

Pervaporation Properties of Polypyrrolidinone-Based Membranes for EtOH/ETBE Mixtures Separation

Samira Touchal, Denis Roizard, Laurent Perrin

LSGC, UPR CNRS 6811, INPL-ENSIC, 1 rue Grandville, BP 451, 54001 Nancy Cedex, France

Received 6 May 2005; accepted 29 July 2005

DOI 10.1002/app.22785

Published online 19 January 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The separation of ethanol/ethyl-*tert*-butylether mixtures by pervaporation was studied with new membranes prepared from *N*-vinyl-pyrrolidinone (NVP) and *N*-[3-(trimethylamoniopropyl)]methacrylamidemethylsulfate (TMA). The pervaporation results showed that highly EtOH selective membranes could be obtained from PVP blends and from pyrrolidinone-based crosslinked copolymers. The influences of the polymer blend composition and the role of the polymer microstructures on the membrane properties were investigated. Whatever the exact NVP/TMA composition used, the membranes strongly favored the pervaporation of ethanol. The ethanol selectivity was higher for the lower PVP/TMA ratio. On the one hand, these results were ascribed to the high pyrrolidinone residues content, which is responsible of the enhanced EtOH sorption affinity. The observed permeation

selectivity was in agreement with the swelling data also recorded with the different polymers, showing higher affinity for ethanol with PVP-enriched materials compared with TMA ones. This is a direct consequence of the Lewis base feature of pyrrolidinone sites towards EtOH molecules. On the other hand, the TMA residues improved the overall stability and selectivity of the membranes thanks to crosslinking reactions, which were induced by thermal treatment. A close comparison made between polymer blend and copolymer pervaporation results helped to clarify the TMA role of the membrane transport properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3622–3630, 2006

Key words: ionomers; blends; copolymerization; membranes; separation techniques

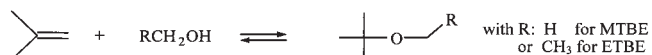
INTRODUCTION

During the last fifteen years, the environmental pollution effects due to human activities have become a major concern all around the earth. Under the pressure of states and public opinion, stringent regulations have been set up to force industries to reduce the environmental impact of their activities (i.e., Kyoto protocol, Clean air act) and to produce more environmental friendly products. Unleaded fuels belong to this category and new octane enhancers have been gradually introduced in fuels to avoid lead dissemination due to automotive transportation¹ and to limit as well the amount of aromatic chemicals in gasoline.² *Tert*-butylethers, i.e., methyl *tert*-butyl ether (MTBE; 2-methoxy-2-methyl-propane) and ethyl *tert*-butyl ether (ETBE; 2-ethoxy-2-methyl-propane), are known to be powerful octane enhancers. Thus, their low cost production has become a challenge in petrochemistry.^{3,4} Indeed, since the ban of tetraalkyl lead compounds, the worldwide production of these ethers has increased to such an extent that MTBE, for instance, is one of the major organic chemicals produced. In the

US, MTBE is now the most oxygenated octane enhancer used.

But MTBE has been detected throughout the hydrologic cycle as a persistent contaminant and then identified as responsible of high-level groundwater contamination.⁵ Taking into account MTBE persistence and toxicity, it is expected that ETBE demand will increase in the next future. In addition, a recent study has shown that ETBE has better antiknock properties than MTBE.⁶ Thus, there is a need for improved processes to get purified ETBE at reasonable costs.

The ETBE purification problem is directly linked to its synthesis route shown here:



As the isobutene feedstock is limited from refinery cracking operations, bulky tertiary ethers are produced with the addition of an excess of alcohol (i.e., EtOH for ETBE production) to ensure a high isobutene conversion.⁷ The obtained alcohol/ether mixtures are difficult to separate by conventional technologies like distillation because of azeotrope formation. Ternary distillation is an efficient mean to break azeotropes but it is also very expensive.⁸ Hence, new technologies able to improve *tert*-butylether purification are currently under investigation.

Among them, membranes-based processes look promising because of membrane separation features.⁹

Correspondence to: D. Roizard (Denis.Roizard@ensic.inpl-nancy.fr).

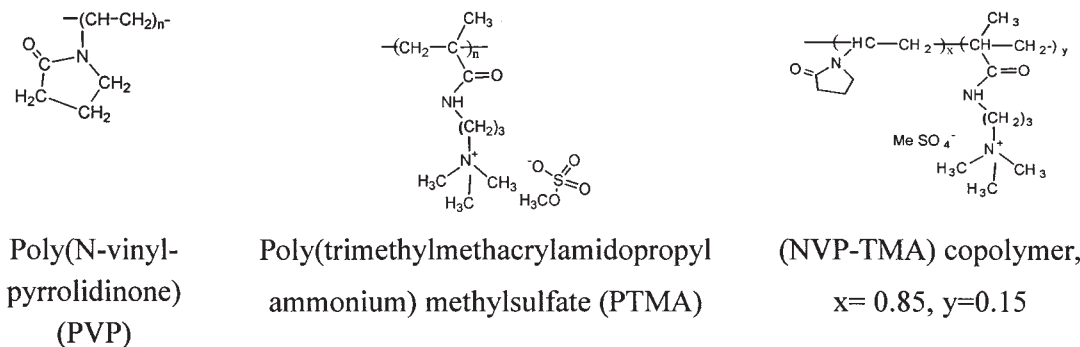


Figure 1 Polymers used for the preparation of PVP-based pervaporation membranes.

