Sorption and Pervaporation Separation of Ethyl Tert–Butyl Ether And Ethanol Mixtures Through a Blended Membrane

G. S. LUO,[1] M. NIANG,[2] P. SCHAETZEL[2]

[1] Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[2] Génie Chimique, IUT, Bd. Maréchal Juin, 14032 Caen Cédex, France

ABSTRACT: A new kind of membrane was prepared by blending poly(acrylic acid) with cellulose acetate propionate for the separation of ethyl tert–butyl ether and ethanol mixtures. The properties of the membranes were evaluated by the pervaporation separation of mixtures of ethyl tert–butyl ether/ethanol and the sorption experiments. The experimental results showed that the selectivity and the fluxes of this membrane depend on the blend composition and on that of processed feed mixtures. With respect to temperature, the ethanol fluxes obey the Arrhenius equation. The fluxes increase with the increase of the poly(acrylic acid) content in the blended membrane, the ethanol concentration in the feed, and the experimental temperature. But the selectivity decreases as the poly(acrylic acid) content and the experimental temperature are raised up. When the feed composition is varied, this membrane shows the special characteristics at the azeotropic composition. In the vicinity of the azeotropic point, the minimum values of ethanol concentration in the permeate and in sorption solution are obtained. The swelling ratios increase with an increase in the temperature and the ethanol concentration. The ethanol concentration in the sorption solution is also influenced by the temperature and composition of the mixtures. When the temperature increases, the sorption selectivity of the membrane decreases. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1631–1638, 1997

Key words: pervaporation; ETBE; ethanol; blended membrane

INTRODUCTION

With the legislation for air pollution being more stringent in the world, now the lead content in gasoline is strictly limited, and lead-free and low-leaded gasoline are encouraged to be used. As very efficient octane value enhancers, the necessary of methyl tert–butyl ether (MTBE) and ethyl tert–butyl ether (ETBE) increased rapidly with the development of environmental senses in recent years.[1–2] Specifically, ethanol may be obtained from farming products by fermentation, so ETBE is being recognized as an environmentally friendly product. ETBE is produced by reacting ethanol (EtOH) with isobutylene. This reaction is limited by the reaction equilibrium. Therefore, an excess of ethanol for this reaction is required to reach much higher conversion degrees of iso-olefin to the corresponding ether. The excess ethanol has to be separated from the production and recycled. The conventional separation process used for the reaction mixture is water washing and distillation. Because ethanol combined with ETBE can form an azeotropic mixture, a very complex flow sheet with several distillation columns was designed. This is a higher capital and energy-intensive separation process.[3,4] The binary azeotropic mixtures of ETBE[5] are listed in Table I.

Table I The Binary Azeotropic Mixture of ETBE

Mixture	Composition (Wt %)	Temperature (°C)
ETBE–H_2O	93.99–6.01	64.9
ETBE–EtOH	78.9–21.1	66.9

Because of its special characteristics, pervaporation separation has been widely considered as an alternative separation process for azeotropic mixtures, close-boiling point mixtures, and isomers.[6–8] Many research works in pervaporation separation of alcohol–ether mixtures have been reported so far. Most of the research works were pervaporation separation of the MTBE and methanol mixtures.[8–14] A hybrid distillation–pervaporation process for MTBE production developed by Air Products & Chemicals, USA has shown that this is a significant cost and energy saving process.[11,12] Until 1995, Noezar et al.[15] reported the cellulose ester-based polymer blend membranes for ethanol–ETBE separation. Some kinds of membranes were tested at 40°C with the mixture containing 20 wt % ethanol, and the results showed binary blends of a cellulose derivative with another polymer or cellulose derivative led to membranes with much better permeability and higher selectivity. They considered with these blended membranes good separation performances for the ETBE–ethanol mixtures could be achieved. Jonquieres et al.[16] studied the pervaporative transport modelling in the following ternary system: ETBE–EtOH–polyurethaneimide. But they didn't give out the results as the experimental conditions were changed. We have studied the pervaporation characteristics of the cellulose acetate propionate (CAP) membrane for separation of the EtOH–ETBE mixture.[17] The results showed that the high selectivity and reasonable fluxes could be obtained with the CAP membrane. We also studied the performance of blended membrane of cellulose acetate butyrate (CAB) with CAP, which showed that a good performance could be achieved by changing the experimental conditions.[18]

This work is to search a better performance membrane for ETBE–ethanol separation; then the characteristics of the pervaporation separation, swelling, and sorption will be studied. A comparison of all the reported works until now will be carried out.

