Characteristic Coefficients for Equilibrium between Solution and Neosepta or Selemion Cation Exchange Membranes

Hirofumi Miyoshi,* Mitsuo Chubachi, Masayuki Yamagami, and Takeshi Kataoka[†]

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

The characteristic coefficients of ions in Neosepta and Selemion cation exchange membranes were measured and compared with those of Nafion cation exchange membranes obtained previously. It was found that the exchange affinities of the cation exchange membranes used were represented as $H^+ < Na^+ < K^+ < Cu^{2+} < Cr^{3+} < Ca^{2+}$. The selectivity coefficients between two monovalent ions (K_{Na}^H, K_{Na}^K, and K_K^H) remained constant. On the other hand, the values of K_{Na}^{Ca} and K_{Na}^{Cu} between monovalent ions and bivalent ions increased linearly with an increase in the concentrations of total cations in the solution (C_0). K_{Na}^{Cr} between monovalent ions and trivalent ions increased in proportion to the square of C_0. Further, it was found that the ratio of $(\alpha Q_0^{-1})_{other}((\alpha Q_0^{-1})_{Neosepta})^{-1}$ was constant, giving the average value of 0.34 for Na^+-Ca^{2+}, Na^+-Cu^{2+}, H^+-Ca^{2+}, H^+-Cu^{2+}, and H^+-Mg^{2+} systems, where α denotes a separation factor and Q_0 is a concentration of an exchange capacity in membrane. $\alpha_{other}(\alpha_{Neosepta})^{-1}$ was constant, too, giving the average value of 1.06 for Na^+-H^+ and Na^+-K^+ systems.

I. Introduction

Functional ion exchange membranes have been mainly employed for the concentration or the desalination of brackish water by electrodialysis (2-4). But they also begin to be used for the recovery of useful ingredients from wastewater by diffusion dialysis (5) and the Donnan dialysis (6-7). Some of the characteristic coefficients (e.g. transport number, electric resistance, burst strength, and thickness of ion exchange membranes) important in the former case had already been measured by membrane makers or membrane investigators. As the driving force in the latter cases, however, is different from that in the former case, it is necessary to know different kinds of characteristic coefficients (e.g. selectivity coefficient, separation factor, and diffusion coefficient etc.) beforehand for the theoretical studies on permeation through the membrane in the latter dialyses. But those values are scarcely measured by membrane makers, and few such characteristic coefficients are available at present for the ion exchange membranes (1, 8-11). In this study, some of the characteristic coefficients of various kinds of cation exchange membranes were measured: exchange capacity, water content, density, concentration of an exchange capacity in membrane, equilibrium relation between solution and membrane, selectivity coefficient, and separation factor. These were further compared with those of Nafion cation exchange membranes obtained previously (1).

II. Experimental Procedure

II.1. Measurement of E_c and Q_0.

Six kinds of cation exchange membranes, viz., Neosepta C66-5T, Neosepta CL-25T, Neosepta CM-1, Neosepta CM-2, Neosepta CMX, and Selemion CMV, were used. All Neosepta type membranes (Tokuyama Soda Co. Ltd.) are homogeneous ones which consist of copolymers of sulfonated styrene and divinylbenzene with varying ratios. A Selemion membrane (Asahi Glass Co., Ltd.) has a chemical composition similar to that of the Neosepta membranes.

Each ion exchange membrane with an area of 64 cm² was cut into nine pieces or more. Those were put into a bottle with a wide mouth, into which ca. 100 cm³ of a HCl solution of 1.0 meq (milliequivalent) cm⁻³ was then poured. The bottle was shaken for 8 h. This procedure was repeated three times, and all counterions of the membrane were exchanged to H⁺ ions.

After being washed with distilled water to remove the solution adhering to the membrane surface, the membranes were put into a NaCl solution of 100 cm³ of 0.5 meq cm⁻³ and were shaken for 8 h. Then, the amounts of the H⁺ ions which moved from membrane to solution were measured by titration with b cm³ of a meq cm⁻³ NaOH solution. After the membranes were dried in a vacuum oven at 40 °C for 24 h, their weights (w/g) were measured. Therefore, an exchange capacity (E_c/(meq g⁻¹)) is calculated by the following equation.

$$E_c = ab/w \qquad (1)$$

A concentration of the exchange capacity per volume of dry membrane (Q_0/(meq cm⁻³)) is calculated from eq 2 using E_c obtained above

$$Q_0 = E_c\rho \qquad (2)$$

where ρ (g cm⁻³) denotes the density of a dry membrane.

