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Membrane Phenomena in Nonisothermal Systems: Part 1. Theory

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Theoretical equations for the thermoosmosis and thermal membrane potential across a charged membrane were derived using a set comprising the energy flux and the coupled logarithmic temperature-difference force as a dissipation function of irreversible processes. In order to obtain phenomenological equations in discontinuous systems by integrating phenomenological equations in continuous systems, it was assumed that temperature and total chemical potential are continuous at the interface between the membrane and the external solution. The new equations were compared with approximate equations derived previously from a set comprising the entropy flux and the coupled temperature-difference force as the dissipation function. Moreover, an equation for the thermal membrane potential was also derived using an alternative method by summing two parts: the equilibrium potential differences between the membrane and the external solutions on both sides of the membrane (two Donnan potentials) and the thermal-diffusion potential in the membrane.

To analyze nonisothermal membrane systems, in general, most of the theories derived by using nonequilibrium thermodynamics have included a dissipation function consisting of the product of a heat flux and the coupled logarithmic temperature difference, and the product of a mass flux and the coupled isothermal chemical potential difference.[1—4] However, these theories could not clearly predict the concentration dependence of nonisothermal membrane phenomena, since the concentration dependence of the heat of transport or the Soret coefficient is not yet known. Therefore, in order to predict concentration dependence of nonisothermal membrane phenomena a set comprising the entropy flux and the coupled temperature-difference force was used as a dissipation function of irreversible processes.[5—8] The theory, based on the entropy flux, is convenient to analyze the concentration dependence of membrane phenomena and the stability of the state of components in the membrane. However, since a membrane is not an infinitely thin film, but has a finite thickness, we must use an approximate method which assumes the entropy flux to be nearly constant over the range of small temperature differences when the phenomenological equations are integrated across the membrane.

In this study a set comprising an energy flux and the coupled logarithmic temperature-difference force was selected as the dissipation function of irreversible processes. This was because the energy flux can be treated as a constant in a steady state due to the conservation of energy when the phenomenological equations are integrated across the membrane and the phenomenological equations derived from this dissipation function can also clearly predict the concentration dependence of nonisothermal membrane phenomena. The equations derived in this study were compared with approximate equations previously obtained by using a set comprising the entropy flux and the coupled temperature-difference force.[5—8]

Theory

If there is no chemical reaction in a system and the fluid is not viscous, the dissipation function is written as[9—11]

$$\begin{aligned}\Phi &= -J_{\mathrm{q}}\cdot\mathrm{grad}(\ln T) - \sum_i J_i\cdot(\mathrm{grad}\,\tilde{\mu}_i)_T \\ &= -J_{\mathrm{e}}\cdot\mathrm{grad}(\ln T) - \sum_i J_i\cdot\mathrm{grad}\,\tilde{\mu}_i \\ &= -J_{\mathrm{s}}\cdot\mathrm{grad}\,T - \sum_i J_i\cdot\mathrm{grad}\,\tilde{\mu}_i, \qquad (1)\end{aligned}$$

where J_{q}, J_{e}, J_{s}, and J_i are the heat flux, the energy flux, the entropy flux, and the mass flux of component *i*. Moreover, *T* is the absolute temperature and $\tilde{\mu}_i$ is the total chemical potential of component *i*. Among these fluxes the following relationships hold:

$$\begin{aligned}J_{\mathrm{e}} &= J_{\mathrm{q}} + \sum_i s_i T J_i \\ &= T J_{\mathrm{s}}, \qquad (2)\end{aligned}$$

where s_i is the partial molar entropy of component *i*. Then J_{e} may be regarded as being the sum of the heat flux and the part due to the mass flux. If we write down phenomenological equations for the energy flux (J_{e}) and the mass flux (J_i) we obtain

$$-J_{\mathrm{e}} = \bar{L}_{\mathrm{qq}}\mathrm{grad}\,(\ln\bar{T}) + \sum_i \bar{L}_{\mathrm{q}i}\mathrm{grad}\bar{\tilde{\mu}}_i, \qquad (3a)$$

$$-J_i = \bar{L}_{i\mathrm{q}}\mathrm{grad}\,(\ln\bar{T}) + \sum_j \bar{L}_{ij}\mathrm{grad}\bar{\tilde{\mu}}_j, \qquad (3b)$$

where $\bar{L}_{\alpha\beta}$ is the phenomenological coefficient and the overbar refers to the membrane phase.