EXPERIMENTAL

Materials

Cellulose acetate propionate (CAP) (46 wt % propionyl content, average $M_w = 75,000$), poly-(acrylic acid) (PAA) (35 wt % solution in water, M_w ca. = 250,000), and ethanol (EtOH) were provided by Aldrich Chemical Company. Ethyl tert-butyl ether was kindly supplied by the Institut Français du Pétrole (IFP, France). All these chemical products were used directly without any further purification.

Membrane Preparation

Polymer blending was performed by a solution method. According to the composition of the blends, PAA and CAP were dissolved in a solvent, dioxane, to obtain the desired polymer solution at room temperature. Homogeneous membranes were prepared by casting the solution on the plate surface of poly(vinyl chloride) (PVC) films and evaporating the solvent under a no-air-flowing condition at room temperature for 48 hours. After drying, the transparent membranes detached from the surface of the films automatically. The average thickness of all these membranes prepared by this method was around 30 μm.

Sorption Experiments

Weighted dry membranes were immersed in various ethanol concentration mixtures at the desired temperature for 24 hours to allow the swelling to reach the equilibrium. After the swollen membranes were rapidly taken out from the mixtures and the solution on the surface of the membranes was carefully wiped with tissue paper, then the membranes were weighed as quickly as possible. After weighing, the swollen membrane was placed into a dry flask, which was connected to cold traps and a vacuum pump. Under the vacuum condition, the sorption solution was collected until the weight of the membrane was the same as that of the dry membrane. The collected solution was analyzed with a VARIAN STAR 3400CX gas chromatograph equipped with a thermal conductivity detector and a 0.7 m long Porapak Q packed column. Hydrogen was used as a carrier. The characteristics of the sorption of the membrane was evaluated by the following swelling ratio, S, and sorption selectivity, β.

$$S = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

$$\beta = \frac{Y_{s,\mathrm{EtOH}} \times (100 - X_{\mathrm{EtOH}})}{X_{\mathrm{EtOH}} \times (100 - Y_{s,\mathrm{EtOH}})} \quad (2)$$

where W_d and W_s indicate the weights of the dry and the swollen membranes, respectively; $Y_{s,\mathrm{EtOH}}$ is the EtOH wt % in the sorption solution; and X_{EtOH} represents EtOH wt % in the feed.

Pervaporation Experiments

The experimental apparatus was explained in our previous works. Dry membrane was installed in the pervaporation cell equipped with a heating jacket. The pervaporation experiments were carried out at 40, 50, and 60°C. The effective membrane area in the cell was 22.8 cm^2. The feed solution was the mixtures of ETBE and EtOH that ranged in EtOH content from 3.1 to 30 wt %. The pressure at the downstream was evacuated to less than 0.75 mm Hg by a vacuum pump. The permeate was collected in the cold traps, which were cooled with liquid nitrogen. The composition of the permeates was analyzed with the gas chromatograph.

The pervaporation properties were characterized by the total, EtOH, and ETBE fluxes, J_{total}, J_{EtOH}, J_{ETBE}, and the separation factor, α. The fluxes were normalized to a membrane thickness of 5 μm, assuming a proportionality between the fluxes and the membrane thickness. The separation factor of the membrane is defined as follows:

$$\alpha = \frac{Y_{\mathrm{EtOH}} \times (100 - X_{\mathrm{EtOH}})}{X_{\mathrm{EtOH}} \times (100 - Y_{\mathrm{EtOH}})} \quad (3)$$

where Y_{EtOH} and X_{EtOH} are EtOH wt % in the permeate and in the feed, respectively.

RESULTS AND DISCUSSION

Determination of the Composition of the Blended Membrane

The blended membrane of CAP with PAA was evaluated by the pervaporation separation of the ETBE–EtOH mixture with 20 wt % in EtOH at 40°C because the azeotropic composition of the mixture is near 20 wt % EtOH in the mixture.

