Mass-Transfer Modeling in the Pervaporation of VOCs from Diluted Solutions

Ane Urtiaga, Daniel Gorri, and Inmaculada Ortiz
Dept. de Ingeniería Química 4, ETS Ingenieros Industriales y de Telecomunicación, Universidad de Cantabria,
39005 Santander, Spain

A generic model is derived for studying the mass-transfer kinetics of the pervaporation of multicomponent mixtures of volatile organochloride compounds. Applying it to the pervaporation of dilute mixtures of trichloromethane, dichloromethane and trichloroethylene using tubular polydimethylsiloxane (PDMS) membranes permits: (1) estimation of the representative mass-transfer parameters, that is, solute diffusivity in the aqueous phase and membrane permeability of the individual components; (2) discrimination of the relative importance of the mass-transport resistances to the pervaporation flux as a function of operation variables; and (3) determination of the selectivity in multicomponent pervaporation. Diffusivity values calculated with the model agree well with predictions by the Wilke−Chang correlation for nonelectrolyte solutes. Permeability values of PDMS membranes change in the trichloroethylene > trichloromethane > dichloromethane direction. The relative importance of mass-transfer resistances for the considered volatile organic compounds depends on the operation variables, that is, flow rate of the feed solution and membrane thickness. Furthermore, for trichloroethylene the main resistance is located in the feed solution, whereas for dichloromethane for high values of feed flow rate the resistance in the membrane could exert a major influence on kinetic control, and the behavior of trichloromethane is intermediate between both compounds.

Introduction

The contamination of natural waters with complex mixtures of volatile organic compounds is a problem of major concern, especially in areas where the primary source of raw water is groundwater (Hand et al., 1986). The occurrence of these mixtures is mainly due to discharges of industrial wastewaters containing either binary solutions of individual volatile organic compounds (VOCs), mainly chlorinated solvents in water, or multicomponent systems containing both polar and nonpolar VOCs in water. The strategies for the elimination of VOCs from these multicomponent systems should include the possibility of separating the VOCs into the pure components according to the attainable selectivity of the separation process.

Considering the group of membrane-based separation techniques, pervaporation has been proved to be a technically feasible process for the removal of VOCs from aqueous solutions, due to the availability of selective membranes with preferential flux of the organic compounds (Mulder, 1996). In the pervaporation operation the liquid feed mixture is maintained into contact with one side of a dense membrane and the permeate is removed from the other side in vapor form by a vacuum pump. The separation is determined by the selective sorption and diffusion of the organic compounds through the membrane.

In the removal of multicomponent mixtures of VOCs from aqueous solutions, the separation factor ($\alpha_{j/i}$) is defined as the relative separation achieved, between the i and j organic compounds, due to the difference in the transport rate of the permeants. Mathematically, the separation factor is ex-

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Correspondence concerning this article should be addressed to I. Ortiz.

pressed as the ratio of the fluxes of two components per unit concentration of each in the feed, as given by Eq. 1

$$\alpha_{j/i} = \frac{y_j/y_i}{x_j/x_i} = \frac{J_j/C_{jf}}{J_i/C_{if}} \tag{1}$$

When dealing with dilute aqueous feeds, it is usual to measure the performance of the pervaporation process by means of the separation factor between the j compound and water. With reference to our previous work (Urtiaga et al., 2001) on the pervaporation of chloroform−water solutions using polydimethylsiloxane (PDMS) membranes, values of $\alpha_{\text{chloroform}/w}$ in the 4,458−9,443 range were obtained.

According to Eq. 1, in order to predict $\alpha_{j/i}$ the fluxes of the components must be estimated. The studies of Psaume et al. (1988), Lipski and Côté (1990), Raghunath and Hwang (1992), and Crowder and Cussler (1998) about the separation of binary solutions of several VOCs in water using silicone tubes as pervaporation membrane are relevant to this matter. From their conclusions it was clear that the liquid-phase boundary-layer resistance was a significant contributing factor to the overall mass-transfer resistance, and consequently the description of liquid-phase hydrodynamics was the key design parameter in the construction of membrane modules for such separations. In a previous article (Urtiaga et al., 1999a), as in the work of Raghunath and Hwang (1992), the modeling of the solute mass transport in the liquid feed phase was performed by solving the continuity equation for the considered solute. It was concluded that the separation of chloroform−water mixtures using thin polydimethylsiloxane (PDMS) tubular membranes can be described by neglecting the mass-transfer resistance of the membrane and using the diffusivity of chloroform in aqueous solution as the only relevant mass-transfer parameter. However, the role of the membrane may become a contributing factor to the mass-transfer resistance as a result of a lower affinity to the organic compound or when using a higher membrane thickness. These aspects recently have been investigated in more detail by Crowder and Cussler (1998), Pereira et al. (1998), and Meuleman et al. (1999).

Furthermore, when dealing with multicomponent aqueous solutions, the permeation of an organic compound may significantly differ from the permeation in binary mixtures, since the diffusivity of the component in the liquid mixture and the solubility and diffusivity in the membrane can be affected by the presence of other compounds. Concerning the pervaporation of multicomponent mixtures of VOCs in water, several authors (Nguyen and Nobe, 1987; Dutta and Sikdar, 1999) concluded that coupling effects are absent when the downstream pressure is close to zero. On the other hand, Visvanathan et al. (1995) reported some flux coupling in the separation of trichloroethylene and 1,1,1-trichloroethane from wastewater by means of sweeping gas pervaporation. Their data could be in agreement with the results of Ji et al. (1994).

In this work the pervaporation of multicomponent diluted mixtures of chloroform (TCM), dichloromethane (DCM), and trichloroethylene (TCE) in water is analyzed. Experimental results obtained in the separation of a single VOC from binary water−TCM, water−TCE, and water−DCM solutions are also discussed, and additional references to the results obtained in previous works (Urtiaga et al., 1999a,b) are also included. The objective is to determine the mass-transfer model that describes the flux of each individual VOC in the separation of multicomponent mixtures and to establish a methodology to differentiate the governing mass-transfer resistances as a function of the values of the operational variables, that is, flow rate of the feed and membrane thickness.

