to dissolve the solvent bubble formed in the sealed end. Then the column was submitted to a vacuum for solvent evaporation. The thickness of the final coating is given by the following equation (Jennings, 1980):

$$\epsilon = \frac{\dfrac{m_p\cdot\phi_i}{4\cdot\rho_p\cdot V_{solv}}}{1+\dfrac{m_p}{\rho_p\cdot V_{solv}}}. \quad (33)$$

In this work four columns were prepared using as stationary phase (polydimethylsiloxane) (PDMS), obtained from the General Electric Company (Silicone Division), and ethene–propene–diene (EPDM), obtained from Miles Inc. (Polymer Rubber Division). PDMS is a polymer widely used in pervaporation applications, mainly for the separation of traces of organic solvents from water (Rautenbach et al., 1992). EPDM has shown good potential to be used in the just mentioned application and has appeared in recent works (Nijhuis, 1990; Borges et al., 1992; Pereira et al., 1997). These reasons led to the choice of these materials in the stationary phase, since the main aim of our work is to achieve further understanding of the pervaporation process.

The PDMS is provided as two oligomers that should be mixed to react resulting in a cross-linked polymer after some hours. In solution, this reaction is inhibited so it only occurs after solvent evaporation. Dicumyl peroxide (Aldrich Inc.) 5% (w/w) was added to the EPDM solution in order to cross-link

Table 2. Characteristics of Columns

Column	ϕ_i (mm)	L (cm)	ϵ (μm)	Coating
S-1	0.56	2039	0.764	PDMS
S-2	0.56	2246	1.558	PDMS
S-3	0.56	1728	1.120	PDMS
E-1	0.56	1935	1.182	EPDM

it. After the solvent evaporation, the columns were put in a gas chromatograph to evaporate the residual solvent and to finish the cross-linking process. The PDMS columns were left in a hydrogen atmosphere at 150°C for 2 h. A nitrogen atmosphere is necessary for the EPDM columns because the reaction with the peroxide must occur in an oxygen free environment. These columns were left at 120°C for 3 h. After this final treatment, the columns were ready for the chromatographic tests.

The characteristics of columns prepared in this work are summarized in Table 2. The length of the columns were obtained counting the number of coils. The inside diameter was assumed to be that given by the drawing machine; the outside diameter was measured at several parts of each column, and its value was 0.89 mm with a difference of about 1% along the column. Since this value is very close to that given by the drawing machine, the inside diameter will also be such. The coating thickness was assumed to be the theoretical one given by Eq. 33. Cross-linked polymers show small variation of volume at moderate temperatures (0–100°C). According to the manufacturer, the expansion coefficient of the PDMS is 27×10^{-5} (cm/cm·°C). Therefore, no correction for volume expansion in the coating thickness is necessary. The polymer densities were assumed to be those given by the manufacturer: 1.02 g/cm^3 for PDMS and 0.85 g/cm^3 for EPDM.

Chromatographic procedure

The chromatographic experiments were carried out using a Chrompack CP-9000 chromatograph with a thermal conductivity detector and adapted to measure the pressure at the inlet and outlet of the column. The pressure drop along the columns was about 8 cm Hg and was never greater than 10 cm Hg. The velocity of the carrier was calculated by the following equation (Bird et al., 1960):

$$\rho_g \cdot V_g = \frac{\dfrac{-32\cdot\eta_g\cdot L}{\phi_i^2} + \sqrt{\left(\dfrac{32\cdot\eta_g\cdot L}{\phi_i^2}\right)^2 - 2\cdot\ln\left(\dfrac{P_i}{P_o}\right)\cdot\dfrac{M_g}{R_g\cdot T}\cdot\left(P_o^2 - P_i^2\right)}}{2\cdot\ln\left(\dfrac{P_i}{P_o}\right)}. \quad (34)$$

In this equation, ideal gas and laminar flow have been assumed. Hydrogen was used as the carrier gas and at chromatographic conditions (low pressure and temperatures about 50°C), it can be considered an ideal gas with negligible error. The viscosity of the gas was estimated according to Prausnitz et al. (1988). Given the conditions (T, P) at any point of the column, it is possible to calculate the gas density (ideal gas) and thereby the carrier velocity. The velocities at the inlet and outlet of the column were calculated and the average velocity was taken as their arithmetic mean. Since the pressure drop along the column is small, the difference between inlet and outlet velocities was about 5% and no greater than 12%.

