A Study on the Preparation and Performance of Polydimethylsiloxane-Coated Polyetherimide Membranes in Pervaporation

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SYNOPSIS

Separation of acetic acid/water mixtures by pervaporation was attempted by silicone rubber-coated polyetherimide membranes. In particular, the effect of the pore size of the polyetherimide membrane and the condition of silicone rubber coating on the performance of the composite membrane was investigated. It was found that the composite membrane could become either water selective or acetic acid selective, depending on the pore size of the support membrane and the condition of the silicone rubber coating. Thus, the overall performance of the composite membrane can be governed, either by the top coated layer or by the bottom support layer.

INTRODUCTION

Although industrial application of pervaporation started only recently, it has been recognized as a versatile separation process in the chemical and other industries.[1] Currently, the industrial applications of pervaporation are divided into two groups; one is dehydration of alcohol and other organic solvents, using hydrophilic or charged polymeric membranes,[2] and the other is the removal of small quantities of volatile organic compounds from water using membranes of a hydrophobic nature.[3] The application of the latter process was investigated in relation to the removal of volatile organic pollutants, such as halogenated hydrocarbons, from water[4] and the concentration of flavor compounds from apple juice.[5] In particular, the concentration polarization occurring during pervaporation was pointed out as being an important factor governing the membrane performance.[6]

As for the process to remove and concentrate volatile organic compounds from the feed aqueous solution into the permeate, there are two commercial membranes currently available. Both are of a composite nature. MTR's pervaporaion membrane adopts two different elastomeric polymers with sufficiently high permselectivity. One of these polymers is coated to a thickness of 0.5 to 3.5 μm on the top of a microporous support and the composite membrane so prepared is mounted to the MTR's spiral wound module.[7] Another membrane, from GFT Corp., is prepared by placing a silicone rubber layer on an asymmetric polyacrylonitrile supporting material.[8] Investigations were also made on the pervaporation performance of a composite membrane that consists of a thin film of polyether–block–polyamides (PEBA) coated on the top of a microporous polyetherimide (PEI) substrate.[3] The top surface layer was thinner than 25, μm having an hydrophobic nature. In all of the above membranes, the elastomeric film of hydrophobic property was expected to govern the overall permselectivity. The porous support was only to strengthen the composite membrane mechanically. In other words, the composite membrane so prepared was supposed to be organic compound selective. It should be noted, however, that all polymeric materials that have been used for the formation of microporous support membranes are relatively hydrophilic and water selective. Therefore, the composite membranes may become water selective, despite initial intention to render them preferentially permeable to volatile organic

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compounds, unless an appropriate balance between the top layer and the porous support layer is maintained. The membranes are even more water selective when the top layer is made thinner in order to increase the permeation rate, since the resistance of the support layer may become increasingly high, relative to the top layer, and may start to dominate the permselectivity of the composite membrane. We can find some experimental evidence in the literature in which the bottom layer, rather than the top layer, governs the pervaporation performance of bilayer membranes. The water selectivity of an aromatic polyamide membrane was intensified when a polydimethylsiloxane membrane was laminated on the top of an aromatic polyamide membrane.[9] Similarly, the preferential permeability of a polyvinylalcohol–polyvinylpyrrolidone blend film to the more hydrophilic component (methanol) of methanol–benzene binary mixtures was intensified by placing a polydimethylsiloxane membrane between the feed solution and the above blend membrane.[10] Obviously, the hydrophilic nature of the membrane, placed at the bottom of the composite membrane, was intensified by lamination of a hydrophobic film in both cases. Although, at a first glance, a simple resistance model seems to explain the above effect, the latter model is not necessarily valid, since the permselectivity was reversed when the positions in lamination of hydrophilic and hydrophobic membranes were interchanged.

The above experimental results suggest that the hydrophilic and hydrophobic property, and the morphology of component barrier layers in a composite membrane and their respective position, are important factors to govern overall permselectivity.

The objective of this work was to study the effect of the pore size of the micoroporous support layer and the method of coating the top layer on pervaporation performance of a composite membrane in a systematic way. Polydimethylsiloxane (PDMS) was used for the top layer, while polyetherimide (PEI) polymer was the material for the microporous support membrane. Pervaporation of acetic acid/water mixtures was adopted for the model separation system. It was shown that both water selective and acetic acid selective membranes could be prepared, depending on the pore size of the porous support membrane and the coating method.

