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A Study of Polydimethylsiloxane/Aromatic Polyamide Laminated Membranes for Separation of Acetic Acid/ Water Mixtures by Pervaporation Process

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ABSTRACT

Separation of acetic acid/water mixtures by pervaporation was attempted over a range of compositions using polydimethylsiloxane (PDMS), aromatic polyamide (PA), and laminated polydimethylsiloxane–aromatic polyamide membranes. PDMS membranes are hydrophobic and acetic acid selective, whereas PA membranes are hydrophilic and water selective. When PDMS and PA membranes were laminated, with PDMS on the top side and in contact with the feed, water selectivity of the bottom PA membrane was intensified. On the other hand, when the PA membrane was on the top side and in contact with the feed, the selectivity was lowered.

Key Words. Gas and vapor permeation; Lamination; Pervaporation; Polydimethylsiloxane and aromatic polyamide membrane

INTRODUCTION

In our earlier discussions on the pervaporation mechanism, we divided the membrane into two regions. In one region the transport takes place by liquid transport and in the other by vapor transport, with a clear boundary between those two regions (1–3). In the former region the membrane is highly swollen and nonselective, whereas in the latter region the membrane is dry and governs the selectivity. It can be concluded from the above mechanism that the depth of penetration of the swollen phase in the membrane should exert a strong influence on the selectivity of the membrane. The above effect will become more pronounced when an asymmetric membrane, in which the pore size increases from one side of the membrane to the other side, is used for pervaporation. Suppose the densest and the least porous side faces the feed liquid mixture. This side is supposed to be the most effective for the separation of a liquid mixture when it is dry, but is now highly swollen. When the depth of penetration of the swollen phase is greater than the thickness of the densest and least porous section of the membrane, the permeant will meet the dry membrane section only after passing the most effective layer, since the dry section is no longer the least porous. As a result, membrane performance will not be as high as it is supposed to be when the least porous section of the membrane is dry and fully contributing to the selectivity. One method to avoid the above problem is to let the porous side of the asymmetric membrane face the feed liquid (4). This, however, would worsen the concentration polarization on the feed side.

Another possible method is to coat the densest and least porous side of the asymmetric membrane with another (not necessarily highly selective) barrier layer. It is expected that this measure will stop swelling in the coated layer and swelling will not penetrate into the asymmetric membrane. The thickness of the coated layer should be large enough so that swelling is only in the coated layer. On the other hand, the thickness of the coated layer should not be so large that the membrane permeation rate will be reduced very much.

The objective of this work was to test the applicability of the above concept to improve membrane selectivity by coating. Asymmetric membranes were prepared from PA material for this purpose, and pervaporation of pure acetic acid, water, and acetic acid/water mixtures was attempted. Similar pervaporation experiments were performed with PDMS membranes. Then the PDMS and PA membranes were laminated and the pervaporation experiments were repeated. If placing the PDMS membrane on top of the PA membrane can effectively prevent the penetration of swelling into the asymmetric PA membrane, the selectivity of the asymmetric PA membrane should be improved. There are other comprehensive studies on the separation of acetic acid/water mixtures by pervaporation (5–7), but none of the previous work was done with the above objective.

EXPERIMENTAL

Pervaporation of pure acetic acid, pure water, and acetic acid/water mixtures was studied using PDMS membranes, PA membranes, and a combination thereof. The permeation cells used for pervaporation were the same as the static cells used for reverse osmosis and ultrafiltration experiments (8). The effective area of the membrane was 9.6 cm^2. About 100 g of feed liquid was loaded into the cell, and a vacuum was applied at the downstream side of the membrane. The permeate sample was condensed and collected in a cold trap cooled with liquid nitrogen. The amount of sample removed was kept below 10% of the initial feed volume. The permeation rate was determined by measuring the weight of the sample collected during a predetermined period. The composition of the sample was determined by refractive index measurement. The temperature was controlled at 23°C throughout the pervaporation experiments. The downstream pressure was controlled within ±1 mmHg. PDMS membranes (thickness, 25 μm) were generously supplied by General Electric Company. PA membranes were laboratory prepared by the method described by Nguyen et al. (9). PA (poly-*m*-phenylene-iso(70)-*co*-tere(30)-phthalamide, 10.3 wt%), LiCl (3.8 wt%), and dimethyl acetamide (85.9 wt%) were mixed and cast on a glass plate. The cast film was then heated at 95°C for 15 minutes before gelation in ice-cold water. The membranes so produced were used for the pervaporation experiments without further treatment. While PDMS membranes are homogeneous, PA membranes are asymmetric in structure.

