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Separation of the Diffusion Potential within a Membrane and the Donnan Potential on the Basis of a Measurement of Transient Membrane Potentials

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In the perfluoro carboxylate cation exchange membrane–aqueous electrolyte systems, two steps appeared in the time course of the membrane potential in response to a pH jump in the external solution. LiCl, NaCl, and KCl were used as the electrolytes. According to the experimentally observed curve of the potential transient, the membrane potential was divided in two portions: the potential difference at the membrane/solution interface (Donnan potential) and the intramembrane diffusion potential. It was found that the differences among the total membrane potentials for three kinds of alkali metal ion systems were mainly attributed to the generation process of the diffusion potential within the membrane. The pH dependencies of the Donnan potential and intramembrane diffusion potential were calculated on the basis of a theory starting at the Nernst–Planck equation for the ion diffusion. Calculations were carried out taking into account the association/dissociation reaction of hydrogen ions and ion exchange groups and the heterogeneous structure of the membrane. By fitting the theoretical equations to the experimental results, the best-fitting values of relative mobility of ion and the dissociation constant of COOH group in the membrane were obtained.

For the ion diffusion in the charged membrane, the driving forces are the gradient of the chemical potential and the gradient of the electrical potential within the membrane phase. Therefore, the potential gradient within the membrane should be clarified to analyze the ion permeation process. However, as is well known, the total membrane potential observed across a charged membrane involves the contribution of the potential difference at the membrane–solution interface originating from the surface charges, i.e., Donnan potential, besides the diffusion potential within the membrane.[1,2] Although, in this case, it is important to estimate the diffusion potential within the membrane and Donnan potential separately, there have been few reports concerning the experimental evaluation of the diffusion potential within a membrane, separated from the total membrane potential, because it is difficult to measure one portion of the total potential and then another portion respectively at the nonequilibrium state.

In a previous paper, we studied the pH dependence of the membrane potential in the aqueous alkali metal chloride–perfluorinated carboxylate polymer membrane.[3] It was found that the time course of the membrane potential in response to a pH change showed the two steps: the fast response and the subsequent slow step. The fast and slow steps in the time course would correspond to the changes in the potential at the membrane/solution interface and the diffusion potential within the membrane, respectively. This assignment enables us to separate the diffusion potential within membrane and the Donnan potential by measuring the potential transient curves in the membrane system. In the perfluorinated ion-exchange membrane, the microheterogeneous structure as an inverted micellar system is taken, of which the hydrophilic region is called an ion-cluster.[4,5] The super selectivity to cation for these membranes have been interpreted in terms of the ion-cluster model, where ions are supposed to be transported through channels in the cluster-network distributed within the membrane.

In this study, the observed time course of the membrane potential in the perfluorinated carboxylate ion-exchange membrane–aqueous alkali metal chloride system was analyzed to obtain the pH dependence of the diffusion potential within the membrane and that of Donnan potential, respectively. A theoretical treatment of the membrane potential taking into account the heterogeneous structure has been described. Transport parameters for each binary ionic system of alkali metal ion and hydrogen ion have been obtained by fitting the theory to the experimental results.

Theoretical

The membrane separates aqueous solution I and II, both containing alkali metal chloride. Aqueous solution I refers to the external solution and aqueous solution II to the internal solution. The internal solution contained 1×10^{-1} mol dm^{-3} alkali metal chloride and the external solution contained 1×10^{-2} mol dm^{-3} alkali metal chloride. The concentration of H^+ ions of the internal solution was kept constant at 1×10^{-3} mol dm^{-3} with hydrochloric acid.

The ion exchange membrane used in this study has a microheterogeneous structure as an inverted micellar dispersed system. The ions existing in the hydrophilic region of the membrane migrate in the network formed by the ion clusters. To the ion transports across the heterogeneous membranes, theories which can be classified into three or four categories have been applied. The dependence of the membrane conductance on the volume fraction of water in the perfluoro sulfonate ion exchange membrane was successfully predicted by modern percolation theory.[5,6] To examine the interactions between counter-ion and solvent flows rigorously, phenomenological coefficients including the cross terms should be determined on the basis of nonequilibrium thermodynamics.[7] The other is the theory starting at the Nernst–Planck equation for the ion diffusion in the field.[8,9] The Fick's equation of diffusion or the Nernst–Planck equation can be alternatively derived according to the absolute rate theory, so that some microscopic insight into the diffusion coefficients of ions is possible.[10] The flux of ion i in the x-axis direction normal to the membrane surface will be expressed by the Nernst–Planck equation as.[10,11]

$$J_i = -D_i\left\{\frac{\mathrm{d}c_i}{\mathrm{d}x} + \frac{c_i z_i F}{RT}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)\right\}. \tag{1}$$

