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Theoretical and Experimental Studies of the Membrane Permeabilities to Ions in Liquid Membrane

Kazuo Nomura,* Akira Matsubara, and Hideo Kimizuka[†]
Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Fukuoka 810
[†]*Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812*

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A theory for the ion transport across liquid ion-exchange membrane was presented on the basis of nonequilibrium thermodynamics with the assumptions that the carrier ions and complexes were present only in the membrane phase, and that there was no volume flow and all chemical reactions were at equilibrium. The equations for "total" fluxes of membrane-permeable ions at steady state were derived from a set of the equations for "individual" fluxes of all mobile species present in the liquid membrane where the complexes were assumed to be partially dissociated. The "total" phenomenological coefficients were able to be expressed in terms of the "individual" coefficients. The diffusional and electroconductional membrane permeabilities to a selective ion in the liquid membrane–single electrolyte system were found to be in the same form as those in the fixed-site membrane–single electrolyte system, if the mean diffusion coefficient and mean mobility of the free species and its complex were used. The rate constants in the permeation process were also related to the diffusional membrane permeability. The experimental examination was made on a liquid cation-exchange membrane–aqueous single electrolyte system at 25 °C. The solution of calcium hexadecyl sulfate in 1-octanol and calcium chloride were used as the liquid membrane and the electrolyte, respectively. All the measured quantities were consistently interpreted by the presented theory.

Since the carrier model was introduced into the transport phenomena across cell membranes, liquid membranes having carrier species have been extensively studied by many investigators.[1,2] On the other hand, various ion-selective electrodes using liquid membranes have been devised and commercialized, because of their high selectivity to a particular ion.[3] Current research has been carried out to provide the underlying principle for the separation of metal ions by liquid membranes.[4,5]

In spite of numerous experimental works, theories proposed for the ion transport across liquid membrane are not as many as for the fixed-site membrane. The theory of Eisenman and his coworkers[6—9] has usually been applied to analyze the ion transport phenomena through liquid membranes, but it has been derived from the Nernst-Planck equation with some assumptions. A rigorous theory for the ion transport across fixed-site membrane has been presented in a previous paper on the basis of nonequilibrium thermodynamics without any assumptions concerning the distributions of concentration and potential within membrane.[10]

In the preceding paper,[11] an electrochemical study of the ion permeation has been made on a liquid membrane–aqueous single electrolyte system. The membrane permeabilities to the membrane-permeable ion p in the presence and absence of electric current, P_p and P_p^0, have been estimated according to the previous theory.[10] A remarkable discrepancy between P_p and P_p^0 has been observed and explained in terms of the permeability matrix. The theory of Eisenman *et al.* can not distinguish these two permeabilities since their theory is based on the Nernst-Planck equation which possesses only one transport coefficient for an ion.

In the preceding paper,[11] the theory of ion transport for the fixed-site membrane has been applied to estimate P_p and P_p^0 in the liquid membrane since the equation describing the ion transport can be deduced to have the same form for both systems.[12] However, the entities of physical representations for the membrane permeabilities, P_p and P_p^0, for the liquid membrane are supposed to be different from those for the fixed-site membrane, because the site ion as well as the complex is mobile in the liquid membrane.

Thus a theory for the liquid membrane was presented on the basis of nonequilibrium thermodynamics by taking into account the movements of the site ions and complexes in the liquid membrane. The experimental examination was also made with a liquid membrane–aqueous single electrolyte system.

Theoretical

System and Assumptions. We shall consider the ion transport phenomena in the system illustrated in Fig. 1. An aqueous phase I is separated by a liquid ion-exchange membrane from another aqueous phase II. The membrane phase is bounded by two planes normal to the x-axis at $x=0$ and $x=\mathrm{d}$. There are stagnant layers on both sides of the membrane phase and their surfaces are in contact with the phase I at $x=-\mathrm{a}$ and phase II at $x=\mathrm{b}$, respectively. The two aqueous phases I and II are homogeneous be-

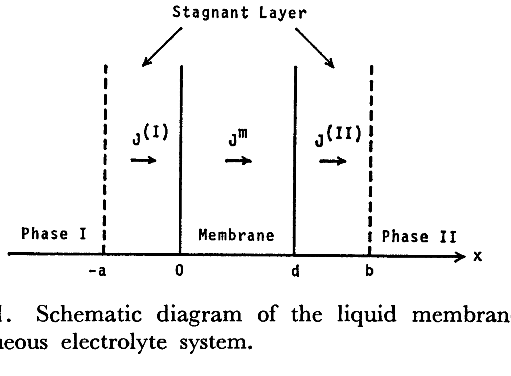

Fig. 1. Schematic diagram of the liquid membrane–aqueous electrolyte system.

cause of being well stirred. It is assumed that the system is isothermal and in a steady state in which there is no volume flow (Assumption 1), and the ion fluxes are constant. Moreover, all the chemical reactions are assumed to be at equilibrium anywhere within the membrane phase (Assumption 2) and a free carrier ion and its electrically neutral complexes are present only within the membrane phase (Assumption 3).

Flux Equation for Individual Species. Only counter- and co-ions can permeate across the liquid membrane, although all the species within membrane are mobile. The total flux of a permeable ion is the sum of the flux of free species and those of complexes. We shall first derive the flux equation for individual species in the membrane which will later be correlated with the total flux for the membrane-permeable species.

According to nonequilibrium thermodynamics, the flux of individual species, j_α, is given as a linear function of all forces that are negative gradients of the total chemical potentials

$$j_\alpha = -\sum_\beta l_{\alpha\beta}\nabla\bar{\mu}_\beta, \tag{1}$$

where α and β refer to all species in the membrane and $l_{\alpha\beta}$ indicates a phenomenological coefficient and satisfies the reciprocal relation of Onsager. Under the condition of chemical equilibrium, we have

$$\bar{\mu}_\mathrm{i} = \sum_\gamma \nu_{\gamma\mathrm{i}}\bar{\mu}_\gamma, \tag{2}$$

where the subscript i refers to the electrically neutral complex formed in the i-th reaction and $\nu_{\gamma\mathrm{i}}$ denotes the stoichiometric coefficient of the free species γ in the i-th reaction. Since the complex is electrically neutral, we have

$$Z_\mathrm{i} = \sum_\gamma Z_\gamma \nu_{\gamma\mathrm{i}} = 0. \tag{3}$$

By substituting Eq. 2 into Eq. 1, the term for the force due to the complex can be eliminated, and the flux equations for all species can be written in terms of the forces for free species as follows:

$$j_\alpha = -\sum_\gamma l'_{\alpha\gamma}\nabla\bar{\mu}_\gamma, \tag{4}$$

where

$$l'_{\alpha\gamma} = l_{\alpha\gamma} + \sum_\mathrm{i} \nu_{\gamma\mathrm{i}} l_{\alpha\mathrm{i}}. \tag{5}$$

The total chemical potential for species α, $\bar{\mu}_\alpha$, is expressed as[10]

$$\bar{\mu}_\alpha = \eta_\alpha + RT\ln a_\alpha + Z_\alpha F\psi = RT\ln\bar{\lambda}_\alpha, \tag{6}$$

where

$$\eta_\alpha = \mu_{\alpha,0} + p\bar{V}_\alpha + \xi_\alpha. \tag{7}$$

$\mu_{\alpha,0}$ denotes the standard chemical potential; a, the activity; ψ, the electric potential; p, the hydrostatic pressure; $\bar{V}$, the partial molar volume; ξ, the excess free energy; $\bar{\lambda}$, the absolute activity; and F, the Faraday constant.

