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A Study of the Transport of Tetraalkylammonium Ions through Ion-exchange Membranes

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The membrane potential and conductance of the cation-exchange membrane–aqueous quaternary tetraalkylammonium chloride systems have been measured by using NH_4^+, tetramethyl-(Me_4N^+), tetraethyl-(Et_4N^+), tetrapropyl-(Pr_4N^+), and tetrabutylammonium ions (Bu_4N^+). The potential change in the concentration cell with these salts was about 58 mV for a tenfold change of concentration. The membrane conductance in the concentration cell increased with the concentration. The membrane permeability, as estimated from the potential and conductance data, was in the order of $NH_4^+ > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$; it is proportional to the geometric mean of the activities of exterior solutions. The effective pore size of the membrane was deduced from the conductance data and found to be *ca.* 10 Å. The selective permeation coefficient has been determined from the potential data of the two- and multi-ionic systems. The selectivity data obtained with the two-ionic system were in agreement with those obtained with the multi-ionic system. The selectivity increased with the chain length of the cation, in contrast to the reversed order of the membrane permeability in the concentration cell. This was attributed to the decreasing mobility with the increasing chain length.

So far, only a few studies of the transport phenomena of organic ions have been reported[1–10] in spite of their importance from the industrial and biological points of view. It is well known that quaternary tetraalkylammonium ions, such as tetramethyl-(Me_4N^+), tetraethyl-(Et_4N^+), tetrapropyl-(Pr_4N^+), and tetrabutylammonium ions (Bu_4N^+), are spherical and that the conductances of these ions in aqueous solutions are generally smaller than those of simple inorganic ions.[12] However, as to the transport of these ions through ion-exchange membranes, it has rarely been reported.[5]

The purpose of this study is to estimate the membrane permeability, the mobility, the selectivity coefficient, and the pore size of the membrane on the basis of measurements of the membrane potential and the membrane conductance of the ion-exchange membrane–organic ion system by using various quaternary ammonium ions and to discuss these physical properties.

Experimental

Materials. The membrane used in this study was a CL-2.5T cation-exchange membrane kindly supplied by the Tokuyama Soda Industry Co., Ltd.; after conditioning it was prepared by immersing the sodium-form membrane in 0.1 M tetraalkylammonium chloride for over a week. The water contents in the membranes of the ammonium and sodium forms were determined from the difference between the weights of the wet and dried membranes. The dried membrane was prepared by heating the wet membrane for a few days at 110 °C until the weight of the membrane attained a constant value. The ion-exchange capacity was measured by means of the back titration of alkali after treating the membrane of the hydrogen form with an excess of a 0.5 M sodium hydroxide solution. The exchange capacity was calculated with respect to the dry weight in the sodium form. The membrane of each form was washed thoroughly with redistilled water and blotted quickly with the filter paper to remove the adhered liquid; its thickness was then measured with the micrometer. The concentration of each counter ion in the wet membrane was calculated on the basis of the exchange capacity and the wet volume of the membrane in the sodium form. The ion-exchange capacity, the water content, and the thickness of the cation-exchange membrane in various forms are summarized in Table 1. The concentrations of the tetraalkylammonium chlorides were determined by the method of Fajans, in which Tween 80 (a nonionic surfactant) was used to decide the end point readily.

TABLE 1. SPECIFIC PROPERTIES OF MEMBRANE[a)]

Substance	Thickness × 10^4	$\bar{C}$[b)]	Water content
	cm	eq/l	wt %
Na^+	1.56	1.6	27
NH_4^+	1.57	1.6	27
Me_4N^+	1.61	1.6	—
Et_4N^+	1.66	1.5	—
Pr_4N^+	1.72	1.5	—
Bu_4N^+	1.77	1.4	—

a) Exchange capacity of membrane: 1.70 meq/g.

b) Molarity in membrane.

Membrane Potential and Conductance. The membrane potential and the conductance were measured by the method described in previous papers.[13,14] There are several methods for conductance measurement.[15–17] Lakshminarayanaiah *et al.*[14] have reported that the mercury method yields a steady value of membrane conductance for the range of the frequencies of the applied electric field of 1000—10000 Hz. Thus, this method was employed for the conductance measurement, and values measured with 1000 Hz were taken throughout this study. The area of the membrane for the measurement was 0.785 cm². The experiments were carried out at room temperature, 20±0.5 °C.

