Kinetic Analysis of the Transitory Overshooting of the H$^+$ Concentration in the Cation-exchange Membrane System

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Overshooting with respect to the H$^+$ concentration was studied quantitatively. Systems of two species of cation and one species of anion were studied for example, the 0.2 M-NaCl (initial, s-side): Collodion-Polystyrene sulfonic acid membrane: 0.02 M-NaCl+0.002 M-HCl (l-side, constant). The volume of the l-side solution was greatly larger than that of the s-side solution. The composition of the former was not altered measurably by the transport of ions across the membrane. Because the cation-exchange membrane used was not highly selective, both cation and anion were permeable. The final composition of the s-side solution became equal to the composition of the l-side solution. In the course of changes toward the final equilibrium, the H$^+$ or HCl concentration temporarily reached far above the final value. An analytical interpretation with two parameters was given, in which the concentration of the most slowly movable ion in the membrane, Cl$^-$, was assumed to decrease monotonously. Moreover, the concentration of next slowly movable ion, Na$^+$, was assumed to change as a result of the force which tends to bring the system toward the imaginary Donnan equilibrium. The Na$^+$ concentration at the imaginary Donnan equilibrium toward which the s-side solution is approaching at any given instant was obtained as follows. The (H$^+$ concentration)/(Na$^+$ concentration) ratio at the equilibrium is the same as the corresponding ratio in the l-side. Moreover, the total concentration of H$^+$ and Na$^+$ at the imaginary Donnan equilibrium is equal to the existing Cl$^-$ concentration in the s-side solution.

Teorell[1)] investigated the transport of ions against their concentration difference between two solutions across a cation-exchange membrane separating these solutions under the simultaneous influence of a concentration gradient and a potential gradient within the membrane. The ions are transported against their concentration difference between outside solutions, but they move in the direction of their electrochemical potential difference. Woermann[2)] reinvestigated the Teorell model quantitatively at a steady state.

Neihof and Sollner[3)] and Sollner[4)] presented electrochemical models which might have potential biological significance in explaining the abilities of living cells. These abilities are: (1) to accumulate electrolytes in their sap up to concentrations far in excess of the surrounding milieu and (2) to take up different species of the same charge in ratios which are vastly different from the ratio in which these ions are present in the surrounding milieu. The Sollner models are based on the transitory effects called the "overshooting" and "depletion" effects. The transitory effects arise in the course of the spontaneous drift toward the Donnan membrane equilibrium of systems in which two or more species of ions of the same charge, coexisting in one solution, exchange at greatly different rates across a membrane of a high anionic or high cationic selectivity against some other species of ions in the other solution. They assumed the existence of a partial membrane equilibrium in which the permeability of the most slowly movable ion was taken to be negligibly small until the system had attained the maximum drift. From the partial membrane equilibrium, they estimated the maximum drift of the effect. Their experimental values of the maximum drifts from the final equilibria were about 90% of the estimated values. In the Sollner model, the membrane of a high anionic or high cationic selectivity was used. That is, only cationic or anionic species of ions are permeable across the cationic or anionic membrane respectively.

It seemed that it would be interesting to extend the Sollner model to a more general membrane model in which a membrane is not perfectly ionic-selective, that is, in which it is permeable to both cation and anion. This makes it possible to apply the overshooting effect to such leaky (low-electrical-resistance) membranes as gastric mucosa and the collecting tubule in the kidney. In this paper we will report on the overshooting with respect to the H$^+$ concentration in systems which have two species of cation and one species of anion, using membranes which do not have perfect cationic selectivity.

Another point we wish to report on here is a quantitative analysis of the overshooting effect. As has been described above, Neihof and Sollner[3)] estimated only the value of the maximum drift. We will formulate the full-time course of the H$^+$ overshooting effect, using a kinetic theory together with the imaginary Donnan equilibrium, to which the system tends to approach.

Description of Systems

The isothermal systems studied in this paper are composed of three compartments; one is the membrane phase that separates the other two compartments of ionic solutions. We shall call these two solutions the s-side and the l-side solutions hereafter. We assumed that the changes in the concentrations of the ionic species in the l-side solution were negligibly small during the experiment. This assumption was made possible by taking the volume of the l-side solution as extremely large compared with that of the s-side solution. For the H$^+$ overshooting effect, the following system was studied. The s-side solution included only NaCl at the initial state (its initial concentration, c_i). The l-side solution included NaCl (c_1) and HCl (c_2), where $c_i > (c_1 + c_2)$. In the system, the H$^+$ concentration is equal to the HCl concentration because the system has only one species of anion, Cl$^-$. The ionic selectivity of the cation-exchange membrane used here was not too high, so the anionic species of ion could also permeate slowly across the membrane. The permeation velocity of Cl^- was very slow compared with the fast permeations of the cations, however. When the test-tube-shaped membrane, which has the s-side solution inside, was immersed in the l-side solution, the H^+ concentration in the s-side solution began to increase rapidly as a result of interdiffusions. In due time, the H^+ concentration reached a maximum that far exceeded the final equilibrium value. Next, it gradually decreased. Finally, it settled to the final equilibrium value, *i.e.*, the H^+ concentration in the l-side solution. It should be noted that, if the system did not have the overshooting effect ($c_i < (c_1 + c_2)$), the H^+ concentration reached its final value without exceeding the final equilibrium value.

