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

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H. C. Park[a]; N. E. Ramaker[a]; M. H. V. Mulder[a]; C. A. Smolders[a]
[a] FACULTY OF CHEMICAL TECHNOLOGY, UNIVERSITY OF TWENTE, ENSCHEDE, THE NETHERLANDS

To cite this Article Park, H. C. , Ramaker, N. E. , Mulder, M. H. V. and Smolders, C. A.(1995) 'Separation of MTBE-Methanol Mixtures by Pervaporation', Separation Science and Technology, 30: 3, 419 — 433
To link to this Article: DOI: 10.1080/01496399508013880
URL: http://dx.doi.org/10.1080/01496399508013880

SEPARATION SCIENCE AND TECHNOLOGY, **30**(3), pp. 419–433, 1995

Separation of MTBE–Methanol Mixtures by Pervaporation

H. C. PARK, N. E. RAMAKER, M. H. V. MULDER,*
and C. A. SMOLDERS
FACULTY OF CHEMICAL TECHNOLOGY
UNIVERSITY OF TWENTE
P.O. BOX 217, 7500 AE ENSCHEDE, THE NETHERLANDS

ABSTRACT

Membranes made of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from methyl *tert*-butyl ether (MTBE) by pervaporation. The influence of the blend composition and the feed composition on the pervaporation performance were investigated. Methanol permeates preferentially through all tested blend membranes, and the selectivity increases with increasing poly(vinyl alcohol) content in the blends. However, a flux decrease is observed with increasing poly(vinyl alcohol) content. With increasing feed temperature the flux increases, and the selectivity remains constant. In addition, the influence of crosslinking on the permselectivity was investigated. The pervaporation flux decreases with increasing crosslinking density, but the selectivity is enhanced. This is due to a more rapid decrease in the component flux of MTBE compared to that of methanol.

INTRODUCTION

The problem of environmental pollution led to the reduction of the amount of lead permitted in gasoline, which created a problem of lowering gasoline octane ratings. To maintain the existing quality specifications, octane boosters such as benzene/toluene/xylene mixtures and oxygenates have been added to lead-free or low-leaded gasolines. Methyl *tert*-butyl ether (MTBE) has been extensively tested and proven to be an octane

* To whom correspondence should be addressed.

enhancer. In recent years MTBE has also been used as an oxygenated fuel additive needed to reformulate gasoline which can meet the requirements of the Clean Air Act amendments of the United States government. For these reasons the demand for MTBE is increasing rapidly. It has been the fastest growing chemical of the 1980s, and it likely will continue this growth throughout the 1990s (1, 2).

MTBE is produced by the reaction of methanol with isobutylene in the liquid phase over a strongly-acidic ion-exchange resin catalyst. The reaction is rapid and selective, but is limited by equilibrium conditions. Therefore, it is desired to improve the conversion by using an excess of methanol. Excess concentrations of methanol up to about 20% of the stoichiometric amount are generally used to achieve high conversions. The use of excess methanol, however, causes a purification problem because methanol forms minimum-boiling azeotropes with MTBE at a composition of 14.3 wt% methanol at 760 mmHg. Presently the reactor effluent is first separated by a debutanizer column into a bottom MTBE product and a near-azeotropic mixture of methanol with MTBE at the overhead of the column. Subsequently methanol is washed out by water, and the water/methanol mixture is then distilled to recover methanol for recycle (3, 4). This conventional separation process is both capital and energy intensive.

Pervaporation has been considered as an alternative separation technique. It may not be practical to separate completely the entire reactor effluents by pervaporation, but a hybrid distillation–pervaporation process may be very attractive. In this case, pervaporation is used only in a limited area of separation such as for breaking the azeotrope. The possibility of a hybrid distillation–pervaporation process can be demonstrated by the Total Recovery Improvement for MTBE (TRIM) process which has been developed by Air Products & Chemicals using cellulose acetate membranes. This process has been developed for both retrofitting an existing MTBE production plant and replacing the water-washing column in a new plant. Laboratory and field-site tests of this process have shown significant energy and cost savings, proving that pervaporation is an option to separate methanol from MTBE and light hydrocarbons (5, 6).

