Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Development of Cellulose Acetate Propionate Membrane for Separation of Ethanol and Ethyl tert-Butyl Ether Mixtures

G. S. Luo[a]; M. Niang[a]; P. Schaetzel[a]
[a] LABORATOIRE D'AUTOMATIQUE ET DE PROCÉDÉS IUT DE CAEN, GÉNIE CHIMIQUE BLD. MARECHAL JUIN, CAEN CEDEX, FRANCE

To cite this Article Luo, G. S. , Niang, M. and Schaetzel, P.(1997) 'Development of Cellulose Acetate Propionate Membrane for Separation of Ethanol and Ethyl tert-Butyl Ether Mixtures', Separation Science and Technology, 32: 6, 1143 — 1156
To link to this Article: DOI: 10.1080/01496399708000952
URL: http://dx.doi.org/10.1080/01496399708000952

SEPARATION SCIENCE AND TECHNOLOGY, 32(6), pp. 1143–1156, 1997

Development of Cellulose Acetate Propionate Membrane for Separation of Ethanol and Ethyl *tert*-Butyl Ether Mixtures

---

G. S. LUO,* M. NIANG, and P. SCHAETZEL
LABORATOIRE D'AUTOMATIQUE ET DE PROCÉDÉS
IUT DE CAEN, GÉNIE CHIMIQUE
BLD. MARECHAL JUIN, 14032 CAEN CEDEX, FRANCE

ABSTRACT

For pervaporation separation of ethanol and ethyl *tert*-butyl ether mixtures, a cellulose acetate propionate membrane was chosen as the experimental membrane because of its high selectivity and good mass fluxes. 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 permeates depend on the ethanol concentration in the feed and the experimental temperature. With increases of the ethanol weight fraction in the feed and the temperature, the total and partial mass fluxes increased. With respect to the temperature, ethanol mass flux obeys the Arrhenius equation. The selectivity of this membrane decreases as the temperature and the ethanol concentration in the feed increase. This membrane shows special characteristics at the azeotropic composition. In the vicinity of the azeotropic point, minimum values of ethanol concentration in the permeate and in sorption solution are obtained. The swelling ratios increase when temperature and the ethanol concentration in the feed are increasing. The ethanol concentration in the sorption solution is also influenced by the temperature and the mixture's composition. When the temperature increases, the sorption selectivity of the membrane decreases.

Key Words. Pervaporation; Cellulose acetate propionate; ETBE; Ethanol

---

* To whom correspondence should be addressed at Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China.

INTRODUCTION

As very efficient octane value enhancers, the use of methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) has increased rapidly as environmental concerns have increased in recent years (1, 2). In particular, ethanol may be obtained from farm products by fermentation, so ETBE is recognized as an environmentally friendly product. ETBE is produced by reacting ethanol with isobutylene. This reaction requires an excess of ethanol (EtOH) in the reactor to reach much higher conversion degrees of iso-olefin to the corresponding ether, and EtOH combined with ETBE can form an azeotropic mixture (21 wt% in ethanol at 760 mmHg). Therefore, a very complex flow sheet with several distillation columns was designed. This is a high capital and energy-intensive separation process (3, 4).

Pervaporation separation has been widely considered as an alternative conventional separation process for azeotropic mixtures, close-boiling-point mixtures, and isomers because of its special characteristics (5–7). Much research work in the pervaporation separation of alcohols/ethers mixtures has been reported (7–12). A hybrid distillation–pervaporation process for MTBE production developed by Air Products & Chemicals has been shown to be a significant cost and energy-saving process (10, 11). However, most research has been on the separation of MTBE/methanol mixtures. In 1995 Noezar and his coworkers (13) reported the use of cellulose ester-based polymer blend membranes for ethanol–ETBE separation. They tested some kinds of membranes with a mixture containing 20 wt% ethanol at 40°C. Jonquieres et al. (14) studied pervaporative transport modeling in a ternary system: ETBE/EtOH/polyurethaneimide, but they didn't report the results of changed experimental conditions.