EXPERIMENTAL

Materials

Polyetherimide polymer (Ultem) was supplied by General Electric Co. and was used after drying at 150°C for 4 h. *N*-methylpyrrolidone was from J. T. Baker Co. and was used without further purification. Curing agent I (tetraethyl orthosilicate) and II (dibutyltin dilaurate) were supplied by Aldrich Chemical Co. Inc. The backing material was a polyester film (Style 3296), supplied by Filtration Science Co. All other chemicals were of reagent grade and were used without further purification.

Membrane Preparation

The composition of casting solutions used to prepare polyetherimide support membranes is given in Table I. The casting solution was cast onto a backing material (polyester film Style 3296) at the casting temperature of 19°C and the relative humidity of 37.8%. The cast film was then gelled in ice-cold water for 2 h. The sequence of solvent exchange and drying

Table I Composition of Casting Solution and Thickness of Polyetherimide Support Membrane

Membrane No.	Composition (wt %) Polymer	NMP	*t*-BuOH	MeOH	Film Thickness (μm)
1	20	80			254 (as cast)
2	23	77			254 (as cast)
3	27	73			254 (as cast)
4	30	70			254 (as cast)
5	9	81.8	3.6	5.5	254 (as cast) 127 (in dry form)
6	17	83			51 (as cast) 30.5 (in dry form)

NMP = N-methylpyrrolidone.

Table II Composition of Dimethylsiloxane Solution and Thickness of Polydimethylsiloxane Coating

Membrane No.	Composition (wt %)				Film Thickness (μm)
	Dimethylsiloxane	Tetraethyl Orthosilicate	Dibutyltin Dilaurate	Haxane	
A	6.58	0.23	0.37	92.83	NA[a]
B	47.4	4.0	1.2	47.4	—[b]
C	65.1	1.9	4.7	28.3	—[b]
D	73.6	6.1	1.9	18.4	101.6 (as cast)
E[c]	—[d]	—[d]	—[d]	—[d]	—[d]

[a] (NA) Not applicable.

[b] Given in the text.

[c] Film laminated on the top of PEI support membrane.

[d] Supplied by General Electric Co.

of membranes was as follows: The water wet membranes, obtained after gelation, were immersed into an ethyl alcohol bath and were kept in the bath for 6 h. Alcohol in the bath was replaced with fresh ethyl alcohol and the membrane was kept in the bath for 16 h. The content of the bath was further replaced with hexane, in which the membrane was kept for 24 h. Then, the membrane was air-dried. One of the PEI membranes (membrane 6) was a thin homogeneous membrane. Gelation procedure was not involved in the preparation of the latter membrane. Instead, the cast film was dried at 95°C for 2 h. Dry asymmetric polyetherimide membranes were either laminated with a polydimethylsiloxane (PDMS) membrane or were coated with PDMS material before being used for pervaporation experiments.

The coating technique of the top PDMS (silicone rubber)-*A* film (see Table II) was the same as that described in detail in the previous article.[11] Briefly, a dry PEI membrane was mounted at the bottom of a cylindrical permeation cell that was filled partially with dimethylsiloxane solution, including curing agents and hexane solvent. The solution was poured out of the cell, which was then kept upside down for 30 min so that any residual solution could be drained and the solvent evaporated. The thin film so produced was further cured at 80°C for 1 h. As for the PDMS coating-*B*, dimethylsiloxane solution was coated on the top surface of a dry PEI membrane by using a casting blade and, after being dried in air at ambient temperature for 16 h, the thin PDMS layer was cured at 80°C for 1 h. As for the PDMS coating-*C*, the dimethylsiloxane solution was coated on the top of the silicone coating-*B*. The PDMS coating-*D* was applied directly to a backing material. Conditions of film drying and coating are summarized in Table III. The PDMS membrane-*E* was supplied generously by General Electric Co.

The membrane codes, listed in Tables I, and II, will be used hereafter. For example, membrane *A*-1 means that the PEI porous support was made under the condition specified for membrane 1 in Table I, while PDMS coating was performed under the condition specified for PDMS coating-*A* in Table II. Membrane-1 means, on the other hand, that the PEI supports membrane-1 without lamination or coating.

The membrane thickness is also listed in Tables I and II. The as-cast thickness indicates the casting gap of the blade, whereas the thickness in dry form was measured using a micrometer.