In the chromatographic runs, a volume about 0.05 μL of probe was injected. At these conditions, infinite dilution of the probe in both phases was assumed. Therefore, the influence of the probe vapor on the carrier-gas properties was neglected. The probes used in this work were dichloromethane (DCM), trichloromethane (TCM), 1,1,1-trichloroethane (TCE), toluene (TOL), ethanol (EtOH), and water, all in an analytic grade. The diffusion coefficient of the probes in the carrier gas was estimated according to Giddings et al. (1966).

The selection of the probes follows the same criteria for the choice of the stationary-phase polymers. Halogenated hydrocarbons and organic solvents can be feasibly withdrawn from water by pervaporation (Nijhuis, 1990; Brüschke, 1991; Rautenbach et al., 1992).

The chromatograph is connected to a digital data-acquisition system provided by the same manufacturer. This system allows an acquisition frequency of 5.5556 Hz, about five points per second. After the probe injection, the system automatically starts the data acquisition with a frequency of 60 Hz, then it is reduced to 5.5556 Hz and the data are sent to a computer. The system software integrates the chromatographic response giving retention times and peak areas. Besides these operations, it is possible to get the raw chromatogram in ASCII, which is the main result for this work.

Pervaporation

The basic pervaporation device used in this work has already been presented (Nobrega et al., 1988). The feed was kept at 50°C and pumped to a pervaporation cell with a permeation surface of 68.65 cm^2. The pressure at the permeate side was maintained under 3 mmHg in order to keep the driving force for the process. The permeate vapors were condensed with liquid nitrogen and weighted at room temperature. Feed and permeate were sampled and analyzed by gas chromatography (Perkin-Elmer, model Autosystem XL). The experiments were carried out at 50°C for a convenient operation of both processes IGC and pervaporation. The experiments were carried out in PDMS and EPDM dense membranes with diluted aqueous solutions of TCM. Further information can be found elsewhere (von Meien, 1997).

Parameters Estimation

In order to obtain the parameters of interest (K, D_p) it is necessary to fit the model to the experimental data. Each raw

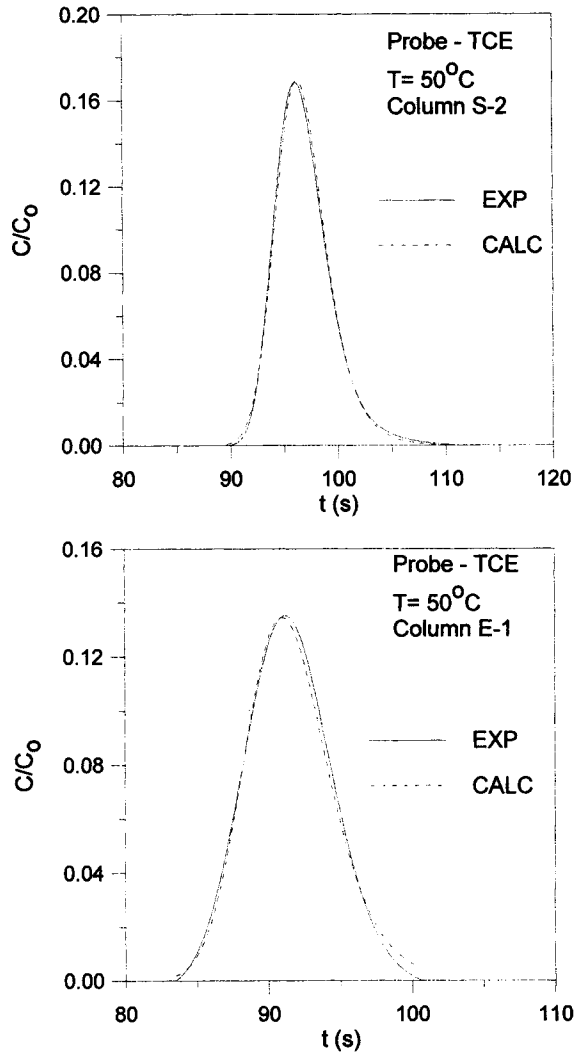

Figure 4. Examples of the fitting procedure for TCE in columns S-2 and E-1.