By use of local electric potential, ψ, and equilibrium local electric potential for free ion γ, ψ_γ, the gradient of $\bar{\mu}_\gamma$ can be expressed alternatively as

$$\nabla\bar{\mu}_\gamma = Z_\gamma F\nabla(\psi-\psi_\gamma). \tag{8}$$

Using Eqs. 4 and 8, the individual ionic current for species α is given by

$$i_\alpha = Z_\alpha F j_\alpha = -\sum_\gamma \kappa'_{\alpha\gamma}\nabla(\psi-\psi_\gamma), \tag{9}$$

where $\kappa'_{\alpha\gamma}$ denotes a part of electric conductivity produced by the effective driving force of ion γ, $\nabla(\psi-\psi_\gamma)$ and given as

$$\kappa'_{\alpha\gamma} = Z_\alpha Z_\gamma F^2 l'_{\alpha\gamma}. \tag{10}$$

Electric Conductivity for Individual Species. According to Eq. 9, the electric conductivity of species α, κ'_α, is given by[13,14]

$$\kappa'_\alpha = \sum_\gamma \kappa'_{\alpha\gamma} = \sum_\gamma Z_\alpha Z_\gamma F^2 l_{\alpha\gamma} = (Z_\alpha F)^2 u_\alpha C_\alpha, \tag{11}$$

where u_α and C_α denote the absolute mobility and concentration of species α, respectively.

Now, the total flux for each free species in the membrane, J^m_γ, may be written as

$$J^\mathrm{m}_\gamma = j_\gamma + \sum_\mathrm{i} \nu_{\gamma\mathrm{i}} j_\mathrm{i}, \tag{12}$$

where the superscript m refers to the membrane phase. When the steady state is attained, the following relation can be realized:

$$J^\mathrm{m}_\gamma = J^\mathrm{(I)}_\gamma = J^\mathrm{(II)}_\gamma \equiv J_\gamma, \tag{13}$$

where $J^\mathrm{(I)}$ and $J^\mathrm{(II)}$ denote the fluxes in the stagnant layers in phases I and II, respectively. According to Eqs. 12 and 13, the total ionic current for each free species, $I_\gamma = Z_\gamma F J_\gamma$, is seen to be expressed in terms of individual fluxes of the free species and of the complexes as follows:

$$I_\gamma = Z_\gamma F j_\gamma + Z_\gamma F\sum_\mathrm{i} \nu_{\gamma\mathrm{i}} j_\mathrm{i} = i_\gamma + \sum_\mathrm{i} i^{(\gamma)}_\mathrm{i}, \tag{14}$$

where $i^{(\gamma)}_\mathrm{i}$ represents the part of the ionic current of species γ carried by the form of complex i.

According to Eq. 14, it is seen that the flux of the complex contributes to the total ionic currents of free species from which the complex is formed even when the complex is electrically neutral. By using Eq. 4, $i^{(\gamma)}_\mathrm{i}$ can be represented by

$$i^{(\gamma)}_\mathrm{i} = Z_\gamma F\nu_{\gamma\mathrm{i}} j_\mathrm{i} = -\sum_\delta Z_\gamma Z_\delta F^2 \nu_{\gamma\mathrm{i}} l'_{\mathrm{i}\delta}\nabla(\psi-\psi_\delta), \tag{15}$$

where the subscript δ refers to the free species. According to Eqs. 14 and 15, the part of the electric conductivity of species γ due to the complex i, $\kappa^{(\gamma)}_\mathrm{i}$, can be expressed as

$$\kappa^{(\gamma)}_\mathrm{i} = \sum_\delta Z_\gamma Z_\delta F^2 \nu_{\gamma\mathrm{i}} l_{\mathrm{i}\delta} = (Z_\gamma F)^2 \nu_{\gamma\mathrm{i}} u_\mathrm{i} C_\mathrm{i}. \tag{16}$$

It is evident from Eq. 16 that the contribution of the diagonal term l_ii to $\kappa^{(\gamma)}_\mathrm{i}$ vanishes when the complex i is electrically neutral.[14] $\kappa^{(\gamma)}_\mathrm{i}$ is correlated with the electric conductivity of the complex i, κ'_i, as follows:

$$\kappa'_\mathrm{i} = \sum_\gamma \kappa^{(\gamma)}_\mathrm{i} = 0, \tag{17}$$

where the superscript γ refers to the membrane-permeable ion as well as the carrier ion.

Total-Flux Equation for Free Species γ. Substituting Eq. 4 into Eq. 12, we have under the condition of the steady state

$$J_\gamma = -\sum_\delta l''_{\gamma\delta}\nabla\bar{\mu}_\delta, \tag{18}$$

where

$$l''_{\gamma\delta} = l'_{\gamma\delta} + \sum_{\mathrm{i}} \nu_{\gamma\mathrm{i}} l'_{\mathrm{i}\delta}. \tag{19}$$

We see in Eq. 19 that the new phenomenological coefficient, $l''_{\gamma\delta}$, is expressed in terms of individual coefficients, $l_{\alpha\beta}$'s, and that the reciprocal relation for individual coefficients verifies that the $l''_{\gamma\delta}$'s also satisfy the reciprocal relation.

According to Eq. 18, the total ionic current for free species γ, I_γ, is expressed as

$$I_\gamma = -\sum_\delta \kappa''_{\gamma\delta}\nabla(\psi-\psi_\delta), \tag{20}$$

where

$$\kappa''_{\gamma\delta} = Z_\gamma Z_\delta F^2 l''_{\gamma\delta} = Z_\delta Z_\gamma F^2 l''_{\delta\gamma} = \kappa''_{\delta\gamma}. \tag{21}$$

Total Electric Conductivity for Free Species γ. According to Eq. 20, the total electric conductivity for ion γ, κ''_γ, is given by

$$\kappa''_\gamma = \sum_\delta \kappa''_{\gamma\delta}. \tag{22}$$

Substituting Eq. 19 into Eq. 21 and using Eqs. 11 and 16, Eq. 22 can be rewritten as

$$\kappa''_\gamma = \kappa'_\gamma + \sum_{\mathrm{i}} \kappa_{\mathrm{i}}^{(\gamma)} = (Z_\gamma F)^2\Big(u_\gamma C_\gamma + \sum_{\mathrm{i}} \nu_{\gamma\mathrm{i}} u_{\mathrm{i}} C_{\mathrm{i}}\Big). \tag{23}$$

