

Pervaporation Separation of Methyl *tert*-Butyl Ether/Methanol Mixtures Using a High-Performance Blended Membrane

MBAYE NIANG,¹ GUANGSHENG LUO,² PIERRE SCHAETZEL¹

¹GRGS, Département Génie Chimique, Bld Marechal Juin, F-14032 Caen Cedex, France

²Departement of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 11 April 1996; accepted 23 August 1996

ABSTRACT: For the separation of methyl *tert*-butyl ether (MTBE) and methanol mixtures, we investigated the pervaporation performance of a blend membrane made from cellulose acetate and cellulose acetate hydrogen phthalate. At first the influence of the blend composition was studied with a certain feed mixture. We found that all the tested membranes permeate methanol preferentially. The selectivity increases and the permeation rate decreases with increasing cellulose acetate content in the blend. Therefore, an optimal blend composition of 30 wt % in cellulose acetate was chosen to evaluate the influence of the feed composition and the experimental temperature on the pervaporation performance. When the feed temperature or the methanol content in the feed increases, the permeation rates are greatly enhanced and the selectivity decreases. However, the temperature effect is more significant at low methanol content in the feed and becomes negligible at high methanol content in the feed where plasticity effects prevail. A comparison, carried out with all the membranes until now used for the separation of MTBE/methanol mixtures, showed that the blended membrane studied in this present work presents good permselective properties. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 875–882, 1997

Key words: pervaporation; methyl *tert*-butyl ether; methanol; blended membrane; cellulose esters

INTRODUCTION

The phase-out of lead antiknock compounds in gasoline has given great interest to the use of some petrochemical products such as benzene, toluene, xylenes, and ethers as alternative octane enhancers for lead-free motor oil. Among them, methyl *tert*-butyl ether (MTBE) quickly appears to be both a good octane enhancer and an excellent oxygenated fuel additive needed to reformulate

gasoline so that it meets the Clean Air Act requirements. For this reason this product has been one of the fastest growing chemicals of the 1980s and it likely will continue to be that way throughout the 1990s.^{1,2} MTBE is produced by reacting methanol with isobutylene from a mixed-C₄ stream in the liquid phase over an acidic ion-exchange resin catalyst. Although rapid and selective, the reaction is limited by the equilibrium. Therefore, an excess of methanol is needed in order to improve the reaction conversion. But unfortunately the unreacted methanol forms azeotropic mixtures with both MTBE at 14.3 wt % methanol at 760 mmHg and with the butenes, which are difficult to separate by distillation. In the conven-

Correspondence to: M. Niang

Contract grant sponsors: Conseil Regional de Basse Normandie; Liaison Committee of Restors' Conferences of Europe.
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/050875-08

tional process scheme, the azeotropic mixture is taken to a butanizer to produce a MTBE bottom product and a binary methanol/ C_4 azeotrope overhead. This stream is then washed with water to remove the excess methanol from C_4 and the water/methanol mixture is distilled to recover the methanol for recycling.³ Unfortunately, the conventional method is both expensive and energy-intensive.⁴

Pervaporation is proven to present a high potential separation alternative because it is less energy-consuming than distillation.⁵ According to recent patents of Air Products and UBE Industries, the combination of distillation and pervaporation to separate MeOH from C_4 hydrocarbons exhibits cost savings as high as 20%.^{4,6,7} Earlier studies in the pervaporation separation of MTBE are related to Chen and coworkers, who investigated cellulose acetate membranes for the separation of alcohols from ethers.^{4,7} Farnand and Noh tested the nafion membrane to separate MeOH from C_4 hydrocarbons.⁸ The use of polyvinylalcohol (PVA) was introduced by Cen and colleagues for the separation of MeOH/MTBE mixtures⁹ and by Pasternak and associates for the separation of MeOH from organic oxygenates.^{10,11} The more recent studies in this field are from Nakagawa and Matsuo, who reported a polyimide membrane for the separation of MeOH from C_4 hydrocarbons in the synthesis of MTBE.⁶ Chen and Martin proposed the use of a thin film of polystyrenesulfonate across the surface of a microporous alumina support membrane.¹² Finally, van Gemert and Cuperus¹³ and Sano and colleagues¹⁴ introduced, respectively, the potential of a newly developed ceramic silica membrane and a silicalite membrane in the separation of organic compounds. Despite all these efforts, the permselective characteristics of these membranes remain insufficient for a large-scale pervaporation application. Thus our task in the present work is the synthesis of and pervaporation experiments on new cellulose acetate (CA) and cellulose acetate hydrogen phthalate (CAHP) polymer blend membranes allowing selectivity and permeation rate improvements. Park and associates¹⁵ have applied and proven the advantages of the polymer blend concept by using a PVA and a polyacrylic acid (PAA) membrane blend for the separation of MTBE and methanol, but the permeation rate and the selectivity obtained are low; therefore, we extensively investigated the effect of the experimental temperature and the feed methanol content on the permselective properties. Moreover, a comparison

