TRANSPORT PHENOMENA IN THE PERVAPORATION OF DICHLOROMETHANE FROM AQUEOUS SOLUTIONS

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ABSTRACT

In this work the mass transfer analysis of the pervaporative separation of dichloromethane from aqueous solutions in hollow fiber devices has been performed. Experimental results were obtained at 40ºC working at different flow rate values (0.02 – 0.105 l/min) and using modules with different thickness of membrane (148 – 433 μm).

In the pervaporation of dichloromethane from dilute aqueous solutions using polydimethylsiloxane hollow fibers, the rate of separation is strongly influenced by the mass transfer resistance in the feed phase. In the laminar flow regime, the resistance of the membrane is not dominant, although it may become significant at higher Reynolds numbers.

A mathematical model resulting from the solution of the continuity equation of the feed phase flowing in laminar regime through the hollow fiber module has been proposed. The analysis by means of the fundamental equations separates the effects of the operation variables such as the hydrodynamic conditions and the geometry of the system from the mass transfer properties of the system, described by the diffusion coefficient in the aqueous phase and the membrane permeability.

INTRODUCTION

The use of the pervaporation process for the separation of chlorinated hydrocarbons from aqueous liquid mixtures has been found a technically viable technology [1-5]. In the pervaporation process, the liquid feed mixture is put into contact with a non-porous solid membrane and the selective sorption of the components of the feed occurs according to the characteristics of the membrane. The absorbed components diffuse through the membrane, evaporate under low pressure on the downstream side and are removed by a vacuum pump or a chilled condenser. The phase change occurs in the membrane and the heat of vaporisation is supplied by the sensible heat of the liquid conducted through the dense membrane.

Concerning the selection of the selective membrane, the family of silicon rubbers provides a good behaviour in the recovery of dilute organics from aqueous solutions, due to the high affinity of these materials towards linear chlorinated hydrocarbons. Commercial membranes of highly hydrophobic polydimethylsiloxane are available. Several groups have studied the enhancement of the separation performance by modifying the properties of the PDMS material either by the incorporation of zeolites into the membrane structure [6] or by the introduction at the molecular level of various organofunctional groups [7].

The low concentration of the organics in the liquid feed and the high affinity of the membrane towards the organic components create a concentration-polarization phenomena at the liquid feed phase, and the removal of dilute organics may be controlled by the mass transfer in the boundary layer at the liquid-membrane interface. Thus achieving fast pervaporation is often compromised by diffusion in the liquid feed phase. However, membrane resistance cannot be always neglected. As the Reynolds number is increased, the liquid film resistance should be reduced and the membrane resistance may become rate controlling.

The gradients at steady state are shown in Figure 1. The feed is rich in water, but the organic component is much more soluble in the PDMS polymer and there is a low concentration of the organic at the upstream face of the membrane ($C_{DCM\ (m)}$). Thus, the gradient of the organic in the liquid is high. The gradient of water, the principal component of the mixture, is negligible.

In this work we present the results obtained in the separation of dilute binary mixtures of water/dichloromethane. The influence of the flowrate of the feed phase and the thickness of the pervaporation membrane were investigated. The kinetic analysis of the separation was performed following the methodology published in a previous paper [3] concerning the separation of water/chloroform mixtures.

