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

Development of a Mixed-Matrix Membrane for Pervaporation

Emin Okumus[a]; Turker Gurkan[a]; Levent Yilmaz[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, MIDDLE EAST TECHNICAL UNIVERSITY, ANKARA, TURKEY

To cite this Article Okumus, Emin , Gurkan, Turker and Yilmaz, Levent(1994) 'Development of a Mixed-Matrix Membrane for Pervaporation', Separation Science and Technology, 29: 18, 2451 — 2473
To link to this Article: DOI: 10.1080/01496399408002203
URL: http://dx.doi.org/10.1080/01496399408002203

SEPARATION SCIENCE AND TECHNOLOGY, **29**(18), pp. 2451–2473, 1994

Development of a Mixed-Matrix Membrane for Pervaporation

EMIN OKUMUS, TURKER GURKAN, and LEVENT YILMAZ*
DEPARTMENT OF CHEMICAL ENGINEERING
MIDDLE EAST TECHNICAL UNIVERSITY
06531 ANKARA, TURKEY

ABSTRACT

In the production of pure alcohol, pervaporation is developing into an important technology. In this study, in order to improve the performance of the pervaporation process, a mixed-matrix polymer-zeolite membrane is developed. In the preparation of these membranes, cellulose acetate as base polymer, acetone or DMF as solvent, and 13X or 4A zeolites as fillers were used. To test the performance of homogeneous and mixed-matrix membranes, a laboratory-scale pervaporation setup was constructed. The effect of the following experimental parameters on the selectivity and flux were experimentally studied to determine the optimum values of operating conditions and to understand the separation mechanism in the indicated ranges: feed concentration, 70–90 wt%; feed temperature, 30–70°C; feed flow rate, 32–76 L/h. It was observed that the addition of zeolite to the membrane matrix improves the flux value twofold with respect to its homogeneous membranes with some loss in their selectivity. For example, for a feed concentration of 74 wt% EtOH at 50°C and 1 mmHg, the flux value for the unfilled membrane is 0.6 L/m^2·h, and for a 30% zeolite-filled membrane, the flux is increased to 1.33. For these cases, the selectivities are 7.76 and 5.0 for the unfilled and filled membranes, respectively. TEM micrographs of the mixed-matrix membranes show a homogeneous distribution of zeolite particles which produce a cave-like porous structure in the matrix. The combined effect of this modified morphology and zeolite selectivity is the possible reason for the observed pervaporation performances of mixed-matrix membranes.

Key Words. Pervaporation; Separation of ethanol–water mixture; Mixed-matrix membrane; Cellulose acetate membrane

---

* To whom correspondence should be addressed.

INTRODUCTION

There is considerable revived interest in the production of fuel-grade ethanol and other chemicals by fermentation because of the increasing price of oil and petrochemicals. The separation and purification steps are very energy-intensive for the production of pure ethanol. In many cases, conventional separation techniques such as distillation, adsorption, liquid–liquid extraction, etc. are often insufficient and uneconomical. Therefore, the application of membrane separation processes is rapidly growing for the separation of azeotropic and close-boiling mixtures and in the field of biotechnology (1–13).

Pervaporation is a membrane separation process in which a liquid mixture is in direct contact with one side of a selective nonporous polymeric membrane and the permeated product is removed in the vapor state from the other side. The actual driving force for the permeation of the different components through the membrane is their chemical potential gradient across the membrane (14).

Pervaporation has some advantages for its applications in biotechnology. It can be operated at any temperature required by the biosystem, and it is particularly well suited to be integrated directly with the fermentation process without any intermediate step. All the conditions for the biosystem in a pervaporation separator can be kept the same as in the fermenter (11).

In the separation of ethanol from fermentation products, to keep the energy consumption as low as possible, pervaporation should be applied with ethanol-permeable membranes for low ethanol concentrations and with water-permeable membranes for high ethanol concentrations in the feed (1). Energy consumption of classical separation processes dramatically increases as the azeotropic composition is approached, especially for concentrated ethanol mixtures. As an alternative separation means, hydrophilic membranes were studied for high ethanol concentration mixtures.

Flux and selectivity are the two characteristics which determine the performance of a membrane used to separate a given binary mixture A–B by pervaporation. Pervaporation fluxes are generally expressed as total mass (or total volume) permeated per unit time per unit membrane area. One measure of selectivity is the separation factor, defined as

$$\alpha = \frac{y_A/y_B}{x_A/x_B}$$

The main aim of all membrane development studies is to improve flux and/or selectivities for the process under study. The physical morphology of polymeric membranes can be classified as homogeneous or heterogeneous. Earlier studies have concentrated on homogeneous membranes (2). Because of their dense structure, homogeneous membranes show a high resistance to mass transport which results in very low fluxes but high selectivities. Heterogeneous membranes can be of the asymmetric, composite, or mixed-matrix type. They usually give high fluxes but low selectivities (2). Therefore, the opposing tendencies of flux and selectivity require optimization.

Many attempts has been made to increase the selectivity and flux by adjusting the hydrophilic–hydrophobic balance and by controlling the specific interaction between the membrane and permeating components for the separation of a water–ethanol mixture from biomass products by pervaporation (15). However, too much hydrophilicity often leads to excessive swelling of the membrane in contact with the aqueous feed solutions. This swelling results in a loss of the mechanical and selective properties of the membrane. Several methods of membrane preparation were tried to avoid such defects and to produce high pervaporation membranes (15, 16). A tentative list of these attempts includes:

Modification of the membrane surface by introducing the hydrophilic polymer on the hydrophobic substrate (17)
Introduction of crosslinking by block or graft copolymerization (15, 18, 19)
Polymer blending (15, 16)
Addition of an adsorptive filler to the membrane (20–22)

There are many studies which developed different membranes by using one of the first three methods on the above list. Although the selectivities obtained from these studies are high, the fluxes obtained are relatively low (22). More research effort is needed on membranes filled with an adsorptive filler as this may lead to higher fluxes together with reasonable selectivities.

It has been observed that membrane performance can be altered by increasing the membrane sorption capacity through the addition of zeolite particles for the preferential permeation of EtOH from dilute alcohol solutions typical to fermenter product streams (7). Different kinds of zeolites have been incorporated into hydrophobic rubbery polymer matrices. The ethanol selectivities of membranes were enhanced by silicate addition but decreased with zeolite A and X addition for 2–10 wt% EtOH. A resistance model has been developed (7) to describe the increased pervaporation flux and selectivity for the separation of an ethanol–water mixture with mixed-matrix and homogeneous membranes. It was claimed that diffusion through the membrane is the rate-determining step, and that the sorption kinetics of feed components into the membrane contribute significantly to the overall permeability for thinner membranes.

Goldman and coworkers (20) prepared an effective novel membrane by combining zeolite NaA and PVC modified by 2,2-butoxyethoxy ethyl thiolate. They modified the polymer by grafting it with suitable hydrophilic side chains and adding zeolites to the polymers in different weight percentages (0–70 wt%). According to this study, when the amount of zeolite was below a definite limit, then the membrane behaves as a pure modified PVC membrane. When the amount of zeolite filler exceeded a certain critical point, the rate-determining step in the overall transport was passage through the zeolite/modified PVC interface.

