Study of Ion Transport across Amphoteric Ion-Exchange Membrane. VI. Multi-Ionic Potential, Membrane Permeability, and Ion-Sieve Effect

Kozue KAIBARA,* Kyoko KUMAGAI-UEDA, and Hiroyoshi INOUE†
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812
† Department of Physiology, Faculty of Medicine, Yamaguchi University, Ogushi, Ube, Yamaguchi 755

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The transport characteristics of an amphoteric ion-exchange membrane were examined by electrochemical measurements for a multi-ionic system, in which NH_4Cl and tetraalkylammonium chloride (TAA·Cl) solution phases are divided by the membrane phase. Membrane permeability values were estimated for two cations, NH_4^+ and TAA^+, and Cl^-, as well as for whole cations as an averaged quantity describing the cation transport process relative to the anion transport process. The present study indicated that ion-sieve permeation characteristics, which have been demonstrated as a fundamental transport mechanism across an amphoteric ion-exchange membrane in the concentration-cell systems, still play a dominant role in the multi-ionic system. Satisfactory linear relationships of the logarithmic membrane permeabilities to NH_4^+, Cl^-, and a series of TAA^+ ions against the hydrated ionic radii of respective ions were obtained. This linear relation was not affected appreciably by the combination of electrolytes separated by the membrane. Thermodynamic analyses on the multi-ionic transport across an amphoteric ion-exchange membrane contribute to improve the selective performances of membrane materials and to survey more efficient operating conditions of the membrane processes.

In earlier papers of the present series, unique transport characteristics of an amphoteric ion-exchange membrane, in which almost equal amounts of positively and negatively charged ion-exchange sites are homogeneously dispersed with high densities, have been investigated. Potentiometric selective response mode observed in a variety of the concentration-cell systems based on the ion-sieve effect is one of the most interesting transport characteristics of a homogeneous type amphoteric ion-exchange membrane.[1—3] It has been suggested that the three-dimensional regular arrangement of alternately charged sites in the amphoteric ion-exchange membrane phase is responsible for shifting out the permeating cations and anions, and consequently, for generating the potentiometric selective responses.[2] The permeant ion size is, indeed, one of the ruling factors in selective transport process of ions across common charged membranes. However, the ion size effect is concealed with ion charge effect in the singly-charged ion-exchange membrane system, especially in case of the usual or commercially available ion-exchange membrane made of highly and strongly charged polymeric resin materials. In these membranes, accordingly, the membrane potential responses depend totally and definitely upon the number of ionic charge of permeants.[3] On the contrary, permselectivities of the binary-charged amphoteric ion-exchange membrane depend essentially upon the size of the hydrated permeating ions and the ion-sieve effect is demonstrated for all the ions regardless of the electrolyte species and of positive or negative charges. The potentiometric selective responses of an amphoteric ion-exchange membrane based on the ion-sieve effect were observed for a series of aqueous metal chlorides and Na salts, as well as NH_4Cl with a series of tetraalkylammonium chlorides.[1—4]

In the present study, the multi-ionic potentials across an amphoteric ion-exchange membrane were investigated in the system where aqueous NH_4Cl or tetraalkylammonium chloride (TAA·Cl) solution is separated by the membrane phase from aqueous solution containing TAA·Cl with different alkyl groups. NH_4Cl and a series of TAA·Cl's were selected as a permeating electrolyte in the present experiments, since the ion-sieve effect was observed typically in the concentration-cell systems of these electrolyte with an amphoteric ion-exchange membrane.[1] Frequently, the mode of ionic membrane permeability in multiple electrolyte systems is modified significantly as compared with that in single electrolyte systems or concentration-cell systems.[5,6] So, the functions of amphoteric ion-exchange membrane as an ion-sieve material were systematically examined by comparing the experimental results both in the single and multiple electrolyte systems. Recently, amphoteric ion-exchange membranes, or charge-mosaic membranes, have been developed so as to be applicable for the separation and purification processes for organic substances of relatively low molecular weight from electrolyte mixtures.[7—10] Thermodynamic analyses on the multi-ionic transport process across an amphoteric ion-exchange membrane would contribute to improve the selective performances of membrane materials and to survey more efficient operating conditions of the membrane-related processes.