In particular, membrane processes are continuous and environmental friendly. Moreover, they are known to be compact technologies and easy to operate. For example, membrane equipments can be easily implemented on conventional technologies. In the specific case of alcohol–ether purification, several membrane methods have already been tested to break the azeotropes mixtures: vapor permeation,¹⁰ reverse osmosis,¹¹ pervaporation,¹² and even hybrid processes such as pervaporation coupled with distillation.¹³ To be complete, it is worth to mention the alternative routes to the synthesis of *tert*-butylethers that can avoid the formation of azeotropes mixtures. They are hybrid processes, which integrate a separation step to the chemical reaction. Starting from isobutyl alcohol with methanol or ethanol, such processes allow for instance the direct elimination of water formed during the reaction either by reactive distillation¹⁴ or through use of a pervaporation membrane reactor.¹⁵

All the above listed membrane processes basically require alcohol selective dense membranes. This paper reports the results obtained for the separation of alcohol–ether by pervaporation with new membranes prepared from *N*-vinyl-pyrrolidinone (VP) based polymers.¹⁶ Indeed, previous works have demonstrated that pyrrolidinone sites have a high affinity for ethanol and thus can dramatically enhance the selective permeation of alcohol from alcohol–ether mixtures.^{17,18,19,20} In the present work, particular membranes containing a high amount of pyrrolidinone sites were prepared from water-soluble polymers, namely poly(*N*-vinyl-pyrrolidinone), poly(trimethylmethacrylamidopropyl ammonium) methylsulfate (PTMA), and a copolymer NVP-TMA (Fig. 1). The TMA monomer was originally chosen to ensure good water solubility and good mechanical resistance to the membranes in ether mixtures. Pervaporation experiments were carried out with EtOH/EBTE mixtures in the 30–50°C temperature range. The influence of the PVP-TMA ratio used to prepare blend membranes is reported. Finally, the transport properties of blend and copolymer membranes, which have the same PVP-TMA ratio, were investigated.

EXPERIMENTAL

Starting polymers

Poly(*N*-vinyl-pyrrolidinone) (PVP) and poly(trimethylmethacrylamidopropyl ammonium) methylsulfate (PTMA) were synthesized from freshly purified monomers, *N*-vinyl-2-pyrrolidinone (NVP) (ALDRICH reagent) and *N*-[3-(trimethylammonio)propyl] methacrylamidomethylsulfate (TMA). The detailed synthesis procedures of TMA from *N*-[3-(dimethylamino)propyl] methacrylamide (DMA) and dimethyl sulfate in dimethylacetamide solution are reported elsewhere.¹⁶

The homopolymers, PVP and PTMA, and the (NVP-TMA) copolymer were prepared in distilled water at 68°C under inert atmosphere by radical polymerization, using 0.1% molar of recrystallised 4,4'-azobis(4-cyanovaleric acid) (ACVA). The aqueous solutions were poured drop wise into dry acetone and the obtained polymers were purified by repeated precipitation in acetone. After filtration, white powders were isolated and dried at 60°C for 24 h under vacuum. These polymers were found to be well soluble in methanol or water, and their molar masses were determined by size exclusion chromatography with a multi angle laser light scattering detector (MALLS miniDawn-Wyatt).

Membrane preparation

Two kinds of membrane were prepared: one from homopolymer blends (PVP and PTMA) and the other from (NVP-TMA) copolymer. Low-concentrated polymer solutions (≈ 3 wt %), either in water or methanol, were stirred during 12 h to ensure a good homogeneity. Dense membranes (area $\approx 5 \times 10^{-3} \text{ m}^2$) were then obtained from slow solvent evaporation, either at 50°C for water or room temperature for methanol solution. After drying, a curing treatment was applied to the films. They were heated stepwise under vacuum, first 1 h at 100°C and then 1.5 h at 180°C. Glassy homogeneous films of $100 \pm 5 \mu\text{m}$ thickness were

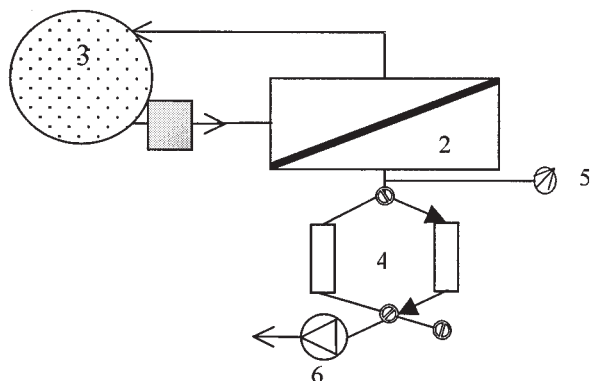


Figure 2 Pervaporation apparatus: 1, circulating pump; 2, pervaporation cell; 3, thermostated feed reservoir; 4, permeate traps; 5, pressure gauge; and 6, vacuum pump.

obtained and stored under dry atmosphere before pervaporation experiments.

Pervaporation measurement

Ethyl-*tert*-butyl ether (ETBE), kindly provided by Institut Français du Pétrole, was distilled twice over sodium before use. Analytical grade EtOH was used. Particular care was taken to use anhydrous solvents.

The pervaporation apparatus consisted of a stainless steel round cell (useful area of $1.5 \times 10^{-3} \text{ m}^2$) connected to a glass apparatus equipped with parallel permeate traps cooled by liquid nitrogen. In the cell, the polymer film was supported by an inorganic porous support. The feed solution was continuously circulated from a thermostated reservoir to the upstream side of the membrane in the cell at the desired temperature (Fig. 2). The downstream pressure was kept at $\approx 50 \text{ Pa}$. The feed and permeate concentrations, respectively, C and C' , were easily determined by gas phase chromatography. They are given in weight fraction. The membrane properties were evaluated from the EtOH permeate concentration (C' in wt %) and the total flux (J). Under steady-state conditions, the EtOH flux, J_{alcohol} , was calculated from the mass of trapped permeate as follows:

$$J_{\text{alcohol}} = \frac{m \cdot C' \cdot e}{A \cdot t \cdot 5} \quad (1)$$

where m is the total amount of permeate, e is the film of a thickness in micron, A is the effective area, and t is the experimental trapping time. Reported EtOH fluxes are normalized values to a thickness of $5 \mu\text{m}$. The normalized flux values allow an easy comparison with data obtained from various sources.