Meng and coworkers (23) studied the separation characteristics of thin film zeolite-filled PDMS composite membranes having a silicate to PDMS ratio of 3.3 by pervaporation and gas permeation. High fluxes and high selectivities were observed in the pervaporation of a 7 wt% aqueous ethanol solution at 22°C.

Bartels-Carpers et al. (24) investigated the dynamic vapor-sorption behavior of various alcohols in zeolite-filled silicon rubber membranes and in PVA-composite membranes. Their results showed that adsorption by the zeolite contributes much more to total sorption than does adsorption by the silicon rubber.

For ethanol–water mixtures, hydrophilic or hydrophobic polymers can be selected as the membrane materials according to the composition of the mixture to be separated. In cases of high ethanol concentration, hydrophilic polymers are preferable since water is selectively removed from the mixture. Conversely in cases of low ethanol concentration, hydrophobic polymers are preferred. As explained above, most of the mixed-matrix membranes studied were of the alcohol selective hydrophobic type. Conversely in this study, cellulose acetate (a relatively hydrophilic polymer), which is a common membrane material widely used to produce various morphologies such as dense homogeneous and asymmetric membranes, was selected as base material to provide for comparison.

Based on the foregoing information the aim of the present work has been set as follows:

To developed a novel zeolite polymer mixed-matrix membrane with better performance by using hydrophilic CA and zeolite 13X or 4A as the filler
To investigate the effect of experimental parameters:
  Feed concentration
  Feed flow rate
  Feed temperature
  Permeate side vacuum pressure
on the selectivity and flux for concentrated ethanol feed solutions.

EXPERIMENTAL

Materials

Cellulose acetate (Sigma Chemical Company) with a 40% acetyl content was employed as the base polymer. Analytical-grade acetone and dimethylformamide (Merck) were used as solvents. In preparation of the feed solutions, absolute ethanol of 99.9 wt% concentration supplied by the Turkish Monopolies was used. Molecular sieve 13X (Alfa Morton Thiokol Inc., 600 Mesh) and 4A (Union Carbide, about 5 μm) zeolites were used as adsorptive fillers. Polymer and solvents were used without further treatment.

Zeolite Treatment

Before preparing the zeolite-filled membrane, pretreatment of zeolite was necessary to remove moisture from the pores. Molecular sieve 13X and 4A zeolites were heated to 400 ± 5°C for 2 hours and then cooled to room temperature and kept in a desiccator.

Adsorption Measurement

A known amount of zeolite sample was put in a Cahn R.G. Vakuum Electrobalance System. It was evacuated with a vacuum pump to a pressure about 0.05 mmHg and heated up to a temperature of 200°C for regeneration. While the pump was still on, the system (Fig. 1) was gradually cooled to room temperature. Sorbate (water and ethanol) which was loaded to the previously evacuated liquid sample tube was allowed to flow to the system. When the sorbate pressure reached the desired value, the flow of sorbate vapor was terminated and the equilibrium weight was recorded.

Membrane Preparation

To prepare a homogeneous cellulose acetate (CA) membrane, an amount of CA was weighed and dissolved in the chosen solvent. Afterwards the solution was cast on a glass plate with to different thicknesses between 500–1000 μm by using a CAMAG Thin Layer Chromatography Film Casting Device. Next, the glass plate was placed in a vacuum oven to evaporate the solvent at 65°C. Then the oven was evacuated to an absolute pressure of 5 mmHg. During this evaporation step to remove the solvent, nitrogen gas was circulated through the oven while the vacuum pump was in operation. After 12 hours the glass plate was removed from the oven and immersed into a water–ethanol solution to remove the membrane from the surface of the glass plate.

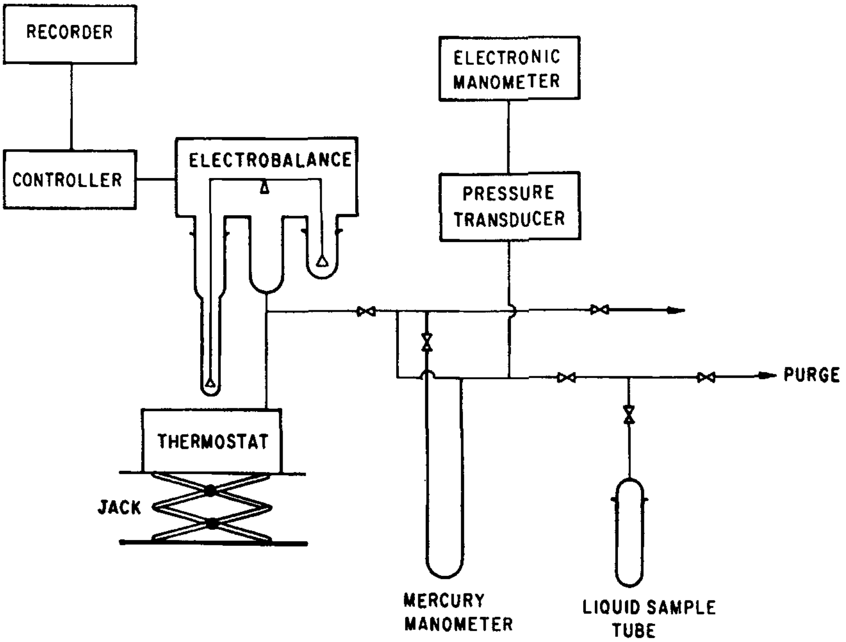


FIG. 1 Schematic diagram of sorption apparatus.

For the preparation of a zeolite-filled membrane, the filler was added to the polymer solution after sieving to −270 mesh to break the agglomerates. After thorough mixing, the mixture was cast by using the same film casting device. The preparation of zeolite-filled membranes involved the same steps as the preparation of homogeneous membranes except for the evaporation step. To prevent cracking of membranes, a suitable pressure above atmospheric was applied instead of vacuum to decrease the evaporation rate. The preparation steps for a zeolite-filled membrane are shown schematically in Fig. 2.

Pervaporation Rate Measurements

Pervaporation experiments can be conducted as either batch or continuous. In the batch mode, concentration polarization should be avoided by using a mixer inside the cell. During batch operation, permeate and retentate compositions change with time, and since the performance of a membrane is strongly composition-dependent, evaluation of the rate becomes difficult. The continuous mode of operation requires a steady supply of a large amount of fresh feed for prolonged experiments. Therefore, a

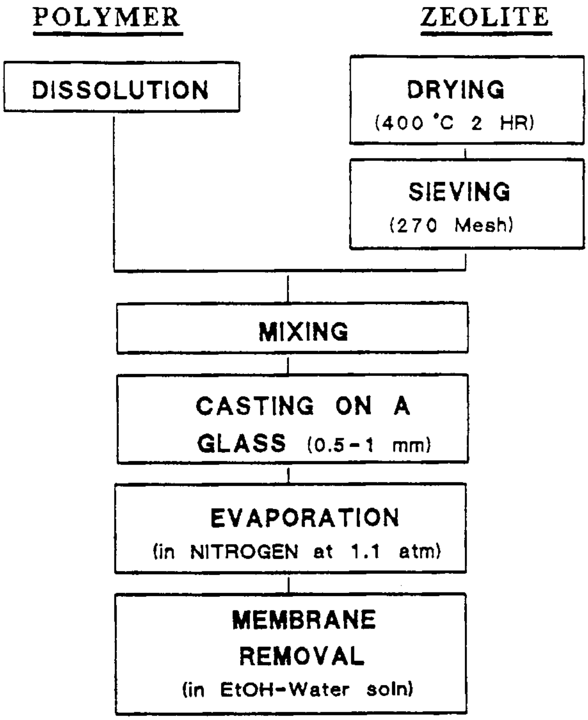


FIG. 2 The preparation steps for homogeneous and zeolite-filled membrane.

mixed mode of operation was selected by recycling retentate to the feed tank. By utilizing a large volume of feed solution in the recycle loop and a high recirculation rate, a constant feed composition could be maintained. The ratio of volume of solution in the tank to cell volume was about 10 in this study. The experimental setup used in this study is shown schematically in Fig. 3.

