

Selective Permeation Properties of Ions through Piezodialysis Membrane

INTRODUCTION

Piezodialysis is a membrane process for desalination utilizing a mosaic membrane under a pressure gradient,¹ and this concept was first predicted in 1932 by Sollner.² The mosaic membrane is composed of anion exchange elements and cation exchange elements and enhances salt permeability by circuit current.³ Various membrane preparation methods for piezodialysis have been reported such as the phase inversion method,⁴ ionotropic gel templates method,⁴ and masking method.⁵ It was reported that a piezodialysis membrane with a good permeation property was prepared by a latex-polyelectrolytes method.⁶ However, the preparation of piezodialysis membranes has been very difficult, and the selective permeation properties have been little studied with piezodialysis membranes.

We prepared a piezodialysis membrane by dispersing ion exchange resins in a poly(vinyl chloride) membrane and investigated the selective permeation properties through the membrane. The selectivities of the salt permeability was high, although the enrichment factor was low. The preliminary study will be reported in this paper.

EXPERIMENTAL

Membrane Preparation. Mosaic membrane were prepared by a casting method. The casting solution was composed of 1 g of cation exchange resin (Amberlite CG-120, 400–600 mesh) and anion exchange resin (Amberlite CG-400, 400–600 mesh), 1 g of polyvinyl chloride, PVC ($n = 1100$) as a binding agent, and 10 mL of tetrahydrofuran. After shaking the solution vigorously for more than 1 h, the solution was cast on a glass plate and evaporated for 1 h. Then, it was immersed in water to obtain a mosaic membrane of 60 μm thickness.

Measurements. Permeability under a pressure gradient was measured with a flow-type or batch-type hyperfiltration apparatus. Permeability, P was determined as follows⁷:

$$P = \frac{\text{concn in permeated solution}}{\text{concn in feed solution}} \quad (1)$$

The term "enrichment factor" was also used with the same implication as permeability in this paper. The concentrations of the salt in the permeated solution and in the feed solution were measured by means of a flame photometer or an atomic absorption spectrophotometer.

The diffusion flux was measured with a dialysis cell which was composed of two cylindrical compartments with 38 mm diameter and 3 mm thickness.⁷ The membrane was set between the two compartments and a concentrated solution (0.1 mol/L), and pure water were pumped to each cell at a rate of 20 cm^3/min . The diffusion flux was calculated from the measurement of the concentration change with time in the dilute solution. The concentrations were measured as described above.

The membrane potential was determined with two glass cells separated by the membrane and with calomel electrodes.⁸ Salt solutions of different concentrations (0.1 and 0.2 mol/L) were circulated from a reservoir to each cell with a micro tube pump.

The volume flux was measured with two glass cells separated by the membrane. After salt solutions of different concentrations (0.1 and 0.2 mol/L) were placed in each cell, a horizontal capillary was attached to each cell. The volume flux was calculated from the movements of the meniscus in the capillaries at 25°C.

RESULTS AND DISCUSSION

The membranes with various ratios of the cation exchange resin to the anion exchange resin were prepared and their transport properties were investigated. Figure 1 shows the effect of membrane compositions on membrane potential, diffusion flux, and permeability for potassium chloride. The

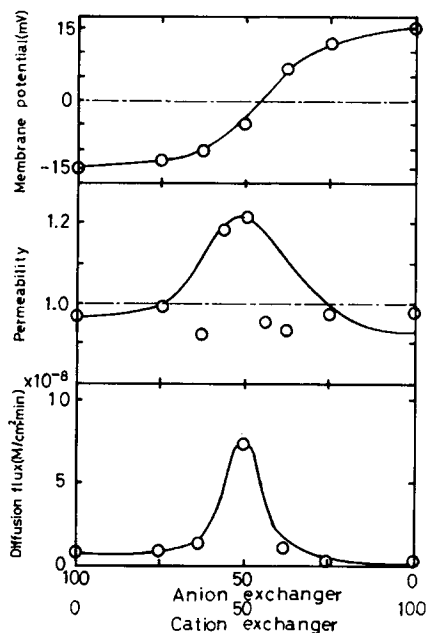


Fig. 1. Effect of mosaic membrane composition. Permeability measurement: 0.1 mol/L KCl feed solution under 40 kg/cm²; membrane potential measurement: 0.1–0.2 mol/L KCl solution; diffusion flux measurement: 0.1 mol/L KCl solution–pure water.

membranes in this experiment consisted of PVC and the resins in the ratio of 2:5 and were 270 μm thick. When the cation exchange capacity was equal to the anion exchange capacity, the membrane potential became close to zero, the diffusion flux was maximum, and salt enrichment occurred under a pressure gradient. The circuit current density, I_{circuit} is defined by the following equation⁹ when the diffusion flux was a maximum:

$$I_{\text{circuit}} = F \times J_s \quad (2)$$

where F is the Faraday constant and J_s is the salt flux through the active membrane area. This membrane did function as a piezodialysis membrane, although the reproducibility of the piezodialysis data of the membrane was too low to compare the selective permeation properties of salts due to mechanical weakness. Then, the selective permeation properties through the mosaic membrane were investigated by dialysis and osmosis experiments under a concentration gradient of various salts.

