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Nonequilibrium Thermodynamics of the Ion and Solvent Transports through Ion-exchange Membrane

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A theory for the ion and solvent transports through membrane has been developed on the basis of nonequilibrium thermodynamics. The fluxes were represented as linear functions of the effective driving potentials. The theory is reduced to that of Katchalsky when the concentration ratio of two aqueous solutions is near unity and the solutions are dilute. The effect of solvent flow on the interionic correlations was discussed. It was pointed out that Despić and Hills' theory of the electroosmotic effect on the membrane conductance is not valid with respect to both theoretical and experimental aspects. The comparison of the present theory with the previous one[1] was also made. The six independent phenomenological coefficients (elements of the conductance matrix) were experimentally determined as a function of concentration with the concentration cell consisting of the amphoteric ion-exchange membrane and aqueous calcium chloride solutions. The membrane properties were discussed in terms of the conductance matrix. The diffusional ion conductance was much greater than the electrical ion conductance, as an indication of the failure of the Nernst-Einstein relation. The cation-anion coupling coefficient was close to unity whereas the ion-water coupling coefficients were less than 0.1. The solvent effects on the interionic conductance elements were found to be small in spite of the fact that the water permeability was extremely high. The distinction between the cationic and amphoteric ion-exchange membranes was explored in terms of the elements of the conductance matrix.

A variety of transport phenomena is known to take place when a membrane system is subject to various driving forces such as the gradients of electric potential, concentration, and hydrostatic pressure. This paper is concerned with an analysis of the transport properties of an isothermal system consisting of an amphoteric ion-exchange membrane, water, and a single salt dissociating into two kinds of ions on the basis of nonequilibrium thermodynamics. Even in this simple case, there are six independent phenomenological coefficients, and hence six independent experiments are required to elucidate the transport properties.

Many papers have appeared on the application of nonequilibrium thermodynamics to the transport phenomena across the membrane, where the fundamental treatments are to determine the coefficients in the phenomenological equations. However, it is usual to make some nonthermodynamic assumptions for studying the membrane phenomena, since it is laborious to perform the detailed study for determining the six phenomenological coefficients. Nevertheless, it is important to complete the detailed study not only for elucidating the transport properties, but also for examining whether the nonthermodynamic assumptions are valid or not.

So far, only a few papers[2-4] have been published on the detailed study of the transport phenomena with the cation exchange membrane–aqueous single electrolyte system. In the preceding paper,[2] the transport phenomena with the cation-exchange membrane–aqueous barium chloride system were studied for determining the six phenomenological coefficients and the transport properties were discussed. However, the preceding theories[2-4] were essentially for the systems with the same concentrations of two external solutions and can not be suitably applied to the concentration cell. Thus a theory for the ion and solvent transports has been developed by extending the previous theory,[1] so that the solvent transport is included.

For estimating the phenomenological coefficients, the ion and solvent transports in the presence and absence of the electric current and the pressure difference should be measured in addition to the membrane potential and membrane conductance. Among these, the accurate determination of the ion transports is especially important in order to estimate the phenomenological coefficients exactly, because the transport number of an ion plays a decisive role in calculating the coefficients from the observed data. Since an accurate determination of the transport number for the co-ion is difficult with the cation- and anion-exchange membranes due to their high selectivity to the counter ions, the amphoteric ion-exchange membrane was used in the present study for the exact determination of the transport number.

In the present paper, the measurements were performed with the concentration cell consisting of the amphoteric ion-exchange membrane and the aqueous calcium chloride solutions. The six independent phenomenological coefficients (elements of a conductance matrix) were estimated from the observed data according to our theory and the membrane properties were discussed in terms of the conductance matrix.

Theory

1. Phenomenological Equation. In the previous paper,[1] the steady ion currents through the membrane have been expressed by linear functions of the effective driving potentials under the assumption of no solvent flow. Even without the assumption, it is easily seen that the flux equations including solvent flux may be written in the similar forms to those in the previous paper.[1] Thus, for the case in which the permeating species are cation α, anion β, and water w, the phenomenological equation can be written as

$$\begin{bmatrix} i_\alpha \\ i_\beta \\ Fj_\mathrm{w} \end{bmatrix} = -\begin{bmatrix} g_{\alpha\alpha} & g_{\alpha\beta} & g_{\alpha\mathrm{w}} \\ g_{\beta\alpha} & g_{\beta\beta} & g_{\beta\mathrm{w}} \\ g_{\mathrm{w}\alpha} & g_{\mathrm{w}\beta} & g_{\mathrm{ww}} \end{bmatrix}\begin{bmatrix} V-V_\alpha \\ V-V_\beta \\ -V_\mathrm{w} \end{bmatrix}, \tag{1}$$

where the subscripts, α, β, and w refer to cation, anion, and water, respectively; i denotes an ion current; j_w, water flux; $g_{\gamma\delta}\,(\gamma,\delta=\alpha,\beta)$ and g_kw $(\mathrm{k}=\alpha,\beta,\mathrm{w})$, the elements of the conductance matrix; V, the transmembrane potential; $V_\gamma(\gamma=\alpha,\beta)$, the pseudo equilibrium potential; V_w, the effective driving potential for water. V_w, V_γ, $g_{\gamma\delta}$, and g_kw are given by

$$FV_\mathrm{w} = RT\ln a_\mathrm{w}^\mathrm{I}/a_\mathrm{w}^\mathrm{II} - \bar{v}_\mathrm{w}\Delta P = \bar{v}_\mathrm{w}(\Delta\pi-\Delta P) \tag{2}$$

$$Z_\gamma FV_\gamma = RT\ln a_\gamma^\mathrm{I}/a_\gamma^\mathrm{II} - \bar{v}_\gamma\Delta P \tag{3}$$

$$g_{\gamma\delta} = Z_\gamma Z_\delta F^2|R|_{\gamma\delta}/|R| \tag{4}$$

$$g_{\gamma\mathrm{w}} = Z_\gamma F^2|R|_{\gamma\mathrm{w}}/|R|, \tag{5}$$

and

$$g_\mathrm{ww} = F^2|R|_\mathrm{ww}/|R|, \tag{6}$$

respectively, where the superscripts I and II refer to phases I and II separated by a membrane, respectively; R, F, and T have usual meanings; Z denotes the charge, a, the activity; v_k, the partial molar volume of a species k; $\Delta\pi$, the osmotic pressure difference; $\Delta P(=P^\mathrm{II}-P^\mathrm{I})$, the external pressure difference; $|R|$, the determinant having $R_\mathrm{kl}(\mathrm{k,l}=\alpha,\beta,\mathrm{w})$ as the kl element of the generalized friction intergrated over the membrane phase, and $|R|_\mathrm{kl}$, the cofactor of R_kl.[1] In Eq. 2, a constant molar volume is assumed for the two aqueous phases I and II. The expression such as Eq. 1 is advantageous for treating the electrical properties of the membrane.