Much higher selectivity with the CAP membrane could be obtained for the separation of the
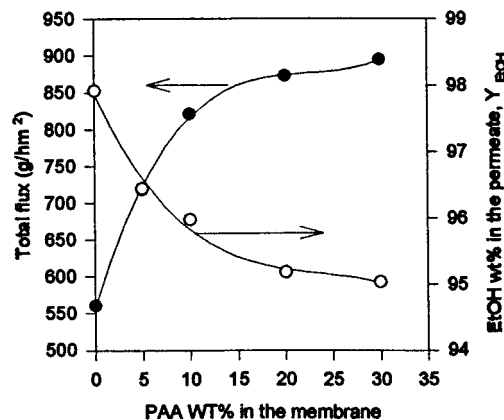

Figure 1 Influence of PAA content on performance of membranes.

EtOH–ETBE mixtures.[17] The EtOH wt % in the permeate can reach 98%. CAP can preferentially interact with EtOH through hydrogen bond formation or even dissolve in EtOH solution at high temperature, but the permeability of this membrane is not very good. Poly(acrylic acid)(PAA), however, presents high affinity with both ETBE and EtOH. Park et al.[19] have reported a blended membrane of PVA with PAA that shows good performance for the separation of methyl tert-butyl ether and methanol mixtures. Therefore, in our works, the blended membranes of CAP with PAA were tested, and it is hoped they may show high selectivity and good permeability for the separation of the EtOH–ETBE mixtures.

As shown in Figure 1, the total flux increases rapidly, and the EtOH wt % in the permeate decreases when the PAA content in the membrane increases. For considering the stability of the blended membrane and the purpose of passing the azeotropic point for the separation of the ETBE and EtOH mixtures, the blended membrane of 10 wt % PAA with 90 wt % CAP was chosen and used in the following experiments. Because the permeate is recycled to the reactor in the process of coupling membrane pervaporation with distillation separation, if the ETBE wt % in the permeate is too high, the reaction will be limited seriously. Under the experimental conditions, this blended membrane is stable; no change in properties have been observed.

Influence of Temperature and EtOH Wt % in Feed on Membrane Sorption

The permeation of molecules through a nonporous polymer membrane is generally described by a
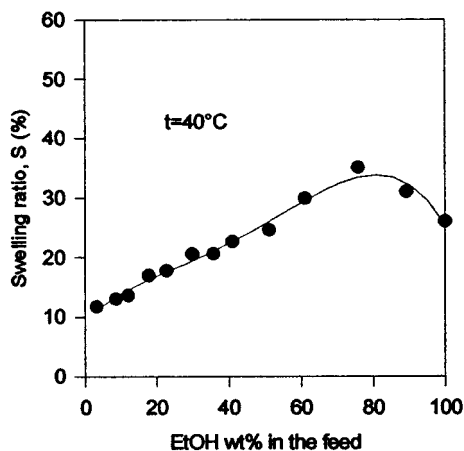
Figure 2 Swelling ratios versus EtOH wt % at 40°C.

Figure 3 Swelling ratios versus EtOH wt % at different temperatures.

solution–diffusion mechanism that occurs in the following three steps: sorption, diffusion, evaporation.[20–24] Due to the low pressure at the downstream, according to this model, the permselective properties of pervaporation of membranes are determined by the solubility and the diffusivity of the permeating components in the membrane. Usually, the component with the highest solubility and largest diffusion coefficient in the polymers permeates preferentially. The characteristics of the sorption depends on (1) the difference between the affinities of the components towards the polymer, (2) the mutual interactions of the components, and (3) the way the interactions with the polymer of each components affect the interactions of the other penetrant with the polymer.[25] Therefore, the properties of the membrane sorption may play an important role in the pervaporation process and decide the performance of the membrane. Some works in this field have been reported.[21]

