

Effect of Operation Conditions in the Pervaporation of Ethanol–Water Mixtures with Poly(1-Trimethylsilyl-1-Propyne) Membranes

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ABSTRACT: Poly(1-trimethylsilyl-1-propyne) (PTMSP) is known to show preferential permeation of ethanol in the pervaporation of ethanol–water mixture. Although this polymer presents good characteristics for the separation of organic–water solutions, operation conditions and membrane characteristics, such as thickness, affect its pervaporation performance. The effect of temperature and feed concentration on pervaporation was studied. During pervaporation of 10 wt % ethanol–water solution, the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) remains almost constant, whereas the permeation flux (F) increases exponentially with operation temperature. On the other hand, the separation factor decreases,

whereas the permeation flux increases with ethanol content in the feed mixture. The membrane thickness also affects the performance of PTMSP polymer films: selectivity increases sharply with membrane thickness up to 50 μm , whereas it remains constant for thicker membranes. The permeation flux decreases with membrane thickness in the whole range studied. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1395–1403, 2004

Key words: pervaporation; ethanol–water mixtures; polyacetylenes; membranes; activation energy

INTRODUCTION

Membrane technology has its main application in the design of new separation processes with high efficiency, with the objective of avoiding the use of separation agents. This kind of process presents economic advantages derived from the elimination of purification and separation steps, and environmental advantages as such minimize generation of residues derived from recovery of solvents. Nevertheless, the main drawback of membrane separation systems is that their efficiency decreases with time because of swelling, degradation, and fouling processes occurring in the membrane.

The main membrane processes are microfiltration, reverse osmosis, ultrafiltration, electrodialysis, gas separation, and pervaporation; the latter is considered as an alternative method for separation of liquid mixtures as the vapor–liquid equilibrium (VLE) can be altered by a selective membrane.

In pervaporation, the feed, at atmospheric pressure, is in contact with a permselective membrane. The permeate undergoes a phase change when it is transported across the membrane and is removed in the vapor state from the opposite side of the membrane, which is kept under low pressure by a vacuum pump (vacuum pervaporation) or swept with a stream of inert gas (sweeping-gas pervaporation). The membrane undergoes anisotropic swelling: the side in contact with the liquid mixture swells, whereas the other side remains almost dry because of the applied vacuum.

The main disadvantage of the pervaporation process is the relatively high energy consumption in comparison with reverse osmosis and ultrafiltration, where the feed does not undergo any phase change. The pervaporation process consumes an amount of energy that is at least equal to the heat of vaporization of the complete pure product to be separated.¹ This can be compensated by using a carrier gas to sweep the permeate solute instead of the vacuum system.²

Although pervaporation is expensive because of the phase change that takes place, it is a process of interest in cases where conventional separation processes either fail or result in a high specific energy consumption and/or high investment costs. The most important categories of separation problems for which pervaporation is promising are mixtures of compounds with small differences in boiling points and azeotro-

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pes or isomers mixtures and the recovery of volatile compounds from diluted solutions. Investigated systems range from aqueous solutions of methanol, ethanol, propanol, and butanol³⁻⁸ to organic binary mixtures⁹⁻¹² and recovery of useful aroma compounds.¹³⁻¹⁵

Characteristics such as selectivity and high flux through the membrane have to be optimized to allow an economical separation process. Poly(1-trimethylsilyl-1-propyne) (PTMSP) is a polymer that exhibits good characteristics for the separation of ethanol from diluted mixtures.^{16,17} This polymer presents high values of separation factor and specific permeation rate, but its transport properties decrease with time.¹⁸⁻²⁰

The objective of this work was to study the effect of operation conditions, such as concentration and temperature of the feed mixture, and membrane thickness on transport properties of PTMSP membranes during pervaporation of ethanol-water mixtures.

EXPERIMENTAL

Materials

1-Trimethylsilyl-1-propyne (TMSP, 99%) and TaCl₅ (99.9%) were purchased from Aldrich; toluene (analytical grade) and methanol (analytical grade) were purchased from Panreac (Barcelona, Spain), and ethanol (analytical grade) was purchased from Merck. TaCl₅ was used as received, with care being taken not to allow decomposition from exposure to moisture and/or air. TMSP and toluene were distilled in the presence of calcium hydride under nitrogen before use.

