Ethanol-Selective Membrane for Reverse Osmosis of Ethanol/Water Mixture

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For the separation of ethanol/water by pervaporation, there are two kinds of membranes: ethanol-permselective and water-permselective membranes. In most cases, water selectively permeate through the membrane from the mixture. However, a limited number of membranes have been reported to have ethanol permselectivity (Kimura and Nomura, 1983; Ishihara and Matsui, 1987; Nagase et al., 1990).

Considering the similarity in the transport mechanism of pervaporation and reverse osmosis, selectivity of both cases should be similar. Many reverse osmosis membranes, which reject ethanol, have water permselectivity in pervaporation. However, only one report has been made on an ethanol-permselective reverse osmosis membrane with a very limited ethanol selectivity (rejection of water was 0.0003[–]) (Hashida et al., 1984).

Recently, Nagase et al. (1990) obtained an ethanol-permselective membrane with an excellent pervaporation separation factor. This result strongly suggests the need to investigate its nature in the reverse osmosis condition. And our experimental results show that this membrane has ethanol selectivity.

Experimental Results

Membrane preparation

An *n*-hexyldimethylsilylated Poly(1-trimethylsilyl-1-propyne) (*n*-hexyldimethylsilylated PTMSP), synthesized by Sagami Chemical Research Center, was used. Its polymer structure is shown in Figure 1. The number- and weight-average molecular weights are 2.50×10^5 and 7.60×10^5, respectively. The molecular weight was determined by gel permeation chromatography using standard polystyrenes to calibrate these values. A ratio of TMSP monomer unit to *n*-hexyldimethylsilylated unit (x/y) of 93/7 was determined by an H^1-NMR spectrometer. Toluene solution of the polymer of about 2 wt % was cast on a polytetrafluoroethylene sheet and the toluene was evaporated over 24 hours. The thicknesses of the membranes used for reverse osmosis and pervaporation were 20 μm and 25 μm, respectively.

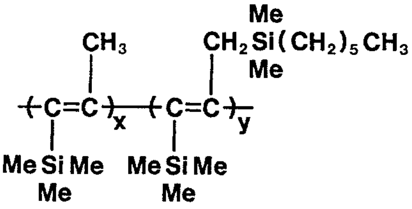

Figure 1. Molecular structure of *n*-hexyldimethylsilylated PTMSP.

Reverse osmosis

A batch-type cell with an effective membrane permeation area of 19.6 cm^2 was used for reverse osmosis (RO). The feed solution was pressurized from 3.9 MPa to 7.8 MPa by nitrogen gas and stirred using a magnetic stirrer. The feed temperature was maintained at 25°C.

Pervaporation

Pervaporation (PV) experiments were carried out to compare the results of Nagase et al. The feed solution at 25°C was circulated by a magnetic pump. The effective membrane permeation area was 26.4 cm^2. Pressure on the permeate side was kept at 2-3 torr (266–399 Pa) using a vacuum pump, and the permeate vapor was trapped using liquid nitrogen.

Results and Discussion

Figure 2 shows the ethanol concentration in the permeate for RO and PV. Under the conditions selected for this study for both

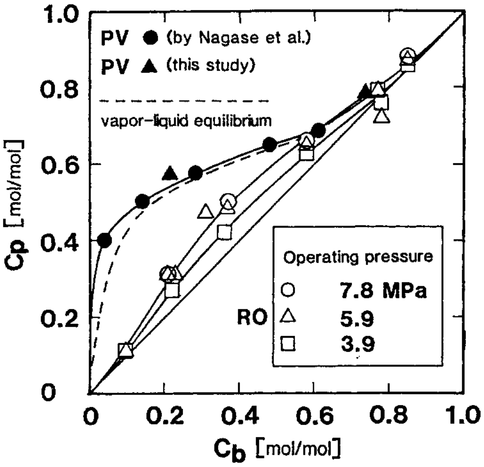

Figure 2. Ethanol concentration: in the permeate, C_p, vs. in the bulk feed, C_b.

RO and PV, the effect of concentration polarization could be ignored. Therefore, the ethanol concentration at the membrane surface on the feed side could be assumed to be the same as that in bulk feed. The PV results of this study and of Nagase et al. were comparable. For RO, an ethanol permselectivity was clearly observed at a medium feed concentration. The difference between the selectivity at 5.9 MPa and at 7.8 MPa is insignificant. A higher ethanol selectivity was observed in the case of PV than in that of RO.

Ethanol activity in the permeate is higher than that in the feed in the ethanol-permselective RO, and ethanol transport is restrained by the osmotic pressure in RO. In contrast to RO, in the ethanol-permselective PV, the ethanol activity in the permeate is lower than in the feed since the permeate side is vacuumed. Therefore, ethanol selectivity can be considered lower in RO than in PV. Furthermore, the phase in the permeate side in PV is vapor. From this point, even if the membrane itself does not have selectivity, the permeate concentration would approach the vapor-liquid equilibrium: i.e., ethanol permselectivity would result in PV.

