Characteristic Coefficients of Cation-Exchange Membranes for Bivalent Cations in Equilibrium between the Membrane and Solution

Hirofumi Miyoshi,* Masayuki Yamagami, Mitsuo Chubachi, and Takeshi Kataoka

Research Institute for Advanced Science and Technology, University of Osaka Prefecture, 1-2 Gakuen-cho, Sakai, Osaka 593, Japan

Characteristic coefficients of four cation-exchange membranes (Neosepta C66-5T, Selemion CMV, Aciplex K101, and Nafion 417 membranes) for three bivalent cations in equilibrium between the membrane and solution were measured. The order of the exchange affinities of the bivalent cations was $Mg^{2+} < Cu^{2+} < Ca^{2+}$ for all the membranes studied. The selectivity coefficients between bivalent cation–bivalent cation systems (*e.g.*, $K_{Ca}{}^{Mg}$) for each membrane remained constant over a 3-order variation of the concentrations of the total cations in solution. The ratios of selectivity coefficients (*e.g.*, $K_{Ca}{}^{Mg}(K_{Ca}{}^{Cu})^{-1}$) were constant among various kinds of membranes for Na^+–H^+, Na^+–K^+, K^+–H^+, Ca^{2+}–Mg^{2+}, Ca^{2+}–Cu^{2+}, and Mg^{2+}–Cu^{2+} systems. In addition, the exchange capacity, water content, density, and thickness of the Aciplex K101 membrane were measured, and compared to those of the Neosepta C66-5T, Selemion CMV, and Nafion 417 membranes.

I. Introduction

Ion-exchange membranes have been used for electrodialysis (*1, 2*), pervaporation (*3, 4*), diffusion dialysis (*5*), and Donnan dialysis (*6, 7*). The latter two dialyses are necessary to know the characteristic coefficients of ions in the membrane between the membrane and solution. There are many studies on the characteristic coefficients of the ion-exchange membranes (*8–11*). We previously studied the characteristic coefficients in relation to equilibrium between the membrane and solution using monovalent ion–monovalent ion systems, and monovalent ion–bivalent ion systems (*13, 14*). However, those coefficients using bivalent ion–bivalent ion systems have not yet been studied.

In this study, selectivity coefficients of various cation-exchange membranes were measured. Further, some of the characteristic constants of the Aciplex K101 cation-exchange membrane which has not been studied in the previous papers (*13, 14*) were measured: exchange capacity, water content, density, and concentration of the exchange capacity in the membrane. These values are compared with those of other cation-exchange membranes.

II. Experimental Procedure

II.1. Measurement of E_c, W_c, ρ, t, and Q_0. The characteristic constants of the Aciplex K101 membrane such as the exchange capacity per unit mass of the dry membrane (E_c (mmol g^{-1})), water content (W_c (dimensionless)), density of the dry membrane (ρ (g cm^{-3})), thickness (t (cm)), and exchange capacity per volume of the dry membrane (Q_0 (mmol cm^{-3})) ($=E_c\rho$) were measured by the same method as reported in the previous papers (*13, 14*).

The concentrations of cations in solution were measured with a Perkin-Elmer 403 atomic absorption spectrophotometer or by a titration method.

II.2. Equilibrium Coefficients. The cation-exchange reaction between B^{z_B+} ions in solution and A^{z_A+} ions in the membrane at equilibrium is represented by eq 1, where R is

$$z_BR_{z_A}\text{–}A + z_AB^{z_B+} \rightleftharpoons z_AR_{z_B}\text{–}B + z_BA^{z_A+} \qquad (1)$$

a fixed ion of the membrane. z_A and z_B are the valences of the A and B ions, respectively. The dimensionless concentration of B^{z_B+} ions in solution (x) and that in the membrane (y) are represented by eqs 2 and 3, where C_0 ($=z_Ac_A + z_Bc_B$),

$$x = \frac{z_Bc_B}{C_0} = \frac{z_Bc_B}{z_Ac_A + z_Bc_B} \qquad (2)$$

$$y = \frac{z_Bq_B}{Q_0} = \frac{z_Bq_B}{z_Aq_A + z_Bq_B} \qquad (3)$$

c_A, and c_B (mol cm^{-3}) are the concentrations of the total cations, A ions, and B ions in solution, respectively. Q_0 ($=z_Aq_A + z_Bq_B$), q_A, and q_B (mol cm^{-3}) are the concentrations of the total cations, A ions, and B ions in the membrane, respectively.