Polymerization procedure

The PTMSP was synthesized by using the method previously described,²¹ adapted from the Masuda et al.'s method.^{22,23} Polymerization of PTMSP was carried out under dry nitrogen at 80°C for 24 h. The catalyst, TaCl₅, was dissolved in toluene and after 10 min the solution became deep yellow. Then, the monomer was added to this solution and the solution became turned dark brown. The reaction mixture was poured into a large amount of methanol where the catalyst was deactivated. The polymer was purified by the solution-precipitation method by using a toluene-methanol system and was dried to constant weight.

Measurement of molecular weight

The molecular weight of the samples was determined by gel permeation chromatography (Water 510 Pump, Waters 410 Differential Refractometer, Waters Styragel HR column). Tetrahydrofuran was used as solvent

and standard polystyrenes were used for calibrating molecular weight.

Membrane preparation

Membranes were fabricated by casting polymer-toluene solutions (1-2 wt %) into a Petri dish, and the solvent was allowed to evaporate slowly over a few days at room temperature. The membranes thus fabricated appeared uniform and dense. Membrane thickness was determined through direct measurement of its weight and a reported density value of 0.75 g cm⁻³²⁴⁻²⁷ and by scanning electron microscopy (SEM; JEOL 6400).

Pervaporation experiments

The pervaporation apparatus was presented in a previous article.²⁸ The effective area of the membrane was 14 cm², and the permeate pressure was kept at about 2 mmHg by a rotary vacuum pump. The ethanol content in the feed, the permeate and the retentate was analyzed by refractive index measurements by using a calibration curve (Refractometer RX-5000, Atago).

The performance of PTMSP membranes in pervaporation was evaluated by the total specific permeation rate (R_{total}) and the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$). R_{total} was calculated by using the expression

$$R_{\text{total}} = \frac{F\delta}{At} \quad (1)$$

where F is the collected amount of permeate (g), δ is the membrane thickness (m), A is the area of the membrane (m²), and t is the sampling time (h).

The separation factor was defined as:

$$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}} = \frac{Y/(1-Y)}{X/(1-X)} \quad (2)$$

where X and Y are the weight fractions of ethanol in the feed and in the permeate, respectively.

EFFECT OF TEMPERATURE

The effect of temperature on transport properties of PTMSP was studied with data obtained after 450 h of pervaporation performance so that the effect of time, thickness, and polymer nature can be excluded. The temperature range studied was 38-75°C.

Separation factor

The effect of temperature on the separation factor was studied with a 100- μm PTMSP membrane with an

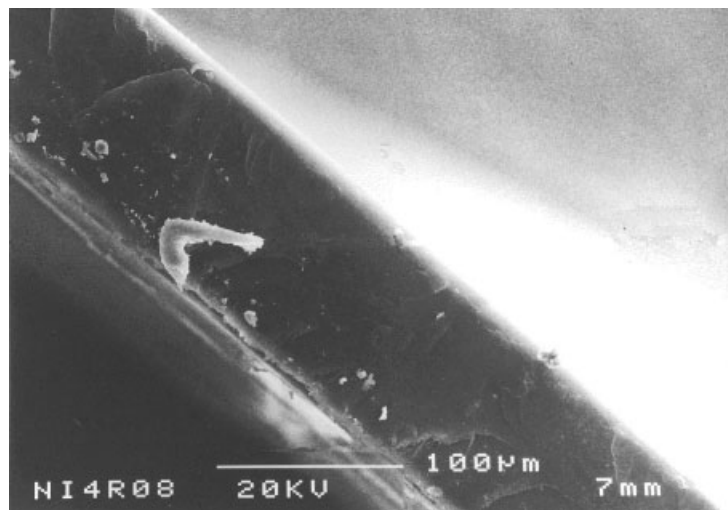


Figure 1 Scanning electron micrograph of the cross section of the PTMSP membrane.

average molecular weight (\bar{M}_w) of $1.2 \times 10^6 \text{ g mol}^{-1}$. Figure 1 shows the cross section of the PTMSP membrane obtained by SEM.

The sampling time was 1 h for higher temperatures ($T > 50^\circ\text{C}$), whereas for lower temperatures, it was increased to 3 h to obtain an amount of permeate large enough to analyze the ethanol content.

