1346 © 1983 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **56**, 1346—1350 (1983) [Vol. 56, No. 5

Study of Ion Transport across Amphoteric Ion Exchange Membrane. II. Transport of Symmetric Tetraalkylammonium Chlorides

Kozue KAIBARA,* Hideaki SONODA, Yoshihiko NAGATA, and Hideo KIMIZUKA
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

(Received December 6, 1982)

Transport characteristics of NH_4Cl, $(CH_3)_4NCl$ (TMA–Cl), $(C_2H_5)_4NCl$ (TEA–Cl), $(n\text{-}C_3H_7)_4NCl$ (TPA–Cl), and $(n\text{-}C_4H_9)_4NCl$ (TBA–Cl) across homogeneous type amphoteric ion exchange membrane (1.0-PA-29, Kanegafuchi Chem. Ind.) were studied. Membrane potentials and conductances of the concentration cell systems were measured to calculate the membrane permeabilities which represent a measure of ionic permselectivity. Membrane potential changed considerably with cationic species and the membrane tended to behave more anionic selectively with increasing bulkiness of cations. The cationic permeabilities calculated from electrochemical data were $P_{NH_4}>P_{TMA}>P_{TEA}>P_{TPA}>P_{TBA}$. Membrane permeabilities to chloride ions, P_{Cl}, were greater than those to cations in all the systems studied and it was interesting that P_{Cl} values and their dependencies on external electrolyte concentration were almost unchanged irrespective of the difference in cationic species. The present experiment was designed in order to examine the effects of ionic size on the transport processes across homogeneous type amphoteric ion exchange membrane. The obtained results indicated that the hydrated radius of permeant ion is an important factor to control the ionic transport processes and to reveal the potentiometric selectivity in these systems. It was suggested that the ion transport across homogeneous type amphoteric ion exchange membrane is strongly affected by hydrodynamic properties of permeant ion, but scarcely influenced by ionic charges of which effects are well known to be exclusive in the uniform cation and anion exchange membranes.

It has been well known that the charge-mosaic and layered type ion exchange membrane systems exhibit unique transport characteristics unexpected for the uniform ion exchange membrane system, such as piezodialysis, circulating electric current, and rectifying phenomena.[1–4] Including these interesting phenomena, the study of fundamental transport characteristics of homogeneous type amphoteric ion exchange membrane has not been systematically carried out yet.

As reported in the preceding paper, our preliminary experiments illustrated the unique transport characteristics of a 1.0-PA-29 amphoteric ion exchange membrane having a homogeneous structure (Kanegafuchi Chemical Industry Co., Ltd.).[5] A 1.0-PA-29 membrane demonstrated the permselectivity in response to ionic size of permeant electrolyte and, therefore, it seems to be possible that the membrane permselectivity is improved by introducing the amphoteric properties into the polymeric membrane structure. It was also suggested in the preceding paper that electrolyte permeation through the 1.0-PA-29 membrane does not depend upon the coupling flow mechanisms and, accordingly, the charge-mosaic membrane model is not suitable to analyse the transport processes across homogeneous type amphoteric ion exchange membrane.[5,6]

The present experiment was carried out to illustrate more clearly the potentiometric selectivity to ions and to confirm the fact that the ionic size of permeant is a dominant factor controlling the ionic transport processes across homogeneous type amphoteric ion exchange membrane. For this purpose, the transport characteristics of ammonium chloride and of a series of symmetric tetraalkylammonium chlorides, such as tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium chlorides, were examined, since a series of tetraalkylammonium ions has similar physicochemical properties except ionic bulkiness. In case of the usual uniform cation exchange membrane (Neosepta CL-25T, Tokuyama Soda Industry Co., Ltd.), membrane potential data for these tetraalkylammonium ions showed the almost ideal Nernstian slope against the logarithmic external electrolyte activity changes irrespectively of the difference in ionic sizes.[7] On the contrary, as shown later the membrane potential data of tetraalkylammonium chloride systems with a 1.0-PA-29 amphoteric ion exchange membrane changed considerably with the hydrated ionic size so as to reveal the potentiometric selectivity. In the present paper, we also discuss to some extent distinctive ion transport characteristics across amphoteric and uniform ion exchange membranes.