The swelling ratios of the membrane at different experimental conditions were compared. The results of swelling ratio versus EtOH wt % in the feed at different temperatures are plotted in Figures 2 and 3. From the two figures, one can see that the swelling ratios of the membrane increase with the temperature increasing. It is because the distance of the molecules is larger than that at low temperature, and the interactions of the molecules of the membrane are weakened when the temperature is raised. As the EtOH wt % in the feed increases, the swelling ratios also increase until the maximum values, and then decrease. The most likely reason is the strong interactions of EtOH molecules with the polymer and the ETBE molecules, which cause the swelling ratios
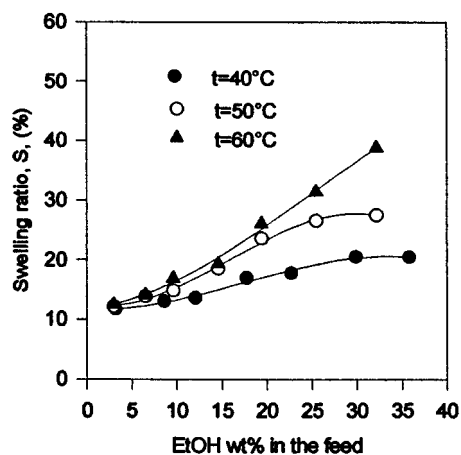
to increase with an increase in the EtOH wt %. When the EtOH wt % in the feed increases further, the interactions between molecules of EtOH would be enhanced and cause the swelling ratios to decrease. In the swelling experiments, the membrane will lose some weight at high temperature and high EtOH wt % (>50 wt %) in the feed due to the dissolution of CAP in EtOH at high temperature. In practice, the EtOH wt % in the feed is usually less than 20%.

The composition of the sorption solution at the different temperatures and feed mixtures was analyzed. The results are shown in Figures 4 and 5. Figures 4 and 5 show that the EtOH wt % in the sorption solution decreases with an increase in the EtOH wt % in the feed. When the feed containing 15–25% EtOH, the minimum values of the EtOH concentration in the sorption solution
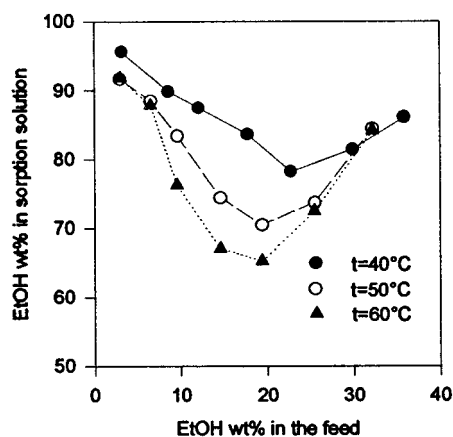

Figure 4 Influence of experimental conditions on sorption selectivity.
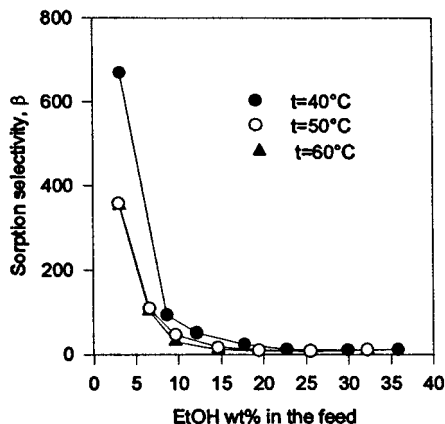
Figure 5 Influence of experimental conditions on sorption selectivity.

are obtained. It is just in the vicinity of the azeotropic composition. After the azeotropic point, the EtOH wt % in the sorption solution increases as the EtOH wt % in the feed increases. The sorption selectivity of the membrane decreases until near constant with the increase of the EtOH wt % in the feed. They also show the EtOH wt % in the sorption solution and sorption selectivity are influenced by the temperature. When the temperature increases, the sorption selectivity decreases. This phenomenon can be explained as the sorption selectivity of the membrane is not only decided by the interactions of the membrane with the molecules of the mixture, but also decided by the mutual interactions of the molecules of the mixture and how these interactions influence other chemical properties of this system. It is likely that for the mixture of ETBE and EtOH, the interactions between these two kinds of molecules are much stronger at the azeotropic composition. Therefore, when EtOH molecules pass through the membrane, much EBTE will pass through the membrane with EtOH in the vicinity of the azeotropic composition, although the interaction between the molecules of EtOH and the membrane is very strong. The interactions between molecules of mixtures and polymer weaken as the temperature increases, so that the sorption selectivity decreases. In this field, the mechanism is not clear, and it is necessary to study it further.

