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Selective Permeation Properties of Inorganic Ions across a Hydrophobic Membrane

Manabu IGAWA,* Rie NISHIURA, Noriyuki MASHIYAMA, and Yoshimi USUDA
Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221

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A hydrophobic membrane was prepared from poly(tetrafluoroethylene-*co*-hexafluoropropylene) by coating method to be a very thin membrane with a high water permeability. The permeation, the diffusion, and the distribution coefficients were measured by time lag method. The permeation coefficient of a salt decreased with the increase of the hydrophilicity of the salt, while hydrophilic salts are permeated readily by the coupling of water flux under a pressure gradient. The characteristic permeation properties of the hydrophobic membrane were caused by the hydrophobic hydration in the pores of the membrane and a hydrophilic ion has a low diffusion coefficient and a high distribution coefficient. The diffusion coefficient of potassium chloride increased with the increases of the temperature or the concentration, while the distribution coefficient had a minimum value at about 55 °C and decreased with the increase of the concentration. Some organics added to the source phase solution affected the hydration structure in the membrane, which changed the permeation properties of salts.

Most of synthetic membranes, such as reverse osmosis membranes, ultrafiltration membranes, and dialysis membranes, are made of the polymers which have both hydrophobic and hydrophilic properties. The hydrophilic region of the membrane separates ion from water and its hydrophobic region supports the membrane structure. Although hydrophobic membranes have not been used for the separation of solutes from water, hydrophobicity of the membrane has a potential of the selective permeation of ions. Satake et al. prepared a dialysis membrane from a derivative of polyamine sulfone and reported that alkaline metal ions were permeated selectively across the membrane for the characteristic interaction of the hydrophobic region of the polymer to the hydrated ions.[1] We have developed, further, a very thin hydrophobic membranes with a high water permeability by coating method.[2] Under a pressure gradient, strongly hydrated ions are permeated readily across the hydrophobic membrane for the coupling with water flux,[3] in contrast with the case of a reverse osmosis membrane.[4] Heavy metal ions are pertracted with chelating agents across a hydrophobic membrane[5,6] and hydrophobic organic solutes are highly distributed to the hydrophobic membrane and enriched by the membrane under a pressure gradient.[7,8]

Hydrophobic membranes have many characteristic permeation properties and in the biological membranes, the hydrophobic region presumably affects the selectivity of the ion permeation. However, the permeation mechanism of ions in the membrane has not been clear. At the surface of the membrane pores, water structure is very different from bulk water and a hydrophobic hydration structure is formed by the hydrophobic interaction of the polymer to the water in the micro space surrounded by the hydrophobic polymer.[9] The hydrophobic hydration is characterized thermodynamically by a large positive entropy change with a small enthalpy term and the overall Gibbs energy change is therefore dominated by the entropy term. The specific environment of the hydrophobic hydration affects on the hydration shell of ions and causes some effects on the distribution and the diffusivity of the ion in the membrane.

In this paper, we will report the selective diffusion and distribution properties of salts in a hydrophobic membrane determined by dialysis experiments, compare them to the permeation properties of salts under a pressure gradient, and propose the selective permeation mechanism of a salt across a hydrophobic membrane.

Experimental

Membrane Preparation. The hydrophobic membrane material used in this study was poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP). The FEP membrane was prepared by coating Teflon® FEP-120 dispersion (Du Pont Co.) on a fluorocarbon polymer membrane filter with 0.2 μm pore, NTF-5200 (Nitto Electric Industry Co., Ltd.). The membrane filter was heated at 300 °C before coating, the 20 fold diluted solution of the dispersion was sprayed on the filter, and dried at 120 °C for 5 min in an oven. The coating and the drying were repeated several times until the coating density on the filter became 0.5 to 0.7 mg cm^{-2} and the coating layer was melted at 300 °C for 10 min in an electric furnace to obtain the FEP membrane. The detail of the membrane preparation was reported previously.[3]

Measurement of Membrane Thickness. The thickness of the membrane was measured by the observation of the cross section of the membrane. To observe the cross section, the membrane was cut after all of the permeation experiments with an acute knife, shadowed with gold in vacuo, and examined with an Electron Beam Lithography System, ELS-3300 (Elionix Inc.). The membrane thickness was determined from the mean value of the measured thickness at the five different points of the membrane.