Table III Conditions of PDMS Film Coating

Membrane No.	Air Drying Period (h)	Curing Temperature (°C)	Curing Period (h)
A	1	80	1
B	16	80	1
C	16	80	1
D	1	80	1.5

Pervaporation Experiments

Pervaporation experiments were carried out as described in our previous work.[12] The cell for the permeation experiments was the same as the static cell used in the reverse osmosis and ultrafiltration experiments.[13] The effective area of the membrane was 10.2 cm^2. About 50 cm^3 of feed liquid was loaded in the permeation cell. A prescribed pressure was applied at the downstream side of the membrane, while the upstream pressure was maintained at an atmospheric pressure. The permeate sample was condensed and was collected in a cold trap with liquid nitrogen. The permeation rate was determined by measuring the weight of the permeate sample collected during a predetermined time. The permeation temperature was controlled by immersing the cell in a constant temperature bath. The downstream pressure was controlled within ±1 mm Hg. The composition of the feed and the permeate sample was determined by gas chromatography.

RESULTS AND DISCUSSION

Performance Data of the Porous PEI Support Membrane

The permeability of air through dry PEI membranes (membranes-1 to -5) is shown as a function of PEI polymer concentration in the casting solution in Figure 1. The permeability decreases with an increase in the PEI concentration, indicating that the pore size of the PEI membranes becomes smaller as the concentration of the polymer in the casting solution increases. The permeate flux and the permeate composition of PEI membranes for pervaporation of feed acetic acid–water mixtures, with feed mole fraction of 0.09, are given in Figure 2 as a function of the polymer concentration in the casting solution. The flux became two orders of magnitude less when the PEI concentration in the casting solution was increased from 20 to 27%. The acetic acid mole fraction in the permeate, on the other hand, decreased from 0.0890 to 0.0648, indicating that PEI membranes are water selective and that the pore size decreases as the PEI concentration in the casting solution increases. This trend, however, was reversed when the PEI concentration in the casting solution was increased from 27 to 30%. The flux of the PEI porous substrate, made from the casting solution containing 9% PEI (membrane-5), was so large that neither the flux nor the permeate concentration could be determined. The latter membrane, however, was nonselective. The porous structure of the substrate membrane was, therefore, characterized by the air permeation rate and the pervaporation performance. A direct measurement of the pore size by SEM was impossible since the pore size involved was too small.

Performance Data of Homogeneous Membranes

Pervaporation fluxes of both acetic acid and water were measured for a homogeneous PEI membrane

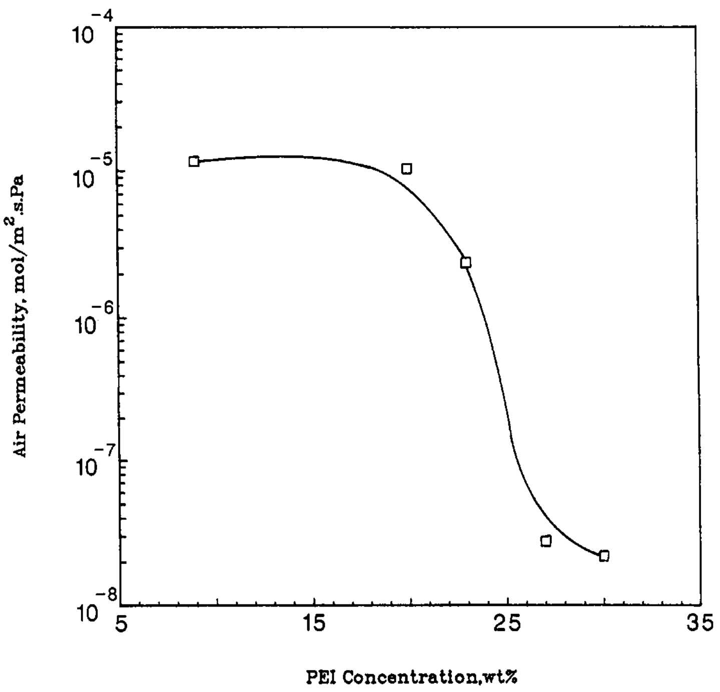

Figure 1 Air permeability through uncoated polyetherimide membranes. Temperature, ambient; upstream pressure, atmospheric; downstream pressure; 12101 Pa (90.8 mm Hg), 3439 Pa (25.8 mm Hg), 115 Pa (0.86 mm Hg), 83 Pa (0.62 mm Hg), and 15,849 Pa (118.9 mm Hg) for membranes 1, 2, 3, 4, and 5, respectively.