II.2. Measurement of Concentrations in Solution and Membrane.

The values of concentrations in solution and membrane were obtained as follows.

Each ion exchange membrane with an area of 64 cm² was cut into nine pieces or more. Those were put into a bottle, into which ca. 100 cm³ of a NaCl solution of 1.0 meq cm⁻³ was then poured. The bottle was shaken for 8 h. This procedure was repeated three times, and all counterions of those were exchanged to Na⁺ ions. Now, the initial amounts of Na⁺ ions in the membrane ($\overline{m_{i,Na}}$/meq) are equal to the initial sum of all ions ($\overline{m_{i,0}}$/meq) in the membrane and are represented by eq 3. On the other hand, an initial amount of M^{n+} ions in the membrane ($\overline{m_{i,M}}$/meq) is zero.

$$\overline{m_{i,Na}} = \overline{m_{i,0}} = E_c w \qquad (3)$$

The mixture solution of v (cm³) of C_0 (meq cm⁻³), into which a relation between a concentration of MCl_n and that of NaCl was varied, was prepared, where C_0 is a total concentration in the solution and v is its volume. The initial concentrations of M^{n+} ions ($c_{i,M}$/(meq cm⁻³)) and Na⁺ ions ($c_{i,Na}$/(meq cm⁻³)) in the solution were measured directly using a Perkin-Elmer 403 atomic absorption spectrophotometer.

Then, these membranes of which all counterions were completely exchanged to Na⁺ ions were put into the above solution and were shaken for 8 h. Thus, the exchange reaction occurs between Na⁺ ions and M^{n+} ions as represented by eq 4, where
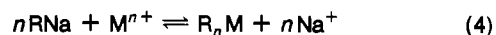
$$n\overline{RNa} + M^{n+} \rightleftharpoons \overline{R_nM} + nNa^+ \qquad (4)$$

Table I. Values of Exchange Capacity (E_c), Water Contents (W_c), Density (ρ), and Exchange Concentration (Q_0) of the Membrane

	Neosepta					Selemion	Nafion[a]		
	C66-5T	C1-25T	CM-1	CM-2	CMX	CMV	417	117	324
E_c/(meq g^{-1})	2.48	1.66	2.32	1.76	1.57	2.08	0.625	0.883	0.629
W_c/–	0.413	0.286	0.322	0.232	0.258	0.266	0.165	0.163	0.137
ρ/(g cm^{-3})	1.14	1.20	1.18	1.23	1.25	1.08	1.50		
$Q_0{}^b$/(meq cm^{-3})	2.84	1.99	2.74	2.16	1.96	2.25	0.938		

[a] The values measured by Miyoshi et al. (*1*). [b] Calculated from $Q_0 = E_c\rho$.

M is a cation, n is its valence, and R is a fixed ion of the membrane. The concentrations of M^{n+} ions (c_M/(meq cm^{-3})) and Na$^+$ ions (c_{Na}/(meq cm^{-3})) in the solution at equilibrium state were measured using the same equipment described above. After the membranes were dried in a vacuum oven at 40 °C for 24 h, their weights (w/g) were measured and used for calculating eq 3.