Time Lag Experiment. The apparatus shown in Fig. 1 was used in this study to obtain the diffusion coefficient and the permeation coefficient and this apparatus is similar to that used by Hirose et al. for the time lag experiment.[10] The membrane area was 4.2 cm^2 and the thickness of the compartment in the cell, which was the thickness of the silicone rubber sheet, was 3 mm. There were two compartments in the cell and the

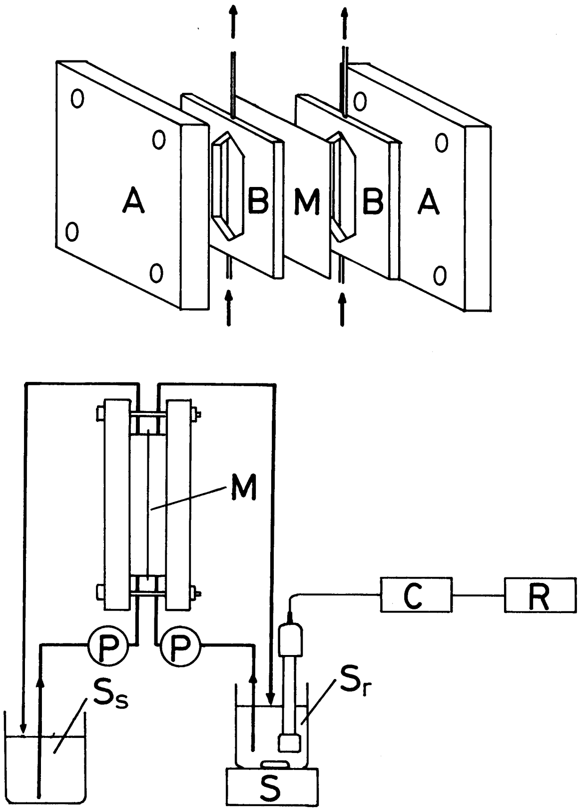

Fig. 1. Dialysis cell and apparatus for the determination of permeation characteristics. A: acrylic resin frame, B: silicone rubber sheet, M: membrane, S_s: source phase solution, S_r: receiving phase solution, S: stirrer, P: tubing pump, C: conductivity meter, R: recorder.

compartment contacted with the coating layer of the membrane was called the source phase compartment and the other compartment was called the receiving phase compartment in this study. The solutions were pumped from the reservoirs to the compartments separately with tubing pumps at the rate of 16 $\mathrm{cm^3\,min^{-1}}$. The cell and reservoirs were thermostatted in a water bath. Before the permeation experiment, methyl alcohol was pumped to both of the compartments to fill the alcohol in the membrane pores and then, pure water was pumped to exchange methyl alcohol in the pores with water. By this treatment, the membrane resulted in transparent from opaque white and water diffused readily in the hydrophobic membrane.

In the permeation experiment, 0.1 $\mathrm{mol\,dm^{-3}}$ salt solution (250 $\mathrm{cm^3}$) and a pure water (80 $\mathrm{cm^3}$) were started to be pumped simultaneously from each reservoir to the source phase compartment and the receiving phase compartment, respectively. The change of the electric conductivity of the receiving phase solution was detected with a conductivity meter (Kyoto Electronics, CM-117) and the conductivity was recorded. The solute diffused across the membrane and the concentration of the receiving phase solution changed linearly with time after a transition period. The time lag is the intercept on the abscissa, when the linear relationship between the concentration and the time was extrapolated to zero concentration. The diffusion coefficient, D, can be obtained from the following equation.

$$D=L^2/(6\tau), \tag{1}$$

where L is the membrane thickness and τ is the time lag. The diffusion coefficient relates on Eq. 2 to the distribution coefficient, K, and the permeation coefficient, P, which can be obtained from the solute flux, J_S, and the concentration difference between the source phase solution and the receiving phase solution, ΔC, in Eq. 3.

$$P=KD/L. \tag{2}$$

$$J_S=P\Delta C. \tag{3}$$

In the calculation of the permeation coefficient, the concentration of the source phase solution was used instead of the concentration difference because J_S was measured while the receiving phase concentration was much lower than that of the source phase solution. The time lag measurement was repeated five times and the mean value was calculated for the conditions of an experiment. The salt flux was obtained from the slope of the linear change of the conductivity with time using the calibration curve between the conductivity and the concentration for each solute and each experimental conditions. After an experiment, 3 $\mathrm{dm^3}$ of a pure water was pumped to both of the compartments to rinse the membrane.