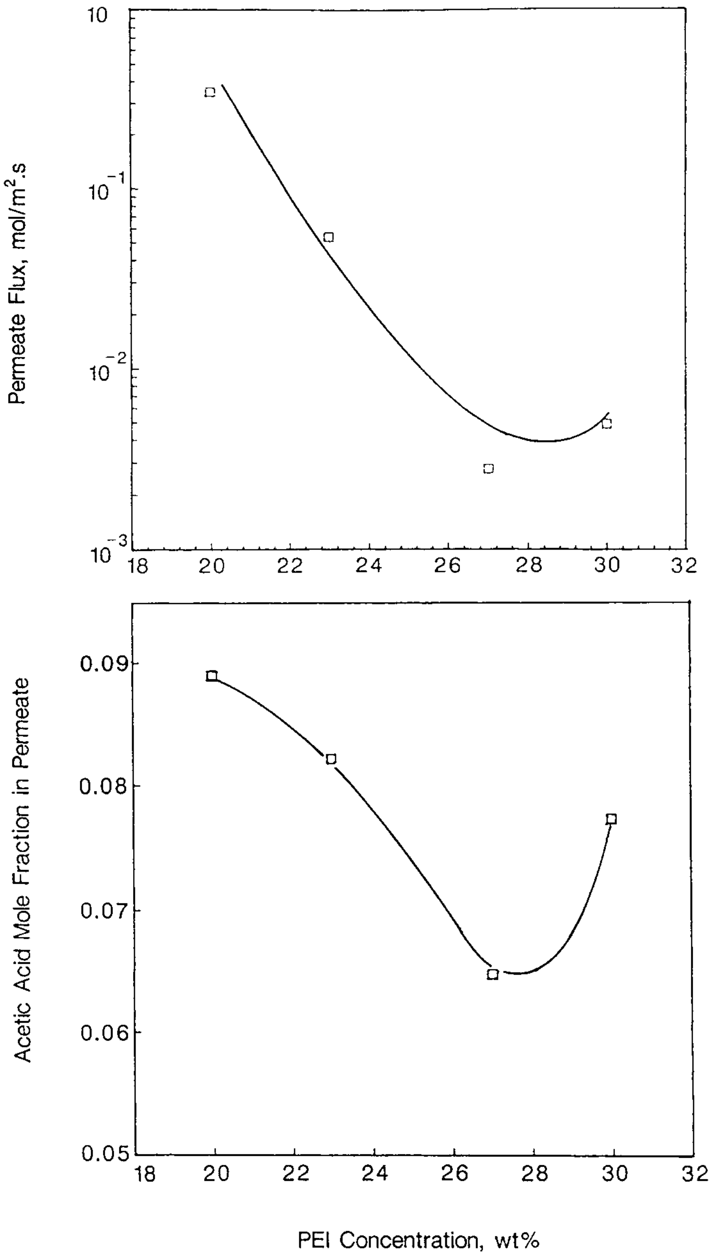

Figure 2 Pervaporation performance of uncoated polyetherimide membranes. Temperature, ambient; downstream pressure, below 733 Pa (5.5 mm Hg); feed acetic acid mole fraction, 0.09.

(membrane-6) at the downstream pressure of 57.3 Pa (0.43 mm Hg). The flux data of this particular membrane were 4.51 × 10^{-5} mol/m^2 s and 2.61 × 10^{-4} mol/m^2 s for acetic acid and water, respectively, indicating that the PEI material was water selective. Similarly, pervaporation fluxes of both acetic acid and water were measured with respect to the homogeneous PDMS membrane (membrane-*D*) at the downstream pressure of 33.33 Pa (0.25 mm Hg). The flux data were 1.14 × 10^{-4} mol/m^2 s and 1.81 × 10^{-5} mol/m^2 s for acetic acid and water, respectively, indicating that this particular membrane was acetic acid selective. The latter data on the PDMS membrane coincides with the data obtained for PDMS membranes supplied by General Electric Co.[9]