Theory

The analysis of mass transfer in the pervaporation of a binary water−VOC mixture has been published in a previous work (Urtiaga et al., 1999a), applied to the separation of diluted chloroform−water solutions. The mass-transfer model describes the change in concentration of the organic solute in the feed liquid when circulating through the membrane module when the mass-conservation equation and the associated boundary conditions are used. The details of the mass-transfer mathematical model are compiled in the Appendix.

This article reports the differentiation of the relevant mass-transfer resistances to pervaporation. To do so, the dimensionless form of the quasi-steady-state mass balance (Eq. A1) will be derived, by defining the following dimensionless variables and parameters:

$$C_j^* = \frac{C_j}{C_{j,z=0}} \tag{2}$$

$$R = \frac{r}{r_i} \tag{3}$$

$$\xi = \frac{zD_j}{4\bar{v}r_i^2} = \frac{1}{Pe(z)} \tag{4}$$

$$Sh_{w,j} = \frac{2P_{m,j}sr_i}{lD_j}. \tag{5}$$

The validity of the quasi-steady-state approximation was checked in the previous work on the pervaporation of chloroform−water mixtures. Then, considering the term $\partial C_j/\partial t$ equal to zero, the following set of dimensionless equations is obtained:

$$[1-R^2]\frac{\partial C_j^*}{\partial \xi} = \frac{2}{R}\frac{\partial}{\partial R}\left(R\frac{\partial C_j^*}{\partial R}\right) \tag{6}$$

$$\text{B.C.1} \quad \text{at } \xi = 0 \quad C_j^* = 1 \quad 0 \le R \le 1 \tag{7}$$

$$\text{B.C.2} \quad \text{at } R = 0 \quad \frac{\partial C_j^*}{\partial R} = 0 \quad 0 \le \xi \le 1 \tag{8}$$

$$\text{B.C.3} \quad \text{at } R = 1 - \frac{\partial C_j^*}{\partial R} = \frac{Sh_{w,j}}{2}C_j^* \quad 0 \le \xi \le 1. \tag{9}$$

The parameter $Sh_{w,j}$ is the Sherwood number of the wall, defined according to Eq. 5, where D_j is the diffusivity of the j organic solute in the aqueous phase, and $P_{m,j}$ is the permeability of the membrane. Thus the value of Sh_w defines the ratio of the mass-transfer resistance in the inner fluid to that in the membrane (Kim and Stroeve, 1989; Urtiaga et al., 1992). For $Sh_w \to \infty$, the membrane resistance is negligible and the mass-transfer rate is dominated by diffusion in the liquid phase. For $Sh_w \rightarrow 0$, the mass-transfer rate is determined by the permeation of the organic compound through the membrane.

Experimental Studies

Pervaporation experiments were performed using capillary PDMS membranes. Hollow-fiber membrane modules were assembled in the laboratory using commercial membranes supplied by Dow Corning. Different modules were built in order to cover a wide range of membrane thickness (1.48×10^{-4}m $< l <$ 4.33×10^{-4} m). Dimensions and specifications of the modules employed in the current study are given in Table 1. The dimensions of the tubes were measured using a digitized microscope (Karl-Zeiss) able to measure in two orthogonal directions. Measurements were made at points randomly selected along the section of the tubing sample. These readings were compared to the values given by the supplier, obtaining a maximum error of 7%. The number of membrane capillaries in each module assembly was selected in order to obtain similar values of the Reynolds number at a given volumetric throughput in the four modules.

A pervaporation system obtained from Sulzer Chemtech was used. The system was operated in batch mode with continuous recirculation of the aqueous phase to the feed tank. Binary aqueous solutions containing dichloromethane ($C_0 =$ 500 mg/L $= 5.9\times10^{-3}$ mol/L), chloroform ($C_0 = 500$ mg/L $= 4.2\times10^{-3}$ mol/L), and trichloroethylene ($C_0 = 250$ mg/L/L $= 1.9\times10^{-3}$ mol/L) were prepared in the laboratory using reagent-grade compounds. Multicomponent solutions of chloroform, dichloromethane, and trichloroethylene in water were also tested. In all the experiments the liquid feed was thermostatized at 40°C and the permeate vacuum side pressure was maintained below 3 mbar. The permeation flux of each individual VOC was determined by analyzing samples of the aqueous feed by gas chromatography (Hewlett-Packard 6890 model) via an electron-capture detector. Detailed descriptions of the experimental system and analytical procedures are given in a previous work (Urtiaga et al., 1999a).

Results and Discussion

Mass-transfer kinetics

The experimental results obtained in the separation of binary mixtures of water–chloroform (TCM), water–dichloromethane (DCM), and water–trichloroethylene (TCE) are described next.

The influence of the flow rate and temperature of the feed on the pervaporation of binary water–TCM mixtures was studied in detail in a previous article (Urtiaga et al., 1999a). Module no. 1 in Table 1 was used in that work, corresponding to a membrane thickness $l = 1.48\times10^{-4}$ m. Working with the mass-transfer model described through Eqs. A1 to A14, it was found that the diffusivity of chloroform in water was the only parameter required to describe the chloroform separation rates obtained at different flow rates and different temperatures. The estimated value for the diffusivity of chloroform in water was $D_{TCM}(40°\text{C}) = 1.55\times10^{-9}$ m^2/s. Therewith it was concluded that when using thin PDMS membranes, the resistance of the membrane to the permeation of chloroform is negligible.

