

# Selective Ion Permeation through Fluorocarbon Polymer Membrane

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## Synopsis

Hydrophobic polymers have rarely been used for membrane materials, but ions permeated selectively through a very thin hydrophobic membrane under a pressure gradient. The membrane was prepared by coating fluorocarbon polymer on a Teflon membrane filter. The permeabilities of strongly hydrated hydrophilic ions and hydrophobic ions are high through the membrane, but those of weakly hydrated ions are low. The selectivities were enlarged in the mixed salts solution of a low concentration at a high pressure. For example, the permeability of KCl was 0.077 and that of LiCl was 0.80 at  $1 \times 10^{-4}$  mol/dm<sup>3</sup> and 40 kg/cm<sup>2</sup>. The coupling between volume flux and ion flux was high for strongly hydrated ions, while the diffusion flux derived by a concentration gradient was high for weakly hydrated ions.

## INTRODUCTION

Selective permeability of ions occurs frequently in biological membranes, but it is scarcely observed artificially despite the case of liquid membranes containing carriers.<sup>1,2</sup> Selectivities in permeation through polymer membranes have also been studied, but they are not large not only for reverse osmosis membranes<sup>3</sup> but also for other membranes such as lactone-contained polymer membranes,<sup>4</sup> macrocyclic polyether-polyamide membranes.<sup>5</sup>

We have reported that alkaline ions permeated selectively through a very thin hydrophobic membrane prepared from polystyrene.<sup>6</sup> Permeability of lithium is higher than that of potassium through a hydrophobic membrane under a pressure gradient and the selectivity increased with increasing hydrophobicity of the membrane, while the diffusion flux of potassium was higher than that of lithium in dialysis experiment with a hydrophobic membrane.<sup>7</sup>

We report here a selective ion permeation through a very thin membrane prepared from fluorocarbon polymer, which is the most hydrophobic polymer (solubility parameter; 6.2 cal<sup>1/2</sup>/cm<sup>3/2</sup> polytetrafluoroethylene, 9.12 cal<sup>1/2</sup>/cm<sup>3/2</sup> polystyrene<sup>8</sup>) and is strong chemically and mechanically, and discuss the mechanism of the selective permeation.

## EXPERIMENTAL

**Membrane Preparation.** Membrane material used in this study was FEP resin, which is a copolymer of polytetrafluoroethylene and polyhexafluoropropylene. Aqueous dispersion of Teflon FEP-120 (DuPont Co.) was diluted 20-fold

with pure water, and this solution was sprayed on a Teflon membrane filter, Fluoropore (Sumitomo Electric Inc., Ltd.), of pore size  $0.1 \mu\text{m}$ , and the membrane was dried at  $120^\circ\text{C}$  for 5 min in an oven. Spraying and drying were repeated some times to an appropriate membrane density ( $0.5$  to  $0.6 \text{ mg/cm}^2$ ), which is the weight per unit area of the membrane coated on a filter and an indication of the membrane thickness. The membrane on the filter was melted by heating at  $300^\circ\text{C}$  for 10 min in an electric furnace to prepare a thin homogeneous membrane.

**Scanning Electron Microscope (SEM) Studies.** The membrane surfaces and the cross section of the coating membrane, which was obtained by cutting the membrane with an acute knife, were examined with a JSM-35C Scanning Electron Microscope (Japan Electric Optics Laboratory Co.), after shadowing with gold *in vacuo*.

**Permeation Experiment.** The ion permeation under a pressure gradient was measured with a flow-type hyperfiltration apparatus. In general, the feed solution contained  $1 \times 10^{-4} \text{ mol/dm}^3$  salt and the operating pressure was  $40 \text{ kg/cm}^2$ . The ion permeation was described with the term, "permeability  $P$ ," defined as follows:

$$P = 1 - R = C_p/C_f \quad (1)$$

where  $R$  is the rejection,  $C_p$  is the concentration in the permeated solution, and  $C_f$  is the concentration in the feed solution. The concentrations of permeated solution and feed solution were measured by atomic absorption analysis.