Farnand and Noh have tested a series of polymers as pervaporation membranes. From the material screening experiments, it was observed that Nafion and a cellulose-based material MT showed similar and the best performance among the polymers tested (7). In addition, poly(vinyl alcohol) and Nafion have been tested by another research group and also showed promising result (8, 9).

In order to promote industrial acceptance of the pervaporation process, research efforts are aimed to develop membranes with better perfor-

mance. In this study, membranes of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) are evaluated for the separation of methanol from MTBE by pervaporation. The influence of blend composition and of crosslinking on the permselectivity have been investigated. In addition, the effect of the feed composition and temperature has also been studied.

EXPERIMENTAL

Materials

Poly(acrylic acid) (M_w = 250,000 g/mol) and poly(vinyl alcohol) 96% hydrolyzed (M_w = 85,000–146,000 g/mol) and 88% hydrolyzed (M_w = 80,000–100,000 g/mol) were purchased from Aldrich Chemical Co. Methyl *tert*-butyl ether, methyl alcohol, and ethyl alcohol (analytical grade) were obtained from Merck Co. They were used without further purification. Water was demineralized before use.

Membrane Preparation

Polymer blending was performed by a solution method. Poly(acrylic acid) and poly(vinyl alcohol) were separately dissolved in water. Two solutions were mixed in various proportions to obtain the proper casting solutions. Homogeneous membranes were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation in a flowing nitrogen atmosphere at room temperature. The thickness of the resulting membranes was around 20 μm.

Membrane crosslinking was performed by heat treatment. Membrane samples were first dried for 1 day at 70°C and then treated at 120°C for various time intervals in a forced nitrogen convection oven.

Pervaporation Experiments

The pervaporation experiments were performed using the same laboratory test apparatus as previously described (20). Dry membranes were installed in the pervaporation cells. The effective membrane area in each cell was 50 cm^2. The feed was circulated through the pervaporation cells from a feed reservoir. The feed temperature was kept at 35°C except for the measurements when the temperature was varied. The pressure at the downstream side was kept below 2 mmHg by a vacuum pump. The permeate was collected in cold traps cooled by liquid nitrogen. The composition of the collected permeate was determined by a gas chromatograph equipped with a thermal conductivity detector.

Pervaporation flux was determined by measuring the weight of liquid

collected during a certain time in the cold trap at the steady state. The fluxes of different membranes were normalized to a membrane thickness of 20 μm, assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_P is defined by

$$\alpha_P = (y_1/y_2)/(x_1/x_2) \quad (1)$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Indices 1 and 2 refer to the more permeable component, methanol in this study, and the less permeable one, methyl *tert*-butyl ether, respectively.

RESULTS AND DISCUSSION

Pervaporation through PAA–PVA Blend Membranes

Membranes made of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from methyl *tert*-butyl ether (MTBE). In previous studies (10) these membranes showed good permselectivities for a similar separation problem, i.e., the separation of methanol and ethanol from mixtures with toluene. Therefore it was expected that these blend membranes would also be good candidates for the separation of methanol from MTBE. Two types of poly(vinyl alcohol) with degrees of hydrolysis of 88 and 96% were used to prepare the polymer blends with poly(acrylic acid). In both cases the PVA content in the blends ranged from 10 to 30 wt%. The pervaporation results are given in Figs. 1 and 2 as a function of the PVA content in the blend. For the feed mixtures containing 5 to 20 wt% methanol, the blend membranes of both types of PVA (88 and 96% hydrolyzed) showed good separation properties without many differences. As the PVA content increased, the selectivity increased but the flux decreased. The decreasing flux with increasing PVA content is caused by a lower swelling of the blend membranes at a certain feed liquid composition similar to what was observed in the case of methanol–toluene and ethanol–toluene liquid mixtures (20).