Table 1. Specifications of Membrane Modules

Module No.	No. of Fibers	ID (m)	Wall Thick. (m)	Memb. Area (m^2)	Shape Factor (s)
1	15	3.27×10^{-4}	1.48×10^{-4}	0.0057	1.405
2	9	5.16×10^{-4}	1.96×10^{-4}	0.0056	1.343
3	7	6.57×10^{-4}	2.53×10^{-4}	0.0055	1.348
4	6	7.78×10^{-4}	4.33×10^{-4}	0.0056	1.488

In the present work the study of the influence of membrane thickness on the rate of TCM pervaporation is reported. The experimental results are given in Figure 1a–1c,

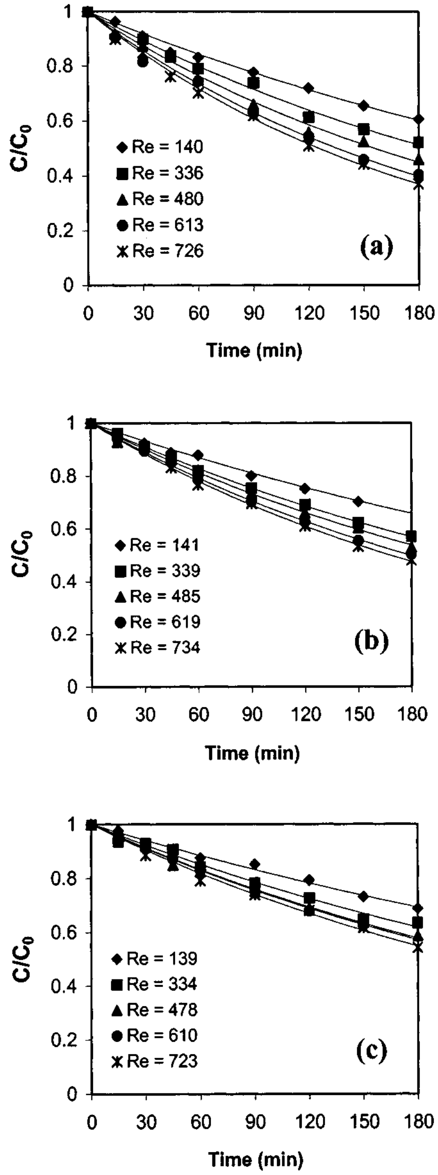


Figure 1. Experimental courses of chloroform concentration in the feed tank: effect of feed flow rate.

(a) Module no. 2; (b) module no. 3; (c) module no. 4. Flowrate values, in m^3/s: (◆) $F = 3.37\times10^{-7}$; (■) $F = 8.1\times10^{-7}$; (▲) $F = 11.58\times10^{-7}$; (●) $F = 14.78\times10^{-7}$; (*) $9F = 17.52\times10^{-7}$.

where it can be observed that the influence of the flow rate of the feed on the TCM rate of removal is lower as the membrane thickness is increased.

The influence of feed flow rate and membrane thickness on the kinetics of the removal of DCM is presented in Figure 2a–2d. The dependence of the rate of removal with the flow rate of the feed indicates that the resistance in the liquid is important in the mass transfer of DCM. Besides, a similar behavior was observed in the four membrane modules under investigation, although the membrane thickness was increased 2.5 times. However, if the kinetics of the pervaporation of DCM are compared with the kinetic results of TCM, it is observed that the separation rate of TCM is faster than the separation rate of DCM for each one of the membrane thicknesses under investigation. This observation could indicate that the resistance of the PDMS membrane to mass transfer cannot be neglected in the pervaporation of DCM, even when using thin membranes. With reference to the relevant literature, Pereira et al. (1998) and Lau et al. (1997) studied the influence of membrane thickness on the flux of water and a group of chlorinated hydrocarbons. The authors concluded that the effect of membrane thickness was particularly important in the separation of DCM.

The results obtained in the separation of TCE from aqueous solutions are given in Figure 3a–3d. As in the removal of TCM and DCM, the higher the flow rate of the liquid feed, the faster the separation kinetics of TCE. If the results of Figure 3a–3d are compared with the data in Figure 1a–1c and 2a–2d, it is observed that the separation rate of TCE is slightly faster than the separation rate of TCM and clearly faster than the separation rate of DCM.

Mass-transfer parameters estimation

According to the mass-transfer model reported in the Appendix, the mass-transfer parameters required to describe the pervaporation of VOCs from diluted aqueous solutions are the diffusion coefficient of each VOC in water, D_j, and the permeability of the pervaporation membrane to each VOC, P_{mj}. In the analysis of the removal of chloroform, the purpose was to verify the limits of the approximation of negligible membrane resistance to the mass transfer of chloroform when using thicker PDMS membranes. Starting from the value of diffusivity obtained in the previous work, the results were simulated using Eqs. A1–A6 and A10. However, only for membrane thickness of $l = 1.96 \times 10^{-4}$ m the simulated curves were in good agreement with the experimental results. Thus, it was concluded that two resistances should be considered for the prediction of the pervaporation flux, that is, the permeability of the membrane was needed in order to describe the pervaporation of chloroform for the membrane thickness of $l = 2.53 \times 10^{-4}$ m and $l = 4.33 \times 10^{-4}$ m. The estimation of $P_{m,TCM}$ was performed by comparing the experimental data with the simulated results obtained using the mass-transfer model in combination with the parameter estimation system gEST, providing a value of $P_{m,TCM} = 4.46 \times 10^{-8}$ m^2/s.

From the experimental results obtained in the pervaporation of DCM, the estimated values of the parameters are $D_{DCM} = 1.84 \times 10^{-9}$ m^2/s and $P_{m,DCM} = 8.97 \times 10^{-9}$ m^2/s. The diffusivity value obtained in this study is very similar to