is carried out with the best of the currently proposed membranes at the same separation and operating conditions.

EXPERIMENTAL

Materials

Cellulose acetate (CA; 39.6% acetyl content, average $M_w = 50,000$) and CAHP (1.2 wt % free acid, 3.5 wt % combined phthalate, 20.7 wt % acetyl content) were purchased from Sigma Aldrich Chemical Company (France). Methanol is 99.8% (chromanorm grade) and the MTBE was kindly offered by ARCO Chemical Company (France). All these products were used directly with no further purification.

Membrane Preparation

Polymer blending was performed by a solution method. CA and CAHP were dissolved in acetone and mixed at various blend compositions. The polymer solution was homogeneous, and was cast on a plate surface of PVC film. The solvent was quickly removed by evaporation at room temperature. The average thickness of all membranes prepared was in the range of 20 to 30 μm .

Pervaporation Experiments

Figure 1 shows the experimental setup used for the pervaporation measurements. Membranes with an effective area of 22.8 cm^2 were installed in a two-compartment stainless-steel cell. About 200 mL of feed mixture were introduced in the upstream compartment, kept at a constant op-

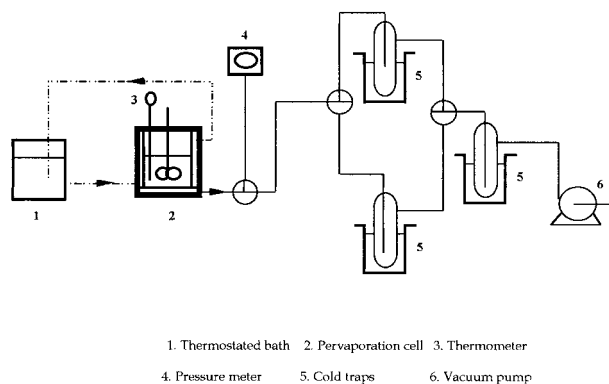


Figure 1 Schematic diagram of experimental apparatus.

erating temperature by circulating water in a thermostatted bath. The membrane upstream side was maintained at atmospheric pressure and the downstream pressure kept to less than 1 mbar by a vacuum pump. The permeate vapor was collected at the membrane downstream side in cold traps which were cooled by liquid nitrogen. Two traps can be used alternatively, allowing the permeate stream to be sampled continuously without interrupting the operation of the unit. All permeate samples were taken when steady-state conditions were reached: the liquid permeate collected in the cold traps was warmed to near room temperature and its composition was analyzed by a gas chromatograph with a 0.7-m long Porapak Q packed column heated at 180°C and equipped with a thermal conductivity detector. Hydrogen was used as gas carrier.

The permselective performance of pervaporation was evaluated in terms of two criteria: the permeate flux and selectivity. The permeate fluxes were determined by measuring the weight of liquid permeate collected in cold traps during a certain time at steady-state conditions. The permeation rates of the different membranes were normalized to a membrane at 5- μm thickness, assuming a proportionality between the total flux and the reciprocal membrane thickness. The pervaporation selectivity is expressed by the separation factor α which is defined by

$$\alpha = \frac{(y_1/y_2)}{(x_1/x_2)}$$

where x and y represent the concentrations in the feed and the permeate, respectively. Indices 1 and 2 refer to the more permeable component (methanol) and the less permeable one (MTBE), respectively.

The experiments were repeated at least 2 to 3 times, giving a deviation from the average of less than 10%.

CHOICE OF THE OPTIMUM BLEND MEMBRANE

CA is very selective for separating methanol from ethers. Indeed, in the permeation of the mixtures of MTBE and methanol through CA membrane, chemical interactions are preferentially between the membrane and methanol through hydrogen bonding and CA is hardly swollen by MTBE. Therefore, the permeate leads to nearly 100%

methanol, but unfortunately the permeation fluxes are very low (700 to 900 $\text{g h}^{-1} \text{m}^{-2}$ at 40°C). This membrane was already represented by Air Products to be very stable even at high temperature and over the range of all wt % methanol in the feed.