RESULTS AND DISCUSSION

Figure 1 illustrates the results of pervaporation experiments with PA (a and b) and PDMS (c and d) membranes. Figures 1(a) and 1(b) illustrate the pervaporation rate of pure acetic acid and water, respectively, through a PA membrane at different downstream pressures. For both acetic acid and water the experimental results showed a typical pervaporation curve with a clear inflection point near the saturation vapor pressure of the permeant. Since the water permeation rate is higher than that of acetic acid, the membrane is water selective. This is natural since PA is a hydrophilic material. Figures 1(c) and 1(d) illustrate the pervaporation rate of pure acetic acid and water, respectively, through a PDMS membrane. Again, typical pervaporation curves were obtained. The selectivity is, however, reversed, and the PDMS membrane is acetic acid selective, which is also natural since PDMS is a hydrophobic material.

Figure 2 illustrates the results of reverse osmosis experiments with PDMS and PA membranes. Since the acetic acid mole fractions in the permeate were nearly equal to those of the feed, both PDMS and PA membranes were not selective in the entire range of the feed mole fraction for the RO process.

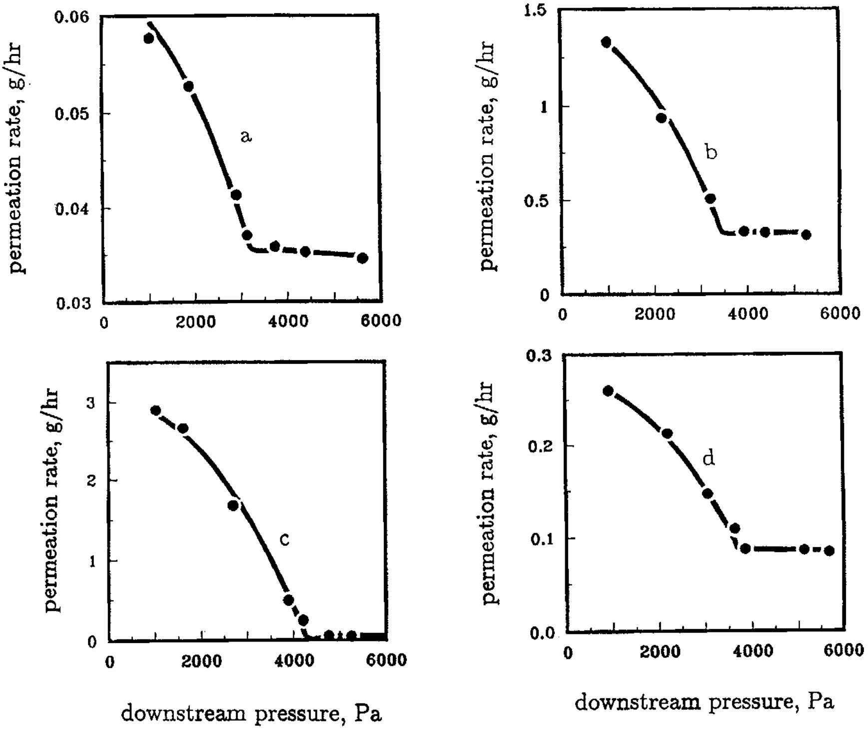

FIG. 1 Permeation rate versus downstream pressure for pervaporation of pure component systems. Upstream pressure, atmospheric; temperature, 23°C. (a) Acetic acid with PA membrane. (b) Water with PA membrane. (c) Acetic acid with PDMS membrane. (d) Water with PDMS membrane.