Mean Activity Coefficient. In order to analyze the experimental results, the mean activity coefficient should be known. Since the mean activity coefficients of tetraalkylammonium ions in concentrations bellow 10^{-1} M have never been reported, they were calculated from the data of the freezing point depression.[18] For concentrations above 10^{-1} M, the values obtained by the gravimetric isopiestic vapor pressure technique[19] were used.

Results and Discussion

Consider the system in which two aqueous phases, I and II, contain electrolytes, M^+X^- and N^+X^-, and in which the aqueous phases are separated by an ion-exchange membrane. According to earlier papers,[13,14,20] the equations for the membrane potential, V_o, and the membrane conductance, G_m, are expressed by:

$$V_o = \frac{RT}{F} \ln \frac{P_M a_M^I + P_N a_N^I + P_X a_X^{II}}{P_M a_M^{II} + P_N a_N^{II} + P_X a_X^I}, \tag{1}$$

and:

$$\begin{aligned} G_m &= \frac{F^2}{RT}(P_M a_M^{II} + P_N a_N^{II} + P_X a_X^I) \exp\left(\frac{FV_o}{2RT}\right) \\ &= \frac{F^2}{RT}(P_M a_M^I + P_N a_N^I + P_X a_X^{II}) \exp\left(-\frac{FV_o}{2RT}\right), \end{aligned} \tag{2}$$

respectively. In Eqs. 1 and 2, the superscripts, I and II, refer to the aqueous phases, I and II, respectively, and the subscripts, M, N, and X, the ion M, N, and X, respectively; R denotes the gas constant; T, the absolute temperature; F, the Faraday constant; P_α, the membrane permeability to the ion, α, and a_α, the activity of the ion, α.

When the two phases contain a single electrolyte, M^+X^-, Eqs. 1 and 2 reduce to:

$$V_o = \frac{RT}{F} \ln \frac{P_M a_M^I + P_X a_X^{II}}{P_M a_M^{II} + P_X a_X^I}, \tag{3}$$

and:

$$\begin{aligned} G_m &= \frac{F^2}{RT}(P_M a_M^{II} + P_X a_X^I) \exp\left(\frac{FV_o}{2RT}\right) \\ &= \frac{F^2}{RT}(P_M a_M^I + P_X a_X^{II}) \exp\left(-\frac{FV_o}{2RT}\right), \end{aligned} \tag{4}$$

respectively.

For the cation-exchange membrane, which is highly permselective to cations, P_X is very small as compared to P_M and P_N. In this case, Eqs. 1—4 can be reduced to:

$$V_o = \frac{RT}{F} \ln \frac{P_M a_M^I + P_N a_N^I}{P_M a_M^{II} + P_N a_N^{II}}, \tag{5}$$

$$\begin{aligned} G_m &= \frac{F^2}{RT}(P_M a_M^I + P_N a_N^I) \exp\left(-\frac{FV_o}{2RT}\right) \\ &= \frac{F^2}{RT}(P_M a_M^{II} + P_N a_N^{II}) \exp\left(\frac{FV_o}{2RT}\right), \end{aligned} \tag{6}$$

$$V_o = \frac{RT}{F} \ln \frac{a_M^I}{a_M^{II}}, \tag{7}$$

and:

$$\begin{aligned} G_m &= \frac{F^2}{RT} P_M a_M^I \exp\left(-\frac{FV_o}{2RT}\right) \\ &= \frac{F^2}{RT} P_M a_M^{II} \exp\left(\frac{FV_o}{2RT}\right), \end{aligned} \tag{8}$$

respectively.

When Phase I contains M^+X^- and Phase II, N^+X^-, *i.e.*, when the system is two-ionic, Eqs. 5 and 6 are reduced to:

$$V_o = \frac{RT}{F} \ln \frac{P_M a_M^I}{P_N a_N^{II}}, \tag{9}$$

and:

$$\begin{aligned} G_m &= \frac{F^2}{RT} P_M a_M^I \exp\left(-\frac{FV_o}{2RT}\right) \\ &= \frac{F^2}{RT} P_N a_N^{II} \exp\left(\frac{FV_o}{2RT}\right), \end{aligned} \tag{10}$$

respectively.