In order to take into account the fact that the membrane is not infinitely thin film, but has a finite thickness, we now adopt the method which was used by Kirkwood in isothermal systems.[12] The energy flux (J_e) and the mass flux (J_i) may be treated as a constant in a steady state because the mass and energy are conserved. By solving Eq. 3 for the forces and integrating them from one side of the membrane (0) to the other (δ), while keeping the fluxes constant, we obtain Eqs. 4a and 4b. Then, we assume that the temperature (T) and the total chemical potential ($\tilde{\mu}_i$) are continuous at the interface between the membrane phase and the external solution phase, although the electric potential and the pressure are not continuous (Fig. 1).[5,13]

$$\begin{aligned} -\int_0^\delta \mathrm{grad}\,(\ln \bar{T})\mathrm{d}x &= -\Delta \ln \bar{T} \\ &= -\Delta \ln T \\ &= \int_0^\delta R_{\mathrm{qq}} J_\mathrm{e} \mathrm{d}x + \int_0^\delta R_{\mathrm{q}i} J_i \mathrm{d}x \\ &= r_{\mathrm{qq}} J_\mathrm{e} + \sum_i r_{\mathrm{q}i} J_i \end{aligned} \tag{4a}$$

$$\begin{aligned} -\int_0^\delta \mathrm{grad}\,\bar{\tilde{\mu}}_i \mathrm{d}x &= -\Delta \ln \bar{\tilde{\mu}}_i \\ &= -\Delta \ln \tilde{\mu}_i \\ &= \int_0^\delta R_{i\mathrm{q}} J_\mathrm{e} \mathrm{d}x + \int_0^\delta R_{ij} J_j \mathrm{d}x \\ &= r_{i\mathrm{q}} J_\mathrm{e} + \sum_j r_{ij} J_j, \end{aligned} \tag{4b}$$

where

$$\frac{|\bar{L}|_{\alpha\beta}}{|\bar{L}|} = R_{\beta\alpha}, \tag{5a}$$

$$r_{\beta\alpha} = \int_0^\delta R_{\beta\alpha}(x)\mathrm{d}x. \tag{5b}$$

The Δ indicates the difference between the two fluid phases on both sides of the membrane, $|L|$ is the determinant of the matrix $L_{\alpha\beta}$, $|L|_{\alpha\beta}$ is the appropriate cofactor, and δ is the thickness of the membrane. By solving Eq. 4 for the fluxes, we obtain

$$-J_\mathrm{e} = L_{\mathrm{qq}} \Delta \ln T + \sum_i L_{\mathrm{q}i} \Delta \tilde{\mu}_i, \tag{6a}$$

$$-J_i = L_{i\mathrm{q}} \Delta \ln T + \sum_j L_{ij} \Delta \tilde{\mu}_i, \tag{6b}$$

where

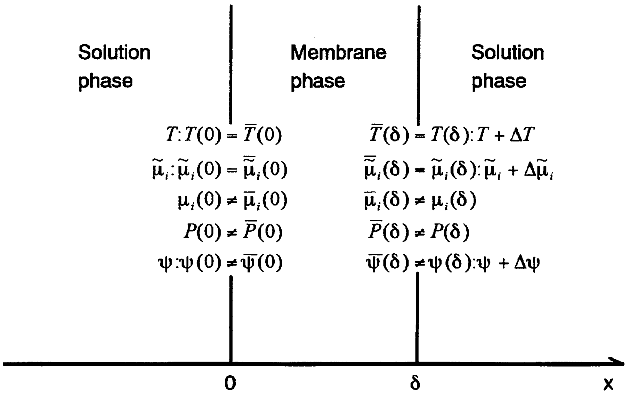

Fig. 1. Illustration of nonisothermal membrane phenomena.

$$L_{\alpha\beta} = \frac{|r|_{\beta\alpha}}{|r|}, \tag{7}$$

and $|r|$ is the determinant of the matrix $r_{\alpha\beta}$ and $|r|_{\alpha\beta}$ is the appropriate cofactor.