We define Δm (meq) as the difference between the initial value and the equilibrium value, as shown in eq 5, where $m_{i,M}$

$$\Delta m = |m_{i,M} - m_M| = |m_{i,Na} - m_{Na}| \tag{5}$$

(meq) and $m_{i,Na}$ (meq) are initial amounts of M^{n+} and Na$^+$ ions in solution and m_M (meq) and m_{Na} (meq) are amounts of M^{n+} and Na$^+$ ions in solution at equilibrium state, respectively. Each value of m (meq) in eq 5 is calculated from eq 6, where c denotes the concentration of each ion in solution.

$$m = cv \tag{6}$$

On the other hand, Δm is an amount of M^{n+} ions transferred from solution to membrane or an amount of Na$^+$ ions transferred from membrane to solution. Thus, at equilibrium, the amount of M^{n+} ions in membrane ($\overline{m_M}$/meq) is equal to Δm, as shown in eq 7, and the amount of Na$^+$ ions in membrane ($\overline{m_{Na}}$/meq) is represented by eq 8.

$$\overline{m_M} = \Delta m \tag{7}$$

$$\overline{m_{Na}} = \overline{m_{i,Na}} - \Delta m \tag{8}$$

Therefore, the concentrations of M^{n+} ions (q_M/(meq cm^{-3})) and Na$^+$ ions (q_{Na}/(meq cm^{-3})) in the membrane at equilibrium state are calculated by eqs 9 and 10, where $\overline{m_0}$ (meq) is an

$$q_M = Q_0\frac{\overline{m_M}}{\overline{m_0}} = Q_0\frac{\overline{m_M}}{\overline{m_M} + \overline{m_{Na}}} \tag{9}$$

$$q_{Na} = Q_0\frac{\overline{m_{Na}}}{\overline{m_0}} = Q_0\frac{\overline{m_{Na}}}{\overline{m_M} + \overline{m_{Na}}} \tag{10}$$

amount of total ions in membrane and is equal to $\overline{m_{i,0}}$ calculated from eq 3. Q_0 (meq cm^{-3}) is a concentration of the exchange capacity of the total ions in dry membrane and is calculated from eq 2.

III. Results and Discussion

III.1. Values of E_c, W_c, ρ, and Q_0. The exchange capacity (E_c), the water contents (W_c/–, where "–" denotes dimensionless unit), then density (ρ), and the exchange concentration (Q_0) of six membranes were measured and are shown in Table I. Those of Nafion exchange membranes obtained previously (*1*) are shown in Table I for comparison, too. The values of E_c, W_c, and Q_0 of Neosepta C66-5T were the largest of all kinds of the membranes used. Thus, this membrane was adopted as representative of the Neosepta type membranes in the following experiments.

III.2. Equilibrium Relation between x and y. At equilibrium, the dimensionless concentration of M^{n+} ions in the solu-
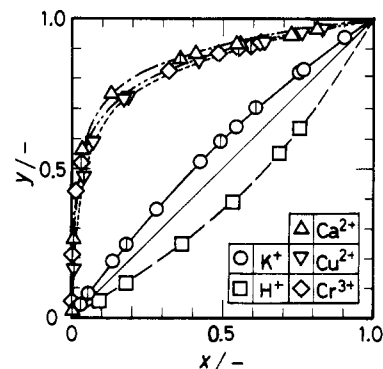
Figure 1. Relation between the concentrations of M^{n+} ions in solution (x) and those in Neosepta C66-5T membrane (y) in the mixture systems of Na$^+$ ions and the respective M^{n+} ions. Each line was drawn using x and y values calculated according to eq 14 or eq 19. Symbols with a vertical line denote the values obtained when C_0 were changed between 0.001 and 1.0 meq cm^{-3}.
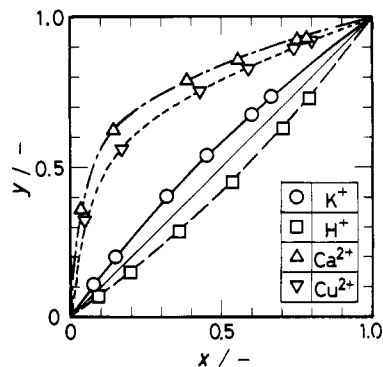
Figure 2. Influence of x on y of M^{n+} ions using Selemion CMV membrane in the mixture systems of Na$^+$ ions and the respective M^{n+} ions. Each line was drawn using x and y values calculated according to eq 14 or eq 19.

tion (x/–) and that in the membrane (y/–) are expressed as eqs 11 and 12.

