NOTES

Permeation Characteristics of Porous Glass and Hydrogel Composite Membrane

Recently the authors[1] proposed a new method for producing a porous glass and hydrogel composite membrane that has the distinctive feature of enabling a switching function in solution permeation rates when a discontinuous volume-phase transition of the hydrogel[2,3] occurs. This capability was demonstrated in previous experiments[1] where the volume fluxes of aqueous solutions permeating the membrane were measured in different swollen states of the hydrogel. It was shown that the volume flux changed rapidly and reversibly according to a change in the degree of swelling of the gel and that the magnitude of the volume flux change was as great as 1000-fold. The present work has been performed to measure the selectivities of the membrane for aqueous polymer solutions in different swollen states of the hydrogel.

EXPERIMENTAL

In the preparation of the composite membrane, a porous glass plate (average pore diameter = 4500 Å, thickness = 1 mm) supplied by Asahi Glass Co. Ltd. was used as a support, on which acrylamide (AAm)/acrylic acid (AAc) copolymer gel was fixed chemically by application of radical polymerization. First, the surface of the porous glass was modified by the condensation reaction of AAc with hydroxyl groups on the glass surface in order to introduce substituents with a double bond. Then the surface-modified porous glass was soaked in an aqueous solution that contained the monomers of AAm and AAc, a crosslinker of N,N'-methylenbisacrylamide and an initiator of potassium persulfate, at total monomer content = 10 wt %, AAm/AAc mol ratio = 4/1, initiator concentration = 2.3×10^{-2} wt %, and crosslinker concentration = 1.2×10^{-1} wt %. The radical polymerization was performed by heating the soaked porous glass to 70°C.

The composite membrane prepared was subjected to permeation experiments, all of which were conducted at 25°C using aqueous acetone solutions as solvents. The solute used was polyethyleneglycol (PEG) in six different molecular weights. Table I shows the molecular weights of PEG measured by gel permeation chromatography. The membrane was placed in a permeation cell equipped with a stirrer. The volume of the cell was 500 cm^3 (diameter = 53 mm, height = 218.4 mm) and the diameter of the stirrer was 43 mm. In each run, the feed solution was agitated with the stirrer at a impeller speed of 500 rpm. Solute concentration in the feed solution was 1 g/L. The pressure difference between the feed and permeate solutions was set with nitrogen at 10 kg/cm^2, and the pressure of the permeation solution was maintained at atmospheric pressure. Solute concentrations in the permeate solutions were determined by liquid chromatography and the observed rejection R_{obs} defined by eq. (1) was calculated:

$$R_{obs} = 1 - C_p/C_f \tag{1}$$

where C_f is the solute concentration in feed solution and C_p that in permeate solution. The volume fluxes of the permeate solutions were measured by a volumetric method, and the compositions of solvents were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Figure 1 shows a comparison of acetone weight fractions measured in the feed and permeate solutions. As reported in our previous work, in the range of acetone weight fractions below 30%

TABLE I
Number-Average Molecular Weight and Dispersity of PEG

	M_n	M_w/M_n
PEG 1000	985	1.03
PEG 2000	2149	1.02
PEG 7500	7210	1.01
PEG 20000	23,573	1.04
PEG 85000	75,787	1.21
PEG 160000	102,135	1.48
PEG 500000	332,735	2.08

the gel was swollen, but in the higher range it was shrunken. In Figure 1, the acetone weight fraction in the permeate solution is the same as that in the feed solution over the whole range of compositions measured. Thus the membrane did not exhibit any selectivity towards the solvent components even when the gel was in swollen or shrunken states. However, this is not the case for the polymer solute in the solutions.

Figure 2 shows the experimental results of R_{obs} for PEG of various molecular weights. In the experiments, pure water and 50 wt % aqueous acetone solution were used as the solvents. As seen from the figure, the value of R_{obs} dramatically changed from the swollen state of the gel in the pure water to its shrunken state in the 50 wt % aqueous acetone solution. The cut-off molecular weight was about 4000 for the pure water, but 80,000 for the 50 wt % aqueous solutions. The volume flux of the permeation solution for the former solvent was 4×10^{-5} cm/s, which was about 500 times smaller than that for the latter solvent.
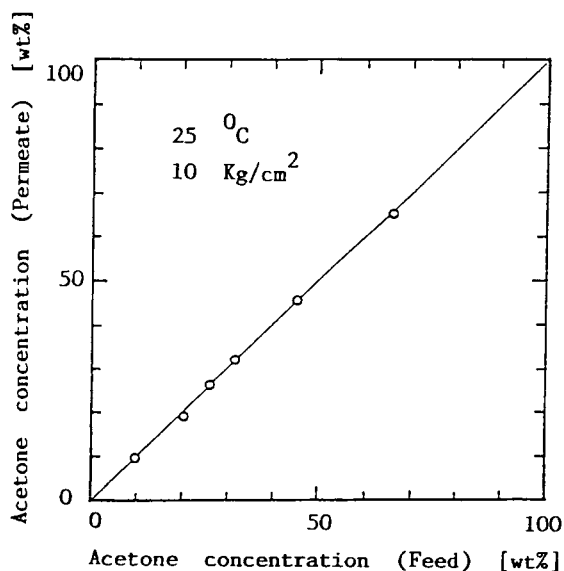

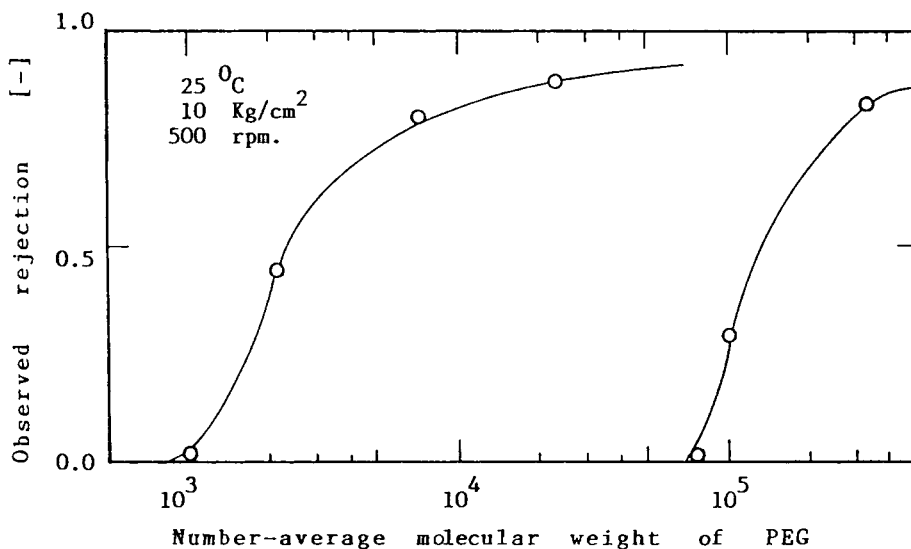Fig. 1.   Solvent composition of feed and permeate solution.

Fig. 2.   Observed rejections of PEG in pure water and 50 wt % aqueous acetone solution.

These experimental results suggest that the gel supported on the membrane has micropores, whose diameter greatly changes according to the degree of the swelling.

References

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