The equation for the membrane current, I, is obtained from Eq. 1 as follows:

$$I = i_\alpha + i_\beta = -g_\alpha(V-V_\alpha) - g_\beta(V-V_\beta) + g_\mathrm{w}V_\mathrm{w} \tag{7}$$

$$= -G_\mathrm{m}(V-V_0), \tag{8}$$

where g_α, g_β, and g_w denote the conductances for permeating species α, β, and w, respectively,

$$g_\mathrm{k} = g_{\mathrm{k}\alpha} + g_{\mathrm{k}\beta}, \tag{9}$$

G_m, the membrane conductance

$$G_\mathrm{m} = g_\alpha + g_\beta, \tag{10}$$

and V_0, the membrane potential at zero membrane current

$$V_0 = t_\alpha V_\alpha + t_\beta V_\beta + t_\mathrm{w}V_\mathrm{w} \tag{11}$$

$$t_\mathrm{k} = g_\mathrm{k}/G_\mathrm{m}, \tag{12}$$

t_k, the transport number of a species k.

When the membrane current is absent, the equation for the ion current, i_γ^0, under this restriction can be written as

$$i_\gamma^0 = -g_\mathrm{k}^0(V_0-V_\gamma) + g_{\gamma\mathrm{w}}^0V_\mathrm{w}, \tag{13}$$

where the superscript 0 refers to the absence of membrane current,

$$\frac{g_\mathrm{k}^0}{g_\mathrm{k}} = 1 - g_{\alpha\beta}\left(\frac{1}{g_\alpha}+\frac{1}{g_\beta}\right), \tag{14}$$

and

$$g_\mathrm{w}^0 = g_{\alpha\mathrm{w}}^0 + g_{\beta\mathrm{w}}^0. \tag{15}$$

Thus, Eq. 11 is seen to be consistent with Eqs. 13—15.

2. *Determination of Phenomenological Coefficient.* Let us consider the way for determining the elements of the conductance matrix.

When the ion and solvent fluxes in the presence and absence of the membrane current are measured, we have from Eqs. 1, 8, and 12

$$i_\gamma - i_\gamma^0 = -g_\gamma(V-V_0) = t_\gamma I$$

$$F(j_\mathrm{w}-j_\mathrm{w}^0) = -g_\mathrm{w}(V-V_0) = t_\mathrm{w}I. \tag{16}$$

Thus, the measurements of the fluxes as a function of the potential enable to estimate g_k's and t_k's $(\mathrm{k}=\alpha,\beta,\mathrm{w})$ according to Eq. 16.

When the membrane current is absent, we have from Eq. 1

$$\begin{bmatrix} i_\alpha^0 \\ Fj_\mathrm{w}^0 \end{bmatrix} = -\begin{bmatrix} g_{\alpha\alpha}-G_\mathrm{m}t_\alpha^2 & g_{\alpha\mathrm{w}}-G_\mathrm{m}t_\alpha t_\mathrm{w} \\ g_{\alpha\mathrm{w}}-G_\mathrm{m}t_\alpha t_\mathrm{w} & g_\mathrm{ww}-G_\mathrm{m}t_\mathrm{w}^2 \end{bmatrix}\begin{bmatrix} V_\beta-V_\alpha \\ -V_\mathrm{w} \end{bmatrix}. \tag{17}$$

Now it is assumed that the addition of nonpermeant neutral substance, *e.g.*, such as sucrose, causes no appreciable change in the phenomenological coefficients as well as the activity coefficients of salt and ions provided the salt concentrations are unaltered.[2] Then we have from Eq. 17

$$\Delta i_\alpha^0 = (g_{\alpha\mathrm{w}}-G_\mathrm{m}t_\alpha t_\mathrm{w})\Delta V_\mathrm{w}, \tag{18}$$

$$F\Delta j_\mathrm{w}^0 = (g_\mathrm{ww}-G_\mathrm{m}t_\mathrm{w}^2)\Delta V_\mathrm{w}, \tag{19}$$

where Δi_α^0 and Δj_w^0 means the changes in fluxes and ΔV_w, the change in the water potential due to the addition of sucrose. Since ΔV_w can be evaluated from the concentration of nonpermeant neutral solute, the measurements of the changes in the salt and solvent fluxes enable us to determine the coefficients $(g_{\alpha\mathrm{w}}-G_\mathrm{m}t_\alpha t_\mathrm{w})$ and $(g_\mathrm{ww}-G_\mathrm{m}t_\mathrm{w}^2)$ according to Eqs. 18 and 19, respectively. Thus $g_{\alpha\mathrm{w}}$ and g_ww can be estimated when g_k's are known. The value of $g_{\beta\mathrm{w}}$ can be estimated according to Eq. 9 provided $g_{\alpha\mathrm{w}}$ is known. Furthermore, $(g_{\alpha\alpha}-G_\mathrm{m}t_\alpha^2)$ can be determined from the i_α^0 data according to Eq. 17, provided $(g_{\alpha\mathrm{w}}-G_\mathrm{m}t_\alpha t_\mathrm{w})$, V_w, and $(V_\beta-V_\alpha)$ are known. Then we can estimate $g_{\alpha\alpha}$ which serves to obtain the values of $g_{\alpha\beta}$ and $g_{\beta\beta}$ successively according to Eq. 9. Thus, the six independent phenomenological coefficients, $g_{\alpha\alpha}$, $g_{\alpha\beta}$, $g_{\beta\beta}$, $g_{\alpha\mathrm{w}}$, $g_{\beta\mathrm{w}}$, and g_ww can be determined according to the procedures mentioned above.

3. *Transformation of Phenomenological Equation.* Equation 1 can be rewritten as follows

$$\begin{bmatrix} i_\alpha \\ I \\ Fj_\mathrm{w} \end{bmatrix} = -\begin{bmatrix} g_{\alpha\alpha} & g_\alpha & g_{\alpha\mathrm{w}} \\ g_\alpha & G_\mathrm{m} & g_\mathrm{w} \\ g_{\mathrm{w}\alpha} & g_\mathrm{w} & g_\mathrm{ww} \end{bmatrix}\begin{bmatrix} V_\beta-V_\alpha \\ E \\ -V_\mathrm{w} \end{bmatrix}, \tag{20}$$

where

$$E = V - V_\beta. \tag{21}$$

Here, we introduce the osmoequilibrium potential for an ion defined as

$$\begin{aligned} Z_\gamma FV_\gamma^* &= RT\ln a_\gamma^\mathrm{I}/a_\gamma^\mathrm{II} - \bar{v}_\gamma\Delta\pi \\ &= Z_\gamma FV_\gamma - \bar{v}_\gamma(\Delta\pi-\Delta P), \end{aligned} \tag{22}$$

then $(V_\beta-V_\alpha)$ may be expressed as

$$V_\beta-V_\alpha = V_\beta^* - V_\alpha^* - \bar{v}_\mathrm{s}V_\mathrm{w}/Z_\alpha\nu_\alpha\bar{v}_\mathrm{w}, \tag{23}$$

where $\bar{v}_\mathrm{s}$ and ν_α are the partial molar volume of the salt and the stoichiometric coefficient of cation, respectively.