$$x = \frac{c_M}{C_0} = \frac{c_M}{c_M + c_{Na}} \tag{11}$$

$$y = \frac{q_M}{Q_0} = \frac{q_M}{q_M + q_{Na}} \tag{12}$$

The relations between x and y obtained are shown in Figure 1 for Na$^+$–H$^+$, Na$^+$–K$^+$, Na$^+$–Ca^{2+}, Na$^+$–Cu^{2+}, and Na$^+$–Cr^{3+} systems using Neosepta C66-5T membrane. Figure 1 shows that the experimental values of y for Na$^+$–H$^+$ system are below the line of $y = x$, and those for other metal ions are above it. It follows that the exchange affinities of Neosepta C66-5T are represented by eq 13.

$$H^+ < Na^+ < K^+ < Cu^{2+} < Cr^{3+} < Ca^{2+} \tag{13}$$
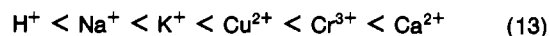
The similar relationship using Selemion CMV is shown in Figure 2. It was found that the exchange affinities of Selemion CMV were also expressed by eq 13. But the curves of the relationship between x and y in Figure 2 are closer to the line

Table II. Selectivity Coefficients $(K/-)$ between Two Monovalent Ions

| | Neosepta | | | | | Selemion | Nafion[a] |
	C66-5T	C1-25T	CM-1	CM-2	CMX	CMV	417
K_H^K	2.52	1.99	1.97	1.72	1.97	1.65	
K_{Na}^H	0.564	0.694	0.747	0.816	0.690	0.705	0.553
K_{Na}^K	1.48					1.41	3.28

[a] The values measured by Miyoshi et al. (1).
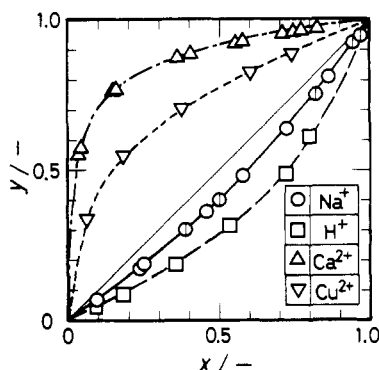

Figure 3. Influence of x on y of M^{n+} ions using Neosepta C66-5T membrane in the mixture systems of K^+ ions and the respective M^{n+} ions. Each line was drawn using x and y values calculated according to eq 14 or eq 19. Symbols with a vertical line denote the values obtained when C_0 were changed between 0.001 and 1.0 meq cm^{-3}.

of $y = x$ than those in Figure 1 are.

The x-y relationships of Neosepta C66-5T for K^+-H^+, K^+-Na^+, K^+-Ca^{2+}, and K^+-Cu^{2+} systems are shown in Figure 3. It is noted that the results from Figure 3 again give the relation of eq 13.

III.3. Selectivity Coefficient. The selectivity coefficient $(K_{Na}^M/-)$ for various M^{n+} ions relative to Na^+ ions in the process of eq 4 was calculated from eq 14 (12, 13).

$$K_{Na}^M = \frac{q_M}{q_{Na}^n} \frac{c_{Na}^n}{c_M}$$
$$= \frac{(1-x)^n y}{x(1-y)^n} \left(\frac{C_0}{Q_0}\right)^{n-1} \tag{14}$$

Selectivity coefficients between two monovalent ions $(K_H^K, K_{Na}^H,$ and $K_{Na}^K)$ for seven cation exchange membranes are shown in Table II.

Using Neosepta C66-5T, the variations of K_{Na}^M vs x were studied (Figure 4). In this figure, C_0 were kept constant at 0.1 meq cm^{-3} except that for the Na^+-K^+ system. Figure 4 shows that all the selectivity coefficients were almost constant against the variations of x and the respective cations. The relationship among K_{Na}^M is represented by eq 15, where each value in parentheses is the average value.

$$K_{Na}^{Cr} (=0.133) < K_{Na}^H (=0.564) < 1 < K_{Na}^K (=1.48) <$$
$$K_{Na}^{Cu} (=1.51) < K_{Na}^{Ca} (=2.45) \tag{15}$$

Similarly, K_K^M of Neosepta C66-5T and K_{Na}^M of Selemion CMV were studied and also found to be approximately constant. The results are expressed by eqs 16 and 17, respectively.

$$K_K^H (=0.397) < K_K^{Na} (=0.674) < 1 \tag{16}$$

$$K_{Na}^H (=0.705) < 1 < K_{Na}^K (=1.41) \tag{17}$$

Each curve in Figures 1-3 is one that was calculated on the basis of the average K values in eqs 15-17. Each curve is seen to fit well with the data plots.