The diffusion coefficient of ion i, D_i, is given as

$$D_i = u_i RT\left(1 + \frac{\mathrm{d}\ln y_i}{\mathrm{d}\ln c_i}\right), \tag{2}$$

where u_i, y_i, c_i, and z_i denote the mobility, the activity coefficient, the concentration, and the charge number of ion i, respectively. ϕ denotes the electrical potential. R, T, and F are gas constant, absolute temperature, and Faraday constant. The anion is assumed to be perfectly excluded from the membrane. We consider the system where the transports of two kinds of counter-ions occur. Consider the membrane system where no ion transport due to the osmotic pressure is observed. Here, we assume that the concentration dependence of y_i is constant. Integrating Eq. 1 under the appropriate boundary conditions for the concentrations of counter ions and the conditions of the constant electric field and steady state, we can derive a flux equation of Goldman's form:

$$J_i = -U_i\left\{c_i^{\mathrm{in}}\exp\left(\frac{F\Delta\phi}{2RT}\right) - c_i^{\mathrm{ex}}\exp\left(-\frac{F\Delta\phi}{2RT}\right)\right\}, \tag{3}$$

$$U_i = \frac{D_i F\Delta\phi/2RT}{l\sinh(F\Delta\phi/2RT)}, \tag{4}$$

where c_i^{ex} and c_i^{in} denote the ion concentration at the membrane surface on the external and internal solution sides, respectively. $\Delta\phi$ denotes the diffusion potential within the membrane, i.e., $\Delta\phi=\phi^{\mathrm{in}}-\phi^{\mathrm{ex}}$, where superscripts ex and in refer to the position at the membrane surface on the external and internal solution sides, respectively. l denotes the membrane thickness. Under the condition of zero electric current across the membrane,

$$F(J_{\mathrm{M}} + J_{\mathrm{H}}) = 0, \tag{5}$$

where subscripts M and H refer to alkali metal ion and hydrogen ion, respectively. Combining Eq. 3 and Eq. 5, we obtain the diffusion potential within the membrane as

$$\Delta\phi = -\frac{RT}{F}\ln\frac{u_{\mathrm{M}}c_{\mathrm{M}}^{\mathrm{in}} + u_{\mathrm{H}}c_{\mathrm{H}}^{\mathrm{in}}}{u_{\mathrm{M}}c_{\mathrm{M}}^{\mathrm{ex}} + u_{\mathrm{H}}c_{\mathrm{H}}^{\mathrm{ex}}}. \tag{6}$$

Provided that Eq. 5 holds, Eq. 6 can be derived without any assumption about the electric field within the membrane in the system where the flows of co-ions (anions) can be neglected.[12]

From the microscopic point of view, the effective concentration is the amount per volume of the hydrophilic region (ion cluster) dispersed in the membrane. The specific volume of the membrane varies with types of counter ions, as described elsewhere,[13,14] because the cluster size is varied with the types of counter ions.[5] Rigorously speaking, therefore, the volume of hydrophilic region on the external side is different from that on the internal side, depending on the mole fraction of the alkali metal ion. In the theoretical expression, we consider that the specific volume of the hydrophilic region varies with counter-ion types but is independent of fraction of alkali metal ion in the membrane. For example, the total amount concentration (molarity) of the ion exchange site, $c_{\mathrm{S}}^{\mathrm{T}}$, is given by the ion exchange capacity, *IEC* ($n_{\mathrm{S}}^{\mathrm{T}}=IEC$), and the volume of hydrophilic region, V_{h}, i.e.,

$$c_{\mathrm{S}}^{\mathrm{T}} = n_{\mathrm{S}}^{\mathrm{T}}/V_{\mathrm{h}}, \tag{7}$$

where the ion exchange capacity and the membrane volume are given in units per weight of the dried membrane of H-form.[14] n_{S} denotes the amount of site and superscript T refers the total amount. The concentration of the ion exchange site can be expressed by using the site concentration in the alkali-metal ion form that is perfectly exchanged with one kind of the alkali metal ions, $c_{\mathrm{S}}(\mathrm{M})$;

