

Dehydration of Light Oil by Pervaporation Using Poly(vinyl alcohol)–Poly(acrylic acid-co-maleic acid) Membranes

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Received 24 April 2001; accepted 21 January 2002

ABSTRACT: A new blended membrane was prepared and tested by pervaporation of light oil, a mixture of five alcohols plus water. The blended membrane was synthesized by blending poly(vinyl alcohol) and poly(acrylic acid-co-maleic acid) sodium salt in the presence of sulfuric acid to dope the reaction. We tested several membranes in order to choose the adequate composition to have the best permselectivity. The PVA(60)–PAA-co-maleic acid(40) membrane was selected as it was found to be highly selective. Sorption experiments were performed using binary and ternary water–alcohol solutions. The influence of temperature and feed composition on the selectivity and flux in pervaporation was investigated for two different binary mixtures (water/etha-

nol, water/isobutanol) and one ternary system (water/ethanol/isobutanol). This membrane presents good permselective properties, high water flux, and good selectivity and can even be used for high-water activities. The performances of this new membrane were compared to those obtained with the PVA(90)–PAA(10) membrane synthesized recently: The fluxes observed for the water–ethanol separation were of the same order of magnitude but the selectivity was found to be much higher. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1709–1716, 2002

Key words: membranes; pervaporation; dehydration

INTRODUCTION

Pervaporation separation has been widely considered as an alternative separation process for azeotropic mixtures to conventional extractive distillation. This process differs from distillation in the way that a membrane constitutes a selective barrier between the liquid phase and the gas phase. In Brazil, ethanol, used as a biofuel, is obtained from sugar cane fermentation. During its purification process by distillation, aqueous solutions of alcohols are formed. Due to the presence of water, these mixtures have azeotropic compositions which simple distillations fail to separate. A specific distillation by-product called light oil contains five alcohols ranging from C₂ to C₅ plus water. These alcohols are considered as natural products which confer them higher commercial value. Up to now, this mixture is not valorized. The average composition of light oil is given in Table I.

Pervaporation/distillation coupling could be a good candidate for the separation of this complex multi-component mixture. Moreover, pervaporation is a significant cost- and energy-saving process as it requires only a partial vaporization of the feed. Nevertheless, we have to look for more efficient membranes to improve the yield of pervaporation processes. Experiments of coupling pervaporation and distillation processes were reported by Chamberlain et al.¹ and Tarjus et al.² on commercial membranes supplied by GFT (now Sulzer/Chemtech, Switzerland) to recover the different alcohols.

The main objective of this work was to develop a highly permselective and water-resistant polymer membrane by blending two polymers for the selective separation of alcohols from water by pervaporation. Poly(vinyl alcohol) (PVA) was chosen for its hydrophilic properties, and to crosslink the polymer chains, poly(acrylic acid-co-maleic acid) (PAA-co-maleic acid) was used. The purpose was first to find an optimal proportion in PAA-co-maleic acid which satisfies both requirements in flux and selectivity. Then, a systematic study was achieved on this membrane with the aim of characterizing its permselective properties. Sorption equilibrium as well as temperature and feed composition effects were also studied.

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Contract grant sponsor: French Minister of Foreign Affairs; contract grant number: PRI 005.

Contract grant sponsor: Carbone Lorraine Co.

TABLE I
Light Oil Composition

Component	Wt %
Ethanol	40.27
1-Propanol	1.85
Isobutanol	14.9
1-Butanol	0.25
Isoamyl alcohol	4.93
Water	37.8

EXPERIMENTAL

Materials

PVA, 99+% hydrolyzed, with a molecular weight of 124,000–186,000, was purchased from Janssen Chemica and PAA-*co*-maleic acid sodium salt with a molecular weight of 70,000 was from Aldrich Chemical Co. The five alcohols were purchased from Pro-labo. All these products were used directly without any further purification.

Membrane preparation³

Polymer films of different compositions were prepared from an aqueous solution containing 7 wt % of PVA and PAA-*co*-maleic acid by mixing the solutions in an appropriate proportion. First, PVA was dissolved in pure water at 100°C under reflux. A sulfuric acid solution was added to dope the solution to make the precipitate disappear. Homogeneous membranes were prepared by casting the polymer solution on PPC film at room temperature. The solvent, water, was slowly removed by evaporation at room temperature and then the membrane was heated to 120°C in an oven for 1 h to promote the crosslinking reaction. The thickness of the resulting membranes was in the range of 15–50 μm .