The Feed tank and permeation cell were constructed from stainless steel. The pervaporation cell consisted of two sections as shown in Fig. 4. The cell was designed so that the cross flow of solution creates turbulence in the cell to prevent concentration polarization. The membrane was supported by filter papers and a metal disk. The rate of flow of the feed solution was monitored by a rotameter and controlled by the by-pass valve of the pump. The temperature of the bath was controlled by a suitable heating element to maintain the temperature at the exit of the cell, measured by a thermocouple, with a precision of ± 1°C. Two parallel liquid nitrogen traps were used to collect the permeate continuously.

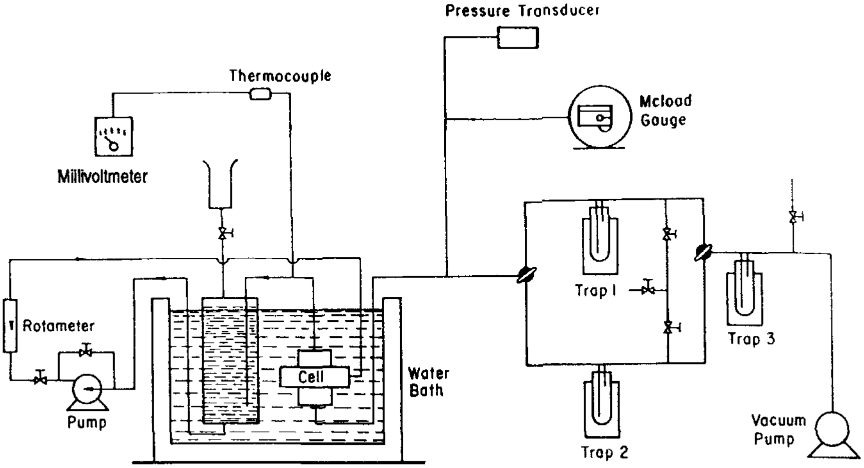


FIG. 3 Experimental setup.

Feed and permeate solution compositions were determined by means of gas chromatography with a 2-m Propak Q column and a thermal conductivity dedector (TCD) [22]. TEM micrographs of membranes were obtained by employing the gold-coating technique.

RESULTS AND DISCUSSION

Adsorption Studies

Since zeolites 4A and 13X were used as fillers in the production of mixed-matrix membranes, their pure equilibrium adsorption capacities were measured at pervaporation conditions and reported in Table 1 to enhance our understanding of the separation mechanism.

The adsorptive dehydration of aqueous ethanol using molecular sieve adsorbents has been studied previously (25–27). Simonot et al. (27) reported the pure sorption isotherm of methanol and ethanol at different temperatures on 13X zeolites. For pure ethanol, the sorption capacity at 25°C and 1 mmHg was reported as 0.24 g/g. For water, the sorption capacities of 4A and 13X at 25°C and 17.5 mmHg were reported as 0.22 and 0.285 g/g, respectively (28). Considering the variation in the origins of zeolites used and the methodology differences, our results, as reported in Table 1, are in agreement with these literature values.

Zeolite 13X has a larger void fraction relative to zeolite 4A and consequently it has a higher adsorption capacity for both water and ethanol, as also observed in our study. But in our research a comparison of the relative

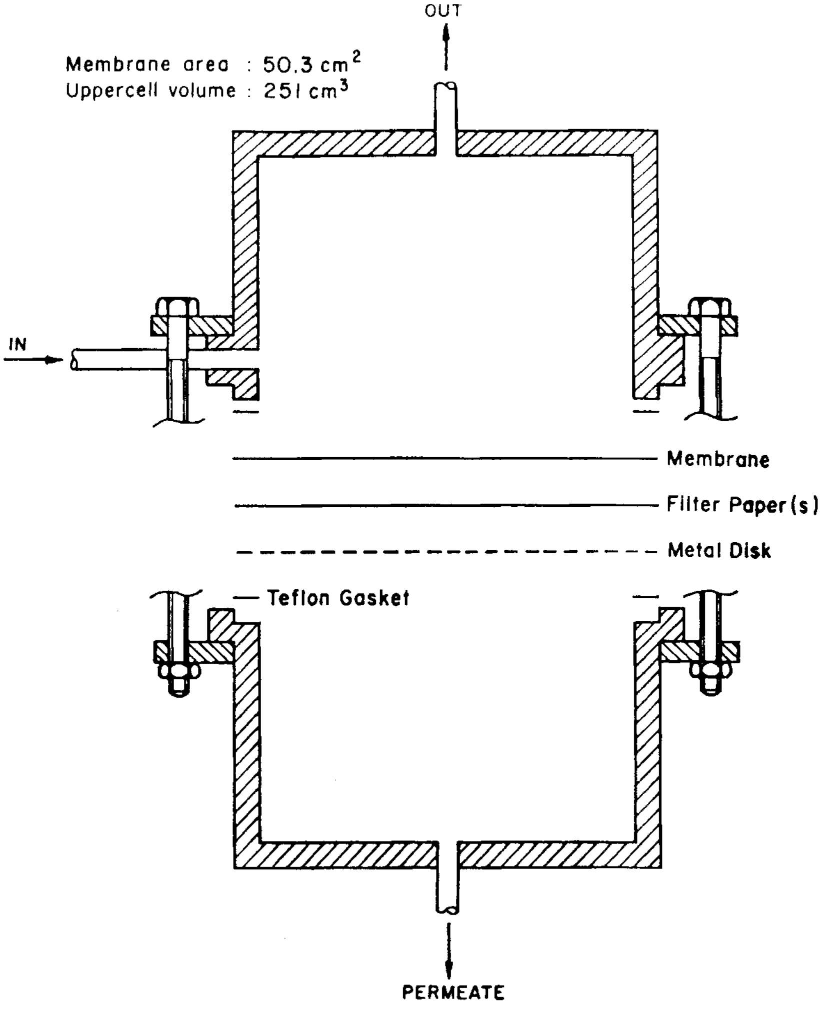


FIG. 4 Details of the pervaporation cell.

adsorption of species (water and ethanol) is more useful than that of total adsorption capacities. As reported in zeolite literature (21, 28, 29), both X- and A-type zeolites, which have high Al/Si ratios, are hydrophilic and have high affinities toward water and polar molecules. As expected by these literature findings, both of our zeolites possessed higher adsorption capacities for water relative to ethanol as reported in last column of Table 1. Therefore, both of them could be useful as fillers in the preparation of

TABLE 1
Pure Equilibrium Adsorption Capacity of Zeolite 13X and 4A to Water and Ethanol at 25°C and 1 mmHg

Zeolite	Water (g/g)	Ethanol (g/g)	Water/ethanol
13X	0.279	0.232	1.20
4A	0.204	0.150	1.36

water selective mixed-matrix membranes. Table 1 also shows that chemical affinity toward water relative to ethanol is somewhat higher for zeolite 4A than for 13X. Therefore, if zeolitic fillers play any direct role in pervaporation mechanism through mixed-matrix membranes, higher selectivities for 4A-filled membranes should be expected.