Introducing the volume flow as a new flux

$$FJ_v/\bar{v}_w = Fj_w + \bar{v}_s i_\alpha/Z_\alpha\nu_\alpha\bar{v}_w, \tag{24}$$

and $(V^*_\beta - V^*_\alpha)$ as a new force, Eq. 20 can be rearranged as

$$\begin{bmatrix} i_\alpha \\ I \\ FJ_v/\bar{v}_w \end{bmatrix} = -\begin{bmatrix} g_{\alpha\alpha} & g_\alpha & g_{\alpha v} \\ g_\alpha & G_m & g_v \\ g_{v\alpha} & g_v & g_p \end{bmatrix}\begin{bmatrix} V^*_\beta - V^*_\alpha \\ E \\ -V_w \end{bmatrix}, \tag{25}$$

where

$$\begin{aligned} g_{\alpha v} &= g_{\alpha w} + g_{\alpha\alpha}\bar{v}_s/Z_\alpha\nu_\alpha\bar{v}_w \\ g_v &= g_w + g_\alpha\bar{v}_s/Z_\alpha\nu_\alpha\bar{v}_w \\ g_p &= g_{ww} + (g_{\alpha w}+g_{\alpha v})\bar{v}_s/Z_\alpha\nu_\alpha\bar{v}_w. \end{aligned} \tag{26}$$

We have from Eq. 25

$$I = -G_m(E-E_0) \tag{27}$$

$$E_0 = t_\alpha(V^*_\alpha - V^*_\beta) + t_v V_w, \tag{28}$$

where

$$t_v = g_v/G_m. \tag{28}$$

The term $t_v V_w$ is the streaming potential referred to the anion reversible electrode, and g_v and t_v may be regarded as the conductance and transport number of volume flow, respectively.

Equation 25 can be rewritten as

$$\begin{bmatrix} J_s \\ I \\ J_v \end{bmatrix} = -\begin{bmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{bmatrix}\begin{bmatrix} \Delta\mu^*_s \\ E \\ \Delta P - \Delta\pi \end{bmatrix}, \tag{30}$$

where

$$\Delta\mu^*_s = Z_\alpha\nu_\alpha F(V^*_\beta - V^*_\alpha) = \bar{v}_s(\Delta\pi - \Delta\pi_s), \tag{31}$$

$$\bar{v}_s\Delta\pi_s = -(\nu_\alpha+\nu_\beta)RT\ln a^{II}_\pm/a^I_\pm, \tag{32}$$

$$J_s = i_\alpha/Z_\alpha\nu_\alpha F, \tag{33}$$

$$\begin{aligned} &L_{11} = g_{\alpha\alpha}/(Z_\alpha\nu_\alpha F)^2,\ L_{12} = g_\alpha/Z_\alpha\nu_\alpha F, \\ &\qquad L_{13} = \bar{v}_w g_{\alpha v}/Z_\alpha\nu_\alpha F^2, \\ &L_{22} = G_m,\ L_{23} = \bar{v}_w g_v/F,\ L_{33} = (\bar{v}_w/F)^2 g_p. \end{aligned} \tag{34}$$

When the external aqueous solutions are dilute and their concentration ratio is close to unity, the approximation given by Kachalsky[5)] may be applied and $\Delta\mu^*_s$ is reduced to

$$\Delta\mu^*_s = \Delta\pi/C_s, \tag{35}$$

where C_s is the mean of the concentrations of external solutions. Thus, Eq. 30 is reduced to the phenomenological equation given by Katchalsky only when the approximation given by Eq. 35 is permitted. Krämer and Meares[6)] found a new force equivalent to Eq. 23, but unfortunately they adopted this approximation to obtain the phenomenological equation equivalent to that of Katchalsky and discussed the transport phenomena. Practically, the most solvent permeation experiments were performed under the condition that Eq. 35 may not be permitted. Equation 30 should be applied in this case.

When the membrane current is absent, we have from Eq. 25

$$\begin{bmatrix} i^0_\alpha \\ FJ^0_v/\bar{v}_w \end{bmatrix} = -\begin{bmatrix} g_{\alpha\alpha} - G_m t^2_\alpha & g_{\alpha v} - G_m t_\alpha t_v \\ g_{\alpha v} - G_m t_\alpha t_v & g_p - G_m t^2_v \end{bmatrix}\begin{bmatrix} V^*_\beta - V^*_\alpha \\ -V_w \end{bmatrix}, \tag{36}$$

which can be rewritten as

$$\begin{bmatrix} \bar{v}_s J^0_s \\ J^0_v \end{bmatrix} = -\begin{bmatrix} L_s & L_{sp} \\ L_{ps} & L_p \end{bmatrix}\begin{bmatrix} \Delta\pi - \Delta\pi_s \\ \Delta P - \Delta\pi \end{bmatrix}, \tag{37}$$

where L_s, L_{sp}, and L_p denote the thermodynamic solute permeability, the mechanical filtration coefficient, and the hydrodynamic permeability, respectively,

$$L_s = \bar{v}^2_s(g_{\alpha\alpha} - G_m t^2_\alpha)/(Z_\alpha\nu_\alpha F)^2 = -[\bar{v}_s J^0_s/(\Delta\pi - \Delta\pi_s)]_{\Delta P=\Delta\pi} \tag{38a}$$

$$\begin{aligned} L_{sp} = L_{ps} &= \bar{v}_s\bar{v}_w(g_{\alpha v} - G_m t_\alpha t_v)/Z_\alpha\nu_\alpha F^2 \\ &= -[J^0_v/(\Delta\pi - \Delta\pi_s)]_{\Delta P=\Delta\pi} \qquad (38b) \\ &= -[\bar{v}_s J^0_s/(\Delta P - \Delta\pi)]_{\Delta\pi=\Delta\pi_s}, \end{aligned}$$

and

$$L_p = (\bar{v}_w/F)^2(g_p - G_m t^2_v) = -[J^0_v/(\Delta P - \Delta\pi)]_{\Delta\pi=\Delta\pi_s}. \tag{38c}$$

Eliminating $(\Delta P - \Delta\pi)$ from Eq. 37, we have

$$J^0_s = -\omega_s(\Delta\pi - \Delta\pi_s) + (1-\sigma)J^0_v/\bar{v}_s, \tag{39}$$

where ω_s is the solute permeability coefficient

$$\omega_s = (L_s - L^2_{sp}/L_p)/\bar{v}_s = [J^0_s/(\Delta\pi - \Delta\pi_s)]_{J^0_v=0}, \tag{40}$$

and σ, the reflection coefficient

$$1 - \sigma = L_{sp}/L_p = (\bar{v}_s J^0_s/J^0_v)_{\Delta\pi=\Delta\pi_s}. \tag{41}$$

According to Eq. 37, the equilibrium is established at the condition

$$\Delta P = \Delta\pi_s = \Delta\pi. \tag{42}$$

There are two cases which satisfy this condition. The one is that the two external solutions possess the same compositions and hence $\Delta P = \Delta\pi_s = \Delta\pi = 0$ and the other, that a nonpermeable polyelectrolyte is present at one side and the osmotic eqilibrium such as the Donnan membrane equilibrium is established, where $\Delta P = \Delta\pi_s = \Delta\pi \neq 0$. Taking the approximation given by Eq. 35, Eqs. 37—41 are reduced to those obtained by Katchalsky.[5)]