Experimental

A 1.0-PA-29 amphoteric ion exchange membrane was kindly supplied by the Central Research Laboratory of Kanegafuchi Chemical Industry Co., Ltd. and the membrane preparation processes were described elsewhere.[6] Ion exchange groups of this membrane are sulfonic acid and trimethylamine types attached to the cross-linked polystyrene skeleton supported by poly(vinyl chloride) network. Basic physicochemical properties are as follows (see also Ref. 5): Cationic and anionic exchange capacity, 1 mequiv./g-wt membrane; cationic/anionic capacity ratio, 1.0±0.2; membrane thickness, 0.1 mm. The closest distance between cationic and anionic exchange sites can be roughly estimated to be *ca.* 0.75 nm when the total ion exchange capacity is 2 mequiv. and the degree of swelling is 0.5; in these situations, it seems to be hard to realize the ion transport mechanisms described with the charge-mosaic model system.[6] Experimental setup and methods were the same as those reported in the previous experiments.[5,8,9]

Electrochemical data, such as the membrane potential and conductance, were measured to estimate the electroconductive membrane permeability. Measurements were carried out on the systems where solution phases I and II were divided by membrane phase; electrolyte concentrations of phase I were varied from 10^{-1} to 10^{-3} mol dm^{-3} and

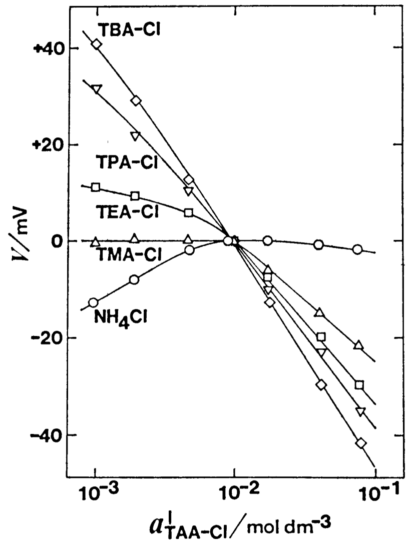

Fig. 1. Membrane potential data as a function of the mean electrolyte activity of phase I.
○: NH$_4$Cl, △: TMA–Cl, □: TEA–Cl, ▽: TPA–Cl, ◇: TBA–Cl.

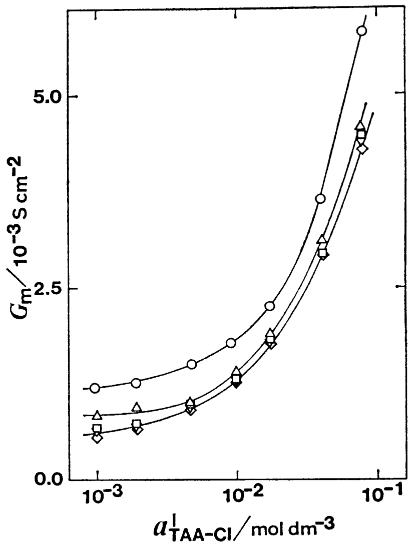

Fig. 2. Membrane conductance data as a function of the mean electrolyte activity of phase I. Symbols are the same as in Fig. 1.

those of phase II were kept constant at 10^{-2} mol dm^{-3}. Electrolyte solutions were prepared from extra pure chemicals (Nakarai Chemicals Ltd.) with conductivity water; ammonium chloride and symmetric tetraalkylammonium chlorides having methyl, ethyl, propyl, and butyl groups were used. All the experiments were carried out under the regulated room temperature, 25±1 °C.

Results and Discussion

Membrane potentials and conductances for the concentration cell systems of NH$_4$Cl, (CH$_3$)$_4$NCl (TMA–Cl), (C$_2$H$_5$)$_4$NCl (TEA–Cl), (n-C$_3$H$_7$)$_4$NCl (TPA–Cl), and (n-C$_4$H$_9$)$_4$NCl (TBA–Cl) were measured to estimate the membrane permeabilities. Figures 1 and 2 illustrate the membrane potential and conductance data as a function of mean electrolyte activity of phase I. As can be seen in Fig. 1, each system exhibits different slope of the membrane potential *vs.* logarithmic electrolyte activity plot; the negative slopes indicate that a 1.0-PA-29 amphoteric ion exchange membrane is more permselective to chloride ion than alkylammonium ions in the present situations. Figure 1 also shows that the permeability to chloride ions in general increases under conditions of higher external electrolyte concentrations. These negative slopes of membrane potential plots in Fig. 1 indicating the anionic selectivity decrease with decreasing bulkiness of respective cations from TBA$^+$ to TMA$^+$ and, in case of the NH$_4$Cl system, the potential plots tend to turn positive slope indicating the cationic selectivity of the membrane.