Materials and Methods

The test-tube-shaped membranes, 8 cm in length and 2 cm in diameter, were made of sulfonated polystyrene and collodion. The polystyrene sulfonic acid was synthesized following the method by Kato, Nakagawa, and Akamatsu;[5] its % of sulfonation was about 75%. Polystyrene sulfonic acids (1.59 g for Membranes 1 and 2 and 2.17 g for Membrane 3) were mixed with 300 ml of a 5% w/w collodion solution. Table 1 summarizes the characteristic data of these membranes—that is, the average membrane thickness, the water content of the membrane, the effective charge density of the membrane in the KCl solution, and the electric resistance of the membrane. The water content of the membrane is defined as the net weight of water absorbed in the membrane phase divided by the total weight of the wet membrane. The effective charge density of the membrane, θ(M), was measured following the method described in a paper by Kobatake, Takeguchi, Toyoshima, and Fujita.[6] The electrical resistance of the membrane (Ω cm^2) was measured on a membrane which had been soaked in a 0.1 M-NaCl solution at 30 °C prior to the measurement.

Table 1. Characteristics and properties for membranes

	Membrane number		
	1	2	3
Membrane thickness (mm)	0.22	0.10	0.024
Water content	0.715	0.359	0.093
θ(M)	-8.3×10^{-3}	-1.07×10^{-2}	-7.14×10^{-2}
Electric resistance (Ω cm^2)	250	240	260
k_1 (min^{-1})	0.043	0.015	0.0028
k_2 (min^{-1})	0.556	0.193	0.0997

The s-side solution (20 ml) was placed in the test-tube-shaped membrane. A combination electrode (Beckmann, Type 39030, Calif., U.S.A.) was immersed in the s-side solution in order to measure the continuous change in the H^+ concentration. The volume of the l-side solution was about 20 l. Both solutions were stirred by bubbling air, and their temperatures were kept at 35 ±0.1 °C

Results

In Fig. 1, the solid lines show the changes in the H^+ concentration in the s-side solution as a function of the time for Membranes 1, 2, and 3. The initial concentrations of NaCl in the s-side solution were 0.2042 M for Membranes 1 and 3 and 0.1950 M for Membrane 2. Moreover, the l-side solution contained 0.0247 M-NaCl and 0.0022 M-HCl for Membranes 1 and 3 and 0.0220 M-NaCl and 0.0024 M-HCl for Membrane 2.

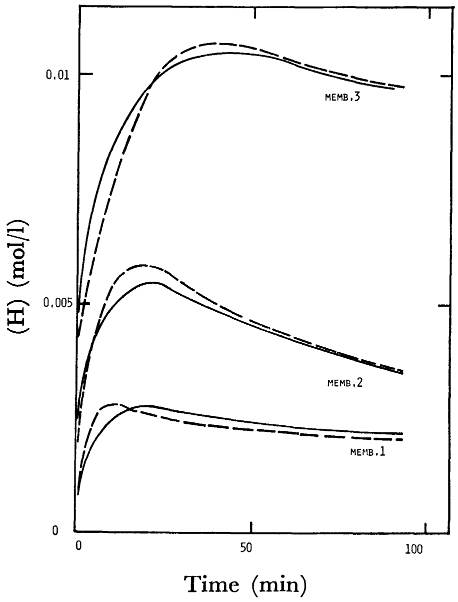

Fig. 1. Time dependencies of the H^+ concentration in the s-side solution. Solid lines show experimental curves for Membranes 1, 2, and 3. Broken lines show calculated curves from Eq. (8) with k_1 and k_2.

The H^+ concentrations of the s-side started from zero and thereafter increased rapidly beyond the final equilibrium values in a few minutes. They went up to the maximum values of 0.0028 M, 0.0054 M, and 0.010 M for Membranes 1, 2, and 3 respectively. Their maximum values were 1.32 times (Membrane 1), 2.25 times (Membrane 2), and 4.37 times (Membrane 3) as large as their final values. After reaching their maximum values, the H^+ concentrations descreased gradually. It took a long time to attain the final equilibrium values (3—24 hr after the start of the experiments).