CAHP, however, presents high affinity for both methanol and MTBE, such that the pervaporation through CAHP membrane is not selective. In fact, the CAHP membrane is highly swollen and even soluble in the feed mixture of MTBE/MeOH. Therefore, the blend of these two components may lead to a very stable membrane whose performance could vary between those of the pure component polymers according to the blend composition. The influence of the blend composition in the pervaporation of the methanol and MTBE mixtures is presented in Figure 2. The experiments investigated the 20 wt % methanol feed at 40°C. As expected, the properties of the membrane tend toward those of the CA membrane when the CA/CAHP ratio in the blend increases. The increase of the CA content in the blend results in a membrane less swollen and more selective for methanol. As a consequence, the permeation fluxes decrease and the selectivity increases when the CA content in the blend increases (Fig. 2). So the selectivity decreases as the permeate rate increases. An optimum composition of the blend is to be found according to the separation requirements. For the separation of the MeOH and MTBE mixtures, a membrane assuring a selectivity of 100 and a permeation flux of 2000 $\text{g h}^{-1} \text{m}^{-2}$ is adequate for industrial purposes. The corresponding composition of the blend is 30% acetate cellulose content and we used this membrane for further experiments.

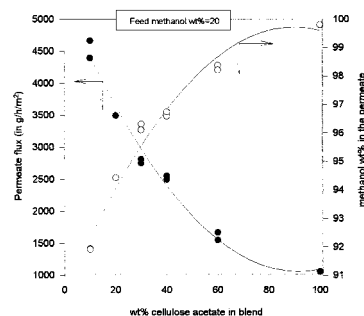


Figure 2 Pervaporation characteristics of blended membranes of CA and CAHP for a 20 wt % MeOH/MTBE mixture feed as a function of the blend composition. Feed temperature is 40°C. Total fluxes are converted to a 5- μm membrane thickness.

PERVAPORATION OF THE MeOH/MTBE MIXTURES: RESULTS AND DISCUSSION

The transport phenomenon of pervaporation separation through a nonporous polymer membrane is generally described by a solution–diffusion mechanism that occurs in the following three steps: sorption, diffusion, and desorption.¹⁶ The desorption step of the vapor at the permeate side is very rapid and nonselective due to the low pressure at the downstream side; only the equilibrium sorption and the transverse diffusion through the membrane to the downstream side of the membrane determine the pervaporation performance. The characteristics of the sorption and the diffusion depend on (a) the difference between the affinities of the components toward the polymer, (b) the mutual interactions of the components, and (c) the way the interactions with the polymer of each component effect the interactions of the other penetrant with the polymer.¹⁷ These interactions are affected both by the temperature and the feed concentration. Thus, in order to evaluate the overall permselective properties, the influence of the feed temperature was studied between 30 and 50°C and the effect of the feed concentration in the range of 5 to 30 wt % MeOH. Because the boiling point of the more volatile component, MTBE, is 55°C, our experiments could not exceed 50°C, to avoid the partial evaporation of the mixture at normal pressure.

Permeation Rate

Figure 3 represents the permeation rate as a function of the MeOH wt % in the feed. For each op-

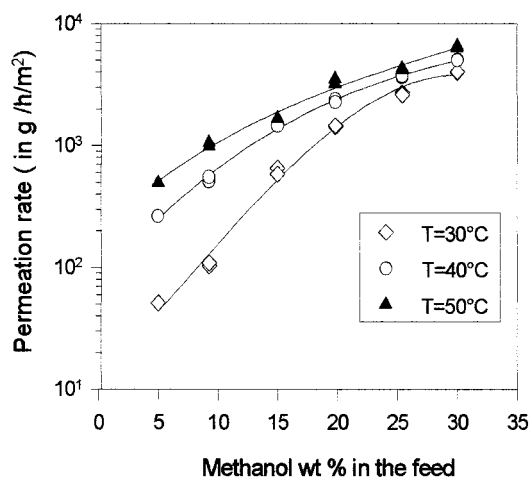


Figure 3 Influence of the feed MeOH wt % on the total permeation rate for various feed temperatures.

erating temperature, the permeation flux rises when the MeOH content of the feed increases. For example, at 40°C, between 10 and 20 wt % MeOH, the flux increases noticeably from 530 to 2500 $\text{g h}^{-1} \text{m}^{-2}$. The reason is that the level of the interactions between the membrane and the permeating molecules is a function of different feed MeOH contents. Indeed, previous experiments showed a preferential and a high solvation of MeOH; the chemical interactions between the membrane and MeOH are stronger than those between MTBE and the membrane. These interactions are realized by hydrogen bonds between the numerous carbonyl functions (heterocycle and C=O groups) of CA and CAHP and the hydrogen of MeOH.