Performance Data of Laminated PDMS-PEI Membrane

Pervaporation experiments were carried out using a laminated PDMS (top)-PEI (bottom) membrane (membrane *E*-5). As a PEI porous support, the most porous PEI membrane was used. The downstream pressure was kept at 33.3 Pa (0.25 mm Hg). Experimental data for the molar flux and the acetic acid mole fraction in the permeate are given as a function of the feed acetic acid mole fraction in Figure 3. The laminated membrane was acetic acid selective. Acetic acid mole fraction in the permeate was higher than that in the feed and also the permeation flux increased with an increase in acetic acid mole fraction in the feed. Figure 3 also includes the data for PDMS membrane without porous PEI substrate (membrane-*E*). While the selectivities of

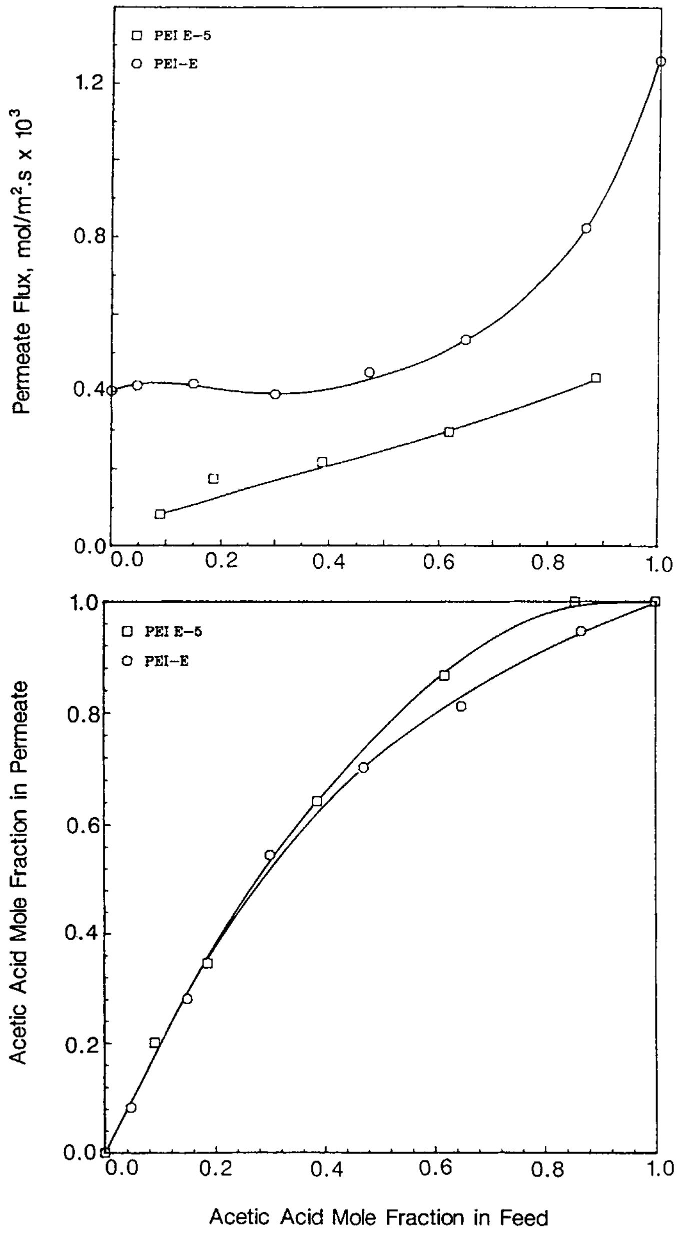

Figure 3 Pervaporation performance of a PDMS membrane[9] (membrane-*E*) and a PDMS/PEI laminated membrane (membrane *E*-5). Temperature, ambient; downstream pressure, 33.3 Pa (0.25 mm Hg).

membrane *E*-5 and membrane-*E* are almost the same, the flux data are different, indicating the effect of the support layer in the former membrane.