Pervaporation Studies

Although pervaporation performances of membranes are generally evaluated by reporting their steady-state fluxes and selectivities, unsteady state trends of these values could also be important, especially for the design of further experiments. A typical example of the unsteady-state period is given in Fig. 5. As seen in this figure, the time elapsed to reach steady-state values of flux and selectivity with the homogeneous CA membrane were approximately the same (3–5 hours). For similar types of membranes reported in the literature, steady-state values were in the range of 2–4 hours (30). The longer unsteady-state periods observed in the present work may be due to swelling of the membrane before starting the pervaporation experiment. Prior to the pervaporation step, feed solution was circulated to saturate the membrane with the solution, and this may cause excessive swelling of the membrane, and abnormally high initial fluxes, and low selectivities. However, preswelling causes a smooth, nonfluctuating approach to steady state. For zeolite-filled membranes, steady state was reached in shorter times (2–3 hours) since the extent of swelling was less.

The pervaporation cell was designed so as to assure thorough mixing by means of high crossflow velocities to prevent concentration polarization. To check this, three experiments were performed at different recirculation flow rates, and it was observed that flux and selectivity values were not affected (Fig. 6). Therefore, the rest of the experiments were performed at a constant flow rate of 76 L/h.

In this study, homogeneous membranes M 1-a and M 1-b were prepared with the same evaporation condition (i.e., 60°C and 5 mmHg in a nitrogen atmosphere). However, mixed-matrix membranes were prepared at room

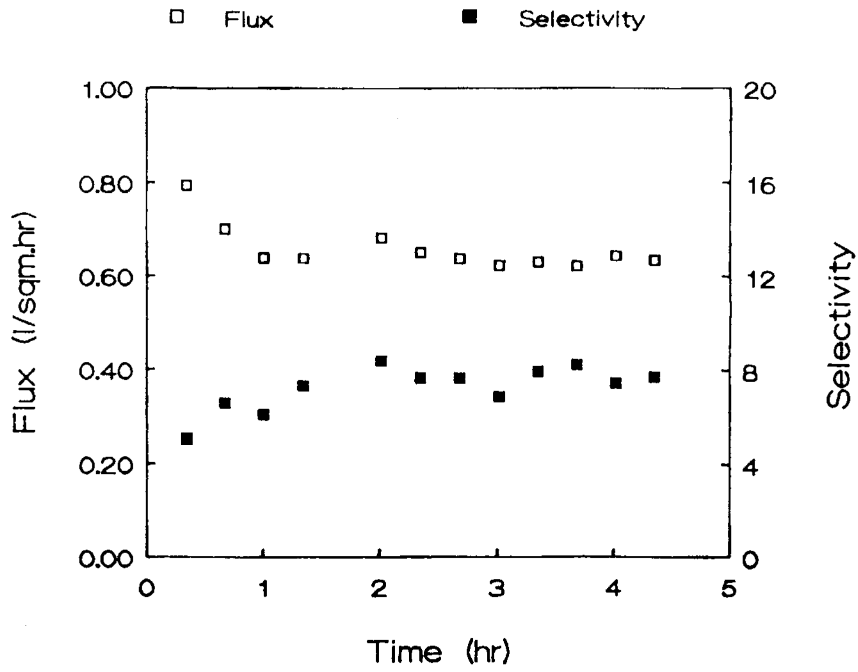


FIG. 5 Approach of selectivity and flux to steady state with M 1-a.

temperature [1.1 atm and a nitrogen atmosphere (M 2 and M 3)]. The initial casting thicknesses were 500 μm for these membranes. Membrane preparation conditions and specifications are summarized in Table 2. Prepared membranes were tested at different pervaporation conditions, and the results are summarized in Table 3.

The reproducibility of experimental results in membrane studies are important and generally difficult to achieve. Table 3 includes reproducibility data for the same membrane and for two different membranes (same type but cast for different times) evaluated at the same operating conditions. For the same membrane, reproducibility was within 5%, which is reasonable. For the two different membranes evaluated at the same operating conditions, reproducibility was 8%, which is also within tolerable limits. Therefore, we conclude that both our pervaporation apparatus and our membrane preparation procedure are satisfactory.

For the preparation of homogeneous CA membrane, acetone and DMF were used as the solvent. At the same pervaporation conditions, membranes prepared with the latter solvent lead to a higher flux with lower selectivity. A possible reason for this could be the different evaporation

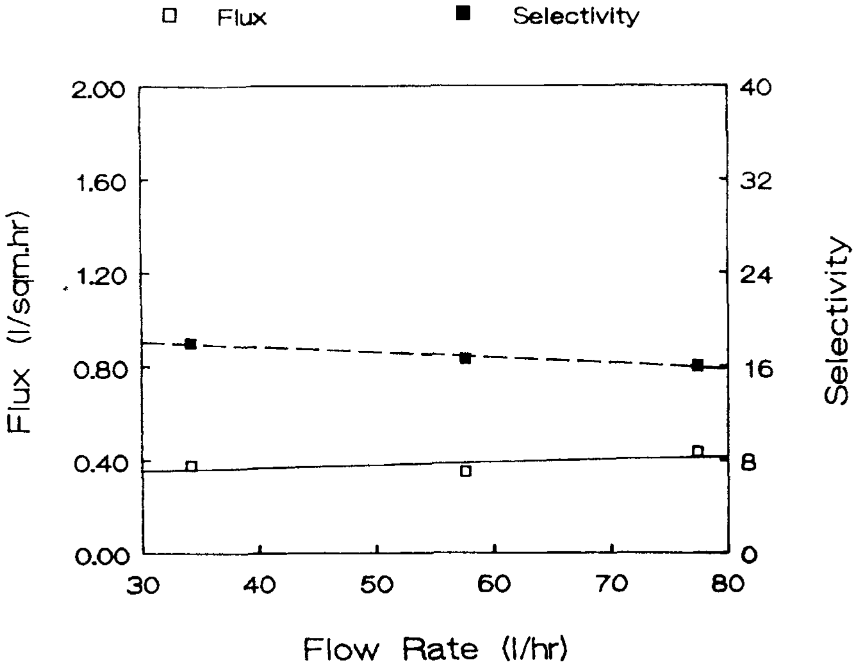


FIG. 6 Effect of recirculation flow rate on selectivity and flux for M 1-a.

