Diffusional and Conductive Membrane Permeabilities to Ions in Liquid Membrane-Aqueous Inorganic Electrolyte System

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Utilizing a liquid membrane-aqueous inorganic electrolyte system, the membrane permeability to ion α estimated from the conductance and potential data, P_α, and that at zero electric current estimated from the salt flow and potential data, P^0_α, were determined. A solution of calcium hexadecyl sulfate dissolved in 1-octanol and calcium chloride were used as the liquid membrane and the inorganic electrolyte, respectively. The results showed that $P^0_{\mathrm{Ca}}/P^0_{\mathrm{Cl}} \approx P_{\mathrm{Ca}}/P_{\mathrm{Cl}} \approx 10$ and $P^0_{\mathrm{Cl}} \approx P^0_{\mathrm{s}}$, where subscript s refers to the salt. The latter result indicates that the diffusion of a salt through the membrane is governed by the co-ion permeation. It was shown that P^0_α is smaller than P_α and that P_α decreases with increase in the concentration of external calcium chloride solution while P^0_α is nearly independent of the concentration. The difference between P_α and P^0_α can be explained in terms of the elements of permeability and conductance matrices estimated from the electrical and salt flow data.

Liquid membranes have been extensively investigated by analytical chemists, because of their high selectivity to a particular ion.[1] They have also drawn the attention of investigators working with biological membranes as a model for a carrier transport.[2] In spite of numerous experimental works, theories proposed for ion transport through liquid membrane are not as many as those for fixed site membranes. The theory of Eisenman *et al.*[3–6] is widely used to analyze the ion transport phenomena through liquid membranes, but it is derived on the basis .of the Nernst-Plank equation.

A theory based on nonequilibrium thermodynamics was presented in a previous paper.[7] It was shown[8] that the equations describing the membrane phenomena for a fixed site membrane is applicable to a liquid membrane with mobile site.

We have carried out an electrochemical study utilizing a cation-exchange liquid membrane containing calcium hexadecyl sulfate for the experimental presentation of the theory.

Experimental

Materials. Calcium hexadecyl sulfate was prepared from sodium hexadecyl sulfate according to the method of Lottermoser and Püschel.[9] Sodium hexadecyl sulfate was prepared from purified 1-hexadecanol obtained by fractional distillation of a commercial sample.[10] All other reagents were of guranteed grade and used without further purification.

Apparatus. The cell assembly is schematically shown in Fig. 1. Two compartments are separated by a liquid membrane supported on a Teflon millipore film (Fluoro Pore, No. EP100, pore size 1.0 μm, thickness 50 μm, from Sumitomo Electric Ind., Ltd.). The liquid membrane was prepared by dissolving calcium hexadecyl sulfate in water-saturated 1-octanol at a concentration of 2.5×10^{-3} mol/dm^3. The diffusional area of the membrane was 0.2 cm^2. Small cells (1.5 cm^3) were used. The concentration of $CaCl_2$ in the internal solution (compartment II) was kept at 4×10^{-3} mol/dm^3, that of the external one (compartment I) being varied from 4×10^{-4} to 10^{-1} mol/dm^3. The whole assembly was thermostated at 25 ± 0.02 °C and the solution in each compartment was stirred with magnetic stirrer at a rate of 200 rpm. The small solubility of calcium hexadecyl sulfate in aqueous solution, an order of 10^{-6} mol/dm^3, was obtained at 25 °C.[11] The dissolution of calcium hexadecyl sulfate in the aqueous phase may be ignored. This was also confirmed by the constancy of the conductance of aqueous calcium chloride solution in contact with the liquid membrane.

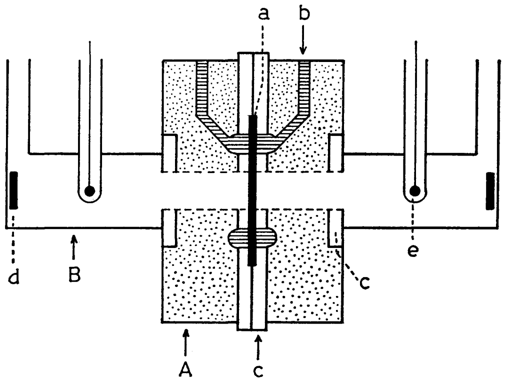

Fig. 1. Schematic diagram of the experimental cell assembly.
A; The holder of the liquid membrane made of two polyethylene-boards. B; The half glass cell. a; The liquid membrane supported on a Teflon millipore film. b; The liquid membrane was retained in the circumference of the supporting film. c; The silicon rubber-packing. d; The magnetic spin bar. e; A pair of platinized platinum electrodes.