4. Electrokinetic Phenomena. It is important to examine how the electroosmosis is involved in the electrical properties of the membrane. Eliminating V_w in Eq. 25, we obtain

$$\begin{aligned} \begin{bmatrix} i_\alpha - g_{\alpha v}FJ_v/g_p\bar{v}_w \\ I - g_v FJ_v/g_p\bar{v}_w \end{bmatrix} &= -\begin{bmatrix} g_{\alpha\alpha} - g^2_{\alpha v}/g_p & g_\alpha - g_{\alpha v}g_v/g_p \\ g_\alpha - g_{\alpha v}g_v/g_p & G_m - g^2_v/g_p \end{bmatrix} \\ &\times\begin{bmatrix} V^*_\beta - V^*_\alpha \\ E \end{bmatrix}, \end{aligned} \tag{43}$$

we have from Eq. 43

$$I - g_v F(J_v - J^0_v)/g_p\bar{v}_w = -(G_m - g^2_v/g_p)(E - E_0), \tag{44}$$

which leads to

$$G'_m = -(I)_{J_v=J^0_v}/(E - E_0) = G_m - g^2_v/g_p, \tag{45}$$

where G'_m denotes the membrane conductance without volume flow. On the other hand we have from Eqs. 25 and 27

$$F(J_v - J^0_v)/\bar{v}_w = -g_v(E - E_0) = FD_e I/\bar{v}_w, \tag{46}$$

where D_e denotes the electroosmotic permeability. Since G'_m is the membrane conductance without volume flow, the L.H.S. of Eq. 44 gives the membrane current without electroomsotic current. Thus, the second term of the L.H.S. of Eq. 44 may be considered as the electroosmotic current I_v accompanied by the volume flow.

Comparing this second term with Eq. 46, we have

$$I_{\mathrm{v}} = g_{\mathrm{v}}F(J_{\mathrm{v}}-J_{\mathrm{v}}^{0})/g_{\mathrm{p}}\bar{v}_{\mathrm{w}} = -\,g_{\mathrm{v}}^{2}(E-E_{0})/g_{\mathrm{p}}. \tag{47}$$

Let X be the charge concentration per unit volume of pore liquid within the membrane, the elctroosmotic current I_{v} may be given by the relation

$$I_{\mathrm{v}} = F(J_{\mathrm{v}}-J_{\mathrm{v}}^{0})X. \tag{48}$$

Comparing Eq. 48 with Eq. 47, we find

$$X = g_{\mathrm{v}}/\bar{v}_{\mathrm{w}}g_{\mathrm{p}}. \tag{49}$$

Combining Eq. 45 with Eqs. 38c and 49, we derive the equation for the part of the membrane conductance due to the electroosmosis as follows:

$$G_{\mathrm{m}} - G_{\mathrm{m}}' = g_{\mathrm{v}}^{2}/g_{\mathrm{p}} = (FX)^{2}L_{\mathrm{p}} + G_{\mathrm{m}}(\bar{v}_{\mathrm{w}}t_{\mathrm{v}}X)^{2}. \tag{50}$$

Taking the capillary model and assuming the membrane controlling process, L_{p} is expressed by[5)]

$$L_{\mathrm{p}} = \phi_{\mathrm{w}}r^{2}\theta/8\eta\Delta x, \tag{51}$$

where ϕ_{w} represents the membrane area available for permeation; r, the capillary radius; θ, the tortuosity factor; η, the viscosity of pore liquid; Δx, the membrane thickness. Substituting Eq. 51 into Eq. 50 and multiplying $\Delta x/\bar{X}$ where $\bar{X}$ is the equivalent concentration of salt per unit volume within the membrane, we have

$$\lambda - \lambda' = (FXr)^{2}\phi_{\mathrm{w}}\theta/8\eta\bar{X} + \lambda(\bar{v}_{\mathrm{w}}t_{\mathrm{v}}X)^{2}, \tag{52}$$

where λ and λ' represent the equivalent conductances of electrolyte with and without the electroosmosis, respectively. For the cation- or anion-exchange membranes, λ and λ' respresent the equivalent conductances of counter ions with and without the electroosmosis, respectively, provided the co-ion concentration may be ignored as compared with the counter ion concentration in the membrane.

Despić and Hills[7)] expressed the equation for the electroomsotic effect on the equivalent conductance of counter ions based on the kinetic approach as follows:

$$\lambda - \lambda' = (Fr)^{2}\bar{X}/8\eta, \tag{53}$$

which differs from Eq. 52. Ignoring the second term of the R.H.S. of Eq. 52 and putting $\phi_{\mathrm{w}}\theta=1$ and $X=\bar{X}$, Eq. 52 is reduced to Eq. 53. The replacement of X by $\bar{X}$ can not be allowed, since X is the charge concentration at the slipping plane of the pore liquid and differs from the counter ion concentration $\bar{X}$. This is experimentally recognized with the polyelectrolyte solution[8)] as well as the charged membrane.[9)] Furthermore, it is well known that the electroosmosis decreases with the increase in the exterior salt concentration. This implies the decrease in X of the pore liquid due to the increase in the ionic strength of the pore solution as is expected from the theory of the electrical diffuse double layer. Despić and Hills[7)] also applied the Nernst-Einstein relation for evaluating λ' from the self-diffusion coefficient of the counter ion. It has been shown[10,11)] that the Nernst-Einstein relation is valid only at the infinite dilution of salt solution and should not be applied to the salt solution of higher concentration[11)] as well as the ion-exchange membrane.[10)] Thus Despić and Hills' theory is seen to be theoretically invalid based on the above arguments. Nevertheless, several authors[12)] performed the experimental studies of Eq. 53 according to Despić and Hills' treatment.[7)] It is unfortunate that their studies have nothing to do with Eq. 53 because of the estimation of λ' from the self-diffusion coefficient of counter ion according to the Nernst-Einstein relation. Such experimental studies should be consulted with Eq. 14 as reported in the preceeding paper.[10)]

5. Solvent Effect on the Apparent Conductance Matrix. In the preceeding paper,[10)] the conductance matrix was determined from the membrane conductance, the transport number and the salt flux data according to the previous theory[1)] developed by assuming no solvent flow. Thus it is of interest to examine, on the basis of the present theory, the effect of solvent flow on the apparent values of the elements of the conductance matrix estimated according to the previous theory.[1)]

It is seen by comparing the present theory with the previous one[1)] that the current-potential relation are the same, although the ion flux-potential relations at non membrane current are different from each other. This implies that the diffusional ion conductance estimated according to the previous theory is the apparent one, although the membrane conductance is identical. We obtain from Eq. 13

$$(g_{\gamma}^{0})_{\mathrm{app}} = -\,i_{\gamma}^{0}/(V_{0}-V_{\gamma}) = g_{\gamma}^{0}(1+f_{\gamma}), \tag{54}$$

where $(g_{\gamma}^{0})_{\mathrm{app}}$ denotes the apparent diffusional conductance and f_{γ}, the solvent effect given by

$$\begin{aligned} f_{\gamma} &= -\,g_{\gamma\mathrm{w}}^{0}V_{\mathrm{w}}/g_{\gamma}^{0}(V_{0}-V_{\gamma}) \\ &= -\,[g_{\gamma\mathrm{w}}-g_{\alpha\beta}t_{\mathrm{w}}/(1-t_{\gamma})]V_{\mathrm{w}}/g_{\gamma}^{0}((V_{0}-V_{\gamma}). \end{aligned} \tag{55}$$