TABLE 2
Membrane Specifications

Membrane code	Initial membrane composition	Final membrane composition	Evaporation medium
M 1-a	20% CA, 80% acetone	CA	N_2 atmosphere, 60°C, 5 mmHg
M 1-b	15% CA, 85% DMF	CA	N_2 atmosphere, 60°C, 5 mmHg
M2	18% CA, 8% 4A, 74% acetone	70% CA, 30% 4A	N_2 atmosphere, room temperature, 1.1 atm
M3	18% CA, 8% 13X, 74% acetone	70% CA, 30% 13X	N_2 atmosphere, room temperature, 1.1 atm

TABLE 3
Experimental Results

Membrane code	Feed temperature (°C)	Feed, wt% EtOH	Pressure, (mmHg)	Fluxes ($L/m^2 \cdot h$)	Selectivity (α)	Experimental variable
M 1-a	50.5	74	1.0	0.60	7.76	Reproducibility
	50.5	75	1.0	0.63	7.37	(Same membrane)
M 2	50.5	73	1.3	1.33	5.00	Reproducibility
	50.5	72	1.3	1.45	4.69	(Different membrane)
M 1-b	50.5	73	0.9	0.78	5.51	Solvent
M 1-a	50.5	72	0.5	0.49	8.60	Feed concentration
	50.5	81	0.5	0.42	10.40	
	50.5	91	0.7	0.35	16.60	
M 1-a	30.0	92	0.5	0.14	13.80	Feed temperature
	50.5	91	0.7	0.35	16.60	
	70.0	92	0.5	0.50	19.70	
M 3	50.5	72	1.2	1.20	4.04	Feed concentration
	50.5	81	1.2	0.99	6.29	
	50.5	90	1.2	0.90	9.41	
M 2	50.5	73	1.3	1.33	5.00	Feed concentration
	50.5	82	1.1	1.01	7.83	
	50.5	91	1.2	0.72	12.11	

rates of the solvents during membrane preparation. When DMF (a less volatile solvent) was used, its lower evaporation rate may produce a looser structure, thereby causing a higher flux and a smaller selectivity.

The variation of selectivity and flux with temperature for a homogeneous CA membrane is shown in Fig. 7. It is observed that as the temperature rises, both flux and selectivity increases. As a general trend, the effect of feed temperature on selectivity and flux in pervaporation may vary widely (31). If selectivity is dominated by sorption selectivity, selectivity should decrease when the temperature increases. But if the selectivity is due to a difference in diffusion rates, then the variation of selectivity will depend on the values of the activation energies of diffusion of each component (31). The activation energy of water (preferential component) is higher than that of ethanol, and therefore the observed selectivity increases with increasing temperatures imply that for the CA membrane of this study, the diffusion rate is controlling. Since a glassy polymer was

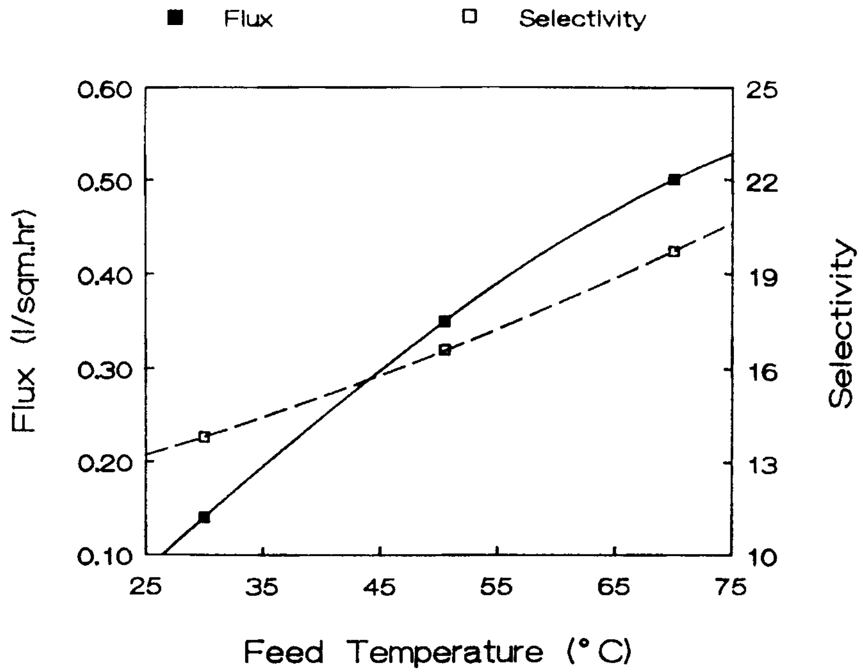


FIG. 7 Effect of temperature on selectivity and flux for M 1-a.

used, this is an expected conclusion. The variation of permeation rate with feed temperature generally shows an Arrhenius-type trend, which is also observed in this study. As the temperature increases, the movements of the polymer segment (CA in this case) also increases, which causes an increase in the flux value.

The concentration of feed solution directly affects the selectivity and flux values achieved during pervaporation. As the concentration increases, flux decreases and selectivity increases for all the membranes under investigation, as shown in Figs. 8 and 9. It is generally observed in the literature (31) that as the feed concentration of the preferentially permeating component increases, flux increases and selectivity decreases due to swelling of the membrane. The same behavior was observed in this study. As the concentration of water in the feed increases, the flux increases but the selectivity decreases. The higher the content of the component that interacts strongly with the polymer, the higher will be the extent of swelling. Thus, the permeation rate increases. A larger concentration of the component of lower affinity can penetrate the swollen system, and this will also contribute to the higher levels of swelling, so selec-

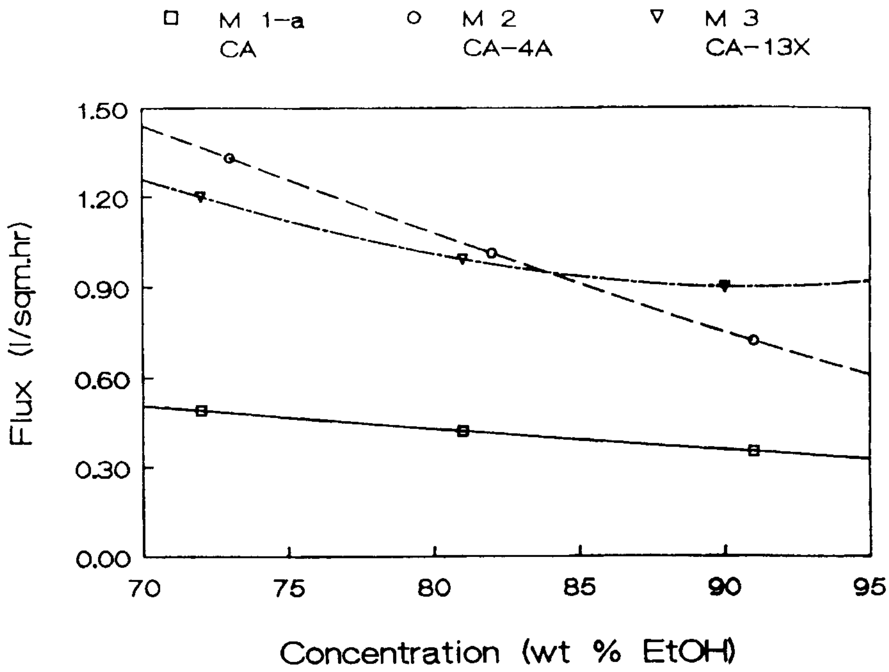


FIG. 8 Effect of feed concentration on flux.

tivity decreases. The effect of concentration on both flux and selectivity for homogeneous and zeolite-filled (mixed-matrix) membranes shows approximately the same trend, implying similar transport mechanisms.