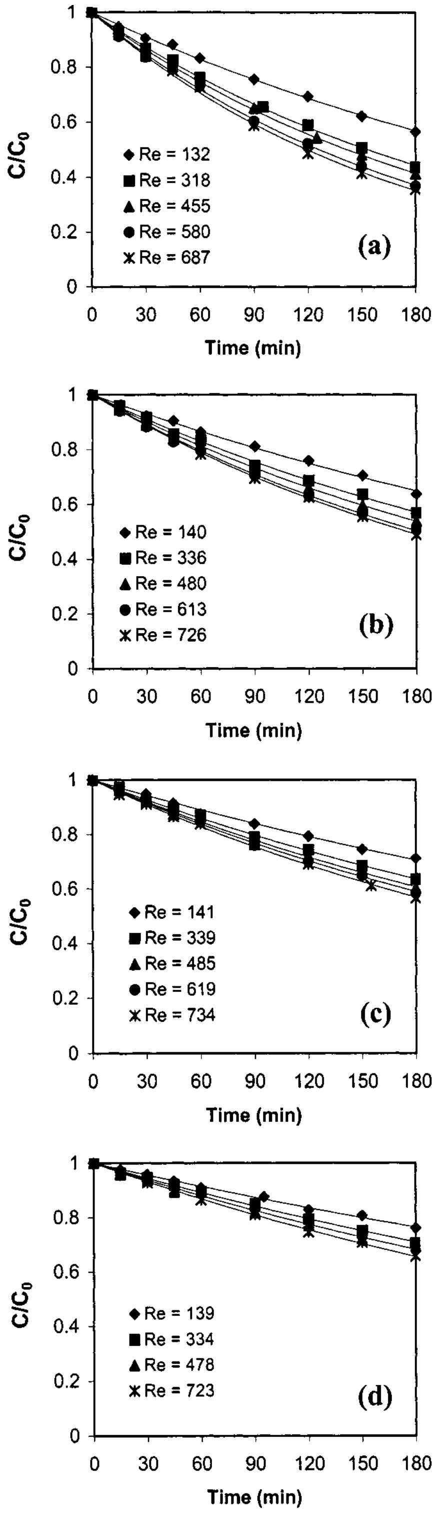


Figure 2. Experimental courses of dichloromethane concentration in the feed tank: effect of feed flow-rate.

(a) Module no. 1; (b) module no. 2; (c) module no. 3; (d) module no. 4. Flow-rate values, in m^3/s: (◆) $F = 3.37 \times 10^{-7}$; (■) $F = 8.1 \times 10^{-7}$; (▲) $F = 11.58 \times 10^{-7}$; (●) $F = 14.78 \times 10^{-7}$; (*) $F = 17.52 \times 10^{-7}$.

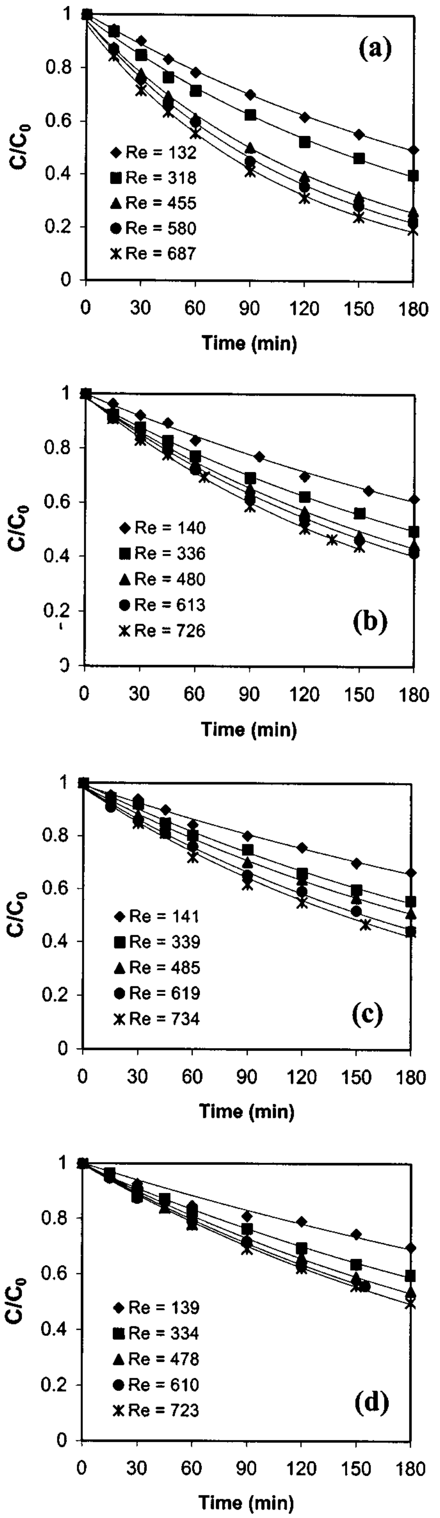


Figure 3. Experimental courses of trichloroethylene concentration in the feed tank: effect of feed flow rate.

(a) Module no. 1; (b) module no. 2; (c) module no. 3; (d) module no. 4. Flow-rate values, in m³/s: (◆) $F = 3.37\times10^{-7}$; (■) $F = 8.1\times10^{-7}$; (▲) $F = 11.58\times10^{-7}$; (●) $F = 14.78\times10^{-7}$; (*) $F = 17.52\times10^{-7}$.

Table 2. PDMS Membrane Permeability for Dichloromethane

T (°C)	$P_{m,DCM}$ (m²/s)	Reference and Remarks
20	5.6×10^{-9}	Hickey and Gooding (1994) Flat membrane: analysis of influence of feed flow rate
30	6.65×10^{-9}	Ji et al. (1994) Flat membranes: analysis of influence of membrane thickness
40	8.97×10^{-9}	This study. Hollow-fiber membrane: combined analysis of influences of membrane thickness and feed flow rate

the value calculated using the Wilke–Chang estimation technique ($D_{DCM,W\text{-}C} = 1.83\times10^{-9}$ m²/s). The good agreement of the model and parameters with the experimental data is confirmed by the value of the standard deviation between experimental data and the simulated values of the dimensionless concentration, $\sigma = 0.0113$. Ninety-eight percent of the simulated results of $C^*_{\text{sim,DCM}}$ fall within the interval $C_{\text{exp},DCM} \pm 5\% C^*_{\text{exp},DCM}$.

The dependence of the membrane permeability of DCM, $P_{m,DCM}$, on temperature was obtained by correlating the value obtained in this work at 40°C with the values reported by other authors, as given in Table 2. It was found that $P_{m,DCM}$ followed an exponential dependency with temperature fitting to a good regression coefficient the values given by Ji et al. (1994) and Hickey and Gooding (1994):

$$P_{m,DCM}\ (\text{m}^2/\text{s}) = 8.5\times10^{-6}\exp(-2{,}150/T), \quad r^2 = 0.97. \tag{10}$$

The permeability coefficient of the membrane is related to the solubility and diffusivity coefficients of the permeating solute in the membrane where both parameters are normally exponentially dependent on temperature (Feng and Huang, 1997; Gonzalez and Ortiz, 2001).