All the given data are average of several experimental points recorded once flux and permeate concentrations were stabilized. Flux measurement was less ac-

curated at low EtOH feed content; maximum flux experimental error was evaluated to be $0.05 \text{ kg h}^{-1} \text{ m}^{-2}$.

The α membrane selectivity was calculated from the concentrations of feed and permeate as follows:

$$\alpha_{\text{alcohol}} = \frac{C'/C}{(100 - C')/(100 - C)} \quad (2)$$

where C and C' are the EtOH concentrations (wt %), respectively, in feed and in permeate.

Note that at a fixed feed concentration (C), the variation of the membrane selectivity can also be directly appreciated from the permeate composition (C').

RESULTS AND DISCUSSION

To improve the separation of alcohol-ether mixtures by pervaporation, we have prepared new membranes from *N*-vinyl-pyrrolidinone (NVP) based polymers according to two synthesis routes. The choice of the pyrrolidinone residue as building unit for EtOH selective membranes is first explained and then the synthesis routes are detailed here.

Choosing *N*-vinyl-pyrrolidinone as building unit for EtOH selective membranes

Numerous papers were published on alcohol/*tert*-butylether separation and a representative overview of the literature is shown in Table I. These studies pointed out that good to excellent separations could be obtained with a variety of membranes^{21,22,23,24,25,26,27,28,29,30} such as cellulose derivatives, polystyrene-sulfonate, or sulfonated poly(ether-sulfone). Nevertheless, one can notice that the common feature of these membranes was the polar characteristic of the used membranes.

This qualitative observation can be easily explained on the basis of the pervaporation transport mechanism. Indeed, pervaporation is a membrane separation method, which involves the partial vaporization of a liquid mixture through a dense active layer. Usually, the membrane upstream side is contacted with the feed mixture under steady state conditions, whereas the downstream side is either kept under vacuum or continuously swept with an inert gas. It is generally acknowledged that pervaporation mass transport through polymer membranes is governed by a "solution-diffusion" mechanism.³¹ Thus, for a given mixture, the solution step is favored for the component, which has the strongest affinity for the membrane. In the particular case of EtOH-ETBE mixtures in contact with polar membranes, ethanol clearly fulfills this condition.

On the other hand, the pervaporation diffusion step is linked to two independent parameters, which are

TABLE I
Literature Overview of the Purification of *tert*-Butyl Ethers

Feed mixtures	Membrane	Literature
Alcohol/ether	CA, PVA, PSf	Chen (1998) ²¹
Alcohol/C4-C7 cut		
MeOH/MTBE	Nafion, cellulose	Farnand and Noh (1989) ²²
MeOH/TAME		
MeOH/MTBE	PPO	Doghieri, et al (1994) ²³
MeOH/MTBE	Silicalite	Sano, et al (1995) ²⁴
MeOH/MTBE	Polystyrenesulfonate	Chen and Martin (1995) ²⁵
EtOH/ETBE	Polyetherurethane	Jonquieres, et al (1996) ²⁶
MeOH/MTBE	Na-Y zeolite	Kita, et al (1997) ²⁷
EtOH/ETBE	PVP-co-Vac—CA blends—blends	Nguyen, et al (1997) ²⁹
MeOH/MTBE	Sodium alginate/chitosan	Kim, et al (2000) ²⁸
MeOH/MTBE	Alumina-supported (PVAc) and (PVP)	Yoshida and Cohen (2003) ¹⁸
MeOH/MTBE	Polyimide/sulfonated poly(ether-sulfone)	Shi, et al (2004) ¹⁰
MeOH/MTBE	Poly(ethylene-co-vinyl acetate)	Gozzelino and Malucelli (2004) ³⁰

first the nature of the polymer network (glassy or rubbery) and second the size of the permeant molecules. For a given liquid mixture, the diffusion selectivity is fixed by the relative size of the molecules. Thus, to improve the separation, the membrane design must focus on the enhancement of polymer-EtOH affinity.

In the present work, the NVP-based membrane design was done according to the above principle. Indeed, former studies have shown the strong affinity of EtOH for pyrrolidinone sites,^{17–18} which can be explained by the Lewis base interaction of the pyrrolidinone cyclic amide.¹⁹ Unfortunately, single use of PVP is prevented because of the bad PVP film properties. Thus the design of new materials containing pyrrolidinone sites needs to be achieved to prepare suitable PVP-based films.

Poly(trimethyl methacrylamidopropyl ammonium) methylsulfate (PTMA) was chosen for this purpose: like PVP, it also contains numerous amide groups combined with methyl sulfate ammonium salt residues, which obviously reinforce the strong polar feature of the material. Thus, several blends of PVP and PTMA were prepared in MeOH or in water solution, and three blend membranes with a high content of

pyrrolidinone sites were finally obtained: Bl-95#1 (95 mol %), Bl-85#2 (85 mol %), Bl-75#3 (75 mol %).

In addition, a fourth membrane (noted Co-85#4) was prepared from a NVP-TMA copolymer. The pyrrolidinone site content of this former membrane was adjusted to 85 mol % to allow comparison with the blend membrane Bl-85#2.

Curing PVP-PTMA membranes procedure

All the membranes prepared were transparent, glassy, and slightly brittle. They were also insoluble in ETBE and other organic solvents of low polarity. Conversely, they were soluble in water, methanol, and ethanol. Hence, to prevent the extraction of PVP chains from the blend membranes during pervaporation experiments, a curing treatment was applied.