Since the carrier species are completely trapped within the membrane phase, the total flux as well as total electric current of carrier species, J_{s} and I_{s}, should be zero at the steady state, *i.e.*,

$$J_{\mathrm{s}}^{\mathrm{m}} = J_{\mathrm{s}}^{(\mathrm{I})} = J_{\mathrm{s}}^{(\mathrm{II})} \equiv J_{\mathrm{s}} = 0, \tag{24}$$

and

$$I_{\mathrm{s}} = Z_{\mathrm{s}} F J_{\mathrm{s}} = 0, \tag{25}$$

where one kind of free carrier species, s, is assumed to be present in the membrane. According to Eq. 25, the total electric conductivity for the carrier species, κ''_{s}, is also zero. Using Eqs. 23 and 17, we obtain

$$\kappa''_{\mathrm{s}} = \kappa'_{\mathrm{s}} + \sum_{\mathrm{i}} \kappa_{\mathrm{i}}^{(\mathrm{s})} = \kappa'_{\mathrm{s}} - \sum_{\mathrm{i}}\sum_\gamma \kappa_{\mathrm{i}}^{(\gamma)} = 0 \quad (\gamma\neq\mathrm{s}). \tag{26}$$

By means of Eq. 24, Eq. 18 can be reduced to a phenomenological relation

$$J_{\mathrm{p}} = -\sum_{\mathrm{q}} l^*_{\mathrm{pq}}\nabla\bar{\mu}_{\mathrm{q}}, \tag{27}$$

where

$$l^*_{\mathrm{pq}} = l''_{\mathrm{pq}} - \frac{l''_{\mathrm{ps}} l''_{\mathrm{sq}}}{l''_{\mathrm{ss}}}, \tag{28}$$

and p and q refer to the membrane-permeable ions. The reciprocal relation of Onsager can be satisfied by l^*_{pq} as well as $l''_{\gamma\delta}$. According to Eq. 27, we have

$$I_{\mathrm{p}} = -\sum_{\mathrm{q}} \kappa^*_{\mathrm{pq}}\nabla(\psi-\psi_{\mathrm{q}}), \tag{29}$$

where

$$\kappa^*_{\mathrm{pq}} = Z_{\mathrm{p}} Z_{\mathrm{q}} F^2 l^*_{\mathrm{pq}} = Z_{\mathrm{q}} Z_{\mathrm{p}} F^2 l^*_{\mathrm{qp}} = \kappa^*_{\mathrm{qp}}. \tag{30}$$

The total electric conductivity for species p, κ''_{p}, given by Eq. 22 can also be expressed by using κ^*_{pq} as follows:

$$\kappa''_{\mathrm{p}} = \sum_{\mathrm{q}} \kappa^*_{\mathrm{pq}}, \tag{31}$$

provided Eq. 26 holds.

Single Electrolyte System. Now, we shall apply our theory to the system in which only a single strong electrolyte, $\mathrm{M}_{\nu'_{\mathrm{M}}}\mathrm{A}_{\nu'_{\mathrm{A}}}$, is present in the aqueous phases. Moreover, the carrier ion is assumed to react only with counter ion to form a neutral complex in the membrane phase. As a result, the components present in the membrane phase are counter ion, $\mathrm{M}^{Z_{\mathrm{M}}+}$, coion, $\mathrm{A}^{|Z_{\mathrm{A}}|-}$, carrier ion, $\mathrm{S}^{|Z_{\mathrm{s}}|-}$, and complex, C.

According to Eq. 29, the ionic current can be expressed as

$$I_{\mathrm{p}} = -\sum_{\mathrm{q}} \kappa^*_{\mathrm{pq}}\nabla(\psi-\psi_{\mathrm{q}}) \qquad (\mathrm{p, q;\ M, A}). \tag{32}$$

Therefore, Eq. 23 can be written as

$$\kappa''_{\mathrm{M}} = \kappa'_{\mathrm{M}} + \kappa_{\mathrm{c}}^{(\mathrm{M})} = (Z_{\mathrm{M}}F)^2\bar{u}_{\mathrm{M}} C_{\mathrm{M}}^{\mathrm{to}}, \tag{33}$$

and

$$\kappa''_{\mathrm{A}} = \kappa'_{\mathrm{A}}, \tag{34}$$

where

$$\kappa'_{\mathrm{M}} = (Z_{\mathrm{M}}F)^2 u_{\mathrm{M}} C_{\mathrm{M}}, \quad \kappa_{\mathrm{c}}^{(\mathrm{M})} = (Z_{\mathrm{M}}F)^2 \nu_{\mathrm{M}} u_{\mathrm{c}} C_{\mathrm{c}}, \tag{35}$$

and

$$\bar{u}_{\mathrm{M}} \equiv f u_{\mathrm{M}} + \nu_{\mathrm{M}}(1-f) u_{\mathrm{c}}. \tag{36}$$

$C_{\mathrm{M}}^{\mathrm{to}}$ and f denote the total concentration and dissociated fraction of ion M ($f = C_{\mathrm{M}}/C_{\mathrm{M}}^{\mathrm{to}}$), respectively, and the subscript c refers to the complex.

If κ^*_{pq} is independent of the externally applied field, Eq. 32 leads to

$$I_{\mathrm{p}} - I_{\mathrm{p}}^0 = -\kappa''_{\mathrm{p}}\nabla(\psi-\psi^0) \qquad (\mathrm{p;\ M, A}), \tag{37}$$

where the superscript 0 refers to the zero electric current. Under the condition of steady state, Eq. 37 can be integrated to give

$$(I_{\mathrm{p}} - I_{\mathrm{p}}^0)\int_{-\mathrm{a}}^{\mathrm{b}} \frac{\mathrm{d}x}{\kappa''_{\mathrm{p}}} = -(V - V^0), \tag{38}$$

where V^0 denotes the membrane potential at zero electric current. Therefore, the ionic membrane conductance of ion p, g_{p}, is expressed as

$$\frac{1}{g_{\mathrm{p}}} = \int_{-\mathrm{a}}^{\mathrm{b}} \frac{1}{\kappa''_{\mathrm{p}}}\mathrm{d}x. \tag{39}$$

The contribution of carrier species to the ionic conductance vanishes outside the membrane.

