Thermal membrane potential and thermoosmosis across charged membranes

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Abstract – When different temperatures are given to simple electrolyte so-
lutions on both side of a membrane, there appears an electrostatic poten-
tial, and osmotic flow of water occurs through the membrane. Thermal mem-
brane potential was determined by flushing two solutions having different
temperatures on the two surfaces of a thick membrane to remove diffusion
layers. Thermoosmotic flow was observed using a capillary. The effective
temperature difference working for thermoosmosis was estimated by measuring
the thermal membrane potential across the membrane. Experimental data thus
obtained were compared with a theory based on nonequilibrium thermodynamics.

INTRODUCTION

When two solutions of a simple electrolyte are placed on both sides of a membrane and no elec-
tric current is passing through the membrane, various phenomena such as membrane potential,
solute flux, solvent flux, etc. are simultaneously found. The driving force for those pheno-
mena is also various: concentration difference, pressure difference, temperature difference,
etc. Although individual phenomenon has been studied in detail, it is most important to
study all these related phenomena on the basis of a common theory. We have been working to
understand various membrane phenomena observed using a simple membrane when there is no
electric current and the hydrostatic pressures are equal, consistently based on a nonequilib-
rium thermodynamics(refs. 1-15). In this paper, our works on nonisothermal membrane pheno-
mena are summerized(refs. 1-9).

The membranes used in the present work are mainly sulfonated polystyrene-collodion interpoly-
mer membranes, which can be regarded as a kind of polyelectrolyte solution. A charge-mosaic
membrane made of pentablock copolymer, which is composed of cation- and anion-exchange ele-
ments and, consequently, has very high permeability for simple electrolytes, is also used for
studying the interaction between solute flux and water flux(ref. 16). The electrolyte solu-
tions placed on both sides of those membranes are generally 1-1 electrolytes.

In literature including our own works, thermal membrane potential is always found to be posi-
tive at the hot side for cation permselective membranes and negative for anion permselective
membranes, respectively.

Concerning the direction of thermoosmosis, however, the conclusions reported in literature
are contradictory. In case of charged membranes the direction of thermoosmosis through mem-
brane is mostly from the cold side to the hot side(refs. 2,5,9,17,18). For noncharged and/or
low charged membranes, however, the direction of thermoosmosis in water or aqueous solutions
is from the hot side to the cold side(refs. 17,19-23). Moreover, it was observed that the
direction of thermoosmosis also changes with change in temperature of external solutions
(refs. 24,25), pore size of membranes(refs. 19,26), and solvent(ref. 21). The magnitude of
the thermoosmotic coefficient changes with the change in the mean temperature of both exter-
nal solutions(refs. 17,20,22,23,25,27,28), and also with the salt concentration(refs. 5,9,21,
27,28).

In closed salt solution systems having no membrane, solvent(water) moves toward the hot side
and solute(potassium chloride, sodium chloride, etc.) towards the cold side under a tempera-
ture gradient(ref. 29).

The permeation of electrolyte through membranes due to temperature difference was so small
that the change of salt concentration could not be found when dealing with charged membranes.
When the membrane used was a charge-mosaic membrane, electrolytes could pass through
the membrane so easily that the direction of electrolyte was found to be from the cold side
to the hot side, in agreement with thermal membrane potential.

BASIC EQUATION OF MEMBRANE PHENOMENA

Applying nonequilibrium thermodynamics to ion transport processes with no chemical reaction, in mechanical equilibrium, the entropy production σ may be given by(refs. 30,31)

$$-T\sigma = J_s \cdot \text{grad}\, T + \sum_i J_i \cdot \text{grad}\, \tilde{\mu}_i \tag{1}$$

where

$$\tilde{\mu}_i = \mu_i + v_i P + z_i F\psi \tag{2}$$

J_s is the total entropy flux and J_i is the absolute mass flux. In addition $\tilde{\mu}_i$ is the chemical potential including contributions due to external forces, μ_i the chemical potential depending on temperature and composition, v_i the partial molar volume, z_i the charge number of component i, P the pressure, F the Faraday constant, T the absolute temperature, and ψ is the electrostatic potential. Thus, the phenomenological equations for the fluxes relative to membrane are given by

$$-J_s = \bar{L}_{ss}\text{grad}\, \bar{T} + \sum_i \bar{L}_{si}\text{grad}\, \tilde{\mu}_i \tag{3}$$

$$-J_i = \bar{L}_{is}\text{grad}\, \bar{T} + \sum_j \bar{L}_{ij}\text{grad}\, \tilde{\mu}_j \tag{4}$$

where the parameters in the membrane phase are denoted by a overbar.