Performance Data of PDMS-Coated PEI Membranes

Air permeation and pervaporation experiments were carried out with respect to the porous PEI support coated with PDMS multilayers. Four PEI support membranes with different pore sizes were used for this purpose and five layers of PDMS coatings were applied, according to the method described as PDMS-*A*, coating in Table II, for each PEI substrate. Therefore, membranes coded as *A*-1, *A*-2, *A*-3, and *A*-4 were involved in this study. The results are summarized in Figure 4, where air permeability, pervaporation flux, and the acetic acid mole fraction

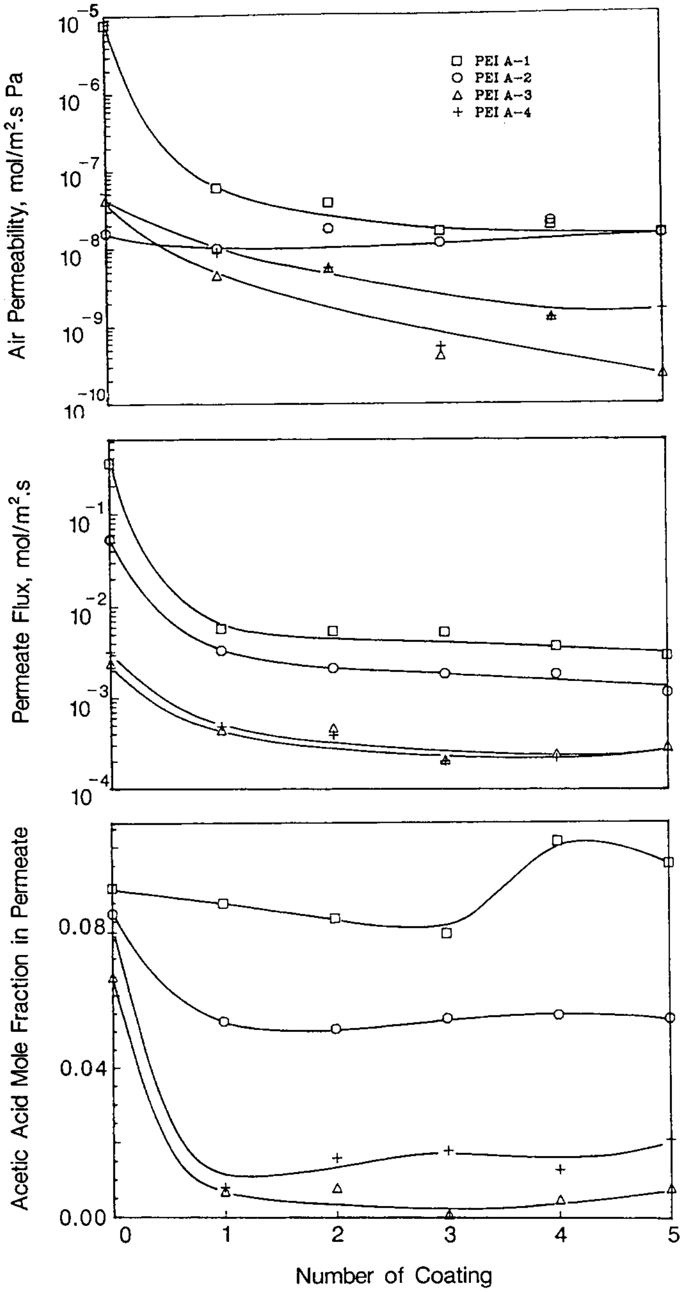

Figure 4 Pervaporation performance of PDMS multilayers coated on PEI support membranes of different pore sizes. Temperature, ambient; downstream pressure, below 200 Pa (1.5 mm Hg), feed acetic acid mole fraction, 0.09.

in the permeate are plotted vs. the number of coatings applied. The feed mole fraction of acetic acid in pervaporation experiments was kept 0.09. Both air permeability and pervaporation flux decreased with the number of coating. The change from the second coating was, however, gradual.

The data for the acetic acid mole fraction of the permeate is interesting. Except the data for the fourth and fifth coating of membrane *A*-1, all the data are below the acetic acid mole fraction in the feed. In other words, membranes were water selective. We have already learned from the data of a homogeneous PEI membrane that PEI membranes are intrinsically water selective. We have also learned, from Figure 2, that water selectivity increases from membrane 1 to 3 as the pore size of the asymmetric PEI membrane decreases. The experimental results, illustrated in Figure 4, indicate that the water selectivity of the PEI support membrane was intensified by the coating with PDMS polymer. Apparently, the water selectivity of the coated membrane depended on that of the uncoated