From Eq. 4 the energy flux (J_e) can be rewritten as

$$\begin{aligned} -J_\mathrm{e} &= (1/r_{\mathrm{qq}})\Delta \ln T + \sum_i (r_{\mathrm{q}i}/r_{\mathrm{qq}}) J_i \\ &= (1/r_{\mathrm{qq}})\Delta \ln T + \sum_i \bar{e}_i J_i, \end{aligned} \tag{8}$$

where $\bar{e}_i$ is the transported energy per mole of component i.

Using a similar method, from Eq. 1 we may write the following equations for the entropy flux (J_s) and the mass flux (J_i):

$$-J_\mathrm{s} = \bar{L}_{\mathrm{ss}} \mathrm{grad}\,\bar{T} + \sum_i \bar{L}_{\mathrm{s}i} \mathrm{grad}\,\bar{\tilde{\mu}}_i, \tag{9a}$$

$$-J_i = \bar{L}_{i\mathrm{s}} \mathrm{grad}\,\bar{T} + \sum_j \bar{L}_{ij} \mathrm{grad}\,\bar{\tilde{\mu}}_j, \tag{9b}$$

If the temperature difference is small we may assume that the entropy flux is nearly constant at the steady state. We then obtain the following approximate equations by a similar method to that used for the energy flux:[8]

$$-J_\mathrm{s} = L_{\mathrm{ss}} \Delta T + \sum_i L_{\mathrm{s}i} \Delta \tilde{\mu}_i, \tag{10a}$$

$$-J_i = L_{i\mathrm{s}} \Delta T + \sum_j L_{ij} \Delta \tilde{\mu}_j, \tag{10b}$$

$$-J_\mathrm{s} = (1/r_{\mathrm{ss}}) \Delta T + \sum_i \bar{\bar{s}}_i J_i, \tag{10c}$$

where $\bar{\bar{s}}_i$ is the mean transported entropy per mole of component i. Substituting Eq. 2 into Eq. 8, we obtain an approximate equation,

$$-J_\mathrm{s} = \left(\frac{1}{r_{\mathrm{qq}} T_\mathrm{m}^2}\right) \Delta T + \sum_i \left(\frac{\bar{e}_i}{T_\mathrm{m}}\right) J_i, \tag{11}$$

where T_m is the mean temperature across the membrane: $T+(\Delta T/2) \fallingdotseq \Delta T/(\Delta \ln T)$. When T_m is fixed at 298 K and ΔT is 20 K, the fraction of the difference between $\Delta \ln T$ and $\Delta T/T_\mathrm{m}$, $\{\Delta \ln T - (\Delta T/T_\mathrm{m})\}/(\Delta \ln T)$, is about 0.0004. Under these conditions Eq. 11 is a good approximate equation. Comparing Eq. 10 with Eq. 11, we obtain

$$r_{\mathrm{ss}} = r_{\mathrm{qq}} T_\mathrm{m}^2, \tag{12a}$$

$$\bar{\bar{s}}_i = \bar{e}_i / T_\mathrm{m}. \tag{12b}$$

If the Onsager reciprocal relationship holds, we obtain

$$L_{\mathrm{q}i} = L_{i\mathrm{q}} = \sum_j \bar{e}_j L_{ji} = \sum_j \bar{e}_j L_{ij}, \tag{13a}$$

$$L_{\mathrm{s}i} = L_{i\mathrm{s}} = \sum_j \bar{\bar{s}}_j L_{ji} = \sum_j \bar{\bar{s}}_j L_{ij}. \tag{13b}$$