Discussion

First, we will check the applicability of the concept of the partial membrane equilibrium to our present system. Following the idea by Neihof and Sollner,[3] the maximum values of the H^+ concentration can be calculated on the basis of the partial membrane equilibrium. The maximum values of the H^+ concentration were calculated as 0.0165 M for Membranes 1 and 3 and 0.0192 for Membrane 2. However, the experimental values were about 1/6, 1/4, and 2/3 times as large as the calculated maximum values for Membranes 1, 2, and 3 respectively. These large discrepancies between the maximum experimental values and the maximum calculated values mean that the permeation of the most slowly movable ion, Cl^-, cannot be neglected even in the initial process. Therefore, we cannot apply the explanation based on the partial membrane equilibrium to a membrane which has a relatively low ionic selectivity, such as the membrane used here.

We shall now propose a kinetic analysis which can formulate the whole time dependence of the transitory effect. The water permeability of the membrane was assumed to be negligibly small. In the system there exist three kinds of ionic species which are movable across the membrane. As for the permeability velocities of these ions through the cation-exchange membrane, the fastest one is H^+, because of its large ionic mobility, the second is Na^+, and the slowest is Cl^-, because of its repulsive interaction with fixed negative membrane charges. Below, the ionic concentration (in M) will be placed within parentheses.

Because its movement in the membrane is the slowest, the transport of Cl^- through the membrane might be rate-determining for this kind of interdiffusion. Hence, its time-dependent change in the concentration is expected to be relatively monotonous in the system. It was assumed that an equation for the first-order reaction could express the decrease in the Cl^- concentration in the s-side solution, (Cl). That is,

$$(\mathrm{Cl}) = [(\mathrm{Cl})_i - (\mathrm{Cl})_f] \exp(-k_1 t) + (\mathrm{Cl})_f \tag{1}$$

where $(\mathrm{Cl})_i$ and $(\mathrm{Cl})_f$ are the initial and final concentrations of Cl^- in the s-side solution respectively ($(\mathrm{Cl})_i = c_i$ and $(\mathrm{Cl})_f = (c_1 + c_2)$) and where k_1 is the velocity rate parameter for Cl^-.

The system, in the course of changing toward the final equilibrium, is not in a steady state, but in a transient state. Therefore, we cannot expect the Donnan equilibrium to be materialized during the experiment except at the end. However, there still exists a driving force which tends to bring the system to the imaginary Donnan equilibrium. The imaginary Donnan equilibrium can be calculated as follows. We made two additional assumptions in the calculation of the imaginary Donnan equilibrium. One is that the permeability of Cl^- is negligibly small in this calculation only. The other is that the activity coefficients of all ions in solutions are unity. The ratio of the imaginary concentrations of two permeable ions in the s-side solution, *i.e.*, $(\mathrm{H})_{\mathrm{imaginary}}/(\mathrm{Na})_{\mathrm{imaginary}}$, should be identical with the ratio of their corresponding concentrations in the 1-side solution from the Donnan equilibrium. That is,

$$c_2/c_1 = (\mathrm{H})_{\mathrm{imaginary}}/(\mathrm{Na})_{\mathrm{imaginary}}. \tag{2}$$

From the electric neutrality condition, the total imaginary cation concentration in the s-side solution may be said to be equal to the existing Cl^- concentration in the s-side solution, *i.e.*:

$$(\mathrm{H})_{\mathrm{imaginary}} + (\mathrm{Na})_{\mathrm{imaginary}} = (\mathrm{Cl}). \tag{3}$$

From Eqs. (2) and (3), we obtain:

$$(\mathrm{Na})_{\mathrm{imaginary}} = [c_1/(c_1+c_2)](\mathrm{Cl}) \equiv \gamma(\mathrm{Cl}) \tag{4}$$

where $\gamma(=c_1/(c_1+c_2))$ is considered to be constant during the experiment.

An important assumption was made regarding the transport of Na^+. The Na^+ concentration in the s-side solution was forced to change by the driving force, which would tend to bring the Na^+ concentration, (Na), toward the calculated Na^+ concentration of the imaginary Donnan equilibrium, (Na)imaginary. This follows:

$$\mathrm{d}(\mathrm{Na})/\mathrm{d}t = -k_2[(\mathrm{Na}) - (\mathrm{Na})_{\mathrm{imaginary}}] \tag{5}$$

where k_2 is another velocity rate parameter for Na^+. Here, $k_2 > k_1$ because the permeability of Na^+ is much greater than that of Cl^-. By combining Eqs. (1), (4), and (5) and by integrating, we get:

$$\begin{aligned}(\mathrm{Na}) = {} & [k_2\gamma/(k_2-k_1)][(\mathrm{Cl})_i - (\mathrm{Cl})_f] \exp(-k_1 t) \\ & + \gamma(\mathrm{Cl})_f + I_0 \exp(-k_2 t)\end{aligned} \tag{6}$$

where I_0 is the integral constant. The I_0 is determined from the initial condition; *i.e.*, at $t=0$, $(\mathrm{Na}) = (\mathrm{Cl}) = (\mathrm{Cl})_i$. That is,

$$I_0 = (\mathrm{Cl})_i - [k_2\gamma/(k_2-k_1)][(\mathrm{Cl})_i - (\mathrm{Cl})_f] - \gamma(\mathrm{Cl})_f. \tag{7}$$