Hyperfiltration Experiment. The ion permeation under a pressure gradient was measured with a flow-type hyperfiltration apparatus. The operating pressure was 40 $\mathrm{kg\,cm^{-2}}$ and the feed solution contained 1×10^{-4} $\mathrm{mol\,dm^{-3}}$ salt. The ion permeation property was described by the salt passage, SP, which is defined as the concentration ratio of the permeated solution to the feed solution and relates on Eq. 4 to rejection, R.[11]

$$SP=1-R. \tag{4}$$

The concentrations of the permeated and the feed solutions were measured by an atomic absorption spectrophotometer (Shimadzu AA-630-02).

Results and Discussion

Characteristics of Membrane. The permselectivity under a pressure gradient was examined at first after the preparation of the membrane. The salt passage of lithium chloride was 0.70 and that of potassium chloride was 0.10 and the water flux was 3.06×10^{-3} $\mathrm{cm\,min^{-1}}$ when the mixed solution of 0.1 $\mathrm{mmol\,dm^{-3}}$ lithium chloride and 0.1 $\mathrm{mmol\,dm^{-3}}$ potassium chloride was used for the feed solution and the operating pressure was 40 $\mathrm{kg\,cm^{-2}}$. This membrane has a high permselectivity and a high water permeability as the membrane reported earlier.[3] Then, this membrane was taken off from the hyperfiltration apparatus and used for time lag experiments.

The membrane used in this study is a composite membrane and the permeation coefficient of the membrane is described as Eq. 7 by substituting Eqs. 3 and 5 to Eq. 6.

$$J_{s,\mathrm{composite}}=J_{s,\mathrm{dense}}=J_{s,\mathrm{support}}. \tag{5}$$

$$\Delta C_{\text{composite}} = \Delta C_{\text{dense}} + \Delta C_{\text{support}}. \quad (6)$$

$$1/P_{\text{composite}} = 1/P_{\text{dense}} + 1/P_{\text{support}}. \quad (7)$$

$P_{\text{composite}}$ and P_{support} values for potassium chloride at 25 °C were obtained by permeation experiments to be 9.19×10^{-5} cm s^{-1} and 1.27×10^{-3} cm s^{-1}, respectively. The P_{dense} value is calculated to be 9.91×10^{-5} cm s^{-1} from Eq. 7 by using these values and the $P_{\text{composite}}$ value was 0.93 times smaller than the P_{dense} for the permeation resistance of support. In this paper, however, the permeation resistance of the support was ignored and the permeation resistance of the composite membrane was regarded to be caused only by the dense membrane because the permeability of a solute in the support membrane was large enough to be regarded as approximately the same level to that in aqueous solution by considering the tortuosity of the support filter. The thickness of the support filter was 76 μm and the diffusion coefficient of potassium chloride in the support filter was calculated to be 0.92×10^{-5} cm^2 s^{-1} on the assumption that the distribution coefficient was 1 while the diffusion coefficient of it in 0.1 mol dm^{-3} aqueous solution is 1.84×10^{-5} cm^2 s^{-1}.[12]

The time lag value obtained experimentally for the composite membrane was 9.87 s and the thickness of the FEP membrane on the filter obtained by the observation of the cross section was 19.7 μm. Then, the diffusion coefficient of potassium chloride at 25 °C was calculated to be 6.70×10^{-8} cm^2 s^{-1} from Eq. 1. The distribution coefficient was calculated to be 2.71 for potassium chloride at 25 °C from Eq. 2 by using the permeation and the diffusion coefficients.

The diffusion coefficients and the distribution coefficients have been reported for many membranes. The diffusion and distribution coefficients of potassium chloride for Visking dialysis membrane, a typical hydrophilic membrane, were reported to be 2.75×10^{-6} cm^2 s^{-1} and 0.70, respectively.[13] The diffusion and distribution coefficients for cellulose acetate membrane are about 1 to 10×10^{-9} cm^2 s^{-1} and about 0.01 to 0.1, respectively.[14] The diffusion coefficients depend primarily on the membrane structure as well as the membrane material, the distribution coefficients are less than one for most cases, and salts are highly rejected at the surface of the hydrophilic membrane, especially in the case of a reverse osmosis membrane. In the case of the hydrophobic membrane, the diffusion coefficient is in the range of the diffusion coefficients reported but the distribution coefficient was larger than 1, which means that the salt are enriched in the hydrophobic membrane. Lee et al. compare the diffusion coefficient obtained by time lag method with those obtained by other method and there was an excellent agreement between the values.[15] The cause of the enrichment phenomenon in the membrane will be discussed afterward.