Thermal Membrane Potential (1). Using the condition of the electrical neutrality, $I=\sum_i z_i F J_i = 0$, from Eq. 6 the electrical potential difference ($\Delta\psi$) is expressed as follows:[5,8]

$$\begin{aligned} -\Delta\psi &= \eta^* \Delta \ln T + \sum_i \tau_i \Delta \mu_i \\ &= \eta \Delta T + \sum_i \tau_i \Delta \mu_i, \end{aligned} \tag{14}$$

where τ_i is the reduced transport number of component i, and η^* and η are thermoelectric coefficients:

$$\tau_i = \sum_j z_j L_{ji} \Big/ \left(\sum_i \sum_j z_i z_j F L_{ij} \right), \tag{15a}$$

$$\eta^* = \sum_i z_i L_{iq} \Big/ \left(\sum_i \sum_j z_i z_j F L_{ij} \right) = \sum_i \tau_i \bar{e}_i = \sum_i \tau_i \bar{\bar{s}}_i T_{\mathrm{m}}, \tag{15b}$$

$$\eta = \sum_i z_i L_{is} \Big/ \left(\sum_i \sum_j z_i z_j F L_{ij} \right) = \sum_i \tau_i \bar{\bar{s}}_i = \eta^* / T_{\mathrm{m}}. \tag{15c}$$

If there is no difference in the concentration of the electrolyte across the membrane, from Eq. 14 $-\Delta\psi/\Delta \ln T$ or $-\Delta\psi/\Delta T$ is given by

$$-\Delta\psi/\Delta \ln T = \sum_i \tau_i (\bar{e}_i - s_i T_{\mathrm{m}}), \tag{16a}$$

$$-\Delta\psi/\Delta T = \sum_i \tau_i (\bar{\bar{s}}_i - s_i), \tag{16b}$$

where s_i is the partial molar entropy of component i in the external solution. If the membrane is ideally perm-selective for counterions, i.e., $t_+=1$, from Eq. 16 we have

$$-\Delta\psi/\Delta \ln T = (RT_{\mathrm{m}}/F) \ln a_+ + \alpha_+{}^*, \tag{17a}$$

$$-\Delta\psi/\Delta T = (R/F) \ln a_+ + \alpha_+, \tag{17b}$$

for cation-exchange membranes, where

$$\alpha_+{}^* = \frac{1}{F}(\bar{e}_+ - s_+^0 T_{\mathrm{m}}) + \tau_0 (\bar{e}_0 - s_0 T_{\mathrm{m}}), \tag{18a}$$

$$\alpha_+ = \frac{1}{F}(\bar{\bar{s}}_+ - s_+^0) + \tau_0 (\bar{\bar{s}}_0 - s_0), \tag{18b}$$

$$\alpha_+{}^* = \alpha_+ T_{\mathrm{m}}. \tag{18c}$$

Thermal Membrane Potential (2). An Alternative Derivation of Thermal Membrane Potential Equation. The membrane potential appearing on both sides of the membrane ($\Delta\psi=\psi(\delta)-\psi(0)$) is the sum of the thermal-diffusion potential inside the membrane ($\Delta\overline{\psi}_{\mathrm{td}}=\overline{\psi}(\delta)-\overline{\psi}(0)$), and the electrostatic-potential differences between the membrane and the external electrolyte solution phases on both sides of the membrane ($\Delta\psi_{\mathrm{e}}=\{\psi(\delta)-\overline{\psi}(\delta)\}+\{\overline{\psi}(0)-\psi(0)\}$). If there is no concentration differences and the electric current is zero, we have from Eq. 3,

$$\begin{aligned} -\operatorname{grad} \overline{\psi} &= \overline{\eta}^* \operatorname{grad} (\ln \overline{T}) + \sum_i \overline{\tau}_i \operatorname{grad} \overline{\mu}_i, \\ &= \overline{\eta} \operatorname{grad} \overline{T} + \sum_i \overline{\tau}_i \operatorname{grad} \overline{\mu}_i, \end{aligned} \tag{19}$$