The membranes were heated at 180°C under vacuum for 90 min. Although this thermal treatment did not modify the solubility of pure PVP samples, it was shown that the membrane containing pyrrolidinone and TMA residues were not anymore soluble in ethanol (Table II). The same crosslinking effect was also obtained after curing the copolymer membrane Co85#4. The mechanism of the crosslinking reaction

TABLE II
Polymer and Membrane Stability *Versus* Solvents (Measured at Solvent Boiling Point) after Thermal Treatment

	Starting materials			Cured membranes			
	PVP	PTMA	Copoly(VP-TMA) 85–15 mol %	Bl-95#1	Bl-85#2	Bl-75#3	Co-85#4
Water	S	SW	SW	SW	SW	SW	SW
Methanol	S	SW	SW	SW	SW	SW	SW
Ethanol	S	SW	S	SW	SW	SW	SW
ETBE	I	I	I	I	I	I	I
HCCl3	I	I	I	I	I	I	I
Toluene	SW	I	I	I	I	I	I

S, soluble; I, insoluble; SW, swelling.

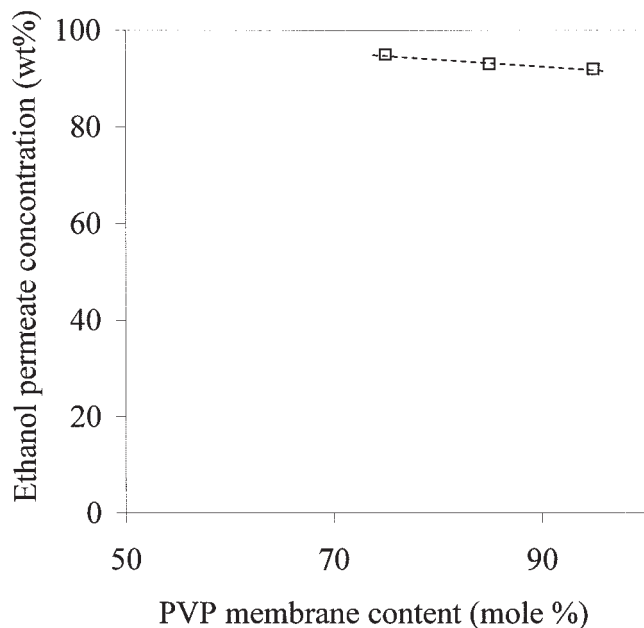


Figure 3 Effect of the PVP-TMA blend membranes ratio on the permeate enrichment at (50°C). Feed: 16 wt % of alcohol, i.e., $a_{\text{EtOH}} = 0.45$.

induced by the curing procedure was not fully elucidated. Nevertheless, it could be deduced from the modification of the solubility properties that the chemical crosslinking was induced by the presence of the TMA residues because neither PVP nor polymethylmethacrylate (PMMA) alone could be crosslinked under the same conditions.

Finally, a further comment can be made from Table II: the observed difference of solubility and swelling between EtOH and ETBE for PTMA and PVP-PTMA underlines a stronger EtOH affinity for PVP than for TMA, conversely to ETBE, which is a non solvent of all samples.

Pervaporation results

The assessment of the PVP-based membranes separation properties was carried out in the temperature range 30–50°C with EtOH-ETBE mixtures. EtOH mole fractions of the mixtures were varied in a wide range from 0.2 to 0.5. This mole fraction range was chosen because it includes the azeotrope compositions at 30 and 40°C, corresponding to 0.2 and 0.4 EtOH mole fraction, respectively. As EtOH-ETBE mixtures are binary systems, which deviate strongly from ideal ones, the 0.2–0.5 mol fraction range corresponds with high thermodynamic activities (a_{EtOH}), which vary from 0.27 to 0.64 at 50°C.

Effect of the PVP-TMA ratio on the blend membranes performances

The first set of results shown on the Figures 3 and 4

present the effect of the pyrrolidinone site content on pervaporation performances for two alcohol-ether mixtures at 50°C. With each mixture, it can be seen that the permeate enrichment recorded are well above 90 wt % for all blend membranes (Fig. 3), the maximum enrichment recorded being 95 wt %.

It clearly demonstrates the ethanol selective feature of the PVP-based membranes in agreement with literature.^{17,19} Nevertheless, it can be seen also the higher permeate enrichment was obtained with the lowest PVP content, not with the highest one as it could be expected at start. Thus, we investigated the relative role of the pyrrolidinone and TMA sites on the selectivity as presented here.

Figure 4 shows that both total permeate fluxes and partial EtOH fluxes are dramatically enlarged with the increase of PVP membrane content, e.g., from ≈ 3.5 to 10 kg/h m² for a mixture containing 16 wt % of alcohol. This means that the membrane affinity for EtOH does not decrease when the PVP membrane content is increased.

Therefore, the reported EtOH concentration decrease of the permeate *versus* PVP content (cf. Fig. 3) can be ascribed to two distinct phenomena, or to their combination: either the EtOH affinity for pyrrolidinone sites is lower than for TMA sites, or a plasticizing effect is induced by the PVP content increase, leading to a coupling transport phenomenon between the two permeants. Indeed, the higher EtOH flux recorded with the BI95#1 indicates that the membrane upstream swelling must be stronger than with BI75#3. Thus, this increased swelling must also favor the simultaneous sorption of ETBE.