Figure 3 shows the influence of the feed mixture composition on the permselectivity of blend membranes containing 10 and 20 wt% PVA of various degrees of hydrolysis. In this figure the flux and selectivity values are presented as a function of the methanol concentration in the feed. As the methanol concentration increases from 5 to 20 wt%, the selectivity decreases slightly but the flux increases drastically. For example, the blend membrane containing 10% of 96% hydrolyzed PVA showed a selectivity decrease from 170 to 45, but the flux increase from 30 to 610 g/m^2·h with an increase in the methanol concentration from 5 to 20 wt%. This increasing flux can be explained in terms of the plasticizing effect exhibited

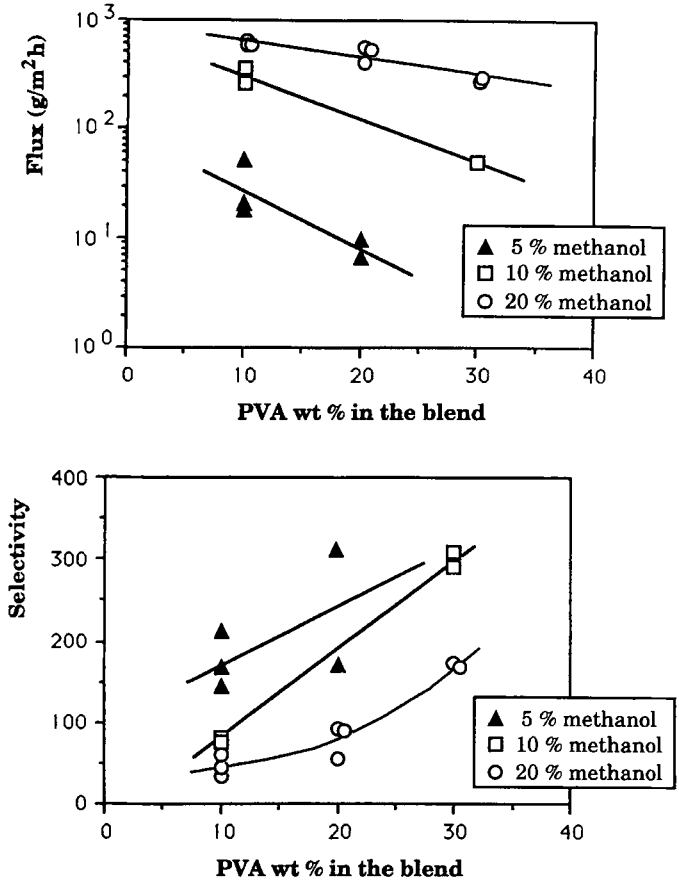

FIG. 1 Pervaporation characteristics of blend membranes of PAA with 96% hydrolyzed PVA for MTBE–methanol liquid mixtures as a function of the blend composition.

by the permeating molecules. As the methanol concentration in the feed increases, the blend membranes become more swollen due to a strong interaction with methanol. As a result, the polymer chains become more flexible, and the resistance for the diffusive transport of penetrants through the membrane becomes less.

Influence of the Feed Temperature

The temperature dependence of pervaporation has been investigated over a temperature range of 23 to 50°C with a PAA–PVA blend membrane