The expression for E_{0} is obtained from Eq. 54 as follows

$$\begin{aligned} E_{0} &= V_{0}-V_{\beta} = (t_{\alpha})_{\mathrm{app}}(V_{\alpha}-V_{\beta}) \\ &= [(\nu_{\alpha}+\nu_{\beta})(t_{\alpha})_{\mathrm{app}}RT/Z_{\alpha}\nu_{\alpha}F]\ln a_{\pm}^{\mathrm{I}}/a_{\pm}^{\mathrm{II}}, \end{aligned} \tag{56}$$

and

$$(t_{\gamma})_{\mathrm{app}} = (g_{\gamma}^{0})_{\mathrm{app}}/(g_{\alpha}^{0}+g_{\beta}^{0})_{\mathrm{app}} = t_{\gamma}(1+f_{\gamma})/(1+t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta}), \tag{57}$$

provided the external pressure difference is absent. It is seen in Eq. 56 that the transport number determined from the membrane potential *vs.* salt activity relation is also the apparent one.

Thus an element of the conductance matrix estimated by the previous treatment[1)] is an apparent one, too. The interionic correlation term is expressed by the relation

$$(g_{\alpha\beta})_{\mathrm{app}} = (t_{\alpha})_{\mathrm{app}}[g_{\beta}-g_{\beta}^{0}]_{\mathrm{app}}, \tag{58}$$

where $(g_{\beta})_{\mathrm{app}}$ is given by $G_{\mathrm{m}}(t_{\beta})_{\mathrm{app}}$. Equation 58 has the same form as the equation for $g_{\alpha\beta}$ obtained by rewriting Eq. 14. Combining Eq. 58 with Eqs. 14, 54, and 57, we derive

$$(g_{\alpha\beta})_{\mathrm{app}} = \frac{(1+f_{\alpha})(1+f_{\beta})}{1+t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta}}\left\{g_{\alpha\beta} - \frac{t_{\alpha}t_{\beta}(t_{\alpha}f_{\beta}+t_{\beta}f_{\beta})}{1+t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta}}G_{\mathrm{m}}\right\}, \tag{59}$$

which satisfies the reciprocal relation, accordingly we have

$$\begin{aligned} (g_{\gamma\gamma})_{\mathrm{app}} &= (g_{\gamma})_{\mathrm{app}} - (g_{\alpha\beta})_{\mathrm{app}} \\ &= \frac{(1+f_{\alpha})(1+f_{\beta})}{1+t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta}}\left\{\frac{g_{\gamma\gamma}-f_{\gamma}g_{\alpha\beta}}{1+f_{\gamma}}\right. \\ &\qquad \left. + \frac{t_{\alpha}t_{\beta}(t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta})}{1+t_{\alpha}f_{\alpha}+t_{\beta}f_{\beta}}G_{\mathrm{m}}\right\}. \end{aligned} \tag{60}$$

It is seen in Eqs. 57, 59, and 60 that the deviations of the apparent values from the true ones can not be evaluated unless all the matrix elements are determined. However, it will be shown later that the apparent values are close to the true ones, as an indication of small f_r's in the present experimental conditions.

It is noted here that the present theory can be applied to both the solid and liquid membranes, since the formulation is unaltered whether the membrane is solid or liquid.

Experimental

Materials. The amphoteric ion exchange membrane used in the present study is a thin crosslinked polystyrene layer with homogeneously dispersed sulfonate and quaternary ammonium groups and is tight contact with a porous support of polyvinyl chloride sheet with *ca.* 0.1 mm in thickness. The ion exchange capacity was 1 mequiv. (g-wt membrane)$^{-1}$ and the cationic/anionic capacity ratio was ranged 1.0 ± 0.2. The membrane is coded as a "1.0-PA-29" which was developed by Central Research Laboratory of Kanegafuchi Chemical Industry Co., Ltd. and kindly supplied for the present study. The details for the preparation of the membrane were described elsewhere.[13] Pure specimen of calcium chloride as well as sucrose and twice redistilled water were used for preparing salt and sucrose solutions. As to aqueous phases separated by a membrane, the salt concentration of phase II was kept at 10^{-2} mol dm^{-3} and that of phase I was varied from 10^{-3} to 10^{-1} mol dm^{-3}. The sucrose concentrations used for the osmotic flux measurement were 0.02 to 0.12 mol dm^{-3}.

Procedures of Experiments. The procedures of experiments were essentially the same as those described in the preceding paper.[2] The experiments were carried out under the regulated room temperature at 25.0 ± 1.0 °C.

The solvent flow j_w was estimated according to the relation

$$j_w = (J_v - \bar{v}_s J_s)/\bar{v}_w. \qquad (61)$$

Results and Discussion

Figure 1 shows the membrane potential, E_0, at zero electric current and the membrane conductance, G_m, as a function of the logarithm of the mean electrolyte activity, $a_\pm^I$, in phase I. The apparent transport number $(t_+)_{app}$ estimated according to Eq. 56 is also shown in this figure. Figure 1 indicates that the membrane is rather selective to anion than cation. Further, G_m increases with the increase in the external salt concentration. This may indicate the increase in the concentrations of cations and anions in the membrane with the increasing external salt concentration.

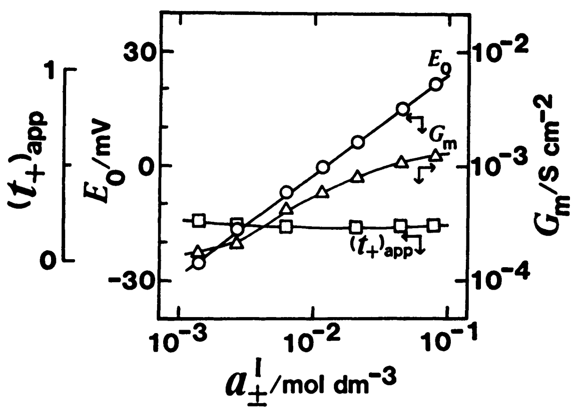

Fig. 1. Membrane potential at zero electric current, E_0, membrane conductance, G_m, and apparent cationic transport number, $(t_+)_{app}$, *vs.* mean electrolyte activity of phase I, $a_\pm^I$.
○, E_0; △, G_m; □, $(t_+)_{app}$.

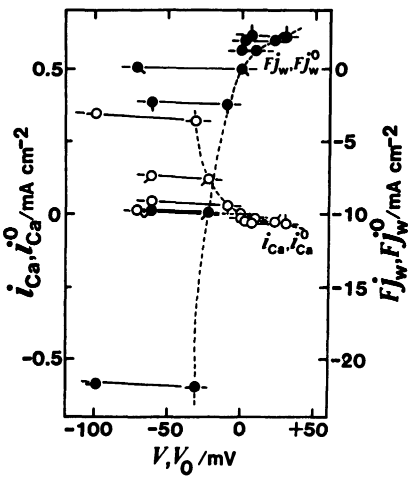

Fig. 2. Cation and water fluxes, i_{Ca} and Fj_w, *vs.* membrane potential, V.
The open and closed circles indicate $i_{Ca}(i_{Ca}^0)$ and Fj_w (Fj_w^0), respectively. Broken lines indicate i_{Ca}^0 and Fj_w^0 at zero electric current.
○, ●, 10^{-3}; ○, ●, 2×10^{-3}; ○, ●, 5×10^{-3}; ○, ●, 10^{-2}; ○, ●, 2×10^{-2}; ○, ●, 5×10^{-2}; ○, ●, 10^{-1}
Figures indicate the concentration of phase I in mol dm^{-3}.