Eq 18 is obtained by transforming eq 14 for K_{Na}^H.

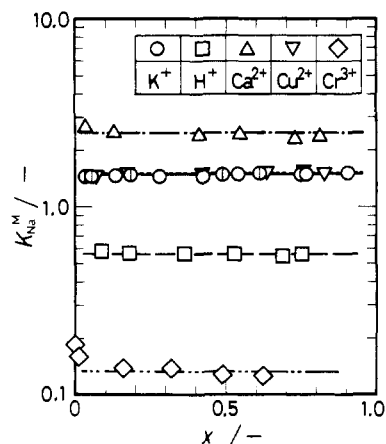$$K_{Na}^H (=0.564) = (K_{Na}^K (=1.48))(K_K^H (=0.397))$$
$$= 0.588 \tag{18}$$

Figure 4. Influence of the concentrations in solution (x) on the selectivity coefficients (K_{Na}^M). Symbols with a vertical line denote the values obtained when C_0 were changed between 0.001 and 1.0 meq cm^{-3}, otherwise C_0 were kept constant at 0.1 meq cm^{-3}.
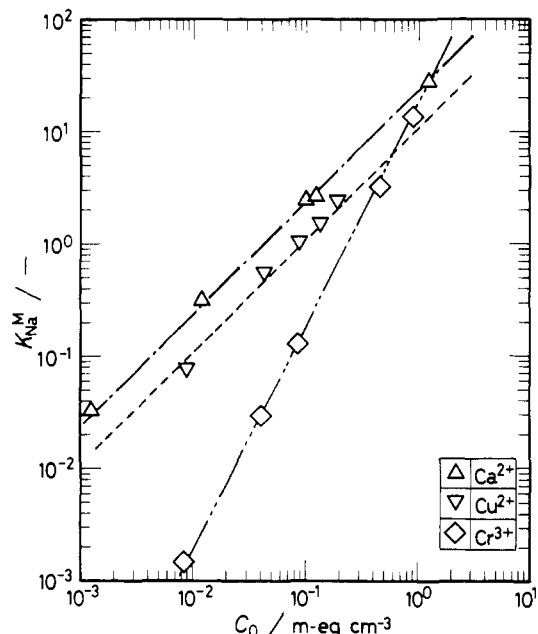

Figure 5. Relation between C_0 and K_{Na}^M using Neosepta C66-5T membrane.

Equation 18 shows that the calculated value of K_{Na}^H $(=0.588)$ is in good agreement with the experimental one $(=0.564)$. Therefore, it is evident that eq 18 is valid for monovalent ions for a same cation membrane.

III.4. Influence of C_0 on K_{Na}^M. Data in Figures 1 and 4 include those that were obtained under the varying values of C_0 $(C_0 = 1, 0.1, 0.01,$ and 0.001 meq cm^{-3}) for Na^+-K^+ system. But all the data plots for Na^+-K^+ system are seen to fit well on the same curve in Figure 1 and on the same line in Figure 4. Therefore, it is evident that K between monovalent ions is not influenced by C_0 and is represented by eq 14.

The influences of C_0 on K_{Na}^{Ca}, K_{Na}^{Cu}, and K_{Na}^{Cr} were studied and are shown in Figure 5. K_{Na}^{Ca} and K_{Na}^{Cu} between monovalent ions and bivalent ions were found to increase linearly with

Table III. Separation Factors (α/–) between Monovalent Ions and Bivalent Ions or Trivalent Ions

	α_{Na}^{Ca}	α_{Na}^{Cu}	α_{Na}^{Cr}	α_{H}^{Ca}	α_{H}^{Cu}	α_{H}^{Mg}	α_{K}^{Ca}	α_{K}^{Cu}
Neosepta C66-5T	69.4	32.4	148	296	7.50	14.3	61.5	8.05
Selemion CMV	18.8	9.12		75.8	2.11	3.68		
Nafion 417[a]	8.26	3.72						

[a] Calculated from the values measured by Miyoshi et al. (*1*).