## RESULTS AND DISCUSSION

The SEM photographs of the surfaces of a Teflon membrane filter, Fluoropore, and the coating membrane and the cross section of the coating membrane are shown in Figure 1. The pores were observed at the surface of Fluoropore, but, after coating, the pores were clogged and a homogeneous thin membrane about  $6\text{--}8 \mu\text{m}$  thick was formed on the Fluoropore, and a part of the molten FEP invaded the pores at the surface of the Fluoropore. Although the pores were not confirmed by the observation of 10,000-fold magnification at the surface of the coating membrane, it was presumed that there was a microporous structure in the coating membrane for the water flux was large ( $5 \times 10^{-4} \text{ cm/min-atm}$ ) despite the hydrophobicity of the membrane and the decrease of the water flux during the membrane compaction was also large.

A solution containing five alkaline metal ions was permeated through the FEP coating membrane, and the permeabilities are plotted in Figure 2 with ion radius as abscissa. Permeabilities increased with the decrease of ion radius through this membrane as polystyrene membrane.<sup>6</sup> The permselective coefficient  $T_A^B$ , which is the permeability of ion B divided by that of ion A,<sup>9</sup> was also measured with the feed solution containing  $10^{-4} \text{ mol/dm}^3$  KCl and  $10^{-4} \text{ mol/dm}^3$  LiCl at  $40 \text{ kg/cm}^2$ .  $T_K^{\text{Li}}$  of this membrane was 10.8, and this value is higher than that of polystyrene membrane reported previously ( $T_K^{\text{Li}} = 7.96$ ).

Permeabilities of various ions are shown in Figure 3 with electric charge-to-ion radius ( $z/r$ )<sup>10</sup> as abscissa. The value of  $z/r$  was used as an indication of hydration intensity and the hydration increases with increasing  $z/r$ .<sup>11</sup> Permeabilities of cations increased linearly with increasing  $z/r$ . Selectivities in Figure 3 is lower

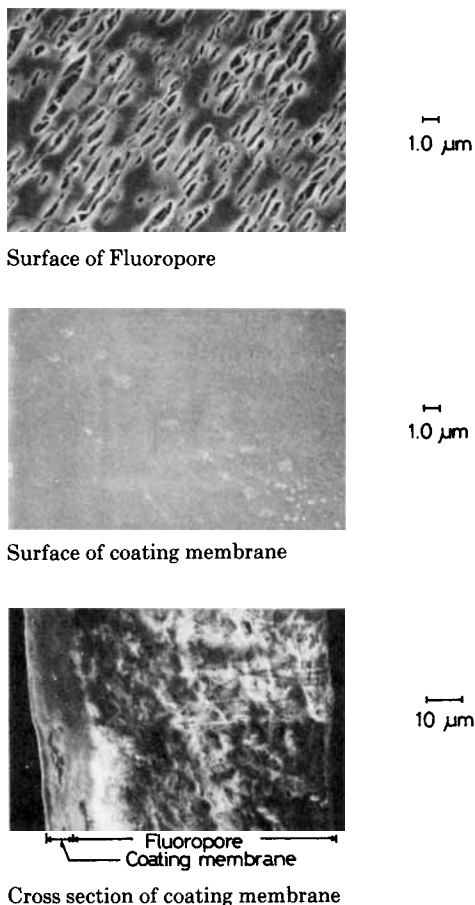


Fig. 1. Scanning electron microscope photographs.

than those in Figure 2 for the feed solution contained a single salt and there was no coexisting salt, which will be explained later in this study.

Permeabilities of anions decreased with increasing  $z/r$ , as opposed to those of cations, and, further, a hydrophobic solute is concentrated by a hydrophobic

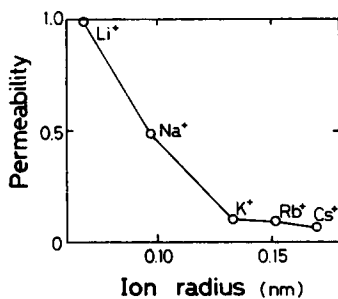


Fig. 2. Permeabilities of alkaline metal ions. Feed solution:  $1 \times 10^{-4}$  mol/dm<sup>3</sup> LiCl,  $1 \times 10^{-4}$  mol/dm<sup>3</sup> NaCl,  $1 \times 10^{-4}$  mol/dm<sup>3</sup> KCl,  $1 \times 10^{-4}$  mol/dm<sup>3</sup> RbCl, and  $1 \times 10^{-4}$  mol/dm<sup>3</sup> CsCl. Pressure: 40 kg/cm<sup>2</sup>.

