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Self-diffusion of a Cation through Cation Exchange Membrane and Membrane Permeability

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The self-diffusion coefficient of an ion and the membrane permeability were studied with a system consisting of two identical electrolyte solutions separated by a cation exchange membrane. The membrane permeability to cation was estimated from the membrane conductance data. The result indicated that the membrane permeability increased with a decrease in electrolyte concentration. The self-diffusion coefficients and the concentrations of Na^+, Cs^+, and Ca^{2+} in the membrane were also measured by the radiotracer method. At concentrations less than 0.1 M, the self-diffusion coefficients more or less increased with increasing concentrations, while the concentrations within membrane remained almost constant. The membrane permeability to ion estimated from the conductance data was in excellent agreement with that calculated by the relation in which the membrane permeability is given as the self-diffusion coefficient times the partition coefficient divided by the membrane thickness.

A number of studies, theoretical and experimental, have been carried out on ion transport through membrane. A theory of ion transport across membrane was presented,[1,2] in which an ion flux was shown to be proportional to the difference in electrochemical activities or total activities of the ion in exterior phases. The proportionality coefficient was defined as the membrane permeability to the ion. Equations for the membrane current, conductance and potential could easily be derived from the flux equation and were found to be suitable for an explanation of the electrochemical data of the living cell membranes.[1,2]

The membrane permeability to an ion in equilibrium was expressed as the diffusion coefficient times the partition coefficient divided by the membrane thickness.[3] The present work is aimed at providing an experimental verification for this physical picture of membrane permeability and discussing related phenomena.

Experimental

Materials. A "CK-1, 1.0 t" cation exchange membrane (Asahi Chemical Industry Co., Ltd.) was used. It was conditioned by the ordinary method before use. The membrane consists of homogeneous sulfonated styrene-divinylbenzene copolymer with an ion exchange capacity of 2.8 meq/g dried membrane and water content of 38 percent. The thickness of the membrane was 1.09 mm after equilibration with 1.0 M sodium chloride solution, and remained almost unaltered even when the electrolyte concentration was changed. Radioactive sodium-22, cesium-137, and calcium-45 in chloride form (Japan Radioisotope Association) were used. Inorganic salts of extra pure grade were used without purification.

Measurement of Tracer Flux. The flux measuring cell consists of two compartments I and II of an equal 3 ml volume, separated by a preconditioned membrane with diffusion area 1 cm². For the measurement, the compartments were filled with the electrolyte solutions of the same concentration, the non-radioactive solution being introduced into compartment I and the radioactive solution, into compartment II. The radioactivities of the solutions were measured after a given time interval with either an Aloka ND-151D γ-ray scintillation counter or a Beckman LS-100 liquid scintillation counter. Compartments I and II were replaced several times with the radioactive and non-radioactive solutions, respectively, until a stationary tracer flux was attained. This could be observed within several hours.

J_M^*, the stationary tracer flux per unit area of membrane, is related to the self-diffusion coefficient, D_M, and the concentration of the tracer in compartment II, C_M^*, as follows[4]

$$J_M^* = D_M \frac{C_M^m}{C_M^s} \frac{C_M^*}{\delta} \tag{1}$$

where the subscript M refers to the ion M, δ denotes the membrane thickness, and C_M^m and C_M^s are the concentrations of the ion M in the membrane and the two electrolyte solutions, respectively. When the diffusion process is membrane-controlled, D_M should be replaced by[5]

$$D_M = D_M^m \Big/ \left(\frac{C_M^m}{C_M^s} + 1\right) \tag{2}$$

where D_M^m is the true self-diffusion coefficient of the ion M through membrane. Combining Eqs. (1) and (2), we obtain

$$D_M^m = \left(\frac{C_M^s}{C_M^m} + 1\right) \frac{\delta J_M^*}{C_M^*}. \tag{3}$$

Let S be the radioactivity per unit volume of the solution in compartment I with V ml in volume, t the time for permeation, A the membrane area, and S_0 the radioactivity per unit volume of the solution in compartment II. We then have

$$J_M^* / C_M^* = VS/AtS_0. \tag{4}$$

According to Eq. (4), J_M^* / C_M^* can be estimated by measuring S_0 and S/t since V and A are known. Hence D_M^m can be evaluated according to Eq. (3) provided the concentration of the ion M within membrane C_M^m is known.