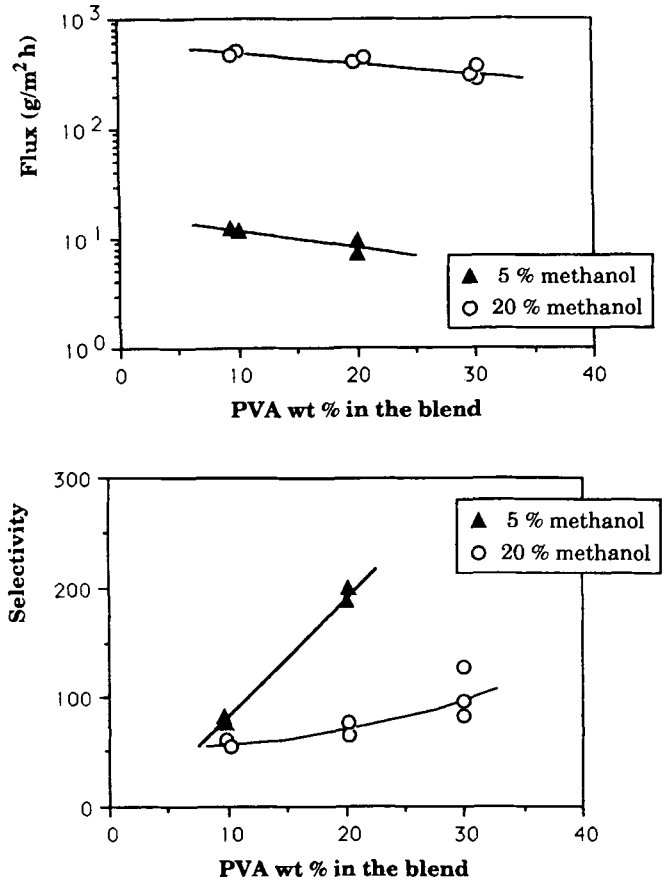

FIG. 2 Pervaporation characteristics of blend membranes of PAA with 88% hydrolyzed PVA for MTBE–methanol liquid mixtures as a function of the blend composition.

containing 20 wt% of 88% hydrolyzed PVA. In Fig. 4 the pervaporation flux and selectivity are given as a function of the feed temperature at a feed concentration of 20 wt% methanol. As can be seen from the figure, the flux increases gradually with the feed temperature. This can be explained by the enhanced diffusivity with temperature. In pervaporation the dependence of diffusivity on temperature is generally described by an Arrhenius-type exponential relation with the apparent activation energy for diffusion (11, 12). According to this relation, diffusivity will increase with temperature when the activation energy has a positive value, which

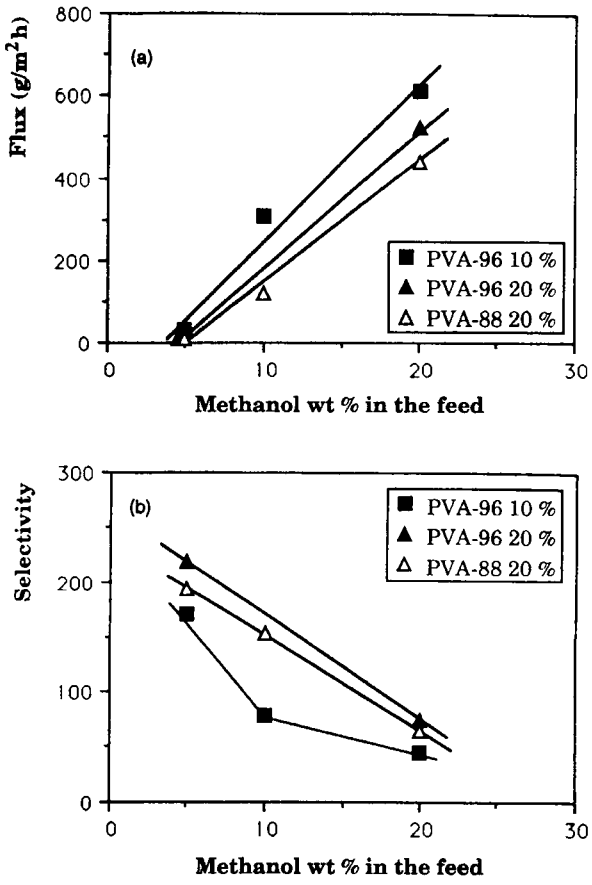

FIG. 3 Influence of the feed composition on the pervaporation flux (a) and selectivity (b) of MTBE–methanol liquid mixtures through various PAA–PVA blend membranes.