Experimental

A 1.0-PA-29 amphoteric ion-exchange membrane (Kanegafuchi Chemical Industry Co.), in which almost equal amounts of sulfonic acid type and trimethylamine type ion-exchange groups are homogeneously dispersed with high densities over the cross-linked polymer networks, was employed in the present experiments.[1,2,7] The distance between positively and negatively charged ion-exchange sites

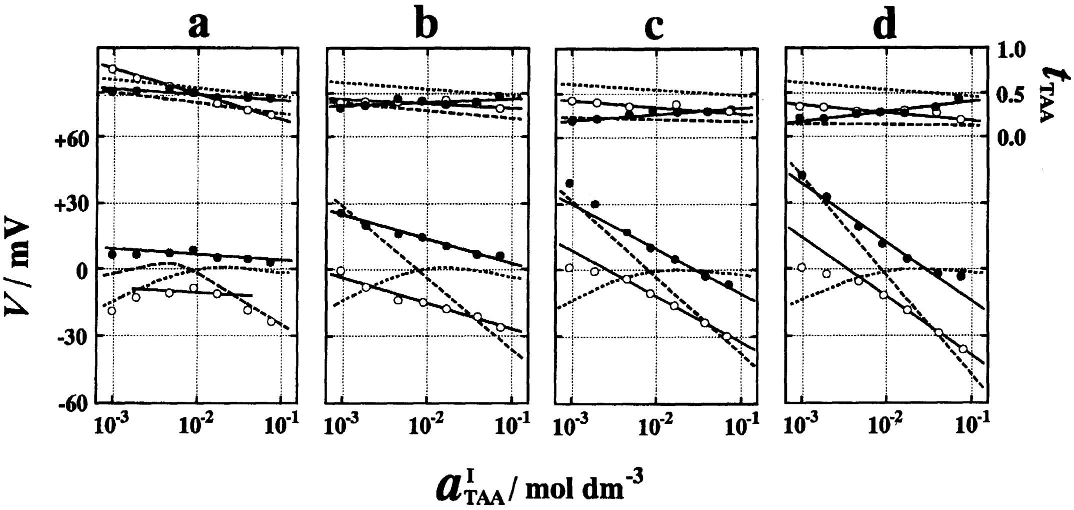

Fig. 1. Membrane potential, V, and transport number to whole cations, t_{TAA}, as a function of the electrolyte activity of phase I. a: NH_4Cl–TMA·Cl system; b: NH_4Cl–TEA·Cl system; c: NH_4Cl–TPA·Cl system; d: NH_4Cl–TBA·Cl system. ● and ○ indicate the NH_4Cl(I)–TAA·Cl(II) and TAA·Cl(I)–NH_4Cl(II) systems, respectively. The dotted and broken lines refer to the data for NH_4Cl(I)–NH_4Cl(II) and TAA·Cl(I)–TAA·Cl(II) systems, respectively.

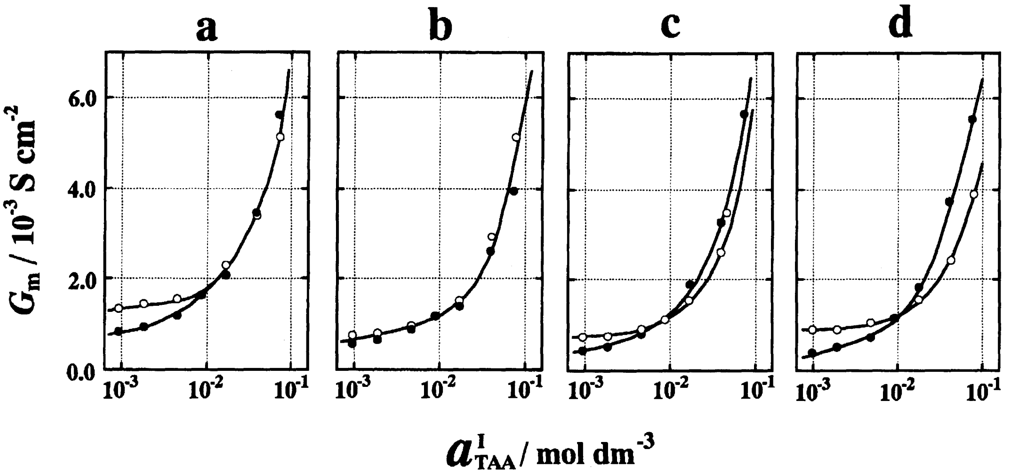

Fig. 2. Membrane conductance, G_m, as a function of the electrolyte activity of phase I. a: NH_4Cl–TMA·Cl system; b: NH_4Cl–TEA·Cl system; c: NH_4Cl–TPA·Cl system; d: NH_4Cl–TBA·Cl system. ● and ○ indicate the NH_4Cl(I)–TAA·Cl(II) and TAA·Cl(I)–NH_4Cl(II) systems, respectively.