Thus, the membrane permeability can be estimated providing that the potential, the conductance, and the activity data are known.

Concentration Cells. In Fig. 1, the membrane potentials are shown for the concentration cells of Pr_4N^+ and Bu_4N^+ chloride as typical examples. The concentration of the salt in Phase II was kept at 10^{-2} M while that in Phase I was altered. The potential change was about 58 mV for a tenfold change in the concentrations from 10^{-3} to 10^{-1} M and the apparent transference numbers of Pr_4N^+ and Bu_4N^+ were 0.97 or 0.98

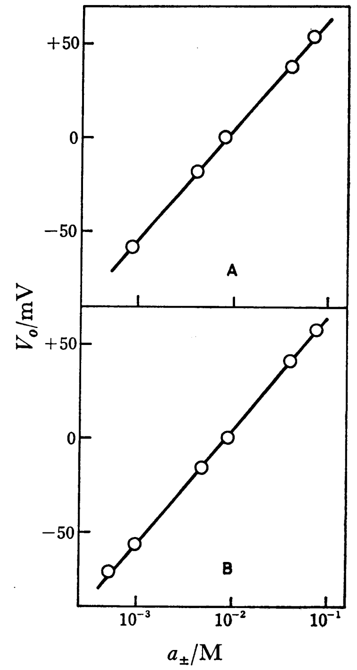

Fig. 1. Membrane potentials as functions of the mean activity of Phase I for the concentration cells.
A: Pr_4N^+, B: Bu_4N^+.

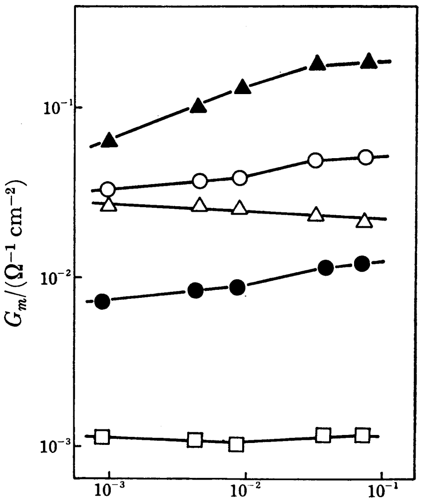

Fig. 2. Membrane conductances as functions of the mean activity of Phase I for various concentration cells. Concentration of Phase II was kept at 10^{-2}M.
▲: NH_4^+, ○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.

respectively. The same results were also obtained with NH_4^+, Me_4N^+, and Et_4N^+. All the data of membrane conductance are shown in Fig. 2. It has been shown that the membrane conductance becomes larger[16,17,21] as the concentration of the external solution increases except for the case of Et_4NCl. In the case of Et_4NCl, a small decrease in the conductance was observed at higher concentrations. The reason for this decrease is not still clear at present. The order of magnitude of the membrane conductance was $NH_4^+ > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$. As has been mentioned previously,[13] the membrane permeability, P_α, was estimated according to Eqs. 7 and 8 by using the experimental results of the membrane potentials and conductances. The membrane permeabilities are plotted against the mean activities in Fig. 3. The results indicate that the membrane permeability decreases with an increase in the concentration and decreases in the order: $NH_4^+ > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$.

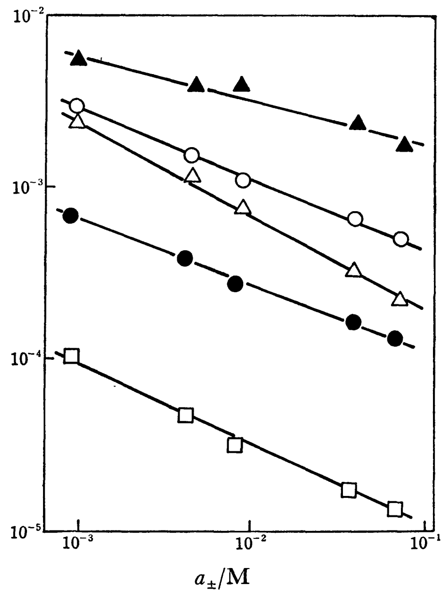

Fig. 3. Permeability *vs.* mean activity diagram for various concentration cells.
▲: NH_4^+, ○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.