Therefore, when the MeOH wt % in the feed increases, the interactions between MeOH and the membrane become statistically more intensive and the MeOH sorption and diffusion ability enhanced. Moreover, Figures 4 and 5 show that MeOH permeation rates are higher than those of MTBE.

The effect of the experimental temperature on the permeation rates can be seen in Figure 6. For a given feed MeOH wt %, the total flux increases when the feed temperature rises. In Figure 3, between 30 and 50°C, the flux can be enhanced from 1300 $\text{g h}^{-1} \text{m}^{-2}$ to 3300 $\text{g h}^{-1} \text{m}^{-2}$ for a constant feed concentration of 20 wt % MeOH. The reason is that at high temperature, (a) the sorption ability is improved because the polymer chains become more flexible and the intermolecular distances greater (more room inside the membrane offered to the penetrants), and (b) the diffusion coefficients of the components are greatly enhanced. Therefore, the permeation flux increases.

In Figure 6, the temperature effect for a given feed concentration is more accentuated at low wt % MeOH, and becomes relatively more constant at the high feed wt % MeOH; the slopes for the curves at 25 wt % and 30 wt % MeOH in the feed are nearly equal. The change in the permeation rates due to the temperature influence is the same for all wt % feed in the range of high MeOH wt %. So at high feed MeOH concentration, the membrane plasticity effect prevails over the temperature effect.

Selectivity

Figures 7 and 8 represent the selectivity of the blended membrane as a function of the temperature and the MeOH wt % in the feed. It appears

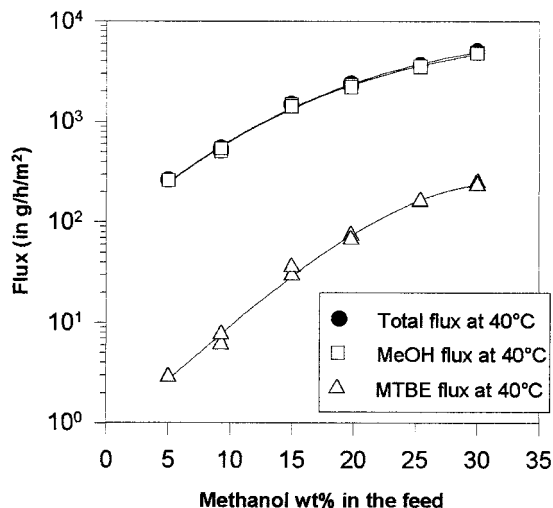


Figure 4 Influence of the feed MeOH wt % on the penetrants' fluxes for various feed temperatures.

that the membrane is very selective for MeOH. The MeOH wt % in the permeate is between 100% and 95% under the experimental conditions investigated. Figure 7 shows, for a constant temperature, a rapid decrease of the MeOH wt % in the permeate when the MeOH wt % in the feed increases from 5 to 30%. At a near azeotropic feed mixture of 14.97 wt % MeOH, the MeOH wt % in the permeate is about 99.4% at 30°C, which represents a separator factor α of about 940. The selectivity decreases drastically when the temperature increases (Fig. 8) or when the MeOH wt % in the feed increases. At the high feed MeOH wt %, the temperature hardly affects the selectivity.

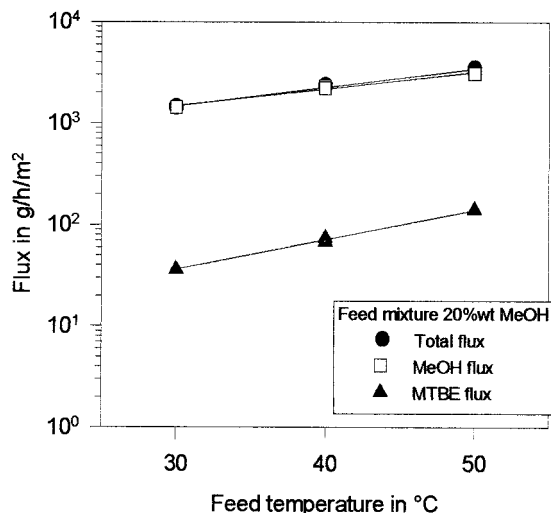


Figure 5 Influence of the feed temperature on the penetrants' fluxes at 20 wt % MeOH in the feed.