Sorption experiments

Thick strips of membranes were dried under a vacuum until no considerable weight change was observed. They were first immersed in water/ethanol, water/isobutanol alcohol, and water/ethanol/isobutanol alcohol mixtures at 60°C, the temperature at which all the sorption experiments were carried out. After sorption equilibrium was reached, the strips were rapidly and carefully blotted between filter paper to remove the adherent liquid and the membranes were weighted as quickly as possible. Then, the strips were placed into a dry flask which was connected to a cold trap and a vacuum pump. Under vacuum conditions, the sorption solution was collected until the weight of the membrane was the same as that of the dry membrane. Finally, the solution collected in the cold trap was analyzed by gas chromatography using

an HP 5890 equipped with a thermal conductivity detector and a 3-m-long Porapak Q packed column heated to 190°C. Hydrogen was used as the carrier gas. Two parameters can therefore be evaluated: the swelling ratio and the volume fraction of the different components sorbed (ϕ_i). The densities of the blend membranes were measured by pycnometry. The sorption equilibria are characterized by the curve relating the volume fraction to the activity. The activities were calculated by ASPEN Plus Release 9.2 using the NRTL method.

Pervaporation experiments

Pervaporation experiments were performed using a stainless-steel cell. The effective membrane area in the cell was 62.21 cm^2 . About 2000 mL of the feed mixture was introduced into the upstream compartment kept at a constant operating temperature. The pervaporation equipment used is a classic apparatus with a circulating bath (volume of the cell about 50 mL). The pressure at the downstream side was kept below 1 mmHg by a vacuum pump. When the steady-state conditions were reached, the permeate was collected in cold traps which were cooled with liquid nitrogen. Two traps were used alternatively to allow a continuous sampling of the permeate stream. Its composition was determined by gas chromatography as described above. Membrane properties were characterized by the following parameters: permeate flux (J) and selectivity (α). The fluxes, expressed in $\text{kg h}^{-1} \text{m}^{-2}$, were determined by measuring the weight of the liquid collected in the cold trap during a certain time. These fluxes were normalized to a membrane thickness of 2.5 μm (the typical thickness of the active layer of the asymmetrical commercial PVA membrane) assuming a proportionality between the fluxes and the reciprocal membrane thickness. The pervaporation selectivity α is defined by

$$\alpha = \left(\frac{\frac{y_1}{x_1}}{\frac{y_2}{x_2}} \right) \quad (1)$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Subscripts 1 and 2 refer to the more permeable component (water in our study) and the less permeable one (ethanol), respectively. We used the weight percent water in the permeate when we worked at a fixed concentration in the feed mixture.

Choice of the optimal membrane

Membranes made of PVA and PAA-*co*-maleic acid were evaluated for the separation of light oil solutions.

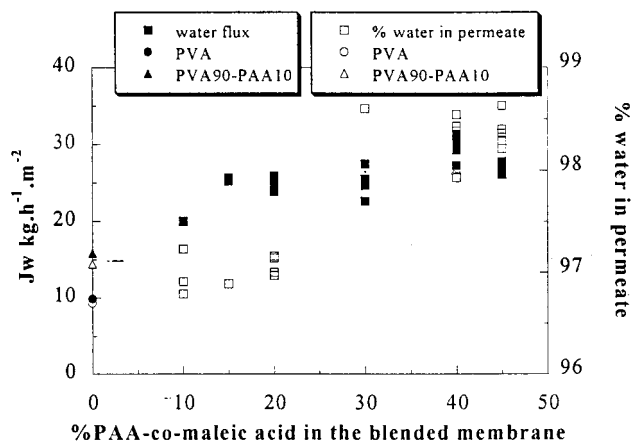


Figure 1 Water flux and selectivity as a function of the PAA-co-maleic acid content in the blended membrane at 60°C. Composition of the mixture in weight percent: water, 35; ethanol, 42; 1-propanol, 1.9; isobutanol, 15.6; 1-butanol, 0.25; isoamyl alcohol, 5.15 (membrane thickness, 2.5 μm).

The experiments were conducted with the same feed mixture of 35 wt % water, conserving the relative proportions of alcohols in light oil, at the constant temperature of 60°C.

