Permeation of organic molecules in water and ethanol-water solutions by reverse osmosis
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Permeation of organic molecules in water and ethanol-water solutions by reverse osmosis

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Abstract

The permeation of different organic molecules in water solvent and in 12% ethanol-water solution by hydrophilic reverse osmosis membrane was studied. The membrane was conditioned to the ethanol-water solution before the experiments. Initially, the membrane was characterized by water and ethanol-water solutions. The permeation of four solutes (tyramine, proline, glucose and tartaric acid) showed that the solute rejections increased with permeate flux and they were than 90% in water solvent, and they were decreased significantly in presence of ethanol.

Keywords: reverse osmosis, ethanol-water mixtures, solute rejection, organic molecules, Spiegler-Kendem model.

1. Introduction

Most of the established reverse osmosis and nanofiltration membrane processes are related to the treatment of aqueous systems, or single organic solvent solution. The use of these process for systems of solvent mixture especially mixture of water and organic solvent is considerably sparse. Furthermore, most of the research is being done with relatively low concentration, and a few results have been reported of solution with high concentration of organic solute in the mixture of organic solvent and water.

Koops *et al.* (2001) and Yang *et al.* (2001) showed that rejections of the same solute are significantly different for a given membrane when measured in solvents with different polarities. The implication of this finding is that the molecular weight cut-off (MWCO) or pore size data provided by membrane manufacturers (which are usually measured in aqueous environments) may not be valid in organic solvents. There is little agreement in the literature on the mechanisms of solute–solvent–membrane interactions in organic solvents.

There is usually a difference in solute rejection and flux in organic solvents when compared with performance in aqueous solutions (Machado *et al.*, 1999). In most cases, rejection of the same molecule in an organic solvent is significantly lower than in aqueous solution for the same membrane and operating conditions (Su *et al.*, 2005). Membrane manufacturers usually supply membranes semi-dry or wet with water. It is important to condition the membranes before to use with organic solvents. Conditioning involves rinsing the membrane and permeating water or the solvent under the appropriate pressure to ensure removal of preservatives and humectants on the membrane surface and from within the pores. The membrane should then be exposed to solvents with gradually changing polarities in sequence, ending with a solvent of a polarity matching that of the membrane. This solvent exchange process was first described by van Oss (1970).

Membrane conditioning ensures complete wetting of membrane by solvent which facilitates solvent permeation and improves its performance. The method of conditioning has a strong effect on flux, membrane integrity and pressure rating of polymeric membranes (Shukla *et al.*, 2002). Swelling and deformation of the membranes when exposed to organic solvents is common and is dealt with by conditioning the membranes through gradual solvent change (Shukla *et al.*, 2003). Once conditioned, the membrane's performance may be significantly different from that in an aqueous system and may have to be described for each individual solute-solvent-membrane system.

The permeability is influenced by these factors as well as molecular size and hydrophobicity. The behavior of the membranes in organic solvents has been described using several different models with varying degrees of success, taking into account characteristics of the solvent such as viscosity, molar volume, and surface tension as well as characteristics of the membranes and solutes (Bhanushali *et al.*, 2001; Van der Bruggen *et al.*, 1999).

In this study, the influence of feed pressure, feed concentration on the permeate flux and rejection of organic molecules have been analyzed in water solvent and in 12% (v/v) ethanol in ethanol-water mixture through low pressure reverse osmosis membrane.

2. Theoretical background

Transport of a binary solution through reverse osmosis membranes can be described by the phenomenological model of Kedem and Katchalsky, which is based on non-equilibrium thermodynamics:

(1) The solvent flux through a membrane, J_v, as a function of differences in applied pressure between both sides of membrane, ΔP, is given by the following expression:

$$J_v = L_p \cdot \left(\Delta P - \sigma \cdot \Delta\pi\right) \qquad (1)$$

where L_p is the solvent permeability, $\Delta\pi$ is the difference in osmotic pressure between both sizes of membrane and σ is the reflection coefficient, which is a measure of the degree of the solute permeation through the membrane and corresponds to the maximum solute rejection.

(2) The steady state transport of a solute, J_s, in a pressure-driven process is described by diffusive and convective transport as:

$$J_s = w \cdot \Delta\pi + (1-\sigma) \cdot J_v \cdot \overline{C} \qquad (2)$$

where w is the solute permeability, and $\overline{C}$ represents the average of the solute concentration between both sides of the membrane and usually is calculated as a logarithm mean. Following this equation, the solute permeation is a function of diffusion and convection flow. As applied pressure increases, the contribution of convection increases and the solute rejection approaches to the reflection coefficient. In contrast, the solute permeability corresponds to purely diffusive transport when convection flux is negligible (solvent flux tends to zero).

Spiegler-Kendem modified the model of Kendem and Katchalsky by a differential form of Equation (2). The Spiegler-Kendem model takes into account the concentration profile inside the membrane.