where

$$\overline{\eta}^* = \sum_i z_i \overline{L}_{iq} \Big/ \left(\sum_i \sum_j z_i z_j F \overline{L}_{ij} \right) = \sum_i \tau_i \bar{e}_i = \sum_i \tau_i \bar{\bar{s}}_i T_{\mathrm{m}} = \eta^*, \tag{20a}$$

$$\overline{\eta} = \sum_i z_i \overline{L}_{is} \Big/ \left(\sum_i \sum_j z_i z_j F \overline{L}_{ij} \right) = \sum_i \tau_i \bar{\bar{s}}_i = \overline{\eta}^* / T_{\mathrm{m}} = \eta. \tag{20b}$$

Integrating Eq. 19 from 0 to δ, we obtain the thermal-diffusion potential ($\Delta\overline{\psi}_{\mathrm{td}}$) in the membrane phase,

$$\begin{aligned} -\Delta\overline{\psi}_{\mathrm{td}} &= \sum_i \tau_i (\bar{e}_i - \bar{s}_i \overline{T}_{\mathrm{m}}) \Delta \ln \overline{T} \\ &= \sum_i \tau_i (\bar{\bar{s}}_i - \bar{s}_i) \Delta \overline{T}, \end{aligned} \tag{21}$$

where $\bar{\bar{s}}_i$ is the partial molar entropy of component i in the membrane phase. For 1–1 electrolytes the equilibrium potential differences at two interfaces between the membrane and the external solution phases, $\Delta\psi_{\mathrm{e}}(\delta)$ and $\Delta\psi_{\mathrm{e}}(0)$, can be calculated from the theory of Donnan:[14,15]

$$\begin{aligned} \Delta\psi_{\mathrm{e}} &= \Delta\psi_{\mathrm{e}}(\delta) + \Delta\psi_{\mathrm{e}}(0) \\ &= \{\psi(\delta) - \overline{\psi}(\delta)\} + \{\overline{\psi}(0) - \psi(0)\} \\ &= \frac{1}{F}\left[v_+ \{\overline{P}(\delta) - P(\delta)\} + \{\overline{\mu}_+^0(\delta) - \mu_+^0(\delta)\} \right. \\ &\qquad \left. + R(T+\Delta T) \ln \frac{\bar{a}_+(\delta)}{a_+(\delta)} \right] \\ &\quad + \frac{1}{F}\left[v_+ \{P(0) - \overline{P}(0)\} + \{\mu_+^0(0) - \overline{\mu}_+^0(0)\} \right. \\ &\qquad \left. + RT \ln \frac{a_+(0)}{\bar{a}_+(0)} \right], \end{aligned} \tag{22}$$

where P is the pressure. If we assumed that $\overline{\mu}_0^0(\delta)-\mu_0^0(\delta)=\overline{\mu}_0^0(0)-\mu_0^0(0)$ and $\overline{\mu}_+^0(\delta)-\mu_+^0(\delta)=\overline{\mu}_+^0(0)-\mu_+^0(0)$, Eq. 22 reduces to Eq. 23.

$$\begin{aligned} \Delta\psi_{\mathrm{e}} &= \left(\frac{v_+}{v_0}\right) \left\{ \frac{R(T+\Delta T)}{F} \ln \frac{a_0(\delta)}{\bar{a}_0(\delta)} + \frac{RT}{F} \ln \frac{\bar{a}_0(0)}{a_0(0)} \right\} \\ &\quad + \frac{R(T+\Delta T)}{F} \ln \frac{\bar{a}_+(\delta)}{a_+(\delta)} + \frac{RT}{F} \ln \frac{a_+(0)}{\bar{a}_+(0)}. \end{aligned} \tag{23}$$