In general, selectivity was dependent on temperature, and in most cases, the separation factor decreased slightly as the temperature increased. Depending on activation energies of the mixture components describing the dependence of flux with temperature, the separation factor showed a different trend. For ethanol-water mixtures, some authors reported a decrease in the separation factor with temperature^{8,29} but others reported a reverse trend.^{30,31} Likewise, it was claimed that selectivity showed no clear dependence with temperature.^{32,33}

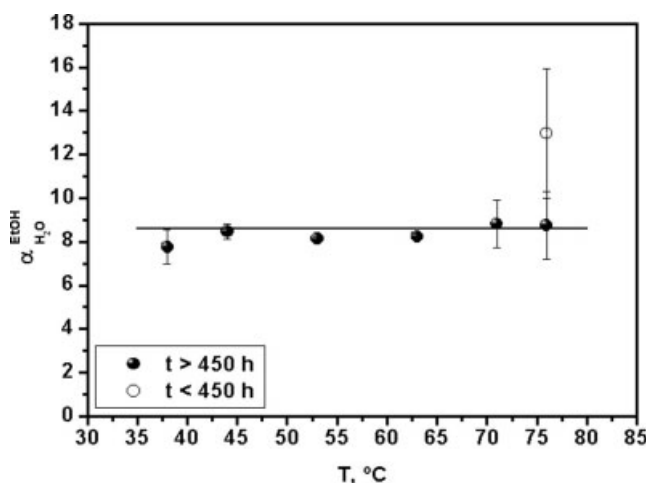


Figure 2 Influence of temperature on the separation factor.

The influence of temperature on the separation factor for a 10 wt % ethanol-water feed mixture is shown in Figure 2, in which the standard deviation was also represented. It can be observed that the selectivity remains almost constant with temperature in the range 38–75°C. There is a blank point at 75°C representing the average value of the separation factors obtained for operating times lower than 450 h that have been used to study the degradation process of PTMSP membranes during the pervaporation process of 10 wt % ethanol solutions.²⁸

Masuda et al.^{34,35} studied the performance of PTMSP membranes for 10 wt % ethanol mixtures in the temperature range 10–50°C. These authors reported that the separation factor showed a maximum at 30°C due to a change in the swollen state of the membrane with temperature. On the other hand, Hickey et al.^{36,37} analyzed the evolution of the selectivity with temperature over the range 0–100°C for 1 and 5 wt % ethanol solutions. They found that it remained almost constant for the more concentrated mixture, whereas, for the diluted solution, the selectivity increased with temperature. Therefore, the effect of temperature was more noticeable at lower ethanol concentrations.

For the poly(dimethylsiloxane) (PDMS) polymer, Garcia et al.³⁸ observed that the separation factor remained constant with temperature in the range 30–80°C during pervaporation of ethanol from a fermentation broth.

We have considered that in our study the selectivity was constant with operation temperature because of the degradation of the polymeric material. Because the membrane was used for the pervaporation of ethanol-water solutions for a period of time of 450 h, the polymeric material underwent a relaxation process

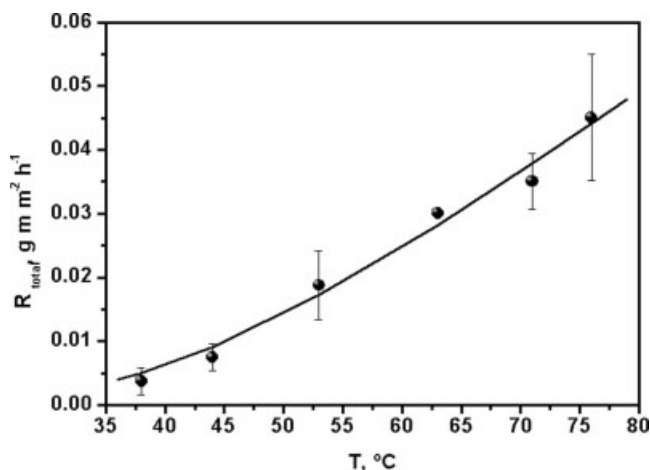


Figure 3 Effect of operation temperature on the specific permeation rate.

and the polymeric chains were rearranged, and, thus, the temperature cannot increase the selectivity of the pervaporation process.

Specific permeation rate

The variation of the total specific permeation rate (R_{total}) with temperature is represented in Figure 3. It can be observed that the value of the total specific permeation rate increases gradually with operation temperature. At 38°C, the total specific permeation rate is $0.0037 \text{ g m m}^{-2} \text{ h}^{-1}$ and reaches a value of about $0.045 \text{ g m m}^{-2} \text{ h}^{-1}$ at 75°C.