The influence of the weight content of PAA-co-maleic acid in the blend membrane is presented in Figure 1. As the PAA-co-maleic acid content increases, the water flux increases and the selectivity increases slightly. One can notice that the performance of this membrane is much better than that of the pure PVA and the PVA(90)-PAA(10) blend membrane.⁴ Flux increased from a 5 to 40 weight content of PAA-co-maleic acid in the blend membrane and then decreased. Above a 45 weight content of PAA-co-maleic acid, the membranes become more fragile and it was impossible to test them by pervaporation—they were too brittle. The weight fraction of water in the permeate for each tested membrane was higher than 97%.

To improve the stability of these blend membranes, we tested them in pure water at 70°C: An important swelling but no dissolution was observed. Considering the stability, selectivity, and water flux, the 40-wt copolymer was chosen for our study. As the main constituents of the light oil were water, ethanol, and isobutanol, our study focused on these three components. Pervaporation and sorption experiments were performed on both the water/ethanol and water/isobutanol binary mixtures and the ternary corresponding system.

RESULTS AND DISCUSSION

The transport phenomena of pervaporation separation through a nonporous polymer membrane is generally described by the solution-diffusion model that occurs in the following three steps: sorption, diffusion, and

desorption.^{5,6} The desorption step of the vapor at the permeate side is known to be generally very rapid and nonselective: Only the sorption and the transversal diffusion through the membrane steps are limiting.⁷

Sorption experiments

According to the solution-diffusion model, the sorption step plays an important role in determining the permselectivity of the membranes. We studied the sorption for the two binary and one ternary systems and then we compared these results with results obtained with the PVA-PAA10 membrane at 60°C.⁴ Figure 2 represents swelling as a function of water activity in feed mixture for the three systems at 60°C.

At equal activity in water, the swelling is nearly the same. From 0 to 0.8 water activity, the membrane swells moderately (60%); then, the swelling reaches 140%. Swelling is lower for the binary water/M2P mixture and the behavior of the ternary system is located between the two binaries.

Figures 3 and 4 show, respectively, the water and ethanol volume fraction as a function of water activity for the different systems. One can notice that, at equal water activity for the binary water/ethanol, the water volume fraction is higher than it is for the binary water/M2P. The M2P volume fraction is nil whatever the water activity in the feed mixture; the presence of M2P seems to prevent water sorption from the ternary and binary water/M2P systems. This could be due to the size of the molecules; isobutylic alcohol is not a linear molecule and its polarity is weaker than that of ethanol and water. So, there are few interactions by hydrogen bonding with PAA-co-maleic acid.

The ethanol volume fraction is very low compared to the water volume fraction. The swelling in the membrane is dependent mainly on polymer-water interactions; hydrogen bonding is "stronger" than are

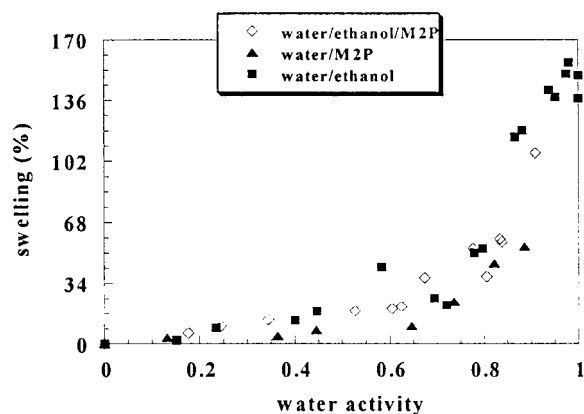


Figure 2 Swelling as a function of water activity in PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C for the ternary system; the ratio of ethanol weight percent to isobutanol weight percent is 40.27/14.9.

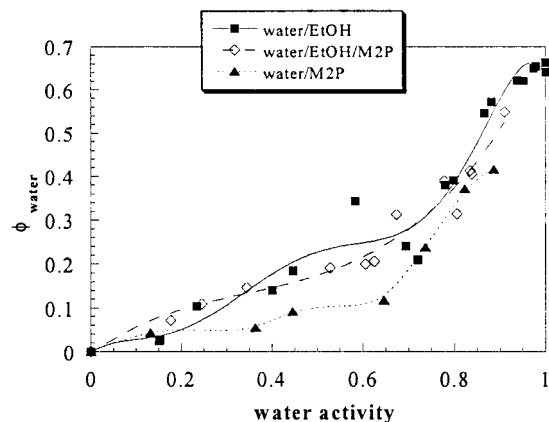


Figure 3 Water volume fraction as a function of water activity in PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C.

ethanol-polymer interactions. The result in sorption experiments is that the ethanol volume fraction is always lower than the volume fraction of water.⁸

At equal water activity for the binary water/ethanol and the ternary systems, the ethanol volume fraction is almost the same. Ethanol sorption depends mainly, as expected, on water activity in the feed mixture. M2P does not inhibit ethanol sorption in the membrane.