is mostly observed in the pervaporation of liquid mixtures (13–16). Besides the enhanced diffusivity, the driving force for mass transport also increases with temperature. The driving force is given by the difference in partial vapor pressure of the permeants between the feed and the permeate side. As the feed temperature increases, the vapor pressure at the feed side increases, while the vapor pressure at the permeate side is not affected. Hence, the driving force increases with temperature. Contrary to the flux, the selectivity was hardly affected by a feed temperature ranging from 23 to 50°C. This indicates that the component fluxes of both

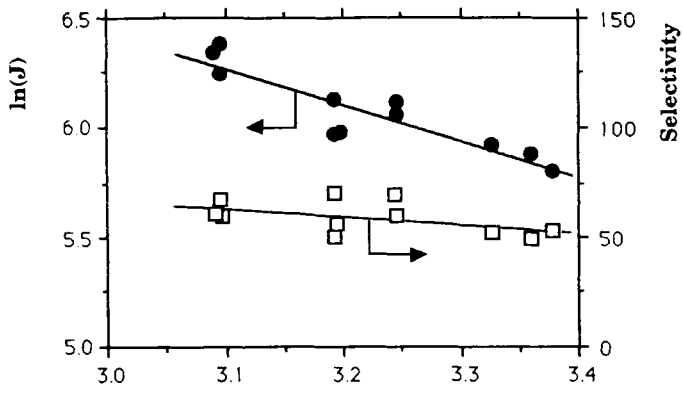

FIG. 4 Influence of the feed temperature on flux J (g/m^2·h) and selectivity of a PAA–PVA blend membrane for a MTBE–methanol liquid mixture containing 20 wt% methanol.

methanol and MTBE were influenced to the same extent by the temperature, which can be seen in Fig. 5. In this figure the total flux and the component fluxes of methanol and MTBE are presented as a function of the feed temperature. One can see that the slopes of the flux curves are almost equal. In this case the optimal pervaporation performance of the membrane can be obtained at the highest temperature possible.

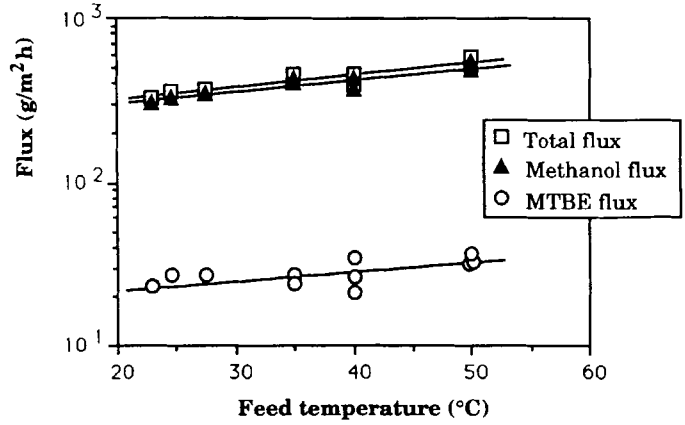

FIG. 5 Total flux and component fluxes of methanol and MTBE through a PAA–PVA blend membrane as a function of the feed temperature.

Crosslinked Membranes

There is growing interest in the improvement of the separation properties of a membrane by crosslinking. As a polymer membrane is crosslinked, the solubility of a liquid feed in the membrane is reduced, as can be deduced from the Flory–Rehner theory (17), see Eq. (2). From the Flory–Huggins thermodynamics for mixing it can be seen that the sorption selectivity increases with decreasing overall solubility (see the Appendix in Chapter 4 of Reference 17). Crosslinking also reduces the mobility of the polymer segments and thus reduces the diffusivity of penetrants through a membrane. For instance, the diffusion coefficient of nitrogen in natural rubber is reported to be reduced tenfold upon crosslinking the rubber with 11% sulfur (18). The reduced diffusivity as well as the reduced solubility might cause a decrease in pervaporation flux but an increase in selectivity.

The PAA–PVA blend membranes were crosslinked by heat treatment at 120°C. This crosslinking temperature was experimentally determined to work satisfactorily. When the blend membranes were treated for 2 hours at higher temperatures (for example, at 140°C), the crosslinked membranes showed extremely low fluxes for the methanol–MTBE mixtures at 20 wt% methanol. Therefore it was decided to perform the heat treatments at 120°C for better control of the crosslinking density.