The selectivity coefficients of the ions between the membrane and solution ($K_A{}^B$ (dimensionless)) are represented by the following equation (*15, 16*):

$$K_A{}^B = \frac{(z_Bq_B)^{z_A}}{(z_Aq_A)^{z_B}}\frac{(z_Ac_A)^{z_B}}{(z_Bc_B)^{z_A}} = \frac{(1-x)^{z_B}y^{z_A}}{x^{z_A}(1-y)^{z_B}}\left(\frac{C_0}{Q_0}\right)^{z_B-z_A} = \alpha_A{}^B\left(\frac{C_0}{Q_0}\right)^{z_B-z_A} \qquad (4)$$

where $\alpha_A{}^B$ (dimensionless) is the separation factor. When z_A is equal to z_B, $K_A{}^B$ becomes equal to $\alpha_A{}^B$.

In order to investigate the equilibrium coefficients between the cation-exchange membrane and solution, we used NaCl, KCl, HCl, $CaCl_2$, $MgCl_2$, and $CuCl_2$ for cation sources, and Neosepta C66-5T (produced by Tokuyama Soda Co. Ltd., Japan), Selemion CMV (Asahi Glass Co. Ltd., Japan), Aciplex K101 (Asahi Chemical Industry Co. Ltd., Japan), and Nafion 417 (DuPont Co. Ltd., U.S.A.) as cation-exchange membranes. The Neosepta C66-5T, Selemion CMV, and Aciplex K101 membranes are sulfonated copolymers of styrene and divinylbenzene with varying ratios. The Nafion 417 membrane is a perfluoro sulfonic acid. Each membrane of an area of 8 × 8 cm^2 was put into a bottle of 100 cm^3 with 1.0 mmol cm^{-3} $MgCl_2$ solution. The bottle was shaken for *ca.* 8 h. This procedure was repeated three times, and all initial counterions were exchanged to Mg^{2+} ions. This membrane was again put into a bottle with 1.0 mmol cm^{-3} $CaCl_2$ solution. The concentration of Mg^{2+} ions in the $CaCl_2$ solution exchanged

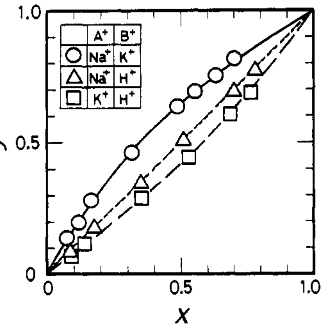

Figure 1. Relationship between the concentrations of cations in solution (x) and those in the Aciplex K101 membrane (y). Each line was drawn using x and y values which were calculated by eq 4 substituted with the $K_A{}^B$'s in Table 2.

Table 1. Exchange Capacity E_c, Water Content W_c, Density ρ, Thickness t, and Exchange Concentration Q_0 of the Four Membranes

	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417
E_c/(mmol g^{-1})	2.48	2.08	1.71	0.625
W_c	0.413	0.266	0.292	0.165
ρ/(g cm^{-3})	1.14	1.08	0.950	1.50
t/cm	0.0133	0.0130	0.0188	0.0418
Q_0/(mmol cm^{-3})	2.84	2.25	1.62	0.938

from the membrane was measured by an atomic absorption spectrophotometer. The concentrations of the cations in the membrane and solution were calculated using eqs 2 and 3. The selectivity coefficients were further calculated by eq 4.

III. Results and Discussion

III.1. Values of E_c, W_c, ρ, t, and Q_0. The characteristic constants E_c, W_c, ρ, t, and Q_0 for the Aciplex K101 cation-exchange membrane are shown in Table 1. The values for the Neosepta C66-5T, Selemion CMV, and Nafion 417 cation-exchange membranes measured previously (*13, 14*) are also shown in Table 1 for reference.

It is evident from Table 1 that the values of E_c, W_c, ρ, t, and Q_0 for the Aciplex K101 membrane are similar to those for the Neosepta C66-5T and Selemion CMV membranes of the same composition, but are different from those for the Nafion 417 membrane of a different composition.