We compared the experimental results obtained with the PVA(90)-PAA(10) membrane⁴ to those observed with the PVA-PAA-co-maleic acid(40) membrane with the water/ethanol mixtures. Figures 5 and 6 represent the water volume fraction as a function of water activity in the feed mixture at 60°C. The presence of maleic acid in the PVA-PAA-co-maleic acid membrane does not seem to modify the sorption behavior, as the swelling is nearly equal for the same water activity: The PVA-PAA10 membrane sorbs more water and ethanol than does the PVA-PAA-co-maleic acid membrane at a water activity equal to 0.9. As the PAA-co-maleic acid membrane sorbs less water

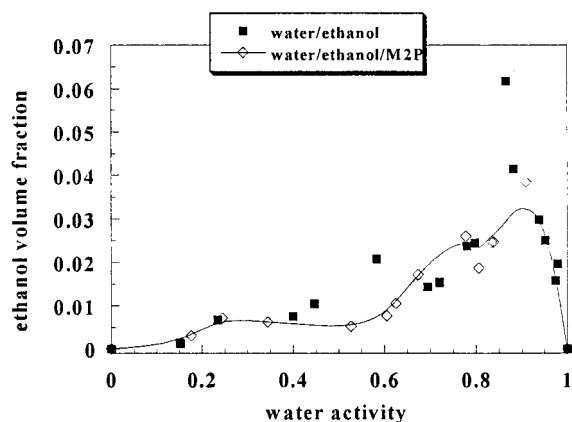


Figure 4 Ethanol volume fraction as a function of water activity in PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

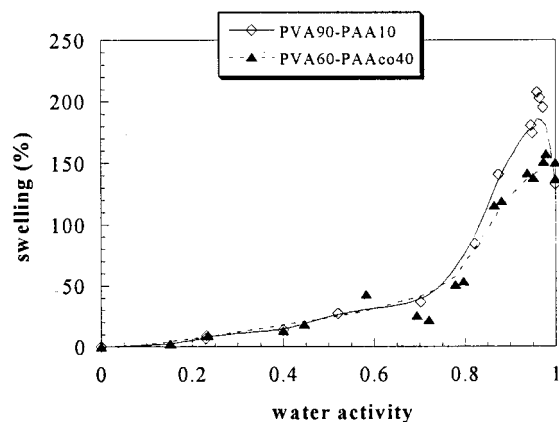


Figure 5 Swelling as a function of water activity in PVA-PAA-co-maleic acid (60-40 in wt %) and in PVA-PAA (90-10 in wt %) membranes at 60°C; water/ethanol mixture.

at high water activity, it could be due to the ester links between the two polymers. Actually, in the case of PVA-PAA-co-maleic acid, the number of carboxylic groups is higher than in the PVA-PAA membrane, so the degree of crosslinking is higher and decreases the water sorption. The presence of the copolymer does not seem to modify the capacity of the membrane to sorb water compared with the PAA.

Influence of temperature

We studied the influence of temperature on the three systems and on pure water to determine the activation energy of the different constituents in the polymer to the Arrhenius law defined by eq. (2), where E_{ai} is the activation energy of component i , expressed in kJ mol^{-1} , and J_{0i} the flux of component i at the reference temperature T_0 . In our case, we took 298.15 K as the reference temperature (R is the ideal gas constant expressed in $\text{kJ mol}^{-1} \text{K}^{-1}$):

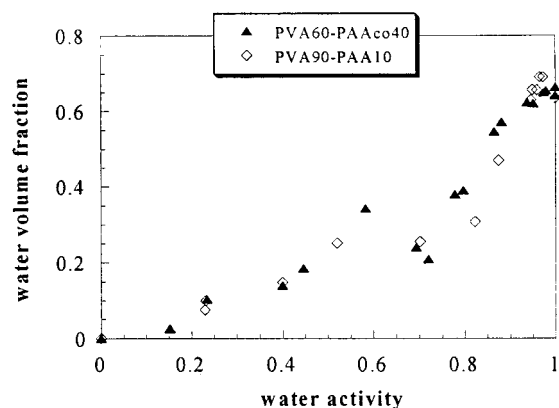


Figure 6 Water volume fraction as a function of water activity in PVA-PAA-co-maleic acid (60-40 in wt %) and in PVA-PAA (90-10 in wt %) membranes at 60°C; water/ethanol mixture.