(3) The solute rejection, which is defined by the permeate and retention concentrations (C_p and C_r, respectively) as $\Re = 1 - C_p / C_r$, for an ideal solution was deduced by Spiegler-Kendem by integration the differential form of solute transport equation and was expressed as a function of reflection coefficient with the following equations:

$$\Re = \frac{(1-F) \cdot \sigma}{1 - \sigma \cdot F} \qquad (3)$$

with

$$F = exp\left(- \frac{(1-\sigma) \cdot J_v}{R \cdot T \cdot w} \right) \qquad (4)$$

Then, the separation process in reverse osmosis is performed by the determination of L_p, w and σ.

3. Experimental

The permeation of four organic solutes was analyzed in water and ethanol-water solutions: tyramine, proline, glucose and tartaric acid. The ethanol concentration in the ethanol-water solutions was fixed to 12%.

The experimental set-up for membrane testing consisted of a thermostatic (25 ± 0.5 ºC) 2 L feed vessel, a positive displacement pump equipped with a closed-pipe pressure dampener to prevent pressure oscillations, supplied by CAT-PUMPS (Kontich, Belgium), a membrane cell for a flat sheet polymeric membrane (Sepa CF membrane cell), supplied by GE Infrastructure Water & Process Technology, pressure gauges to measure the inlet and outlet pressures in the membrane cells and flow meters for retentate and permeate flux rate measurements.

The reverse osmosis membrane was supplied by Toray (ref. UTC70). This flat sheet (155 cm^2) polysulfone-polyamide nanofiltration membrane has salt rejection of 97.2%. The membrane system was operated in steady state mode, in which both retentate and permeate streams are recycled to the feed vessel. The time needed to reach the steady state was 60 minutes. The performance of the process was determined by measuring the solute concentrations in the retentate and permeate streams, the transmembrane pressure and the resulting permeate flux rate. The membrane was conditioned to ethanol solvent. The membrane was initially soaked in 12% (v/) aqueous ethanol overnight at room temperature and atmospheric pressure. The membrane was then placed in the cell and the flux of 12% ethanol measured as a function of pressure. This procedure was repeated until the flux was constant.

4. Results and discussions

The solvent permeate flux depends on not only operational conditions (i.e., transmembrane pressure, temperature) and membrane properties, but also interaction between solution and membrane, which are determined by solution and membrane properties. Figure 1 shows the water and ethanol-water permeate fluxes as a function of transmembrane pressure and ethanol volume fraction. Linear relationships with transmembrane pressure were obtained for both solutions. The ethanol-water fluxes were much lower than those of the water. The experimental data was well correlated by Equation (1), and the fitted and calculated values of Splieger-Kendem model are shown in Table I. L_p and $\sigma \cdot \Delta\pi$ depended on ethanol volume fraction, while $\sigma \cdot \Delta\pi$ increased, L_p decreased with ethanol volume fraction.

As water has the highest affinity for hydrophilic membranes, the addition of ethanol has a stronger effect on the solvent permeability. Therefore, ethanol-water mixtures have lower permeabilities than water ones. This fact could be due to the polarity differences and surface phenomena (i.e., swelling), since the presence of a relative low alcohol concentrations decreases the mixture polarity, leading to higher resistance at the membrane-solvent interphase. As a result, ethanol has lower affinity for hydrophilic membranes.

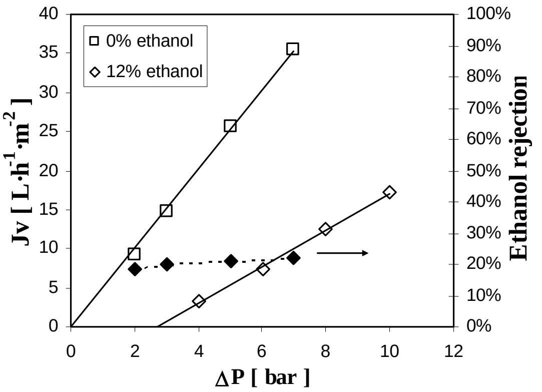

Figure 1. Evolution of solvent permeate flux (open symbols) and ethanol rejection (filled symbols) as a function of transmembrane pressure for the two solvent solutions.

Table I. Solvent permeability and $\sigma \cdot \Delta\pi$ as a function of ethanol concentration.