At zero electric current, the following relation must hold

$$I_{\mathrm{M}}^0 + I_{\mathrm{A}}^0 = 0. \tag{40}$$

By means of Eq. 40, one of the forces in Eq. 32 can be eliminated to give

$$I_{\mathrm{p}}^0 = -\kappa_{\mathrm{p}}^0\nabla(\psi^0-\psi_{\mathrm{p}}) \qquad (\mathrm{p;\ M, A}), \tag{41}$$

where

$$\kappa_{\mathrm{p}}^0 = \frac{\kappa^*_{\mathrm{pp}}\kappa^*_{\mathrm{qq}} - (\kappa^*_{\mathrm{pq}})^2}{\kappa''_{\mathrm{q}}} \qquad (\mathrm{p, q;\ M, A}). \tag{42}$$

According to Eq. 41, the flux equation at zero electric current is given by

$$J_{\mathrm{p}}^0 = -\frac{\kappa_{\mathrm{p}}^0}{(Z_{\mathrm{p}}F)^2}\nabla\bar{\mu}_{\mathrm{p}}^0, \tag{43}$$

where $\bar{\mu}_{\mathrm{p}}^0$ denotes the total chemical potential at zero electric current. Since Eq. 43 should be of the form of the Nernst-Planck equation, it can be written as

$$J_{\mathrm{p}}^{0} = -\frac{\bar{D}_{\mathrm{p}} C_{\mathrm{p}}^{\mathrm{to}}}{RT} \nabla \bar{\mu}_{\mathrm{p}}^{0}, \tag{44}$$

where $\bar{D}_{\mathrm{p}}$ and $C_{\mathrm{p}}^{\mathrm{to}}$ denote the diffusion coefficient and the total concentration of ion p, respectively, and

$$\frac{\kappa_{\mathrm{p}}^{0}}{(Z_{\mathrm{p}}F)^{2}} = \frac{\bar{D}_{\mathrm{p}} C_{\mathrm{p}}^{\mathrm{to}}}{RT}. \tag{45}$$

Comparing Eq. 45 with Eqs. 33, 35, and 36, we have

$$\bar{D}_{\mathrm{M}} = f(\kappa)\bar{u}_{\mathrm{M}}RT = fD_{\mathrm{M}} + (1-f)D_{\mathrm{c}}, \tag{46}$$

and

$$D_{\mathrm{A}} = f(\kappa)u_{\mathrm{A}}RT, \tag{47}$$

where

$$f(\kappa) = 1 - \kappa_{\mathrm{MA}}^{*}\left(\frac{1}{\kappa_{\mathrm{M}}''} + \frac{1}{\kappa_{\mathrm{A}}''}\right) = \frac{\kappa_{\mathrm{p}}^{0}}{\kappa_{\mathrm{p}}''}, \tag{48}$$

and D_{M} and D_{c} denote the diffusion coefficients of ion M, and of complex C, respectively. As seen in Eq. 48, the total electric conductivity at zero electric current, κ_{p}^{0}, is different from the total electric conductivity, κ_{p}'', unless the cross term κ_{pq}^{*} is zero. Under the condition of the steady state, Eq. 41 can also be integrated to give

$$I_{\mathrm{p}}^{0} \int_{-\mathrm{a}}^{\mathrm{b}} \frac{\mathrm{d}x}{\kappa_{\mathrm{p}}^{0}} = -(V^{0} - V_{\mathrm{p}}), \tag{49}$$

where V_{p} denotes the equilibrium membrane potential of ion p. Therefore, κ_{p}^{0}, can be related to the ionic membrane conductance at zero electric current, g_{p}^{0}, as follows:

$$\frac{1}{g_{\mathrm{p}}^{0}} = \int_{-\mathrm{a}}^{\mathrm{b}} \frac{1}{\kappa_{\mathrm{p}}^{0}} \mathrm{d}x. \tag{50}$$

Experimental

The materials, the apparatus and the procedures for measuring membrane potential, membrane conductance and salt flux were described in detail in the preceding paper.[11]

Partition of $CaCl_2$ between 1-Octanol and Aqueous Phases. The partition ratio, R^{wm}, was determined as the ratio of equilibrium concentration of $CaCl_2$ in 1-octanol phase to that in aqueous phase. The measurements were carried out both in the presence and absence of carrier species in 1-octanol phase. Preconditioned 1-octanol was layered on the aqueous $CaCl_2$, of which the initial concentration was 0.964 mol dm^{-3}. Whole system was vigorously shaken for thirty hours at 25 °C and allowed to stand until both phases became clear, then the sample was pipetted from 1-octanol phase for determining the equilibrium concentration of $CaCl_2$. The concentration was determined with a Nippon Jarrell-Ash atomic absorption spectrophotometer Model AA-8500. The partition ratio obtained for the system without carrier species was 1.7×10^{-4} which agreed well with the value obtained by the radiotracer method.[15] The partition ratio for the system with carrier species was 6.2×10^{-4}, where the concentration of calcium hexadecyl sulfate in 1-octanol phase was 2.5×10^{-3} mol dm^{-3}.

Molar Conductivity Measurement of Calcium Hexadecyl Sulfate in 1-Octanol. The electric conductivity of calcium hexadecyl sulfate in water-saturated 1-octanol was measured by use of a Yanagimoto conductivity outfit Model MY-7. The measurements were carried out with a pair of Pt–Pt electrodes immersed in 1-octanol solution of calcium hexadecyl sulfate at 25 °C. The cell constant, *ca.* 0.05, was determined by use of a standard solution of KCl. The molar conductivity is plotted against the square root of concentration in Fig. 2.

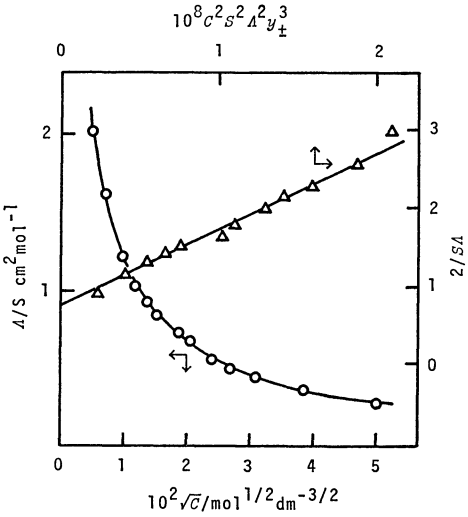

Fig. 2. Molar conductivity of calcium hexadecyl sulfate in 1-octanol as a function of square root of the concentration (○) and Shedlovsky's plot (△).

The limiting molar conductivity, Λ^{∞}, and the dissociation constant, K_{I}, were determined from Shedlovsky's plot,[16,17] $2/S\Lambda$ *vs.* $C^{2}S^{2}\Lambda^{2}y_{\pm}^{3}$, where

$$S = [z/2 + \{1 + (z/2)^{2}\}^{1/2}]^{2}, \tag{51}$$

and

$$z = \frac{2A'}{(\Lambda^{\infty})^{3/2}}\sqrt{C\Lambda}. \tag{52}$$

A' is Onsager's coefficient; C, the concentration; $y_{\pm}$, the mean activity coefficient; and Λ, the molar conductivity. For the calculation of A', the values of viscosity[18] and relative permittivity[19] for pure solvent, *i.e.*, $\eta = 0.0721$ P and $\varepsilon = 9.85$, were used, respectively. The limiting transport number was assumed to be equal to that in water, $t_{\mathrm{Ca}}^{\infty} = 0.76$.[20] The mean activity coefficient was calculated by means of the Debye-Hückel equation in which the diameter of sodium hexadecyl sulfate, 9.9 Å, was used as an ion parameter. The diameter was estimated from its partial molar volume in water obtained by the extrapolation of the values for sodium alkyl sulfates of C_2–C_{12}.[21,22]

The Shedlovsky plot is also shown in Fig. 2. The values of Λ^{∞} and K_{I} obtained from the plot were 2.8 S cm^{2} mol^{-1} and 4.1×10^{-9} mol^{2} dm^{-6}, respectively. The degree of dissociation, θ, was 0.25 at 2.5×10^{-3} mol dm^{-3}, *i.e.*, the concentration of calcium hexadecyl sulfate in the liquid membrane studied.