Measurement of Concentration within Membrane. The membrane with 1 cm square was preconditioned by equilibration with a metal chloride solution of a given concentration and immersed in the 500 ml of the radioactive solution having the same concentration as the preconditioning solution. The membrane was taken out at a given time interval, the

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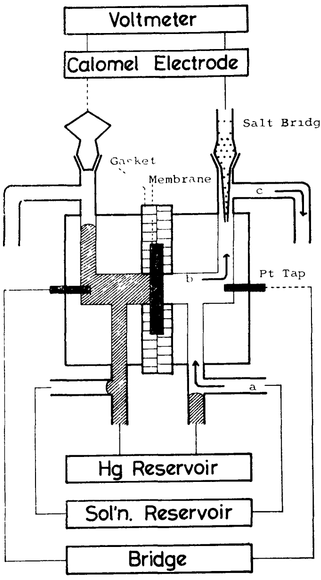

Fig. 1. Schematic diagram of the cell used for the measurements of membrane conductances. The arrows a, b, and c indicate the direction of the solution flow.

adhering solution being removed with filter paper, and the radioactivity entering the membrane was measured. The sample membrane was then brought back into the radioactive solution. Radioactivity measurements were carried out until an attainment of equilibrium which was within several hours.

The ratio C_M^m/C_M^s at equilibrium can be evaluated according to the following relation

$$\frac{C_M^m}{C_M^s} = \frac{S_0^s - S_\infty^s}{S_\infty^s}\cdot\frac{V^s}{V^m} = \frac{r^s S_\infty^m}{r^m S_\infty^s}\cdot\frac{V^s}{V^m} \qquad (5)$$

where superscripts m and s refer to the membrane phase and the solution phase, respectively, S_0 and S_∞ denote the radioactivity per unit volume at the initial and final states, respectively, V denotes volume, and r specific activity.

Membrane Conductance Measurement. The cell is illustrated in Fig. 1. The membrane conductance was measured with a 4255 A universal bridge and a 4440 B decade capacitor (Yokogawa-Hewlett-Packard, Ltd.). Before the measurement, slow streams of salt solutions were introduced from the solution reservoirs, running through and overflowing the two solution chambers of the cell. Equilibrium was attained within several hours. Mercury was then introduced from the reservoirs so that the salt solutions were pushed out and the solution chambers were filled up with mercury. The bridge was connected to the platinum plugs of the cell and the membrane conductance was measured. The temperature was kept at 20±1 °C.

Results and Discussion

The C_M^m values are plotted against C_M^s in Fig. 2. The concentrations of Na^+ were almost the same as those of Cs^+ within experimental error. The values of C_M^m at external salt concentrations less than 0.2 M were found to be almost constant at 1.7±0.2 M, which is close to the fixed charge density of membrane. Since the external salt concentrations for the measurements of the membrane conductance and the tracer flux were less than 0.1 M, we may regard C_M^m as a constant. The C_M^m increased at higher salt concentrations due to the Donnan effect.

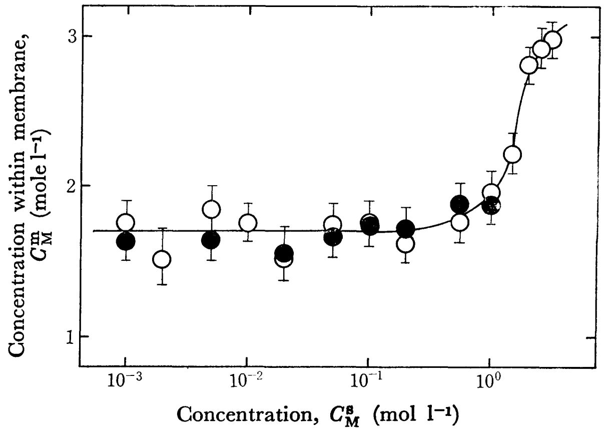

Fig. 2. Cationic concentration within membrane *vs.* external electrolyte concentration curve. The symbols ● and ○ denote C_{Na}^m and C_{Cs}^m, respectively.

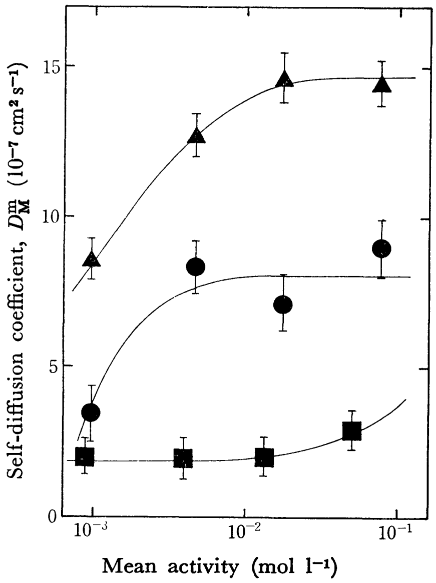

Fig. 3. Self-diffusion coefficient of cation through membrane *vs.* mean activity of salt in the external solution. The symbols ●, ▲, and ■ indicate D_{Na}^m, D_{Cs}^m, and D_{Ca}^m, respectively.