III.2. Relationship between x and y in the Monovalent Cation–Monovalent Cation Systems. The relationships between x and y for Na^+ (A^+ ions)–K^+ (B^+ ions), Na^+ (A^+ ions)–H^+ (B^+ ions), and K^+ (A^+ ions)–H^+ (B^+ ions) systems, *viz.*, monovalent cation–monovalent cation systems, using an Aciplex K101 membrane are shown in Figure 1. Figure 1 shows that the experimental values of y for the Na^+–K^+ system are above the line of $y = x$, those for the Na^+–H^+ system are on it, and those for the K^+–H^+ system are below it, suggesting that the exchange affinity of K^+ cations for the membrane is a little larger than those of Na^+ and H^+ ions. There is no selectivity between the membrane and solution for the Na^+–H^+ system. The latter result of this membrane is different from the previous results for other membranes (*13, 14*). It was found that the exchange affinities between the monovalent cations for this membrane are represented by the following equation:

$$H^+ \simeq Na^+ < K^+ \tag{5}$$

III.3. Relationship between x and y in the Bivalent Cation–Bivalent Cation Systems. The x–y relationships of Ca^{2+} (A^{2+} ions)–Mg^{2+} (B^{2+} ions), Ca^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions), and Mg^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions) systems, *viz.*, bivalent cation–bivalent cation systems, using a Neosepta C66-5T membrane are shown in Figure 2. Figure 2 shows that the exchange affinities between these cations using this membrane are expressed by the following equation:

$$Mg^{2+} < Cu^{2+} < Ca^{2+} \tag{6}$$

The x–y relationships of the Ca^{2+} (A^{2+} ions)–Mg^{2+} (B^{2+} ions) system using four kinds of cation-exchange membranes, *viz.*, Neosepta C66-5T, Selemion CMV, Aciplex K101, and Nafion 417 membranes, are shown in Figure 3. The x–y relationships of Ca^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions) and Mg^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions) systems are shown in Figures 4 and 5, respectively. Figures 3–5 show that the same relations as represented by eq 6 are obtained in each system. Also there was no discernible difference in affinity between these membranes.

III.4. Selectivity Coefficient for Monovalent Cations on the Aciplex K101 Membrane. The values of $K_A{}^B$ for the Aciplex K101 membrane calculated using eq 4 are shown in Table 2. The values of $K_A{}^B$ measured previously on the Neosepta C66-5T, Selemion CMV, and Nafion 417 membranes (*13, 14*) are shown again in this table for reference. Table 2 suggests that various $K_A{}^B$'s measured for the Aciplex K101 membrane are represented by the following equations:

$$K_{Na}{}^{H} < K_{Na}{}^{K} \tag{7}$$

$$K_{K}{}^{H} < K_{K}{}^{Na} \tag{8}$$

The relationship in eq 7 for the Aciplex K101 membrane is in agreement with those for other membranes, *i.e.*, Neosepta C66-5T, Selemion CMV, and Nafion 417 membranes, but the

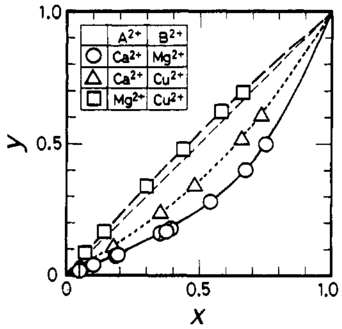

Figure 2. Influence of x on y using the Neosepta C66-5T membrane. Each line was drawn using x and y values which were calculated by eq 4 substituted with the $K_A{}^B$'s in Table 3. Symbols with a vertical line denote the values obtained when C_0 was changed between 0.0005 and 0.5 mmol cm^{-3}.

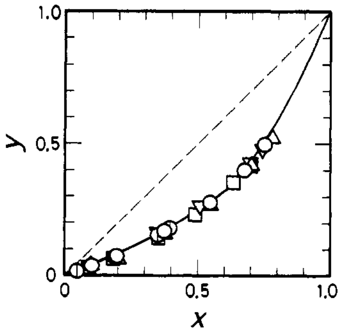

Figure 3. Effect of x on y using the Ca^{2+} (A^{2+} ions)–Mg^{2+} (B^{2+} ions) system using Neosepta C66-5T (○), Selemion CMV (△), Aciplex K101 (▽), and Nafion 417 (□) membranes. A line was drawn using x and y values which were calculated by eq 4 substituted with the $K_{Ca}{}^{Mg}$'s of the Neosepta C66-5T membrane in Table 3. Symbols with a vertical line denote the values obtained when C_0 was changed between 0.0005 and 0.5 mmol cm^{-3}.

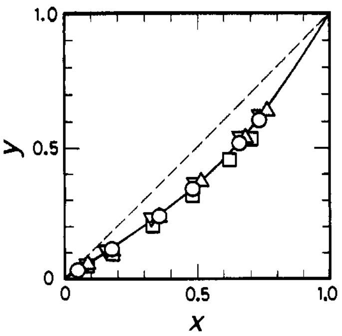

Figure 4. Dependence of x on y using the Ca^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions) system using Neosepta C66-5T (○), Selemion CMV (△), Aciplex K101 (▽), and Nafion 417 (□) membranes. A line was drawn using x and y values which were calculated by eq 4 substituted with the $K_{Ca}{}^{Cu}$'s of the Neosepta C66-5T membrane in Table 3.