Downstream pressure is another factor that effects the flux and selectivity in pervaporation. Selectivity decreases with an increase in the downstream pressure for homogeneous CA membrane M 1-a (Table 3). As downstream pressure increases, the driving force decreases and the downstream region of the membrane becomes more swollen. This causes a lower diffusion resistance for ethanol and water molecules. The penetration of ethanol molecules into an unswollen CA polymer can be much more difficult than in a more swollen network, so selectivity decreases with an increase in the downstream pressure. But there is a limit to the reduction of downstream pressure because of operational difficulties and economic considerations (31).

It is observed in Figs. 8 and 9 that the addition of zeolites to cellulose acetate to produce mixed-matrix membranes strongly affects membrane performance. Both mixed-matrix membranes, cerated by addition of the same amounts of zeolites 13X and 4A, respectively, possessed much

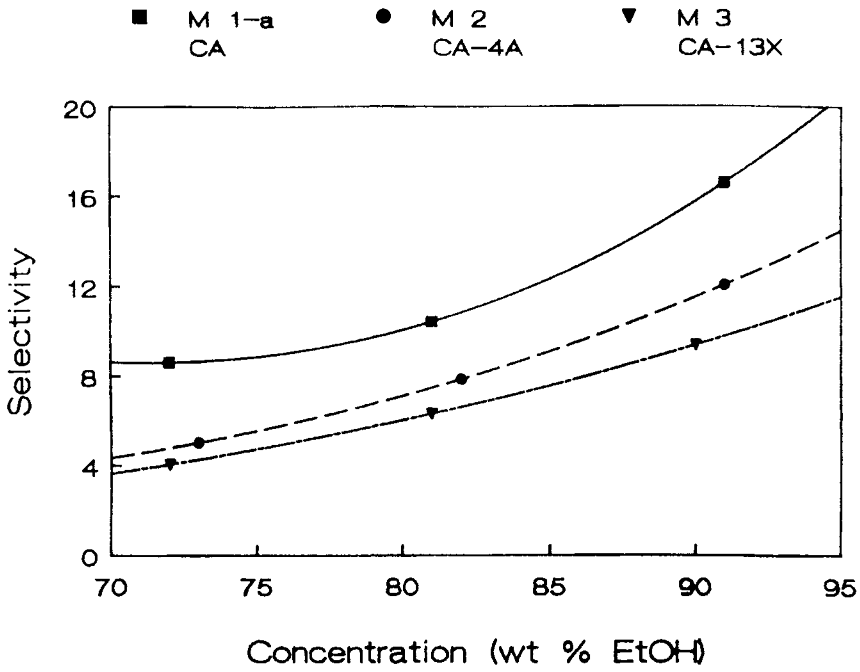


FIG. 9 Effect of feed concentration on selectivity.

higher fluxes relative to homogeneous CA membranes prepared under the same conditions. The concentration dependency of fluxes for mixed-matrix membranes is much stronger, especially for 4A-filled membranes, which implies a much stronger interaction of feed components with the membrane matrix. Contrary to the big improvements in fluxes, a certain amount of selectivity decrease is observed for mixed-matrix membranes, indicating a loosening of the membrane structure. As seen from Fig. 9, loss of selectivity is smaller for the 4A-filled membrane (M 2) relative to the 13X-filled membrane (M 3). Since particle sizes and adsorbent concentrations were the same for both mixed-matrix membranes, this selectivity difference demonstrates that the interaction of feed components with zeolites also play a role in the transport mechanism through mixed-matrix membranes. This implication was also supported by our previously mentioned adsorption results that higher chemical affinity of 4A zeolite toward water molecules relative to 13X may improve selectivities. Indeed, the losses of selectivities for 4A-filled membranes are smaller than those of 13X-filled membranes, as shown by Fig. 9.

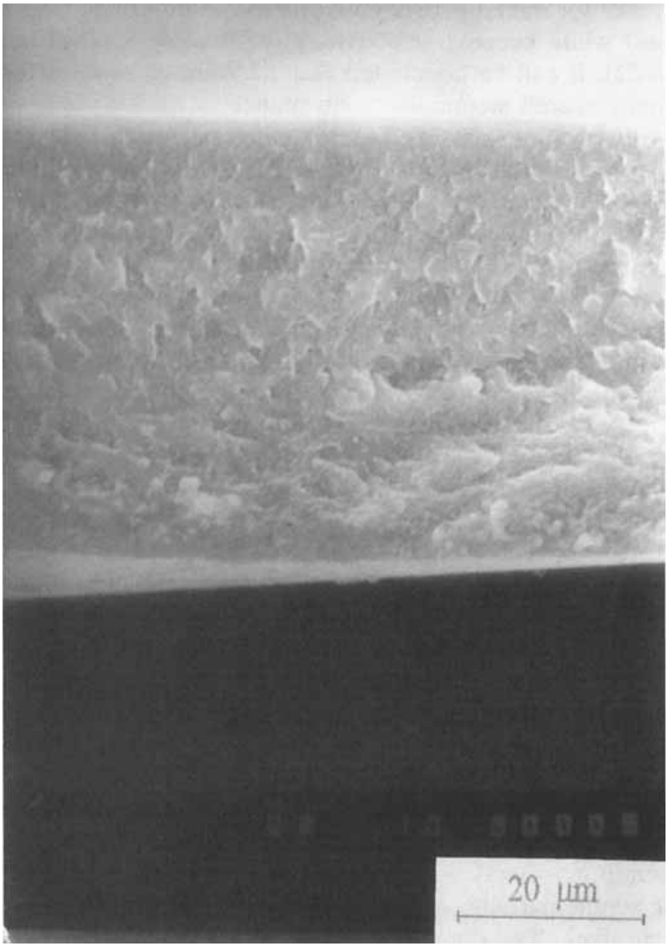
Since fluxes for mixed-matrix membranes are improved tremendously (2 to 3-fold) while keeping selectivities (with some loss) at acceptable levels (20–22), it can be concluded that addition of zeolites (especially 4A) improves overall membrane performance.

Various observations on mixed-matrix membrane performance reported by other research groups differ from our observations. Goldman et al. (20) observed that as zeolite content increases, flux value of membranes increases but selectivity shows a variation according to transport mechanism. Hennepe et al. (21) recognized that ethanol selectivity of a membrane was enhanced with silicate incorporation but decreased with zeolite A and X incorporation at low ethanol concentrations. These comparisons imply that mixed-matrix membranes and their performances for water–alcohol pervaporations may vary widely depending on the specific properties of selected polymers and adsorbents, emphasizing the importance of specific interactions among polymer matrices and adsorbents and the interaction of feed components with these structures beyond simple molecular sieving.