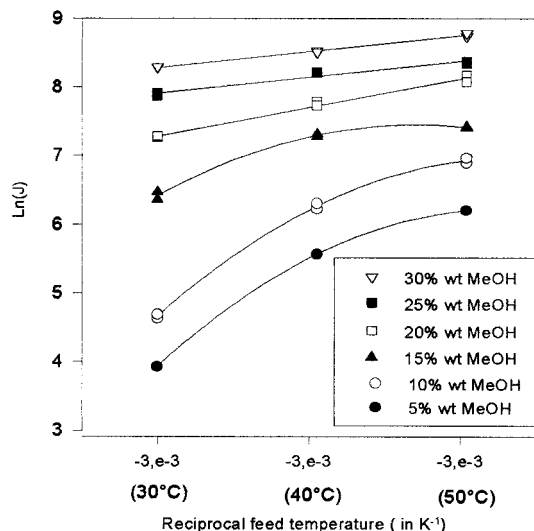


Figure 6 Influence of the feed temperature on the total permeation rate for various MeOH wt % in the feed.

The transport properties of the penetrants are not influenced to the same extent by the temperature according to the feed composition. The relative MTBE transport improvement due to temperature increase is nearly negligible at low concentrations and, on the other hand, at high MeOH wt %, the mobility of MTBE is facilitated by the enhancement of the MeOH transport properties of MeOH through the membrane.

The Arrhenius law could be fitted to predict this effect of temperature on the permeate flux for the high wt % MeOH feed.

The dependency of penetrants' fluxes, J_{MeOH}

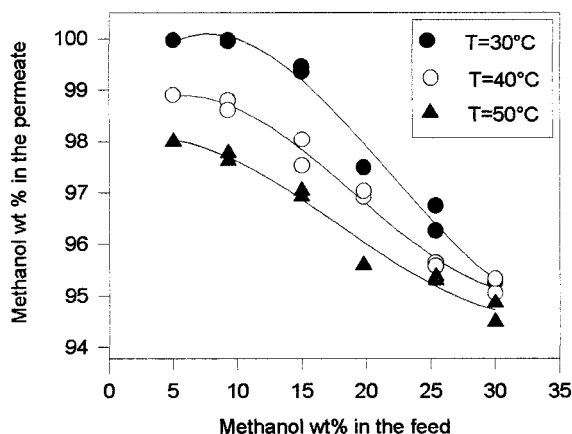


Figure 7 Influence of the feed mixture wt % MeOH on the permeate concentration for various feed temperatures.

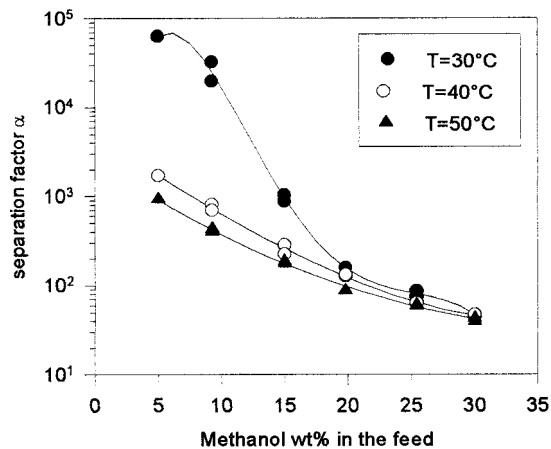


Figure 8 Influence of the MeOH wt % in the feed on the selectivity for various feed temperatures.

and J_{MTBE} , is well represented in Figure 9, where the total flux (J_{total}) is fitted by the same linear function of J_{MeOH} whatever the temperature of the feed between 30 and 50°C and for the MeOH composition in the feed between 10 and 30%. The equation $J_{total} = 1.0512 \times J_{MeOH} - 21.386$ can be used for rapid evaluations of the total flux.