chromatogram obtained by the acquisition system suffers an earlier "cleaning," which consists of removing the base line and getting the peak in a dimensionless way. The acquisition system provides the raw data in mV. Since the acquisition frequency is known, it is possible to calculate the time of each point. The detector response is a linear function of the concentration, so the integration of the raw chromatogram gives a number that is proportional to the total concentration. Therefore, the dimensionless chromatogram is obtained by dividing each point by the peak area. So, the model can be fitted to this dimensionless chromatogram in order to obtain the parameters. The fitting procedure is done according to the maximum-likelihood principle following Anderson and Abrahans (1978). Two examples of the fitting results are given in Figure 4. As can be observed in that figure, the model fits the experimental data well, as do the further data sets.

Results and Discussion

The parameters K and D_p obtained from the fitting procedure are presented in Table 3. The partition coefficients obtained for each different column made of PDMS are about the same. A wide variation of this parameter is not observed when the coating thickness is changed for the same material (PDMS). The partition coefficients for the EPDM are, in general, slightly higher. The diffusion coefficients presented in Table 3 should be the same for the three PDMS columns; however, they vary. Since the columns have a different coating thickness, it is important to check if the obtained diffusion coefficients depend on that parameter. An analysis of the results shows that the variations are random, so it is fair to conclude that the diffusion coefficients obtained by the present technique do not rely on the coating thickness. In spite of this fact, the diffusion coefficients show larger variations than the partition coefficients. This occurs because the partition coefficient depends mostly on the retention time, while the diffusion coefficient depends on the peak shape. The retention time is relatively easy to reproduce from one experiment to another; however, the peak shape is not. The latter depends on the equipment dead volume and the way in which the operator injects the probe and eventual electronic oscillations. These parameters cannot be completely controlled and always affect the results. The problem is that the diffusion coefficient is very sensitive to the peak shape. In Figure 5 a simulation is shown where the diffusion coefficient is made to vary 50% around a value of 20×10^{-8} cm^2/s. It can be observed that the variation of the peak shape, in particular the peak height, is relatively small compared to the diffusion-coefficient variation. Since small changes in the peak shape are difficult to control experimentally, the random results for the diffusion coefficients can be explained. The diffusion coefficients obtained in the EPDM column are, in general, smaller than those in the PDMS columns. These results imply that EPDM is a less permeable material than PDMS, which is supported in the literature (Rufino et al., 1996).

In spite of the limitations of the procedure, the order of magnitude of the results obtained are in agreement with those in the literature (Pawlisch et al., 1987, 1988; Arnould and Laurence, 1992, 1994; Bonifaci et al., 1992; Danner et al., 1993, 1995; Faridi et al., 1996). Pawlisch et al. (1987) and Danner and Romdhane (1993) compared their results to extrapolations from finite concentration data. Nevertheless, these extrapolations are made from logarithmic plots, and differences of one order of magnitude can be easily concealed in these cases. As a result, we do not think that extrapolation from finite concentration data is an adequate tool to assure the reliability of data obtained at infinite dilution conditions.

In order to verify the reliability of the thermodynamic results, it is interesting to compare them to those reported in the literature. However, for the systems chosen in our work it is difficult to get data from the literature. In Wohfarth (1994) the weight fraction Henry constant for many organic probes in PDMS at 100°C is given. This constant is related to the specific retention volume, the basic parameter of IGC, through the following relation:

$$H_A = \frac{R_g \cdot T}{M_A \cdot V_e}, \tag{35}$$

and the specific retention volume is related to the partition coefficient by the following relation:

Table 3. Results (K, D_p) for Each Column at 50°C

Probe	K	$D_p \times 10^8$ (cm^2/s)	V (cm/s)	Ω^∞
		Column S-1		
DCM	38.82 ± 0.07	25.19 ± 2.32	53.53	6.05
TCM	90.31 ± 0.07	32.68 ± 1.43	53.49	3.74
TCE	127.74 ± 0.20	24.78 ± 1.63	53.58	3.62
TOLUENE	388.40 ± 1.30	5.58 ± 0.36	53.45	6.29
ETOH	23.16 ± 0.04	25.16 ± 0.04	52.62	87.44
		Column S-2		
DCM	37.68 ± 0.05	46.37 ± 2.12	54.82	6.24
TCM	83.78 ± 0.06	44.34 ± 0.88	54.82	4.03
TCE	117.09 ± 0.06	26.55 ± 0.30	54.82	3.95
TOLUENE	346.93 ± 2.94	18.03 ± 0.76	54.82	7.05
ETOH	22.69 ± 0.06	37.16 ± 2.88	54.82	89.25
		Column S-3		
DCM	43.43 ± 0.08	38.99 ± 2.91	48.18	5.41
TCM	101.62 ± 0.09	61.65 ± 2.42	48.18	3.39
TCE	138.26 ± 0.26	38.89 ± 2.41	47.56	3.34
TOLUENE	415.64 ± 4.00	7.94 ± 0.67	47.56	5.88
ETOH	23.77 ± 0.04	42.83 ± 3.76	46.79	85.19
		Column E-1		
DCM	42.00 ± 0.04	21.04 ± 0.69	48.73	4.66
TCM	121.51 ± 0.04	13.91 ± 0.11	48.92	2.31
TCE	147.56 ± 0.10	8.02 ± 0.12	48.88	2.61
TOLUENE	572.54 ± 16.53	10.70 ± 0.61	48.91	3.56
ETOH	23.84 ± 0.05	10.00 ± 0.41	48.89	70.79

$$V_e = K/\rho_p. \tag{36}$$

Although it is possible to compare the V_e, a better comparison of the results can be made through the rational activity coefficient (Vilcu and Leca, 1990):

$$\ln \Omega_1^\infty = \ln\left(\frac{R_g T}{P_1^s \cdot V_e \cdot M_A}\right) - \frac{P_1^s}{R_g T}\cdot(B_{11} - v_1^0). \tag{37}$$

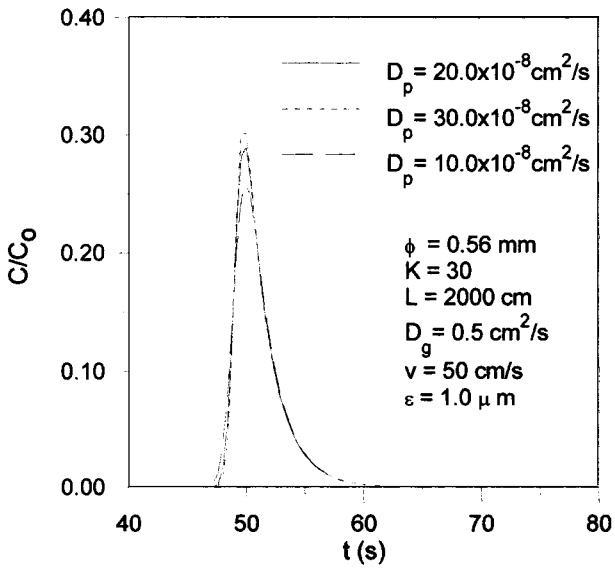

Figure 5. Dependence of the diffusion coefficient on the peak shape.

The probe properties (P_1^s, B_{11}, and v_1^0) were estimated according to correlations given in Prausnitz et al. (1988).

In order to compare the literature data and the results of this work, a set of experiments at 100°C were made using column S-3. In Table 4 both sets are compared and, in general, there is a satisfactory agreement between them. A larger rational activity coefficient means a lower interaction between the probe and the polymer. The tendency of our results is the same as that presented in the literature. In Table 3 the rational activity coefficients of all probes in the four columns at 50°C are also present. The tendency of the results presented in Table 3 is the same as that presented in Table 4. However, the former results are in general slightly lower than the latter. Although the interaction between the polymer and the probes increases with an increase in temperature, the volatility of the probes also increases, which explains these results. The rational activity coefficients of all probes in EPDM are smaller than those in PDMS, so it is possible to conclude that the former polymer has a greater affinity to the probes.