Although the crosslinking mechanism is not identified, it probably occurs through an esterification reaction. The carboxyl functionality of PAA can react with the hydroxyl functionality of PVA, resulting in an ester linkage by the elimination of water. An esterification reaction has been used previously to crosslink PVA with diacids; this is comparable with the PAA–PVA system (19).

A blend membrane of poly(acrylic acid) and 88% hydrolyzed poly(vinyl alcohol) containing 20 wt% PVA was heat-treated over various periods of time. To determine the crosslinking density, the equilibrium solubility of pure ethanol at room temperature was measured. The sorption results are given in Table 1. As the time of the heat treatment increases, the solubility of ethanol decreases rapidly. When the membrane was treated for 16 hours, it was hardly swollen by ethanol. From this result it appears that the blend membranes can be crosslinked by heat treatment and that the crosslinking density can be controlled by adjusting the heating time.

The crosslinking density or molecular weight between two adjacent crosslinks can be calculated from the Flory–Rehner theory (18). According to this theory, the chemical potential of a solvent $\Delta\mu_i$ in a polymer is given as a function of the volume fraction of the polymer ϕ_p:

$$\Delta\mu_i/RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip}\phi_p^2 + (\rho V_i/M_c)(\phi_p^{1/3} - \phi_p/2) \quad (2)$$

TABLE 1
The Solubility of Ethanol in Crosslinked PAA–PVA Blend Membranes (PVA content: 20 wt%)[a] at Room Temperature and the Molecular Weight between Two Adjacent Crosslinks (M_c) Calculated from Eq. (2)

Crosslinking time (h) at 120°C (g/g)	Ethanol solubility fraction	Polymer volume parameter	Binary interaction (g/mol)	M_c
0	2.43	0.1875	0.5728	—
2	1.78	0.2395	—	29,000
5	0.26	0.6832	—	220
7	0.10	0.8486	—	70
16	0	1	—	—

[a] Density of the blend = 1.40 g/cm^3.

where ρ and M_c are the density of dry polymer and the molecular weight between two adjacent crosslinks, respectively. V_i is the molar volume of the solvent. The last term on the right-hand side of Eq. (2) represents the contribution of the elastic effect. At swelling equilibrium, $\Delta\mu_i/RT = 0$. The volume fraction of the polymer ϕ_p can be determined from an equilibrium sorption experiment. Therefore, when the M_c value is known, the binary interaction parameter χ_{ip} can be calculated from Eq. (2), or vice versa.

In the case of sorption into the uncrosslinked blend membrane, the elastic term can be neglected compared to the first three terms. In such a situation the binary interaction parameter χ_{ip} can be calculated from Eq. (2) by using the experimental volume fraction of the membrane ϕ_p. A value of 0.5728 was calculated for the interaction parameter between ethanol and the uncrosslinked PAA–PVA blend membrane. For the calculation of M_c, the molecular weight between two adjacent crosslinks, it was assumed that the interaction parameter between ethanol and the blend membranes did not vary with crosslinking. This means that the interaction parameter calculated for the uncrosslinked membrane is equally valid for the crosslinked membranes. The calculated M_c values under this assumption are given in Table 1. As the crosslinking time increases, the ethanol solubility decreases drastically, which is also expressed by a smaller M_c value indicating a higher crosslinking density. However, the numerical values of M_c are unrealistically low, which may be due to the assumption of a constant interaction parameter. Nevertheless, this result clearly confirms that the PAA–PVA membrane can be crosslinked by heat treatment and that the crosslinking density can be controlled by adjusting the heating time.

The influence of crosslinking on the pervaporation flux and selectivity was investigated using the blend membrane of 88% hydrolyzed PVA (20 wt% in the blend). The results are presented in Fig. 6 for a methanol–MTBE mixture containing 20 wt% methanol. This figure shows that the flux decreases but the selectivity increases with increasing crosslinking time. This can be explained by the reduced solubility and diffusivity, as discussed before.