The H^+ concentration in the s-side solution, (H), is given as follows from the electric neutrality condition:

$$\begin{aligned}(\mathrm{H}) = (\mathrm{Cl}) - (\mathrm{Na}) = {} & (1-\gamma)(\mathrm{Cl})_f + [1 - k_2\gamma/(k_2-k_1)] \\ & \times [(\mathrm{Cl})_i - (\mathrm{Cl})_f][\exp(-k_1 t) - \exp(-k_2 t)] \\ & - [(\mathrm{Cl})_f - \gamma(\mathrm{Cl})_f] \exp(-k_2 t).\end{aligned} \tag{8}$$

In order to determine the two parameters, k_1 and k_2, from the experiment, we got a limiting equation from Eq. (8). Considering γ as near unity ($c_1 \gg c_2$) and neglecting the term of $\exp(-k_2 t)$ in the third brackets on the right-hand side of Eq. (8) compared with the term of $\exp(-k_1 t)$ in the range of large t values because $k_2 > k_1$, we obtain:

$$\begin{aligned}\log[(\mathrm{H}) - (1-\gamma)(\mathrm{Cl})_f] = {} & -k_1 t/2.303 \\ & + \log\{[1 - k_2\gamma/(k_2-k_1)][(\mathrm{Cl})_i - (\mathrm{Cl})_f]\}.\end{aligned} \tag{9}$$

In Fig. 2, the left-hand side of Eq. (9) is plotted against t for Membranes 1, 2, and 3. From their gradients and the intercepts of straight broken lines in the range of large t values, k_1 and k_2 were obtained. In Table 1,

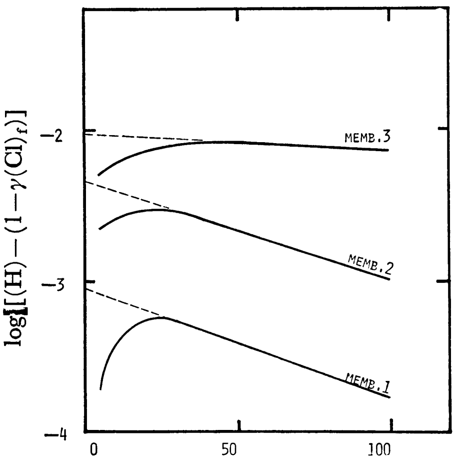

Fig. 2. Plots of $\log[(\mathrm{H}) - (1-\gamma)(\mathrm{Cl})_f]$ *vs.* time t.
From gradients and intercepts of straight broken lines, k_1 and k_2 were obtained. Solid lines show experimental data.

k_1 and k_2 are shown along with other membrane characteristics.

The time dependencies of the H+ concentration for Membranes 1, 2, and 3 calculated from Eq. (8) with k_1 and k_2 in Table 1 are represented in broken lines in Fig. 1. The coincidence between experimental curves and calculated curves was found to be generally good. Although it is felt that the analysis is rather too simple, this good coincidence could mean that the most significant aspects of the phenomena are included in the above analysis. It may be noted that the overshooting effect becomes larger as k_1 and k_2 become smaller and as the effective charge density of the membrane, θ, becomes larger.

A partial derivative of Eq. (8) with time becomes zero at the time when the overshooting effect reaches its maximum. Thus, the time t at the maximum effect, $t_{\max}$, is given as:

$$(k_2-k_1)t_{\max} = \ln(k_2/k_1) + \ln I_0 - \ln[1-k_2\gamma/(k_2-k_1)] - \ln[(\mathrm{Cl})_i-(\mathrm{Cl})_f]. \tag{10}$$

The $t_{\max}$ values were calculated from Eq. (10) to be 8, 17, and 39 min for Membranes 1, 2, and 3 respectively. The calculated $t_{\max}$ values are in good agreement with the experimental values. When $(\mathrm{Cl})_i<(\mathrm{Cl})_f$, Eq. (10) has no solution. In fact, experiments under the condition of constant 1-side composition (0.0247 M-NaCl+0.0022 M-HCl) showed that the overshooting effects were not found at 0.01 M and 0.02 M-NaCl initial concentrations in the s-side solution, although the effects *were* observed at an initial concentration higher than 0.05 M-NaCl in the s-side solution.

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