Effect of the feed ethanol concentration

Plots of the EtOH fraction in permeate *versus* the EtOH feed concentration showed for each blend membrane

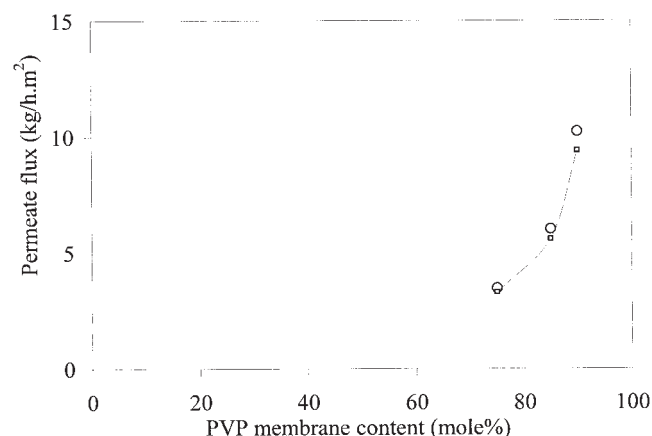


Figure 4 Effect of the PVP-TMA blend membranes ratio on the permeate fluxes at (50°C). Feed: EtOH 16 wt % at 50°C, i.e., $a_{\text{EtOH}} = 0.45$. ○: Total flux; □: EtOH flux.

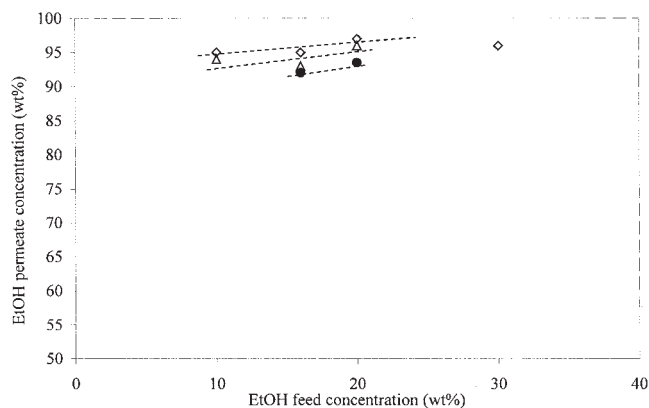


Figure 5 Effect of the EtOH/ETBE feed composition on the permeate enrichment at 50°C. Results for the PVP-TMA blend membranes (PVP mol %): ●, BI-95#1; △, BI-85#2; and ◇, BI-75#3.

a continuous increase of the permeate enrichment, which reaches 97 wt % starting from the EtOH 20 wt % in the feed (Fig. 5). The higher enrichments were obtained with BI75#3, and the lower with BI-95#1, which has a higher PVP content. It means that the influence of the membrane composition (i.e., NVP/TMA ratio) on the selectivity was the same whatever the EtOH feed content (cf. Fig. 3).

On the other hand, a sharp alcohol flux increase *versus* the EtOH feed concentration was recorded with the three PVP-based membranes (Fig. 6), but this effect was less pronounced with BI75#3 than with BI95#1. Figure 5 also shows much lower fluxes with BI85#2

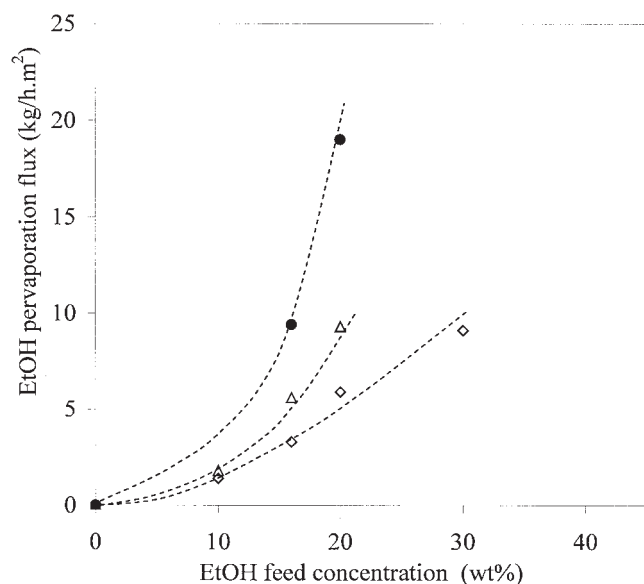


Figure 6 Effect of the EtOH/ETBE feed composition on the pervaporation flux at 50°C. Results for the PVP-TMA blend membranes (PVP mol %): ●, BI-95#1; △, BI-85#2; and ◇, BI-75#3.

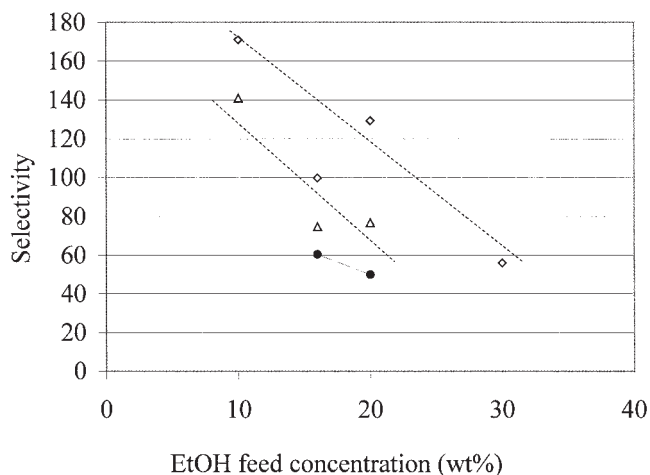


Figure 7 Effect of the EtOH/ETBE feed composition on the pervaporation selectivity at 50°C. Results for the PVP-TMA blend membranes (PVP mol %): ●, BI-95#1; △, BI-85#2; and ◇, BI-75#3.

and BI75#3. These transport property modifications related to the TMA content and to the EtOH feed concentration revealed that the TMA residues act more as crosslinking agents than as EtOH affinity sites.

