

Permselectivity between Anions in Anion-Exchange Membranes

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In order to control hydrophilicity of anion-exchange membranes, modified anion-exchange membranes were prepared by the reaction of a copolymer membrane composed of chloromethylstyrene and divinylbenzene with triethylamine, 2,2-diethylaminoethanol, N-ethyl-diethanolamine and triethanolamine. The ion-exchange equilibrium constant, the mobility ratio and ion selectivity coefficient between fluoride ions and chloride ions were measured using these membranes. The increase of the ion-exchange equilibrium constant with increasing the hydrophilicity of the anion-exchange groups indicates that the strongly hydrated fluoride ions are ion-exchanged more easily in the membrane with high hydrophilicity, in comparison with the less-hydrated chloride ions. The mobility ratio of fluoride ions to chloride ions in the membranes decreases with decreasing membrane water content. This means that the mobility of the strongly hydrated fluoride ions decreases more steeply in the membrane with low water content than that of the less-hydrated chloride ions.

Key words: Permselectivity, Anion, Anion exchange membrane, Electrolysis

1. INTRODUCTION

The excess of fluoride ions in ground water is found in many regions, such as Africa,¹ America,² Europe,^{3,4} and Asia.⁵⁻⁶ The ions in drinking water have caused serious health problems. There are several methods to remove fluoride ions and to improve the quality of drinking water.⁷⁻⁹ It was reported that fluoride ions are difficult to permeate through conventional anion-exchange membranes because the ion-exchange equilibrium constant of the ions compared with chloride ions is extremely low.^{10,11} However, electrolysis^{1,12,13} is one of the most effective methods to remove fluoride ions if ion-exchange membranes having permselectivity for the ions are developed. Sata et al.¹⁴⁻¹⁹ have studied about dependence of membrane hydrophilicity on permselectivity between ions with the same sign and the same valence. They reported that the permeation of fluoride ions increased relative to chloride ions by impregnating compounds containing ether bonds into anion exchange membranes.¹⁹

In this study, anion-exchange membranes having

different degree of hydrophilicity were prepared by the reaction of a copolymer membrane composed of chloromethylstyrene and divinylbenzene with various kinds of amine groups. We prepared anion-exchange membranes having different degree of hydrophilicity by changing anion exchange groups. We measured the permeability coefficient, the ion exchange equilibrium constant and the ionic mobility ratio of various anions in the membranes to analyze the relationship between the permselectivity of fluoride ions and membrane hydrophilicity.

2. EXPERIMENTAL

2.1. Sample membranes

Anion-exchange membrane with different anion-exchange groups were prepared by the reaction of the copolymer membrane composed of chloromethylstyrene-divinylbenzene with triethylamine, 2,2-diethylaminoethanol, N-ethyl-diethanolamine and triethanolamine. The copolymer membrane was prepared by the same methods as shown elsewhere.²² The obtained copolymer membrane was

reacted at 60°C with the amines: a 1M triethylamine alcohol solution for 24h, a 1M 2,2-diethylaminoethanol alcohol solution for 48h, a 1M N-ethyl-diethanolamine alcohol solution for 240h and a 1 M triethanolamine alcohol solution for 480h. After the reaction, the membranes were thoroughly washed with a 1.0 hydrochloric acid solution. The membranes were equilibrated with an aqueous 1.0 N hydrochloric acid solution and a 0.5 N sodium chloride solution alternately, and then stored in a 0.5 N sodium chloride solution. The characteristics of the anion-exchange membranes are listed in Table I.

Table I: Amines, ion exchange capacity, Q , water content, H and thickness, d , of the anion exchange membranes.

Name	M1	M2	M3	M4
Amines	A1*	A2*	A3*	A4*
Q ¹⁾	1.55	1.57	1.52	1.37
H ²⁾	32.6	25.7	17.6	13.3
d [mm]	0.145	0.141	0.137	0.113

*A1:Triethylamine, A2:2-Diethylaminoethanol, A3:N-Ethyl-diethanolamine, A4:Triethanolamine