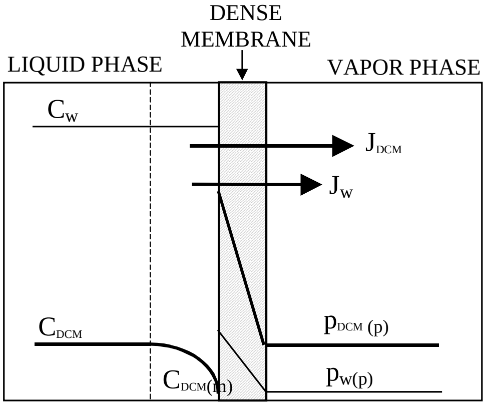
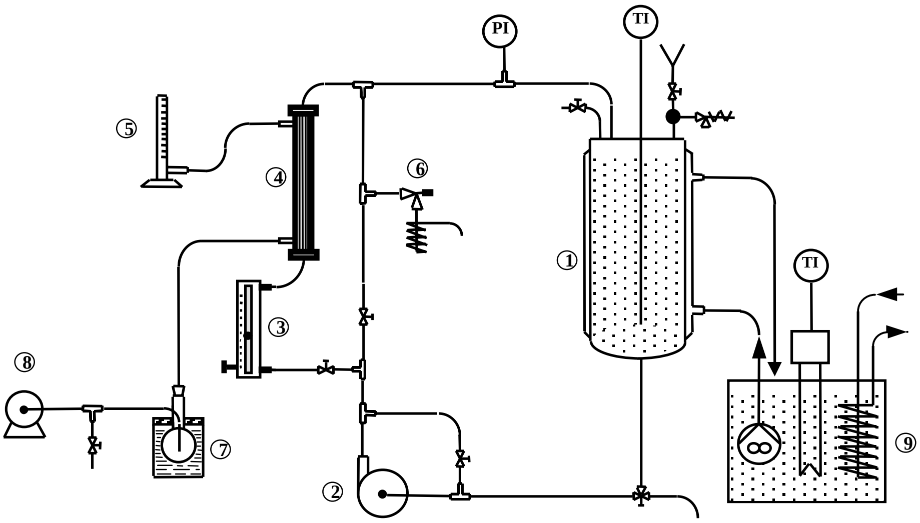


Figure 1. Diagram of concentration gradients in a three phase pervaporation system

EXPERIMENTAL

In all cases the aqueous feed solutions were prepared in the laboratory using reagent grade dichloromethane in deionized water. The initial concentration in the feed was 0,5 kg/m^3 each of dichloromethane. The temperature of the feed was maintained constant at T = 40 ºC. Dense polydimethylsiloxane hollow fibers were used to assemble the membrane modules in the laboratory. The dimensions of the fibers are given in Table 1. A diagram of the experimental system is given in Figure 2. The aqueous feed was introduced through the bore of the hollow fibers. The system was operated in batch mode with the continuous recirculation of the aqueous phase to the feed tank. The permeate was removed in vapor form from the shell-side of the membrane module by the suction of a vacuum pump. Cold traps refrigerated by liquid nitrogen were used to condense and recover the permeate vapors. The detailed descriptions of the experimental system and analytical procedures are given elsewhere [3].



1 - Feed vessel   2 - Feed pump   3 – Flowmeter   4 - Hollow fiber module   5 - Vacuum gauge
6 - Sampling valve   7 - Liquid N_2 cold trap   8 - Vacuum pump   9 - Temperature control bath