The estimation of the mass-transport parameters for trichloroethylene was performed following the same procedure as in the DCM–water separation. It was found, however, that the mathematical model did not show sensitivity to the value of the parameter $P_{m,TCE}$. It was believed that this behavior was caused by the negligible resistance of the PDMS membrane to the transport of TCE. Under this assumption, the mass-transport model contains only one parameter, the diffusivity of TCE in water, as the estimated value of $D_{TCE}(40°\text{C}) = 1.52\times10^{-9}$ m²/s. The simulated concentrations using the diffusivity in water as the only mass-transport parameter are compared to the experimental concentrations to arrive at a value for the standard deviation of $\sigma = 0.018$. Ninety-two percent of the simulated results of $C^*_{\text{sim},TCE}$ fall within the interval $C^*_{\text{exp},\,TCE} \pm 5\% C^*_{\text{exp},TCE}$.

Table 3 shows that the estimated values of the diffusivity of the three VOCs in water are very similar to those calculated using the Wilke–Chang semiempirical correlation (Reid et al., 1987). This fact proves the validity of the proposed mass-transfer model and parameters and the adequacy of the well-known Wilke–Chang equation for estimating diffusion coefficients of halogenated VOCs in water. With reference to

Table 3. Estimated Mass-Transfer Parameters and Theoretical Diffusivity of Organics in Water

Compound	D_j (m^2/s) Est. in This Study	$D_{j,\,W\text{-}C}$ (m^2/s) Wilke–Chang Equation	$P_{m,j}$ (m^2/s) Est. in This Study
Chloroform (TCM)	1.55×10^{-9}	1.53×10^{-9}	4.46×10^{-8}
Dichloromethane (DCM)	1.84×10^{-9}	1.83×10^{-9}	8.97×10^{-9}
Trichloroethylene (TCE)	1.52×10^{-9}	1.46×10^{-9}	$>5\times10^{-7}$

Note: Temperature = 40°C.

the literature, Raghunath and Hwang (1992) followed a similar methodology for the estimation of the diffusion coefficients of chlorobenzene, benzene, and toluene in water. These authors also used a mass-transfer model based on the solution of the continuity equation, but they found that the values of the diffusivity of the organic compounds in water obtained from the fitting of their experimental data differed substantially from those calculated with the Wilke–Chang equation. The authors ascribed these differences to the experimental errors and an insufficient amount of data. In agreement with other authors (Visvanathan et al., 1995), it was found in this work that one important source of experimental error in the pervaporation of volatile organic compounds arises from the use of the condensed permeate in the determination of the permeation flux of the organic compounds, which is a result of the difficulty in achieving the complete condensation of the vapor permeate. For this reason, it was decided to sample the liquid feed instead of using the condensed permeate.

Discrimination of mass-transfer resistances

Figure 4 shows the variation of Sh_{ov}, with the Peclet number as a function of Sh_w, where the overall Sherwood number is expressed as

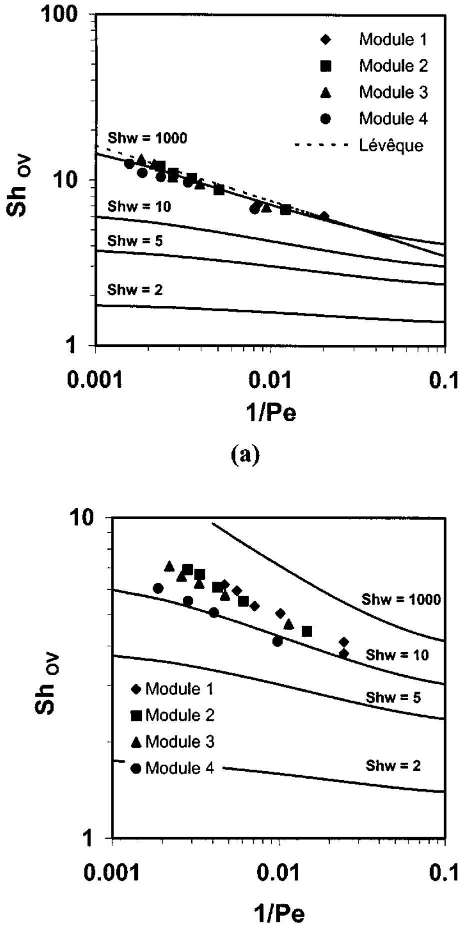
$$Sh_{ov,j} = \frac{-\ln\left(\bar{C}^*_{j,L}\right)}{4\xi_{z=L}} = \frac{-\ln\left(\bar{C}^*_{j,L}\right)}{4(1/Pe)}. \qquad (11)$$

In Eq. 11, $\bar{C}^*_{j,L}$ is the dimensionless mixing-cup concentration of the j component at the module outlet, as defined in the Appendix. $\xi_{z=L}$ is the value of the dimensionless variable ξ at the module outlet, and is equal to the inverse of the Peclet number. For a given solute (fixed ρ and D) and a given geometry of the membrane tubes (fixed r_i and L), an increase in the value of the Reynolds number of the inner fluid is equivalent to a decrease in the value of $(1/Pe)$.

The contribution of the membrane to the total mass-transfer resistance can be obtained by considering the resistances in series expression,

$$\frac{1}{Sh_{ov,j}} = \frac{1}{Sh_{L,j}} + \frac{1}{Sh_{w,j}}. \qquad (12)$$

On the righthand side of Eq. 12 the term $1/Sh_{L,j}$ accounts for the resistance to mass transfer of the liquid phase, and the term $1/Sh_{w,j}$ accounts for the resistance to mass transfer of the pervaporation membrane. For each permeating compound, the value of $1/Sh_{L,j}$ is dependant on the flow rate of the feed, while the term $1/Sh_{w,j}$ has a constant value for a given module.



(a)

(b)

Figure 4. Variation of Sh_{ov} with $(1/Pe)$ as a function of Sh_w: (a) TCE data; (b) DCM data.

In Figure 4 it is observed that for $(1/Pe) < 0.03$ the slope of the line with $Sh_w = 1000$ is approximately equal to $-1/3$, which is coincident with Léveque's solution to the Graetz problem (Skelland, 1974):

Léveque's equation:

$$Sh_L = 1.62 Re^{1/3} Sc^{1/3} (d/L)^{1/3} = 1.62 Pe^{1/3}. \qquad (13)$$

Equation 13 is valid for the description of mass transfer in the liquid boundary layer for a fully developed velocity profile in laminar flow. Thus, for $Sh_w \to \infty$, $Sh_{ov} = Sh_L$, which is to say, the total resistance to mass transfer is located in the liquid boundary layer. The decrease in the value of Sh_w is accompanied by a reduction in the slope of the Sh_{ov}-$(1/Pe)$ courses. At low values of the parameter Sh_w the mass-transfer rate is only slightly influenced by the value of $(1/Pe)$, because the overall permeation rate is mainly determined by the permeation rate through the membrane.