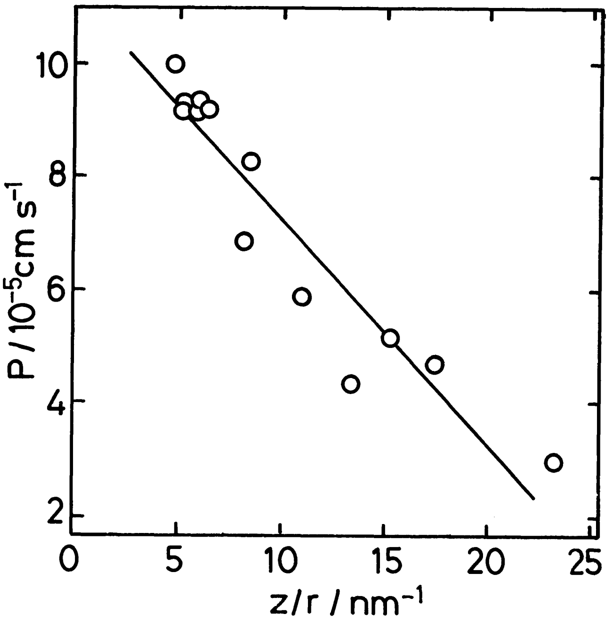

Fig. 2. Permeation coefficient in hydrophobic membrane vs. ratio of electric charge to ion radius. *P*: permeation coefficient in hydrophobic membrane, *r*: ion radius (nm), *z*: electric charge, concentration of source phase solution: 0.1 mol dm^{-3}, temperature: 25 °C.

Permeation Properties of Many Ions. The permeation (*P*), the diffusion (*D*), and the distribution (*K*) coefficients were measured for many salts (LiCl, NaCl, KCl, RbCl, CsCl, KF, KBr, KI, $MgCl_2$, $CaCl_2$, $BaCl_2$, and $SrCl_2$). Figure 2 shows the relationship between the permeation coefficient and the ratio of the electric valence to the ion radius, which is a indication of the hydration of an ion.[16] The solid line in Fig. 2 is the regression line ($P=-0.40\times z/r+11.3\times10^{-5}$) and the correlation factor is −0.95. The permeation coefficients decreased with the increase of the hydration of the salt as reported,[1] while the salt passage in hyperfiltration across a hydrophobic membrane increased with increasing hydration.[3] The diffusion coefficient decreased with increasing hydration of salts, whereas the distribution coefficient increased with increasing hydration. The dependence of the diffusion coefficients for the salts on their hydration is the same as that of the permeation coefficients because the difference in the distribution coefficients for many salts is smaller than that in the diffusion coefficients. For example, in the chloride salts of alkaline metals, lithium chloride is the most hydrated and cesium chloride is the least hydrated and the permeation properties were as follows; D_{LiCl}, 3.54×10^{-8} cm^2 s^{-1}; K_{LiCl}, 3.28; D_{CsCl}, 8.93×10^{-8} cm^2 s^{-1}; K_{CsCl}, 2.03.

The diffusion coefficients of the salts through the hydrophobic membrane were plotted versus the diffusion coefficients in the infinitely diluted aqueous solution[12] in Fig. 3. There is a linear relationship between the values

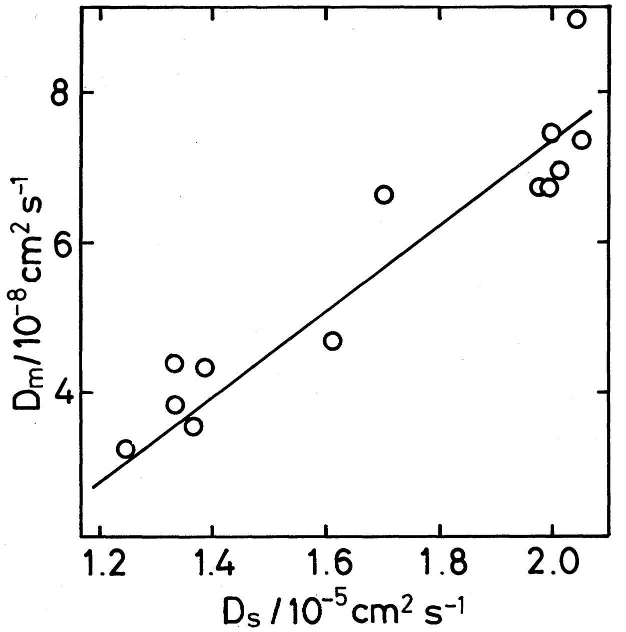

Fig. 3. Diffusion coefficient in hydrophobic membrane vs. diffusion coefficient in solution. D_m: diffusion coefficient in hydrophobic membrane, D_s: diffusion coefficient in solution, concentration of source phase solution: 0.1 mol dm^{-3}, temperature: 25°C.