¹⁾meq./g-dry membrane ²⁾g-H₂O/g-dry membrane

2.2 Measurements of ion selective coefficient in electro dialysis

Fig. 1 shows four-compartment cell with Ag/AgCl for electro dialysis to measure ion selective coefficient of fluoride ions to chloride ions. After an anion-exchange membrane had been placed in the cell, the two middle compartments were filled with 100cm³ of a 1:1 mixed sodium chloride and sodium fluoride solution. Its concentration was 0.01N or 0.04N as sodium ion concentration. The anolyte and the catholyte were sodium chloride solutions, which were separated by cation exchange membranes (NEOSEPTA CM-2, made by Tokuyama), and their concentration was the same as that of the mixed salt solution in the middle compartments. Electro dialysis was carried out at the current density of 1mA/cm² under vigorous agitation (1500 rpm with stirrers) for 60 min at 25.0°C. After electro dialysis, the solutions were analyzed by an ion

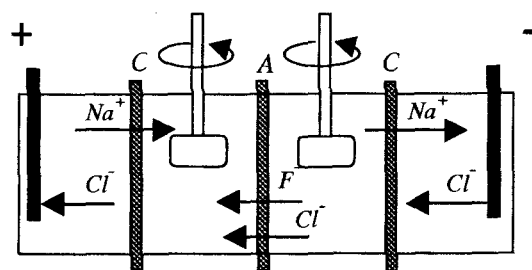


Fig. 1 Apparatus for measurement of ion selective coefficient of fluoride ions to chloride ions. C: cation exchange membrane; A: anion exchange membrane; effective membrane area: 2cm × 5cm; volume of each compartment: 100cm³

chromatograph (TOSHO CCPD, IC-8010). The ion selective coefficient, P_{Cl}^F , was calculated from the following equation:

$$P_{Cl}^F = \frac{C_F(L) - C_F(R)}{C_{Cl}(L) - C_{Cl}(R)} \quad (1)$$

where $C_i(L)$ and $C_i(R)$ ($i=Cl$ or F) are the anion concentration at the compartment at side L and at side R, respectively.

2.3 Measurements of membrane electrical resistance

Electrical resistance of the anion-exchange membranes was measured by 1000Hz AC, using Hewlett Packard LCR-4263 meter at 25.0°C and a two compartment cell (effective membrane area is 1.0cm²) with platinum black electrodes. The electrical resistance was measured using 0.50N sodium chloride and sodium fluoride.

2.4 Ion exchange equilibrium constant between ions

The ion exchange equilibrium constant between fluoride ions and chloride ions was determined as follows: after the membranes had been equilibrated with a 1:1 mixed sodium chloride and sodium fluoride solution whose concentration was 0.01N or 0.04N as sodium ion concentration, both the anions had been eluted with 0.1M sodium sulfate, and then the concentration of the anions was determined by the ion chromatograph. The equilibrium constant, K_{Cl}^F , was defined as:

$$K_{Cl}^F = \frac{\bar{C}_F}{\bar{C}_{Cl}} \quad (2)$$

where \bar{C}_F and \bar{C}_{Cl} were the concentration of fluoride

and chloride ions ion-exchanged in the membranes.

The water content and ion-exchange capacity of the membrane were measured according to conventional methods.

3. RESULTS AND DISCUSSION

Fig. 2 shows the effect of species of anion-exchange groups on the ion exchange equilibrium constant, K_{Cl}^F . K_{Cl}^F increases with increasing number of hydroxyl groups in the ion-exchange groups. Hydrophilicity of the ion-exchange groups increases with increasing number of hydroxyl groups. Fluoride ions are strongly hydrated compared with chloride ions (the Gibbs hydration energies of fluoride and chloride ions are -434 and -317 kJ mol^{-1} , respectively). Hence, it is thought that the strongly hydrated fluoride ions are ion-exchanged more easily in the membrane with high hydrophilicity, in comparison with the less-hydrated chloride ions. K_{Cl}^F increases with increasing concentration of the mixed salt solutions. This means that the effect of hydrophilicity of the charged groups on ion-exchange equilibrium increases with decreasing salt concentration.

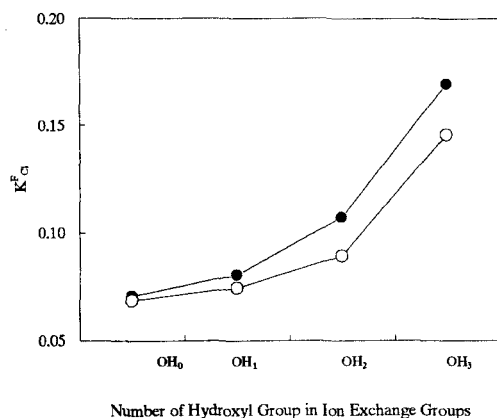


Fig. 2 Effect of species of anion-exchange groups on the ion-exchange equilibrium constant, K_{Cl}^F : ●: 0.005N NaF+0.005N NaCl ; ○: 0.02N NaF+0.02N NaCl.