Table 4. Rational Activity Coefficient at Infinite Dilution for the Organic Probes in PDMS at 100°C

Probe	Column S-3 Ω^∞ This work	Ω^∞ (Wohfarth, 1994)
DCM	6.58	4.34
TCM	3.90	3.12
TCE	3.91	3.16
TOLUENE	6.30	5.75
ETOH	83.75	51.09

Special case of water

In addition to the tests with organic probes, tests with water were also made. The results obtained were unexpected, as the peaks of water are highly tailed. According to the literature (Pawlisch et al., 1987, 1988; Arnould and Laurence, 1992), the tailing in the elution curves of some substances is due to their low diffusion coefficients. Substances with low diffusion coefficients present a high resistance to mass transfer, so the majority of the solute remains in the gas phase, and the response is a pulse. The smaller portion of the solute retained by the stationary phase is released slowly, and its response is therefore a long tail. The same could be concluded from simulations using our model. However, the results in the literature (Rufino et al., 1996) show that the water permeability in PDMS and EPDM is not small enough to justify such low values of the diffusion coefficients. Therefore, other phenomena must be present in order to explain that behavior. Adsorption of water on the column wall is a possible reason.

In order to verify whether there is an important adsorption effect, experiments in a column without a stationary phase were made. A 2073-cm-long glass capillary, with 0.56 mm ID, 0.89 mm OD, was treated following the procedure described in the Experimental section. According to the literature (Grob, 1986), this treatment should prevent any interaction between the probes and the capillary wall. This empty column was placed in the chromatograph, and then air, water, and organic probes (dichloromethane (DCM), toluene (TOL), and ethanol (EtOH)) were injected. The result is shown in Figure 6. The organic probes have the same retention time and approximately the same peak shape as air, which is an inert probe. Therefore, it can be concluded that there is a negligible interaction with the capillary wall for these probes. The situation is the opposite with water, as its elution curve showed a significant skewness. The adsorption effect shown by water may be due to its strong interactions with the groups [—Si-O—] of the glass. Although the glass treatment was not able to prevent adsorption in the case of water, it proved to be efficient for the organic probes, even using a polar compound like ethanol.

Due to the flexibility of the proposed model, it is easy to incorporate the adsorption effect. In order to do this, the following sorption–desorption equation for the capillary wall was assumed:

$$\frac{\partial a}{\partial t} = K_{ad} \cdot q(R+\epsilon, z, t) - K_{ds} \cdot a(z,t). \tag{38}$$

It is thus necessary to include another initial condition:

$$a(z,0) = 0, \tag{39}$$

and to modify the boundary condition at the polymer–capillary interface wall (Eq. 10):

$$-\frac{D_p}{\epsilon}\frac{\partial q(z,r,t)}{\partial r}\bigg|_{r=R+\epsilon} = K_{ad} \cdot q(R+\epsilon, z, t) - K_{ds} \cdot a(z,t). \tag{40}$$

The other equations of the model are the same and the solution of the resulting system can be achieved using the numerical procedure described previously.

If no adsorption occurred, the constants K_{ad} and K_{ds} would be zero and tailing would not appear in response. However, if the probe interacted with the capillary wall, its peak shape would be modified by this extra mass-transfer resistance. Since an adsorption–desorption kinetics occurs, part of the probe will be delayed and the response will present tailing. This behavior is similar to that caused by low diffusion coefficients. Simulation of the adsorption effect is presented in Figure 7. As can be seen, the peak skewness is dramatically affected by adsorption.