Figure 2. Schematic diagram of the experimental set-up

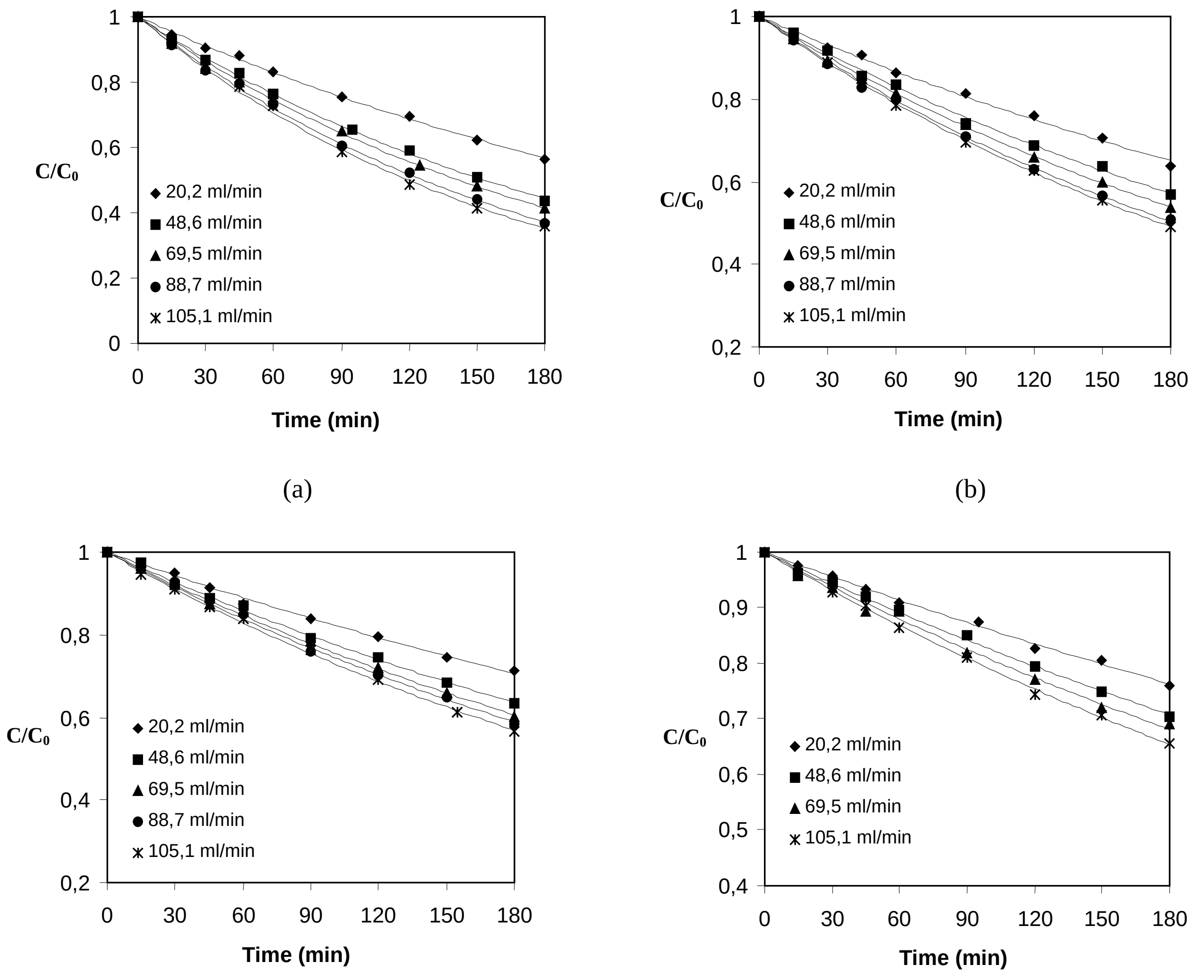
Table 1
Dimensions of the PDMS Hollow Fibers

Module #	Inner diameter (μm)	Thickness (μm)	# of fibers
1	327	148	15
2	516	196	9
3	657	253	7
4	778	433	6

RESULTS AND DISCUSSION

Figure 3 shows that increasing the flowrate of the feed phase increased the kinetics of the removal of dichloromethane, thus indicating that the mass transfer resistance of the liquid boundary layer has a strong influence on the flux of the organic component. The same behaviour was observed with the four modules under investigation.

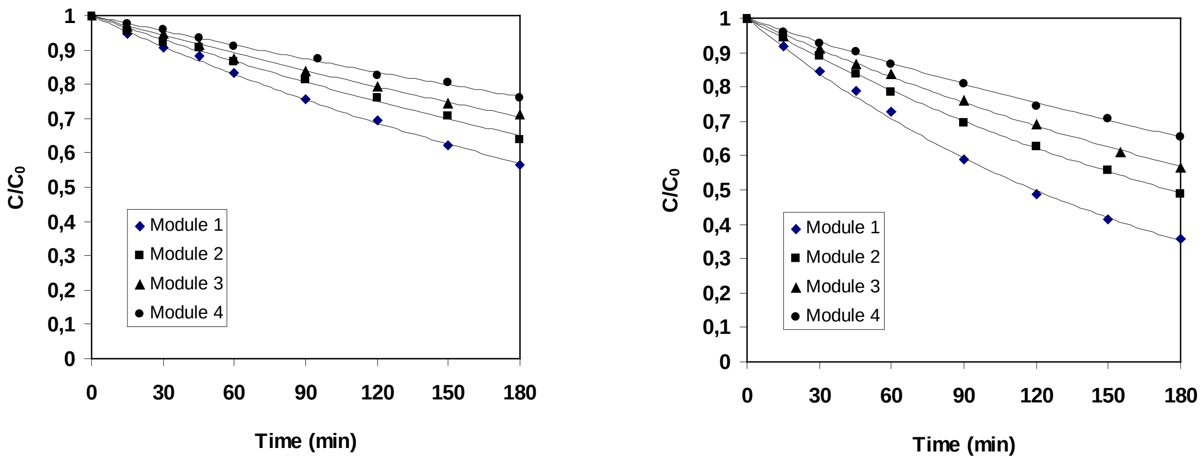
However, Figure 4 shows that at a constant Reynolds number the rate of the dichloromethane separation decreases as the thickness of the membrane is increased. Thus in the range of Reynolds numbers under investigation ($132 < Re < 734$) the mass transfer resistance across the membrane, is significant enough as to be taken into consideration.



