

Cation-Exchange Membranes Having High Permselectivity For Multi-Valent Ions

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In order to examine the relationship between permselectivity for multi-valent ions in a Donnan dialysis system and membrane water content, cation-exchange membranes with high water content in comparison with conventional cation-exchange membranes were prepared from a hydrophilic matrix, poly(vinyl alcohol), and a polyanion. Permeation of copper ions and potassium ions across the membranes and a conventional cation-exchange membrane (NEOSEPTA CM-1, Tokuyama Co.) was measured in the system of mixed HCl, KCl and CuSO_4 electrolyte solutions. The permeation experiments show that in the system, the CM-1 membrane has permselectivity for potassium ions, but the membranes made from PVA matrix for copper ions. This result indicates that the mobility of the strongly hydrated copper ions in a membrane decreases more steeply with decreasing membrane water content than the less-hydrated potassium ions does. The permeability of both the cations across the CM-1 membrane is larger than that across the PVA membranes because of high charge density of the CM-1 membrane.

Key words: Ion selectivity, Donnan dialysis, Cation exchange membrane, Mobility, Poly(vinyl alcohol)

1. INTRODUCTION

Ion-exchange membranes are widely used in industrial waste treatment and water purification¹⁻³ because of their highly selective properties in the separation processes. The specific membrane process which makes use of the Donnan equilibrium principle⁴ and coupled transport of counter ions in a ion-exchange membrane is "Donnan dialysis", introduced for the first time by Wallace.⁵ In Donnan dialysis, An ion-exchange membrane, e.g., an cation-exchange membrane separates two cells which contain different kinds of electrolytes each other. The cation-exchange membrane is permeable to cations but not to anions. Hence, the cations will diffuse through the membrane in either direction, whereas anions diffuse through it very slowly. The condition that electric current is zero in the system requires the countercurrent fluxes of cations to be coupled. In case that the concentration of an electrolyte in one cell is much larger than that in the other cell, the cations of the electrolytes are transported against their concentration gradients. Teorell⁶ pioneered the

quantitative study of the transport by using a cation-exchange membrane. After his reports, many studies have been made concerning the transport.⁷⁻¹¹ Recently, Higa et al.¹² have studied about simulation of the transport in nonstationary states. Their simulations show that both the initial flux and the maximum concentration of bivalent ions are larger than those of univalent ions. This means that a Donnan dialysis system using a cation-exchange membrane has permselectivity for bivalent ions. However, the permselectivity was not observed in their experiments by using a conventional cation-exchange membrane because of low water content of the membrane. Donnan dialysis is one of the most effective methods to remove high-valent ions, such as Cu^{2+} ion, Cd^{2+} ion from industrial waste water if ion-exchange membranes having permselectivity for high-valent ions are developed.

In this study, cation-exchange membranes with high water content in comparison with conventional cation-exchange membranes were prepared from a hydrophilic matrix, poly(vinyl alcohol), and a polyanion. In order to

examine relationship between permselectivity for bivalent ions and membrane water content, permeation of Cu^{2+} ion and K^+ ion across the membranes and a conventional cation-exchange membrane was measured in the system of mixed HCl, KCl and CuSO_4 electrolyte solutions.

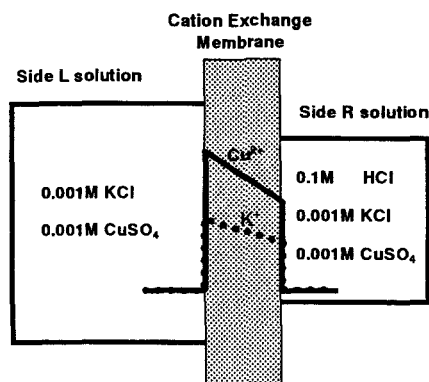


Fig. 1 Donnan dialysis system in this study and schematic diagram of the concentration gradient of Cu^{2+} ion and K^+ ion in a cation-exchange membrane.