$$c_{\mathrm{S}} = c_{\mathrm{S}}(\mathrm{M})/\sigma, \tag{8}$$

where $\sigma=V_{\mathrm{h}}/V_{\mathrm{h}}(\mathrm{M})$ and $c_{\mathrm{S}}(\mathrm{M})=n_{\mathrm{S}}/V_{\mathrm{h}}(\mathrm{M})$. $V_{\mathrm{h}}(\mathrm{M})$ denotes the volume of the hydrophilic region in the alkali metal ion form. For the charged membrane, the potential distribution at the boundary region of the membrane/solution arises from the surface charge of the membrane. Since the ions can permeate across the membrane/solution interface, the diffuse structure of the potential also appears near the interface on the membrane side as well as on the solution side, which obeys the Poisson–Boltzmann equation. The surface concentration in the equation of diffusion potential is determined by the boundary condition at the interface. We assume the Donnan equilibrium as follows

$$y_i^{\mathrm{ex}}c_i^{\mathrm{ex}} = a_i^{\mathrm{I}}b_i^{\mathrm{ex}}\exp(-FU^{\mathrm{I}}/RT): \tag{9}$$

$$y_i^{\mathrm{in}}c_i^{\mathrm{in}} = a_i^{\mathrm{II}}b_i^{\mathrm{in}}\exp(-FU^{\mathrm{II}}/RT): \tag{10}$$

Here U^{I} and U^{II} denote the difference between the potential at the membrane surface and that in the solution bulk on the external and internal sides, respectively. b_i^{ex} and b_i^{in} refer to the partition coefficient of ion i between the membrane and the external solution and that between the membrane and the internal solution, respectively; a_i^{I} and a_i^{II} are the activity of ion i in the external solution and that in the internal solution, respectively. In the cluster, a concentration distribution of counter ions in the direction normal to the charged wall of the water pool would be formed as pointed out for the reverse micellar systems.[15] The ion concentration in the membrane that appears in Eqs. 9 and 10 is therefore supposed to be the quantity averaged over the space in the ion cluster within the membrane.

The Donnan potential will be derived in a manner described below. The acid dissociation constant for the ion exchange site, COOH group, in the membrane is expressed by

$$K_a = f(y)c_S c_H / c_{SH}, \tag{11}$$

$$f(y) = y_S y_H / y_{SH}, \tag{12}$$

where y_i denotes the activity coefficient of species i. The subscripts S and SH stand for the free site and undissociated form of site, respectively. It is assumed that the electroneutrality is analytically held in the ion cluster;

$$c_S^{ex} = c_M^{ex} + c_H^{ex}. \tag{13}$$

The total concentration of ion exchange sites, c_S^T, which is defined by ion exchange capacity per volume of hydrophilic region as mentioned above, is given by the sum of the concentration of each site species as

$$c_S^T = c_S + c_{SH}. \tag{14}$$

We consider only the association reaction between the hydrogen ion and the ion exchange site. Combining Eqs. 9, 10, 11, 12, 13, and 14, we obtain

$$\exp(-FU^I/RT) = \frac{-B_I + (B_I^2 + 4B_I A_I c_S^T)^{1/2}}{2B_I A_I}, \tag{15}$$

where

$$A_I = y_S^{ex} a_H^I b_H^{ex} / K_a \tag{16}$$

$$B_I = a_M^I b_M^{ex} / y_M^{ex} + a_H^I b_H^{ex} / y_H^{ex}. \tag{17}$$

Similarly we obtain for the side of internal solution:

$$\exp(-FU^{II}/RT) = \frac{-B_{II} + (B_{II}^2 + 4B_{II} A_{II} c_S^T)^{1/2}}{2B_{II} A_{II}}, \tag{18}$$

with

$$A_{II} = y_S^{in} a_H^{II} b_H^{in} / K_a, \tag{19}$$

$$B_{II} = a_M^{II} b_M^{in} / y_M^{in} + a_H^{II} b_H^{in} / y_H^{in}. \tag{20}$$

The membrane potential, U_m, is given by the sum of the diffusion potential within membrane and the difference of the Donnan potentials, U^I and U^{II} as

$$U_m = \Delta\phi + U^I - U^{II}. \tag{21}$$

Results and Discussion

The perfluoro carboxylate polymer membrane, Flemion 230, kindly supplied by Asahi Glass Co. with the ion exchange capacity of 1.4 mmol univalent ion/g dry membrane, was used as a cation exchange membrane. It had no reinforcing material over the membrane surface. The procedure for the measurement of membrane potential, U_m, was described in a previous paper.[3] The difference of electric potentials in the internal solution, ϕ^{II}, and in the external solution, ϕ^I, i.e., $U_m = \phi^{II} - \phi^I$, was measured by means of a pair of Ag/AgCl reference electrodes, each having a liquid junction assembled in the case; these were commercially obtained. The internal solution contained 1×10^{-1} mol dm^{-3} alkali metal chloride, MCl, and 1×10^{-3} mol dm^{-3} HCl. Stepwise changes in pH of the external alkali metal chloride solution were achieved by injecting HCl solution while keeping the concentration of MCl at 1×10^{-2} mol dm^{-3}. As the alkali metal chloride, LiCl, NaCl, and KCl were used. The measurements of membrane potentials were carried out at 25.0 °C.