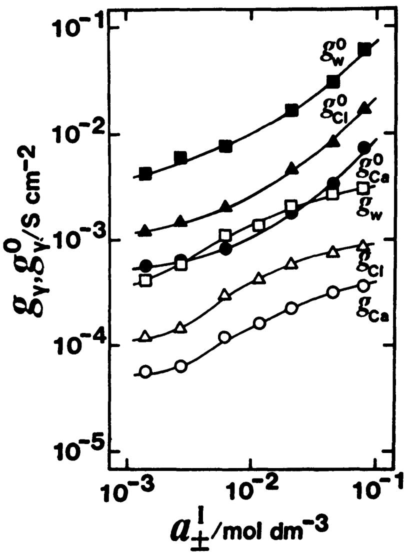

Fig. 3. Electrical ion and water conductances (g_{Ca}, g_{Cl}, g_w) and diffusional ion and water conductances (g_{Ca}^0, g_{Cl}^0, g_w^0) *vs.* mean electrolyte activity of phase I.
○, g_{Ca}; △, g_{Cl}; □, g_w; ●, g_{Ca}^0; ▲, g_{Cl}^0; ■, g_w^0.

Figure 2 shows the changes in i_α and Fj_w as functions of the applied potential V. All the fluxes were shown to be linear against V in this figure as an indication of the constancy of the conductances under the present experimental condition.

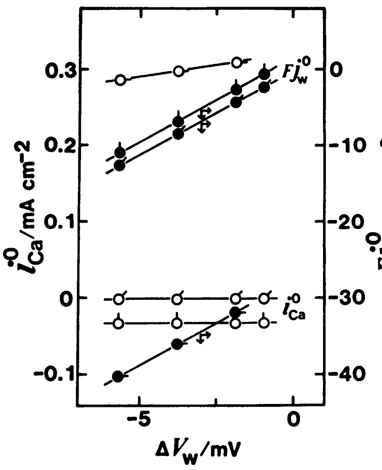

Fig. 4. Effect of osmotic pressure difference (ΔV_w) on ion and water fluxes at zero electric current. Open and closed circles are i^0_{Ca} and Fj^0_w, respectively.
○,●, 10^{-3}; ○,●, 10^{-2}; ○,●, 10^{-1}
Numericals indicate the concentration of phase I in mol dm^{-3}.

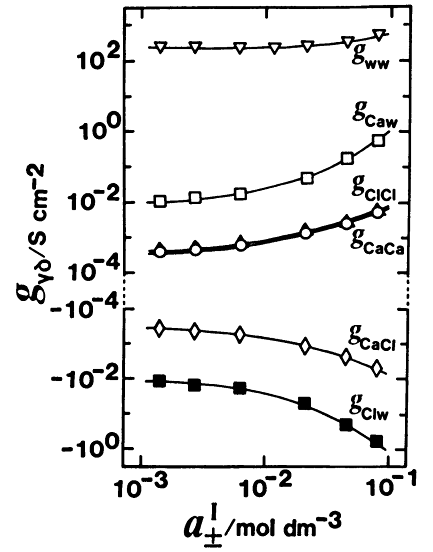

Fig. 5. Elements of conductance matrix *vs*. mean electrolyte activity of phase I.
○, g_{CaCa}; △, g_{ClCl}; ◇, g_{CaCl}; □, g_{Caw}; ■, g_{Clw}; ▽, g_{ww}.

The values of g_{Ca} and g_w can be estimated according to Eq. 16 and hence g_{Cl} can be calculated according Eq. 10. These are plotted as functions of $a^I_\pm$ in Fig. 3 together with g^0_γ calculated according to Eq. 14.

The deviation of the apparent transport number $(t_+)_{app}$ from the true one $t_{Ca}(=g_{Ca}/G_m)$ was found to be very small less than one percent and within the experimental error. This indicates that the solvent effect on the membrane potential at no membrane current, E_0, may be ignored under the present experimental conditions. This can be confirmed also by comparing E_0 with the calculated value of $t_w V_w$.

Figure 4 indicates the effect of the osmotic pressure difference ΔV_w caused by the addition of sucrose on the salt and water fluxes. The fluxes were linear against ΔV_w as shown in this figure. It is found in this figure that the slope of the i^0_α *vs*. ΔV_w relation agrees well with the intercept of the Fj^0_w *vs*. ΔV_w relation. This indicates the validity of the reciprocal relation assumed in the present theory. The membrane potential changed little by the addition of sucrose, and the change was within experimental error, probably due to the small solvent effect on the membrane potential. The phenomenological coefficients can be estimated stepwise as described in the theoretical section from the data shown in Figs. 1, 3, and 4. The estimated elements of the conductance matrix are shown in Fig. 5 as functions of the mean activity of salt in phase I.

This figure indicates that $g_{CaCa} \approx g_{ClCl} > -g_{CaCl}$ and all these coefficients are the same order of magnitude in contrast to the result in the cation-exchange membrane,[10] $g_{CaCa} \gg g_{CaCl} > g_{ClCl}$. In the preceding paper,[2] the l_{kl}(k,l$=\alpha,\beta$,w) coefficients were determined with the cation-exchange membrane-barium chloride system. The $g_{\gamma\delta}(\gamma,\delta=\alpha,\beta)$ may be calculated according to the relation, $g_{\gamma\delta}=Z_\gamma Z_\delta F^2 l_{\gamma\delta}\Delta x$, where Δx is the membrane thickness. The order of $g_{\alpha\beta}$ is found to be $g_{BaBa} \gg g_{BaCl} > g_{ClCl}$ at the external salt concentrations less than 0.1 mol dm^{-3}. On the other hand, g_{BaCl} becomes negative at the concentrations more than 0.4 mol dm^{-3} and the order of $g_{\gamma\delta}$ is found to be $g_{BaBa} \simeq g_{ClCl} > -g_{BaCl}$ as a similar result to the amphoteric membrane. An appreciable amount of the Donnan salt may migrate in the cation-exchange membrane when the external salt concentration becomes comparable with the fixed ion concentration. Thus, the negative cross coefficients in the cation and amphoteric ion exchange-membranes may correspond to the positive $l_{\alpha\beta}(\alpha \neq \beta)$ coefficient in the salt solution.[11]