Figures 3 and 4 show the acetic acid mole fraction in the permeate and the total permeation rate as a function of the acetic acid mole fraction in the feed. As expected, the PDMS membrane, when used individually, was acetic acid selective, and the acetic acid mole fraction in the permeate was higher than in the feed. The permeation rate increased with an increase in the acetic acid mole fraction in the feed. On the other hand, the PA membrane, when used individually, was water selective, and the acetic acid mole fraction in the permeate was less than in the feed. The permeation rate decreased with an increase in the acetic acid mole fraction in the feed. Interestingly, water selectivity of the PA membrane was intensified significantly when PDMS and PA membranes were laminated, with the PDMS membrane being in contact with the feed mixture. The total permeation rate was almost constant in the entire range of feed compositions.

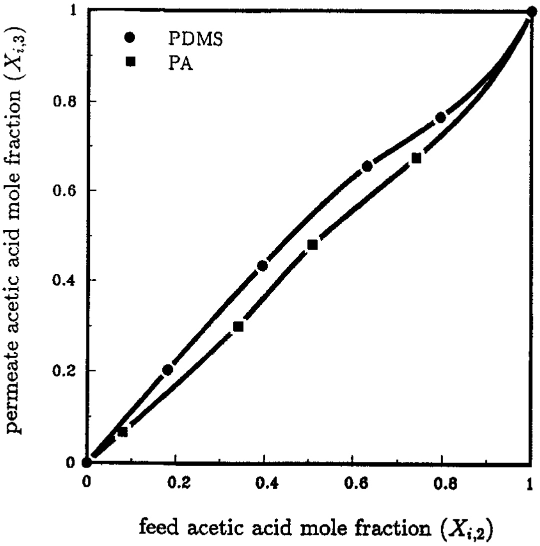

FIG. 2 Experimental results of reverse osmosis separation of acetic acid/water mixtures. Operating pressure, 3447 kPa (gauge) (= 500 psig).

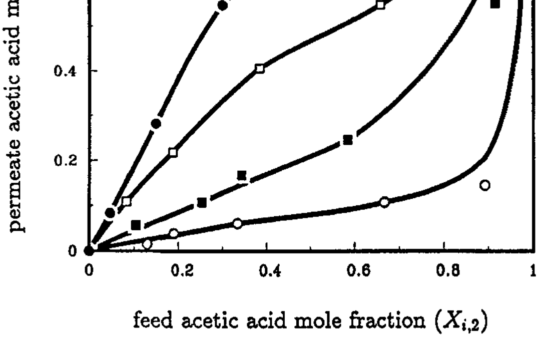

FIG. 3 Experimental separation results of pervaporation of acetic acid/water mixtures. Downstream pressure, 1000 Pa; temperature, 23°C.

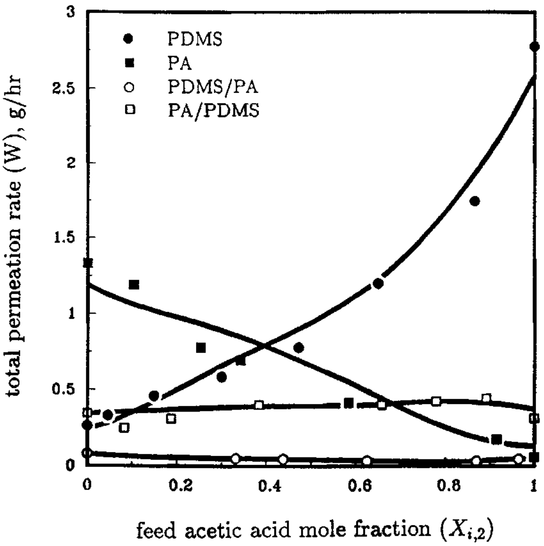

FIG. 4 Experimental total permeation rate results of pervaporation of acid/water mixtures. Downstream pressure, 1000 Pa; temperature, 23°C.