Table IV. Relative Separation Factors

	$\dfrac{\alpha_{Na}^{Cu}/}{\alpha_{Na}^{Ca}}$	$\dfrac{\alpha_{Na}^{Cr}/}{\alpha_{Na}^{Ca}}$	$\dfrac{\alpha_{H}^{Ca}/}{\alpha_{Na}^{Ca}}$	$\dfrac{\alpha_{H}^{Cu}/}{\alpha_{Na}^{Ca}}$	$\dfrac{\alpha_{H}^{Mg}/}{\alpha_{Na}^{Ca}}$
Neosepta C66-5T	0.467	2.13	4.27	0.108	0.206
Selemion CMV	0.485		4.03	0.112	0.196
Nafion 417[a]	0.450				

[a] Calculated from the values measured by Miyoshi et al. (*1*).

Table V. Separation Factors of Selemion CMV or Nafion 417 Relative to Those of Neosepta C66-5T Including Monovalent Ions and Bivalent Ions, Viz., $(\alpha_A^M)_{other}((\alpha_A^M)_{Neosepta})^{-1}$

	A = Na		A = H		
	M = Ca	M = Cu	M = Ca	M = Cu	M = Mg
Selemion CMV	0.271	0.281	0.256	0.281	0.257
Nafion 417[a]	0.119	0.115			

[a] Calculated from the values measured by Miyoshi et al. (*1*).

Table VI. Values of $\alpha_A^M Q_0^{-1}$ of Selemion CMV or Nafion 417 Relative to Those of Neosepta C66-5T Including Monovalent Ions and Bivalent Ions, Viz., $(\alpha_A^M Q_0^{-1})_{other}((\alpha_A^M Q_0^{-1})_{Neosepta})^{-1}$

	A = Na		A = H		
	M = Ca	M = Cu	M = Ca	M = Cu	M = Mg
Selemion CMV	0.342	0.356	0.324	0.356	0.325
Nafion 417[a]	0.360	0.348			

[a] Calculated from the values measured by Miyoshi et al. (*1*).

Table VII. Separation Factors of Selemion CMV or Nafion 417 Relative to Those of Neosepta C66-5T Including Two Monovalent Ions, Viz., $(\alpha_{Na}^M)_{other}((\alpha_{Na}^M)_{Neosepta})^{-1}$

	M = H	M = K
Selemion CMV	1.25	0.953
Nafion 417[a]	0.980	2.22

[a] Calculated from the values measured by Miyoshi et al. (*1*).

an increase in C_0 in accordance with eq 14. On the other hand, K_{Na}^{Cr} between monovalent ions and trivalent ions increased in proportion to the square of C_0.

III.5. Separation Factor. K_{Na}^M were influenced by C_0 when n of M^{n+} ions were more than 2. However, data in Figures 1–3 for the varying values of C_0 for Na⁺–Ca²⁺, Na⁺–Cu²⁺, Na⁺–Cr³⁺, K⁺–Ca²⁺, and K⁺–Cu²⁺ systems are well represented by a respective single curve. Thus, in order to discuss the equilibrium state in terms of a constant value, a separation factor α_{Na}^M is introduced, where α_{Na}^M is defined using x and y as in eq 19.

$$\alpha_{Na}^M = K_{Na}^M (Q_0/C_0)^{n-1}$$
$$= \frac{(1-x)^n y}{x(1-y)^n} \qquad (19)$$

The values of α_{Na}^M calculated from eq 19 using varying values of x, y, C_0, and Q_0 were found to be constant with the error less than 5% for all combinations between monovalent ions and bivalent ions or trivalent ions. Thus, each average value of α_{Na}^M, α_H^M, and α_K^M measured for varying x, y, C_0, and Q_0 are shown in Table III for three kinds of cation exchange membranes, respectively. The dotted–dashed, dotted, and two-dotted–dashed curves in Figures 1 and 2 for Na⁺–Ca²⁺, Na⁺–Cu²⁺, and Na⁺–Cr³⁺ systems, respectively, were calculated by eq 19 using average values of α_{Na}^M in Table III. The curves in Figure 3 were calculated in a similar manner as that discussed above. Each curve in Figures 1–3 is seen to fit well with data plots. Therefore, we conclude that the relation between x and y for monovalent ions vs bivalent ions or trivalent ions can be calculated easily from eq 19 when one value of α_{Na}^M is available.