The values of P_{Cl} were found to be very small as compared with those of cations; *i.e.*, P_{Cl}/P_{NH_4} and P_{Cl}/P_{R_4N} were less than 1/100, where R_4N denotes the tetraalkylammonium ion.

According to a previous paper,[20] the membrane permeability is expressed by:

$$P_\alpha = \frac{RT}{|Z_\alpha|F}\frac{\bar{U}_\alpha\bar{C}_\alpha}{\delta(a^{\rm I}_\alpha\cdot a^{\rm II}_\alpha)^{1/2}}, \tag{11}$$

provided the membrane is permselective to the ion, α, and the process is membrane-controlling, where Z_α denotes the ionic charge; $\bar{U}_\alpha$, the mobility; $\bar{C}_\alpha$, the concentration of the ion, α, within membranes; δ, the membrane thickness and $a^{\rm I}_\alpha$ and $a^{\rm II}_\alpha$, the activities of the ion, α, in Phases I and II respectively.

Thus, the permeabilities are plotted against $(a^{\rm I}_\alpha\cdot a^{\rm II}_\alpha)^{-1/2}$ in Fig. 4. Figure 4 indicates that P_α is approximately proportional to $(a^{\rm I}_\alpha\cdot a^{\rm II}_\alpha)^{-1/2}$ for all the systems studied. According to Eq. 11, this implies that $\bar{U}_\alpha\bar{C}_\alpha$ is almost constant. Since the concentration of the cation in the membrane may be regarded as constant within the range of concentrations studied,[22] this means that the mobilities are constant. The mobilities were then evaluated according to Eq. 11; they are summarized, together with the limiting equivalent conductance[11] and ionic radii,[12] in Table 2. The mobility in the membrane in Table 2 are plotted against the limiting equivalent conductance of each ion, λ_α, in Fig. 5.

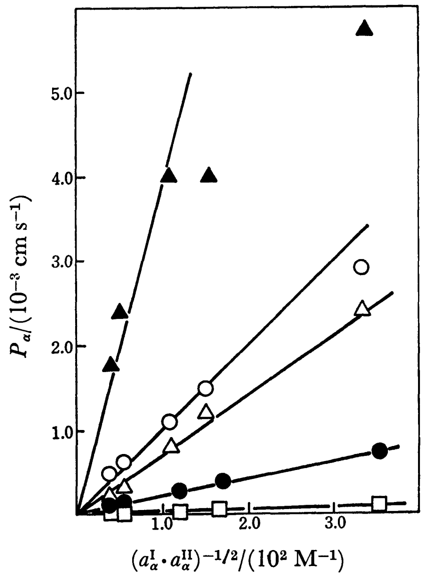

Fig. 4. Permeabilities as functions of the reciprocal of geometric means of the activities of Phase I and Phase II.
▲: NH_4^+, ○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.

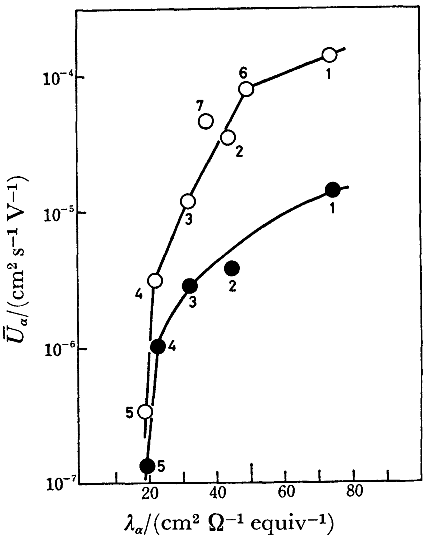

Fig. 5. Mobility in the membrane as a function of the limiting equivalent conductance in aqueous solution.
1: NH_4^+, 2: Me_4N^+, 3: Et_4N^+, 4: Pr_4N^+, 5: Bu_4N^+, 6: Na^+, 7: Li^+.
●: The data obtained in this study with Cl-2.5T.
○: The data obtained by Kawabe *et al.*[5] with AC-1 (Asahi Chem.) at 10^{-1} M.