Figure 5 also indicates the positive g_{Caw} and the negative g_{Clw}. A similar result, the positive g_{Baw} and the negative g_{Clw}, may be deduced from the $l_{\gamma w}$ data observed with the cation-exchange membrane[2] at the external salt concentrations more than 0.2 mol dm^{-3}. On the other hand, both g_{Baw} and g_{Clw} are postive at the concentrations less than 0.2 mol dm^{-3}. Similar to $g_{\gamma\delta}$, the concentration dependence of $g_{\gamma w}$ in the cation-exchange membrane may be ascribed to the increase of the Donnan salt within the membrane with increasing salt concentration. Thus it may be concluded that the behaviors of the cation and amphoteric ion exchange-membranes are quite different each other at the concentrations of external salt solutions less than 0.1 mol dm^{-3} where the major migrating ionic species in the former is cations and in the latter, both cations and anions. This reflects to the relation between the diffusional and conductive membrane conductances, *i.e.*, $g_\gamma \gg g^0_\gamma$ in the cation-exchange membrane[10] and this order is reversed in the amphoteric membrane as shown in Fig. 3. The values of g_γ and g^0_γ are estimated from $g_{\gamma\delta}$'s according to Eqs. 9 and 14, and related to the electrical absolute mobility $\bar{U}_\gamma$ and the diffusion coefficient $\bar{D}_\gamma$ within the membrane, respectively, as follows:[14]

$$\begin{aligned} g_\gamma &= (Z_\gamma F)^2 \bar{U}_\gamma \bar{C}_\gamma / \Delta x \\ g^0_\gamma &= (Z_\gamma F^2) \bar{D}_\gamma \bar{C}_\gamma / RT\Delta x, \end{aligned} \qquad (62)$$

where $\bar{U}_\gamma$ and $\bar{D}_\gamma$ denotes the mean electrical absolute mobility and the mean diffusion coefficient of ion γ within the membrane, respectively, and $\bar{C}_\gamma$ the mean concentration of ion γ within the membrane. Comparing Eq. 14 with Eq. 62, we have

$$\lambda_\gamma - \lambda_\gamma^0 = (g_\gamma - g_\gamma^0)\Delta x/\bar{C}_\gamma = (Z_\gamma F)^2(\bar{U}_\gamma - \bar{D}_\gamma/RT) \tag{63}$$

$$= g_{\alpha\beta}\Delta x/\bar{C}_\gamma(1-t_\gamma), \tag{64}$$

where λ_γ and λ_γ^0 are the equivalent electrical and diffusional ion conductances, respectively. Despić and Hills evaluated the electroosmotic effect according to Eq. 63, although they derived Eq. 53.[7] It is evident that Despić and Hills' treatment has no relation to their theoretical expression, Eq. 53. The disagreement between g_γ and g_γ^0 implies the failure of the Nernst-Einstein relation. The order, $g_\gamma^0 \gg g_\gamma$, in the amphoteric membrane indicates that the usual dialysis is energetically more effective than the electrodialysis for removing the salt through the amphoteric membrane.

It is seen in Eq. 25 that this phenomenological equation involves $g_{\alpha\mathrm{v}}$, g_v, and g_p as new conductance elements. These coefficients can be evaluated from the original set of conducatnce matrix elements according to Eq. 26. The deviation of the new elements from the corresponding original elements are found to be small as shown in Fig. 6. L_s, L_sp, L_p, and ω_s calculated according to Eqs. 38a, b, c, and 40, are plotted against $a_\pm^\mathrm{I}$ as shown in Fig. 7. Since the value of σ calculated by Eq. 41 is almost unity over the range of concentrations studied in the present paper, it is not plotted in Fig. 7. In the phenomenological equation, a flux is given by a linear combination of forces with phenomenological coefficients and *vice versa*. This implies that the processes are more or less coupled and the coupling phenomena can be discussed in terms of the phenomenological coefficients.[5] In this respect, it is interesting to consider the phenomena in terms of the degree of coupling.[15,16] The degree of coupling can be expressed by the coupling coefficient which is an important parameter for treating the energy conversion.[15,16]

For the phenomena dealing with the two and three processes, *e.g.*, those expressed by Eqs. 37 and 1, respectively, the coupling coefficients are given by

$$q = L_\mathrm{sp}/(L_\mathrm{s}L_\mathrm{p})^{1/2}, \tag{65}$$

and

$$q_{kl} = -|g|_{kl}/(|g|_{kk}|g|_{ll})^{1/2}, \tag{66}$$

respectively, where $|g|_{kl}$ is the cofactor of an element g_{kl} in the conductance matrix. The coupling coefficient q_{kl} can be regarded as the extent to which the k-th flow is dragged by the l-th flow when no other flow is present and the force conjugate to the k-th flow is zero. The absolute values of q, $q_{\alpha\beta}$, $q_{\alpha\mathrm{w}}$ and $q_{\beta\mathrm{w}}$ calculated according to Eqs. 65 and 66, respectively are shown in Fig. 8 as functions of $a_\pm^\mathrm{I}$. It is shown in this figure that q_CaCl is close to unity, although q_Caw and q_Clw are less than 0.1. This indicates that the interionic processes are strongly coupled, although the coupling between the water and ionic fluxes is weak. This might be reflected to the small solvent effects on the interionic conductance elements. Actually, deviations of the apparent interionic conductance elements, $(g_{\gamma\delta})_\mathrm{app}$, estimated according to the previous treatment[10] from the true ones is within the experimental error as shown in Fig. 9. Thus it is seen that the coupling coefficient plays an important role

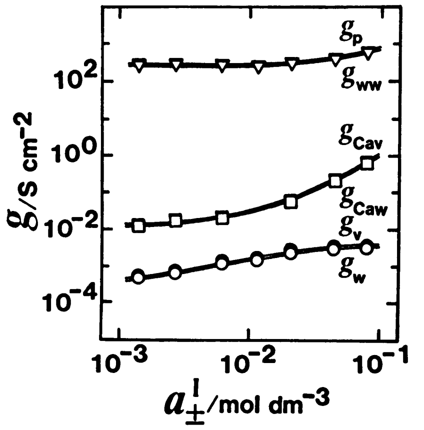

Fig. 6. Deviations of g_v, g_Cav, and g_p from g_w, g_Caw, and g_ww, respectively.
○, g_w; ●, g_v; □, g_Caw; ■, g_Cav; ▽, g_ww; ▼, g_p.

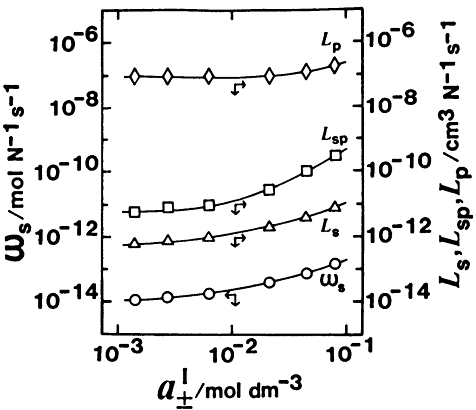

Fig. 7. Solute permeability (ω_s), thermodynamic permeability (L_s), mechanical filtration coefficient (L_sp) and hydrodynamic permeability (L_p) *vs.* mean electrolyte activity of phase I.
○, ω_s; △, L_s; □, L_sp; ◇, L_p.