Let us assume that all gradients in the membrane are in the x direction perpendicular to the membrane surfaces and, at steady state, temperature T, and general chemical potential, $\tilde{\mu}_i$, at points $x = 0$ and $x = \delta$ in the membrane(at opposite surfaces of the membrane), are equal to those in the contiguous solutions. That is,

$$\Delta\tilde{\mu}_i = \tilde{\mu}_i(\delta) - \tilde{\mu}_i(0) = \bar{\tilde{\mu}}_i(\delta) - \bar{\tilde{\mu}}_i(0) = \Delta\bar{\tilde{\mu}}_i \tag{5}$$

$$\Delta T = T(\delta) - T(0) = \bar{T}(\delta) - \bar{T}(0) = \Delta\bar{T} \tag{6}$$

where Δ shows the difference between two fluid phases on either side of the membrane. By solving eqs.(3) and (4) for forces and integrating them from one side of the membrane to the other, keeping the fluxes constant, we have(refs. 2,8,32,33)

$$-J_s = L_{ss}\Delta T + \sum_i L_{si}\Delta\tilde{\mu}_i \tag{7}$$

$$-J_i = L_{is}\Delta T + \sum_j L_{ij}\Delta\tilde{\mu}_j \tag{8}$$

where $L_{\alpha\beta}$ is the permeability coefficient of the membrane of finite thickness.

If $\Delta T = 0$, from eq.(8) we have

$$-J_i = \sum_j L_{ij}\Delta\tilde{\mu}_j \qquad \text{or} \qquad -\Delta\tilde{\mu}_j = \sum_i R_{ji}J_i \tag{9}$$

For solvent flux, J_0, that is the osmotic flow through the membrane, we have(ref. 6)

$$-J_0 = (1/R_{00})\Delta\mu_0 + \sum_i (R_{0i}/R_{00})J_i \tag{10}$$

and electric current, I, can be written as

$$I = \sum_i z_i F J_i \tag{11}$$

The physical quantities which characterized the membrane properties are also written as

$$t_i = (z_i F J_i/I)_{\Delta T=0, \Delta P=0, \Delta\mu_i=0} \tag{12}$$

$$\tau_i = (J_i/I)_{\Delta T=0, \Delta P=0, \Delta\mu_i=0} \tag{13}$$

$$\tau_0 = (J_0/I)_{\Delta T=0, \Delta P=0, \Delta\mu_0=0} = -(1/R_{00})\sum_i' (R_{0i}t_i/z_i F) \tag{14}$$

where the sum $\sum'$ is taken over all ionic species without water.

If the membrane is ideally permselective for component i, i.e., $t_i = 1$, the value of R_{0i}/R_{00}, which means the interaction between water and component i, can be directly obtained by measuring electroosmosis. Here, we would like to point out that the interactions between water and salt fluxes, R_{0i}/R_{00}, are most important to understand the osmotic flow of water.

The membrane potential can be calculated from the condition $I = 0$ and $\Delta P = 0$(ref. 1). That is,

$$-\Delta\psi = \eta\Delta T + \sum_i \tau_i \Delta\mu_i \tag{15}$$

where the thermoelectric potential coefficient is

$$\eta = \sum_j z_j L_{js} / \sum_i \sum_j z_i z_j L_{ij} F \tag{16}$$

and the reduced transport number of species i is

$$\tau_i = \sum_j z_j L_{ji} / \sum_i \sum_j z_i z_j L_{ij} F \tag{17}$$

Equation (17) is derived from eq.(13) using the Onsager reciprocal relationship $L_{ij} = L_{ji}$. Moreover, if the transported entropy $\bar{\bar{s}}_j$ is defined in terms of the phenomenological coefficients(refs. 32-34)

$$L_{is} = \sum_j L_{ij} \bar{\bar{s}}_j \tag{18}$$

from eq.(16) we have(ref. 6)

$$\eta = \sum_j \tau_j \bar{\bar{s}}_j \tag{19}$$

$\Delta\mu_i$ in eq.(15) is composed of two terms due to the temperature difference and due to the composition:

$$\Delta\mu_i = -s_i \Delta T + (\Delta\mu_i)_T \tag{20}$$

where

$$s_i = s_i^\circ - R \ln a_i - RT(\partial \ln a_i / \partial T) \tag{21}$$

s_i is the partial molar entropy of component i.