Salt Flow Measurement. The salt flow was studied by measuring the change in the concentration of the solution. Concentration changes were followed by the electric conductance of the external and internal solutions measured by means of the two Pt-Pt electrodes connected to the Yanagimoto conductivity outfit Model MY-7. The solutions were replaced with fresh ones several times, until a steady membrane resistance was obtained. It took more than 24 h on some occasions to attain a steady salt flow.

A theory for the liquid membrane has been presented[8] by assuming 1) steady state, 2) absence of the flow of water as well as organic solvent, 3) the dissociation equilibrium for the mobile site-counter ion binding within the liquid membrane, and 4) presence of the mobile site only within the liquid membrane. It has been shown that the equations describing transport phenomena for the fixed site membrane[7] is equally applicable to the system with a mobile site membrane.

The membrane permeability to ion α, P_α^0, as well as that to salt, P_s^0, at zero electric current can be estimated by using the equations[7)] for the flux, J_α^0 and the salt flux, J_s:

$$J_\alpha^0 = \nu_\alpha J_s = -P_\alpha^0 \Delta \bar{a}_\alpha = -P_\alpha^0 \{a_\alpha^{\mathrm{II}} \exp(Z_\alpha \Phi_0/2) - a_\alpha^{\mathrm{I}} \exp(-Z_\alpha \Phi_0/2)\}, \tag{1}$$

and

$$J_s = -P_s^0 \Delta a_s = -P_s^0 (a_s^{\mathrm{II}} - a_s^{\mathrm{I}}), \tag{2}$$

where

$$\Phi_0 = FV_0/RT, \tag{3}$$

ν, Z, F, α, V_0, R, and T denote the stoichiometric coefficient, the charge number, Faraday constant, the activity, the membrane potential at zero electric current, gas constant and absolute temperature, respectively. Superscripts I and II refer to compartments I and II, respectively, and subscripts α and s to ion α and salt s, respectively.

Membrane Potential and Conductance Measurements. The membrane potential was measured by means of two calomel electrodes connected to the Orion digital pH meter Model 701. The calomel electrode was connected to each compartment through an agar bridge. In experiments at lower concentrations, the solutions were replaced by fresh ones several times in order to avoid contamination with KCl diffusing from the agar bridge.

The membrane resistance was measured by means of the two Pt-Pt electrodes connected to the same conductivity outfit as used for the salt flow measurement. The membrane resistance was obtained by subtracting the solution resistance from the total one. After the steady state was attained, the membrane resistance remained constant. Errors inherent to the measurement of the membrane resistance were 4—5 percent.

The membrane permeability to ion α, P_α, is related to ion conductance, g_α, by[7)]

$$g_\alpha = t_\alpha G_m = \frac{(Z_\alpha F)^2}{RT} P_\alpha (a_\alpha^{\mathrm{I}} a_\alpha^{\mathrm{II}})^{1/2} \frac{\sinh Z_\alpha(\Phi_0 - \Phi_\alpha)/2}{Z_\alpha(\Phi_0 - \Phi_\alpha)/2}, \tag{4}$$

where

$$\Phi_\alpha = FV_\alpha/RT, \tag{5}$$

and t_α denotes the apparent transport number, G_m the membrane conductance, and V_α the equilibrium membrane potential for the ion α.

Results and Discussion

The membrane potential, V_0, the membrane conductance, G_m, and the salt flow, J_s, are plotted against the mean activity of $CaCl_2$ in the external solution ($a_\pm^{\mathrm{I}}$) in Fig. 2. The apparent transport number, t_{Ca}, estimated from the potential *vs.* logarithm of mean activity relation was nearly constant, 0.96, within the range of concentration studied.

Membrane permeability at zero electric current, P_{Ca}^0, P_{Cl}^0 and P_s^0, can be estimated from the potential and salt flow data according to Eqs. 1 and 2. P_{Ca} and P_{Cl} can be estimated from the potential and conductance data according to Eq. 4. The results are shown in Fig. 3.