TABLE 2. MOBILITY IN THE MEMBRANE AND LIMITING EQUIVALENT CONDUCTANCES IN AQUEOUS SOLUTION AND IONIC RADII

Substance	$\bar{U}_\alpha$ cm^2 s^{-1} V^{-1}	λ_α cm^{-2} Ω^{-1} equiv^{-1}	r_α Å
NH_4^+	1.4×10^{-5}	73.50	3.31
Me_4N^+	4.2×10^{-6}	44.92	3.67
Et_4N^+	3.0×10^{-6}	32.66	4.00
Pr_4N^+	1.0×10^{-6}	23.42	4.52
Bu_4N^+	1.3×10^{-7}	19.47	4.94

Kawabe *et al.*[5] measured the membrane conductances with the alkali metal cation and tetraalkylammonium ions in order to estimate the effective pore size of the ion-exchange membranes. According to their method, the mean pore size of a membrane was estimated from our experimental results of Et_4N^+, Pr_4N^+, and Bu_4N^+. These quaternary ions may be regarded as indicating that they are not hydrated.[12] By comparing the results of Et_4N^+–Pr_4N^+ and Pr_4N^+–Bu_4N^+, the pore radii of the membrane in this study were found to be 5.4 Å and 5.2 Å respectively. Thus, it can be suggested that the mean effective pore size of the membrane is approximately 10 Å, since the ionic radius of Bu_4N^+ is 4.94 Å and the mobilities of Pr_4N^+ and Bu_4N^+ decrease steeply, as is shown in Fig. 5.

Two-ionic System. The two-ionic membrane potentials for the system expressed by the following scheme were studied.

(II)		(I)
NH_4Cl	Membrane	Tetraalkylammonium chloride
10^{-2} M		10^{-3} M to 10^{-1} M

The concentration of the salt in Phase II was kept at 10^{-2} M NH_4Cl, while that in Phase I was altered from 10^{-3} M to 10^{-1} M. The results are shown in Fig. 6.

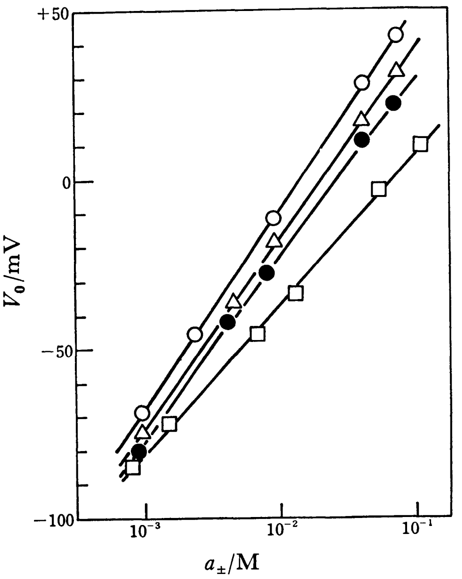

Fig. 6. Membrane potentials as functions of the mean activity of Phase I for two-ionic systems.
○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.

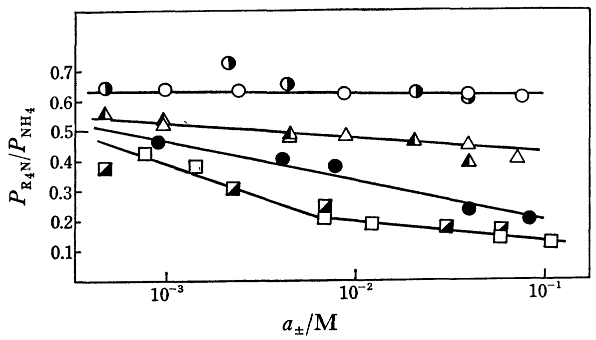

Fig. 7. Permeability ratios as functions of the mean activity of Phase I for two-ionic and multi-ionic systems.
Two-ionic system;
○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.
Multi-ionic system;
◑: Me_4N^+, ▲: Et_4N^+, ◪: Bu_4N^+.

For the NH_4^+–Me_4N^+ and NH_4^+–Et_4N^+ systems, the plots of the potentials *vs.* the logarithmic activities were found to be linear, with the slope of 58 mV. The results are in agreement with that expected from Eq. 9 provided the membrane permeability ratios are constant. Small deviations from the slope of 58 mV, however, were observed with the NH_4^+–Pr_4N^+ and –Bu_4N^+ systems. The membrane permeability ratios, P_{R_4N}/P_{NH_4}, calculated according to Eq. 9 are shown in Fig. 7. It may be seen in this figure that the longer the chain, the smaller the values of P_{R_4N}/P_{NH_4}, and that the tendency to decrease with the concentration becomes greater as the ionic radius increases. A more detailed study will be required to elucidate the concentration dependence of the permeability ratio.