It is the most remarkable feature of the 1.0-PA-29 amphoteric membrane that the potentiometrically selective responses are observed even for ions of the same number of electric charge, as also discussed in the preceding paper.[5] In case of the system with usual uniform cation exchange membranes (*e.g.*, Neosepta CL-25T, Tokuyama Soda Co., Ltd.), similar membrane potential responses indicating the ideal Nernstian characteristics were observed to a series of cations from NH$_4^+$ to TBA$^+$; therefore, these membranes developed mainly for the desalination processes are ideally permselective to all the univalent cations and the characteristic potential responses specific to each cation were not observed.[7] Situations are the same in the uniform anion exchange membrane; membrane potential data for bulky surfactant anions were almost the same as those for simple anions.[10,11]

Membrane conductance data are summarized in Fig. 2. Membrane conductance values were not so distinctive to each system as membrane potential values but slightly dependent upon the cationic size. By the way, there is a striking difference between the conductance values of amphoteric ion exchange membrane and those of uniform cation exchange membrane. In case of the usual cation exchange membrane composed of various types of synthetic polymer, such as ACI (Asahi Chemical Industry Co., Ltd.), AMF C-103 (American Machine and Foundry Co., Ltd.), or CL-25T, the membrane conductance values of NH$_4$Cl amount to over hundred times as those of TBA–Cl system.[6,12]

On the basis of these electrochemical data, electroconductive membrane permeabilities to cation and chloride ion were estimated for each system; electroconductive permeabilities are defined and introduced to describe transport processes related to ionic mobility on the basis of nonequilibrium thermodynamics.[5,9,13] Electrochemical quantities are expressed as a function of membrane permeabilities to tetraalkylammonium ion (or ammonium ion) and chloride ion, P_{TAA} and P_{Cl}:

$$\begin{aligned} V_0 &= t_{\mathrm{TAA}}V_{\mathrm{TAA}} + t_{\mathrm{Cl}}V_{\mathrm{Cl}} \\ &= (g_{\mathrm{TAA}}/G_{\mathrm{m}})V_{\mathrm{TAA}} + (g_{\mathrm{Cl}}/G_{\mathrm{m}})V_{\mathrm{Cl}} \\ &= -(RT/F)\ln[(P_{\mathrm{TAA}}a^{\mathrm{II}}_{\mathrm{TAA}}+P_{\mathrm{Cl}}a^{\mathrm{I}}_{\mathrm{Cl}})/(P_{\mathrm{TAA}}a^{\mathrm{I}}_{\mathrm{TAA}}+P_{\mathrm{Cl}}a^{\mathrm{II}}_{\mathrm{Cl}})] \end{aligned} \tag{1}$$

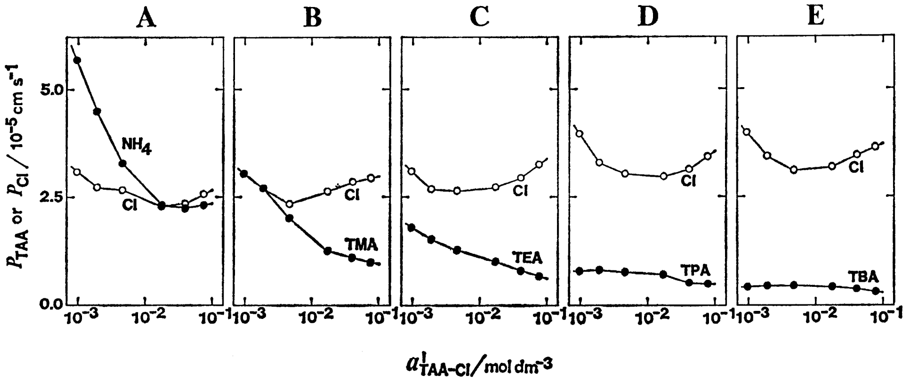

Fig. 3. Electroconductive membrane permeabilities as a function of the mean electrolyte activity of phase I. Closed and open circles indicate membrane permeabilities to cation and chloride ion, P_{TAA} and P_{Cl}, respectively.
A: NH_4Cl, B: TMA–Cl, C: TEA–Cl, D: TPA–Cl, E: TBA–Cl.