The purpose of our work was to use cellulose acetate propionate (CAP) membrane, a good performance membrane, for ETBE/ethanol separation. The pervaporation separation characteristics of the membranes and the sorption properties were studied.

EXPERIMENTAL

Materials

Cellulose acetate propionate (CAP) (46 wt% propionyl content, average MW = 75,000), and ethanol (EtOH) were purchased from Aldrich Chemical Company. ETBE was kindly supplied by Institut Français du Pétrole (IFP). All these chemical products were used directly without any further purification.

Membrane Preparation

CAP was dissolved in acetone to obtain the desired polymer solution at room temperature. Homogeneous membranes were prepared by casting the solution on the plate surface of PVC films and evaporating the solvent, acetone, under the no-air-flowing condition at room temperature for 24 hours. When they were dried, the transparent membranes detached from the films automatically. The average thickness of membranes prepared by this method was in the 30–40 μm range.

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 equilibrium. After the swollen membranes were rapidly taken out from the mixtures and the solution on the surface of the membranes wiped carefully with tissue paper, the membranes were weighted as quickly as possible. Then the swollen membrane was placed into a dry flask which was connected to cold traps and a vacuum pump. Under 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 Chromatographer equipped with a thermal conductivity detector and a 0.7-m long Porapak Q packed column. Hydrogen was used as carrier. The characteristics of the sorption of the membrane were evaluated by the swelling ratio S and sorption selectivity β:

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

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

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

Figure 1 is a schematic diagram of the experimental apparatus used in the work. A dry membrane was installed in the pervaporation cell equipped with a heating jacket. Warm water was circulated to keep the experimental temperature at the desired temperature. The pervaporation experiments were carried out at 40, 50, and 60°C. The effective membrane

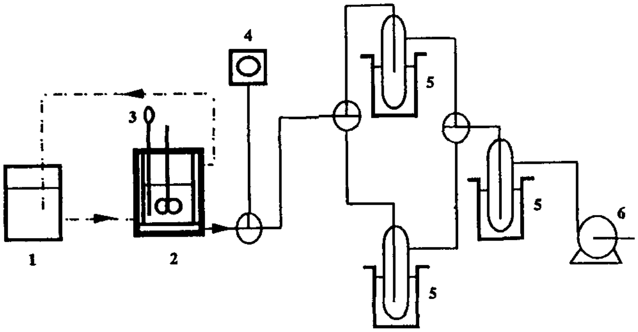

FIG. 1 Schematic diagram of experimental apparatus: (1) thermostated bath, (2) pervaporation cell, (3) thermometer, (4) pressure meter, (5) cold traps, (6) vacuum pump.

area in the cell was 22.8 cm^2. The feed solutions were mixtures of ETBE and EtOH that ranged in EtOH content from 3.1 to 30 wt%. The feed was stirred in the cell at the speed of 1000 rpm. The pressure at the downstream was evacuated to less than 0.75 mmHg 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 chromatographer.

The pervaporation properties were characterized by the total, EtOH, and ETBE fluxes (J_{total}, J_{EtOH}, and 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 was defined by

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

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

RESULTS AND DISCUSSION

Influence of Temperature and EtOH wt% in the Feed on the Membrane Sorption

The permeation of molecules through a nonporous polymer membrane is generally described by a solution–diffusion mechanism that occurs in the following three steps: sorption, diffusion, evaporation (15–19). 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 (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 affect the interactions of the other penetrant with the polymer (20). Therefore, the membrane sorption properties may play an important role in the pervaporation process.