According to the free-volume theory, the randomly thermal motion of polymer chains produces free volume. As temperature increases, the frequency and amplitude of the chain jumping increases, and the resulting free volumes become larger; therefore, the molecules can diffuse better through these free volumes. Thus, when temperature is high, the diffusion rates of isolated permeating and associated permeating molecules are also high.³⁹

Hickey et al.³⁶ reported the same increasing tendency of the specific permeation rate with operation temperature for 1 and 5 wt % ethanol solutions with PTMSP and PDMS membranes. They suggested that permeability of ethanol to water in the membrane seemed to slightly increase with temperature, being the diffusivity of ethanol is more affected than that of the water. On the other hand, Masuda et al.³⁵ related the increasing tendency of the specific permeation rate with temperature to the swelling of the PTMSP membrane.

Permeation flux

The effect of temperature on permeation flux is shown in Figure 4. A good linearity of total and partial fluxes

with the inverse of the absolute temperature can be observed. This tendency was fitted according to an Arrhenius relationship,

$$F = B \exp\left(-\frac{E_p}{RT}\right) \quad (3)$$

where F is the permeation flux, B is a preexponential factor, E_p is the apparent activation energy, R is the gas constant, and T is the temperature.

According to the solution-diffusion model, the apparent activation energy can be expressed as a combination of the apparent activation energy for the diffusion of molecules through the membrane, and the heat of sorption of molecules in the membrane, because the solubility and the diffusion of permeants determine the permeability in these polymeric membranes. The apparent activation energy of permeation can be attributed to the activation of the diffusive transport, as the heat of sorption is generally smaller.⁴⁰

Hickey and Slater³⁶ analyzed the effect of temperature on permeation flux during pervaporation with PTMSP membranes and found that flux increased exponentially with temperature. They also studied the performance of PDMS membranes under the same operation conditions and reported that both polymers showed the same behavior during pervaporation. However, whereas for PDMS, the flux remained constant for extended operation at higher temperatures, it decreased slightly for PTMSP.

Huang³⁹ reported that the apparent activation energy of permeation usually varied in the range of 4–8.7 kcal mol⁻¹. On the other hand, Nguyen⁴⁰ determined that the apparent energy activation varied in the range of 4–15 kcal mol⁻¹, and the permeation rate

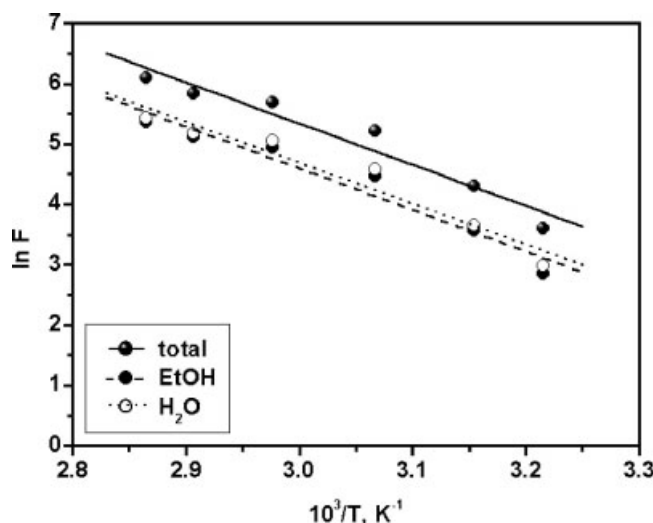


Figure 4 Effect of operation temperature on permeation flux.