Also included in Figure 4 are the experimental data points corresponding to the separation of DCM and TCE at different flow rates and different membrane thickness. For clarity of exposition, we have omitted the data of chloroform, which is the behavior of chloroform intermediately between trichloroethylene and dichloromethane. The slope of the linear regression of the experimental data in Figure 4 was determined. In the case of TCE, all the experimental data were fitted to a single regression line and the resulting slope is -0.33, thereby indicating that for TCE the mass-transfer resistance is only located in the liquid phase. In the case of DCM, the data obtained in module 4, which has the highest membrane thickness, can be clearly distinguished from the data obtained in modules 1, 2 and 3, and two different slopes were calculated: slope 1 (data from modules 1, 2, and 3) $= -0.26$; slope 2 (data from module 4) $= -0.23$. Thus, increasing the thickness of the membrane causes an increase in the membrane resistance to mass transfer. However, in the case of DCM, that influence is only important for high values of the membrane thickness.

It is observed that each set of experimental results shows a trend that can be associated with a certain value of the wall Sherwood number. The data points of TCE fall over the $Sh_w = 1000$ line, while the data points of DCM are plotted slightly over $Sh_w = 10$ line. Therefore, the value of Sh_w that corresponds to each compound and membrane module was calculated using a parameter estimation technique to give $11 < Sh_{w,DCM} < 18$; $50 < Sh_{w,TCM} < \infty$; $250 < Sh_{w,TCE} < \infty$, being the varation range determined by the dependency of Sh_w on the diameter and wall thickness of the membrane.

For instance, using module no. 1 (membrane thickness $l = 1.48 \times 10^{-4}$ m) to remove DCM, the values of the overall Sherwood number varied in the range $4 < Sh_{ov} < 6.2$ in the interval of Reynolds number of the feed $132 < Re < 687$, while the estimated value of the wall Sherwood number is $Sh_w = 16.7$. As a result, the percentage the membrane contributes to the total resistance to mass transfer varies between 24 and 37%. Thus we conclude that in the pervaporation of DCM the resistance of the PDMS membrane may become dominant at higher Reynolds numbers.

Behavior of multicomponent mixtures

The mass-transfer model given in the Theory section has been applied to the separation of binary VOC–water mixtures. In this section we check that the model is valid to describe the pervaporation of multicomponent VOCs–water mixtures. For that purpose the experimental results obtained in the pervaporation of multicomponent aqueous solutions of DCM, TCM, and TCE are presented. The aqueous feed solution was prepared with the following initial concentrations: TCM, 4.2×10^{-3} mol/L; DCM, 5.9×10^{-3} mol/L; and TCE, 1.9×10^{-3} mol/L. The influence of the flow rate was analyzed in the range of Re number $140 < Re < 735$, corresponding to feed flow rates of 20.2, 48.6, 69.5, 88.7 and 105.1 mL/min. All the experiments were performed using module no. 3, with an intermediate value of the membrane thickness ($l = 2.53 \times 10^{-4}$ m). As a representative example, Figure 5 shows the kinetic results obtained for $Re = 734$. In the graph the multicomponent results are compared to the evolution of the concentration of each individual VOC in the separation of binary mixtures. As it is qualitatively observed, the separation rate of each individual VOC is not affected by the presence of other VOCs in the dilute range of concentrations under consideration. A parity graph of the concentrations obtained in the separation of binary mixtures versus the data obtained in the separation of multicomponent mixtures is given in Figure 6. The standard deviation of the data in Figure 6 is $\sigma = 0.022$. Thus the presence of coupling phenomena in the flux of the organic solutes can be ignored.

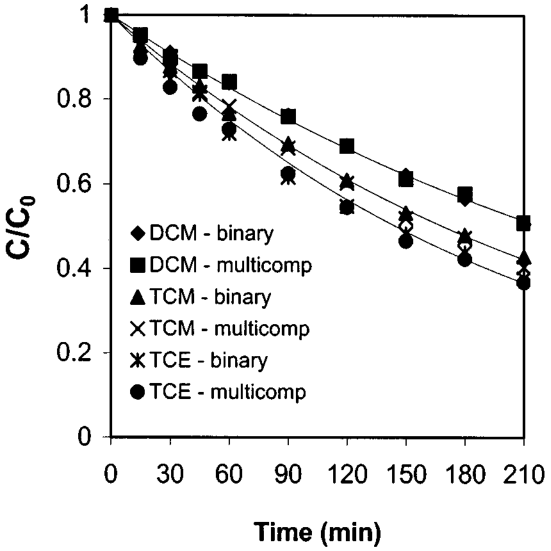


Figure 5. Experimental courses of concentration for binary mixtures (1 VOC–water) and multicomponent mixtures (3 VOC–water), module no. 3, $Re = 734$.

It then can be concluded that due to the low concentration of the VOCs in the aqueous feed solutions the diffusion process of each individual solute in the liquid phase is not significantly altered by the presence of other solutes, neither the

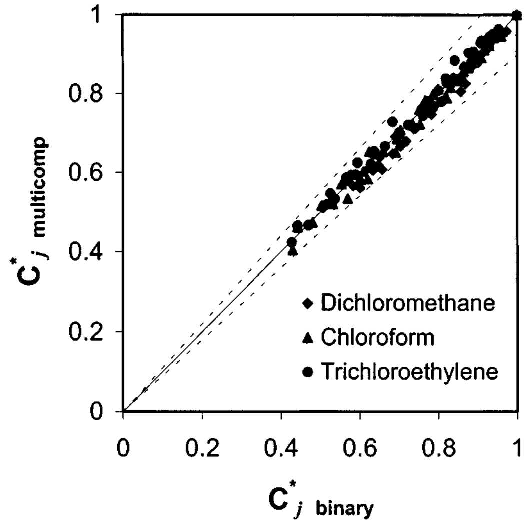


Figure 6. Parity.