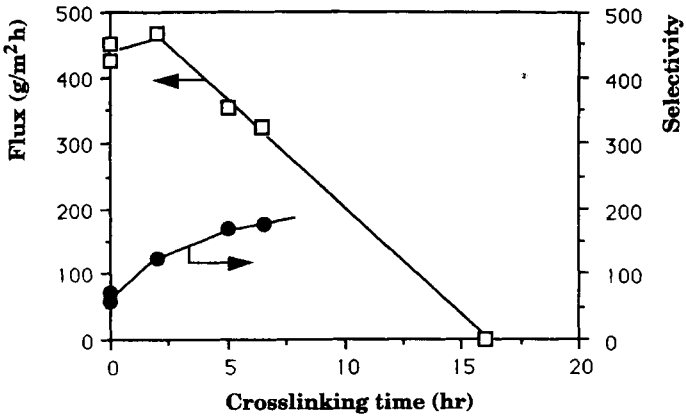

FIG. 6 Influence of membrane crosslinking on pervaporation flux and selectivity of a PAA–PVA blend membrane (20% PVA) for a methanol–MTBE liquid mixture containing 20 wt% methanol as a function of the crosslinking time.

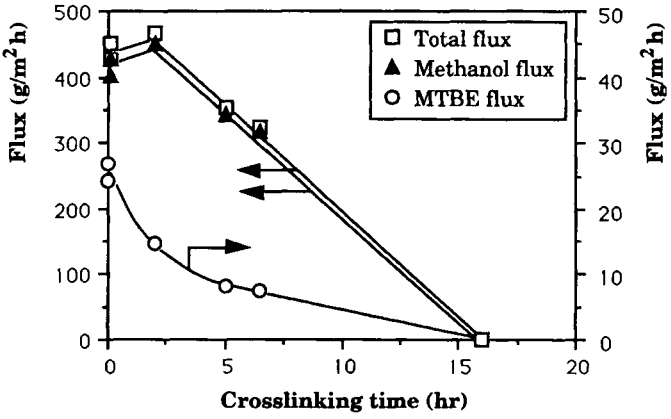

FIG. 7 Total flux and component fluxes of methanol and MTBE through crosslinked PAA–PVA blend membranes as a function of the crosslinking time.

The improvement of the separation factor is caused by a more rapid decrease of the MTBE flux compared to methanol (Fig. 7). In the crosslinking time interval of 0 to 7 hours the methanol component flux shows a rather linear decrease, but the decrease of MTBE component flux shows a more concave curve. This can be due to the different molecular sizes of the permeants. The molar volumes of methanol and MTBE are 40.73 and 119.04 cm^3/mol, respectively, at 25°C. Therefore, with even the same reduction in polymer chain flexibility, the larger molecule of MTBE should experience a larger frictional force in diffusion than the smaller methanol molecule.

CONCLUSIONS

Membranes of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from MTBE. For feed mixtures of 5 to 20 wt% methanol, blend membranes containing 10 to 30 wt% PVA showed both high fluxes and high selectivities. Furthermore, it was observed that the separation characteristics of the blend membrane could easily be controlled by adjusting the blend composition. As the poly(vinyl alcohol) content in the blends increased, fluxes decreased gradually but selectivities increased. In addition, a strong influence of the feed mixture composition on the separation characteristics was also observed.

The temperature of the feed liquid showed a favorable effect on the separation performance of the system studied. The flux increased with temperature, while the selectivity was hardly affected. This implies that an optimal pervaporation performance can be obtained at the highest temperature possible.

By crosslinking the membranes, the flux decreases but the selectivity increases. From a comparison of the component fluxes, it appeared that the MTBE flux was more reduced than that of methanol.