It is worth to note the variation range of the membrane performances at a fixed EtOH feed concentration. For instance at EtOH 20 wt %, a permeate enrichment decrease of only 4 wt % was observed from BI75#3 (i.e., the most selective membrane) to BI95#1 (i.e., the less selective one), whereas the flux increase is over 300%. Thus, the possibility to tune easily the membrane properties looks very promising for EtOH-EBTE separation.

The variation of the membrane selectivity (i.e., α criterion) as a function of the EtOH feed concentration is shown in Figure 7. Despite some deviations due to measurement accuracy, the observed trend (i.e., negative slopes) is the same for the three membranes: in fact, the decrease of the α selectivity is mainly due to the mathematical expression of α (cf. Eqn2) combined with the fact that very high permeate enrichments ($\geq 95\%$) are already reached at 10 wt % EtOH feed content.

More significant, when α selectivity recorded for different feed contents is plot *versus* the PVP membrane content (Fig. 8), the two dashed lines drawn from the experimental points intersect to a lower selectivity range. This range corresponds with the combination of the intrinsic pyrrolidinone affinity counterbalanced by the maximum plasticizing effect occurring at high PVP content. Conversely, for lower PVP content, i.e., at higher TMA content, the crosslinking effect due to the ammonium sulfate residues notably favors the membrane selectivity.

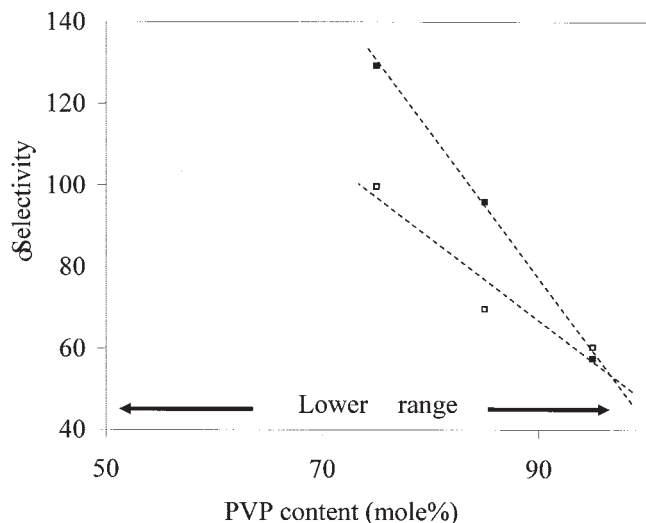


Figure 8 Effect of the PVP-TMA blend membranes ratio on the pervaporation selectivity for EtOH/ETBE mixtures at 50°C. ■, 20 wt % of alcohol and □, 16 wt % of alcohol.

Comparison of blend and copolymer membranes performances: effect of the polymer network architecture on the membrane transport

Besides the preparation of enriched pyrrolidinone membranes prepared according to the above blending method, we have also investigated the synthesis of copolymers from (*N*-vinyl-pyrrolidinone) and (trimethylmethacrylamidopropylammonium) methylsulfate.¹⁶ Taking into account the monomer reactivity ratios, i.e., $r_{\text{NVP}} = 0.04$ and $r_{\text{TMA}} = 4.47$, particular reaction conditions were worked out to get a copolymer, which had the same pyrrolidinone/TMA ratio than the membrane Bl85#2. Films were easily prepared from water of methanol solutions and then cured at 180° under vacuum. The observed solubility is given in Table II.

The pervaporation results are shown in Figures 9 and 10. For the whole studied EtOH concentration range (5–30 wt %), the fluxes recorded with the copolymer membrane are two to three times lower than with Bl-85#2 membrane, which is revealing a significant effect of the polymer network microstructure on the mass transfer properties.

On the other hand, only small differences in EtOH permeate enrichment were found between these two membranes. However, the copolymer selectivity was clearly the highest at high EtOH feed content (Fig. 10). As both membranes had the same bulk composition and were prepared according to the same curing procedure, the distinct pervaporation transport properties revealed by these experiments underlined the role of the polymer network architecture on the separation performances. This aspect is discussed hereafter.

The copolymer chain microstructure is closely related to the monomer reactivity ratio values and to the

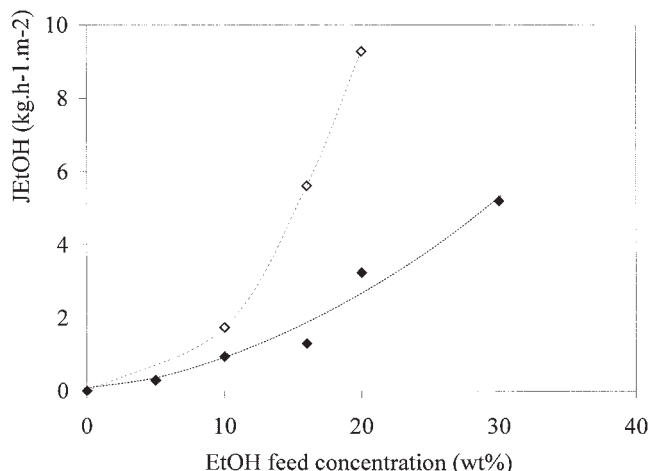


Figure 9 Effect of the pyrrolidinone-TMA network architecture on the EtOH pervaporation flux at 50°C. ◇, Bl-85#2 and ◆, Co-85#4.

VP/TMA monomer ratio used to synthesize the copolymer. As a consequence, the copolymer chains are composed of short TMA sequences, induced by the high TMA reactivity ratio, surrounded by a majority of pyrrolidinone residues (85 mol %). Obviously, the copolymer microenvironment is markedly different from the blend one.