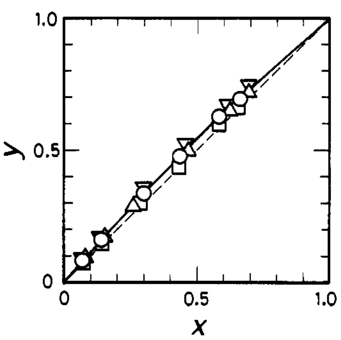

Figure 5. Relationship between x and y of the Mg^{2+} (A^{2+} ions)–Cu^{2+} (B^{2+} ions) system using Neosepta C66-5T (○), Selemion CMV (△), Aciplex K101 (▽), and Nafion 417 (□) membranes. A line was drawn using x and y values which were calculated by eq 4 substituted with the $K_{Mg}{}^{Cu}$'s of the Neosepta C66-5T membrane in Table 3.

Table 2. Selectivity Coefficients $K_A{}^B$ between Two Monovalent Ions

	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417
$K_{Na}{}^{K}$	1.48	1.41	1.88	3.28
$K_{Na}{}^{H}$	0.564	0.705	0.975	0.553
$K_{K}{}^{H}$	0.397	0.606	0.753	
$K_{K}{}^{Na}$	0.674	0.708	0.533	0.305

Table 3. Selectivity Coefficients $K_A{}^B$ between Two Bivalent Ions

	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417
$K_{Ca}{}^{Mg}$	0.108	0.0986	0.114	0.101
$K_{Ca}{}^{Cu}$	0.310	0.305	0.341	0.253
$K_{Mg}{}^{Ca}$	9.26	10.15	8.77	9.94
$K_{Mg}{}^{Cu}$	1.38	1.28	1.63	1.08

relationship in eq 8 for the Aciplex K101 membrane is different from those for the other membranes.

III.5. Selectivity Coefficient for Bivalent Cation–Bivalent Cation Systems. The values of $K_A{}^B$ calculated for four kinds of cation-exchange membranes are shown in Table 3. The relationship between $K_A{}^B$ obtained for the bivalent cation–bivalent cation systems is represented by the following equations for all the membranes employed:

$$K_{Ca}{}^{Mg} < K_{Ca}{}^{Cu} \tag{9}$$

$$K_{Mg}{}^{Cu} < K_{Mg}{}^{Ca} \tag{10}$$

This trend is equal to those of the exchange affinities obtained in Figures 2–5.

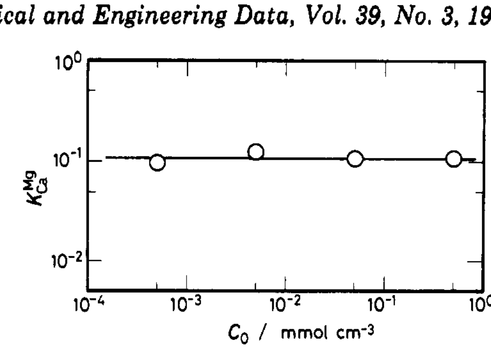

Figure 6. Relationship between the total concentration (C_0) and the selectivity coefficient ($K_{Ca}{}^{Mg}$) using the Neosepta C66-5T membrane.

Table 4. Ratios of Selectivity Coefficients $K_A{}^B/K_C{}^D$ between Two Monovalent Ions and Two Bivalent Ions

	Neosepta C66-5T	Selemion CMV	Aciplex K101	Nafion 417	mean value
$K_{Na}{}^{H}/K_{Na}{}^{K}$	0.380	0.499	0.519	0.169	0.466
$K_{K}{}^{H}/K_{Na}{}^{H}$	0.703	0.859	0.773		0.778
$K_{Ca}{}^{Cu}/K_{Ca}{}^{Mg}$	2.87	3.10	2.99	2.51	2.87
$K_{Mg}{}^{Cu}/K_{Ca}{}^{Cu}$	4.45	4.19	4.77	4.26	4.42