Fig. 3 shows mobility ratio of fluoride ions to chloride ions in the membranes as a function of membrane water content, H . As shown in Table I, the membrane water content decreases in order of membrane M1, M2, M3 and M4, in other words, with increasing

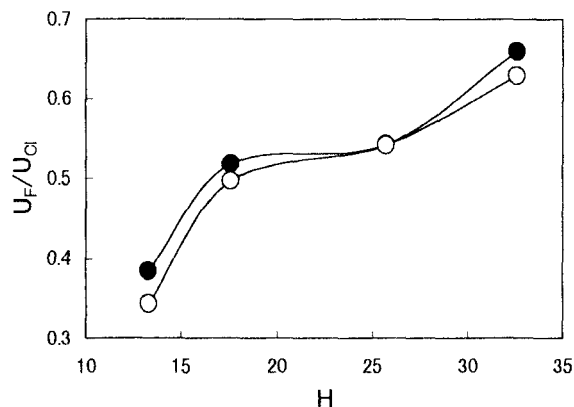


Fig. 3 Mobility ratio of fluoride ions to chloride ions in the membranes, U_F/U_{Cl} , as a function of membrane water content, H : ●: 0.005N NaF+0.005N NaCl ; ○: 0.02N NaF+0.02N NaCl.

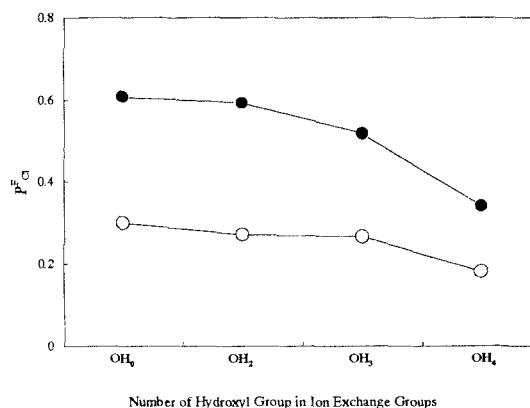


Fig. 4 Ion selective coefficient, P_{Cl}^F , of the ion-exchange membranes vs. number of hydroxyl group: ●: 0.005N NaF+0.005N NaCl ; ○: 0.02N NaF+0.02N NaCl.

number of hydroxyl groups in the ion exchange groups. The mobility ratio of fluoride ions to chloride ions in the membranes decreases with decreasing H . In an aqueous solution, the mobility ratio is 0.73.²⁰ This means that fluoride ions are strongly hydrated compared with chloride ions, and the radius of the hydrated fluoride ions is larger than that of chloride ions. In Fig. 3, the ratio in the membranes is almost the same as that in an aqueous solution when the membranes have high water content. The mobility of strongly hydrated fluoride ions decreases more steeply with decreasing H in compared with less-hydrated chloride ions.

Fig. 4 shows the ion selective coefficient, P_{Cl}^F , of the ion exchange membranes vs. number of hydroxyl group.

P_{Cl}^F in all the membranes are smaller than unity. This means that these membranes have the selectivity for chloride ions. P_{Cl}^F decreases slightly with increasing number of hydroxyl group. The ion selective coefficient is equal to the ion exchange equilibrium constant times the mobility ratio in a membrane. Hence, The slight decrease of P_{Cl}^F indicates that the effect of the decrease of the mobility ratio on the selectivity for fluoride ions is larger than that of the increase of ion exchange equilibrium constant in the membranes. P_{Cl}^F in the 0.01N mixed solution is larger than that in the 0.04N mixed solution in all the membranes because K_{Cl}^F in the former is larger than that in the latter while the mobility ratio does not change with the concentration.

4. CONCLUSIONS

In order to increase the hydrophilicity of anion-exchange membranes, We made anion exchange membranes with various kinds of anion exchange groups. The data of the ion exchange equilibrium constant indicates that the strongly hydrated fluoride ions are ion-exchanged more easily in the membrane with high hydrophilicity, in comparison with the less-hydrated chloride ions. The data of the electrical resistance shows that the mobility of the strongly hydrated fluoride ions decreases more steeply in the membrane with low water content than that of the less-hydrated chloride ions. These results indicate that an anion-exchange membrane which has high water content and consists of hydrophilic charge groups and/or hydrophilic matrix, such as poly(vinyl alcohol) will have higher permselectivity for fluoride ions than conventional ion exchange membranes.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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