If we assume that $\bar{a}_0(\delta)=\bar{a}_0(0)=\bar{a}_0$, $\bar{a}_+(\delta)=\bar{a}_+(0)=\bar{a}_+$, $\bar{a}_-(\delta)=\bar{a}_-(0)=\bar{a}_-$, $a_0(\delta)=a_0(0)=a_0$, $a_+(\delta)=a_+(0)=a_+$, and $a_-(\delta)=a_-(0)=a_-$, for 1–1 electrolytes thermal membrane potential can the written as the sum of the thermal-diffusion potential in the membrane phase ($\Delta\psi_{\mathrm{td}}$) and Donnan potentials ($\Delta\psi_{\mathrm{e}}(0)$ and $\Delta\psi_{\mathrm{e}}(\delta)$):

$$\begin{aligned} -\Delta\psi &= -(\Delta\overline{\psi}_{\mathrm{td}} + \Delta\psi_{\mathrm{e}}) \\ &= -\left(\frac{v_+}{v_0}\right) \frac{R\Delta T}{F} \ln \frac{\bar{a}_0}{a_0} - \frac{R\Delta T}{F} \ln \frac{\bar{a}_+}{a_+} \\ &\quad + \frac{t_+ \Delta T}{F} (\bar{\bar{s}}_+ - s_+^0 + R \ln \bar{a}_+) \\ &\quad - \frac{t_- \Delta T}{F} (\bar{\bar{s}}_- - s_-^0 + R \ln \bar{a}_-) + \tau_0 (\bar{\bar{s}}_0 - \bar{s}_0) \Delta T \\ &= \frac{t_+ \Delta T}{F} (\bar{\bar{s}}_+ - s_+^0 + R \ln a_+) \\ &\quad - \frac{t_- \Delta T}{F} (\bar{\bar{s}}_- - s_-^0 + R \ln a_-) + \tau_0 (\bar{\bar{s}}_0 - s_0) \Delta T \\ &= \sum_i \tau_i (\bar{\bar{s}}_i - s_i) \Delta T, \end{aligned} \tag{24}$$

where $F\tau_0=v_+/v_0$ is assumed. The relationship between $\Delta\psi$ and ΔT in Eq. 24 is the same as in Eq. 16. Figure 2 schematically shows the thermal membrane potential across a cation-exchange membrane, assuming $\bar{a}_0=a_0$.

Thermoosmosis. Substituting Eq. 16 into Eq. 6 or Eq. 10, the mass flux of component i is written as[7,8]

$$\begin{aligned} -J_i &= \sum_j (L_{ij} - \tau_i \tau_j F^2 L_{\mathrm{e}}) \{(\bar{e}_j - s_j T_{\mathrm{m}}) \Delta \ln T + (\Delta\mu_j)_T\} \\ &= \sum_j (L_{ij} - \tau_i \tau_j F^2 L_{\mathrm{e}}) \left\{(\bar{\bar{s}}_j - s_j) \Delta T + (\Delta\mu_j)_T\right\}, \end{aligned} \tag{25}$$

where L_{e} is the electric permeability, $L_{\mathrm{e}}=\sum_i \sum_j z_i z_j L_{ij}$. If the difference in the chemical potential due to the composition

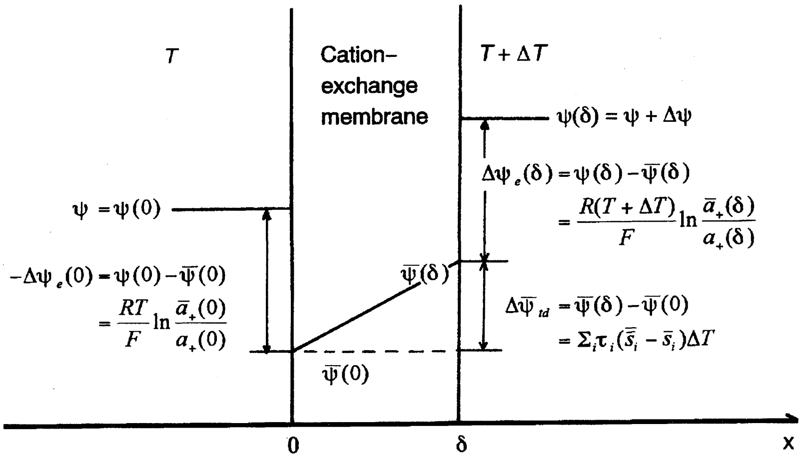

Fig. 2. Illustration of thermal membrane potential across a cation-exchange membrane assuming $\overline{a}_0=a_0$: $\Delta\psi=\Delta\psi_e(0)+\Delta\overline{\psi}_{td}+\Delta\psi_e(\delta)$.