$$
\begin{aligned}
G_m &= g_{TAA} + g_{Cl} \\
&= \frac{F^2}{RT}\left\{(a^{I}_{TAA}a^{II}_{TAA})^{1/2}P_{TAA}\frac{\sinh[F(V_0-V_{TAA})/2RT]}{F(V_0-V_{TAA})/2RT}\right. \\
&\quad \left. + (a^{I}_{Cl}a^{II}_{Cl})^{1/2}P_{Cl}\frac{\sinh[F(V_0-V_{Cl})/2RT]}{F(V_0-V_{Cl})/2RT}\right\}, \qquad (2)
\end{aligned}
$$

where V_0 is the membrane potential in the absence of electric current, G_m is the membrane conductance, a is the activity, t is the transport number, and g is the ionic membrane conductance; V_{TAA} and V_{Cl} are the Nernst equilibrium membrane potentials to tetraalkylammonium ion (or ammonium ion) and chloride ion; F, R, and T indicate usual physical meanings; the subscripts TAA and Cl refer to tetraalkylammonium ion (or ammonium ion) and chloride ion; the superscripts I and II refer to solution phases I and II divided by membrane phase, respectively. Electroconductive membrane permeabilities, P_{TAA} and P_{Cl}, represent the membrane permselectivities to respective ions by indicating the order of electrical migration speed across membrane phase.

Membrane permeability values calculated by Eqs. 1 and 2 with electrochemical data are summarized in Fig. 3. As illustrated in this figure, the values of permeability to chloride ions show only a small change independently of difference in paired cationic species, while those to cations decrease with increasing bulkiness of respective cations as: $P_{NH_4}>P_{TMA}>P_{TEA}>P_{TPA}>P_{TBA}$. It can be also seen that the membrane permeability to smaller cations increases with decreasing external electrolyte concentrations of phase I, but for larger cations, this tendency is reduced and the permeability values are depressed to almost constant low level as shown by P_{TPA} and P_{TBA} values.

The membrane permeability ratios, P_{NH_4}/P_{Cl}, P_{TMA}/P_{Cl}, P_{TEA}/P_{Cl}, P_{TPA}/P_{Cl}, and P_{TBA}/P_{Cl}, are plotted as a function of mean electrolyte activity of phase I in Fig. 4. As expected from the respective permeability values, the permeability ratios decrease with increasing cationic bulkiness. Also in a uniform cation exchange membrane such as a Neosepta CL-25T, P_{TAA} values decrease with increasing cationic bulkiness in the same manner as the present experiment; however, P_{TAA}/P_{Cl} values are more than 100 and constant independently of cationic bulkiness.[7] These are reasonable results as expected from Eq. 1, since the almost ideal Nernst membrane potentials were observed for the CL-25T membrane system and, accordingly, P_{TAA}/P_{Cl} ratios should be constant and approach to infinitely large values.

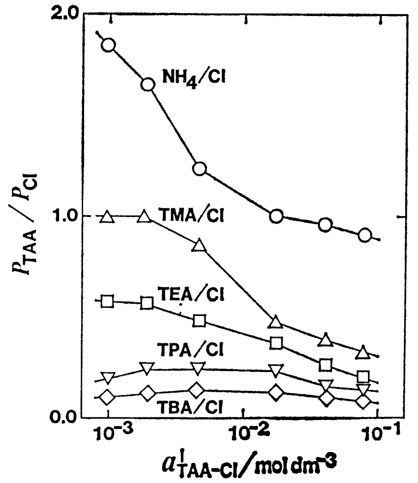

Fig. 4. Membrane permeability ratios as a function of the mean electrolyte activity of phase I.
○: P_{NH_4}/P_{Cl}, △: P_{TMA}/P_{Cl}, □: P_{TEA}/P_{Cl}, ▽: P_{TPA}/P_{Cl}, ◇: P_{TBA}/P_{Cl}.