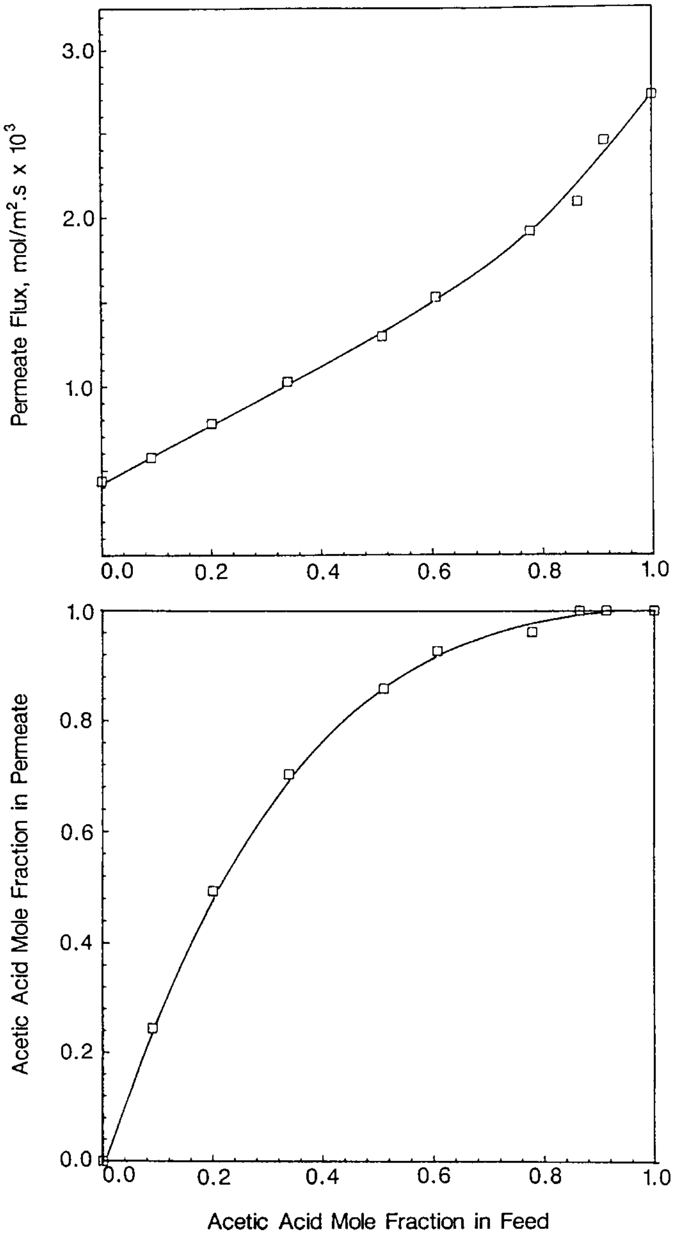

Figure 5 Pervaporation performance of a PDMS-coated PEI porous support membrane (membrane *CB*-5). Temperature, ambient; downstream pressure, 13.3 Pa (0.1 mm Hg).

membrane. The membrane-3, which showed the highest water selectivity when uncoated, became the most water selective membrane after the PDMS coating. The effect of the coating on the selectivity seems to be the most marked after the first coating. It is interesting to note that there was practically no acetic acid in the solution that permeated through the membrane *A*-3 after the third coating. PDMS material is intrinsically acetic acid selective, as our previous data show. The coating of a PEI porous support membrane, which is water selective, with PDMS layers, which are acetic acid selective, resulted in a water selectivity higher than that of the PEI support membrane. These experimental data are similar to those reported in the earlier work,[9] where the water selectivity of aromatic polyamide membranes was increased by lamination (on the top side) of a PDMS film.

We have pointed out that the above effect can be explained either by the resistance model, where it is assumed that the lamination of a PDMS membrane on the top of the porous PEI support layer prevents the leak of the feed solution through large pores on the latter PEI membrane, thereby revealing more explicitly the intrinsic property of the PEI material, or by another mechanism that assumes the repulsion of feed liquid by the PDMS membrane, resulting in a lesser degree of swelling of the top skin layer of the PEI membrane that is supposed to be the most selective in a dry form. More work is necessary to discover the mechanism that is effective.

Figure 4 also shows that the acetic acid mole fraction in the permeate tended to increase at the fourth and fifth coating. The above tendency was observed for most of the PEI support membranes. This effect was probably due to the increased effect of the PDMS layer on the selectivity when the PDMS layer became thicker.