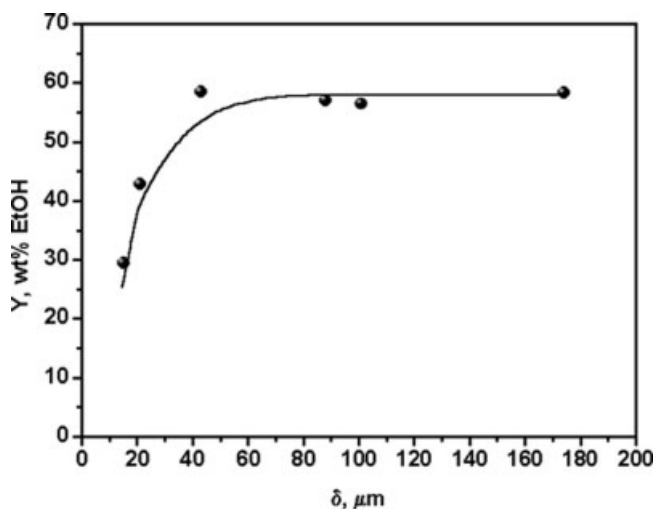


Figure 5 Ethanol content in the permeated fraction as a function of the membrane thickness.

might increase many times for each 10°C temperature increment.

From the analysis of the slope of the Figure 4, the apparent activation energy obtained in this study is of $\sim 13 \text{ kcal mol}^{-1}$. The values obtained for water and total flux are similar to that of the ethanol. It suggests that the effect of temperature on permeation flux of ethanol and water is the same, and thus, selectivity remains constant with operation temperature as it was discussed above.

Mochizuki et al.⁴¹ studied the separation of water-ethanol mixtures with polysaccharide membranes and suggested that, as the apparent activation energies for each component were nearly equal for the separation through a chitosan membrane, the separation factor was almost independent of temperature.

EFFECT OF THE MEMBRANE THICKNESS

The effect of membrane thickness on transport properties of PTMSP membranes was evaluated by studying the evolution of the specific parameters of pervaporation at 75°C with 10 wt % ethanol solutions.

Separation factor

Figure 5 shows the effect of the membrane thickness on the ethanol content in the permeated fraction. It can be observed that ethanol content in the permeated fraction, and thus, selectivity, increases with thickness sharply up to $\sim 50 \mu\text{m}$, and for thicker membranes, it remains constant.

The resistance to mass transfer is located in the interface polymer-permeate where the membrane is virtually dry because of the applied vacuum. The fact that the selectivity increases with membrane thickness

suggests that the polymeric film is an active part in the separation process, whereas in other membrane processes, the separation is only due to superficial phenomena.

In the literature, different results about the evolution of the separation factor with thickness of PTMSP membranes were found. Wang et al.⁴² reported that, for a 10 wt % ethanol-water solution at 30°C in the range $10\text{--}70 \mu\text{m}$, the separation factor increased up to $50 \mu\text{m}$ and, for thicker membranes, it remained almost constant. Masuda et al.³⁵ observed that, for a 10 wt % ethanol solution at 30°C , the separation factor increased slightly in the range of $0\text{--}100 \mu\text{m}$. On the other hand, Camera-Roda et al.⁴³ studied the effect of membrane thickness in the range $10\text{--}55 \mu\text{m}$ for 10 wt % ethanol solutions and found that the separation factor increased up to $\sim 35 \mu\text{m}$ and for thicker membranes it decreased slightly.

Permeation flux

The ethanol permeation flux was represented versus the inverse of the membrane thickness in Figure 6. The solution-diffusion model predicts that total flux is inversely proportional to the membrane thickness. As can be seen from Figure 6, for the thicker membranes, there is a linear relationship between the total flux and the inverse of the membrane thickness, whereas the thinner membranes present lower values than those predicted for the solution-diffusion model.

From the evolution of the separation factor and the permeation flux with the membrane thickness, we have considered that both parameters present lower values than that predicted by the solution-diffusion model because of the presence of cracks or pinholes in the polymeric membranes.

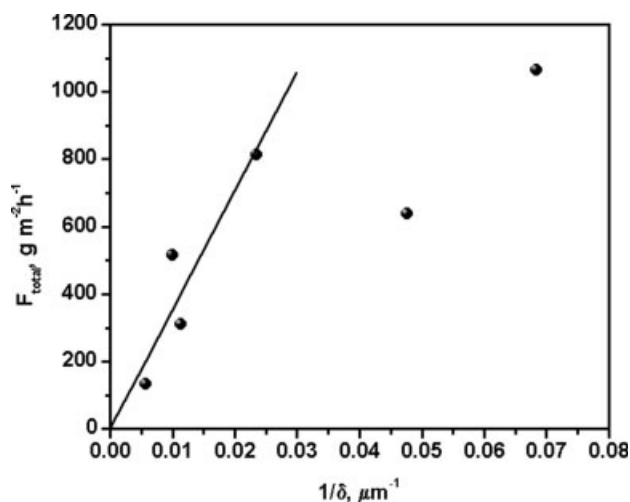


Figure 6 Permeation flux as a function of the reciprocal membrane thickness.