at a temperature constant is zero, $(\Delta\mu_j)_T=0$, the volume flux, $J_v=\sum\limits_i \nu_i J_i$, is expressed by

$$\begin{aligned} -J_v &= D^{e}\Delta\ln T \\ &= D\Delta T, \end{aligned} \tag{26}$$

where

$$D^{e}=\sum_i\sum_j \nu_i(L_{ij}-\tau_j\sum_k L_{ik}z_kF)(\overline{e}_j-s_jT_m), \tag{27a}$$

$$\begin{aligned} D&=\sum_i\sum_j \nu_i(L_{ij}-\tau_j\sum_k L_{ik}z_kF)(\overline{\overline{s}}_j-s_j) \\ &=D^{e}/T_m. \end{aligned} \tag{27b}$$

Moreover, for cation-exchange membrane and 1−1 electrolyte systems the thermoosmotic coefficients (D^{e}) are written by

$$D^{e}=D^{e(0)}+D^{e(1)}+D^{e(2)}, \tag{28}$$

where

$$D^{e(0)}=\overline{c}_0 l_{v0}(\overline{e}_0-s_0T_m)/\delta, \tag{29a}$$

$$D^{e(1)}=-\tau_0F\phi Xl_{v\pm}(\overline{e}_0-s_0T_m)/\delta, \tag{29b}$$

$$D^{e(2)}=(\overline{c}_-+t_-\phi X)l_{v\pm}(\overline{e}_s-s_sT_m)/\delta, \tag{29c}$$

and

$$L_{ij}=\overline{c}_j l_{ij}/\delta, \tag{30a}$$

$$l_{vi}=\sum_j \nu_j l_{ji}, \tag{30b}$$

$$\overline{e}_s=\overline{e}_++\overline{e}_-, \tag{30c}$$

$$s_s=s_s+s_-, \tag{30d}$$

$$\overline{c}_+=\overline{c}_-+\phi X. \tag{30e}$$

Here, ϕX is the effective concentration of fixed charges, and l_{ij} and l_{vi} are coefficients defined by Eqs. 30a and 30b. We may assume that $l_{v+}=l_{v-}=l_{v\pm}$ because the electroosmosis and streaming potential tend to zero at high salt concentrations.[16] If a membrane has no fixed charges, and the solution does not contain an electrolyte, $D^{e(1)}$ and $D^{e(2)}$ disappear and we have $D^{e}=D^{e(0)}$. If the membrane has fixed charges, the additional frictional interaction between the fixed charges and water flow must be considered. The charge effect is predicted by $D^{e(1)}$ of Eq. 29b. $D^{e(2)}$ is zero at low electrolyte concentrations because the transport number and the concentration of co-ions are zero in the membrane. Since the transport number of the co-ions increases with increasing concentration of the electrolyte, the absolute value of $D^{e(2)}$ would monotonically increase with the concentration.

If cation-exchange membrane have ideal perm-selectivity for counterions, the volume flux (J_v) across the membranes due to a temperature difference and an osmotic pressure difference can be written as

$$\begin{aligned} -J_v &= D^*\{(\overline{e}_0-s_0T_m)\Delta\ln T-v_0\Delta\pi\} \\ &= D^*\{(\overline{\overline{s}}_0-s_0)\Delta T-v_0\Delta\pi\}, \end{aligned} \tag{31}$$

where

$$D^*=(1/\delta)(\overline{c}_0 l_{v0}-\tau_0F\phi Xl_{v+}), \tag{32}$$

If there is no osmotic pressure difference, Eq. 30 becomes

$$-J_v=D^{e}\Delta\ln T, \tag{33a}$$

$$D^{e}=(\overline{e}_0-s_0T_m)D^*. \tag{33b}$$

Moreover, if there is no temperature difference, Eq. 30 becomes

$$-J_v=L_p\Delta\pi, \tag{34a}$$

$$L_p=-v_0D^*, \tag{34b}$$

where L_p is the hydraulic permeability.