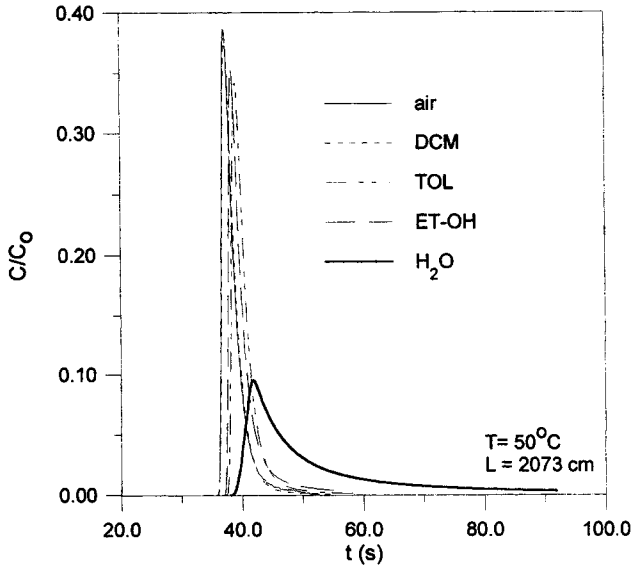

Figure 6. Experimental chromatograms of air, water, and organic probes in an empty column at 50°C.

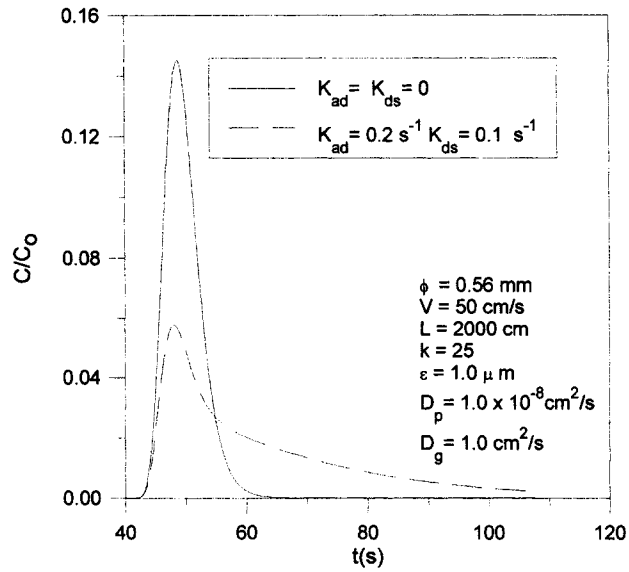

Figure 7. Simulation of the adsorption effect on the peak shape.

Table 5. Results for Water in Each Column at 50°C

Column	K	$D_p \times 10^8$ (cm²/s)	K_{ad} (s^{-1})	K_{ds} (s^{-1})	Ω_1^∞	V (cm/s)
S-1	13.10±0.07	1.16±0.03	0.3403±0.0035	0.1503±0.0017	941.99	52.51
S-2	14.26±0.14	5.36±0.36	0.2563±0.0041	0.1196±0.0017	865.36	54.82
S-3	17.34±0.14	1.63±0.06	0.2602±0.0036	0.1217±0.0016	711.65	46.79
E-1	20.07±0.42	1.03±0.42	0.2783±0.0077	0.1501±0.0029	514.17	48.90

Admitting the adsorption effect means having two more parameters (K_{ad}, K_{ds}) in addition to the parameters of interest (K, D_p). All four parameters were obtained by fitting the model to experimental elution curves as described above. The results of the four columns are presented in Table 5. The constants of adsorption and desorption should be the same for all the columns, because they were made with the same glass and were submitted to the same treatment. According to the results present in Table 5, it is fair to assume that these constants have the same value for the different columns. This fact shows the reliability of the model, since the four parameters were estimated at the same time in each case. If the adsorption were not taken into account, the diffusion coefficient obtained would be two orders of magnitude lower. This occurs because the model would try to fit the experimental peak tailing by decreasing the diffusion coefficient.

In Figure 8 results of the fitting procedure with and without the adsorption effect are shown. First of all, it is possible to note that the fitting is much better when the adsorption is taken into account. Moreover, the diffusion coefficient of water at 50°C in column S-1, taking into account that the adsorption is estimated at 1.16×10^{-8} cm²/s and neglecting the adsorption at 4.58×10^{-10} cm²/s. Therefore, the results obtained admitting the adsorption effect are closer to the data in the literature (Brun and Larchet, 1985; Rufino et al., 1996).