We see that $P_{Ca}^0 > P_{Cl}^0$, $P_{Ca} > P_{Cl}$, $P_{Ca}^0 < P_{Ca}$, and $P_{Cl}^0 \approx P_s^0 < P_{Cl}$. Since the membrane is a cation exchanger, the results $P_{Ca}^0 > P_{Cl}^0$ and $P_{Ca} > P_{Cl}$ are as expected. The ratio of P_{Ca}^0 to P_{Cl}^0 and that of P_{Ca} to P_{Cl} are both about ten. The result, $P_{Cl}^0 \approx P_s^0$, indicates that the diffusion of salt through the liquid membrane is governed by co-ion permeation.

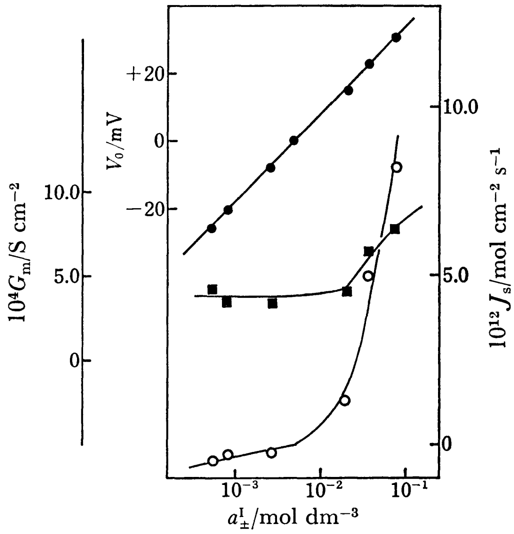

Fig. 2. The membrane potential (●), the membrane conductance (■), and the salt flow (○), each as a function of the mean activity of external solution. The concentration of the internal solution was kept at 4× 10^{-3} mol/dm^3.

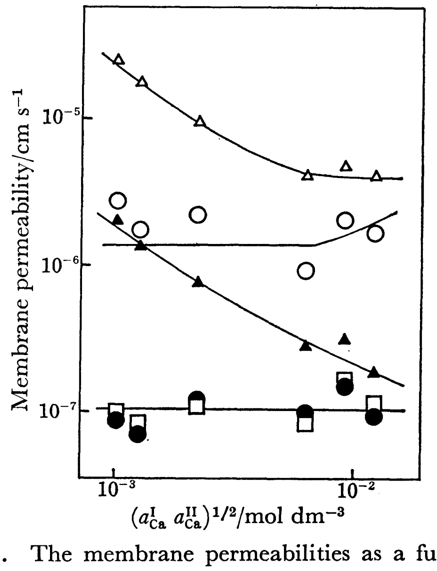

Fig. 3. The membrane permeabilities as a function of the geometric mean of the activity of external and internal solutions. △; P_{Ca}, ▲; P_{Cl}, ○; P_{Ca}^0, ●; P_{Cl}^0 □; P_s^0. The solid lines indicate the values of P_α^0 and P_α calculated from $P_{\alpha\beta}$ (Fig. 5) according to Eqs. 6 and 7, respectively.

P_{Ca} and P_{Cl} decrease with the increase in the geometric mean of the activities of external and internal solutions as shown in Fig. 3. On the other hand, P_{Ca}^0, P_{Cl}^0, and P_s^0 show no appreciable concentration dependence. P_α^0, P_α and P_α^0/P_α can respectively be expressed as functions of the elements of permeability matrix $P_{\alpha\beta}$'s and of conductance matrix $g_{\alpha\beta}$'s ($\alpha \neq \beta$) as follows.

$$P_\alpha^0 = (P_{\alpha\alpha} P_{\beta\beta} - P_{\alpha\beta} P_{\beta\alpha})/P_\beta, \tag{6}$$

$$P_\alpha = P_{\alpha\alpha} + Z_\beta P_{\beta\alpha}/Z_\alpha, \tag{7}$$

and

$$\frac{P_\alpha^0}{P_\alpha} = 1 - \frac{Z_\beta P_{\beta\alpha}}{Z_\alpha P_\alpha} - \frac{Z_\alpha P_{\alpha\beta}}{Z_\beta P_\beta} = 1 - g_{\alpha\beta}\left(\frac{1}{g_\alpha} + \frac{1}{g_\beta}\right). \tag{8}$$