As shown in Figure 10, the distillation and the pervaporation performances, through the permeating and the V–L equilibrium curves, are compared at the same operating temperature of 30°C. The V–L equilibrium curve was evaluated with the UNIFAC method by using the AspenPlus Release 9.2. The great separation potential of pervaporation is apparent because the permeate concentration at 30°C is much higher than the vapor phase concentration that we obtained from the V–

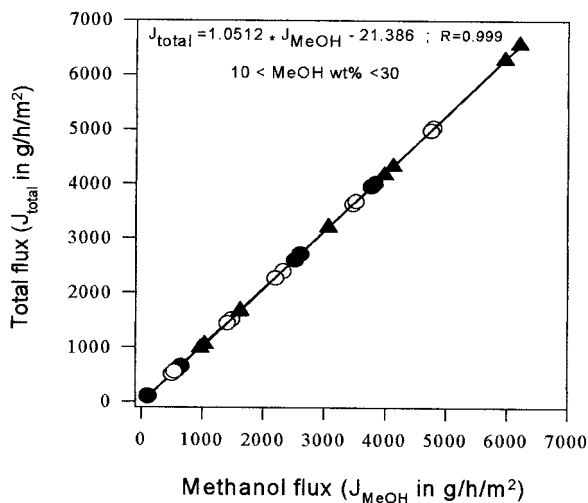


Figure 9 The relation between J_{total} and J_{MeOH} .

L equilibrium curve during distillation separation. Moreover, the azeotropic separation limitation is easily overcome by the pervaporation process.

The selectivity of pervaporation separation can sometimes be related to the nature of the mixture to be separated, i.e., the possible interactions between the component molecules. In this case, the MeOH–MTBE mixture presents a minimum-boiling azeotrope (maximum azeotrope). From a thermodynamic standpoint, in these mixtures the intensities of the different interactions between components MeOH/MeOH, MTBE/MTBE, and MeOH/MTBE are such that molecules of the same nature tend to autoassociate instead of generating intermolecular association. It appears the permeation is favorable to a high pervaporation selectivity because the transport of the permselective component is facilitated by the spontaneous molecular segregation from the other component due to these interactions between particles of the same components. To the contrary, with maximum boiling azeotropes the result is traduced by the existence of preferential interactions between molecules of different natures and then by possible bad selectivity. Consequently the initial choice of the membrane appears to be very important in the separation of this minimum-boiling azeotrope mixture. Swelling experiments, which have shown essentially no interactions between the blended membrane and MTBE, are a good means of predicting high selectivity during the pervaporation separation of MeOH and MTBE mixtures.

A comparison is carried out with the best mem-

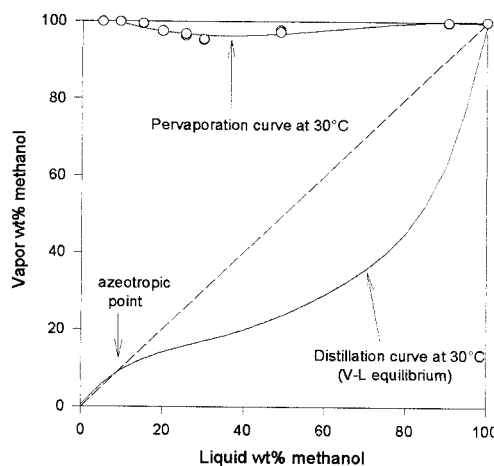


Figure 10 Comparison between the distillation and the pervaporation performances.

Table I Summary of Separation Performance of Various Membranes for the Separation of MTBE/MeOH Mixtures

Membrane Type	MeOH in Feed (wt %)	Separation Factor $\alpha(\text{MeOH/MTBE})$	Permeation Rate ($\text{g h}^{-1} \text{m}^{-2}$) ^a	Temperature (°C)	Reference
PVA/PAA (20 wt % PVA 88% hydrolyzed)	20	57–65	1,440–2,054	30–50	[15]
PVA	5–30	3–4	240–320	45	[9]
Nafion 117	3.2–5.3	25	107	RT ^b	[8]
Nafion 417	3.2–5.3	25	380	RT ^b	[8]
		35	1275	50	[8]
Polycrystalline silicalite on porous stainless steel support	5.3–51.6	3–8	7,300–11,000	30	[14]
Polycrystalline silicalite on porous stainless steel support	51.6	9–3	11,000–13,500	30–50	[14]
PSS/A12O3 Na (27.5 mol %)	5–14.3	5,000–1,200	8–150	25	[12]
PSS/A12O3 Mg (27.5 mol %)	5–14.3	35,000–25,000	3–55	25	[12]
Ceramic silica (silica deposited on γ -alumina membrane)	9–15.5	18.7–5.9	40.8–37.5	35	[13]
CA/CAHP (30 wt % CA)	20	175–100	1,440–3,365	30–50	This work
CA/CAHP (30 wt % CA)	20	130	2330	40	This work
CA/CAHP (30 wt % CA)	5–20	190,000–175	51–1,440	30	This work

^a All permeate rates are normalized at 5 μm of membrane thickness.