The present results suggest that the possible origin of the potentiometric selectivity of 1.0-PA-29 amphoteric ion exchange membrane is a sieve effect on permeant ions as also discussed in the preceding paper.[5] To examine further correlations between the membrane permeability and ionic size, the permeability values and permeability ratios are plotted against the values of hydrated radii of permeant ions, r_H,[14,15] in Figs. 5 and 6, respectively. These figures illustrate the reasonable correlation of hydrated ionic radius to both the permeability and the permeability ratio. The hydrated radii of tetraalkylammonium ions are almost the same as the crystal ionic radii owing to poor hydration. These results suggest that the transport process across amphoteric ion exchange membrane is strongly affected by the hydrated radius of permeant

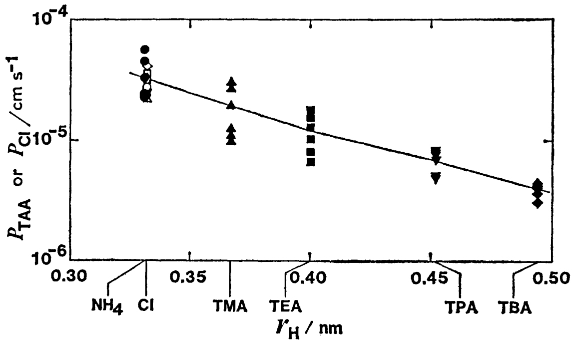

Fig. 5. Electroconductive membrane permeability *vs.* hydrated ionic radius plots.

●: P_{NH_4}, ▲: P_{TMA}, ■: P_{TEA}, ▼: P_{TPA}, ◆: P_{TBA}. P_{Cl}'s are indicated by corresponding open symbols. Solid line traces the average values of respective ions.

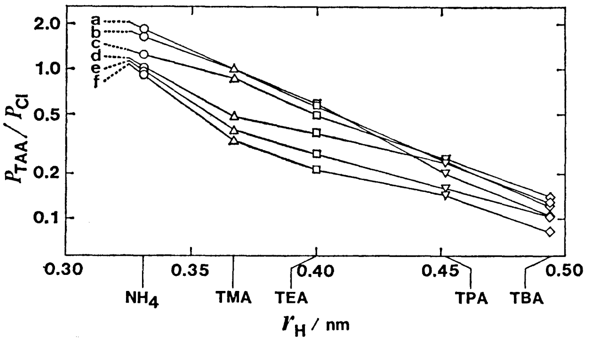

Fig. 6. Membrane permeability ratio *vs.* hydrated ionic radius plots. Symbols are the same as in Fig. 4. a, b, c, d, e, and f refer to the systems in which the electrolyte concentrations of phase I are 1×10^{-3}, 2×10^{-3}, 5×10^{-3}, 2×10^{-2}, 5×10^{-2}, and 1×10^{-1} mol dm^{-3}, respectively.

ion. Since the electroconductive membrane permeability is a function of the ionic mobility within membrane phase,[9,13,16] it is likely that the permeability values are inversely proportional to ionic size, although the mobility of permeant ion within membrane phase is not always the same as that in free solution phase and the ion movement through polymeric substance having charged sites is rather deviated from the movement in free media due to various effects.