A typical time dependence of the membrane potential, U_m, in response to a pH jump in the external solution is shown in Fig. 1. The total membrane potential can be divided into two portions: the change in the Donnan potential at the interface, ΔU_b, and that in the diffusion potential within the membrane, ΔU_d. Assuming the Donnan potential to have reached the stationary value before the second step starts, the height of the potential change in the first step can be obtained from the point where the second rise starts in the course of the potential change for the final steady potential. In the symmetric membrane system in which the ionic compositions of both aqueous phases are the same, the Donnan potential and diffusion potential are both supposed to be zero. To obtain the values of $U_b(=U^I - U^{II})$ and $U_d(=\Delta\phi)$ from ΔU_b and ΔU_d, respectively, one must measure the potential change starting at the steady state in a symmetric membrane system initially. In this study, the system where the external solution as well as the internal solution contained 1×10^{-1} mol dm^{-3} MCl and 1×10^{-3} mol dm^{-3} HCl was selected as the reference system. The results are shown in Figs. 2 and 3 as a function of the concentration of hydrogen ions in the external solution. The magnitude of U_d is not so large as U_b for every alkali metal ion–hydrogen ion system. However, the difference among the total membrane potentials was found to be determined almost entirely by the diffusion potential

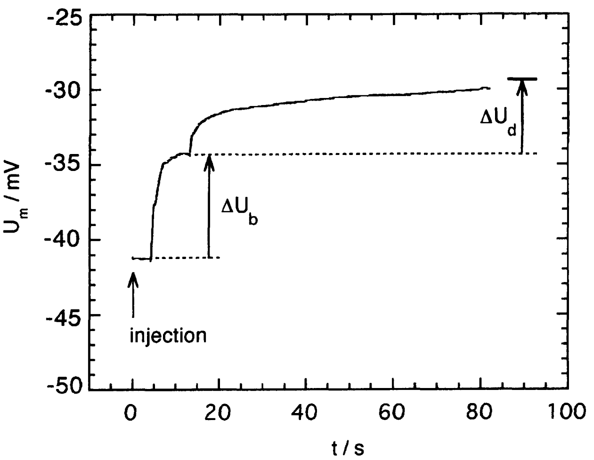

Fig. 1. A time dependence of the membrane potential in a transition between two steady states. The pH of external solution was changed by injecting 100 µl of HCl solution while keeping the concentration of LiCl at 1×10^{-2} mol dm^{-3} from pH 3.1 to pH 2.9. The injection was started at zero time. It took 500 ms to complete the injection.

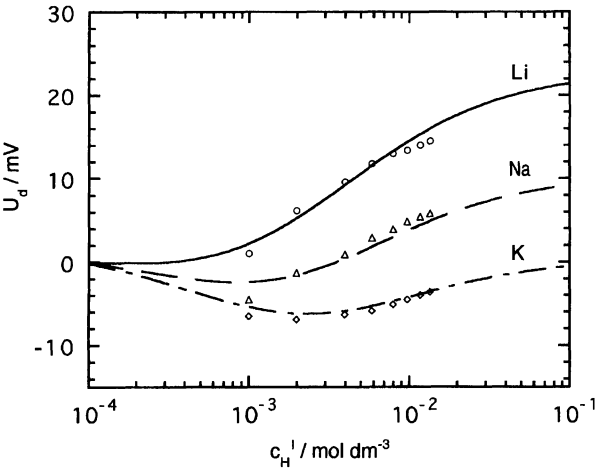

Fig. 2. The diffusion potential within membrane, U_d, as a function of the concentration of hydrogen ions in the external solution. ○, LiCl system; △, NaCl system; ◇, KCl system. The lines show the theoretically calculated values. —, LiCl; ---, NaCl; ---, KCl.