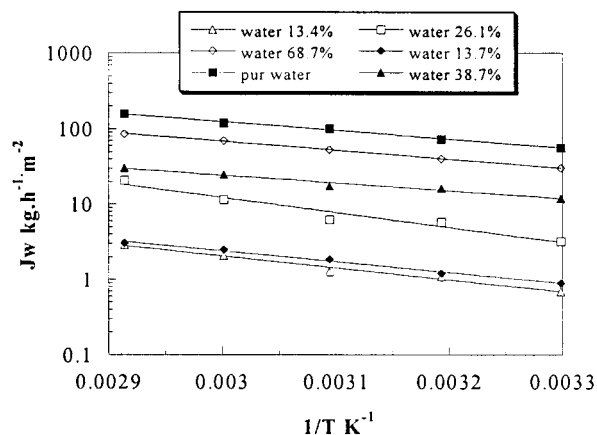


Figure 7 Water flux as a function of reciprocal temperature in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane for the binary water/ethanol mixture (membrane thickness, 2.5 μm).

$$J_i = J_{oi} \times \exp\left(\frac{-E_{ai}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (2)$$

Figures 7 and 8 represent the water and ethanol flux as a function of the reciprocal temperature for the binary water/ethanol. Figures 9 and 10 show the water flux for the binary water/M2P and for the ternary water/ethanol/M2P. The apparent activation energies of water and ethanol are calculated from the Arrhenius plot. We do not calculate the M3B activation energy because the membrane is too selective to this product.

One can notice that the water and ethanol fluxes increase with temperature according to the Arrhenius law. Indeed, when temperature increases, the polymer chains become more flexible; the intermolecular distance increases, which favors a better permeation. The percentage of water in the permeate is shown in Figures 11 and 12 as a function of temperature for the

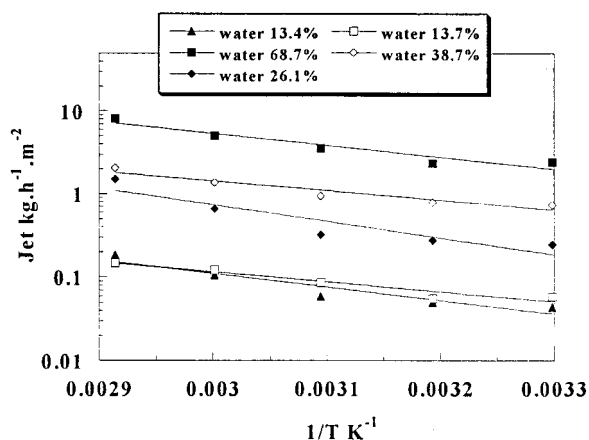


Figure 8 Ethanol flux as a function of reciprocal temperature in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane for the binary water/ethanol mixture (membrane thickness, 2.5 μm).

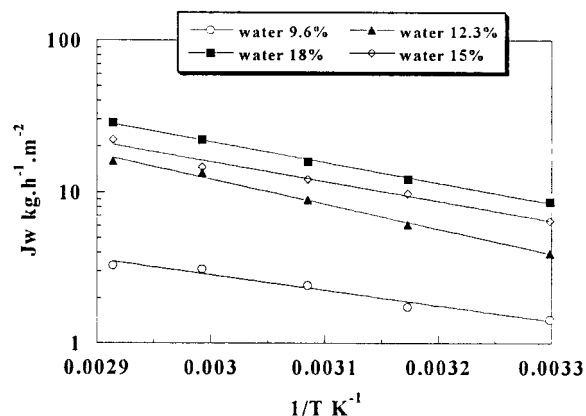


Figure 9 Water flux as a function of reciprocal temperature in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane for the binary water/M2P mixture (membrane thickness, 2.5 μm).

binary water/ethanol and the ternary water/ethanol/M2P systems. We notice that the water mass fraction in the permeate decreases when the temperature increases: This is because the polymer chains are more mobile. This accounts for the fact that the ethanol molecules are more permeated.