APPENDIX: EFFECT OF MEMBRANE PRECONDITIONING

The permeation property of a glassy polymer membrane can be influenced by preconditioning. Jordan et al. showed that the permeability of a polycarbonate membrane for various gases can be improved very much by preconditioning the membrane with CO_2 at high pressure (21). Preconditioning may also strongly affect the pervaporation property of a glassy polymer membrane for a liquid mixture.

A blend membrane of poly(acrylic acid) and poly(vinyl alcohol) containing 30 wt% PVA was preconditioned in methanol–MTBE mixtures with various compositions before performing a pervaporation experiment. The blend is in the glassy state, as has been proved from glass transition tem-

perature measurements. The pervaporation results of this blend for a methanol–MTBE (1/9 by weight) mixture at 35°C are given in Fig. 8 and 9. A membrane which was swollen in a liquid mixture containing 10 wt% methanol showed the same flux as a membrane which was not preconditioned. However, when membranes were swollen in liquid mixtures con-

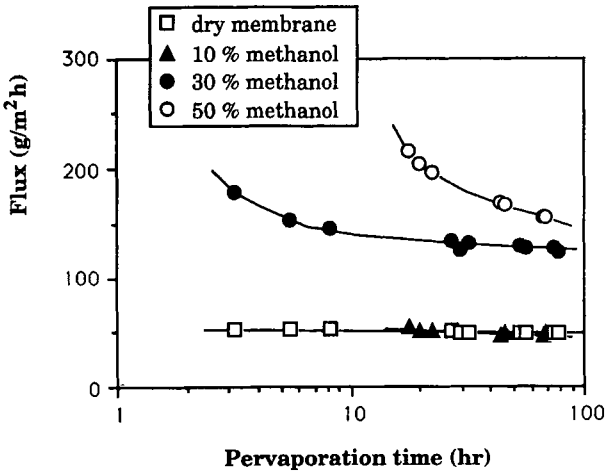

FIG. 8 Influence of membrane preconditioning on the pervaporation flux of a methanol–MTBE (1/9 by weight) mixture through a PAA–PVA blend (30% PVA) membrane as a function of the pervaporation time.

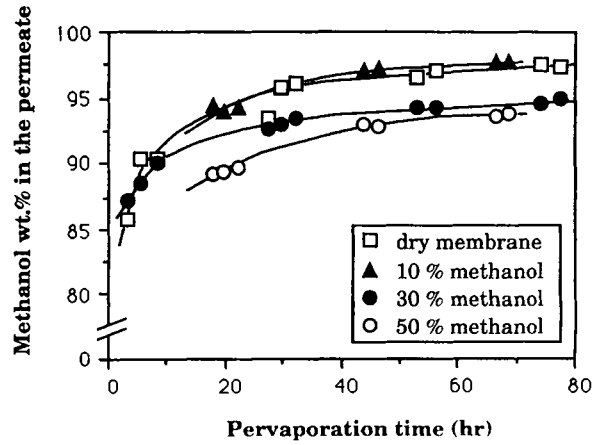

FIG. 9 Influence of membrane preconditioning on the methanol concentration in the permeate for the pervaporation of a methanol–MTBE (1/9 by weight) mixture through a PAA–PVA blend (30% PVA) membrane as a function of the pervaporation time.

taining more methanol, i.e., 30 and 50 wt%, much higher fluxes were obtained. Furthermore, the flux increases with increasing methanol content in the preconditioning liquid. The flux decreases with the pervaporation time, but more rapidly for a more swollen membrane. However, it can be seen from Fig. 1 that it will take quite a long time until the fluxes of more swollen membranes to approach that of a dry membrane.

Different preconditioning also shows a strong effect on the permeate composition. When a membrane is swollen in the feed, the methanol concentration in the permeate is almost the same as that obtained with a dry membrane. However, membranes which are swollen in liquid mixtures containing 30 and 50 wt% methanol show a lower methanol concentration in the permeate.

The preconditioning effect seems to be related to subtle morphological alterations in a glassy polymer matrix. For more detailed information, the reader is referred to the literature (22).

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Economical Affairs in The Netherlands and by DSM.

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Received by editor May 16, 1994