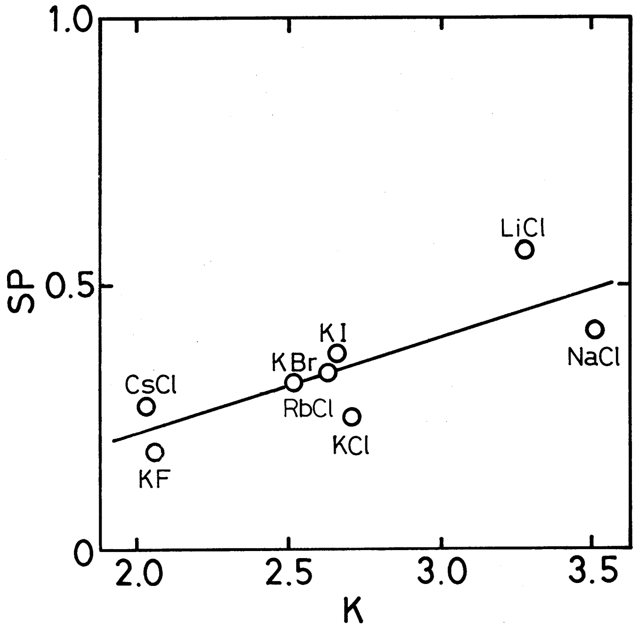

Fig. 4. Salt passage vs. distribution coefficient. *SP*: literature value[3] of salt passage, *K*: distribution coefficient, concentration of source phase solution: 0.1 mol dm^{-3}, temperature: 25°C.

although the values in the solution are much larger than those in the membrane. The solid line in Fig. 3 is the regression line ($D_m=0.00562\times D_s-3.92\times10^{-8}$) and the correlation factor is 0.94. The less hydrated salt diffuses readily in the solution because its hydrated ion radius is small. In the hydrophobic membrane, the salt in the hydrophobic hydration structure in a membrane pore jumps to the other membrane pore when it diffuses. Then, it must be very difficult for a strongly hydrated salts to move between the hydrophobic regions and a slightly hydrated salt can diffuse readily in the membrane.

The distribution coefficient increased with increasing hydration and the hydrophilic salts were concentrated in the hydrophobic membrane. This is a very strange phenomenon but the selectivity is corresponding well with the selective salt passage across a hydrophobic membrane under a pressure gradient. The salt passage of hydrophilic salt is larger than that of hydrophobic salt under a pressure gradient. Figure 4 shows the relationship between the salt passage reported earlier[3] and the distribution coefficient for the salts of potassium halide and alkali metal chlorides. The solid line is the regression line ($P=0.18\times K-0.14$) and the correlation factor is 0.80. The slope was about two times larger for the salts with the divalent cations than those of salts in Fig. 4 but the correlation factor is small (0.36). Under a pressure gradient, highly distributed hydrophilic ions were permeated selectively with the water flux across the hydrophobic membrane. In hyperfiltration, the salts are transported by the coupling with the water flux as shown in the following equation.[17]

$$J_s=\omega\Delta\pi+(1-\sigma)C_m J_v, \tag{8}$$

where J_v is the volume flux, σ is the reflection coefficient, ω is the solute permeability, and $\Delta\pi$ is the osmotic pressure difference across the membrane. The contribution of the coupling effect of the solute flux increased with the increase of the volume flux and the term of the coupling effect, $(1-\sigma)C_m$. In the reverse osmosis membrane, the coupling effect is negligible,[18] the salt passage decreased with increasing hydration of the salt,[4] and the selective salt passage is reverse to that of hydrophobic membrane, although reverse osmosis membranes have somewhat hydrophobic property.

In reverse osmosis membranes, the hydration layer is formed at the wall of the membrane pore and the distribution coefficients of most of the salts are very small but some hydrophobic salts, such as KSCN, have the distribution coefficients more than 1 and enriched by hyperfiltration. It must be caused by the extraction of such salt to the membrane phase by the formation of the ion pair.[19] In the hydrophobic membrane, hydrophobic solutes are also highly distributed and enriched by the membrane under a pressure gradient.[6,7] Highly hydrated solutes have also distribution coefficients larger than 1 in the hydrophobic membrane, although these solutes are not enriched under a pressure gradient. Wiggins reported that a hydrophobic hydration is formed in the hydrophobic membrane pore, the properties of the water in the membrane is much different to those of bulk water, which has the random defective network of the normal liquid, and there is a stretched-water structure in the pore.[20] He also reported that potassium chloride had stretched-water/water distribution coefficient which was greater than one and the coefficient tended to one as the concentration increased. It has been reported that the hydrophilic salts break the water structure when they invade the water of the hydrophobic hydration.[21] The salts are enriched in the hydrophobic membrane because the water structure is changed to vapor like water from stretched-water by the salt and the chemical potential of the pore water decreases.[20]