Substituting eqs.(19) and (20) into eq.(15), we have(ref. 6)

$$-\Delta\psi = \sum_i \tau_i \{ (\bar{\bar{s}}_i - s_i)\Delta T + (\Delta\mu_i)_T \} \tag{22}$$

Similarly, for the mass flux of component i we have

$$-J_i = \sum_j (L_{ij} - \tau_i \tau_j F^2 L_e) \{ (\bar{\bar{s}}_j - s_j)\Delta T + (\Delta\mu_j)_T \} \tag{23}$$

where L_e is the electric permeability(refs. 35,36):

$$L_e = \sum_i \sum_j z_i z_j L_{ij} \tag{24}$$

In the case of $\Delta T = 0$ we have the well-known equation for concentration membrane potential,

$$-\Delta\psi = \sum_i \tau_i (\Delta\mu_i)_T \tag{25}$$

The permeation velocity of salt is given by eq.(9) and from eq.(23) the water flux is given by

$$-J_0 = \sum_j (L_{0j} - \tau_0 \tau_j F^2 L_e)(\Delta\mu_j)_T \tag{26}$$

which is equivalent to eq.(10). $\Delta\psi$ and J_s are not discussed in this paper but a brief discussion will be given to J_0 at $\Delta T = 0$ in relation to the nonisothermal osmosis.

In nonisothermal systems and also if there is no concentration difference on both sides of membrane, the volume flux, $J_V = \sum_i v_i J_i$, due to ΔT (thermoosmosis) may be calculated from eq. (23) as(ref. 8)

$$-J_V = D\Delta T \tag{27}$$

where

$$D = \sum_i v_i \sum_j (L_{ij} - \tau_i \tau_j F^2 L_e)(\bar{\bar{s}}_j - s_j) \tag{28}$$

The above equations can be applied to every systems, but in the following the application of the equations is limited to 1-1 electrolyte systems with cation permselective membranes for simplicity, except specified cases.

INTERACTION BETWEEN IONS AND WATER

Volume flow is observed through a membrane if two solutions of different concentrations of an electrolyte are separated by the membrane. However, the volume flow is not always proportional to the difference in the osmotic pressure on the two sides of the membrane if the membrane has fixed charges. Such anomalous membrane phenomena are caused by a strong interaction between the flows of ions and water. The reduced transport number of water is a measure of the interaction. From eq.(15) the reduced transport number of water can be written as

$$\tau_0 = -(R_{0+}/R_{00})t_+ + (R_{0-}/R_{00})t_- \tag{29}$$

As seen from eq.(10) R_{0+}/R_{00} means the interaction between cation and water or the number of moles of water accompanied with one mole of transported ions. If the membrane is ideally permselective for counterions, we can obtain the value of R_{0+}/R_{00} or R_{0-}/R_{00} from the electroosmotic experiments. These values are approximately inversely proportional to the mobilities of these ions(ref. 13). In the case $I = 0$, from eq.(10) the solvent flux can be written as

$$-J_0 = (1/R_{00})\Delta\mu_0 + (R_{0+}/R_{00} + R_{0-}/R_{00})J_\pm \tag{30}$$

where $J_\pm$ is the salt flux. Since $\Delta\mu_0$ is proportional to the concentration difference, $c'' - c'$, $\log[-J_0 - (R_{0+}/R_{00} + R_{0-}/R_{00})J_\pm]$ must be linear to $\log c'$ with the slope of unity.

Figure 1 shows examples of the solvent flux through sulfonated polystyrene-collodion interpolymer membrane i-m in solution of various electrolytes where the concentration ratio of two solutions $c''/c' = 8$. In solutions of sodium chloride and lithium chloride, the so-called negative osmosis was observed because the second term of eq.(30) becomes larger than the first term. Figure 2 shows the relationship between the calcuted values of $\log [-J_0 - (R_{0+}/R_{00} + R_{0-}/R_{00})J_\pm]$ and the electrolyte concentration. All the plots are found to be linear with a slope of approximately unity, as expected from the theory.

Similarly, the water flux through charge-mosaic membranes are shown in Fig. 3. In the range 0.001 to 0.1 mol/dm^3, negative osmosis is shown for potassium chloride, sodium chloride, and lithium chloride solutions because of the high salt fluxes(ref. 14).