Experimental concentrations obtained in the separations of binary mixtures vs. experimental concentrations obtained with multicomponent mixtures.

sorption nor the diffusion processes of DCM through the pervaporation membrane.

Values of the separation factor of the multicomponent separation were determined using Eq. 1. The experimental fluxes needed to calculate $\alpha_{j/i}$ were obtained as

$$J_j = k_{ov,j} C_j, \tag{14}$$

where $k_{ov,j}$ was obtained from the slope of the linear regression of the experimental data as follows

$$\ln\left(\frac{C_j^T}{C_{j,0}^T}\right) = -\left(\frac{k_{ov,j} A_m}{V}\right) t. \tag{15}$$

As was discussed in the previous work (Urtiaga et al., 1999a), the experimental data fit this simple description adequately, based on overall mass-transfer parameters. However, due to the difficulty of describing the experimental behavior observed with changing flow rate and temperature, this simple description was not used to predict the mass-transfer rates. Consequently, the distributed parameter mass balance given by Eq. A1 was needed to perform the mathematical prediction of the selectivity, using the mass-transfer parameters obtained for the binary systems that are given in Table 3.

Figure 7 shows the experimental and simulated values of the separation factor as a function of the Reynolds number of the feed. The experimental values of $\alpha_{j/i}$ were obtained from the pervaporation data of multicomponent mixtures. In Figure 7a it is observed that in all cases the selectivity $\alpha_{TCE}/_{DCM}$ is higher than unity, while the ratio of diffusion coefficients is $D_{TCE}/D_{DCM} = 0.83$. Thus the contribution of the membrane resistance to the DCM flux enhances the selectivity of the pervaporation of TCE over DCM. It is also observed that the experimental values of the separation factor become higher as the Reynolds number is increased. This behavior is also due to the fact that the feed flow rate has more influence on the mass transfer of TCE than on the mass transfer of DCM, since the latter is also limited by resistance to permeation through the membrane.

A similar behavior is observed with the selectivity of the separation of chloroform and dichloromethane mixtures, $\alpha_{TCM/DCM}$. Figure7b shows the selectivity results for modules no. 1 and no. 2 with thin PDMS membranes. As long as the membrane thickness does not affect the rate of chloroform separation, the values of the separation factor in the two modules follow the same trend. The situation changes for higher membrane thickness (Figure 7c), showing increasing values of $\alpha_{TCM/DCM}$ as the membrane thickness is increased, since $P_{m,TCM} > P_{m,DCM}$.

Figure 7d indicates that the separation factor of the TCM/TCE separation is lower than unity. The two compounds have a very similar diffusion coefficient in water, but the flux of TCM is reduced due to the permeability of the membrane when compared to the flux of TCE.

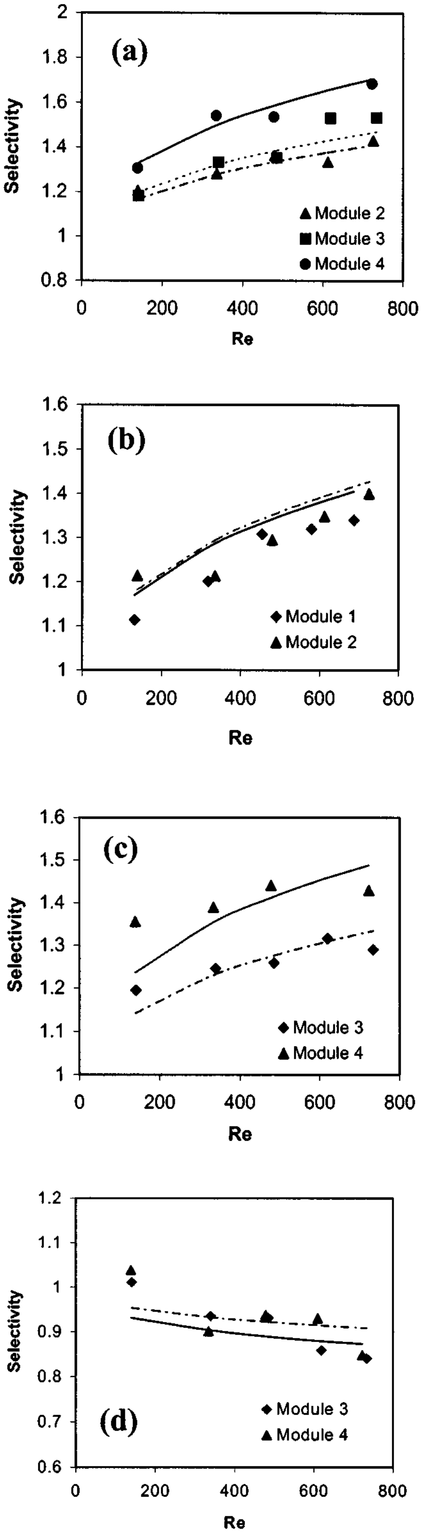


Figure 7. Experimental and simulated separation factor of multicomponent pervaporation.

(a) $\alpha_{TCE/DCM}$; (b) $\alpha_{TCM/DCM}$; (c) $\alpha_{TCM/DCM}$; (d) $\alpha_{TCM/TCE}$.

Conclusions

In this work a general mass-transfer analysis of the pervaporation of multicomponent mixtures of VOCs in water using PDMS capillary membranes is reported. Three VOCs have been analyzed—trichloromethane, dichloromethane, and trichloroethylene—and the relevant mass-transfer parameters of each compound have been determined using the methodology previously reported by the authors (Urtiaga et al., 1999a). The influence of the flow rate of the feed and the thickness of the membrane were experimentally studied. For the three compounds the higher the feed flow rate, the faster the kinetics of the separation. It was also found that the TCE separation rate is slightly faster than the TCM separation rate, and clearly faster than the DCM separation rate.

The mass-transfer parameters required to describe the pervaporative separation of VOCs were the diffusion coefficient in water and the permeability of the membrane. The estimated values of the diffusion coefficient of TCM, DCM, and TCE in water were very similar to those obtained using the Wilke–Chang semiempirical correlation. After the characteristic parameters of the pervaporation of each VOC were determined, a schematic method for differentiating the mass-transfer resistances as a function of the operation variables, feed flow rate, and membrane thickness was reported. The method, which was based on the use of dimensionless numbers, showed that the studied VOCs exhibited different behavior. In the removal of TCE the resistance of the membrane is negligible, while in the separation of DCM the contribution of the membrane to the total resistance varies between 21 and 37% in the experimental range of variables.