Temperature Effect on Permeation Characteristics. The effect of temperature on the permeation characteristics was investigated from 25 °C to 75 °C for potassium chloride and shown in Fig. 5. The diffusion coefficient increased with increasing temperature. The distribution coefficient decreased with increasing temperature but it had minimum value at around 55 °C and increased with the temperature over the temperature. With the increase of temperature, the hydrophobic bonding becomes stronger but has a maximum value at 58 °C.[22] The temperature dependence of this permeation characteristics corresponded well with this temperature dependence of water structure. The salt passage across a hydrophobic membrane under a pressure gradient also changed with temperature and increased linearly with decreasing value of the reciprocal of the absolute temperature, T, but the slope becomes steep over 55 °C.

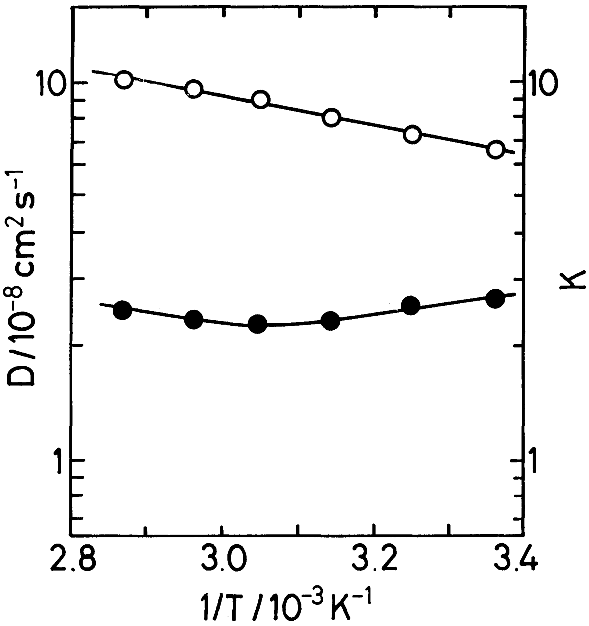

Fig. 5. Effect of temperature on diffusion coefficient and distribution coefficient. D: diffusion coefficient (○), K: distribution coefficient (●), T: absolute temperature, source phase: 0.1 mol dm^{-3} KCl aqueous solution.

The activation energy of diffusion can be calculated from the following equation.

$$\ln(D_1/D_2) = -E_a/R\cdot(1/T_1 - 1/T_2), \qquad (9)$$

where D_1 and D_2 correspond to the diffusion coefficients at the temperature, T_1, and at the temperature, T_2, respectively, E_a is the diffusion activation energy, and R is the gas constant. The activation energy of potassium chloride is calculated to be 7.31 kJ mol^{-1} from Fig. 5. The diffusion activation energy reported for sodium chloride across the cellulose acetate reverse osmosis membrane was 10 to 20 kJ mol^{-1} [23] and the value was the same level as the value across hydrophobic membrane by considering the difference of the hydration between the salts.

The Gibbs energy change of the transfer from bulk solution to the membrane phase can be calculated from the following equation.

$$\ln(K_1/K_2) = -\Delta G/R\cdot(1/T_1 - 1/T_2), \qquad (10)$$

where K_1 and K_2 correspond to the distribution coefficient at the temperature, T_1, and at the temperature, T_2, respectively, and ΔG is the Gibbs energy change. Under 55 °C, the energy change was −5.7 kJ mol^{-1} and potassium chloride became stable in the membrane as estimated in the preceding chapter. Over 55 °C, the energy change was 4.9 kJ mol^{-1} and potassium chloride became unstable in the membrane.