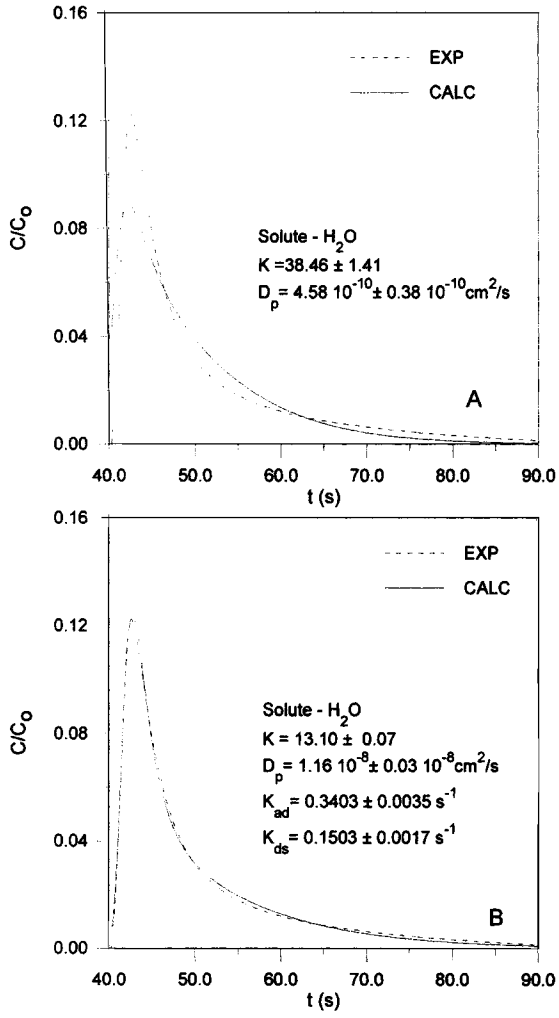

Figure 8. Fitting procedures in column S-1 at 50°C: (a) model without adsorption; (b) Model with adsorption.

Comparison to pervaporation results

The pervaporation results are given in Table 6. The permeate flux of the TCM in both membranes is a linear function of its feed concentration. The permeate flux of the water can be assumed constant, despite the increase of the organic feed concentration. These results are in agreement with the literature (Brun and Larchet, 1985; Nijhuis, 1990; Borges et al., 1992; Rufino et al., 1996; Pereira et al., 1997) and indicate that neither plastisizing nor flux coupling occurs. The scattering observed in the results obtained for water is due to the experimental error of this kind of test, which also has been noted in the literature (Brun and Larchet, 1985; Nijhuis, 1990; Borges et al., 1992; Rufino et al., 1996; Pereira et al., 1997). According to Table 6 the permeate flux of TCM in PDMS is much larger than it is in EPDM. TCM has a smaller Ω_1^∞ in EPDM than in PDMS (see Table 3), so it dissolves better in the former polymer. However, TCM permeability is larger in PDMS, as shown in Table 6. When the concentration of the

Table 6. Pervaporation Results for the Removal of TCM from Water by Pervaporation Using PDMS and EPDM Membranes at 50°C

TCM in Feed (PPM)	J_{total} kg/h m² ×10²	J_{TCM} kg/h m² ×10²	$J_{água}$ kg/h m² ×10²
	Membrane PDMS		
928	5.75	5.13	0.62
770	4.10	3.64	0.46
397	3.18	2.16	1.02
274	2.96	1.60	1.36
159	2.24	1.24	1.00
151	2.02	1.21	0.81
136	1.86	1.28	0.58
	Membrane EPDM		
1043	1.29	1.15	0.14
877	0.95	0.82	0.13
625	0.71	0.61	0.10
341	0.36	0.24	0.12

Table 7. Permeabilities Obtained by Pervaporation from the Literature and by IGC in this Work