As it was previously shown that the permeate flux amount was linked to the quantity of TMA residues and that the flux recorded for Bl-85#2 was higher than for copoly(NVP-TMA), it means that the crosslinking induced by the thermal treatment is more efficient in the copolymer structure than in the blend one. This could be well related with the random distribution of the TMA residues among the network that can be better achieved with copolymer chains than with poly-

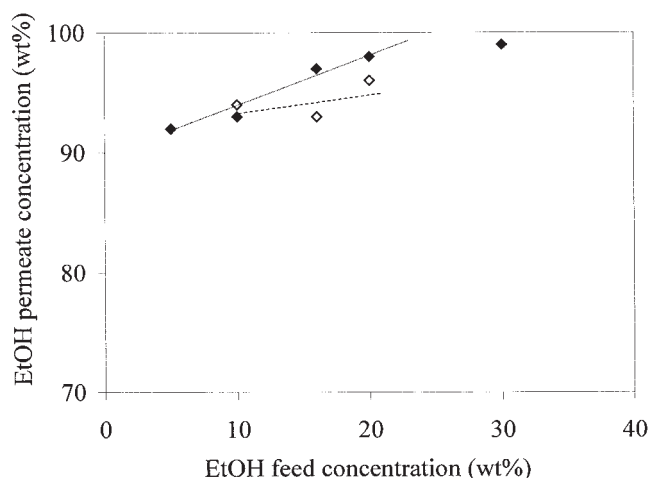


Figure 10 Effect of the pyrrolidinone-TMA network architecture on the EtOH permeate enrichment at 50°C. ◇, Bl-85#2 and ◆, Co-85#4.

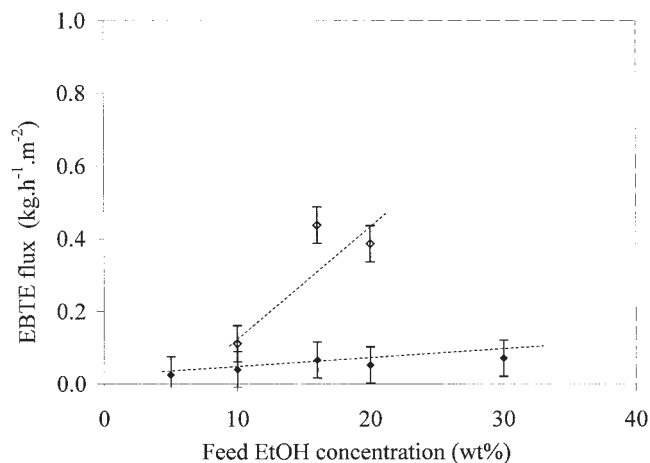


Figure 11 Plasticization effect on pervaporation ETBE fluxes recorded at 50°C. -◇, BI-85#2 and -◆, Co-85#4.

mer blends. Therefore, even if the bulk pyrrolidinone-TMA ratio is the same for the two membranes, the resulting crosslinking effect is stronger for the copolymer structure and induces much lower fluxes for EtOH and ETBE.

Finally, these results also clarify the role of TMA residues with respect to the membrane selectivity. Indeed, with the same global membrane composition, different selectivity was obtained, which means TMA residues do not enhance membrane affinity for EtOH directly, but limit ETBE diffusion *versus* EtOH.

In addition, the coupling transport phenomenon due to the EtOH plasticizing effect was also observed with the copolymer membrane: the higher the ethanol feed content, the higher the ether flux (Fig. 11).

Comparison with literature results

In Figure 12, a literature overview of pervaporation results obtained for EtOH/ETBE separation at different temperatures is presented for comparison with this work. Among published data only membranes that had an α membrane selectivity higher than 76 (i.e., EtOH permeate enrichment ≥ 95 wt % for a 20 wt % EtOH feed concentration) and fluxes higher than $0.1 \text{ kg h}^{-1} \text{ m}^{-2}$ were selected. These data correspond with different types of membranes, i.e., interpenetrated networks (IPN),¹⁷ block copolymers,^{19,26} polymer blends,^{29,32,33} crosslinked blends [this work], and methacrylate copolymers [this work].

Thus, it can be seen that the NVP-based membranes results reported in our work compete well with previously reported pervaporation results. These enhanced membrane properties, which combine high selectivity ($76 \geq \alpha \geq 196$) with good flux ($J_{\text{EtOH}} \geq 1 \text{ kg h}^{-1} \text{ m}^{-2}$), can be ascribed to the high pyrrolidinone membrane content coupled to TMA crosslinking, which prevent too high network swelling.

CONCLUSIONS

New EtOH selective films were prepared from polymers based on pyrrolidinone (NVP) and ionic *N*-substituted methacrylamide (TMA) monomers. These starting materials were easily synthesized by radical polymerization in aqueous medium and they led to the preparation of highly selective membranes for the separation of EtOH-ETBE mixtures by pervaporation. Two distinct series of glassy films were studied: the first one was prepared from the blends of homopolymers, while the other one was prepared from copolymers of NVP and TMA.

Thanks to the presence of the TMA residues, the water soluble films could be thermally crosslinked previously to their use in pervaporation. This curing treatment led to improved membrane stability during the pervaporation experiments.

From the sorption and pervaporation results, the specific roles played in the pervaporation transport by the two NVP and TMA residues were underlined. On the one hand, the pyrrolidinone sites were found to be mainly responsible for strong EtOH membrane affinity. As a drawback, it was shown that the EtOH flux enhancement, due to the higher amount of pyrrolidinone residues, induced a coupling effect of the ETBE pervaporation transport leading in turn to a selectivity decrease.

On the other hand, the TMA residues were shown to act mainly as crosslinking sites and to prevent to some extent the membrane swelling due to ethyl alcohol. Thus, the higher amount of TMA in the polymer structures, the lower the pervaporation flux and the higher the membrane selectivity.