Diffusion across Water–Octanol Interface. The kinetics of diffusion of $CaCl_2$ across the water–1-octanol interface was studied, where the concentration of carrier species in 1-octanol phase was 2.5×10^{-3} mol dm^{-3}. The modified apparatus of the type proposed by Davies[23], which is shown in Fig. 3, was used. The diffusion area was *ca.* 12.6 cm^{2}. Concentration change in aqueous phase was followed by measuring the electric conductance. A known amount of preconditioned 1-octanol was layered on the aqueous $CaCl_2$ solution with the initial concentration of 3.86×10^{-4} mol dm^{-3}. After the conductance of an aqueous phase became constant, 1-octanol solution of $CaCl_2$ was injected into the oil phase. The initial concentration of $CaCl_2$ in 1-octanol phase was 1.05×10^{-4} mol dm^{-3}. The measurement was carried out at 25 °C, and both phases were stirred at the

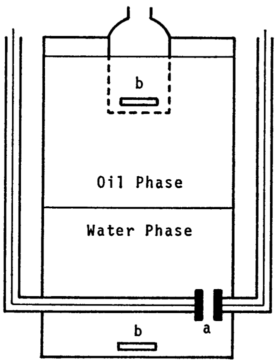

Fig. 3. Schematic diagram of the glass cell used for the measurement of diffusion across the oil–water interface. a: Pt–Pt electrodes, b: magnetic spin bar.

same rate as used for the salt flux measurements.

Results and Discussion

The membrane permeabilities evaluated from the electrical data, P_{Ca} and P_{Cl}, and those at zero electric current evaluated from the membrane potential and flux data, P^0_{Ca} and P^0_{Cl}, have already been reported in the preceding paper.[11] These values were again evaluated in the present study and are shown in Fig. 4. The general features of this figure are similar to those of the preceding paper, but somewhat lower values were obtained with P_{Ca} and P_{Cl}, being due to lower membrane conductance. After repeated measurements, it turned out to be essential for obtaining consistent membrane conductance that the liquid height of the membrane solution in the reservoir was kept constant. We shall, therefore, adopt the present results for analyzing the membrane permeability according to the presented theory.

Since the system is close to equilibrium with respect to calcium ion, we have[10]

$$P_{\mathrm{Ca}} \approx \frac{RT}{(Z_{\mathrm{Ca}}F)^2}\frac{g_{\mathrm{Ca}}}{(a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}}, \tag{53}$$

where superscripts I and II refer to the aqueous phases I and II, respectively. We shall assume that the ion transport is membrane-controlled. From Eqs. 33 and 39, the ionic conductance, g_{Ca}, can be expressed in terms of the absolute mobilities and concentrations of free calcium ion and its complex:

$$\frac{1}{g_{\mathrm{Ca}}} = \int_0^{\mathrm{d}} \frac{\mathrm{d}x}{(Z_{\mathrm{Ca}}F)^2(u_{\mathrm{Ca}}C_{\mathrm{Ca}}+\nu_{\mathrm{Ca}}u_{\mathrm{c}}C_{\mathrm{c}})}. \tag{54}$$

Combining Eq. 53 with Eq. 54, we have

$$\frac{1}{P_{\mathrm{Ca}}} \approx \frac{(Z_{\mathrm{Ca}}F)^2}{RT}(a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}\int_0^{\mathrm{d}} \frac{\mathrm{d}x}{(Z_{\mathrm{Ca}}F)^2(u_{\mathrm{Ca}}C_{\mathrm{Ca}}+\nu_{\mathrm{Ca}}u_{\mathrm{c}}C_{\mathrm{c}})}. \tag{55}$$

Since carrier species are completely trapped within membrane, we can obtain from Eq. 26

$$\kappa''_{\mathrm{s}} = (Z_{\mathrm{s}}F)^2u_{\mathrm{s}}C_{\mathrm{s}} - (Z_{\mathrm{Ca}}F)^2\nu_{\mathrm{Ca}}u_{\mathrm{c}}C_{\mathrm{c}} = 0. \tag{56}$$

Using Eq. 56, the term for the complex in Eq. 55 can be replaced by that for carrier ion, s,

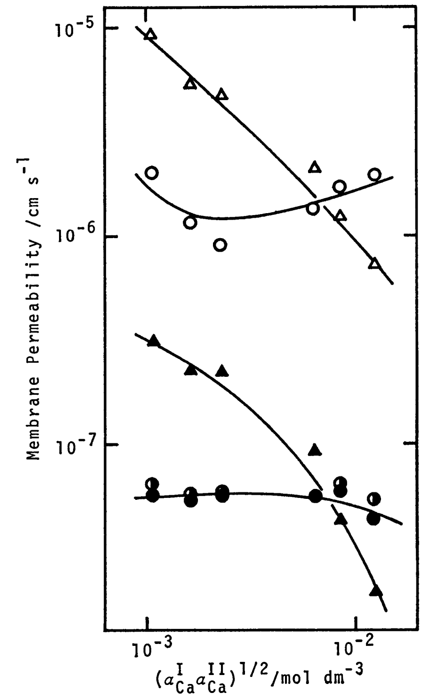

Fig. 4. The membrane permeabilities as a function of geometric mean of the activities of phases I and II. ○: P^0_{Ca}, ●: P^0_{Cl}, △: P_{Ca}, ▲: P_{Cl}. The membrane permeability to salt, P^0_{sa}, is also shown, ◑. The concentration of $CaCl_2$ in phase II was kept at 4×10^{-3} mol dm^{-3} and that in phase I being varied from 4×10^{-4} to 10^{-1} mol dm^{-3}. Solid lines indicate P^0_{p} and P_{p} calculated from P_{pq} according to Eqs. 6 and 7 in Ref. 11, respectively.

$$\frac{1}{P_{\mathrm{Ca}}} \approx \frac{(Z_{\mathrm{Ca}}F)^2}{RT}(a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}\int_0^{\mathrm{d}} \frac{\mathrm{d}x}{(Z_{\mathrm{Ca}}F)^2u_{\mathrm{Ca}}C_{\mathrm{Ca}}+(Z_{\mathrm{s}}F)^2u_{\mathrm{s}}C_{\mathrm{s}}} \tag{57}$$

$$= \frac{(Z_{\mathrm{Ca}}F)^2}{RT}\frac{(a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}d}{(Z_{\mathrm{Ca}}F)^2\tilde{u}_{\mathrm{Ca}}\tilde{C}_{\mathrm{Ca}}+(Z_{\mathrm{s}}F)^2\tilde{u}_{\mathrm{s}}\tilde{C}_{\mathrm{s}}}, \tag{58}$$

where $\tilde{u}$ and $\tilde{C}$ denote the mean absolute mobility and mean concentration within membrane, respectively.

