

SHORT COMMUNICATIONS

## Pervaporation of Water-Ethanol through Synthetic Polymer Membranes Having Cationic Charge Sites

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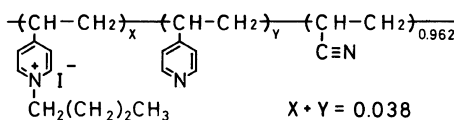
Separation of organic substrates from aqueous solution through membranes was extensively studied. For instance, synthetic polymer membranes having imide groups,<sup>1,2</sup> N-substituted imide groups,<sup>3</sup> carboxylic acid moieties,<sup>4,5</sup> or N-substituted imide and ester group,<sup>6,7</sup> selectively permeated water from aqueous ethanol (alcohol) or aqueous acetic acid solution by the pervaporation technique using hydrogen-bonding interactions. Especially, the poly{1-(2-methylpropenoxyloxy)-succinimide-co-acrylonitrile} membrane gave a high separation factor, which exceeded 2000 for water.<sup>6</sup> Although these membranes permeated water preferentially, the flux values were less than 100 g m<sup>-2</sup> h<sup>-1</sup>. From the viewpoint of industrial utilization of synthetic polymer membranes for the separation of aqueous ethanol (alcohol) solution, the membrane should have the following properties: a separation factor toward water over 50 and a flux value over 500 g m<sup>-2</sup> h<sup>-1</sup>.<sup>8</sup>

The separation factor of water from water-ethanol solution was attempted through ion exchange membranes by pervaporation using coulombic interactions instead of hydrogen-bonding interactions.<sup>9</sup> Another attempt was

made to pervaporate water through a partially quaternized poly(4-vinylpyridine) membrane.<sup>10</sup>

Based on industrial considerations, synthetic polymer membranes having cationic charges, poly(1-butyl-4-vinylpyridinium iodide-co-acrylonitrile) membranes, were prepared and the selective separation of a water-ethanol mixture through the present membranes was investigated.

Poly(4-vinylpyridine-co-acrylonitrile) (1), whose unit mol fraction of 4-vinylpyridine was 0.038, was synthesized by a radical copolymerization of 4-vinylpyridine and acrylonitrile initiated by 2,2'-azobisisobutyronitrile in *N,N*-dimethylformamide (DMF) solution at 45°C. Poly(1-butyl-4-vinylpyridinium iodide-co-ac-



Polymer	X	Y	Fraction of quaternization/%
1	0	0.038	0
2	0.015	0.023	39.5
3	0.038	0	100

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rylonitrile)s (**2** and **3**) were prepared by the reaction of **1** and iodobutane in DMF solution at 60°C. The chemical compositions of **2** and **3** were measured by <sup>1</sup>H NMR spectra recorded on a JEOL FX200 (199.5 MHz).

Membranes were prepared from DMF solution. Their thickness was 20–28 μm. Pervaporation of the water–ethanol mixture was carried out as described previously.<sup>1–7</sup> The separation analysis was carried out on a Shimadzu GC-8A Gas Chromatograph equipped with a 1-m long column packed with Porapak Q. The separation factor,  $\alpha$ , is defined as

$$\alpha = \frac{Y_{\text{Water}}/Y_{\text{Ethanol}}}{X_{\text{Water}}/X_{\text{Ethanol}}}$$

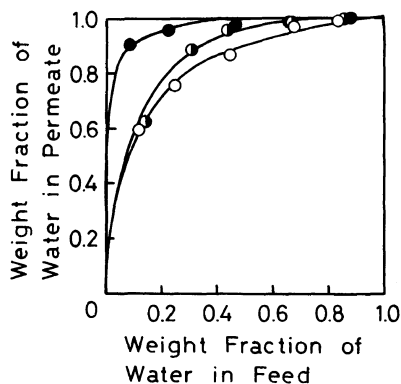
where  $Y_i$ 's are the weight fractions of the permeates and  $X_i$ 's those of the feeds.

Figure 1 indicates the results of pervaporation at 15°C through these three membranes. The weight fractions of water in permeates were plotted against those in the feeds. Figure 1 shows that as the fraction of quaternization increases, the more preferentially is water permeated through the membranes.

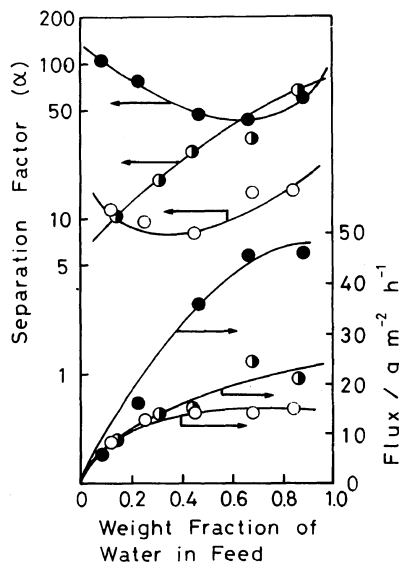
Figure 2 gives the effects of feed composition on flux and the separation factor,  $\alpha$ , at 15°C. In Figure 2, the  $\alpha$  values for membranes **1** and **2** increased with water fraction in the feeds, while those for membrane **3** to increase with decreasing water fraction. On the other hand, the total flux increased with water content in the feeds as expected from the fact that the present membranes preferentially permeate water.

In order to study the permeation mechanism, we separated the observed fluxes into their respective water and ethanol components, so that each component-flux could be plotted against its feed concentration. The separated fluxes are shown in Figure 3.