Finally, the mass-transfer model was used to calculate the separation factor in the pervaporation of multicomponent mixtures, and predictions were compared to experimental results. It was observed that in all cases the selectivity, $\alpha_{TCE/DCM}$, is higher than unity; however, the ratio of diffusion coefficients is $D_{TCE}/D_{DCM} = 0.83$. Thus the contribution of the membrane resistance to the DCM flux enhances the selectivity, $\alpha_{TCE/DCM}$.

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Notation

A_m = mass-transfer area of the membrane, m^2
C = solute concentration in the feed along the membrane module, mol/m^3
C^T = solute concentration in the feed tank, mol/m^3
C^* = dimensionless solute concentration along the membrane module
C_{in}^T = concentration of the fluid at the entrance to the feed tank
C_0 = initial solute concentration in the feed, mol/m^3
$\overline{C}_L^*$ = dimensionless mixing-cup concentration
d = inner diameter of the hollow-fiber membranes, m
D = diffusion coefficient, m^2/s
F = total volumetric flow rate of the feed, m^3/s
J_j = flux of the component j through the membrane, mol/m^{2}s
k_m = membrane mass-transfer coefficient, m/s
k_{ov} = averaged overall mass-transfer coefficient, m/s
l = membrane thickness, m
L = effective length of the hollow fiber module, m
P_m = permeability coefficient of the membrane, m^2/s
Pe = Peclet number in $z = L$, $Pe = (d/L)ReSc$
$Pe(z)$ = Peclet number, $Pe(z) = 4\bar{v}r_i^2/zD_j$
r = radial coordinate
r_i = inner radius of the hollow fiber, m
r_o = outer radius of the hollow fiber, m
R = dimensionless radial coordinate
Re = Reynolds number
s = shape factor, $s = \{[r_o - r_i]/[r_i \ln(r_o/r_i)]\}$
S_{LM} = distribution coefficient defined by Eq. A7
Sc = Schmidt dimensionless number
Sh_L = liquid-phase Sherwood number
Sh_{ov} = overall Sherwood number
Sh_w = wall Sherwood number, Eq. 5
t = time, s
T = temperature, K
$\bar{v}$ = average linear velocity of the fluid, m/s
$v_z(r)$ = axial velocity of the fluid inside the hollow fiber, m/s
V = volume of the feed, m^3
x = molar fraction in the liquid feed
y = molar fraction in the vapor permeate
z = axial coordinate

Greek letters

$\alpha_{j/i}$ = separation factor
α = portion of the total volumetric flow rate that circulates along the module ($0 < \alpha < 1$)
ξ = dimensionless variable, Eq. 4

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Appendix

The continuity equation and the associated boundary conditions for the fluid circulating through the membrane module are written as follows,

$$\frac{\partial C_j}{\partial t} + 2\bar{v}\left[1-\left(\frac{r}{r_i}\right)^2\right]\frac{\partial C_j}{\partial z} = D_j \frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial C_j}{\partial r}\right] \tag{A1}$$

$$\text{B.C. 1:} \quad t=0 \quad C_j = C_{j,0} \quad \text{for all } r \text{ and all } z \tag{A2}$$

$$\text{B.C. 2:} \quad z=0, \quad C_j = C_j^T, \quad \text{for all } r \tag{A3}$$

$$\text{B.C. 3:} \quad r=0 \quad \frac{\partial C_j}{\partial r} = 0, \quad \text{for all } z \tag{A4}$$

$$\text{B.C. 4:} \quad r=r_i \quad -D_j\frac{\partial C_j}{\partial r} = s * k_{m,j}\left(C^1_{j,\text{membrane}} - C^2_{j,\text{membrane}}\right), \quad \text{for all } z. \tag{A5}$$

The fourth boundary condition dictates the continuity of the j flux compound at the fluid/membrane interface.

The low pressure of the permeate side allows us to consider

$$C_{\text{permeate}} = C^2_{\text{membrane}} = 0, \quad \text{for all } z. \tag{A6}$$

The solute concentration in the membrane cannot be directly measured. Using a distribution coefficient,

$$S_{ML,j} = \frac{C^1_{j,\text{membrane}}}{C_{r=r_i}}. \tag{A7}$$

The mass-transport coefficient of the membrane $k_{m,j}$ is related to the permeability of the membrane $P_{m,j}$

$$\frac{1}{k_{m,j} * S_{ML,j}} = \frac{l}{P_{m,j}}. \tag{A8}$$

By substitution of Eqs. A7 and A8 into Eq. A6,

$$\text{B.C. 4} \quad r=r_i \quad -D_j\frac{\partial C_j}{\partial r} = \frac{P_{m,j}}{l} * s * C_j, \quad \text{for all } z. \tag{A9}$$

When the pervaporation membrane shows a high affinity for the organic solute, the B.C. 4 can be simplified by considering the negligible resistance of the membrane to the transport of the j compound. Thus

$$\text{B.C. 4:} \quad r=r_i, \quad C_j = 0 \quad \text{for all } z. \tag{A10}$$

Integration of the preceding system of differential equations will provide values of $C_j(r,z)$. The mixing-cup concentration of the organic component at the module outlet is obtained as

$$\overline{C}_{j,z=L} = \frac{\int_0^{r_i} v_z(r) C_j(r,L) r\, dr}{\int_0^{r_i} v_z(r) r\, dr}. \tag{A11}$$

The mass-transfer model of the system under consideration is completed with the mass balance to the feed tank, Eqs. A12 and A13, and the mixing point, Eq. A14:

$$V\frac{dC_j^T}{dt} = F\left(C^T_{j,in} - C_j^T\right). \tag{A12}$$

Initial condition $t=0$

$$C_j^T = C_{j,0} \tag{A13}$$

$$(1-\alpha) * F * C_j^T + \alpha F * \overline{C}_{j,z=L} = F * C^T_{j,in}. \tag{A14}$$

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