Concentration Effect on Permeation Characteristics. The effect of the salt concentration on the diffusion coefficient and the distribution coefficient for potassium chloride are shown in Fig. 6. In the diluted solution, the distribution coefficient was very high to be over 4 and the permeation resistance across the membrane was high. With the increase of the salt concentration, the hydration water structure was disordered and the characteristic permeation properties decreased. The selective permeation properties also decreased remarkably with the increase of the concentration under a pressure gradient for the membrane.[3]

Effect of the Addition of Organics on Permeation Properties. Some organics were added to potassium chloride solution to investigate the effect of water structure change on the permeation properties of salts. Figure 7 shows the effect of methyl alcohol content in the salt solution on the permeation characteristics. When the permeation properties of potassium chloride in 50% (v/v) methyl alcohol–water solution was investigated, the membrane was equilibrated with the aqueous solution containing 50% methyl alcohol and then, the source phase and receiving phase solutions were changed to 50% methyl alcohol–water solution containing 0.1 mol dm^{-3} potassium chloride and to 50% methyl alcohol–pure water solution, respectively. With the increase of

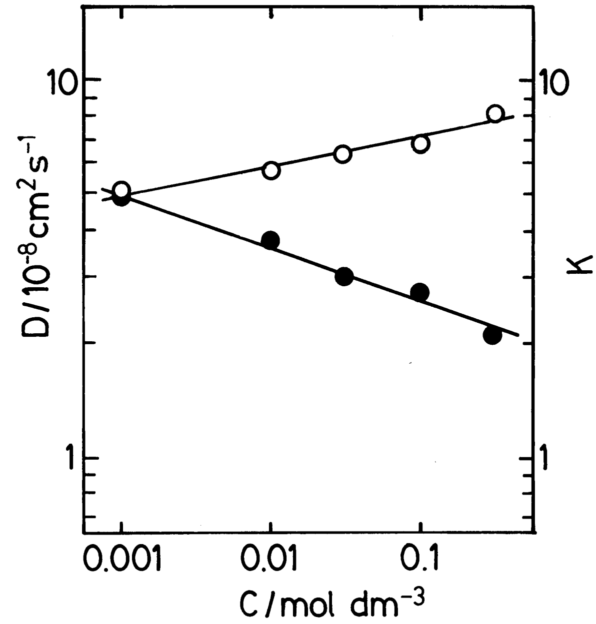

Fig. 6. Concentration effect on diffusion coefficient and distribution coefficient. *D*: diffusion coefficient (○), *K*: distribution coefficient (●), *C*: concentration of source phase solution, source phase: KCl aqueous solution, temperature: 25 °C.

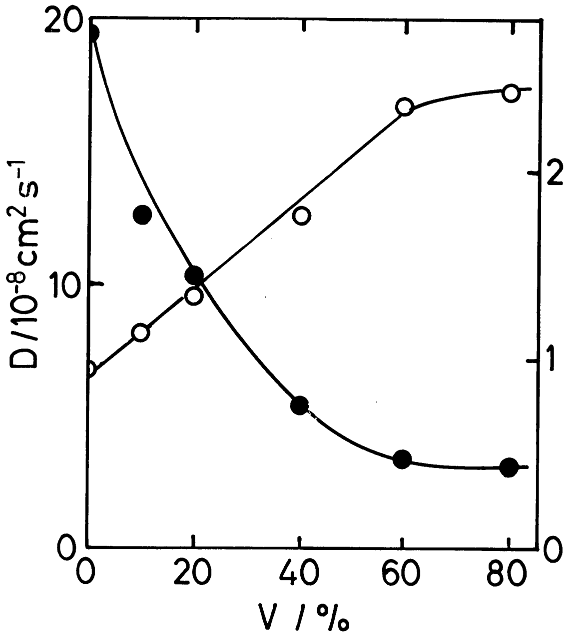

Fig. 7. Effect of methyl alcohol on permeation characteristics. *D*: diffusion coefficient (○), *K*: distribution coefficient (●), *V*: volume percentage of methyl alcohol in aqueous solution, source phase: KCl aqueous solution containing methyl alcohol, receiving phase: aqueous solution containing methyl alcohol, temperature: 25 °C.

methyl alcohol content, the distribution coefficient decreased and the diffusion coefficient increased. When methyl alcohol was added, the repulsion between the solution and the membrane material decreased and salt readily diffused in the membrane and the distribution coefficient became lower than 1 as the hydrophilic membrane. Both of the coefficients became constant when the methyl alcohol content was over 60%. The effect of ethyl alcohol was also investigated and there was the same tendency as the case of methyl alchol but the effect was larger than that of methyl alcohol. The coefficient became constant when the ethyl alcohol content was over 40% and the constant value of the diffusion coefficient was 26.8×10^{-8} cm^2 s^{-1} and that of distribution coefficient was 0.31.