III.6. Separation Factors between Two Membranes Including Monovalent Ions and Bivalent Ions. Ratios of α_{Na}^M to α_{Na}^{Ca} and α_H^M to α_{Na}^{Ca} were calculated for each membrane, as summarized in Table IV. Table IV shows that the ratio of $\alpha_{Na}^M(\alpha_{Na}^{Ca})^{-1}$ or $\alpha_H^M(\alpha_{Na}^{Ca})^{-1}$ is constant for the given M^{n+} ions among three membranes.

The next step was to calculate the values of α_{Na}^M and α_H^M of Selemion or Nafion membrane relative to those of Neosepta membrane as standards (Table V). Table V shows that values of $(\alpha_A^M)_{Selemion}((\alpha_A^M)_{Neosepta})^{-1}$ or $(\alpha_A^M)_{Nafion}((\alpha_A^M)_{Neosepta})^{-1}$ are approximately constant for the same membrane.

Then, in order to make better use of the results obtained from Tables IV and V, the next relative value, that is, $\alpha_A^M Q_0^{-1}$, of Selemion CMV or Nafion 417 relative to those of Neosepta C66-5T including monovalent ions and bivalent ions, viz., $(\alpha_A^M Q_0^{-1})_{other}((\alpha_A^M Q_0^{-1})_{Neosepta})^{-1}$ is introduced, which is conveniently rewritten as eq 20.

$$\frac{(\alpha_A^M Q_0^{-1})_{other}}{(\alpha_A^M Q_0^{-1})_{Neosepta}} = \frac{(K_A^M C_0^{-1})_{other}}{(K_A^M C_0^{-1})_{Neosepta}} \qquad (20)$$

The values calculated by eq 20 are shown in Table VI. All values in this table were approximately constant, giving 0.34 ± 0.014 on the average. Therefore, it is now possible to calculate K_A^M value of another membrane by eq 20 if a K_A^M value of one membrane is available.

III.7. Separation Factors between Two Membranes Including Only Monovalent Ions. The values of α_{Na}^M of Selemion CMV or Nafion 417 relative to those of Neosepta C66-5T between two monovalent ions, viz., $(\alpha_A^M)_{other}((\alpha_A^M)_{Neosepta})^{-1}$, are shown in Table VII. Each value in this table is approximately constant at 1.06 ± 0.13 on the average except for the α_{Na}^K value of the Nafion 417 membrane relative to that of the Neosepta C66-5T membrane. We now think that the α_{Na}^K value obtained previously may have some systematic error and needs reinvestigation.

IV. Conclusions

The following conclusions were obtained.

(1) E_c, W_c, and Q_0 of Neosepta C66-5T membrane were the largest of all the membranes used.

(2) The exchange affinities of the cations could be represented by eq 13.

(3) The relationship between x and y was represented by one curve, though x and C_0 were changed.

(4) K values between two monovalent ions were constant, independent of C_0. When C_0 was constant, K values between monovalent ions and bivalent ions or trivalent ions were constant, too.

(5) The relation among K's between two monovalent ions was represented by the relative equation of eq 18.

(6) K_{Na}^M between monovalent ions and bivalent ions were increasing linearly with an increase in C_0. K_{Na}^M between mo-

novalent ions and trivalent ions were increasing in proportion to two powers of C_0.

(7) α_{Na}^M became constant although each value of x, y, C_0, and Q_0 was changed.

(8) $(\alpha_A^M Q_0^{-1})_{other}((\alpha_A^M Q_0^{-1})_{Neosepta})^{-1}$ was constant giving the average value of 0.34 between monovalent ions and bivalent ions, and $(\alpha_A^M)_{other}((\alpha_A^M)_{Neosepta})^{-1}$ was a constant value of 1.06 between monovalent ions.