Finally, by comparison of the results gained from blend and copolymer films having the same NVP/TMA composition, the effect of the polymer network

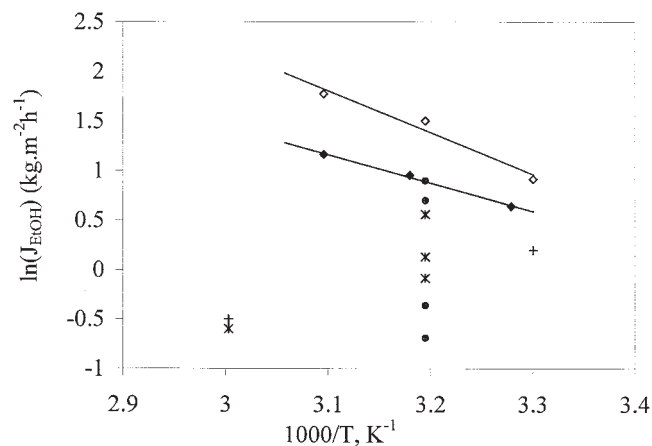


Figure 12 EtOH/ETBE pervaporation (feed: EtOH 20 wt %). Effects of temperature and of membrane type on EtOH permeate fluxes. -◆, Co-85#4; 224, BI-75#3; +, block copolymers;^{26,19} * Polymer blends;¹⁷ ○ IPN membranes;^{29,32,22,33}

microstructure was shown: in the copolymer structure, the more homogeneous distribution of the monomer residues led to a limited coupling effect. As a consequence, the copolymers film was more selective to ethanol.

References

1. Stickers, D. E. *Sci Total Environ* 2002, 299, 37.
2. BTX content regulations: Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC Official J L 350, 28/12/1998, 0058-0068, 1998.
3. Louder, K. E. U.S. Pat. 3,726,942 (1973).
4. Ancillotti, F.; Fattore, V. *Fuel Process Tech* 1998, 57, 163.
5. Happel, A. M.; Beckenbach, E. M.; Halden, R. U. An evaluation of MTBE impacts to California groundwater resources. Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-130897, 1998; p 80.
6. da Silva, R.; Cataluna, R.; et al. *Fuel* 2005, 84, 951.
7. Girard, M. *Pétrol Tech* 2001, 433, 63.
8. Streicher, C. U.S. Pat. 5,607,557 (1997).
9. Mulder, M. *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic Publishers: Dordrecht, 1996.
10. Shi, B.; Wuand, Y.; Liu, J. *Desalination* 2004, 161, 59.
11. Farnand, B. A.; Sawatzky, H. *Sep Sci Technol* 1988, 23, 1667.
12. Feng, X.; Huang, R. Y. M. *Ind Eng Chem Res* 1997, 36, 1048.
13. Lu, Y.; Zhang, L.; Chen, H.-L.; Qianand, Z.-H.; Gao, C.-J. *Desalination* 2002, 149, 81.
14. Quitain, A.; Itohand, H.; Goto, S. *J Chem Eng Jpn* 1999, 32, 539.
15. Yang, B.-L.; Goto, S. *Sep Sci Technol* 1997, 32, 971.
16. Touchal, S.; Jonquieres, A.; Clement, R.; Lochon, P. *Polymer* 2004, 45, 8311.
17. Nguyen, Q. T.; Noezar, I.; Clement, R.; Streicher, C.; Brueschke, H. *Polym Adv Tech* 1997, 8, 477.
18. Yoshida, W.; Cohen, Y. *J Membr Sci* 2003, 213, 145.
19. Roizard, D.; Léger, C.; Noezar, I.; Perrin, L.; Nguyen, Q. T.; Clément, R.; Lenda, H.; Lochon, P.; Néel, J. *Sep Sci Technol* 1999, 34, 369.
20. Steinhauser, H. A.; Brüsckhe, H. E. A. *Eur. Pat.* 0 674 940 A3 (1995).
21. Chen, M. S.; Eng, R. M.; Glazer, J. L.; Wensley, C. G. (to Air Products and Chemicals, Inc.) U.S. Pat. 4,774,365 (1998).
22. Farnand, B. A.; Noh, S. H. *AIChE Symposium Series* 1989, 85, 89.
23. Doghieri, F.; Nardella, A.; Sarti, G. C.; Valentini, C. *J Membr Sci* 1994, 91, 283.
24. Sano, T.; Hasegawa, M.; Kawakamiand, Y.; Yanagishita, H. *J Membr Sci* 1995, 107, 193.
25. Chen, W.-J.; Martin, C. R. *J Membr Sci* 1995, 104, 101.
26. Jonquieres, A.; Roizard, D.; Cuny, J.; Lochon, P. *J Membr Sci* 1996, 121, 117.
27. Kita, H.; Inoue, T.; Asamura, H.; Tanaka, K.; Okamoto, K. *Chem Commun* 1997, 45.
28. Kim, S.-G.; Lim, G.-T.; Jegal, J.; Lee, K.-H. *J Membr Sci* 2000, 174, 1.
29. Nguyen, Q. T.; Léger, C.; Billard, P.; Lochon, P. *Polym Adv Tech* 1997, 8, 487.
30. Gozzelino, G.; Malucelli, G. *Colloid Surface Physicochem Eng Aspect* 2004, 235, 35.
31. Huang, R. Y. M. *Pervaporation Membrane Separation Processes*; Elsevier: Amsterdam, 1991.
32. Luo, G. S.; Niangand, M.; Schaetzel, P. *J Membr Sci* 1997, 125, 237.
33. Funkhouser, G. P.; Frost, K. A. *Polymeric Compositons and Methods for Use in Low Temperature Well Applications*; 1997.