Finally, Figure 5 showed the results of the experiments with respect to membrane *CB*-5. As Table I indicates, PEI membrane-5 is the most porous membrane cast from the solution with the lowest concentration of PEI polymer. As explained earlier, PDMS coating *CB* consists of two PDMS layers (*C* on top of *B*), each formed by applying dimethylsiloxane solutions, the concentrations of which were much higher than that of coating *A*. The total thickness of the silicone rubber layer was measured by a micrometer after peeling the silicone layer off the substrate membrane. It was less than 25 μm. The results, shown in Figure 5, are almost the same as those of a single PDMS membrane (membrane-*E*) and a laminated PDMS membrane (membrane *E*-5). However, both selectivity and flux of *CB*-5 were higher than those of membranes-*E* and *E*-5.

CONCLUSIONS

From the above experimental results for pervaporation of acetic acid–water mixtures, the following conclusions can be drawn.

1. Polyetherimide (PEI, Ultem) membranes are water selective, whereas PDMS membranes are acetic acid selective.
2. The selectivity of membranes, prepared by coating a PDMS film on the top of a porous PEI support layer, depends on the pore size of the support layer and the method of PDMS coating.
3. When the PEI concentration in the casting solution used for preparation of the support membrane is high, and the concentration of dimethylsiloxane solution coated on the top of the dry PEI support layer is low, the composite membrane becomes water selective.
4. When both the PEI and dimethylsiloxane concentrations in the respective casting solution are low, the composite membrane is nonselective.
5. When the PEI concentration is low and the dimethylsiloxane concentration is high in the respective casting solution, the membrane becomes acetic acid selective.

Analysis of experimental data by pervaporation transport equations is underway in order to elucidate the mechanism of pervaporation through the composite membrane.

REFERENCES

1. G. Tusel, *Market Potential of Pervaporation System*, in: R. Bakish (Ed.), Proc. of Second Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1987, pp. 277–286.
2. H. E. A. Brüschke, *State-of-Art of Pervaporation*, in: R. Bakish (Ed.), Proc. of Fourth Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1989, pp. 1–12.
3. K. W. Böddeker, G. Bengston, and E. Bode, *J. Membrane Sci.*, **53** 143 (1990).
4. R. Y. M. Huang, *Pervaporation Membrane Separation Processes*, Elsevier, New York, 1991.
5. E. Bengtsson, G. Trägåardh, and B. Hallström, *En-*

richment of Aroma Compounds by Pervaporation, W. E. L. Spiess and H. Schubert (Eds.), Engineering and Food, Vol. 3, Advanced Processes, Elsevier, New York, 1990, pp. 270–279.

6. P. Côté and C. Lipski, *Mass Transfer Limitation in Pervaporation for Water and Waste Water Treatment,* in: R. Bakish (Ed.), Proc. of Third Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1988, pp. 449–462.
7. J. Kaschemekat, J. G. Wijmans, R. W. Baker, and I. Blume, *Separation of Organics from Water Using Pervaporation,* in: R. Bakish (Ed.), Proc. of Third Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1988, pp. 405–412.
8. R. Clément, Z. Bendjama, Q. T. Nguyen, and J. Néel, *Extraction of Ethyl Acetate from Aqueous Solutions by Pervaporation Through the GFT Organophilic Composite Membrane,* in: R. Bakish (Ed.), Proc. of Fifth Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1991, pp. 282–290.
9. S. Deng, S. Sourirajan, and T. Matsuura, *Separation of Acetic Acid/Water Mixtures by Pervaporation Using Laminated Hydrophobic and Hydrophilic Membranes,* in: R. Bakish (Ed.), Proc. of Fourth Int. Conf. on Pervaporation Processes in the Chem. Ind., Bakish Materials Corp., Englewood, New Jersey, 1989, pp. 84–92.
10. A. Mochizuki, Y. Sato, H. Ogawara, and Y. Tanaka, Maku (Membrane), **9,** 279 (1984).
11. Y. Chen, T. Miyano, A. Fouda, and T. Matsuura, *J. Membrane Sci.,* **48,** 203 (1990).
12. T. Okada and T. Matsuura, *J. Membrane Sci.,* **59,** 133 (1991).
13. S. Sourirajan and T. Matsuura, *Reverse Osmosis/Ultrafiltration Process Principles,* National Research Council of Canada, Ottawa, 1985.

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