can be roughly estimated at 0.75 nm based on the ion-exchange capacity, water content, and density values. Electrolytes used in the present experiments were NH_4Cl and a series of symmetric TAA·Cl's with methyl, ethyl, propyl, and butyl residues (TMA, TEA, TPA, and TBA). Aqueous electrolyte solutions were prepared from conductivity water and extra-pure salt without further purification. Transmembrane potentials and conductances were measured with an experimental setup essentially the same as reported earlier.[5] A high-input-impedance digital voltmeter (TR6877D, Advantest Co.) and impedance measuring equipments (YHP4255A and YHP4440B, Yokogawa-Hewlett-Packard Co.; KC-530, Kokuyo Electric Co.) were employed. Experimental systems consisted of solution phase I, where electrolyte concentration was varied from 10^{-1} to 10^{-3} mol dm^{-3}, and phase II with a fixed concentration of 10^{-2} mol dm^{-3} separated by the membrane phase. The two aqueous solution phases I and II contained different electrolyte species, NH_4Cl or TAA·Cl, from each other. Systems in which NH_4Cl solution phase is separated from TAA·Cl solution phase by the 1.0-PA-29 membrane were mainly investigated. All the measurements were carried out at regulated room temperature, 25±1°C.

Results and Discussion

Membrane Transport Equations. Phenomenological analyses of the permselective transport process of ions across a charged membrane can be performed by means of evaluating the electroconductive membrane permeabilities from the electrochemical measurement data.[11] For the present systems in which three ionic species, two cations and Cl^- ion, permeate across the 1.0-PA-29 amphoteric ion-exchange membrane, the