Fig. 3 shows the self-diffusion coefficients of metal ions through the membrane which are less than those in aqueous solution by a factor of the order of 1 or 2. It is seen that D_{Na}^m and D_{Cs}^m are almost constant at higher concentrations of external solutions and decrease at lower concentrations, while D_{Ca}^m is almost constant at lower concentrations and increases at higher concentrations.

The membrane permeability to the ion M, P_M, in equilibrium is related to D_M^m and C_M^m as follows[3]

$$P_M = \frac{D_M^m}{\delta}\frac{C_M^m}{a_M} \qquad (6)$$

where a_M denotes the activity of the ion M in the external solution. Since the quantities on the right-hand side are known, P_M can be calculated.

The results of the membrane conductance measurements are shown in Fig. 4. This figure indicates that

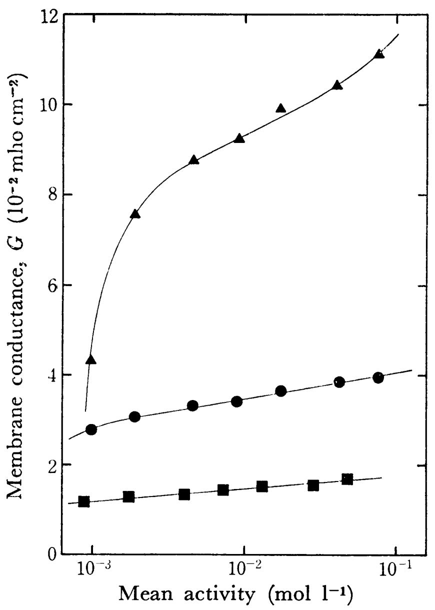

Fig. 4. Membrane conductance *vs.* mean activity of external salt solution. The symbols ●, ▲, and ■ indicate the membrane conductances in the NaCl, CsCl, and $CaCl_2$ system, respectively.

the membrane conductances increase more or less with the increase in the concentration of the external solution. The membrane permeability to cation M can be estimated by the relation[1]

$$G = \frac{Z_M F^2}{RT} P_M a_M \tag{7}$$

where G denotes the membrane conductance per unit area, Z_M the charge, and F, R, and T have their usual meanings. In Eq. (7), the contribution of an anion to the membrane conductance is ignored since the sample membranes can be regarded as ideally selective for cation permeation.

The values of P_M calculated from the self-diffusion coefficients and the ion concentrations in membrane are compared with those calculated from the conductance data (Fig. 5). The agreement is satisfactory.

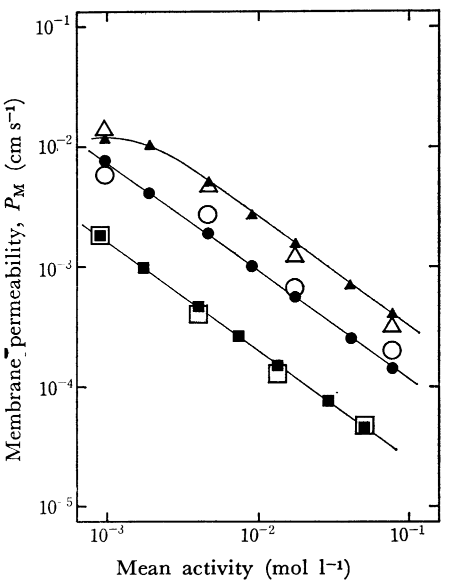

Fig. 5. Memrane permeability *vs.* mean activity of external salt solution diagramms. The symbols ●, ▲, and ■ denote electrochemically estimated P_{Na}, P_{Cs}, and P_{Ca}, respectively, and ○, △, and □, those estmated by tracer method, respectively.

Combining Eq. (6) with Eq. (7) we have

$$\delta G = \frac{Z_M F^2}{RT} D_M^m C_M^m = \kappa \tag{8}$$

where κ denotes the specific membrane conductance. The diffusion coefficients estimated from the conductance data by using Eq. (8) were always greater than those estimated from the tracer diffusion by using Eq. (1).[6] Mackay and Meares[7] attributed this to the contribution due to the electro-osmosis.

From our result it is pointed out that the disagreement was caused by neglecting the correction term indicated by Eq. (2).

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