The swelling ratios of the CAP membrane at different experimental conditions were compared. The results of swelling ratio vs EtOH wt% in the feed at different temperatures are plotted in Figs. 2 and 3. From the two figures it can be seen that the swelling ratios of the membrane increase with increasing temperature. This is because the distance between the molecules is larger than at low temperature, and the interactions of the molecules of the membrane weaken when the temperature is raised. As the EtOH wt% in the feed increases, the swelling ratios also increase until they reach the maximum values and then decrease. The reason is likely the strong interactions of EtOH molecules with the polymer and the ETBE molecules. When the EtOH wt% in the feed increases further, the interactions between molecules of EtOH are enhanced and cause the swelling ratios to decrease. In the swelling experiments the membrane loses some weight at high temperature and high EtOH wt% (>40 wt%) in the feed due to the dissolution of CAP in EtOH at high temperature.

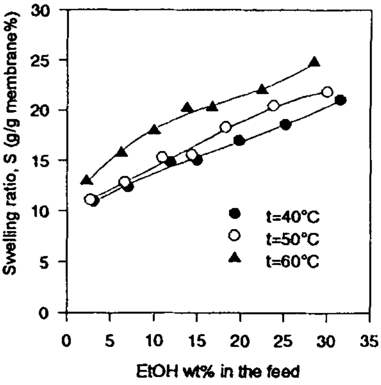

FIG. 2 Influence of temperature and EtOH wt% on swelling ratios.

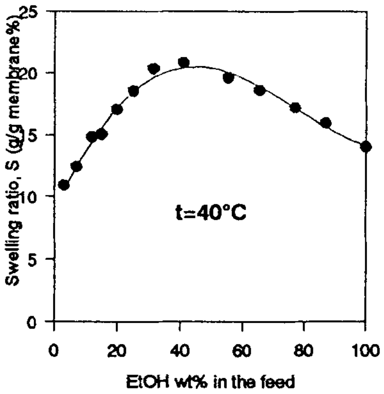

FIG. 3 Influence of EtOH wt% on swelling ratios.

The composition of the sorption solution at different temperatures and feed mixtures was analyzed. The results, illustrated in Figs. 4 and 5, show that the EtOH wt% in the sorption solution decreases as the EtOH wt% in the feed increases. When the feed contains 15–20% EtOH, minimum values of the EtOH concentration in the sorption solution are obtained. These are in the vicinity of 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

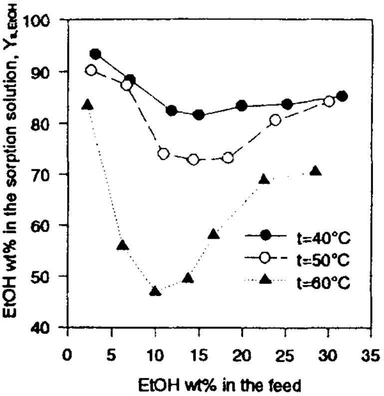

FIG. 4 Influence of temperature and EtOH wt% on EtOH wt% in sorption solution.

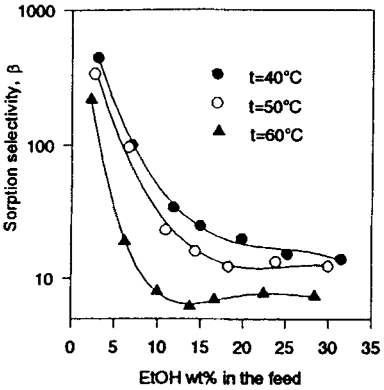

FIG. 5 Influence of temperature and EtOH wt% on sorption selectivity, β.

with the increase of the EtOH wt% in the feed until it is nearly constant. The curves also show that 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 follows: The selectivity sorption of the membrane is not only decided by the interactions of the membrane with the molecules in the mixture, but also by the mutual interactions of the molecules in 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 also 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 sorption selectivity decreases. The mechanism is not clear and will require further study.