Figure 3 shows the rejection of water calculated by the following equation:

$$R = \frac{C_p - C_b}{1 - C_b}$$

where R is the rejection of water. C_b and C_p are the ethanol mol fractions in bulk feed and in the permeate, respectively. R

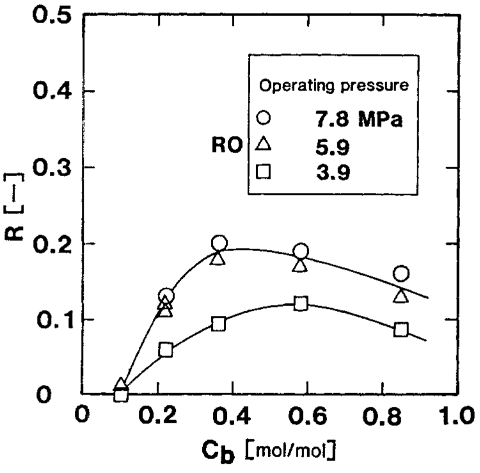

Figure 3. Rejection of water, R, vs. ethanol concentration in the bulk feed, C_b.

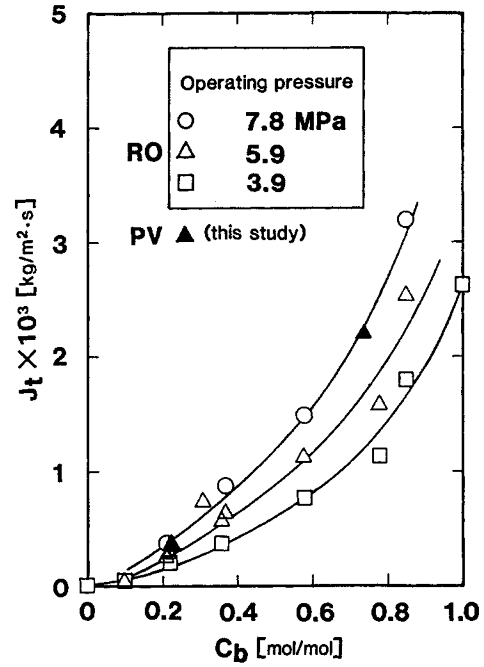

Figure 4. Dependence of total flux, J_t, on ethanol concentration in the bulk feed, C_b.

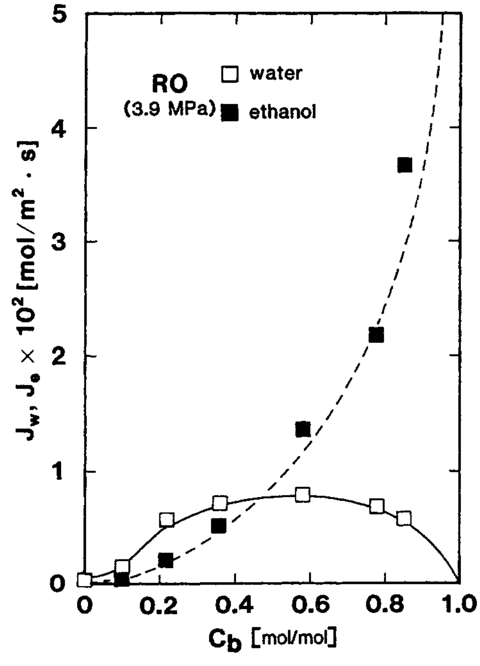

Figure 5. Dependence of water flux, J_w, and ethanol flux, J_e, on ethanol concentration in the bulk feed, C_b.

reaches a maximum at about 0.4–0.6 mol/mol of ethanol concentration.

Total flux is shown in Figure 4. It increases significantly with the increase in the ethanol concentration of the feed. This tendency is opposite to that of water-permselective RO membranes (Ohya et al., 1981). Flux in PV was multipled by 25/20 in order to compare PV with RO, because the thickness of the membranes used for RO and PV were 20 μm and 25 μm, respectively, as described previously. Total flux in PV was nearly equal to that in RO at the operating pressure of 7.8 MPa.

Water and ethanol flux for RO are given in Figure 5. Ethanol flux increases greatly with the increase in ethanol concentration in the feed, whereas water flux reaches a maximum at medium concentration.

Acknowledgment

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Notation

R = rejection of water
C_b = ethanol mol fraction in the bulk feed
C_p = ethanol mol fraction in the permeate
J_t = total flux
J_w = water flux
J_e = ethanol flux

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