Pervaporation Characteristics of Blended Membrane of 10% PAA with 90% CAP

Influence of Temperature and Feed Composition on Fluxes

A systematic study of the pervaporation characteristics of the membrane of 10% PAA with 90%
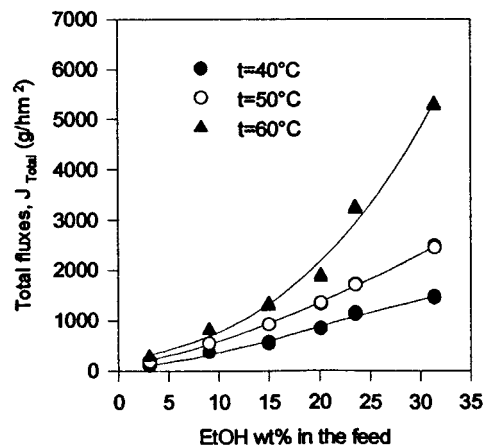
CAP was carried out. The influence of the EtOH wt % in the feed and the experimental temperature were studied. Figures 6 and 7 represent the influence of EtOH wt % in the feed and the experimental temperature on the total and EtOH fluxes.

As shown in Figures 6 and 7, the total and EtOH fluxes increase quickly with the increase of the temperature and the EtOH wt % in the feed. This is because the molecules of the mixture move more quickly when the temperature is raised up, and the diffusion coefficients of EtOH and ETBE in the membrane increase. As the EtOH wt % in the feed increases, the swelling ratios of the membrane increase; this causes the fluxes to increase. But due to the strong interactions between the polymer and EtOH molecules, the EtOH flux is much higher than that of ETBE.
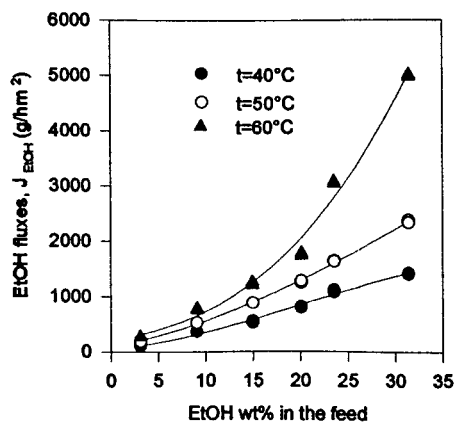

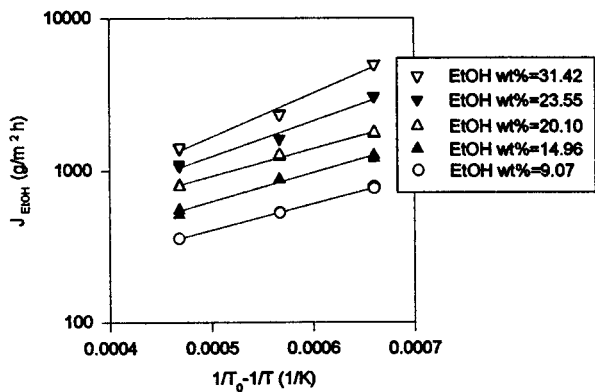**Figure 6** Performance of total fluxes of the membrane.

Figure 7 Performance of EtOH fluxes of the membrane.

Figure 8 J_{EtOH} versus $\left(\dfrac{1}{T} - \dfrac{1}{T_0} \right)$.

Figure 8 is the diagram of J_{EtOH} versus $\left(\dfrac{1}{T} - \dfrac{1}{T_0} \right)$ at different EtOH wt % in the feed.

From these figures, one can see that the relationship of EtOH flux with the temperature and EtOH wt % in the feed can be represented by the Arrhenius equation. The equation is

$$J_{\text{EtOH}} = (K_1 X + K_2 X^2) \cdot e^{-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (4)$$

where J_{EtOH} stands for the EtOH flux (g m^{-2} h), K_1 and K_2 are the constants of the equation, (g m^{-2} h), and X represents EtOH wt % in the feed. E is the activation energy in the unit of J mol, which depends strongly on the nature of the membrane and on that of the mixture. T is absolute temperature, K, and $T_0 = 273$ K. R indicates the gas constant.