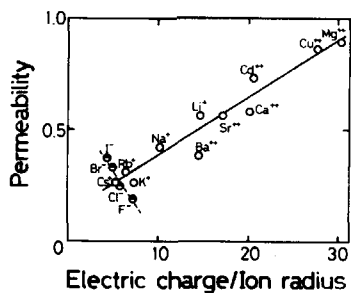


Fig. 3. Permeability vs. electric charge/ion radius. Feed solution: (O)  $1 \times 10^{-4}$  mol/dm<sup>3</sup> chloride salt; (●)  $1 \times 10^{-4}$  mol/dm<sup>3</sup> potassium salt. Pressure: 40 kg/cm<sup>2</sup>.

membrane.<sup>12</sup> Then, it is presumed that the relationship between permeability and  $z/r$  has a minimum value. It was proved by the measurement of permeabilities of tetraalkylammonium ions, whose ion radius are larger than those of alkaline metal ions. Table I shows the permeabilities of alkylammonium chlorides and permeability of tetraethylammonium ion was the lowest in tetraalkylammonium ions, although  $z/r$  decreases with increasing carbon number. Permeabilities of monoalkylammonium ions changed little with carbon number, for the effect of carbon number on the hydration property for monoalkylammonium ion was less than that for tetraalkylammonium ion.<sup>13</sup> Further, a steric hindrance also affects the permeability, the permeability decreases with increasing volume of ion.

This selective permeability of ions may be caused by the interaction between hydration of ion and hydrophobic hydration<sup>14</sup> of a hydrophobic membrane. Water is repelled by a hydrophobic membrane, but water permeates into the membrane under a pressure gradient and hydrophobic hydration is formed at the surface and the pores of the membrane. When hydrophilic ion hydrated strongly permeates in the membrane under a pressure gradient, the interaction between the hydrophilic hydration layer of the ion and the hydrophobic hydration layer of the membrane breaks the iceberg structure<sup>15</sup> of the water in the membrane and causes the high permeability of the ion. When hydrophobic ion permeates in the membrane under a pressure gradient, an affinity between hydrophobic ion and the hydrophobic membrane occurs<sup>15</sup> and the partitioning of the ion to the membrane causes the high permeability of the ion.<sup>16</sup> When the ion with the intermediate hydration property permeates in the membrane, the iceberg structure of the water in the membrane hinders the permeation of the

TABLE I  
Permeabilities of Alkylammonium Chloride<sup>a</sup>

Salt	Permeability	Salt	Permeability
NH <sub>4</sub> Cl	0.48		
Me <sub>4</sub> NCl	0.47	MeNH <sub>3</sub> Cl	0.55
Et <sub>4</sub> NCl	0.44	EtNH <sub>3</sub> Cl	0.55
<i>n</i> -Pr <sub>4</sub> NCl	0.71	<i>n</i> -PrNH <sub>3</sub> Cl	0.53
<i>n</i> -Bu <sub>4</sub> NCl	0.69	<i>n</i> -BuNH <sub>3</sub> Cl	0.49

<sup>a</sup> Concentration in feed solution:  $1 \times 10^{-4}$  mol/dm<sup>3</sup>. Pressure: 40 kg/cm<sup>2</sup>.

ion through the membrane. This selectivity in ion permeabilities was large in low concentration and it decreased with increasing feed concentration, because water structure in the membrane and that around the ion were distorted when the concentration of the feed solution was high.

Ion permeation properties of strongly hydrated ion,  $\text{Cu}^{2+}$  and weakly hydrated ion  $\text{Cs}^+$  were investigated by changing operating pressure. Figure 4 shows permeability vs. pressure using  $10^{-4}$  mol/dm<sup>3</sup>  $\text{CuCl}_2$  solution or  $10^{-4}$  mol/dm<sup>3</sup>  $\text{CsCl}$  solution. From the irreversible thermodynamic theory, the volume flux  $J_v$  and the salt flux  $J_s$  change with an operating pressure difference  $\Delta P$  and an osmotic pressure difference  $\Delta\pi$  on the following equation<sup>17</sup>:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad (2)$$