2. EXPERIMENTAL

2.1. Sample membranes

Aqueous solutions of a mixture of PVA [poly(vinyl alcohol), aldrich] and AP-2 [Kuraray Co. Ltd.] were cast for cation-exchange membranes. The AP-2 polymer contains sulfonic groups which provide cation-exchange sites. The volume fraction of PVA to AP-2 was changed to control the charge densities. After annealing the membranes at 160°C for 20 min., they were crosslinked in an aqueous solution of 20% Na_2SO_4 , 1% H_2SO_4 and 0.1% glutaraldehyde at 25°C to obtain membranes with low water content.

A conventional cation-exchange membrane (NEOSEPTA CM-1, Tokuyama Co.) was also used as a reference membrane.

2.2 Definition of membrane charge density

Membrane potential was measured as a function of external KCl concentration of a dialysis system by the same apparatus and the same conditions as described elsewhere.¹¹ The charge density was estimated from the data by the same methods as described elsewhere.¹¹

2.3 Measurement of membrane water content

Membrane water content is defined as the following equation:

$$H = W_s / W_d \quad (1)$$

where W_s and W_d are the weights of a membrane at the equilibrium swollen and dry states, respectively.

Membrane charge density, ion exchange capacity, water content and thickness of the anion exchange membranes are listed in Table I.

Table I: Membrane charge density, C_x , Ion exchange capacity, Q , water content, H and thickness, d , of the anion exchange membranes.

Name	CM-1	C-2	C-3
C_x ¹⁾	-	0.60	0.64
Q ²⁾	1.55	-	-
H ³⁾	32.6	76.5	58.1
d [mm]	0.138	0.260	0.185

¹⁾mol/l, ²⁾meq./g-dry membrane ³⁾g- H_2O /g-dry membrane

2.4 Permeation experiments

The permeation of K^+ ions and Cu^{2+} ions was measured by the same apparatus as shown elsewhere.¹¹ Figure 1 shows the dialysis system in the experiment. Initially, the cell L contains 0.001M of KCl and CuSO_4 , and the cell R 0.001M of KCl and CuSO_4 , and 0.1M HCl. The side R solution was sampled to measure the ion concentrations by atomic absorption spectrophotometry (HITACHI 170-50A).

Permeability of ions across the membranes, P_i , is defined as:

$$P_i = \frac{V^R d \Delta C_i^{init}}{C_o S \Delta t} \quad (4)$$

where $\Delta C_i^{init} / \Delta t$ is the initial concentration change with time; S is membrane area. Permselectivity between Cu^{2+} ion and K^+ ion, P_K^{Cu} , is defined as

$$P_K^{Cu} = P_{Cu} / P_K \quad (5)$$

3. RESULTS AND DISCUSSION

Fig. 2 shows time-concentration curves of K^+ ion and Cu^{2+} ion at side R cell in the system using the C-2

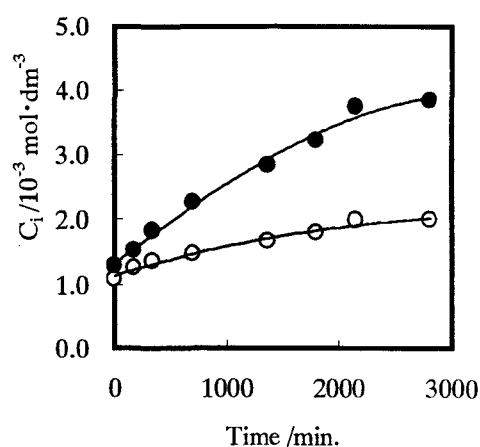


Fig. 2 Time-concentration curves of K^+ ion and Cu^{2+} ion at side R cell in the system using the C-2 membrane. ●, Cu^{2+} ion; ○, K^+ ion.