Pervaporation Characteristics of CAP Membrane

Influence of Temperature and EtOH wt% in the Feed on Mass Fluxes

A systematic study of the pervaporation characteristics of the membrane was carried out. The influences of the EtOH wt% in the feed and the experimental temperature were studied. Figures 6 and 7 represent the

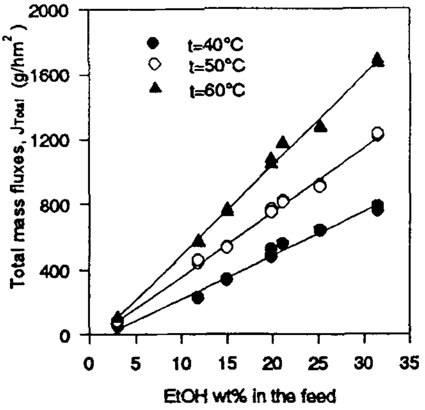

FIG. 6 Influence of EtOH wt% (X_{EtOH}) and temperature on total flux (J_{total}).

influence of EtOH wt% in the feed and the experimental temperature on the total and EtOH fluxes.

Figures 6 and 7 show that the total and the EtOH fluxes increase quickly with increases of the experimental temperature and the EtOH wt% in the feed. This is because the molecules of the mixtures move more quickly as the temperature is increased, and the diffusion coefficients of EtOH and ETBE in the membrane increase. When the EtOH wt% in the feed

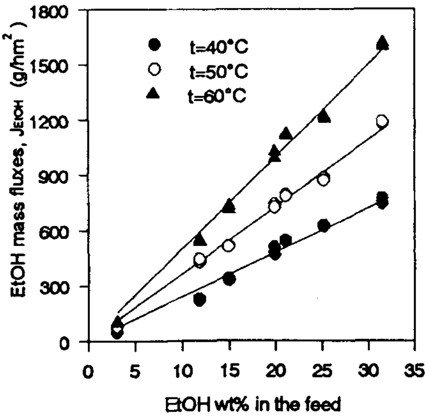

FIG. 7 Influence of EtOH wt% (X_{EtOH}) and temperature on EtOH flux (J_{EtOH}).

increases, the swelling of the membrane increases, and this causes the fluxes to increase. However, due to the strong interaction of CAP with EtOH, the EtOH flux is much higher than that of ETBE.

From the curves in Fig. 7 it can be seen that all these lines pass through the original point. Therefore, the relationship of EtOH flux with the temperature and EtOH wt% in the feed can be represented by the Arrheniuns equation. The equation is

$$J_{\mathrm{EtOH}} = K_1 X_{\mathrm{EtOH}} e^{-E/R(1/T - 1/T_0)} \tag{4}$$

where J_{EtOH} stands for the EtOH flux (g/m^2·h), K_1 is an equation constant (g/m^2·h), and X_{EtOH} represents EtOH wt% in the feed. E is the activation energy in units of J/mol, which depends strongly on the nature of the membrane and of the mixture. T is the absolute temperature in K, and $T_0 = 273$ K. R is the gas constant (J/mol·K). At a certain temperature, the Eq. (4) can be written

$$J_{\mathrm{EtOH}} = K_{\mathrm{T}} X_{\mathrm{EtOH}} \tag{5}$$

where $K_T = K_1 e^{-E/R(1/T - 1/T_0)}$. K_{T} at different temperatures can be obtained from Fig. 7. The diagram of $\ln(K_{\mathrm{T}})$ vs $(1/T - 1/T_0)$ is shown as Fig. 8, and Fig. 9 is the diagram of $\ln(J_{\mathrm{EtOH}})$ vs $(1/T - 1/T_0)$ at different EtOH wt% values in the feed. K_1 and E were evaluated from the experimental data: $K_1 = 1.83$ and $E = 1.39 \times 10^4$ J/mol.

Therefore, the relationship of EtOH flux with temperature and EtOH wt% in the feed can be written

$$J_{\mathrm{EtOH}} = 1.83 X_{\mathrm{EtOH}} e^{-1.39 \times 10^4/R(1/T - 1/T_0)} \tag{6}$$

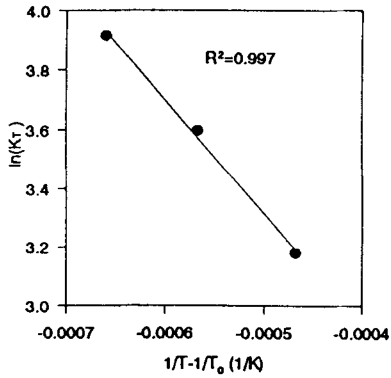

FIG. 8 Diagram of $\ln(K_{\mathrm{T}})$ vs $[(1/T) - (1/T_0)]$.