Multi-ionic System. The multi-ionic potentials of the following system were examined:

(II)		(I)
NH_4Cl	Membrane	$R_4NCl:NH_4Cl=1:1$
10^{-2} M		5×10^{-4} M to 5×10^{-2} M

The concentration of the salt in Phase I, where the concentration ratio of R_4N^+ to NH_4^+ was kept at 1: 1, was altered from 5×10^{-4} M to 5×10^{-2} M. Here, the activity coefficient was used without further correction for the mixed electrolyte solutions. The permeability ratio was calculated according to Eq. 5 and shown in Fig. 7. As shown in this figure, P_{R_4N}/P_{NH_4} in the two-ionic system was agreed with that in the multi-ionic system.

According to Eq. 11, $P_\alpha/\bar{U}_\alpha$ may give the measure of the partition of the ion, α, in the membrane; hence:

$$K^{\mathrm{R_4N}}_{\mathrm{NH_4}} = \frac{P_{\mathrm{R_4N}}\bar{U}_{\mathrm{NH_4}}}{\bar{U}_{\mathrm{R_4N}}P_{\mathrm{NH_4}}} \qquad (12)$$

corresponds to the ion-exchange selectivity coefficient. The values of $K^{\mathrm{R_4N}}_{\mathrm{NH_4}}$ calculated according to Eq. 12 are shown in Table 3. $K^{\mathrm{R_4N}}_{\mathrm{NH_4}}$ shows an increase with an increase in the alkyl chain length which agrees with the result reported by Kressman and Kitchener.[23,24] At this stage, it is interesting to compare the relative permeabilities, P_{R_4N}/P_{NH_4}, in the two- and multi-ionic systems with those calculated from the permeabilities

Table 3. Selectivity coefficient[a)]

Substance	$K^{R_4N}_{NH_4}$
Me_4N^+	2.2
Et_4N^+	2.2
Pr_4N^+	5.3
Bu_4N^+	19

a) The data were calculated at 10^{-1} M.

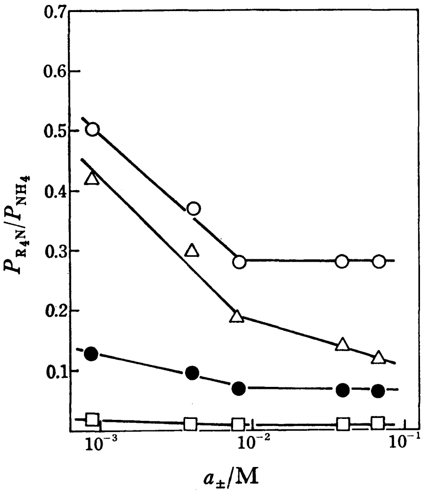

Fig. 8. Permeability ratio, P_{R_4N}/P_{NH_4}, *vs.* mean activity diagram for concentration cells.
○: Me_4N^+, △: Et_4N^+, ●: Pr_4N^+, □: Bu_4N^+.

in the concentration cell given in Fig. 8. Those permeability ratios showed a tendency to decrease against the increase in the concentration of the external solution, *i.e.*, Phase I. However, the values in the concentration cell were found to be much smaller than those in the two- and multi-ionic systems. It is noted that the longer the chain of the organic ion, the smaller the value of P_{R_4N}/P_{NH_4}. This behavior is more or less different from the earlier results in the case of simple inorganic ions.[13,14] These facts imply that the transport phenomena of the organic ions are strongly dependent on the compositions of the ionic species present in the membrane. That is, when only a single species of an ion is present in the membrane, the permeability to the quaternary tetraalkylammonium ion decreases remarkably as their ionic radii increase, as may be seen in Fig. 3. On the other hand, when two species of ions are present together in the membrane, it may be presumed that the relative permeability is governed by the interdiffusion in the membrane and that, therefore, the permeabilities of coexisting ions become closer. However, a more detailed study of the permeability in the two- and multi-ionic systems will be required to confirm the deduction described here.

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