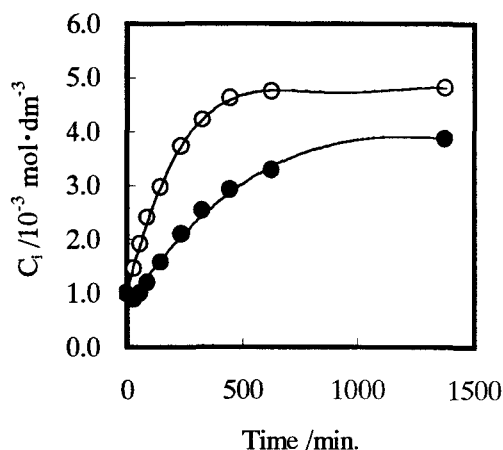


Fig. 3 Time-concentration curves of K^+ ion and Cu^{2+} ion at side R cell in the system using the CM-1 membrane. ●, Cu^{2+} ion; ○, K^+ ion.

membrane. The concentration increase of the two cations indicates that both the ions are transported against their concentration gradients, driven the diffusion of hydrogen ion. The initial flux of Cu^{2+} ion is larger than that of K^+ ion though the mobility of Cu^{2+} ion in an aqueous solution is smaller than that of K^+ ion (the mobility of Cu^{2+} ion and K^+ ion are $7.89 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$ and $2.88 \times 10^{-13} \text{ mol m}^2 \text{ J}^{-1} \text{ s}^{-1}$, respectively¹³). This means that the system using the C-1 membrane has permselectivity for the bivalent ion. The permselectivity of the system is due to the following effects: (1) The bivalent ion receives two times stronger electric force than the univalent ion does by the diffusion potential generated by the diffusion of the driving electrolyte. (2)

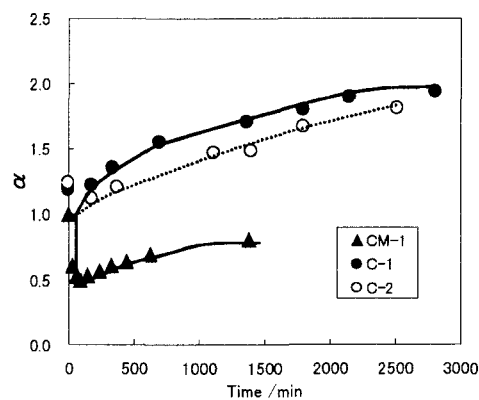


Fig. 4 The concentration ratio of Cu^{2+} ion to K^+ ion in the side R cell, α , as a function of time. ▲, ○, and ● are the data of CM-1, C-2 and C-3 membrane, respectively.

The Donnan equilibrium equation indicates that the concentration of the bivalent ion in the membrane is much larger than that of the univalent ion as shown in Fig. 1. The ionic flux proportions to the ionic concentration in the membrane; thus, the flux of the bivalent ion is much larger than that of the univalent ion.

Fig. 3 shows time-concentration curves of K^+ ion and Cu^{2+} ion at side R cell in the system using the CM-1 membrane. On the contrary to the result in Fig. 2, The initial flux of K^+ ion is larger than that of Cu^{2+} ion. This means that the system using the CM-1 membrane has permselectivity for univalent ion. The less flux of Cu^{2+} ion than that of K^+ ion indicates that the mobility of the ion in the membrane is much smaller than that in an aqueous solution because of the low water content of the membrane.

Fig. 4 shows the concentration ratio of Cu^{2+} ion to K^+ ion in the side R cell, α , as a function of time. The ratio in both the C-1 and C-2 membranes increases with time. This means that the flux of Cu^{2+} ion in the system is larger than that of K^+ ion in all the diffusion time. The ratio of the C-1 membrane is larger than that of the C-2 membrane. As shown in Table I, the water content of the C-1 membrane is larger than that of the C-2 membrane while the two membranes have almost the same charge density. Hence, the difference of α between the two membranes indicates that permselectivity for bivalent ions increases with membrane