Thus, the interaction between ions and water plays an important role on solvent flux or volume flux across membranes. Anomalous
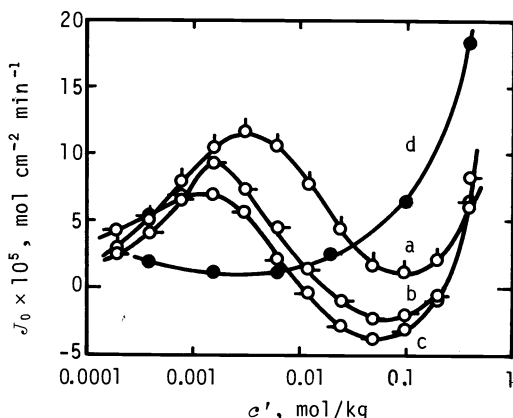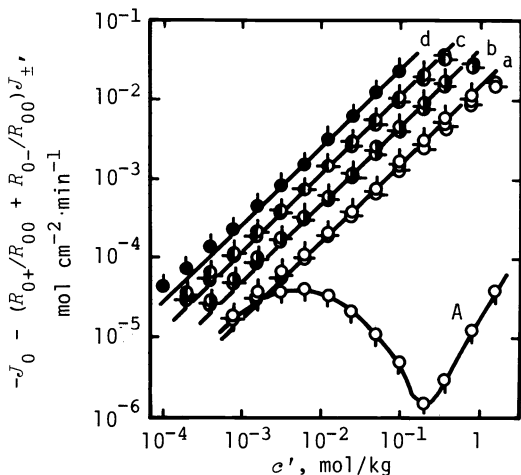

Fig. 1. Examples of solvent flow through membranes in solution of various electrolytes: $c''/c' = 8$; i-m: a, KCl; b, NaCl; c, LiCl; collodion membrane: d, KCl(ref. 10). Experiments at $c''/c' = 2$ and 4 are similar.

Fig. 2. The dependence of $-J_0 - (R_{0+}/R_{00} + R_{0-}/R_{00})J_\pm$ on molality of various electrolytes for membrane i-m(ref. 10). c''/c': a, 2; b, 4; c, 8; d, 16. Electrolytes: ●, KCl; ○, NaCl; –○, LiCl. A, the dependence of J_0 on molality of KCl at $c''/c' = 2$.
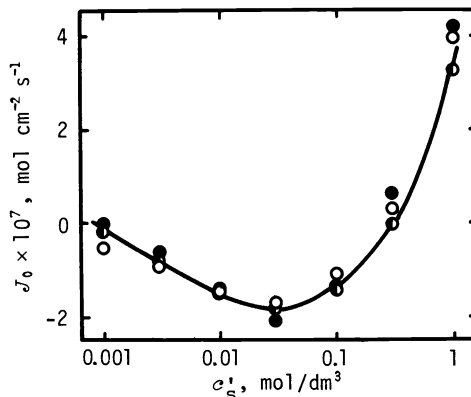

Fig. 3. Water fluxes, J_0, through charge-mosaic membrane TUN-1002-QS against lower electrolyte concentration, c_s'. Electrolytes: ○, KCl; ●, NaCl; ◐, LiCl. $c_s''/c_s' = 2$(ref. 14).

osmosis and negative osmosis through low charged membranes and charge-mosaic membranes can well be explained by eq.(30)(refs. 10-12,37,38).

THERMAL MEMBRANE POTENTIAL

If there is no difference in molalities of electrolyte across the membrane, from eq.(15) $-\Delta\psi/\Delta T$ is given by(refs. 1,38,39)

$$-\Delta\psi/\Delta T = \eta - \sum_i \tau_i \{s_i^\circ - R \ln a_i - RT(\partial \ln a_i/\partial T)\}$$

$$\approx \eta - \sum_i \tau_i (s_i^\circ - R \ln a_i) \tag{31}$$

If the membrane is ideally permselective for counterions, i.e., $t_+ = 1$, from eq.(31) we have