Effects of the membrane thickness and the amount of the exchange resin were investigated to obtain a mosaic membrane which generated an effective circuit current. The diffusion flux of the mosaic membrane increased with decreasing the membrane thickness, but the salt leakage could not be ignored when the membrane thickness was less than 50 μm . The salt leakage was estimated by comparison with the membrane containing only cation exchange resin prepared in the same way as that of the mosaic membrane. The amount of the ion exchange resin in the membrane also affected the membrane characteristics and the salt flux increased with increasing the amount of the resin. However, the salt leakage also increased with increasing amounts of resin due to the difference between the swelling properties of ion exchange resins and PVC. Then, the membranes prepared as described in the experimental section were used hereafter.

Selective permeation properties were studied for alkali metal chlorides, and the membrane potential, the diffusion flux of salt, and the volume flux are shown in Figure 2. The membrane potential increased with increasing ion radius of the alkali metal ions. The membrane potential E of the membrane whose fixed charge density is zero is described as follows¹⁰:

$$E = \frac{RT}{F} \frac{U_C - U_A}{U_C + U_A} \ln \frac{C_2}{C_1} \quad (3)$$

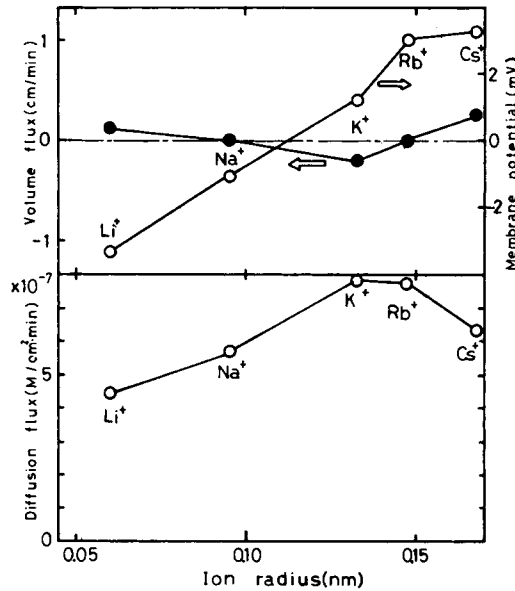


Fig. 2. Effect of ion radius. Volume flux measurement: 0.1–0.2 mol/L salt solution; diffusion flux measurement: 0.1 mol/L salt solution–pure water; membrane potential measurement: 0.1–0.2 mol/L salt solution.

where U_C , U_A , C_2 , C_1 are the mobilities of cation and anion and the concentrations of the concentrated solution and the dilute solution, respectively. The theoretical values calculated from the ion mobilities¹¹ were -5.84 mV, -3.70 mV, -0.32 mV, $+0.18$ mV, and $+0.11$ mV for LiCl, NaCl, KCl, RbCl, and CsCl, respectively. The experimental values differed from the theoretical values mainly because the ion mobility in solution was different from that in the membrane. When the membrane potential was zero, the diffusion flux was maximum and negative osmosis, which was the volume flux from the concentrated solution to the dilute solution, was realized. The membrane functioned as a cation exchange membrane to the salts generating a positive membrane potential and the membrane functioned as an anion exchange membrane to the salts generating a negative membrane potential. In these cases, the diffusion flux was low and a normal osmosis was observed.

Selective permeation properties of bivalent, univalent and bivalent electrolytes were also studied and are shown in Table I. The interaction of an ion exchange resin with multivalent counterion is much larger than that with univalent counterion, and the mobilities of multivalent counterion are low in ion exchange resins.¹² The absolute values of the membrane potential for the symmetric salts were smaller than that for asymmetric salts. All the salt in this table generated a normal osmosis, and the asymmetric salts generated larger volume flux than the symmetric salts. The diffusion flux of the salt containing bivalent ion was small because of the low mobility of these ions in the mosaic membrane.

TABLE I
Volume Flux, Diffusion Flux, and Membrane Potential of Some Salts^a

Salt	V (mV)	$J_V \times 10^5$ (cm/min)	$J_s \times 10^8$ (mol/cm ² ·min)
K ₂ SO ₄	+13.6	+2.6	40.8
MgCl ₂	-13.4	+1.6	14.6
MgSO ₄	+1.19	0.0	6.11

^a Volume flux measurement: 0.1–0.2 mol/L salt solution; diffusion flux measurement; 0.1 mol/L salt solution–pure water; membrane potential measurement: 0.1–0.2 mol/L salt solution.

Piezodialysis was also carried out for a feed solution of 10^{-2} mol/L KCl and 10^{-2} mol/L $MgCl_2$ and the permeability was 1.09 for KCl and 0.65 for $MgCl_2$. Consequently, the separation of multi-valent electrolytes from univariant electrolytes is possible by permeation through a mosaic membrane.

CONCLUSION

A mosaic membrane prepared by casting a PVC solution containing cation exchange resin and anion exchange resin functioned as a piezodialysis membrane if the cation exchange capacity was equal to the anion exchange capacity. The mosaic membrane revealed selective permeation properties of salts depending on the mobilities of the ions in the membrane.

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