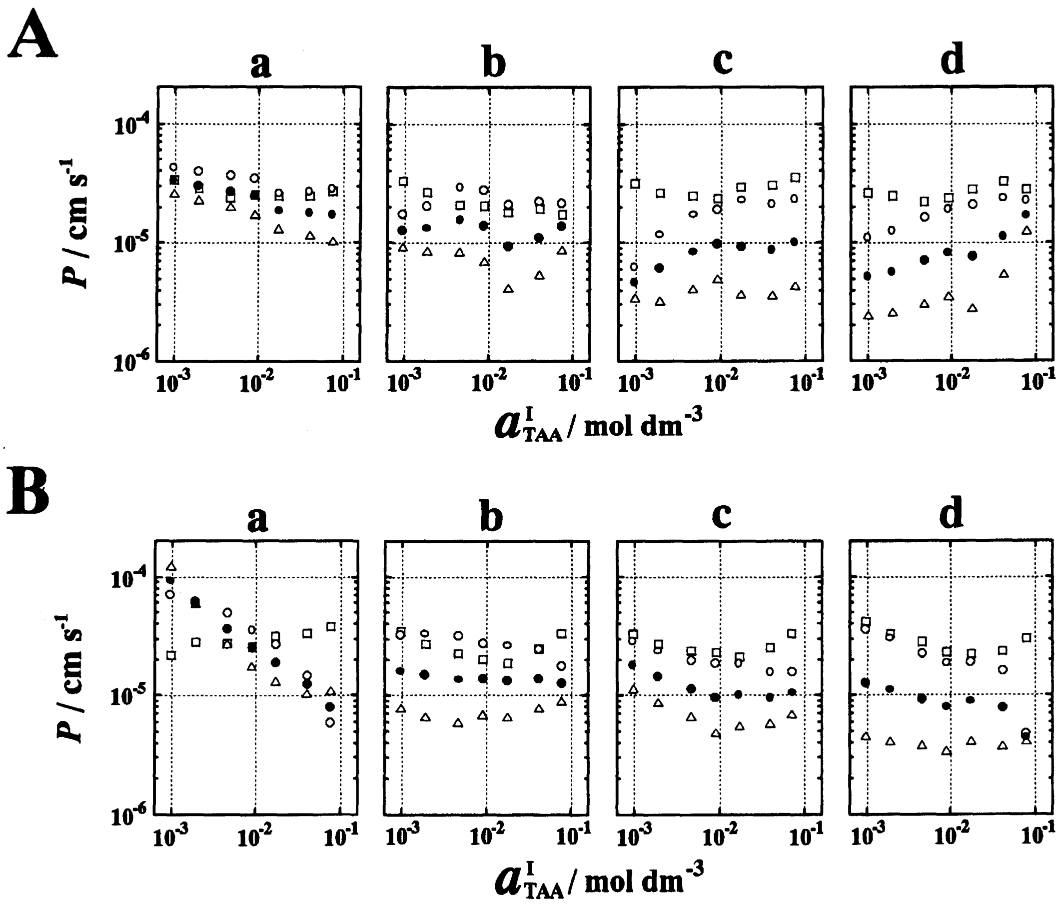

Fig. 3. Membrane permeability, P, as a function of the electrolyte activity of phase I. A: NH_4Cl(I)–TAA·Cl(II) system; B: TAA·Cl(I)–NH_4Cl(II) system. a: NH_4Cl–TMA·Cl system; b: NH_4Cl–TEA·Cl system; c: NH_4Cl–TPA·Cl system; d: NH_4Cl–TBA·Cl system. ○: P_{NH_4}; △: P_{TAA-I} or P_{TAA-II}; □: P_{Cl}; ●: P_{TAA}.

membrane processes can be described as follows:[6,12)]

$$\begin{aligned} I = {} & F\Bigl\{P_{\text{TAA-I}}a^{\text{I}}_{\text{TAA-I}}\exp\left(-FV/2RT\right) \\ & -P_{\text{TAA-II}}a^{\text{II}}_{\text{TAA-II}}\exp\left(FV/2RT\right) \\ & +P_{\text{Cl}}\left[a^{\text{II}}_{\text{Cl}}\exp\left(-FV/2RT\right)-a^{\text{I}}_{\text{Cl}}\exp\left(FV/2RT\right)\right]\Bigr\} \end{aligned} \tag{1}$$

$$\begin{aligned} = {} & -2F\Bigl\{P_{\text{TAA}}\left(a^{\text{I}}_{\text{TAA-I}}a^{\text{II}}_{\text{TAA-II}}\right)^{1/2} \\ & \sinh\left[F\left(V-V_{\text{TAA}}\right)/2RT\right] \\ & -P_{\text{Cl}}\left(a^{\text{I}}_{\text{Cl}}a^{\text{II}}_{\text{Cl}}\right)^{1/2}\sinh\left[-F\left(V-V_{\text{Cl}}\right)/2RT\right]\Bigr\} \end{aligned} \tag{2}$$

$$= -g_{\text{TAA}}\left(V-V_{\text{TAA}}\right)-g_{\text{Cl}}\left(V-V_{\text{Cl}}\right) = -G_{\text{m}}\left(V-V_0\right) \tag{3}$$

where I is the total membrane electric current, V is the transmembrane potential, P is the membrane permeability, and a is the ionic activity; F, R, and T are the Faraday constant, gas constant, and absolute temperature; the superscripts I and II refer to the aqueous solution phase I and II separated by the membrane phase; the subscripts TAA-I and TAA-II indicate NH_4^+ or TAA^+ ion in the external solution phases I and II, respectively; the subscript Cl indicates Cl^- ion. The membrane permeability to whole cations, P_{TAA}, is defined as an averaged quantity of the respective cationic membrane permeabilities, $P_{\text{TAA-I}}$ and $P_{\text{TAA-II}}$: $P_{\text{TAA}}=(P_{\text{TAA-I}}P_{\text{TAA-II}})^{1/2}$.[6)]