As mentioned earlier, differences in electrochemical properties of tetraalkylammonium systems between the usual highly selective ion exchange membrane and the homogeneous type amphoteric ion exchange membrane are as follows: In the former membrane system, the membrane potential responses depend upon strictly the number of ionic charges so as to show the almost ideal Nernst potential for all the systems, but the membrane conductances are spread over wide range of values. In case of the latter membrane system as shown in the present results, the potentiometric selectivity to univalent cations of different ionic sizes is revealed, but the membrane conductances stay at similar values for all the systems. These experimental facts and estimated permeability values suggest some differences in possible ion transport mechanisms of uniform and amphoteric ion exchange membranes. It is generally realized that the ion transport process across uniformly charged membrane is controlled by the co-ion permeation.[16] Only the extremely small electrolyte fluxes are observed in the uniform ion exchange membrane under the steady conditions without membrane electric current, since the co-ion penetrations into membrane phase from external phase are prevented by high electric potential barrier. On the contrary, relatively large salt fluxes were observed in the homogeneous amphoteric membranes irrespectively of the low electrical membrane conductance.[17] It is especially interesting that the membrane permeability to chloride ion is maintained at nearly constant level for all the electrolyte systems having different size of cations as can be seen in Fig. 3. These results suggest that both the cations and anions independently migrate through the membrane phase with the interaction to electric fields built up by positively and negatively charged sites. Three dimensional array of the positive and negative charge, in which each site is adjacent at about 0.75 nm distance to oppositely charged sites, could effectively function rather as a sieve to select the size of permeant ions than as an electrical barrier. Under these situations, the ion transport across homogeneous type amphoteric ion exchange membrane seems to resemble preferably to that in free aqueous electrolyte solution, and consequently the large salt flux is expected.

As a matter of course, the ion permeability of 1.0-PA-29 membrane depends not only upon the hydrated ionic radius but also upon factors such as specific interactions of ions to exchange groups and to matrix polymer of membrane. It is, however, conceivable as shown in the present results that the effects of hydrated ionic size play an important role in the transport process of ions across the amphoteric ion exchange membrane with a homogeneous binary charged structure. On the contrary, the ionic size effects are almost concealed with the ionic charge effects in the uniform ion exchange membrane, and accordingly the potentiometric selectivity to univalent cations is not exposed. The most noticeable property of the 1.0-PA-29 membrane system with ammonium and tetraalkylammonium chlorides is that the slope of membrane potential *vs.* logarithmic electrolyte activity curve is changed stepwise in relation to the cationic hydrated radius as an indication of the appreciable variation in the relative membrane permeability with the constant chloride permeability. The present results suggest that the transport processes of ions across amphoteric ion exchange membrane explicitly reflect the hydrodynamic properties of permeant ions, while the ionic charge effects are dominant in the uniform ion exchange membrane.

We thank members of Central Research Laboratory of Kanegafuchi Chemical Industry Co., Ltd., especially Dr. Tamiyuki Eguchi, for preparing and supplying the amphoteric membrane, 1.0-PA-29, used in this work. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) R. Neihof and K. Sollner, *J. Gen. Physiol.*, **38**, 613 (1955).

2) O. Kedem and A. Katchalsky, *Trans. Faraday Soc.*, **59**, 1918 (1963).

3) J. N. Weinstein, B. M. Misra, D. Kalif, and S. R. Caplan, *Desalination*, **12**, 1 (1973).

4) A. A. Sonin and G. Grossman, *J. Phys. Chem.*, **76**, 3996 (1972).

5) A. Yamauchi, S. Tsuruyama, H. Masumori, Y. Nagata, K. Kaibara, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **55**, 3297 (1982).

6) T. Eguchi, S. Mori, and M. Shimokawa, *Membrane*, **3**, 289 (1978).

7) K. Inenaga, A. Yamauchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **50**, 2584 (1977).

8) K. Kaibara, H. Ito, N. Inoue, and H. Kimizuka, *Mem. Fac. Sci., Kyushu Univ. Ser. C*, **12**, 125 (1980).

9) K. Kaibara and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **55**, 1743 (1982).

10) K. Kaibara, T. Nakahara, I. Satake, and R. Matuura, *Mem. Fac. Sci., Kyushu Univ. Ser. C*, **7**, 1 (1970).

11) K. Shirahama, *Kolloid Z. Z. Polym.*, **250**, 620 (1972).

12) H. Kawabe, H. Jacobson, I. Miller, and H. P. Gregor, *J. Colloid Interface Sci.*, **21**, 79 (1966).

13) H. Kimizuka and K. Kaibara, *J. Colloid Interface Sci.*, **52**, 516 (1975).

14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths & Co., London (1959).

15) E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).

16) H. Kimizuka, K. Kaibara, E. Kumamoto, and M. Shirōzu, *J. Memb. Sci.*, **4**, 81 (1978).

17) H. Kimizuka, K. Kaibara, and Y. Nagata, 7th International Biophysics Congress, Mexico City, August 1981, Abstr. 348.