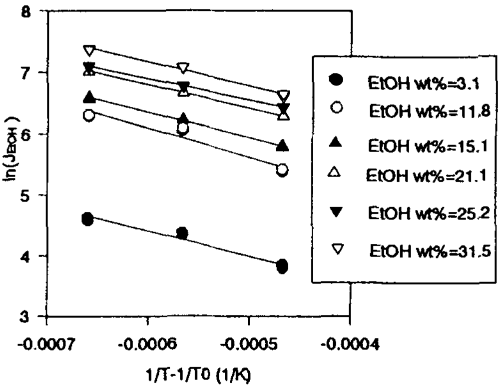

FIG. 9 Diagram of $\ln(J_{\mathrm{EtOH}})$ vs $[(1/T) - (1/T_0)]$.

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

For comparison of the selectivity of the membrane at different experimental conditions, the separation factor (α) and the EtOH wt% in the permeate (Y_{EtOH}) were chosen as compared constants. Figures 10 and 11 show the function of α and Y_{EtOH} versus the temperature and EtOH wt% in the feed.

When the EtOH concentration in the feed is low, EtOH wt% in the permeate and the separation factor decrease quickly with increasing tem-

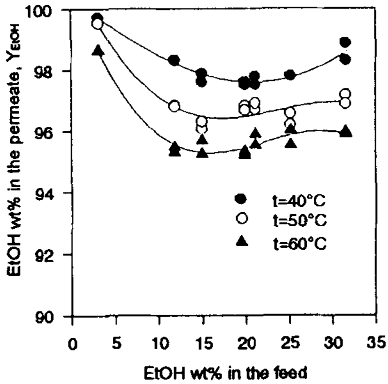

FIG. 10 The function of Y_{EtOH} as temperature ana EtOH wt%.

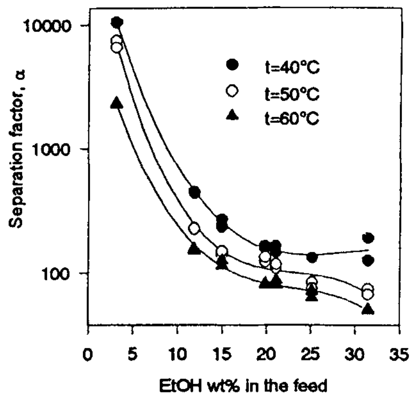

FIG. 11 Influence of the temperature and EtOH wt% on separation factor, α.

perature, but when EtOH wt% in the feed increases, the influence of temperature on the selectivity is not as large as that at a low concentration of EtOH in the feed. When the experimental temperature is constant, the EtOH wt% in the permeate first decreases, reaches a minimum point, and then increases. The separation factor, α, decreases when the concentration of EtOH in the feed increases. In the vicinity of the azeotropic composition of the mixture, Y_{EtOH} is at its lowest value. The main reason is that the swelling ratios of the membrane change with temperature. Therefore, the ability of the membrane to prevent movement of the ETBE molecule is weakened. At the azeotropic composition, although the interaction of the membrane with EtOH molecules is very strong, the interaction of ETBE molecules with EtOH molecules is also very strong, but the selectivity of the membrane is enough to pass the azeotropic point for the separation of ETBE/EtOH mixtures.