In 1990, Huang suggested that the lower values of flux obtained for thin membranes were attributed to interactions between the polymer and the components of the feed solution. The deviation from Flick's law (nonlinear relationship of the reciprocal thickness below a certain value) was probably due to differences in the conformation of polymer chains: in thin casted films, chains have less time to be rearranged to a compact structure than in thicker films because of a shorter evaporation time.³⁹

It can be observed that variation of permselectivity is the reverse of that of the permeation flux, that is to say, diminishing membrane thickness cannot improve both the flux and the selectivity. When the membrane thickness is $>50 \mu\text{m}$, selectivity does not show further improvement, whereas the flux decreases continuously. On the other hand, for membranes with thickness $< 50 \mu\text{m}$, high fluxes are obtained, but when the thickness is smaller and smaller, the membrane can present pinholes or cracks. Therefore, to obtain high efficiency in the separation of ethanol from diluted solutions, the membrane thickness should allow us to obtain high values of selectivity as well as high permeation fluxes.

Camera-Roda et al.⁴³ reported that, for PTMSP membranes, the ethanol flux was independent of membrane thickness in the range of 15–55 μm . They suggested that the mass transfer resistance due to the diffusion of alcohol was independent of the total membrane thickness, and the effective resistance was confined to a portion of the membrane layer whose thickness remains constant.

EFFECT OF FEED CONCENTRATION

The effect of ethanol content on pervaporation parameters has been evaluated with a membrane of 48 μm and an average molecular weight (\bar{M}_w) of about $1.7 \times 10^6 \text{ g mol}^{-1}$. Although the study of membrane thickness effect was carried out at 75°C, the effect of feed concentration was studied in the whole range of ethanol composition at 50°C. It was observed that, at 75°C, the polymeric film did not present enough mechanical strength due to the high ethanol content and high temperature of the feed solution, and thus, the effect of feed composition at 75°C was only evaluated in the range of 10–70 wt %. The evolution of the characteristic parameters of pervaporation resulted the same in the studied range for the two temperatures; in this article, the evolution of experimental data obtained at 50°C in the whole range of ethanol composition in the feed mixture will be discussed.

Separation factor

Nguyen in 1986⁴⁰ established that a change in feed composition affected the sorption phenomena at the

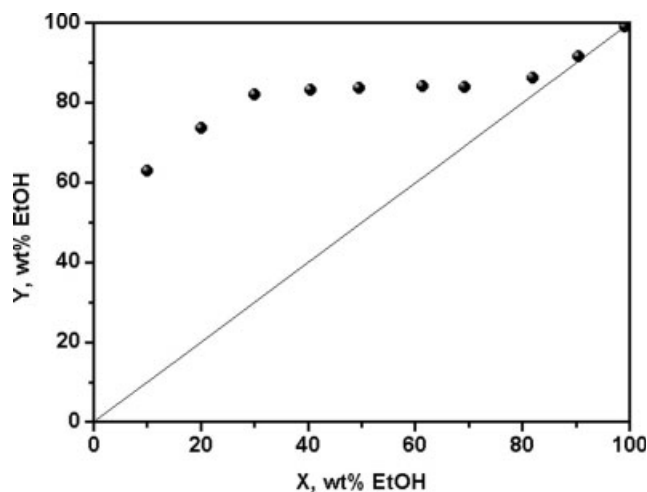


Figure 7 Relationship between the ethanol content in the permeate and in the feed.

liquid–membrane interface. The activity of the mixture components can vary more or less with the change in composition depending on the chemical nature of the mixture. In general, the higher the content of the component that interacts strongly with the polymer, the better the swelling is, and thus, the amount of lower affinity molecules that diffuse through the membrane is higher and contributes to the swelling of the membrane. On the other hand, when the content of the preferential component in the mixture is lower, the swelling is less extended and consequently, the selectivity of the process is higher.

The evolution of ethanol content in the permeated fraction (Y) with ethanol content in the feed mixture (X) is represented in Figure 7.