The activation energies obtained are presented in Table II. The ethanol activation energy is higher in the ternary system than in the binary water/ethanol, due to the higher interactions between ethanol and M2P. The presence of M2P has a negative effect on the ethanol activation energy. The pure water apparent activation enthalpy is higher in the PVA60–PAA-*co*-maleic acid(40) membrane than in the PVA–PAA10 membrane. The ethanol apparent activation energy is higher in the PVA–PAA10 membrane (ranging from 60.8 to 52.6 kJ mol^{-1} for the water–ethanol mixture with a water mass fraction ranging from 10 to 30%). The presence of maleic acid and the weight content of PAA in the membrane favors water permeation.

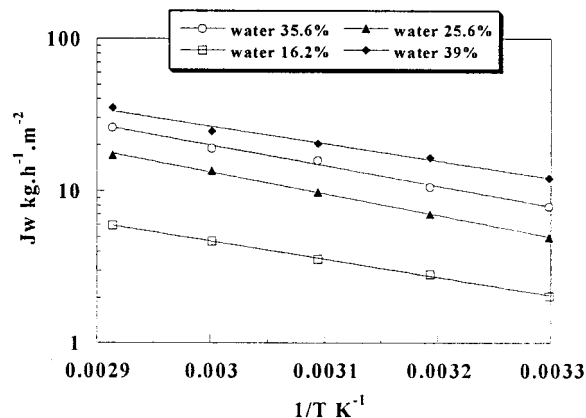


Figure 10 Water flux as a function of reciprocal temperature in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane for the ternary water/M2P/ethanol mixture (membrane thickness, 2.5 μm).

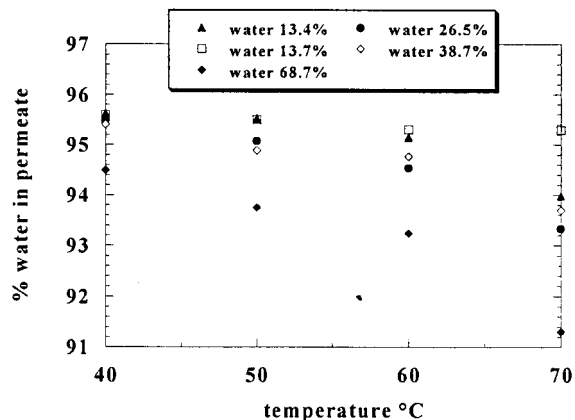


Figure 11 Percentage of water in permeate as a function of temperature for the binary water/ethanol system in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane (membrane thickness, 2.5 μm).

TABLE II
Water and Ethanol Apparent Activation Energy in Different Mixtures

PVA(60)–PAA- <i>co</i> -maleic acid(40)	Weight fraction of water in the feed (%)	E_a water (kJ mol ⁻¹)	E_a ethanol (kJ mol ⁻¹)
Water/ethanol	13.37	30.7	28.61
	13.72	27.1	19.86
	26.53	38.9	36.06
	38.7	19.9	20.03
	68.7	22.6	24.3
Pure water	100	21.9	
Water/M2P	9.6	19.27	
	12.3	28.25	
	15	25.36	
	18	25.9	
Water/ethanol/M2P	25.2	27.34	63.74
	35.6	22.15	40.43
	39	25.72	37.55

Influence of the nature of feed mixture

We studied the influence of the water weight content in the feed mixture for the ternary and binary mixtures at 60°C. Figure 13 represents water flux as a function of water activity in the feed mixture. As expected, the water flux increases when the water activity increases. We can notice that, at equal activity, fluxes for the binaries and ternary systems are different. The fluxes are very weak for the ternary system as well as for the binary water/M2P. At equal activity for the binary water/M2P and for the ternary systems, the fluxes are not noticeably different.

Figure 14 represents the ethanol flux as a function of water in the feed mixture for the binary water/ethanol solution and for the ternary mixture. Ethanol flux is more important for binary water/ethanol than for the ternary system, with a maximum value for an activity equal to 0.9. Water carries more ethanol in the case of the binary than in case of the ternary system. Isobutyl

alcohol seems to inhibit water permeation through the membrane as well as does ethanol. Figure 15 shows the selectivity α as a function of water activity in the feed mixture for the binary water/ethanol and the ternary systems. As the water activity in the feed mixture increases, the selectivity α decreases while the water permeation increases. This phenomenon can be explained by the plasticizing effect of water. As was seen above, when water activity increases, the water volume fraction increases and the membrane is more swollen, so the polymer chains become more mobile and favor water and ethanol permeation (highly interactive systems).⁹ In pervaporation, this membrane is not permeable to M2P as could be expected from the observed results in sorption; furthermore, the presence of this component seems to inhibit ethanol permeation for the ternary system. Water has stronger interactions with the membrane than does M2P because water is more polar and has a higher ability to