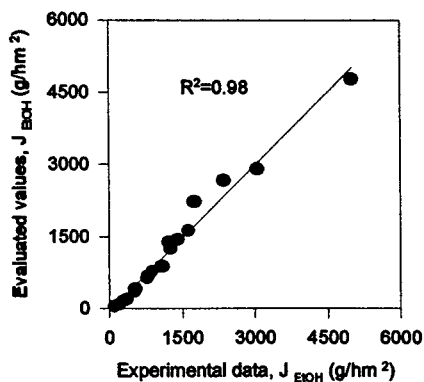K_1, K_2, and E were evaluated from the experi-

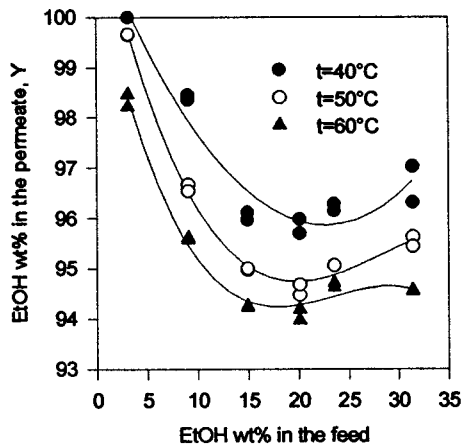**Figure 9** Comparison of experimental data with evaluated values.

Figure 10 Function of Y_{EtOH} as the temperature and EtOH wt %.

mental data, which are $K_1 = 0.61$, $K_2 = 0.06$, and $E = 753.86$ J mol. As shown in Figure 9, the agreement between the experimental data and the evaluated values is very well. Therefore, relationship of the EtOH flux with the temperature and the EtOH wt % in the feed can be written as follows:

$$J_{\text{EtOH}} = (0.61X + 0.06X^2) \cdot e^{-\frac{753.86}{R} \left(\frac{1}{T} - \frac{1}{T0} \right)} \quad (5)$$

Influence of Temperature and EtOH Wt % on the Separation Factor, α

For the comparison of the selectivity of the blended membrane at the different experimental conditions, separation factor, α, and EtOH wt % in the permeate, Y_{EtOH}, were chosen as compared
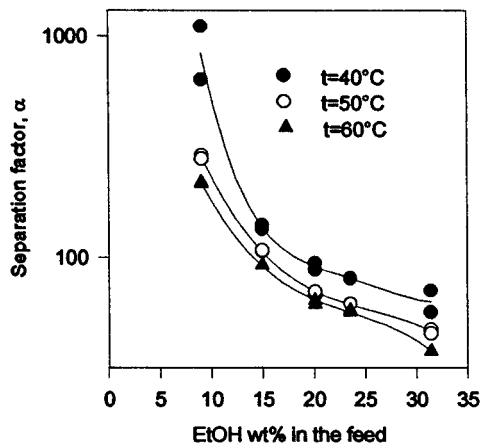

Figure 11 Function of α as the temperature and EtOH wt %.

constants. Figures 10 and 11 show the function of α and Y_{EtOH} as the temperature and EtOH wt % in the feed.

For the same feed, the EtOH wt % in the permeate decreases quickly with the temperature increasing. When the temperature is not changed, the EtOH wt % in the permeate decreases until the minimum value, then increases with the EtOH concentration in the feed increasing. In the vicinity of the azeotropic composition of the mixture, the lowest value of the selectivity is observed. The separation factor decreases until near a constant value when the temperature and EtOH wt % increase. When the EtOH wt % in the feed is low, the separation factor decreases quickly with the temperature increasing; but as the EtOH wt % in the feed is raised up, the influence of the temperature on the separation factor is not so serious as that at low EtOH concentration in the feed. The main reason is due to the swelling of the membrane with the temperature changed. At the azeotropic composition, although the interactions between the polymer and EtOH molecules are strong, the interactions of ETBE molecule with EtOH molecule are also very strong. Therefore, the lowest selectivity appears in the vicinity of the azeotropic point, but the selectivity of the membrane is enough to pass the azeotropic point for the separation of the ETBE–EtOH mixtures. As the EtOH wt % in the feed increases further, due to the interactions of the membrane with EtOH, the selectivity increases, even though the membrane is much more swollen.