It can be noticed that the ethanol content in the permeation fraction increases with ethanol content in the feed mixture, remaining constant in a value of about 80 wt % for feed mixtures with ethanol contents in the range 30–70 wt %. For more concentrated feed solutions, the ethanol content in the permeated fraction is similar to the amount of ethanol in the feed mixture, and therefore, the value of selectivity obtained is close to unity. The values of selectivity obtained for ethanol contents > 70 wt % are not very reliable, because PTMSP membranes are suitable for diluted solutions, and therefore, the structure of the membrane is modified for high ethanol contents in the feed mixture.

The relationship between the separation factor with ethanol content in the feed mixture at 50°C is shown in Figure 8.

It was found that, when the ethanol content in the feed mixture increases from 10 to 50 wt %, the selectivity decreases from ~ 17 to 5. For more concentrated solutions, the decrease of the separation factor is less pronounced, reaching a value of about 1 for ethanol

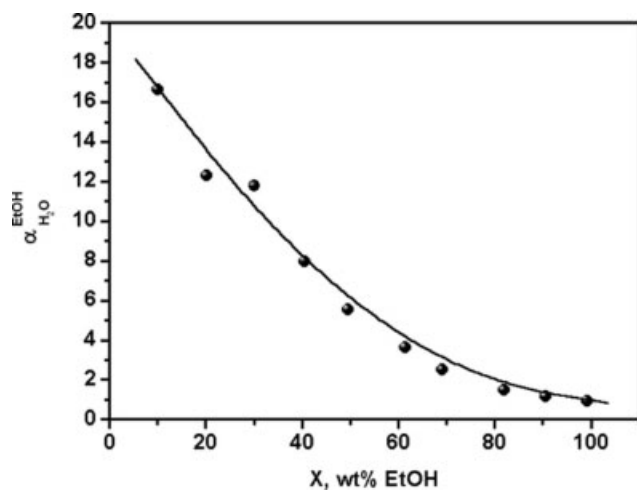


Figure 8 Evolution of the separation factor with ethanol content in the feed mixture.

contents higher than 80 wt % in the feed mixture, in accordance with that observed in Figure 7.

Working at lower temperatures (30°C), some authors have reported that the separation factor presented the same tendency with ethanol content in the feed solution as the one obtained in this work. Masuda et al.³⁵ observed that for a 30- μm PTMSP membrane, the separation factor increased markedly when the ethanol content of the feed mixture decreased. They reported a value of 17 for the separation factor and established that the PTMSP membranes were suitable for the separation of ethanol from diluted solutions because of the high values of selectivity. On the other hand, Wang et al.⁴² found that in the 5–50 wt % ethanol concentration range the selectivity decreased with ethanol content in the feed solution because the high ethanol content made the water transport easier through the polymeric membrane.

Permeation flux

The evolution of permeation flux with ethanol content in the feed mixture at 50°C is shown in Figure 9.

Ethanol and total flux increase with ethanol content in the feed solution in the concentration range 10–70 wt %, whereas water flux increases very slowly. For more concentrated mixtures, ethanol and total flux increase very sharply, whereas water flux decreases to very low values.

The results obtained for ethanol contents in the feed mixture up to 70 wt % are in agreement with the general tendency, that is, when the membrane is in contact with concentrated feed solutions, the swelling of the membrane is higher. Ethanol and water molecules can diffuse faster through the membrane, and thus, higher permeation fluxes can be observed in the whole concentration range. Nevertheless, as can be seen from Figure 9, water

flux decreases to very low values when ethanol content in the feed is higher than 70 wt %.

The evolution of the water flux when ethanol content is higher than 70 wt % is not the expected one due to the following reasons: (1) PTMSP membranes are appropriated for the separation of diluted ethanol-water solutions, and as the polymer has been in contact with very concentrated feed mixtures, the structure of the membrane was modified, its diameter being reduced; and (2) because the membrane undergoes a swelling process in the presence of high ethanol content, the water flux should have presented the same tendency as that of ethanol and total flux. Somehow, the high ethanol content might have blocked water permeation through the polymeric membrane, decreasing water permeation flux.

The increase of permeation flux with solvent content that interacts strongly with the membrane might be explained by using the dependence of thermodynamic and kinetic parameters on concentration. The exponential increase of permeation was due to the superposition of the exponential dependence of diffusion coefficients on the concentration of permeants sorbed by the membrane, and the increase of sorbed amounts with the content of preferential solvent in the feed.⁴⁰

Wang et al.⁴² established that permeation flux through a PTMSP membrane increased markedly with ethanol content in the concentration range 5–50 wt % at 30°C. In our study, the higher the operation temperature, the higher the values of permeation flux, because, as shown previously, flux increases exponentially with operation temperature.