Comparison of the Results of Pervaporation and Sorption

In order to investigate the potential of the membrane for the separation of EtOH/ETBE mixtures, the results of sorption and pervaporation at 40°C were compared with the vapor–liquid equilibrium calculated by ASPEN PLUS RELEASE 9.2 with the UNIFAC method. As shown in Fig. 12, the pervaporation curve, the vapor–liquid equilibrium curve, and the polymer–liquid mixture equilibrium curve show the same tendency with a change of the EtOH wt% in the feed. The EtOH selectivity of pervaporation is considerably higher than that of distillation, indicating the membrane permeates EtOH preferential. It also shows the CAP membrane

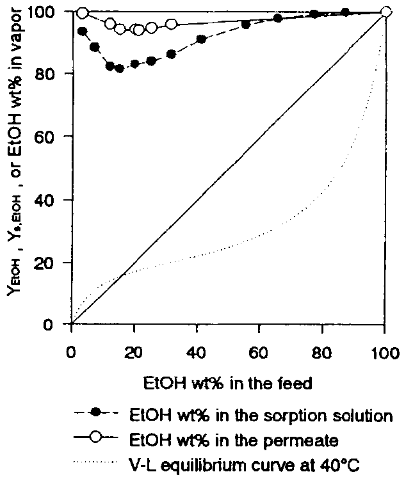

FIG. 12 Comparison of results of sorption and pervaporation with vapor–liquid (V–L) equilibrium at 40°C.

absorbs EtOH molecules preferentially based on data of the sorption experiments, although the value of the sorption selectivity is smaller than that of pervaporation selectivity. From the above discussion we conclude that pervaporation selectivity is determined by the sorption and diffusion steps, and that the diffusion coefficient of EtOH is much bigger than that of ETBE. We will study this project further to determine the diffusion coefficients of the two components in the CAP membrane.

Table 1 is the summary of the performance of various membranes for the separation of the EtOH/ETBE mixture. From this table it can be seen

TABLE 1
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 ($g/m^2 \cdot h$)	Temperature (°C)	Reference
Cellulose acetate	20	100	90	40	14
Cellulose acetate butyrate	20	79.70	2980	40	14
Cellulose triacetate	20	100	70	40	14
Polyurethaneimide	20	<50	<650	30	15
CAP	20	98.0	560	40	This work
CAP	3–30	95.3–99.7	50–1700	40–60	This work

that higher selectivity and mass fluxes can be allowed with the CAP membrane. The CAP membrane is stable for the separation of this mixture, and this property may decide if the membrane can be used commercially.

CONCLUSION

A new kind of CAP membrane was prepared. The properties of this membrane were evaluated by the pervaporation separation of ethyl *tert*-butyl ether and ethanol mixture. The experimental results showed that the selectivity and the fluxes of this membrane are high, and depend on the mass fraction of feed and the experimental temperature. With increases in both the ethanol concentration in the feed and the experimental temperature, the total mass and ethanol fluxes increase. The ethanol mass flux obeys the Arrhenius equation with respect to the experimental temperature.

The mechanism by which the experimental conditions affect the characteristics of the membrane is very complicated. Selectivity decreases when the temperature is raised. With a change of ethanol concentration in the feed, the EtOH wt% in the permeate is at the minimum value in the vicinity of the azeotropic composition. Curves of ethanol concentration in the sorption solution versus ethanol content in the feed at different temperatures show the same tendency. This fact may be explained as follows: The characteristics of the membrane are not only decided by interactions between the polymer and the molecules in the mixture, but also by interactions of the molecules in the mixture. Therefore, in the vicinity of the azeotropic point, the selectivity of the membrane and the EtOH wt% in the sorption solution are at their lowest.

ACKNOWLEDGMENT

G.S.L. thanks the Liaison Committee of Restores' Conferences of Europe for its financial support of him as a postdoctoral researcher.