$$J_s = \omega\Delta\pi + (1 - \sigma)C_s J_v \quad (3)$$

$$C_s = (C_f + C_p)/2 \quad (4)$$

where  $L_p$ ,  $\sigma$ ,  $\omega$ , and  $C_s$  are water permeability, reflection coefficient, solute permeability, and the concentration in the membrane, respectively. In this experiment,  $J_v$  was proportional to  $\Delta P$ , for the salt concentration in the feed solution was low. The experimental values of  $\omega\Delta\pi$  is very difficult to be obtained, for the hydrophobic membrane and Fluoropore filter repel the solution when  $\Delta P = 0$ . Then, the values of  $\omega\Delta\pi$  are estimated by extrapolation of  $J_s$  to  $\Delta P = 0$  in Figure 4 to be  $1.7 \times 10^{-10}$  mol/cm<sup>2</sup>·min for  $\text{CuCl}_2$  and  $2.7 \times 10^{-10}$  mol/cm<sup>2</sup>·min for  $\text{CsCl}$ , for  $J_s = \omega\Delta\pi$  when  $J_v = 0$ . The values of  $(1 - \sigma)$ , which was obtained by the slope of permeability against pressure, were 0.78 for  $\text{CuCl}_2$  and 0.29 for  $\text{CsCl}$ . These values were obtained without consideration of concentration polarization, which was not able to be ignored for more detailed study. The value of  $\omega\Delta\pi$  is equal to diffusion flux and it decreases with increasing hydration as previously reported,<sup>6,7</sup> while in hyperfiltration through a hydrophobic membrane the permeability increases with increasing hydration and the coupling effect between ion flux and volume flux is strong for a hydrophilic ion.

The effect of coexisting ion on ion permeability is weak for reverse osmosis membranes,<sup>18</sup> but it is very strong for hydrophobic membranes. Figure 5 shows the effect of composition of the feed solution containing  $\text{LiCl}$  and  $\text{KCl}$ . The permeability of chloride changed linearly with mole fraction, but the permeability of potassium decreased rapidly when lithium was added to the feed solution. If

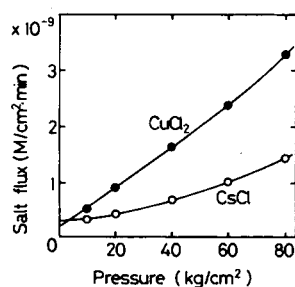


Fig. 4. Salt flux vs. pressure. Feed solution: (O)  $1 \times 10^{-4}$  mol/dm<sup>3</sup>  $\text{CsCl}$ ; (●)  $1 \times 10^{-4}$  mol/dm<sup>3</sup>  $\text{CuCl}_2$ .

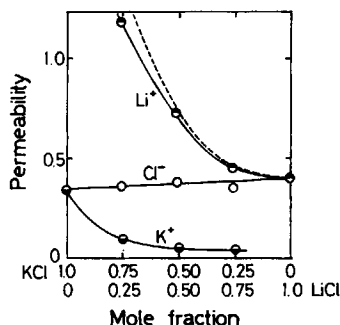


Fig. 5. Permeability vs. mole fraction: (---) calculated value of  $\text{Li}^+$  permeability. Total concentration of KCl and LiCl in feed solution:  $2 \times 10^{-4} \text{ mol/dm}^3$ . Pressure:  $40 \text{ kg/cm}^2$ .

the permeability of potassium was assumed to be zero in the mixed solution, the permeabilities of chloride ion and lithium ion were as follows:

$$P_{\text{Cl}} = P_{\text{KCl}} + (P_{\text{LiCl}} - P_{\text{KCl}}) \times \gamma \quad (5)$$

$$P_{\text{LiCl}} = P_{\text{Cl}} \times 1/\gamma \quad (6)$$

where  $\gamma$  is the mole fraction of lithium in the feed solution. A dotted line in this figure shows a calculated value of lithium permeability based on empirical equation (6), and it agreed well with experimental value. Lithium was concentrated when the mole fraction of lithium is small. When chloride ion permeated through a hydrophobic membrane, it selected more permeable cation as the counterion and coexisting co-ion affected ion permeability.

## CONCLUSION

A very thin hydrophobic membrane prepared by coating fluorocarbon polymer on a Teflon membrane filter revealed selective permeabilities of ions. The permeabilities of strongly hydrated hydrophilic ions and hydrophobic ions were high, and those of weakly hydrated ions were low, for the ions variously affected iceberg structure of water caused by the hydrophobic hydration in a hydrophobic membrane. The coupling between volume flux and ion flux was large for a strongly hydrated ion and the order of ion permeability under a pressure gradient was reversed to that under a concentration gradient. The effect of a coexisting co-ion on ion permeability was large, and the selectivity was large in a mixed salts solution of a low concentration at a high pressure.

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