From the observed values of θ and R^{wm}, we see that the concentration of Donnan salt is negligible compared with that of free calcium ion. Under this condition, *i.e.*, $C_{\mathrm{Ca}} \gg C_{\mathrm{Cl}}$, Eq. 58 can be reduced to

$$P_{\mathrm{Ca}} \approx \frac{RT}{(Z_{\mathrm{Ca}}F)^2}\frac{\tilde{\Lambda}^{\mathrm{i}}\tilde{\theta}\tilde{C}^{\mathrm{to}}_{\mathrm{Ca}}}{(a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}d}, \tag{59}$$

$$\Lambda^{\mathrm{i}} = \nu_{\mathrm{Ca}}\Lambda_{\mathrm{Ca}} + \nu_{\mathrm{s}}\Lambda_{\mathrm{s}}, \tag{60}$$

where Λ_{Ca} and Λ_{s} denote the molar conductivity of calcium ion and of carrier ion, respectively, and Λ^{i} is the hypothetical molar conductivity that the complex would have if it be completely dissociated and is related to the observed molar conductivity, Λ, as follows:[24]

$$\theta\Lambda^{\mathrm{i}} = \Lambda. \tag{61}$$

The molar conductivity within liquid membrane, $\tilde{\Lambda}$, must be independent of the external concentrations, because the total concentration of calcium ion within membrance is nearly constant, as stated above. Therefore, the dependence of P_{Ca} on the external

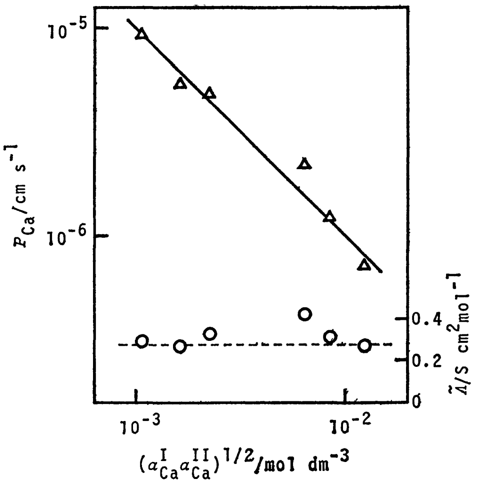

Fig. 5. The membrane permeability, P_{Ca} (△), and the molar conductivity in the liquid membrane estimated from P_{Ca}, $\tilde{\Lambda}$(○), as a function of the geometric mean of the activities of calcium ion in the aqueous phases I and II. Broken line indicates the molar conductivity of calcium hexadecyl sulfate measured in the bulk solution.

concentrations shown in Fig. 5 can well be described by Eq. 59. According to Eq. 59, $\tilde{\Lambda}$ was calculated from P_{Ca} and is compared with the molar conductivity measured in the 1-octanol solution of calcium hexadecyl sulfate in the same figure. We see from this figure that the agreement is satisfactory. This result implies that the electroconductional process of calcium ion is membrane-controlled and the effect of co-ion on this process is negligible.

From Eqs. 45 and 50, the diffusional ionic conductance at zero electric current, g^0_{Ca}, can be expressed as

$$\frac{1}{g^0_{Ca}}=\int_{-a}^{b}\frac{RT}{(Z_{Ca}F)^2\bar{D}_{Ca}C^{to}_{Ca}}dx. \tag{62}$$

The membrane permeability of calcium ion at zero electric current is related to g^0_{Ca} as[10)]

$$P^0_{Ca}\approx\frac{RT}{(Z_{Ca}F)^2}\frac{g^0_{Ca}}{(a^{I}_{Ca}a^{II}_{Ca})^{1/2}}, \tag{63}$$

when the system is close to equilibrium for calcium ion. Combining Eq. 63 with Eq. 62, P^0_{Ca} is expressed in terms of the mean diffusion coefficient, $\tilde{\bar{\bar{D}}}_{Ca}$, and mean total concentration, $\tilde{C}^{to}_{Ca}$, as

$$P^0_{Ca}\approx\frac{\tilde{\bar{\bar{D}}}_{Ca}\tilde{C}^{to}_{Ca}}{(a^{I}_{Ca}a^{II}_{Ca})^{1/2}d}, \tag{64}$$

provided the diffusion of calcium ion is membrane-controlled.

According to Eq. 64, $\tilde{\bar{\bar{D}}}_{Ca}$ was calculated from P^0_{Ca} and is shown in Fig. 6. We see from the small value of partitioning of CaCl$_2$, $R^{wm}=6.2\times10^{-4}$, and the concentrations of external CaCl$_2$ solutions less than 10^{-1} mol dm^{-3} that the concentration of Donnan salt is negligible. The mean total concentration of calcium ion in the membrane is nearly equal to 2.5×10^{-3} mol dm^{-3} which is a half of the concentration of membrane site and is almost independent of the external electrolyte concentration. Therefore, the diffusion coefficient of calcium ion in the membrane phase would be almost independent of the external concentration of CaCl$_2$. Contrary to the expectation, a remarkable concentration dependence was found as shown in Fig. 6. A similar result has been obtained with an ion-exchange resin membrane and has been explained by assuming the energy barrier at the interface.[25)] Thus the observed concentration dependence of $\tilde{\bar{\bar{D}}}_{Ca}$ may be attributed to the presence of energy barrier at the interface.

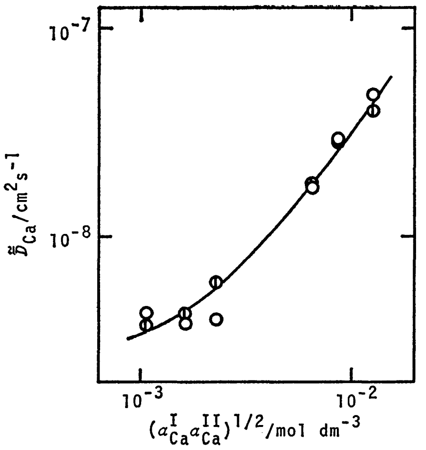

Fig. 6. Diffusion coefficient, $\tilde{\bar{\bar{D}}}_{Ca}$, as a function of the geometric mean of the activities in phases I and II. ○: Estimated from the observed P^0_{Ca}. ⦶: Estimated from P^0_{Ca} calculated from P_{pq} according to Eq. 6 in Ref. 11.