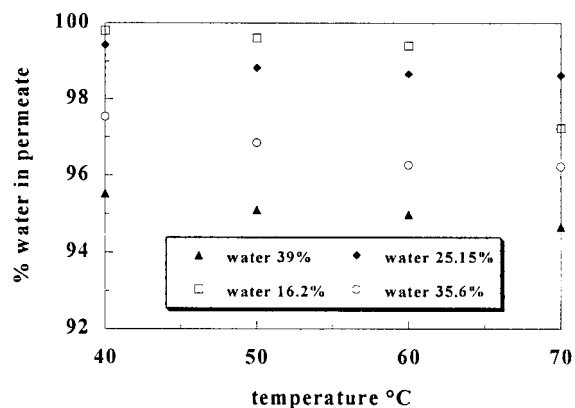


Figure 12 Percentage of water in permeate as a function of temperature for the ternary water/ethanol/M2P system in the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane (membrane thickness, 2.5 μm).

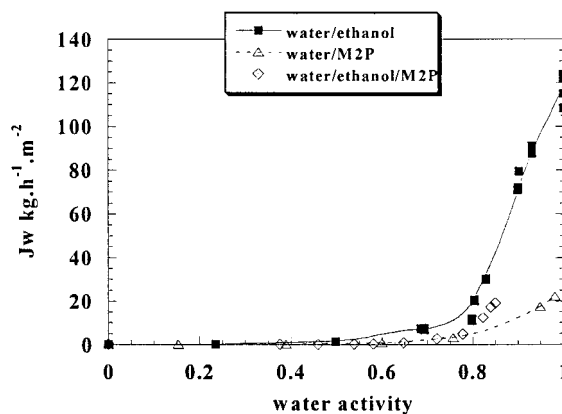


Figure 13 Water permeation flux as a function of water activity in the feed side of the PVA–PAA-*co*-maleic acid (60–40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

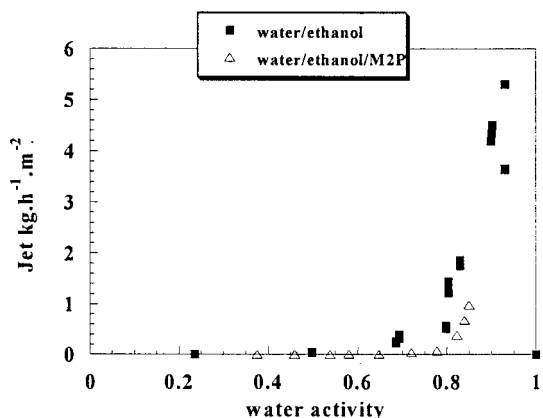


Figure 14 Ethanol permeation flux as a function of water activity in the feed side of the PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

form hydrogen bonding. These stronger interactions result in a higher sorption and, therefore, in higher permeation; in addition, the difference in the molar size favors water permeation. Selectivity for this system is better than what was observed for the binary water/ethanol solution, particularly at a lower water activity in the feed solution.

Water fluxes for the three systems studied are presented in Figure 16 as a function of the water volume fraction at 60°C. The water volume fractions were calculated using a polynomial fitting of ϕ_{water} as a function of a_{water} obtained from the sorption experiments.

Figures 17 and 18 represent the water flux and the selectivity α as a function of the water activity in the feed mixture for the membranes PVA(60)-PAA-co-maleic acid(40) and PVA(90)-PAA(10). Water flux for the PVA(90)-PAA(10) seems slightly superior than that observed for the PVA(60)-PAA-co-maleic acid(40) membrane, and selectivity of the PVA(60)-PAA-co-

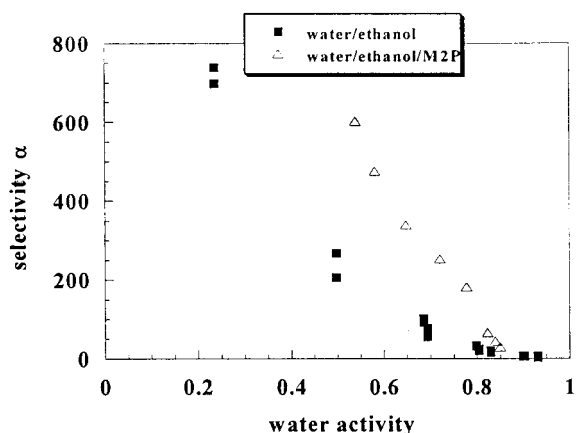


Figure 15 Selectivity as a function of water activity in the feed side of the PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