In order to explain these performance differences and to improve our understanding of the pervaporation mechanism, micromorphology of these membranes should be considered. If TEM micrographs of homogeneous and mixed-matrix membranes, as given in Fig. 10(a–d), are examined, major difference in microstructures can easily be seen. Pure polymeric membranes have a uniform homogeneity and a relatively looser structure, thus indicating a possible reason for their relatively higher fluxes and lower selectivities in comparison to M 1-a (Fig. 10a).

Contary to pure membranes, mixed-matrix membranes (Figs. 10c and d) have a very different and complex heterogeneous micromorphology. These micrographs imply a random distribution of zeolites in the matrix, where the zeolite particles create cave-like porous structures in which to place themselves. The creation of this porous cave-like network is believed to occur from the partial incompatibility of polymer chains and zeolite crystals, implying that the chemical and physical interactions of polymeric matrices and adsorbent fillers may play a very important role in determining microstructure and hence the performance of mixed-matrix membranes.

Some of the performance characteristics of our mixed-matrix membranes can be explained by their heterogeneous microstructures. The cave-like porous network, created by partial incompatibility of polymer matrix and zeolitic fillers, may provide an alternate path for feed component molecules and porous passages for zeolite particles, which offer different resistances and chemical affinities. This microporous network in the membrane matrix may help the transportation of both components



a) For M 1-a (× 1000)

FIG. 10 TEM micrographs of the membranes.

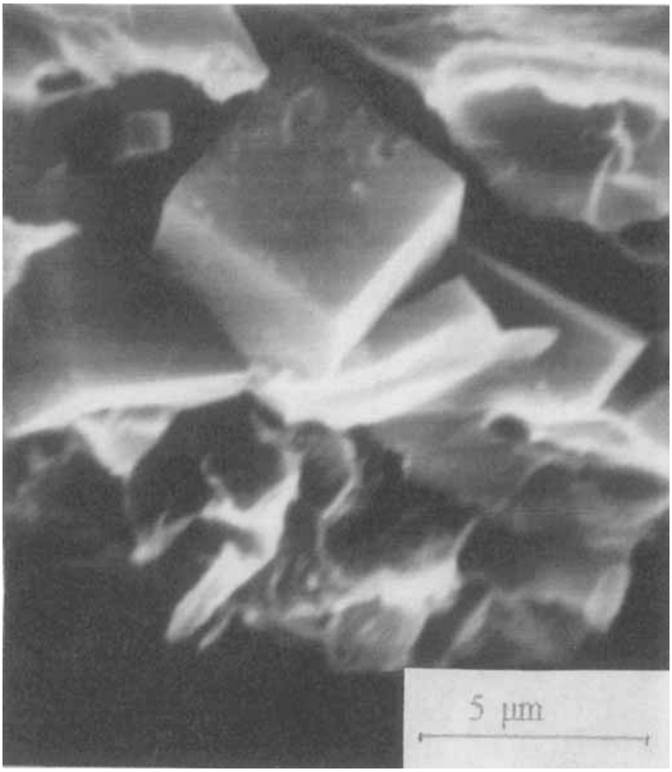
through the membrane and thereby cause the flux to increase. Related to this, a cavity network also causes the selectivity of a membrane to decrease if the pore sizes are larger than both molecules. Flux increases were much higher than selectivity losses. Since the chemical interactions of zeolites and their adsorptive capacities were different for water and alcohol during their passage through the membrane, the interaction of these molecules with zeolite particles will affect their transportation times differently. The selectivity of membranes filled with zeolite 4A is larger

b) For M 1-b (× 1500)

FIG. 10 Continued.

(continued)

than those with 13X, as shown in Fig. 9. This can be because of the combined effect of microstructure and chemical interactions. The higher selectivity of 4A-filled membranes may be affected by the fact that the distance between zeolite particles for 4A is shorter than for 13X as seen from TEM micrographs (c and d), producing tighter and intertwined porous structures combined with the effect of selective sorption capacities of the adsorbents in the structure. This was verified by electrogravimetric sorption studies. All these observations indicates that zeolite particles in the membrane may play an active role in the transport mechanism, both

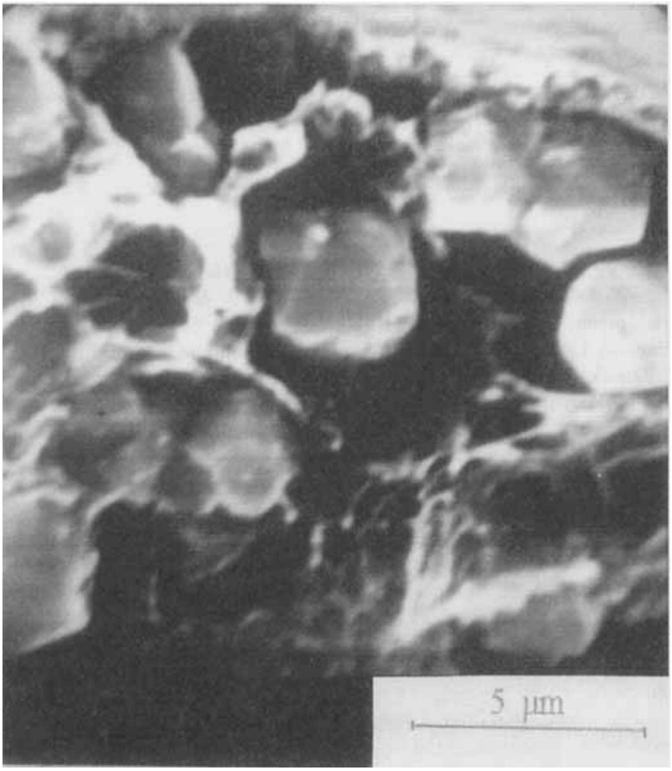


c) For M 2 (× 10000)
FIG. 10 Continued.

by creating a complex heterogeneous micromorphology and by interacting with feed components.

CONCLUSIONS

1. A novel scheme for the preparation of homogeneous and mixed-matrix crack-free membranes with relatively long operational times and with reasonable reproducibility properties was developed.
2. Effects of process parameters on membrane performance for the pervaporation of water–ethanol separations were investigated. As feed temperature increases, flux and selectivity also increase. If downstream pressure increases, flux and selectivity decrease. As the feed concentration of ethanol increases, the flux decreases but the selectivity increases.
3. Different solvents for the preparation of membranes were used, and it was observed that the choice of initial casting solvent strongly affects



d) For M 3 (× 10000)

FIG. 10 Continued.

the pervaporation performance of homogeneous membranes. The lower evaporation rate of DMF yields a looser structure with lower selectivity and higher flux relative to a membrane prepared by using acetone as solvent.

4. The effect of the addition of zeolite on flux and selectivity was investigated. In general, their presence was found to improve the flux (2 to 3-fold in this study) substantially with some loss in selectivity.