The cationic equilibrium membrane potential, V_{TAA}, is generated only by cations TAA-I and TAA-II without Cl^-. Similarly, V_{Cl} is the Nernstian equilibrium membrane potential for Cl^-. Namely, V_{TAA} and V_{Cl} should be observed under the conditions where $P_{\text{Cl}}=0$ and $P_{\text{TAA-I}}=P_{\text{TAA-II}}=0$, respectively. These equilibrium membrane potentials appeared in Eq. 2 are defined as:

$$\begin{aligned} V_{\text{TAA}} &= -\left(RT/F\right)\ln\left(P_{\text{TAA-II}}a^{\text{II}}_{\text{TAA-II}}/P_{\text{TAA-I}}a^{\text{I}}_{\text{TAA-I}}\right) \\ V_{\text{Cl}} &= \left(RT/F\right)\ln\left(P_{\text{Cl}}a^{\text{II}}_{\text{Cl}}/P_{\text{Cl}}a^{\text{I}}_{\text{Cl}}\right) \end{aligned} \tag{4}$$

The transmembrane potential in absence of membrane electric current, V_0, is expressed as a function of these equilibrium membrane potentials:

$$\begin{aligned} V_0 &= t_{\text{TAA}}V_{\text{TAA}}+t_{\text{Cl}}V_{\text{Cl}} \\ &= -\left(RT/F\right)\ln\Bigl[\Bigl(P_{\text{TAA-II}}a^{\text{II}}_{\text{TAA-II}}+P_{\text{Cl}}a^{\text{I}}_{\text{Cl}}\Bigr) \end{aligned}$$

$$\Big/ \left(P_{\mathrm{TAA\text{-}I}}a^{\mathrm{I}}_{\mathrm{TAA\text{-}I}} + P_{\mathrm{Cl}}a^{\mathrm{II}}_{\mathrm{Cl}}\right)\Big] \qquad (5)$$

The transport numbers to whole cations, t_{TAA}, and to Cl^-, t_{Cl}, satisfy the relation, $t_{\mathrm{TAA}}+t_{\mathrm{Cl}}=1$, inevitably. P_{TAA}, defined previously, and t_{TAA} were introduced to indicate a measure of the cation transport relative to the anion transport.

The membrane conductance measured by the electrochemical experiments, G_{m}, a summation of the cationic and anionic membrane conductances, g_{TAA} and g_{Cl}, is expressed as a function of the membrane permeabilities:

$$\begin{aligned} G_{\mathrm{m}} &= g_{\mathrm{TAA}} + g_{\mathrm{Cl}} \\ &= \left(F^2/RT\right)\left(P_{\mathrm{TAA\text{-}I}}a^{\mathrm{I}}_{\mathrm{TAA\text{-}I}} + P_{\mathrm{Cl}}a^{\mathrm{II}}_{\mathrm{Cl}}\right) \\ &\quad \exp\left(-FV_0/2RT\right) \\ &= \left(F^2/RT\right)\left(P_{\mathrm{TAA\text{-}II}}a^{\mathrm{II}}_{\mathrm{TAA\text{-}II}} + P_{\mathrm{Cl}}a^{\mathrm{I}}_{\mathrm{Cl}}\right) \\ &\quad \exp\left(FV_0/2RT\right) \end{aligned} \qquad (6)$$

The ionic membrane conductances are also expressed as a function of the membrane permeability:

$$\begin{aligned} g_{\mathrm{TAA}} &= \frac{F^2}{RT}P_{\mathrm{TAA}}\left(a^{\mathrm{I}}_{\mathrm{TAA\text{-}I}}a^{\mathrm{II}}_{\mathrm{TAA\text{-}II}}\right)^{1/2} \\ &\qquad \frac{\sinh\left[F\left(V-V_{\mathrm{TAA}}\right)/2RT\right]}{F\left(V-V_{\mathrm{TAA}}\right)/2RT} \\ g_{\mathrm{Cl}} &= \frac{F^2}{RT}P_{\mathrm{Cl}}\left(a^{\mathrm{I}}_{\mathrm{Cl}}a^{\mathrm{II}}_{\mathrm{Cl}}\right)^{1/2}\frac{\sinh\left[-F\left(V-V_{\mathrm{Cl}}\right)/2RT\right]}{-F\left(V-V_{\mathrm{Cl}}\right)/2RT} \end{aligned} \qquad (7)$$

The present membrane transport process can be examined by means of evaluating the transport parameters based on the above equations and electrochemical data.