^b Room temperature.

branes already proposed in the literature for the same purpose and same operating conditions, in order to have an idea of the permselective properties we can perform with this blended membrane. The permeating fluxes of the different membranes were brought to a 5- μm membrane thickness to allow an objective comparison. The results collected in Table I lead to the conclusion that the selectivity and permeation rates of the blended membrane of CA with CAHP are much better than those of any other membrane published until now and used for the separation of the MeOH and MTBE mixtures.

CONCLUSIONS

The blended membrane concept is very useful because different separation requirements can easily be achieved by adjusting the blend composition. In this case, as the cellulose acetate content in the membrane increases the selectivity increases and the permeate flux decreases. The temperature influence on pervaporation characteristics, studied from 30 to 50°C and for various feed concentrations from 5 to 30 wt % MeOH, shows the decrease of the selectivity and the high in-

crease of the fluxes when the temperature increases. The temperature effect is more intensive at low MeOH content feed and becomes nearly negligible at high MeOH content feed. It was observed that the influence of the MeOH content in the feed is very strong.

Finally, the CA/CAHP blend membrane exhibits real opportunities for the pervaporation separation of the MeOH/MTBE mixtures. The permselective performance of this membrane is among the highest in comparison with those of the polymers already investigated for the separation of the MeOH/MTBE mixtures.

The authors thank the Conseil Regional de Basse Normandie and the Liaison Committee of Restors' Conferences of Europe for their financial support of our research.

REFERENCES

1. MTBE forte croissance prévue en Europe, *Informations Chimie*, 308, Aug–Sep 1989, 177–189.
2. S. J. Ainsworth, *Chem. Eng. News*, 13 (1990).
3. L. S. Bitar, E. A. Hazbun, and W. J. Piel, *Hydrocarbon Process.*, **63**, 63 (1984).

4. M. S. K. Chen, G. S. Markiewicz, and K. G. Venugopal, *AIChE Symp. Ser.*, **85**, 82 (1989).
5. J. L. Humphrey and A. F. Seibert, *Chem. Eng. Prog.*, **32** (1992).
6. K. Nakagawa and M. Matsuo, U.S. Patent 5292963, 1994.
7. M. S. Chen, R. M. Eng, J. L. Glazer, and C. G. Wensley, U.S. Patent 4774365, 1988.
8. B. A. Fernand and S. H. Noh, *AIChE Symp. Ser.* **85**, 89 (1989).
9. Y. Cen, M. Wesslein, and R. N. Lichtenthaler, in *Proceedings of the 4th International Conference on Pervaporation Processes in the Chemical Industry*, R. Bakish, Ed., 1989, p. 522.
10. M. Pasternak, C. R. Bartels, J. Reale, and V. M. Shah, U.S. Patent 4960519, 1990.
11. V. M. Shah, C. R. Bartels, M. Pasternak, and J. Reale, *AIChE Symp. Ser.*, **85**, 93 (1989).
12. W. J. Chen and C. R. Martin, *J. Membr. Sci.*, **104**, 101 (1995).
13. R. W. van Gemert and F. P. Cuperus, *J. Membr. Sci.*, **105**, 287 (1995).
14. T. Sano, M. Hasegawa, Y. Kawakami, and H. Yanagishita, *J. Membr. Sci.*, **107**, 193 (1995).
15. H. C. Park, N. E. Ramaker, M. H. V. Mulder, and C. A. Smolders, *Sep. Sci. and Technol.*, **30**, 419 (1995).
16. J. Neel, *Pervaporation Membrane Separation Process*, in R. Y. M. Huang, Ed., Elsevier, Amsterdam, 1991, Chap. 1.
17. G. S. Luo, M. Niang, and P. Schaetzel, *J. Membr. Sci.*, to appear.