Probe	$P\,(K \times D_p) \times 10^6$ (cm²/s) (Pereira et al., 1997) 25°C	$P\,(K \times D_p) \times 10^6$ (cm²/s) (This work) 50°C
DCM	0.48	8.84
TCM	2.16	16.90
TOLUENE	8.48	61.26

penetrants in the membrane are low, as in this case, the permeability can be estimated from IGC results. The average partition and diffusion coefficients for TCM in PDMS obtained by IGC are, respectively, 90 and 45×10^{-8} cm²/s, and in the case of EPDM are 120 and 14×10^{-8} cm²/s. An estimate for the permeability can be obtained from the product of these two coefficients. The results are 40.5×10^{-6} cm²/s for TCM in PDMS and 16.8×10^{-6} cm²/s in EPDM. As a consequence, the permeability of TCM in both polymers obtained by IGC is in agreement with the pervaporation results. Moreover, since IGC results give transport and thermodynamic parameters, it is possible to get a comprehensive picture of the pervaporation process. A similar analysis can be made in the case of water.

Pereira et al. (1997) carried out pervaporation experiments on the removal of several organic compounds from water. They obtained the permeability of these compounds in EPDM at 25°C and the results are reproduced in Table 7. In this same table, the results of the permeabilities obtained from IGC data (see Table 3) at 50°C are presented. Of course, the effect of the temperature has to be taken into account, because permeability increases at higher temperatures. Despite the differences in the absolute values, due to the different temperatures, the trend of both sets of results is the same. So, these results can be analyzed on the basis of IGC data. For example, although DCM is a smaller molecule and, therefore, has a larger diffusion coefficient in EPDM, its permeability is much smaller than that of toluene. Analyzing the IGC results in Table 3, one can conclude that this is due to the higher solubility of toluene. So, in this case it is also possible to get a further insight into the pervaporation process from the IGC results.

Conclusion

In this article, we proposed a fairly realistic model for gas chromatography. Simplifications can be made based on the simulation results. We have shown that these simplifications do not change the response of the model and enable the improvement of the numerical solution. The fitting procedure has shown adequate results. However, the procedure suffers from experimental limitations not reported in the literature, such as the high sensitivity of the diffusion coefficient on the peak shape. In spite of these limitations, on the whole the obtained results are satisfactory and in agreement with the literature. Therefore, the advantages of the IGC technique, in particular the fast data collection, still make it a convenient tool for the study of mass transfer and thermodynamic properties of small penetrants in polymers. The adsorption on the capillary wall suggested in the case of water has been undoubtedly proven by the experiments made with an empty column. The model proposed for the chromatograph process was improved by taking into account the adsorption effect. The results obtained for the adsorption–desorption constants assure the reliability of the model. The diffusion coefficients obtained for water are much more reliable when the adsorption effect is considered. The results obtained with the IGC procedure can give further understanding into the pervaporation process. Because IGC enables a fast data collection, it is interesting to have a bank of chromatographic columns with stationary phases made of the polymers that are often used in the membrane separation process.

Notation

a = solute concentration on the column wall
B_{11} = probe second virial coefficient
c = solute concentration in the mobile phase
c_0 = feed solute concentration
D_g = diffusion coefficient in the mobile phase
D_p = diffusion coefficient in the stationary phase
H_A = weight fraction Henry constant
K = partition coefficient
K_{ad} = adsorption constant
K_{ds} = desorption constant
L = column length
l_j = Lagrange interpolator polynomial
M_A = molecular weight of the probe
M_g = carrier molecular weight
m_p = polymer mass
P = flow rate
p = injected volume/t_{inj}
P_i = column inlet pressure
P_1^s = probe saturation pressure at column temperature
P_o = column outlet pressure
q = solute concentration in the stationary phase
R = column inside radius
r = radial coordinate
R_g = universal gas constant
T = temperature
t = time
t_{inj} = injection time
V = average velocity in the mobile phase
v_1^0 = molar volume of the probe as a pure liquid
V_e = specific retention volume
V_{inj} = admission chamber volume
V_{solv} = solvent volume
z = axial coordinate
ϵ = film thickness
η_g = carrier viscosity
ρ_p = polymer density
ρ_g = carrier density
ϕ_i = capillary inside diameter

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