The diffusion of CaCl$_2$ across the interface was studied in the two-phase system of water and 1-octanol with carrier species. The flux of calcium ion at zero electric current can be expressed by Eq. 44. By substituting Eq. 6 into Eq. 44, we have

$$J^0_{Ca}=-\frac{\bar{D}_{Ca}C^{to}_{Ca}}{\bar{\lambda}_{Ca}}\nabla\bar{\lambda}_{Ca}. \tag{65}$$

Integrating Eq. 65 under the condition of steady state, we derive the equation for the flux across phase boundary as follows:

$$\begin{aligned}J^0_{Ca}=&-P^{(b)}_{Ca}\{a^{w}_{Ca}\exp[(Z_{Ca}F\psi^{w}+\eta^{w}_{Ca}-Z_{Ca}F\psi^{m}-\eta^{m}_{Ca})/2RT]\\&-a^{m}_{Ca}\exp[-(Z_{Ca}F\psi^{w}+\eta^{w}_{Ca}-Z_{Ca}F\psi^{m}-\eta^{m}_{Ca})/2RT]\},\end{aligned} \tag{66}$$

where

$$\frac{1}{P^{(b)}_{Ca}}=\left(\frac{a^{m}_{Ca}a^{w}_{Ca}}{\bar{\lambda}^{m}_{Ca}\bar{\lambda}^{w}_{Ca}}\right)^{1/2}\int\frac{\bar{\lambda}_{Ca}}{\bar{D}_{Ca}C^{to}_{Ca}}dx. \tag{67}$$

The integration extends over the boundary region interposing the interface. The superscript (b) refers to the boundary region, m and w, to the oil and aqueous phases, respectively. Equation 66 can be rewritten as[26)]

$$J^0_{Ca}=-k_1C^{w}_{Ca}+k_2C^{m}_{Ca}, \tag{68}$$

where

$$\begin{aligned}k_1=P^{(b)}_{Ca}y^{w}_{Ca}\exp\{[(Z_{Ca}F\psi^{w}+\eta^{w}_{Ca})\\-(Z_{Ca}F\psi^{m}+\eta^{m}_{Ca})]/2RT\},\end{aligned} \tag{69}$$

and

$$k_2 = P_{\mathrm{Ca}}^{(\mathrm{b})} y_{\mathrm{Ca}}^{\mathrm{m}} \exp\{[(Z_{\mathrm{Ca}}F\psi^{\mathrm{m}} + \eta_{\mathrm{Ca}}^{\mathrm{m}}) - (Z_{\mathrm{Ca}}F\psi^{\mathrm{w}} + \eta_{\mathrm{Ca}}^{\mathrm{w}})]/2RT\}. \tag{70}$$

y_{Ca} denotes the activity coefficient of calcium ion.

Assuming that the degree of dissociation of calcium hexadecyl sulfate in the membrane phase is not so much affected by the addition of a small amount of $\mathrm{CaCl_2}$, the conservation law of mass holds for free calcium ion:

$$C_{\mathrm{Ca}}^{\mathrm{m}} v^{\mathrm{m}} + C_{\mathrm{Ca}}^{\mathrm{w}} v^{\mathrm{w}} = C_{\mathrm{Ca}}^{\mathrm{m(e)}} v^{\mathrm{m}} + C_{\mathrm{Ca}}^{\mathrm{w(e)}} v^{\mathrm{w}}, \tag{71}$$

where v denotes the volume of each phase and the superscript (e) refers to the equilibrium state. At the equilibrium state, we have from Eq. 68

$$\frac{k_2}{k_1} = \frac{C_{\mathrm{Ca}}^{\mathrm{w(e)}}}{C_{\mathrm{Ca}}^{\mathrm{m(e)}}}. \tag{72}$$

By means of Eqs. 71 and 72, Eq. 68 can be converted into a convenient form:[26,27]

$$\frac{\mathrm{d}C_{\mathrm{Ca}}^{\mathrm{w}}}{\mathrm{d}t} = k(C_{\mathrm{Ca}}^{\mathrm{w(e)}} - C_{\mathrm{Ca}}^{\mathrm{w}}), \tag{73}$$

where

$$k = A\left(\frac{k_1}{v^{\mathrm{w}}} + \frac{k_2}{v^{\mathrm{m}}}\right), \tag{74}$$

and t and A denote time and the diffusion area, respectively. By integrating Eq. 73 and replacing the concentration with the resistance of aqueous phase, R, we have

$$\ln\left(\frac{1}{R^{\mathrm{e}}} - \frac{1}{R}\right) = -kt + \text{const.}, \tag{75}$$

where R^{e} denotes the resistance of aqueous phase at equilibrium. According to Eq. 75, k can be obtained from the slope of the logarithmic plot shown in Fig. 7. By using Eqs. 72 and 74, k_1 and k_2 were estimated and it was found that $k_1 = 2.8 \times 10^{-6}\ \mathrm{cm\,s^{-1}}$, and $k_2 = 2.3 \times 10^{-6}\ \mathrm{cm\,s^{-1}}$. In order to verify the relation of Eq. 72, the estimated values of k_1 and k_2 were substituted into Eq. 68 which was derived without the above assumption and J_{Ca}^{0} was calculated. The agreement between the calculated and observed J_{Ca}^{0}'s was excellent.

Combining Eq. 69 with Eq. 67, we have

$$\frac{y_{\mathrm{Ca}}^{\mathrm{w}}}{k_1} = \left[\exp\left(-\frac{Z_{\mathrm{Ca}}F\psi^{\mathrm{w}} + \eta_{\mathrm{Ca}}^{\mathrm{w}}}{2RT}\right)\right]\left(\frac{a_{\mathrm{Ca}}^{\mathrm{w}}}{\bar{\lambda}_{\mathrm{Ca}}^{\mathrm{w}}}\right)^{1/2} \int \frac{\bar{\lambda}_{\mathrm{Ca}}}{\bar{D}_{\mathrm{Ca}} C_{\mathrm{Ca}}^{\mathrm{to}}} \mathrm{d}x, \tag{76}$$

$$= \int \frac{a_{\mathrm{Ca}} \exp(U/RT)}{\bar{D}_{\mathrm{Ca}} C_{\mathrm{Ca}}^{\mathrm{to}}} \mathrm{d}x, \tag{77}$$

where U denotes the free energy of partition as

$$U \equiv Z_{\mathrm{Ca}}F\psi + \eta_{\mathrm{Ca}} - (Z_{\mathrm{Ca}}F\psi^{\mathrm{w}} + \eta_{\mathrm{Ca}}^{\mathrm{w}}). \tag{78}$$