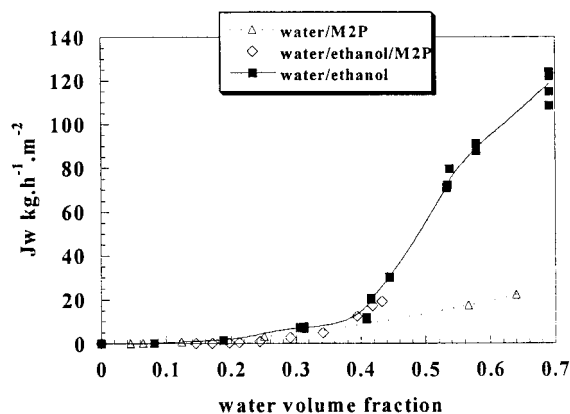


Figure 16 Water permeation flux as a function of water volume fraction in the PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

maleic acid(40) membrane is much better at lower water activity in the feed mixture than that measured for the PVA(90)-PAA(10) membrane.

CONCLUSIONS

This new membrane, prepared by the reaction of PVA with PAA-co-maleic acid sodium salt, has shown interesting permselective properties for the dehydration of light oil, water/ethanol, and water/isobutanol mixtures. This membrane is very resistant, stable, and selective (in sorption and pervaporation); only water and ethanol are sorbed and diffused through it.

The performances of this membrane are strongly influenced by the nature of the feed mixture. For each system studied (water/ethanol, water/M2P, and water/ethanol/M2P), fluxes increase and selectivity decreases when water activity increases. The presence of M2P in the feed mixture, for the binary and ternary

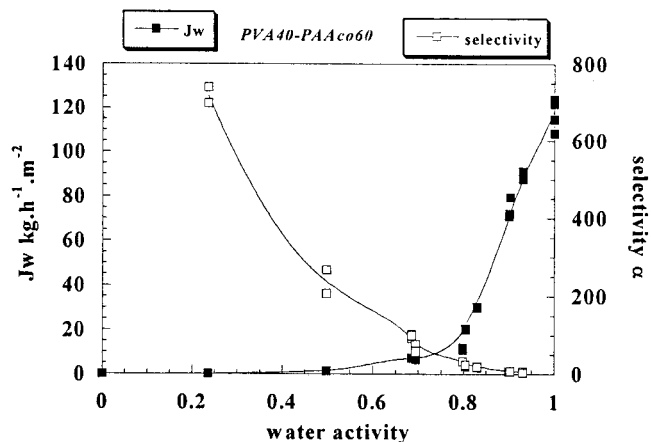


Figure 17 Water permeation flux and selectivity as a function of water activity in the feed side of the PVA-PAA-co-maleic acid (60-40 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

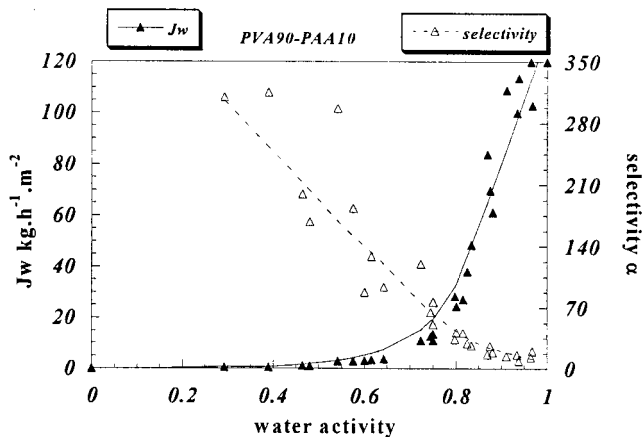


Figure 18 Water permeation flux and selectivity as a function of water activity in the feed side of the PVA–PAA (90–10 in wt %) membrane at 60°C (membrane thickness, 2.5 μm).

systems, enhances the water sorption and reduces flux.

The presence of maleic acid modifies the properties of the pure PVA membrane: Selectivity and water flux

are enhanced. The water flux is slightly lower than that obtained with the PVA(90)–PAA(10) membrane recently synthesized, but the selectivity for water in pervaporation is enhanced.

This work was financially supported by the French Minister of Foreign Affairs (PRI 005) and the Carbone Lorraine Co.

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