Acknowledgment

Nomenclature

a: concentration of NaOH solution (meq cm^{-3})
b: volume of NaOH solution (cm^3)
C: concentration of the total ions in solution (meq cm^{-3})
c: concentration of each ion in solution (meq cm^{-3})
E_c: exchange capacity per weight of dry membrane (meq g^{-1})
K_{Na}^M: selectivity coefficient of M^{n+} ions relative to Na^+ ions between membrane and solution
m: amounts of each ion (meq)
Δm: value difference between $m_{i,M}$ and m_M or $m_{i,Na}$ and m_{Na} (meq)
Q: concentration of total ions, that is, the exchange capacity per volume of dry membrane (meq cm^{-3})
q: concentration of each ion in membrane (meq cm^{-3})
v: volume of mixture solution with M^{n+} ions and Na^+ ions (cm^3)
W_c: water content (-)
w: weight of dry membrane (g)
x: dimensionless concentration of M^{n+} ions in solution (-)
y: dimensionless concentration of M^{n+} ions in membrane (-)

Greek Letters

α_{Na}^M: separation factor (-)
ρ: density of dry membrane (g cm^{-3})

Superscripts

M: M^{n+} ion
n: valence of M^{n+} ion
-: in the membrane

Subscripts

A: A^+ ion
i: initial
M: M^{n+} ion
Neosepta: Neosepta cation exchange membrane
other: Selemion or Nafion cation exchange membrane
0: total ions

Literature Cited

(1) Miyoshi, H.; Yamagami, M.; Kataoka, T. Chem. Express 1990, 5, 717.
(2) Miyoshi, H.; Fukumoto, T.; Kataoka, T. Sep. Sci. Technol. 1988, 23, 585.
(3) Miyoshi, H.; Kataoka, T. Sep. Sci. Technol. 1989, 24, 507.
(4) Mizutani, Y. J. Membr. Sci. 1990, 49, 121.
(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.; Melsheimer, S. S. Ind. Eng. Chem. Fundam. 1983, 22, 311.
(11) Petropoulos, J. H.; Kimura, Y.; Iijima, T. J. Membr. Sci. 1988, 38, 39.
(12) Kagaku Kogaku Hen. Kagaku Kogaku Binran; Maruzen: Tokyo, 1988; p 614.
(13) Perry, J. H. Chemical Engineers' Handbook; McGraw-Hill: New York, 1963; pp 16-8.

Thermodynamics of Binary Mixtures Containing Alkenes. 1. Excess Enthalpies of Some Alkenes and Polyenes + n-Heptane or Cyclohexane Mixtures[†]

Barbara Pittau, Bruno Marongiu,* and Silvia Porcedda

Dipartimento di Scienze Chimiche, Universita'di, Cagliari, Via Ospedale 72, 09124 Cagliari, Italy

A flow microcalorimeter had been used to measure the excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing alkenes and polyenes with n-heptane or cyclohexane. The values of H^E are small and positive: This behavior is attributed to interactions between the π electrons of the double bonds, on the analogy of π–π interactions between the aromatic hydrocarbon molecules.

Introduction

This work is part of a systematic study of the thermodynamic properties of liquid organic mixtures, the TOM-Project (1–4) with the purpose of characterizing the type and magnitude of molecular interactions in binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic excess functions.

Although there is a great industrial interest about the alkenes, their mixtures had been relatively little studied. Recently Woycicki (5), Letcher (6), and Ghassemi et al. (7) have started a more systematic study about the excess enthalpies of the mixtures containing alkenes. In order to verify and to complete the literature data and to better characterize the behavior of the C=C group, we decide to measure, in a systematic way, H^E for mixtures of alkenes: 2-hexene (cis), 2-hexene (trans), 3-hexene (trans), 1-octene, 1-decene, and 1,7-octadiene with n-heptane or cyclohexane.

Experimental Section

The molar liquid phase molar excess enthalpy, H^E, was determined by means of a flow microcalorimeter (model 2277, LKB-Producter AB, Bromme, Sweden). The detailed description