The dependence of water flux on water concentration in the feed exhibited a typical Michaelis–Menten profile (Figure 3(a)). In other words, the fluxes approached asymptotic limits as the water concentration in the feed



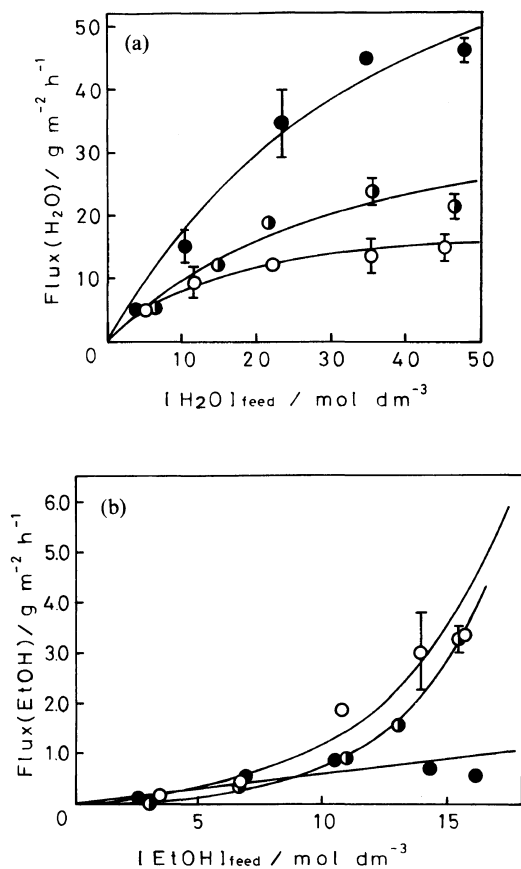
**Figure 1.** Effects of feed composition on the separation of a water–ethanol mixture through membranes **1**, **2**, and **3** at 15°C: ○, membrane **1**; ●, membrane **2**; ●, membrane **3**; down-stream pressure, 400 Pa (3.0 torr).



**Figure 2.** Effects of feed composition on flux and the separation factor,  $\alpha$ , through membranes **1**, **2**, and **3** at 15°C: ○, membrane **1**; ●, membrane **2**; ●, membrane **3**; down-stream pressure, 400 Pa (3.0 torr).

increased. This result strongly supports that water is permeated through the three membranes by a carrier-mediated mechanism, where a carrier (pyridine or (and) pyridinium cation) is immobilized in the membrane.

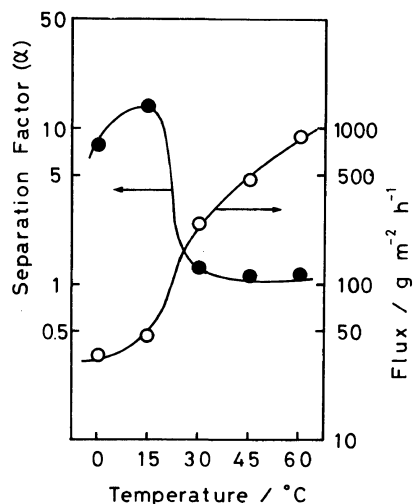
On the other hand, ethanol flux through membranes **1** and **2** showed exponential profiles. This may be due to microscopic swelling



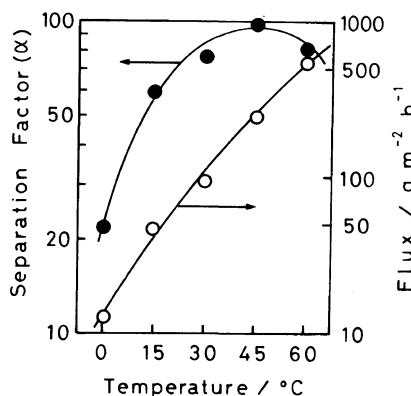
**Figure 3.** Effects of water and ethanol concentration on their fluxes in water-ethanol pervaporation through membranes 1, 2, and 3 at 15°C: ○, membrane 1; ◐, membrane 2; ●, membrane 3; down-stream pressure, 400 Pa (3.0 torr).

which did not affect water permeation, forming a permeation path for ethanol. Membrane 3 had less dependence of the ethanol flux on the ethanol feeds, and was hardly observed in the microscopic swelling. This might be due to the high concentration of pyridinium cations in the membrane. As reported for a charge-mosaic membranes,<sup>11</sup> the incorporation of cationic charge sites into the membrane caused depression of the permeation of neutral organic compounds such as ethanol.

We previously reported,<sup>1,4,6,7</sup> that selectivity and flux are remarkably dependent on operat-



**Figure 4.** Effects of operating temperature on water-ethanol pervaporation through membrane 2: Weight fraction of water in feed, *ca.* 0.86; down-stream pressure, 400 Pa (3.0 torr).



**Figure 5.** Effects of operating temperature on water-ethanol pervaporation through membrane 3: Weight fraction of water in feed, *ca.* 0.88; down-stream pressure, 400 Pa (3.0 torr).

ing temperatures. Accordingly, the effects of the permeation through membranes 2 and 3 were investigated. Figures 4 and 5 show the dependence of membrane permeabilities on operating temperatures through membranes 2 and 3. In both systems, the flux values increased with operating temperature. Especially, membrane 3 showed good results over 30°C; that is, the  $\alpha$  value exceeded 77 and the

flux value was 100—550 gm<sup>-2</sup> h<sup>-1</sup>.

As mentioned above, the incorporation of cationic charge sites into the membrane made it possible to selectively separate water from aqueous ethanol solution by pervaporation as reported by Wenzlaff *et al.*<sup>9</sup> Variables such as the kind of alkyl group (quaternized reagents), counter ions such as Br<sup>-</sup>, Cl<sup>-</sup>, SCN<sup>-</sup>, and OH<sup>-</sup>, the fraction of quaternization, and the concentration of a fixed carrier in the membrane may lead to the preparation of better membranes for water permeation than those already reported. Further investigation is in progress and results will be reported shortly.

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