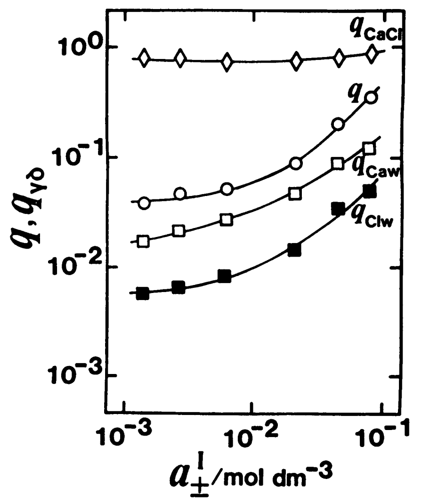

Fig. 8. Coupling coefficient *vs.* mean electrolyte activity of phase I.
○, q; ◇, q_CaCl; □, q_Caw; ■, q_Clw.

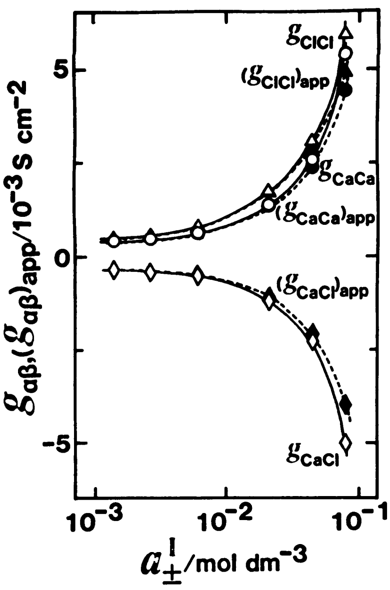

Fig. 9. Comparison of the true interionic conductance elements with the apparent ones.
○, g_{CaCa}; ●, $(g_{CaCa})_{app}$; ◇, g_{CaCl}; ◆, $(g_{CaCl})_{app}$; △, g_{ClCl}; ▲, $(g_{ClCl})_{app}$.

in the cross phenomena. The small V_w due to the small concentration difference in the concentration cell will be also responsible to little solvent effect as deduced from Eq. 55.

The electroosmosis is an example of the coupling phenomena. The electroosmotic contribution to the membrane conductance is given by g_v^2/g_pG_m as shown by Eq. 45. The factor g_v^2/g_pG_m corresponds to the square of the coupling coefficient for the membrane current-volume flow coupling in the case of no concentration difference between the two external solutions. The contribution is found to be a negligible order of 10^{-3} and the same order as that for the cation-exchange membrane.[10] This may be attributed to the low charge concentration of the flowing pore liquid X which is evaluated according to Eq. 49. In the present study, X is found to be an order of 10^{-4} mol dm^{-3} over the concentration range studied. Even for the cation-exchange membrane with the fixed ion concentration of *ca.* 2 mol dm^{-3}, the value of X evaluated from the observed phenomenological coefficient[2] is an order of 10^{-2} mol dm^{-3} and much less than the counter ion concentration within the membrane, $\bar{X}$. The strong interaction of the counter ions with the fixed charges may be the cause of the lower charge concentrations of flowing pore liquid. It is seen in Eqs. 48 and 50 that the small electroosmotic current with an appreciable volume flow may be ascribed to the low X. It is seen in the foregoing discussion that there is no appreciable contribution of the solvent effect on the interionic conductance elements, $g_{r\delta}$'s, for the amphoteric and cation-exchange membranes as far as the concentrations of the external salt solutions are dilute as compared with the fixed ion concentrations. This also verifies the previous treatment[10] for estimating the $g_{r\delta}$'s in the cation-exchange membrane-aqueous calcium chloride system.

It should be pointed out here that the small coupling coefficient for the coupling between solvent and ion flows is responsible to these results. It is shown in Fig. 5 that g_{ww} is extremely high and much greater than $g_{r\delta}$'s by a factor of 10^5. A similar result has been observed with the cation-exchange membrane.[2] Thus, the fact that $g_{ww} \gg g_{r\delta}$ suggests the small coupling coefficient. On the other hand, this fact also invalidates the assumption of no solvent flow in the previous theory.[1] The assumption should be revised as the assumption of little solvent effect on the ion transports. The small coupling coefficients may, in turn, imply no appreciable salt effect on the solvent flow.

Comparing Eq. 41 with Eq. 62, we have

$$\sigma = 1 - q(L_s/L_p)^{1/2} \tag{67}$$

which implies that the small coupling coefficient and and $L_p \gg L_s$ are the recommended conditions for the reverse osmosis.

When the external salt concentration becomes higher, the deviation of $(g_{r\delta})_{app}$ from $g_{\delta r}$ will be greater as can be deduced from Eq. 55. This tendency may already be seen even in Fig. 9 and in fact, a remarkable deviation occurs in the cation-exchange membrane-barium chloride system at higher salt concentrations more than 0.1 mol dm^{-3}.[2] This may be related to the increasing coupling coefficient with salt concentration.[2]

For the membrane with higher water content and lower fixed charges, the ions move as fast as the solvent molecule and hence the coupling coefficient q_{rw} will be greater. This may be the cause of an anormalous osmosis.[17]

Whether the water content and fixed ion concentration of a membrane is high or not, the detailed study for determining all the phenomenological coefficients should be required for describing the membrane properties precisely.

It has been shown in the present paper that the cross coefficients play an important role for elucidating the membrane properties. Thus the nonthermodynamic assumption such as ignoring the cross term should be avoided unless it is verified experimentally.

References

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

2) E. Kumamoto and H. Kimiuzka, *J. Phys. Chem.*, **85**, 635 (1981).

3) T. Foley, J. Klinowski, and P. Meares, *Proc. R. Soc. London, Ser. A*, **336**, 327 (1974).

4) T. Foley and P. Meares, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1105 (1976).

5) A. Katchalsky and P. F. Curran, "Non-Equilibrium Thermodynamics in Biophysics," Harvard University Press, Cambridge, MA, (1965).

6) H. Krämer and P. Meares, *Biophys. J.*, **9**, 1006 (1969).

7) A. Despič and G. J. Hills, *Discuss. Faraday Soc.* **21**, 150 (1956).

8) B. E. Conway and R. G. Barradas "Chemical Physics in Ionic Solution," John Willey and Sons, New York, London, Sydney (1966).

9) Y. Toyoshima, Y. Kobatake, and H. Fujita, *Trans. Faraday Soc.*, **63**, 2814 (1967).

10) H. Kimizuka, K. Kaibara, E. Kumamoto, and M. Shirōzu, *J. Membr. Sci.*, **4**, 81 (1978).

11) E. Kumamoto and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **52**, 2145 (1979).

12) N. Lakshminarayanaiah "Transport Phenomena in Membranes," Academic Press, New York and London (1969).

13) A. Yamauchi, S. Tsuruyama, H. Masumori, Y. Nagata, K. Kaibara, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **55**, 3297 (1982).

14) K. Nomura, A. Matsubara, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **54**, 1324 (1981).

15) O. Kedem and S. R. Caplan, *Trans. Faraday Soc.*, **61**, 1897 (1965).

16) S. R. Caplan, *J. Phys. Chem.*, **69**, 3801 (1965); *J. Theor. Biol.*, **10**, 209 (1966); **11**, 346 (1966).

17) M. Tasaka, C. Wada, and M. Nagasawa, *J. Membr. Sci.*, **6**, 171 (1980).