(a) (b)

(c) (d)

Figure 3. Evolution of the dimensionless concentration in the feed tank. Influence of the flow rate of the feed. T=40 ºC. (a) module 1, (b) module 2, (c) module 3, (d) module 4.



(a) (b)

Figure 4. Evolution of the dimensionless concentration in the feed tank. Influence of the thickness of the membrane. T=40 ºC. (a) 132 < Re < 141, (b) 688 < Re < 734.

The analysis of the results was performed using the mathematical model reported in a previous work for the separation of chloroform [3]. The analysis by means of the fundamental equations separates the effects of the operation variables such as the hydrodynamic conditions and the geometry of the system from the mass transfer properties of the system, described by the diffusion coefficient in the aqueous phase and the membrane permeability. The mass balance to the hollow fiber membrane module and the associated boundary conditions are written as follows,

$$\frac{\partial \mathrm{C^m}}{\partial \mathrm{t}} + 2\,\overline{\mathrm{v}}_\mathrm{z}\left[1-\left(\frac{r}{r_i}\right)^2\right]\frac{\partial \mathrm{C^m}}{\partial z} = D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \mathrm{C^m}}{\partial r}\right) \tag{1}$$

$$\text{BC 1 :} \qquad t = 0, \quad \mathrm{C^m} = \mathrm{C_0} \qquad \text{all } r \text{ and all } z \tag{2}$$

$$\text{BC 2 :} \qquad z = 0, \quad \mathrm{C^m} = \mathrm{C^T} \qquad \text{all } r \tag{3}$$

$$\text{BC 3:} \qquad r = 0, \quad \frac{\partial \mathrm{C^m}}{\partial r} = 0 \qquad \text{all } z \tag{4}$$

$$\text{BC 4:} \qquad r = r_i\,, \quad -D\,\frac{\partial \mathrm{C^m}}{\partial r} = \frac{P_m}{\delta} * s * \mathrm{C^m} \qquad \text{all } z \tag{5}$$

The fourth boundary condition imposes the continuity of flux of dichloromethane at the fluid/membrane interface. The left-hand side of the equation gives the solute flux arriving at the membrane wall from the bulk due to radial diffusion. The right-hand side of the equation accounts for the transport of solute through the membrane due to diffusion in the solid PDMS. D is the diffusivity of the solute in the aqueous phase and P_m is the permeability of the membrane. In eq. (5) the shape factor s as defined by Noble [8] is:

$$s = \frac{r_o - r_i}{r_i\; ln\dfrac{r_o}{r_i}} \tag{6}$$

The parameter s is based in the internal mass transfer area of the membrane and relates the flux though the membrane in a cylindrical geometry to the flux in a flat geometry.