water content. On the contrary, the ratio in the CM-1 membrane decreases with time at the initial stage, and has a minimum value at the diffusion time, $t = 150$ min., and then increases with time. This means that the flux of Cu^{2+} ion in the system is smaller at the initial stage, but is larger after 300 min. than that of K^+ ion. When $t = 150$ min, the K^+ ion concentration in the side R cell is 2.8×10^{-3} mol/dm³, and that in the side L cell is estimated as by 0.55×10^{-4} mol/dm³ from the initial concentration and the volume of the two cells. The concentration ratio of K^+ ion between the two cells at the time is 5.1 while that of Cu^{2+} ion is 1.8. Hence, it is difficult for K^+ ion to be transported against its concentration gradient because of the high concentration difference between the two cells. Therefore, the flux of Cu^{2+} ion becomes larger than that of K^+ ion after the time. This result implies that α will decrease with increasing the volume of the side L cell in the system using the CM-1 membrane.

Table II: Permeability of ions, P_i , and permselectivity between Cu^{2+} ion and K^+ ion, P_K^{Cu} of the cation-exchange membranes.

Name	CM-1	C-2	C-3
P_K^{-1}	4.3	0.33	0.23
P_{Cu}^{-1}	2.1	0.97	0.40
P_K^{Cu}	0.49	2.9	1.8

*1 $\times 10^9$ m²/s

P_i and P_K^{Cu} in the membranes are listed in Table II. The data in Table I and II indicate that the permselectivity for the bivalent ion increases with increasing membrane water content. Permeability of both the cations across the CM-1 membrane is larger than that of the C-1 and C-2 membranes in spite of the low water content of the CM-1 membrane because the CM-1 membrane has higher charge density than the C-1 and C-2 membrane does.

4. CONCLUSIONS

Permeation experiments in a Donnan dialysis system of HCl-KCl-CuSO₄ solutions show that the system using a cation-exchange membrane with low water content has permselectivity for univalent ions, but the system using the membrane with high

water content for bivalent ions. This means that the mobility of the strongly hydrated Cu^{2+} ion in a membrane decreases more steeply with decreasing membrane water content in comparison with the less-hydrated K^+ ion. The initial flux of the two cations in the CM-1 membrane is larger than that in the PVA membranes because of the high charge density of the CM-1 membrane. These results indicate that a cation-exchange membrane which has high water content and high charge density will be very useful for removing heavy metal ions from industrial waste water in the system of Donnan dialysis.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- (1) Y. Oda, A. Nishihara, H. Hani and T. Yawataya, *Ind. Eng. Chem. Prod. Res. Dev.*, 3, 244(1964).
- (2) H. K. Lonsdale, *J. Membr. Sci.*, 10, 81(1982).
- (3) W. Pusch and A. Walch, *Angew. Chem., Int. Ed. Engl.*, 21, 660(1982).
- (4) F. G. Donnan, *Chem. Rev.*, 1, 73(1925).
- (5) R. M. Wallace, *Ind. Eng. Chem., Process Des. Dev.*, 6, 423(1967).
- (6) T. Teorell, *Proc. Natl. Acad. Sci. U.S.A.*, 21, 152(1935); *Trans. Faraday Soc.*, 33, 939(1937).
- (7) T. Shimizu, M. Yoshikawa, M. Hasegawa and K. Kawakatsu, *Macromolecules*, 14, 170(1981).
- (8) T. Uragami, F. Yoshida and M. Sugihara, *J. Appl. Polym. Sci.*, 28, 1361(1983).
- (9) M. Yoshikawa, Y. Yatsuzuka, K. Sanui and N. Ogata, *Macromolecules*, 19, 995(1986).
- (10) E. L. Cussler, R. Aris and A. Bhowm, *J. Membr. Sci.*, 43, 149(1989).
- (11) M. Higa, A. Tanioka and K. Miysasaka, *J. Membr. Sci.*, 37, 251(1988); 49, 145(1990); 64, 255(1991).
- (12) M. Higa and A. Kira, *J. Phys. Chem.*, 96, 9518(1992).
- (13) *International critical tables*, McGraw-Hill, NY, 1949.