According to a previous paper,[25] $\bar{D}_{\mathrm{Ca}}$ can be expressed as

$$\bar{D}_{\mathrm{Ca}} = \bar{D}_{\mathrm{Ca}}^{\circ} \exp[(U-E)/RT], \tag{79}$$

where $\bar{D}_{\mathrm{Ca}}^{\circ}$ and E denote the diffusion coefficient of calcium ion in bulk phase and the energy barrier at the interface, so that $E-U$ could be considered the apparent energy barrier for the diffusion of calcium ion. Substituting Eq. 79 into Eq. 77, we have

$$\frac{y_{\mathrm{Ca}}^{\mathrm{w}}}{k_1} = \int \frac{a_{\mathrm{Ca}}/C_{\mathrm{Ca}}^{\mathrm{to}}}{D_{\mathrm{Ca}}^{\circ} \exp(-E/RT)} \mathrm{d}x. \tag{80}$$

We see from Eq. 80 that $y_{\mathrm{Ca}}^{\mathrm{w}}/k_1$ may almost be independent of the concentration of the external aqueous phase, since $\bar{D}_{\mathrm{Ca}}^{\circ}$, E and $a_{\mathrm{Ca}}/C_{\mathrm{Ca}}^{\mathrm{to}}$ can be regarded as constant. This agrees well with the experimental observation[28] that k_1 is almost constant independent of the concentration of aqueous phase.

We shall compare k_1 with P_{Ca}° determined from the salt flux across membrane. There are two interfaces in the liquid membrane–aqueous electrolyte system. Thus, the system may be regarded as that composed of the two o/w systems. The first consists of phase I and a half of the membrane, the second, phase II and another half of the membrane. According to Eq. 76, we find for the former system

$$\frac{y_{\mathrm{Ca}}^{\mathrm{I}}}{k_1^{(\mathrm{I})}} = \left[\exp\left(\frac{Z_{\mathrm{Ca}}\Phi^{0}}{2}\right)\right]\left(\frac{a_{\mathrm{Ca}}^{\mathrm{I}} a_{\mathrm{Ca}}^{\mathrm{II}}}{\bar{\lambda}_{\mathrm{Ca}}^{\mathrm{I}} \bar{\lambda}_{\mathrm{Ca}}^{\mathrm{II}}}\right)^{1/2} \int_{-\mathrm{a}}^{\mathrm{d}/2} \frac{\bar{\lambda}_{\mathrm{Ca}}}{\bar{D}_{\mathrm{Ca}} C_{\mathrm{Ca}}^{\mathrm{to}}} \mathrm{d}x, \tag{81}$$

where $-$a and d/2 indicate the positions of the surface of the stagnant layer and of the middle of the membrane, respectively, and

$$\Phi^{0} = F(\psi^{\mathrm{II}} - \psi^{\mathrm{I}})RT. \tag{82}$$

Similarly we obtain

$$\frac{y_{\mathrm{Ca}}^{\mathrm{II}}}{k_1^{(\mathrm{II})}} = \left[\exp\left(-\frac{Z_{\mathrm{Ca}}\Phi^{0}}{2}\right)\right]\left(\frac{a_{\mathrm{Ca}}^{\mathrm{I}} a_{\mathrm{Ca}}^{\mathrm{II}}}{\bar{\lambda}_{\mathrm{Ca}}^{\mathrm{I}} \bar{\lambda}_{\mathrm{Ca}}^{\mathrm{II}}}\right)^{1/2} \int_{\mathrm{d}/2}^{\mathrm{b}} \frac{\bar{\lambda}_{\mathrm{Ca}}}{\bar{D}_{\mathrm{Ca}} C_{\mathrm{Ca}}^{\mathrm{to}}}, \tag{83}$$

where b indicates the position of the surface of the stagnant layer in phase II. On the other hand, the

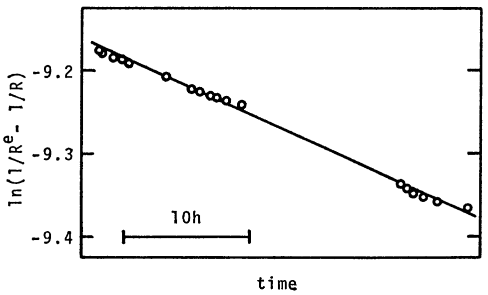

Fig. 7. Plot of $\ln(1/R^{\mathrm{e}} - 1/R)$ *versus* time.

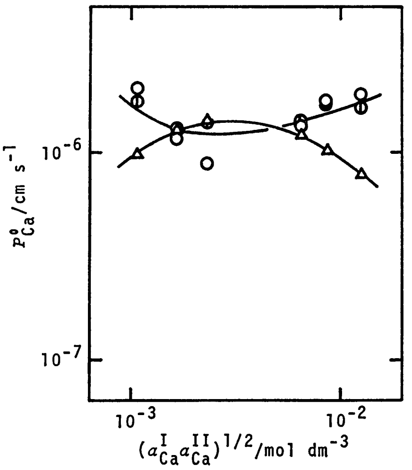

Fig. 8. Comparison of P_{Ca}° estimated from k_1 according to Eq. 85 (△) with P_{Ca}° observed in the liquid membrane–aqueous electrolyte system (○). P_{Ca}° calculated from P_{pq} according to Eq. 6 in Ref. 11 (⦶) is also shown.

diffusional membrane permeability to calcium ion can be obtained from Eq. 65 in a similar way to that described previously:[10)]

$$\frac{1}{P^0_{\mathrm{Ca}}}=\left(\frac{a^{\mathrm{I}}_{\mathrm{Ca}}a^{\mathrm{II}}_{\mathrm{Ca}}}{\bar{\lambda}^{\mathrm{I}}_{\mathrm{Ca}}\bar{\lambda}^{\mathrm{II}}_{\mathrm{Ca}}}\right)^{1/2}\int_{-\mathrm{a}}^{\mathrm{b}}\frac{\bar{\lambda}_{\mathrm{Ca}}}{\bar{D}_{\mathrm{Ca}}C^{\mathrm{to}}_{\mathrm{Ca}}}\mathrm{d}x. \tag{84}$$

Comparing Eq. 84 with Eqs. 81 and 83, we have

$$\frac{1}{P^0_{\mathrm{Ca}}}=\frac{y^{\mathrm{I}}_{\mathrm{Ca}}\exp\left(-Z_{\mathrm{Ca}}\Phi^0/2\right)}{k_1^{(\mathrm{I})}}+\frac{y^{\mathrm{II}}_{\mathrm{Ca}}\exp\left(Z_{\mathrm{Ca}}\Phi^0/2\right)}{k_1^{(\mathrm{II})}}. \tag{85}$$

According to Eq. 85, P^0_{Ca} can be estimated from k_1. The estimated P^0_{Ca} is compared with the observed P^0_{Ca} determined from the salt flux measurement on the membrane–electrolyte system in Fig. 8. We see from this figure that the estimated value agrees well with the observed one.

Thus the fact that the diffusional membrane permeability is less dependent on the external aqueous concentration can be attributed to the presence of an apparent energy barrier at interface. The diffusional fluxes of ions across liquid membranes have been measured by some workers.[15,29,30)] However, they have not fully investigated the concentration dependence of the membrane permeability.

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