Analyses of Membrane Transport Phenomena: Comparisons with Concentration-Cell Systems. Transmembrane potential and conductance data are summarized in Figs. 1 and 2 for the systems in which $\mathrm{NH_4Cl}$ and TAA·Cl aqueous solution phases are separated by the 1.0-PA-29 amphoteric ion-exchange membrane, $\mathrm{NH_4Cl}$(I)–TAA·Cl(II) and TAA·Cl(I)–$\mathrm{NH_4Cl}$(II) systems. It was shown that the membrane potential vs. logarithmic activity slopes in these systems remain at limited values between the slopes of $\mathrm{NH_4Cl}$ and respective TAA·Cl concentration-cell systems with the 1.0-PA-29 membrane, $\mathrm{NH_4Cl}$(I)–$\mathrm{NH_4Cl}$(II) and TAA·Cl(I)–TAA·Cl(II) systems. Accordingly as shown in the upper frames of Fig. 1, the estimated values of the transport number to whole cations, t_{TAA}, are suppressed within the limited values between $t_{\mathrm{NH_4}}$ and t_{TAA} values observed in the respective concentration-cell systems. Moreover, the membrane conductance values presented in Fig. 2 changed within the limits of the conductance values lower than those of $\mathrm{NH_4Cl}$ concentration-cell system and higher than those of respective TAA·Cl concentration-cell system. These results suggest that permeating $\mathrm{NH_4^+}$ and $\mathrm{TAA^+}$ ions bind competitively to available cation-exchange sites of the 1.0-PA-29 amphoteric ion-exchange membrane, in the same manner as a usual cation-exchange membrane system.[5,6] Figure 3 shows the membrane permeabilities, $P_{\mathrm{NH_4}}$, $P_{\mathrm{TAA-I}}$ or $P_{\mathrm{TAA-II}}$, P_{Cl}, and P_{TAA}, as a function of the mean electrolyte activity of phase I estimated based on these electrochemical measurements with Eqs. 1, 2, 3, 4, 5, 6, and 7. Concentration dependent changes in the respective membrane permeability values were relatively small within the external electrolyte concentration ranges studied as similarly to those observed in the concentration-cell systems with the 1.0-PA-29 membrane.[1]

In Fig. 4A, the membrane permeabilities to $\mathrm{NH_4^+}$, respective $\mathrm{TAA^+}$ cations, and $\mathrm{Cl^-}$ averaged for overall systems in the present experiments are plotted as a function of the hydrated ionic radius. Actually for a series of $\mathrm{TAA^+}$ cations, the hydrated radii are almost equal to the crystal radii due to poor hydration characteristics of these cations.[13] The averaged membrane permeability values in the present multi-ionic systems