Comparison of the Results of Pervaporation and Sorption

In order to investigate the potential of the blended membrane for the separation of the EtOH–ETBE mixture, the results of the sorption and the pervaporation at 40°C were compared with the vapor–liquid equilibrium calculated by ASPEN PLUS RELEASE 9.2 with UNIFAC method. As shown in Figure 12, the pervaporation curve, the vapor–liquid equilibrium curve, and the polymer–liquid mixture equilibrium curve show the same tendency with the change of the EtOH wt % in the feed. The selectivity of pervaporation is considerably higher than that of distillation, indicating that the membrane permeates EtOH preferentially. It also shows that the blended membrane absorbs EtOH molecules preferentially from the data of sorption experiments, although the value of the sorption selectivity is smaller than that of
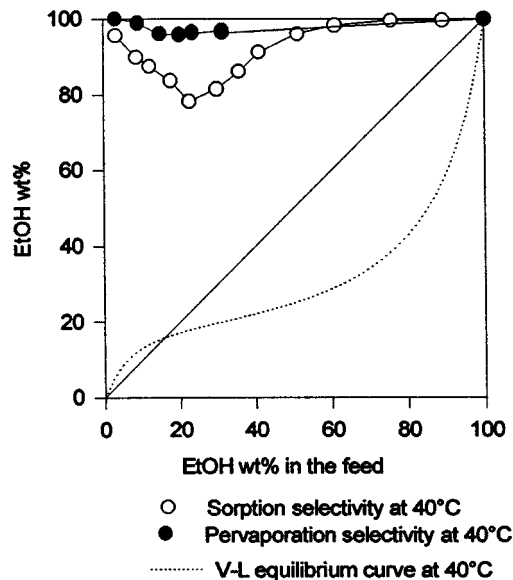

Figure 12 Comparison of sorption and pervaporation with the vapor–liquid equilibrium curve.

pervaporation selectivity. From the above discussion, we may conclude that the pervaporation selectivity is determined by the sorption and diffusion steps and that the diffusion coefficient of EtOH is much bigger than that of ETBE.

Table II is the summary of the performance of various membranes for the separation of the EtOH–ETBE mixture. From this table, one can see that higher selectivity and mass fluxes with the blended membrane can be allowed.

CONCLUSION

A new kind of membrane was prepared by blending poly(acrylic acid) with cellulose acetate propionate. The properties of this membrane were evaluated by the pervaporation separation of the ethyl tert–butyl ether/ethanol mixtures. With the increase of the content of poly(acrylic acid) in the membrane, the fluxes increase and the selectivity decreases. High permeability and good selectivity could be reached by changing the composition of the blend.

For the membrane of 10% PAA with 90% CAP, the experimental results showed that the selectivity and the fluxes of this membrane depend on the feed composition and the experimental temperatures. When ethanol concentration in the feed and the experimental temperature are raised up,

Table II Summary of the Performance of Various Membranes for the Separation of the EtOH–ETBE Mixture

Membrane	EtOH Wt % in Feed	EtOH Wt % in the Permeate	Total Flux (g m^{-2} h)	Temperature (°C)	Reference
Cellulose acetate	20	100	90	40	15
Cellulose acetate butyrate	20	79.70	2980	40	15
Cellulose triacetate	20	100	70	40	15
Polyurethaneimide	20	< 50	< 650	30	16
CAP	20	98.0	560	40	17
CAP	3–30	95.3–99.7	50–1700	40–60	17
70% CAP + 30% CAB	20	94.7	1140	40	18
70% CAP + 30% CAB	3–30	92.3–99.6	42–4625	40–60	18
90% CAP + 10% PAA	20	95.87	835	40	This work
90% CAP + 10% PAA	3–30	94.18–99.7	98–5260	40–60	This work

the total flux and ethanol flux increase. The ethanol flux obeys the Arrhenius equation.