III.6. Relationship between Each Selectivity Coefficient. The ratios of one selectivity coefficient ($K_A{}^B$) to another selectivity coefficient ($K_A{}^C$ or $K_C{}^B$), *i.e.*, $K_{Na}{}^{H}/K_{Na}{}^{K}$, $K_{K}{}^{H}/K_{Na}{}^{H}$, $K_{Ca}{}^{Cu}/K_{Ca}{}^{Mg}$, and $K_{Mg}{}^{Cu}/K_{Ca}{}^{Cu}$, are shown in Table 4. In the table, the ratio of only $K_{Na}{}^{H}/K_{Na}{}^{K}$ on the Nafion 417 membrane is different from those on the other membranes. The mean values of each ratio are shown again in this table, excluding the value for $K_{Na}{}^{H}/K_{Na}{}^{K}$ on the Nafion 417 membrane. Each ratio in Table 4 is clearly close to the corresponding mean values, although the values include an average error of 7.1%. Table 4 suggests that we can estimate the $K_A{}^B$ value of bivalent cations between the membrane and solution when we know the $K_A{}^C$ value of the same membrane.

III.7. Influence of the Concentration on $K_A{}^B$. The relationship between the selectivity coefficient ($K_{Ca}{}^{Mg}$) and the total concentration (C_0) is shown in Figure 6 for the Neosepta C66-5T membrane. Figure 6 clearly shows that $K_{Ca}{}^{Mg}$ is not influenced by C_0 in the wide concentration range of 3 orders. When z_A is equal to z_B, $K_A{}^B$ is equal to $\alpha_A{}^B$ and is not influenced by the concentration of cations in the membrane and solution. Therefore, the result obtained in Figure 6 was found to lend support to eq 4.

IV. Conclusions

(1) Values of E_c, W_c, ρ, t, and Q_0 of the Aciplex K101 membrane were measured and found to be similar to those of the Neosepta C66-5T and Selemion CMV membranes but different from those of the Nafion 417 membrane.

(2) The exchange affinity of the Aciplex K101 membrane is expressed by eqs 5 and 6.

(3) The magnitude of the various $K_A{}^B$'s in the cation-exchange membranes is expressed by eqs 7–10.

(4) $K_A{}^B$ in the bivalent cation–bivalent cation systems is not influenced by the variation of the concentration of the total cations in solution.

Acknowledgment

We would like to thank Dr. Takaaki Dohmaru of the University of Osaka Prefecture for his helpful discussion. We also thank Asahi Chemical Industry Co. Ltd. for supplying the Aciplex K101 cation-exchange membrane.

Literature Cited

(1) Miyoshi, H.; Fukumoto, T.; Kataoka, T. *Sep. Sci. Technol.* **1988**, *23*, 585.

(2) Miyoshi, H.; Kataoka, T. *Sep. Sci. Technol.* **1989**, *24*, 507.

(3) Miyoshi, H.; Böddeker, K. W.; Hattenbach, K.; Wenzlaff, A. *Membrane* **1988**, *13*, 109.
(4) Miyoshi, H.; Böddeker, K. W.; Hattenbach, K.; Wenzlaff, A. *Chem. Express* **1989**, *4*, 209.
(5) Miyoshi, H.; Fukumoto, T.; Kataoka, T. *Desalination* **1983**, *48*, 43.
(6) Wallace, R. W. *J. Phys. Chem.* **1964**, *68*, 2418.
(7) Cwirko, E. H.; Carbonell, R. G. *J. Membr. Sci.* **1990**, *48*, 155.
(8) Yeager, H. L.; Steck, A. *Anal. Chem.* **1979**, *51*, 862.
(9) Kojima, T.; Furusaki, S.; Takao, K.; Miyauchi, T. *Can. J. Chem. Eng.* **1982**, *60*, 642.
(10) Manning, M. J.; Melshelmer, S. S. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 311.
(11) Miyoshi, H.; Hattenbach, K.; Böddeker, K. W.; Wenzlaff, A. *Chem. Express* **1987**, *2*, 503.
(12) Petropoulos, J. H.; Kimura, Y.; Iijima, T. *J. Membr. Sci.* **1988**, *38*, 39.
(13) Miyoshi, H.; Yamagami, M.; Kataoka, T. *Chem. Express* **1990**, *5*, 717.
(14) Miyoshi, H.; Chubachi, M.; Yamagami, M.; Kataoka, T. *J. Chem. Eng. Data* **1992**, *37*, 120.
(15) Kagaku Kogaku Hen. *Kagaku Kogaku Binran*; Maruzen: Tokyo, 1988; p 614.
(16) Perry, J. H. *Chemical Engineers' Handbook*; McGraw-Hill: New York, 1963; p 16-8.

Received for review December 15, 1993. Accepted March 3, 1994.®

® Abstract published in *Advance ACS Abstracts*, April 1, 1994.