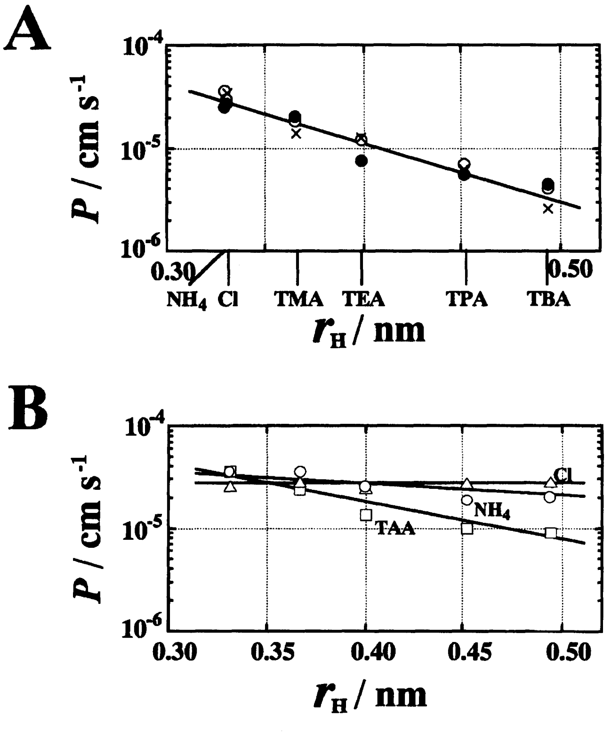

Fig. 4. Logarithm of averaged membrane permeability vs. hydrated ionic radius relationships. In A, each plot was based on the averaged value covering overall systems. ● and ○ refer to the present multi-ionic system and previous concentration-cell system, respectively. × refers to the data estimated for the TEA·Cl(I)–TMA·Cl(II) and TBA·Cl(I)–TPA·Cl(II) systems. In B, $P_{\mathrm{NH_4}}$ (○), P_{Cl} (△), and P_{TAA} (□) values were averaged for the respective $\mathrm{NH_4Cl}$-TAA·Cl systems and plotted against the hydrated radius of TAA-I or TAA-II cation. The left-end data plotted on the hydrated radius of $\mathrm{NH_4^+}$ correspond to the $\mathrm{NH_4Cl}$(I)–$\mathrm{NH_4Cl}$(II) system.