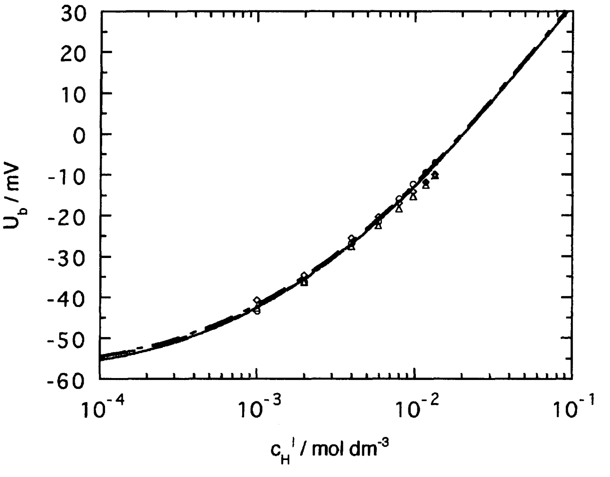

Fig. 3. The Donnan potential, U_b, as a function of the concentration of hydrogen ions in the external solution. ○, LiCl system; △, NaCl system; ◇, KCl system. The lines show the theoretically calculated values. —, LiCl; ---, NaCl; ---, KCl.

within the membrane.

We have obtained the expressions for the diffusion potential within a membrane for binary ionic systems. We found them to be a function of the relative mobilities, partition coefficients of ions, and the ion concentrations at the membrane surfaces on the external and internal solution sides. The ion concentrations at the membrane surfaces on both sides are given by a function of the dissociation constant of COOH group in the membrane and the partition coefficients of permeable ions under the condition of the Donnan equilibrium. We calculated U_d for each membrane system according to the theory. Activity coefficients of cations in the aqueous phases are calculated according to the Debye–Hückel equation. We compared the calculated diffusion potential within membrane with the experimental values obtained in the pH range below apparent pK_a. The theoretical curves are also shown in Fig. 2 for diffusion potentials and in Fig. 3 for Donnan potentials. In Fig. 4, the calculated value of the ratio of the concentration of alkali metal ion at the membrane surface on the external solution side to that on the internal solution side, c_M^{ex}/c_M^{in}, for each alkali metal ion-hydrogen ion system is shown together with the experimental values obtained using the observed Donnan potential and the ion concentration in the aqueous phase.

The values of u_H/u_M and pK_a for each alkali metal ion system are obtained by a curve fitting method by assuming the ratios, $b_M^{ex}y_H^{ex}/b_H^{ex}y_M^{ex}$ and $b_M^{in}y_H^{in}/b_H^{in}y_M^{in}$, to both be unity. The results are cited in Table 1. The best fitting value of pK_a approaches to the pK_a of the trifluoroacetic acid in aqueous solution.[16,17] In the case where the concentration in the membrane determined on the basis of the homogeneous model[14] was used, large values of pK_a's were obtained (ca. 0.82). The values of pK_a's are slightly varied with counter-ion types, which are in the order, $Li^+ > Na^+ > K^+$. This would be due to the difference in the electrostatic screening effect of counter ions around the COOH groups embedded in the wall of the water pool in the ion cluster. Moreover, the water activity in the cluster would vary with the kinds of alkali metal ions. The relative mobilities of alkali metal to hydrogen ions are in the order: $K^+ > Na^+ > Li^+$. Thus, for each alkali metal ion–hydrogen ion system, the diffusion potential within a membrane and the Donnan potential obtained on the basis of the transient potential measurement were theoretically reproduced by using a modified charged membrane model,

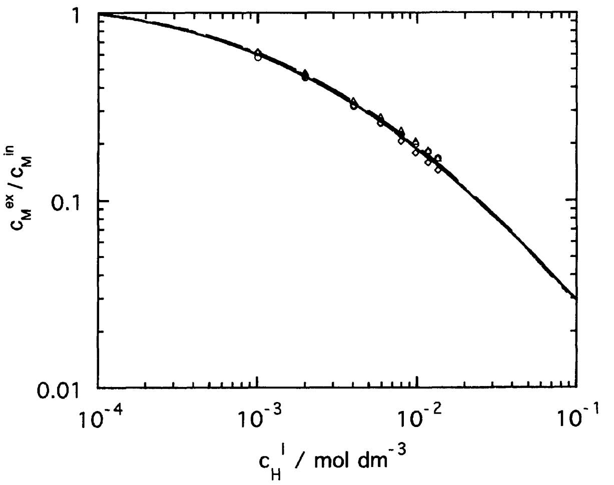

Fig. 4. The ratio of the concentration of the alkali metal ion at the membrane surface on the external solution side and that on the internal solution side. ○, LiCl; △, NaCl; ◇, KCl. The lines show the theoretically calculated values. —, LiCl; ---, NaCl; ---, KCl.

Table 1. Mobility Ratio, u_H/u_M, and pK_a, for Three Alkali Metal Ion Systems

M^+	u_H/u_M	pK_a
Li^+	9.8	0.41
Na^+	5.6	0.16
K^+	3.8	0.14

in which the nonuniformity of the membrane structure was considered.

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