Therefore, if we experimentally obtain the values of D and D^*, we can estimate the value of $(\overline{e}_0-s_0T_m)$ or $(\overline{\overline{s}}_0-s_0)$:

$$\begin{aligned} (\overline{e}_0-s_0T_m)&=(\overline{\overline{s}}_0-s_0)T_m \\ &=D^{e}/D^* \\ &=-v_0D^{e}/L_p. \end{aligned} \tag{35}$$

Conclusions

(1) The equations of nonisothermal membrane phenomena derived using a set comprising an energy flux and the coupled

logarithmic temperature difference are practically the same as the approximate equations derived using a set comprising an entropy flux and the coupled-temperature difference in the experimental errors.

(2) The thermal membrane potential could also be expressed as the sum of the thermal-diffusion potential in the membrane phase and the Donnan potentials at both interfaces between the membrane and the external solutions.

A part of this work was reported at Membrane Symposium in Kyoto, 1994.

List of Symbols

The overbar refers to the membrane phase and the subscripts +, −, and 0 refer to cations, anions, and water molecules respectively.

a_i	activity of component i
c_i	concentration of component i (mol cm^{-3})
D	thermoosmotic coefficient defined by Eq. 27b
D^{e}	thermoosmotic coefficient defined by Eq. 27a
$\bar{e}_i$	transported energy per mole of component i in the membrane phase (J mol^{-1})
J_{e}	energy flux (J cm^{-2} s^{-1})
J_i	mass flux of component i (mol cm^{-2} s^{-1})
J_{q}	heat flux (J cm^{-2} s^{-1})
J_{s}	entropy flux (J cm^{-2} s^{-1})
J_{v}	volume flux (cm^{-2} s^{-1})
L_{e}	electric permeability: $\sum_i \sum_i z_i z_i L_{ij}$
L_{p}	hydraulic permeability (cm Pa^{-1} s^{-1})
$\lvert L \rvert$	determinant of matrix $L_{\alpha\beta}$
$\lvert L \rvert_{\alpha\beta}$	appropriate cofactor
$L_{\alpha\beta}$	phenomenological coefficient
l_{ij}	coefficient defined by Eq. 30a
$l_{\mathrm{v}i}$	coefficient defined by Eq. 30b
P	pressure (Pa)
$R_{\alpha\beta}$	phenomenological coefficient defined by Eq. 5a
$r_{\alpha\beta}$	phenomenological coefficient defined by Eq. 5b
$\lvert r \rvert_{\alpha\beta}$	appropriate cofactor
s_i	partial molar entropy of component i (J K^{-1} mol^{-1})
$\bar{\bar{s}}_i$	mean transported entropy per mole of component i in the membrane (J K^{-1} mol^{-1})
T	absolute temperature (K)
T_{m}	mean temperature: $T+\Delta T/2$ (K)
t_i	transport number of component i
v_i	partial molar volume of component i (cm^3 mol^{-1})
α	coefficient defined by Eq. 18b
α^*	coefficient defined by Eq. 18a
Δ	difference across the membrane
$\Delta\psi_{\mathrm{td}}$	thermal-diffusion potential (V)
$\Delta\psi_{\mathrm{e}}$	Donnan potential (V)
δ	thickness of the membrane (cm)
η	thermoelectric coefficient defined by Eq. 15c
η^*	thermoelectric coefficient defined by Eq. 15b
μ_i	chemical potential of component i (J mol^{-1})
μ_i^0	standard chemical potential of component i (J mol^{-1})
$\tilde{\mu}_i$	total chemical potential of component i (J mol^{-1})
π	osmotic pressure (Pa)
τ_i	reduced transport number of component i (mol C^{-1})
ϕX	effective concentration of fixed charges (mol cm^{-3})
ψ	electric potential (V)

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