When urea was added to the solution, the tendency was the reverse to that of the alcohols and the distribution coefficient increased and the diffusion coefficient decreased with increasing concentration of urea. When the concentration of urea was 5 mol dm^{-3}, the diffusion and the distribution coefficients were 4.45×10^{-8} cm^2 s^{-1} and 3.41, respectively. These differences were caused by the difference effect of the organics on the hydrophobic hydration and the ion hydration. Urea is well-known to have a structure breaking effect to the hydrophobic hydration[24] and then potassium chloride plays a roll in the hydrophobic membrane as a strongly hydrated salt such as lithium chloride.

Conclusion

The permeation properties of salts in a hydrophobic FEP membrane were governed by the water of the hydrophobic hydration structure adjacent to the wall of the hydrophobic membrane, the ion, and the water around the ion. The mutual effects were very complicated and the hydrophobic membrane had some characteristic permeation properties different from those of the reverse osmosis membranes.

Under a concentration gradient without a pressure gradient, the weakly hydrated ions were much more permeable than strongly hydrated ions across a hydrophobic membrane. The dependency of the distribution coefficients of ions on their hydration properties was reverse to that of the diffusion coefficients and was corresponded well with that of the salt passage under a pressure gradient. Salts were stabilized in the water in the membrane by the interaction with the hydrophobic hydration and were enriched in the membrane.

The hydration properties of the hydrophobic membrane and the salt changed with the salt concentration, the temperature, and the addition of some organics. The representative permeation properties across the membrane were revealed in the low salt concentration and were diminished by the addition of alcohols to the source phase solution.

References

1) I. Satake, H. Nakajima, and H. Noguchi, *Membrane,* **2,**

225 (1977).

2) M. Igawa, Y. Nakamura, K. Takahashi, M. Tanaka, and M. Seno, *J. Polym. Sci., Polym. Lett. Ed.,* **20**, 165 (1982).

3) M. Igawa, K. Torii, M. Tanaka, and M. Seno, *J. Appl. Polym. Sci.,* **29**, 117 (1984).

4) M. Igawa, S. Yoshida, T. Yamabe, and N. Takai, *Desalination,* **17**, 257 (1975).

5) M. Igawa, M. Seno, H. Takahashi, and T. Yamabe, *J. Membr. Sci.,* **2**, 263 (1977).

6) M. Igawa, A. Saito, N. Sasamura, and M. Seno, *J. Membr. Sci.,* **14**, 59 (1983).

7) M. Igawa, T. Tachibana, K. Yoshida, M. Tanaka, and M. Seno, *Chem. Lett.,* **1984**, 1527.

8) M. Igawa, T. Anzai, and M. Seno, *Chem. Lett.,* **1985**, 1703.

9) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.,* **36**, 3401 (1962).

10) S. Hirose, E. Yasukawa, and M. Hayashi, *J. Membr. Sci.,* **11**, 177 (1982).

11) R. Bautenbach and R. Albrecht, "Membrane Proceses," John Wiley & Sons, Chichester (1989), p. 67.

12) "Kagaku Binran Kisohen," ed by Japan Chemical Society, Maruzen, Tokyo (1984), p. II-66.

13) R. Paterson and P. Doran, *J. Membr. Sci.,* **26**, 289 (1986).

14) H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polym. Sci.,* **9**, 1341 (1965).

15) E. K. L. Lee, H. K. Lonsdale, R. W. Baker, E. Drioli, and P. A. Bresnahan, *J. Membr. Sci.,* **24**, 125 (1985).

16) F. Basolo and R. Johnson, "Coordination Chemistry," W. A. Benjamin, New York, N. Y. (1964), p. 122.

17) O. Kedem and A. Katchalsky, *Biochim. Biophys. Acta,* **27**, 229 (1958).

18) S. B. McCray, V. L. Viker, and K. Nobe, *J. Membr. Sci.,* **59**, 317 (1991).

19) T. Matuura, "Gouseimaku No Kiso," Kitami Shobo, Tokyo (1981), p. 171.

20) P. M. Wiggins, *Prog. Polym. Sci.,* **13**, 1 (1988).

21) J. E. Desnoyer, M. Arei, G. Perron, and C. Jolicoeur, *J. Phys. Chem.,* **73**, 3346 (1969).

22) K. Miyajima, *Kagaku no Ryoiki, Zokan-go,* **106**, 83 (1974).

23) S. Prabhakar and B. M. Misra, *J. Membr. Sci.,* **29**, 143 (1986).

24) N. Takeguchi, *Kagaku no Ryoiki, Zokan-go,* **106**, 111 (1974).