Similar phenomena were reported by Mochizuki et al. in 1984 (10). They studied the pervaporation performance of PDMS and polyvinyl alcohol/polyvinylpyrrolidone (PVA/PVP) blend membranes to separate benzene/methanol mixtures. Both membranes were dense and homogeneous. When the membranes were used individually, the PDMS membrane was benzene selective whereas the PVA/PVP blend membrane was methanol selective. This is natural since PDMS and PVA/PVP blend polymers are hydrophobic and hydrophilic, respectively. When they were laminated, with the PDMS membrane being in contact with the feed mixture, the bilayer membrane became methanol selective. On the other hand, when they were laminated with the PVA/PVP membrane in contact with the feed mixture, the bilayer membrane became benzene selective. In both cases the selectivity was governed by the membrane that was not in direct contact with the feed mixture. Mochizuki et al. explained this phenomenon in the following way. The membrane that is in contact with the feed liquid mixture is highly swollen and does not contribute to membrane selectivity, whereas the membrane on the downstream side is dry and governs membrane selectivity.

The same principle may apply to our experiments where PDMS and PA membranes were laminated; i.e., the PA membrane, placed on the downstream side, remained dry and governed the selectivity of the bilayer membrane. However, there is some difference between the experiment of Mochizuki et al. and ours. While both membranes used by Mochizuki et al. were dense and homogeneous, our PA membrane was asymmetric. It is well known that there is a gradient of the pore size across the cross section of an asymmetric membrane; i.e., the pore size increases gradually from one side of the membrane to the other. Suppose an asymmetric PA membrane without lamination is used for pervaporation, the most dense and least porous side being in contact with the feed liquid. While this side is supposed to be the most effective for separation of the feed mixture, it now faces the feed liquid and is highly swollen. The permeant should penetrate through the dense skin layer deeply into the membrane until it meets a dry section. This section is no longer the densest and least porous. Therefore, the observed selectivity of the PA membrane does not necessarily correspond to the highest selectivity of the asymmetric membrane. When, on the other hand, a PDMS membrane is laminated on top of an asymmetric PA membrane, swelling stops inside the PDMS membrane and the densest section of the PA membrane can be maintained dry. Therefore, the most effective section of the PA membrane can contribute to membrane selectivity. This is the reason why a laminated membrane in which the PDMS membrane is in contact with the feed liquid showed water selectivity higher than that of the PA membrane itself.

When PDMS and PA membranes were laminated, with the PA membrane in contact with the feed liquid, the acetic acid mole fraction in the permeate was between those of individual PDMS and PA membranes. As a result, the selectivity of such a bilayer membrane is very poor. These results indicate that the lamination had no favorable effect on the selectivity of the PDMS membrane.

The above explanation can also be justified by the following observations. The surface of a wet PA membrane was blotted and a drop of water was placed on it. There was no change on the membrane surface. On the other hand, when a drop of acetic acid was placed on it, wrinkles formed on the surface, indicating swelling of the membrane surface.

The second observation is concerned with the PA membranes used. Three PA membranes were involved. One was a PA membrane without lamination (PA(a)), the second was a PA membrane laminated to the top of a PDMS membrane (PA(b)), and the third one was a PA membrane laminated to the bottom of a PDMS membrane (PA(c)). After pervaporation experiments were performed with acetic acid/water mixtures for 2 weeks, the PA membrane was peeled off the PDMS membrane and its surface was observed. While the PA(a) and PA(b) membranes were swollen and wrinkled, the PA(c) membrane remained smooth. This observation indicates that the top PDMS membrane protected the PA(c) membrane from swelling.

CONCLUSIONS

The following conclusions can be drawn from the above experimental results.

1. When two membranes are laminated, both component membranes contribute to the overall selectivity of the bilayer membrane.
2. When a hydrophobic homogeneous membrane and an asymmetric hydrophilic membrane are laminated, with the former membrane in contact with the feed liquid, the water selectivity of the latter membrane is intensified. This is because the densest and least porous section of the asymmetric membrane is kept dry and contributes to the selectivity of the bilayer membrane most effectively.

The above conclusions are extremely important for the design of highly selective membranes. It is desirable to coat a very thin layer of hydrophobic material on top of an asymmetric hydrophilic membrane to utilize fully the separation capability of the latter membrane while maintaining a reasonably high permeation rate.

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