The mass balance to the feed tank is given as

$$\mathrm{V^T}\frac{d\mathrm{C^T}}{dt} = \dot{\mathrm{V}} * \left(\mathrm{C^T_{in}} - \mathrm{C^T}\right) \tag{7}$$

$$t = 0 \qquad \mathrm{C^T} = \mathrm{C_0} \tag{8}$$

Additionally,

$$\overline{\mathrm{C}}^\mathrm{m}_\mathrm{z=L} = \frac{4}{r_i^2}\int_0^{\mathrm{r_i}} \mathrm{C^m}(r,\mathrm{L})\; r\left(1 - \left(\frac{r}{r_i}\right)^2\right)\mathrm{d}r \tag{9}$$

Eqs. (1)-(9) were integrated using the numerical integration package gPROMS in combination with the parameter estimator gEST. A comparison between the experimental and the simulated results allowed to obtain the values of the parameters D and P_m, the diffusivity of the organic compound in the aqueous phase and the permeability of the membrane respectively (Table 2).

Table 2
Diffusivity in Water and Permeability of the PDMS Membrane, T = 40 ºC

Organic compound	Diffusivity in water at 40ºC, m^2/s, this work	Diffusivity in water at 40ºC, m^2/s, Wilke-Chang equation	Permeability of the membrane, m^2/s
Dichloromethane	1.84×10^{-9}	1.83×10^{-9}	8.97×10^{-9}

Several findings are concluded from this table. First, the value obtained for diffusivity of dichloromethane in aqueous phase from the fitting of experimental results to the reported model is very similar to the value obtained by using the well-known Wilke-Chang correlation. Second, although no previous reference has been found in the literature reporting the permeability of dichloromethane at 40ºC, Hickey and Gooding [9] in 1994 reported a value of $P_m = 5.6 \times 10^{-9}\ m^2/s$ at 20ºC, and Ji et al. [10] in 1994 reported a value of $P_m = 6.65 \times 10^{-9}\ m^2/s$ at 30ºC, both working with flat membranes. Thus, the value obtained in this work is in good accordance with previously reported data.

The good agreement of the model and parameters with the experimental data is confirmed by the value $\sigma = 0.0113$ of the standard deviation between experimental data and the simulated values of the dimensionless concentration, defined by eq. (10).

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}\left(C^*_{exp} - C^*_{sim}\right)^2}{N-1}} \tag{10}$$

Finally, Figure 5 shows a parity graph of simulated concentration values versus experimental concentrations, where it is observed that 98% of the results of C^*_{sim} falls within the interval $C^*_{exp} \pm 5\%\ C^*_{exp}$, thus confirming the adequacy of the reported model and parameters.

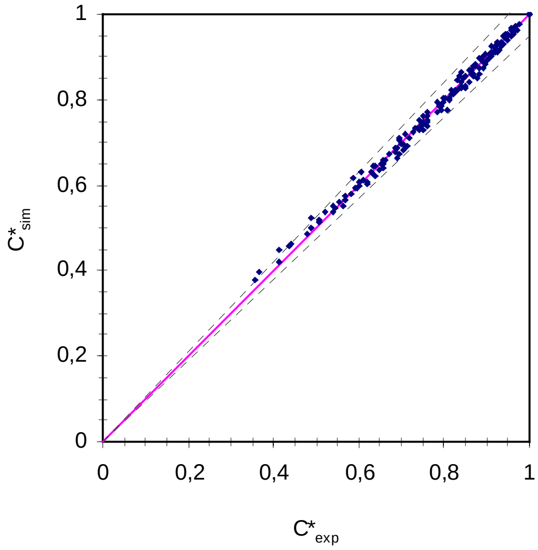


Figure 5. Parity graph of simulated dichloromethane concentration vs. experimental dichloromethane concentration.

CONCLUSIONS

It can be concluded that in the pervaporation of dichloromethane from dilute aqueous solutions using polydimethylsiloxane hollow fibers, the rate of separation is strongly influenced by the mass transfer resistance in the feed phase. In the laminar flow regime, the resistance of the membrane is not dominant, although it may become significant at higher Reynolds numbers. The proposed mass transfer model includes two parameters, the diffusivity of dichloromethane in water and the permeability of dichloromethane in the PDMS membrane. Diffusivity of dichloromethane in aqueous phase took a value of 1.84 x 10^{-9} m^2/s and the permeability through the polydimethylsiloxane PV membrane took a value of 8.97 x 10^{-9} m^2/s.

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