5. Addition of zeolites created a complex heterogeneous micromorphology. The introduction of a microporous cave-like network in which zeolite particles places themselves demonstrates a degree of polymer–zeolite interaction and their partial incompatibility.

6. Changes in membrane performance are due both to the creation of a complex micromorphology because of polymer–zeolite interactions and to the differing interactions of feed components with zeolitic particles and the polymeric matrix.

ACKNOWLEDGMENT

This work has been supported by METU University Grant AFP 88-03-04-02. The authors wish to express their gratitude.

REFERENCES

1. M. H. V. Mulder, J. O. Hendrikman, H. Hegeman, and C. A. Smolders, "Ethanol–Water Separation by Pervaporation," *J. Membr. Sci.*, *16*, 269 (1983).
2. I. Frennesson, G. Tragardh, and B. Hahn-Hagerdal, "Pervaporation and Ethanol Upgrading—A Literature Review," *Chem. Eng. Commun.*, *45*, 277 (1986).
3. J. H. Patrick and C. S. Slater, "The Selective Recovery of Alcohols from Fermentation Broths by Pervaporation," *Sep. Purif. Methods*, *19*, 93 (1990).
4. U. Sander and P. Soukup, "Design and Operation of a Pervaporation Plant for Ethanol Dehydration," *J. Membr. Sci.*, *36* 463 (1988).
5. H. L. Fleming, "Membrane Pervaporation: Separation of Organic/Aqueous Mixtures, *Sep. Sci. Technol.*, *25*, 1239 (1990).
6. Z. Changluo, L. Moe, and X. Wei, "Separation of Ethanol Water Mixtures by Pervaporation—Membrane Separation Process," *Desalination*, *62*, 299 (1987).
7. B. D. Gupta and A. K. Mukherjii, "Separation of Liquid Mixtures by Pervaporation," *Polym-Plast. Technol. Eng.*, *29* 299 (1990).
8. H. R. Acharya, S. A. Stern, Z. Z. Liu, and I. Cabasso, "Separation of Liquid Benzene/Cyclohexane Mixtures by Perstraction and Pervaporation," *J. Membr. Sci.*, *37*, 205 (1988).
9. L. Kraetz, "Dehydration of Alcohol Fuels by Pervaporation," *Desalination*, *70*, 481 (1988).
10. H. Strathmann, *Fundamental of Membrane Separation Processes*, Presented at Chromatographic and Membrane Processes in Biotechnology, Azores, Portugal, July 1990.
11. H. Strathmann, *Pervaporation in Biotechnology*, Presented at Chromatographic and Membrane Processes in Biotechnology, Azores, Portugal, July 1990.
12. J. Neel, P. Aptel, and R. Clement, "Basic Aspect of Pervaporation," *Desalination*, *5*, 297 (1985).
13. I. Cabasso, "Organic Liquid Mixture: Separation by Permselective Polymer Membranes 1. Selection and Characteristics of Dense Isotropic Membranes Employed in the Pervaporation Processes," *Ind. Eng. Chem., Prod. Res. Dev.*, *22*, 313 (1983).
14. H. Strathmann, C. M. Bell, and J. Kerres, "Gas Separation and Pervaporation-Membrane and Module Development," *Desalination*, *77*, 259 (1990).
15. Y. F. Xu and R. Y. M. Huang, "Pervaporation Separation of Ethanol Water Mixtures Using Ionically Crosslinked Blended PAA-Nylon 6 Membrane," *J. Appl. Polym. Sci.*, *36*, 1121 (1988).
16. Q. Nguyen, L. Blanc, and J. Nell, "Preparation of Membranes from PAN-PVP Blend," *J. Membr. Sci.*, *22*, 245 (1985).
17. C.-M. Hu and W.-Y. Chiang, "Separation of Liquid Mixtures by Using Polymer Membranes. III. Water–Alcohol Separation by Pervaporation through Modified PAN Membrane," *J. Appl. Polym. Sci.*, *42*, 1829 (1991).
18. K. Ishihara and K. Matsui, "Pervaporation of Ethanol–Water Mixture through Composite Membranes Composed of Styrene–Fluoroalkyl Acrylate Graft Copolymers and Crosslinked PDMS Membrane," *Ibid.*, *34*, 437 (1987).

19. G. H. Hsive, Y. S. Yang, and J. F. Kno, "Pervaporation and Separation of Aqueous Alcohol Solutions through Grafted Polyvinyl Alcohol Latex Membranes," *Ibid.*, *34*, 2187 (1987).
20. M. Goldman, D. Fraenkel, and G. Levin, A Zeolite/Polymer Membrane for Separation of Ethanol–Water Azeotrope," *Ibid.*, *37*, 1791 (1989).
21. H. J. C. Hennepe, D. Bargeman, M. H. V. Mulder, and C. A. Smolders, "Zeolite-Filled Silicon Rubber Membranes: Part I. Membrane Preparation and Pervaporation Results," *J. Membr. Sci.*, *35*, 39 (1987).
22. H. J. C. Hennepe, "Zeolite Filled Polymeric Membranes. A New Separation Technology Concept in Membrane Separation," Ph.D. Thesis, University of Twente, 1988.
23. M.-D. Jia, K.-V. Pienemann, and R.-D. Behling, "Preparation and Characterization of Thin-Film Zeolite–PDMS Composite Membrane," *J. Membr. Sci.*, *73*, 119 (1992).
24. C. Bartels-Carpers, E. Tusel-Langer, and R. N. Linchtenthaler, "Sorption Isotherms of Alcohols in Zeolite-Filled Silicone Rubber and in PVA-Composite Membranes," *Ibid.*, *70*, 75 (1992).
25. W. K. Teo and D. M. Ruthen, "Adsorption of Water Aqueous Ethanol Using 3-A Molecular Sieves," *Ind. Eng. Chem., Proc. Des. Dev.*, *25*, 17 (1986).
26. A. Carton, G. Gounzales, A. I. Torre, and J. L. Cabezas, "Separation of Ethanol–Water Mixture Using 3-A Molecular Sieve," *J. Chem. Tech. Biol. Biotechnol.*, *39*, 125 (1987).
27. M. H. Simonot-Grange, J. J. Guilleminot, J. C. Setior, and F. Meunier, "The Liquid–Gas Zeolite Stationary State and The Sorption Cycle—Compared Sorption of Methanol, Ethanol and Water by Zeolite 13X," *Proceedings of The Fifth International Conference on Zeolites, Naples, Italy, June 1980.*
28. A. L. Kohl and F. C. Risenfield, *Gas Purification*, 3rd ed., Gulf Publishing Company, Houston, 1979.
29. M. E. Flanigen, "Molecular Sieve Zeolite Technology the First Twenty-Five Years," *Pure Appl. Chem.*, *50*, 2191 (1980).
30. M. H. V. Mulder and C. A. Smolders, "On the Mechanism of Separation of Ethanol–Water Mixture by Pervaporation, I. Calculation on Concentration Profile," *J. Membr. Sci.*, *17*, 289 (1984).
31. T. Q. Nguyen, "The Influence of Operating Parameters on the Performance of Pervaporation Process," *AIChE Symp. Ser.*, *82*, 1 (1982).

Received February 22, 1994