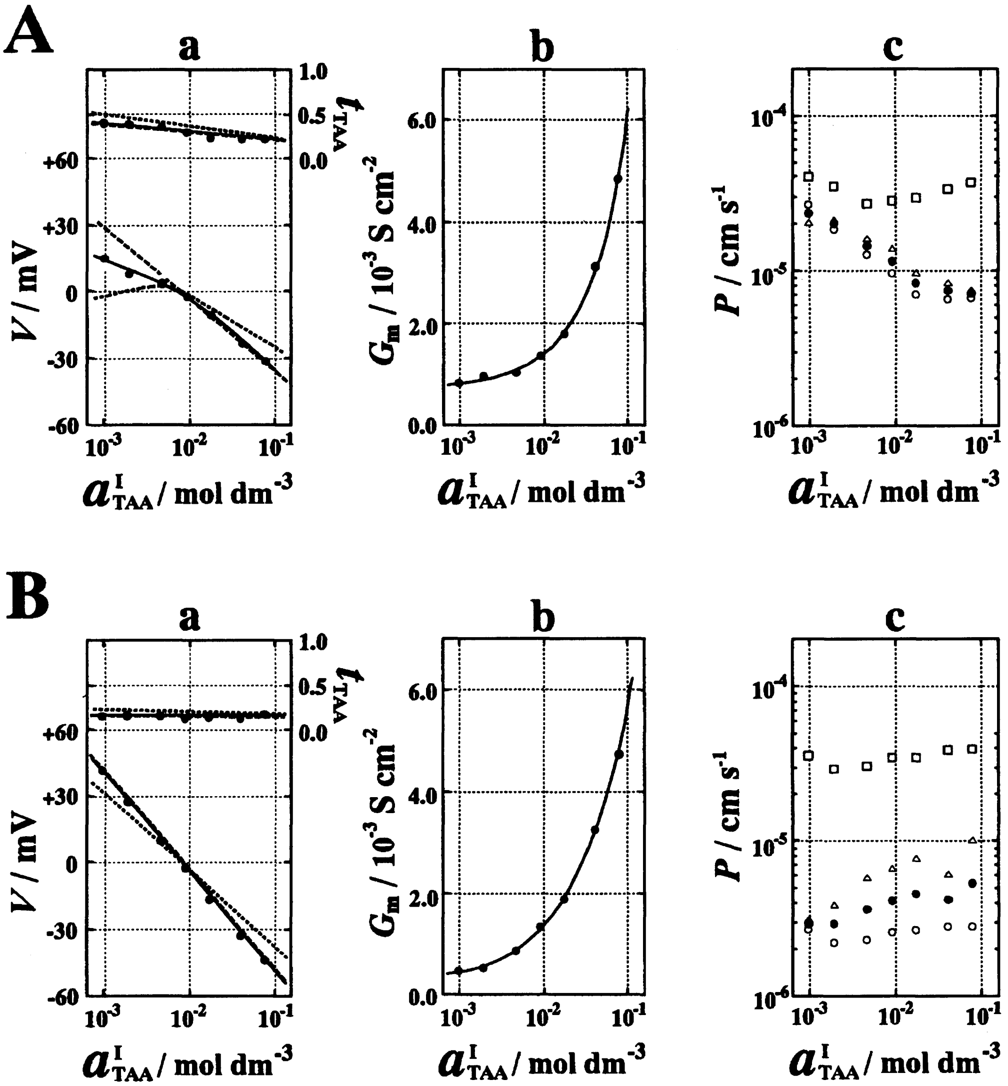

Fig. 5. Membrane potential and transport number to whole cations (a), membrane conductance (b), and membrane permeability (c) as a function of the electrolyte activity of phase I for the TEA•Cl(I)–TMA•Cl(II) (A) and TBA•Cl(I)–TPA•Cl(II) (B) systems. In A-a, the dotted and broken lines refer to the data for TMA•Cl(I)–TMA•Cl(II) and TEA•Cl(I)–TEA•Cl(II) systems, respectively. In A-c, ○: $P_{\rm TMA}$; △: $P_{\rm TEA}$; □: $P_{\rm Cl}$; ●: $P_{\rm TAA}$. In B-a, the dotted and broken lines refer to the data for TPA•Cl(I)–TPA•Cl(II) and TBA•Cl(I)–TBA•Cl(II) systems, respectively. In B-c, ○: $P_{\rm TPA}$; △: $P_{\rm TBA}$; □: $P_{\rm Cl}$; ●: $P_{\rm TAA}$.

were also examined to compare with those estimated in the respective concentration systems in Fig. 4A. These results indicate that the permeability differences between concentration-cell systems and multi-ionic systems with the 1.0-PA-29 amphoteric ion-exchange membrane were quite small for all permeating ions studied. Figure 4B shows $P_{\rm NH_4}$ and $P_{\rm Cl}$ values, as well as $P_{\rm TAA}$ values, as a function of the hydrated radius of TAA$^+$ in the external solution phase I or II. The left-end plots correspond to the $\rm NH_4Cl$ concentration-cell system, $\rm NH_4Cl$(I)–$\rm NH_4Cl$(II). It is clearly shown that the $P_{\rm Cl}$ changes were fairly small against the alterations of counter cations and coupling electrolyte separated by the membrane phase. In case of the amphoteric ion-exchange membrane, the Cl$^-$ permeation is performed independently of the cation transport through the pathway of the positively charged sites, whereas in the cation- and anion-exchange membrane, Cl$^-$ permeation characteristics are swayed definitely by the transport process of cation as a counter-ion or co-ion to the charged membrane site. In fundamentally counter transport processes of cations, $\rm NH_4^+$ and TAA$^+$, $P_{\rm NH_4}$ values decreased slightly with increasing hydrated radius of paired TAA$^+$ cation.

In the preceding papers,[1—3)] it has been demonstrated for the concentration-cell systems that there is a linear relation between the logarithmic membrane permeability and the radius of the hydrated permeant ion regardless of the electrolyte species and of positive or negative charges. Consequently, it has been pointed out that the membrane potential response for an electrolyte system with an appropriate combination of cations and anions can be estimated theoretically. The satisfactory linear relationships of logarithmic membrane permeability vs. hydrated ionic radius for a multi-ionic system in Fig. 4A suggest that expected potential responses of the multi-ionic system can be evaluated from Eqs. 4 and 5 with the hydrated radius data of a set of permeating ions. In this context, additional experiments examining the transport characteristics of TEA•Cl(I)–TMA•Cl(II) and TBA•Cl(I)–TPA•Cl(II) systems were carried out to check the above supposition. Figure 5 summarizes the membrane potential and conductance data, as well as the estimated membrane permeability values. Qualitative descriptions of the electrochemical transport process in these multi-ionic systems were the same as those in the NH_4Cl–TAA•Cl systems mentioned earlier, such as the restricted membrane potential vs. logarithmic activity slope, cationic transport number, and membrane conductance values within the limited ranges of those data in the concentration-cell systems. Furthermore as can be seen in Fig. 4A, the logarithms of the averaged P_{TMA}, P_{TEA}, P_{TPA}, P_{TBA}, and P_{Cl} values of these systems followed the same linear relationships against the hydrated ionic radius as for the previous NH_4Cl–TAA•Cl systems.

The present results indicated that the cation transport process controlled by the interactions of cations with sulfonic acid type exchange sites proceeds almost independently of the anion transport process controlled by the interactions of anion with trimethylamine type exchange sites. The ion-sieve mechanisms of membrane transport through the three-dimensional-array of alternately charged sites are still active in the multiple ion permeation process as in the single salt permeation process reported earlier.[1—3)]

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