Ethanol concentration	**L_p ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)**	$\sigma \cdot \Delta\pi$	**r^2**
0%	5.05	0	0.997
12%	2.34	2.71	0.999

In general, the retention of organic species in water solvent can be considered very high for reverse osmosis. Figure 2 shows the solute rejections as a function of permeate flux for both solvents. The solute rejection increased with permeate flux tending to the reflection coefficient of the solute, σ. The Spiegler-Kendem model was well correlated with the experimental data for the best values of solute permeability, *w*, and reflection coefficient, σ, following Equations (3) and (4). The best fitting curves are illustrated in Figure 2 as solid lines and the results are shown in Table II. The solute rejections were higher than 90% in water solvent, and they were decreased significantly in presence of ethanol. The higher rejection in water solvent than in ethanol-water mixture could suggest that the complexation of water molecules with the solute molecules makes their effective size larger in water solvent than in ethanol-water mixture. Rejections were approximately the same for all solutes because of the comparable molecular size, if molecular size is taken as a factor determining the separation, without taking any effect of the solvent into account.

Solute permeability, showed in Table II, depended on solute type and increased in presence of ethanol. This fact could be due to the reduction of solvent polarity. Therefore, the decrease in solute rejection with ethanol-water mixture is due to the reduction of solvent flux although solvent permeability increased.

Mechanisms and mathematical models for retention of organic solutes by reverse osmosis have been well developed for water solvent, while transport and retention mechanisms in presence of organic solvents need further investigation for the determination of the solute-solvent-membrane interactions.

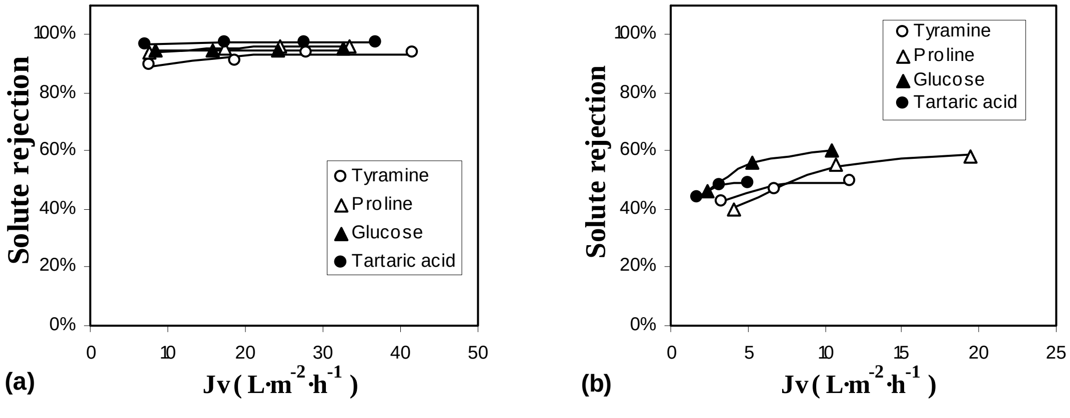

Figure 2. Solute rejections as a function of solvent fluxes: (a) water solvent and (b) 12% ethanol in ethanol-water mixture.

Table II. Reflection coefficient and solute permeability in different solvent.

Solvent	Solute	σ (-)	w (mol· h^{-1}·m^{-2}· bar^{-1})
Water	Tyramine	0.935	0.0234
	Proline	0.960	0.0122
	Glucose	0.949	0.00753
	Tartaric acid	0.976	0.00570
Ethanol-water (12% ethanol)	Tyramine	0.495	0.0481
	Proline	0.601	0.112
	Glucose	0.607	0.0480
	Tartaric acid	0.490	0.0208

5. Conclusions

In this study, it has been studied the permeation of four organic solutes in water solvent and in ethanol-water mixture with an ethanol volume fraction of 12%. The permeate flux of the ethanol-water mixture was lower than that of the pure water for the hydrophilic membrane and the result was theoretically analyzed. The solute rejections increased with permeate flux and they were than 90% in water solvent, and they were decreased significantly in presence of ethanol. The experimental data was well correlated by the Spiegler-Kendem model.

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References

Bhanushali, D., Kloos, S., Kurth, C., and Bhattacharyya, D. (2001) *Journal of Membrane Science*, 189, 1–21.
Koops, G.H., Yamada, S. and Nakao, S.I., (2001) *Journal of Membrane Science*, 189, 241–254.
Machado, D.R., Hasson, D. and Semita, R., (1999) *Journal of Membrane Science*, 163, 93-102.
Shukla, R. and Cheryan, M., (2002) *Journal of Membrane Science*, 198, 75-85.

Van der Bruggen, B., Schaep, J., Wilms, D., and Vandecasteele, C. (1999) *Journal Membrane Science*, 156, 29–41.

Shukla, R. and Cheryan, M., (2003) *Separation Science and Technology*, 38, 1533–1547.

Su, B., Wang Z., Wang, J. and Wang, S., (2005) *Journal of Membrane Science*, 251, 189-200.

van Oss, C.J., *Progress in Separation and Purification*, vol. 3, Wiley/ Interscience, New York (1970).

Yang, X.J., Livingston, A.G. and Freitas dos Santos, L., (2001) *Journal of Membrane Science*, 190, 45–55.