$P_{\alpha\beta}$ is related to an element of conductance matrix $g_{\alpha\beta}$:

$$g_{\alpha\beta} = \frac{Z_\alpha Z_\beta F^2}{RT} P_{\alpha\beta}(a^{\mathrm{I}}_\beta a^{\mathrm{II}}_\beta)^{1/2} \frac{\sinh Z_\beta(\Phi_0 - \Phi_\beta)/2}{Z_\beta(\Phi_0 - \Phi_\beta)/2}, \tag{9}$$

and $g_{\alpha\beta}$ can be estimated according to the equation

$$g_{\alpha\beta} = g_{\beta\alpha} = G_{\mathrm{m}} t_\alpha t_\beta - \frac{(Z_\alpha \nu_\alpha F)^2 P^0_{\mathrm{s}} \Delta a_{\mathrm{s}}}{\nu_{\mathrm{s}} \Delta \mu_{\mathrm{s}}}, \tag{10}$$

where

$$\nu_{\mathrm{s}} = \nu_\alpha + \nu_\beta,$$

and $\Delta\mu_{\mathrm{s}}$ denotes the chemical potential difference of salt across membrane. The diagonal elements of conductance matrix, $g_{\alpha\alpha}$ and $g_{\beta\beta}$, are given by

$$g_{\alpha\beta} = g_\alpha - g_{\alpha\alpha} = g_\beta - g_{\beta\beta}. \tag{11}$$

The value of $g_{\alpha\beta}$ was evaluated by means of Eq. 10 where the activity data of calcium chloride in phases I and II were taken from Handbook of Chemistry (Chemical Society of Japan). The other elements $g_{\alpha\alpha}$ and $g_{\beta\beta}$ were calculated by means of Eq. 11. These elements were plotted against the mean activity of calcium chloride in phase I as shown in Fig. 4. The elements of permeability matrix were estimated by means of Eq. 9 and the results are shown in Fig. 5.

The ratio P^0_α/P_α may be calculated from Eq. 8 by using the elements of the permeability matrix. A comparison of the observed values with calculated ones is given in Fig. 6. The agreement is satisfactory.

The full lines in Fig. 3 represent P^0_α and P_α calculated by means of Eqs. 6 and 7, respectively. We see that the agreement between theory and experiment is satisfactory.

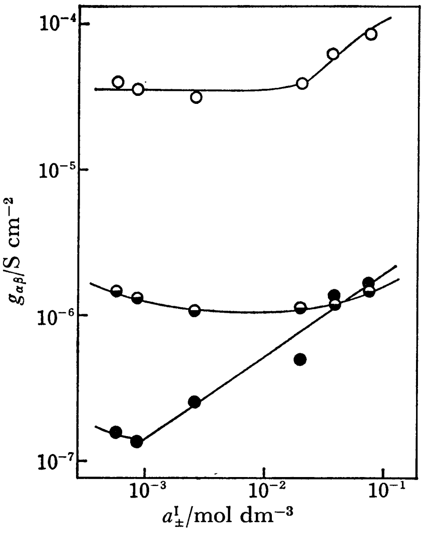

Fig. 4. The elements of the conductance matrix as a function of the mean activity of external solution. The concentration of internal solution was kept at 4×10^{-3} mol/dm^3. ○; $g_{\mathrm{Ca.Ca}}$, ◒; $g_{\mathrm{Ca.Cl}}$, ●; $g_{\mathrm{Cl.Cl}}$.

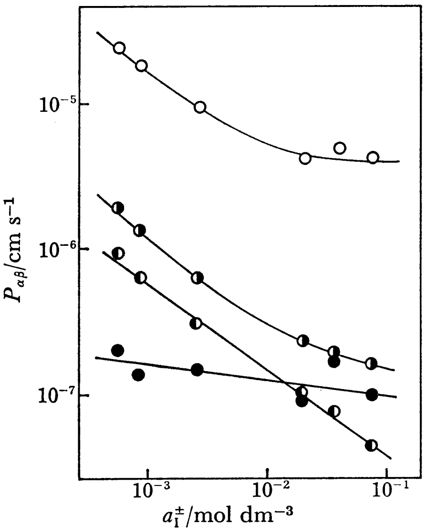

Fig. 5. The elements of the permeability matrix as a function of the mean activity of external solution. The concentration of internal solution was kept at 4×10^{-3} mol/dm^3. ○; $P_{\mathrm{Ca.Ca}}$, ◑; $-P_{\mathrm{Cl.Ca}}$, ◐; $-P_{\mathrm{Ca.Cl}}$, ●; $P_{\mathrm{Cl.Cl}}$.