The selectivity decreases with the increase of the temperature; but as the ethanol concentration in the feed is changed, the minimum value of the selectivity is observed in the vicinity of the azeotropic composition of the mixture. The same tendency results in the sorption experiments have been obtained. This fact may be explained as the characteristics of the blended membrane are not only decided by the interactions between the polymer and the molecules of the mixture, but also decided by the interactions of molecules of the mixture. Therefore, the selectivity of the membrane and the EtOH wt % in the sorption solution are at the minimum values in the vicinity of the azeotropic composition.

REFERENCES

1. M. S. Reish, *Chem. Eng. News,* **72,** 12 (1994).
2. G. Pecci and T. Floris, *Hydrocarbon Proc.,* **56,** 98 (1977).
3. I.F.P., Venice Symposium, France, 1989.
4. A. Chauvel, G. Lefebvre, and L. Castex, *Procédés de Prétrochimie,* Tome 1, 1985.
5. M. Matoqu, A. T. Quitain, K. Takahashi, and S. Goto, *Ind. Eng. Chem. Res.,* **35,** 982 (1996).
6. D. R. Seok, S. G. Kang, and S.-T. Huang, *J. Membrane Sci.,* **33,** 71 (1987).
7. I. Blume, J. G. Wijmers, and R. W. Baker, *J. Membrane Sci.,* **49,** 253 (1990).
8. W. J. Chen and C. R. Martin, *J. Membrane Sci.,* **104,** 101 (1995).
9. H. C. Park, N. E. Ramaker, and M. H. V. Mulder, *Sep. Sci. Technol.,* **30,** 419 (1995).
10. V. M. Shah, C. R. Bartels, M. Pasternak, and J. Reale, *AIChE Symp. Ser.,* **85,** 93 (1989).
11. M. S. Chen, R. M. Eng, J. L. Glazer, and C. G. Wensley, U.S. Pat. 4,774,365 (1988).
12. M. S. K. Chen, G. S. Markiewicz, and K. G. Venugopal, *AIChE Symp. Ser.,* **85,** 82 (1989).
13. T. Sano, M. Hasegawa, Y. Kawakami, and H. Yanagishita, *J. Membrane Sci.,* **107,** 193 (1995).
14. M. Niang, G. S. Luo, and P. Schaetzel, *J. Appl. Polym. Sci.,* 1997.
15. I. Noezar, Q. T. Nguyen, R. Clement, J. Neel, and H. Bruschke, *Proceedings of Euromembrane '95,* University of Bath, U.K., 1995, p. I-368.
16. A. Jonquieres, R. Clement, D. Roizard, and P. Lochon, *J. Membrane Sci.,* **109,** 65 (1995).
17. G. S. Luo, M. Niang, and P. Schaetzel, *Sep. Sci. Technol.,* **32,** 1143 (1997).
18. G. S. Luo, M. Niang, and P. Schaetzel, *J. Membrane Sci.,* **125,** 237 (1997).
19. H. C. Park, N. E. Ramaker, M. H. V. Mulder, and C. A. Smolers, *Sep. Sci. Technol.,* **30,** 419 (1995).
20. J. Neel, in *Pervaporation Membrane Separation Process,* R. Y. M. Huang, Ed., Elsevier, Amsterdam, 1991, Chap. 1.
21. Y. M. Lee, D. Bourgeois, and G. Belfort, *J. Membrane Sci.,* **44,** 161 (1989).
22. W. J. Rhim and R. Y. M. Huang, *J. Membrane Sci.,* **46,** 335 (1989).
23. C. K. Yeom and R. Y. M. Huang, *J. Membrane Sci.,* **67,** 39 (1992).
24. J. G. Wijmans and R. W. Baker, *J. Membrane Sci.,* **79,** 101 (1993).
25. C. Bartels-Caspers, E. Tusel-Langer, and R. N. Lichterthaler, *J. Membrane Sci.,* **70,** 75 (1992).
26. X. Y. Ni, Z. L. Xu, and Y. J. Shi, *Water Treatment,* **9,** 265 (1994).