REFERENCES

1. M. S. Reish, "Top 50 Chemicals Production Rose Modestly Last Year," *Chem. Eng. News*, *72*, 12 (1994).
2. G. Pecci and T. Floris, "Ethers Ups Antiknocks of Gasoline," *Hydrocarbon Process.*, *56*, 98 (1977).
3. I.F.P., *Etherfication Technology, the MTBE, ETBE and TAME Processes*, Venice Symposium, 1989.
4. A. Chauvel, G. Lefebvre, and L. Castex, *Procédés de Prétrochimie*, *Tome 1* (1985).
5. D. R. Seok, S. G. Kang, and S.-T. Huang, "Use of Pervaporation for Separation of Azeotropic Mixtures Using Two Different Hollow Fiber Membranes," *J. Membr. Sci.*, *33*, 71 (1987).

6. I. Blume, J. G. Wijmers, and R. W. Baker, "The Separation of Dissolved Organic from Water by Pervaporation," *Ibid.*, *49*, 253 (1990).
7. W. J. Chen and C. R. Martin, "Highly Methanol-Selective Membranes for the Pervaporation Separation of Methyl *t*-Butyl Ether/Methanol Mixtures," *Ibid.*, *104*, 101 (1995).
8. H. C. Park, N. E. Ramaker, and M. H. V. Mulder, "Separation of MTBE–Methanol Mixtures by Pervaporation," *Sep. Sci. Technol.*, *30*, 419 (1995).
9. V. M. Shah, C. R. Bartels, M. Pasternak, and J. Reale, "Opportunities for Membranes in the Production of Octane Enhancers," *AIChE Symp. Ser.*, *85*, 93 (1989).
10. M. S. Chen, R. M. Eng, J. L. Glazer, and C. G. Wensley, "Pervaporation Process for Separating Alcohols from Ethers," US Patent 4,774,365 (1988).
11. M. S. K. Chen, G. S. Markiewicz, and K. G. Venugopal, "Development of Membrane Pervaporation TRIM Process for Methanol Recovery from $CH_3OH/MTBE/C_4$ Mixtures," *AIChE Symp. Ser.*, *85*, 82 (1989).
12. T. Sano, M. Hasegawa, Y. Kawakami, and H. Yanagishita, "Separation of Methanol/Methyl-*tert*-butyl Ether Mixture by Pervaporation," *J. Membr. Sci.*, *107*, 193 (1995).
13. I. Noezar, Q. T. Nguyen, R. Clement, J. Neel, and H. Bruschke, "Cellulose Ester-Based Polymer Blend Membranes for Ethanol–ETBE Separation," in *Proceedings of Euromembrane '95*, University of Bath, UK, 1995, p. 1-368.
14. A. Jonquieres, R. Clement, D. Roizard, and P. Lochon, "Pervaporative Transport Modelling in a Ternary System: Ethyltertiarybutylether/Ethanol/Polyurethaneimide," *J. Membr. Sci.*, *109*, 65 (1995).
15. J. Neel, "Introduction to Pervaporation," in *Pervaporation Membrane Separation Process* (R. Y. M. Huang, Ed.), Elsevier, Amsterdam, 1991, Chap. 1.
16. Y. M. Lee, D. Bourgeois, and G. Belfort, "Sorption, Diffusion, and Pervaporation of Organics in Polymers Membranes," *J. Membr. Sci.*, *44*, 161 (1989).
17. W. J. Rhim and R. Y. M. Huang, "On the Prediction of Separation Factor and Permeability in the Separation of Binary Mixtures by Pervaporation," *Ibid.*, *46*, 335 (1989).
18. C. K. Yeom and R. Y. M. Huang, "Modelling of the Pervaporation Separation of Ethanol–Water Mixtures through Crosslinked Poly(Vinyl Alcohol) Membrane," *Ibid.*, *67*, 39 (1992).
19. J. G. Wijmans and R. W. Baker, "A Simple Predictive Treatment of the Permeation Process in Pervaporation," *Ibid.*, *79*, 101 (1993).
20. C. Bartels-Caspers, E. Tusel-Langer, and R. N. Lichterthaler, "Sorption Isotherms of Alcohols in Zeolite-Filled Silicone Rubber and in PVA-Composite Membranes," *Ibid.*, *70*, 75 (1992).

Received by editor March 29, 1996
Revision received June 20, 1996