Garcia et al.³⁸ determined that the permeation flux in PDMS membranes increased with ethanol content in the same way as reported in this work.

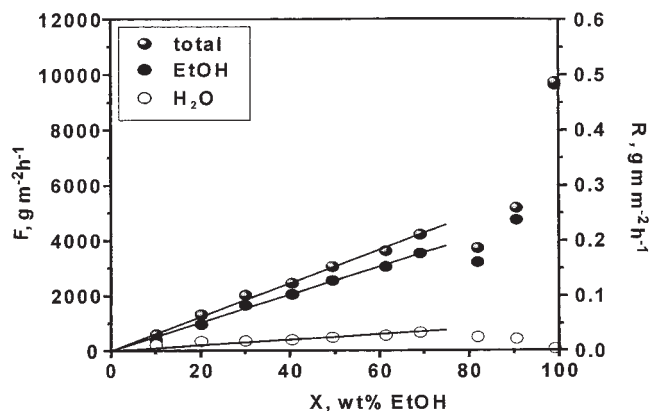


Figure 9 Flux and specific permeation rate as a function of ethanol content in the feed mixture.

Specific permeation rate

The effect of ethanol content in the feed mixture on the specific permeation rate was also represented in Figure 9.

It can be seen that the specific permeation rate increases with ethanol content in the feed mixture in the same way that permeation flux because both parameters are related according to eq. (1).

Masuda et al.³⁵ studied the effect of ethanol content over specific permeation rate at 30°C and determined that the ethanol-specific permeation rate increased markedly with ethanol content in the concentration range 5–85 wt %, whereas the water-specific permeation rate increased in the same ratio in the range 5–30 wt % and, for more concentrated solutions, this variable increased slowly.

Nagase et al.⁴⁴ observed that the ethanol-specific permeation rate increased with ethanol content in the feed mixture for a poly(1-phenyl-1-propyne) (PPP)/PDMS membrane, whereas water-specific permeation rate remained almost constant for higher ethanol contents, and for diluted solutions, the amount of water that permeated through the membrane increased.

CONCLUSION

The operation conditions affected in different ways the parameters of the pervaporation performance. It was observed that an increase in the temperature feed caused an increase in the permeability of ethanol and water because the chains of polymer had higher mobility at elevated temperatures. The flux showed an Arrhenius relationship with temperature, whereas the selectivity remained almost constant. Thus, to obtain high permeation fluxes, the operation temperature should be the highest provided the stability of the membrane was unaffected.

The effect of membrane thickness might also be taken into account to evaluate the performance behavior of PTMSP membranes. The flux increased as the thickness decreased; so, to obtain high fluxes, very thin membranes might be fabricated, which can be easily obtained with the PTMSP. On the other hand, the selectivity increased with thicknesses up to ~ 50 μm, and for thicker membranes, it could be considered that the selectivity remained almost constant. Thus, there should be an optimal thickness for which high values of selectivity and flux could be obtained.

The separation factor decreased with ethanol content in the feed mixture because the high ethanol content made the membrane swell and therefore the molecules could permeate through the polymeric membrane quickly. On the other hand, the permeation flux, and thus, the specific permeation rate, increased with ethanol concentration in the feed solution. On the other hand, the PTMSP is a polymer that presents

good separation characteristics for diluted solutions, and therefore, high yields in the separation of ethanol from aqueous solutions could be expected.

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NOMENCLATURE

A	Area of the membrane, m ²
B	Preexponential factor, g m ⁻² h ⁻¹
E_p	Activation energy of permeation, kcal mol ⁻¹
F_-	Collected amount of permeate, g
\bar{M}_w	Average molecular weight, g mol ⁻¹
R	Gas constant, cal mol ⁻¹ K ⁻¹
R_{total}	Specific permeation rate, g m m ⁻² h ⁻¹
t	Sampling time, h
T	Operation temperature, °C
X	Weight fraction of ethanol in the feed, wt %
Y	Weight fraction of ethanol in the permeate, wt %

Greek symbols

$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$	Separation factor, dimensionless
δ	Membrane thickness, μm

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