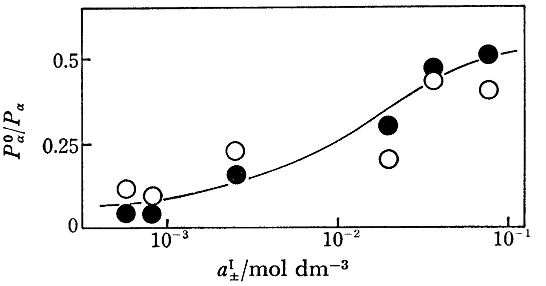

Fig. 6. The ratio P^0_α/P_α as a function of the mean activity of external solution. The concentration of internal solution was kept at 4×10^{-3} mol/dm^3.
○; $P^0_{\mathrm{Ca}}/P_{\mathrm{Ca}}$, ●; $P^0_{\mathrm{Cl}}/P_{\mathrm{Cl}}$. The solid line was calculated from $P_{\alpha\beta}$ according to Eq. 8.

P^0_α can be expressed by

$$\frac{1}{P^0_\alpha} = \frac{1}{P^0_\alpha(\mathrm{I})} + \frac{1}{P^0_\alpha(\mathrm{m})} + \frac{1}{P^0_\alpha(\mathrm{II})}, \tag{12}$$

where (I) and (II) refer to the boundary layers in phases I and II, respectively, and (m) denotes the membrane phase.[7] Since the system is close to equilibrium with respect to calcium ions, we can put

$$\frac{1}{P^0_{\mathrm{Ca}}(\mathrm{I})} = \frac{l(\mathrm{I})}{D_{\mathrm{Ca}}(\mathrm{I}) \cdot C_{\mathrm{Ca}}(\mathrm{I})} (a^{\mathrm{I}}_{\mathrm{Ca}} a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2} \tag{13}$$

and

$$\frac{1}{P^0_{\mathrm{Ca}}(\mathrm{II})} = \frac{l(\mathrm{II})}{D_{\mathrm{Ca}}(\mathrm{II}) \cdot C_{\mathrm{Ca}}(\mathrm{II})} (a^{\mathrm{I}}_{\mathrm{Ca}} a^{\mathrm{II}}_{\mathrm{Ca}})^{1/2}, \tag{14}$$

where l, D, and C denote the boundary layer thickness, the diffusion coefficient in boundary layer and the concentration, respectively. Assuming that the thickness of boundary layers to be 100 μm, the values of $1/P^0_{\mathrm{Ca}}$ (I) and $1/P^0_{\mathrm{Ca}}$ (II) were found to be in the order of 10^3 cm^{-1} s, while $1/P^0_{\mathrm{Ca}}$ was the order of 10^5—10^6 cm^{-1} s, *i.e.*,

$$P^0_{\mathrm{Ca}} \approx P^0_{\mathrm{Ca}}(\mathrm{m}). \tag{15}$$

It can be concluded that the transport process is the membrane control. Since the membrane resistance was obtained by subtracting part of the solution resistance from the total one, we have

$$P_{\mathrm{Ca}} \approx P_{\mathrm{Ca}}(\mathrm{m}). \tag{16}$$

The theory based on the Nernst-Plank equation can not differentiate P_α from P^0_α.[7] Thus an explanation for the transport phenomena should be made on the basis of nonequilibrium thermodynamics.

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References

1) R. A. Durst, Ed., "Ion Selective Electrode," Dept. of Commerce, National Bureau of Standards Special Publication 314, Washington, D. C. (1969), Chaps. 1 and 2.

2) G. M. Shean and K. Sollner, *Ann. N. Y. Acad. Sci.*, **137**, 759 (1966).

3) F. Conti and G. Eisenman, *Biophys. J.*, **6**, 227 (1966).

4) J. L. Walker and G. Eisenman, *Biophys. J.*, **6**, 513 (1966).

5) J. P. Sandblom, G. Eisenman, and J. L. Walker, *J. Phys. Chem.*, **71**, 3862 (1967).

6) J. L. Walker, G. Eisenman, and J. P. Sandblom, *J. Phys. Chem.*, **72**, 978 (1968).

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

8) A. Yamauchi, T. Minematsu, and H. Kimizuka, *Membrane*, **2**, 69 (1977).

9) A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933).

10) R. Matuura, H. Kimizuka, S. Miyamoto, and R. Shimozawa, *Bull. Chem. Soc. Jpn.*, **31**, 532 (1958).

11) A. Matsubara, K. Nomura, and H. Kimizuka, *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **10**, 111 (1977).