$$-\Delta\psi/\Delta T = (R/F)\ln a_+ + \alpha_+ \tag{32}$$

for cation-exchange membranes, where

$$\alpha_+ = \eta - s_+^\circ/F - \tau_0 s_0 \tag{33}$$

Membrane potential in nonisothermal systems was measured by flushing the two solutions having different temperatures on the two surfaces of a thick membrane to remove diffusion layers(ref. 1). Membrane potential cell is schematically shown in Fig. 4. The nozzle of the inlet tube, whose internal diameter was 2 to 3 mm, was fixed at a position 2 to 3 mm apart from the membrane surface. While in isothermal systems a reproducible stationary membrane potential was observed at relatively low flow rates of electrolyte solutions (60-150 cm^3/min) and with thin membranes, in nonisothermal systems high flow rates (250-300 cm^3/min) and thicker membranes (of about 1 mm thickness) were required to obtain reproducible membrane potentials independent of the flow rate. An example of the dependence of membrane potential on flow rate is shown in Fig. 5.
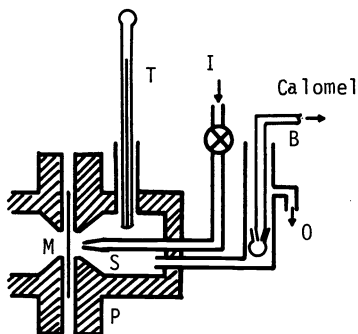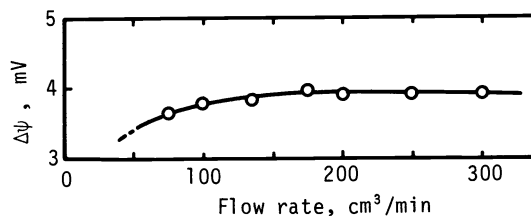

Fig. 5. The influence of flow rate on membrane potential for heterogeneous cation-exchange membrane M-10/0 at 0.1 mol/kg KCl solution(ref. 1). Membrane thickness, 1.13 mm; ΔT, 10 K.

Fig. 4. Membrane potential cell(ref. 1). B, salt bridge; I, solution inlet; M, membrane; O, solution outlet; S, solution; T, thermometer.

In the range of small temperature differences (< 10 K), linear relationships were observed between $\Delta\psi$ and the temperature difference, ΔT(refs. 1-3). The electrical potential of the hot side solution was always positive for cation permselective membranes and negative for anion permselective membranes. These phenomena mean that ions are forced to move from the hot side to the cold side across a membrane.

In Figs. 6 and 7, the temperature coefficient of the thermal membrane potential, $-\Delta\psi/\Delta T$, with cation-exchange membranes is plotted as a function of activities of electrolytes(refs. 3,40). The absolute value of $-\Delta\psi/\Delta T$ decreases with increasing ionic radius of hydrated alkali metal ions. As shown by eq.(33), α_+ is made of three terms: η, s_+°/F, and $\tau_0 s_0$. The value of s_+° are known as the molar entropy of ions referred to that of hydrogen ion and the value of s_0 may be approximated by the molar entropy of water, i.e., $s_0 = 3.99$ J K^{-1} mol^{-1}, neglecting the effect of hydration of ions on the molar entropy of water(ref. 41). The value of τ_0 can be obtained by the measurement of electroosmosis. Thus, using eq.(33) we can calculate values of pure thermoelectric coefficient η. These values are also shown in Tables 1 and 2. The value of η increases with increasing the mobility of counterions. In general, the absolute value of $-\Delta\psi/\Delta T$ becomes high when the water content of the membrane is low, because τ_0 is small and the value of the transported entropy of counterions $\bar{s}_+$ would be much smaller. For anion-exchange membranes(ref. 3), phospholipid bilayer films(refs. 40,

42), and anion permselective liquid membranes(refs. 43-45), the theory agreed with experi-
mental results.

For polyvalent type electrolyte solutions we have

$$-\Delta\psi/\Delta T = (R/z_+F)\ln a_+ + \alpha_+ \tag{34}$$

for cation-exchange membranes, where

$$\alpha_+ = \eta - s_+^\circ/z_+F - \tau_0 s_0 = (\bar{\bar{s}}_+ - s_+^\circ)/z_+F + \tau_0(\bar{\bar{s}}_0 - s_0) \tag{35}$$

The slopes of the temperature coefficient of thermal membrane potential, $-\Delta\psi/\Delta T$, against
logarithmic activities of counterions in the external solution were predicted to be $R/2F$ for
2-1 electrolytes with cation-exchange membranes and $-R/2F$ for 1-2 electrolytes with anion-
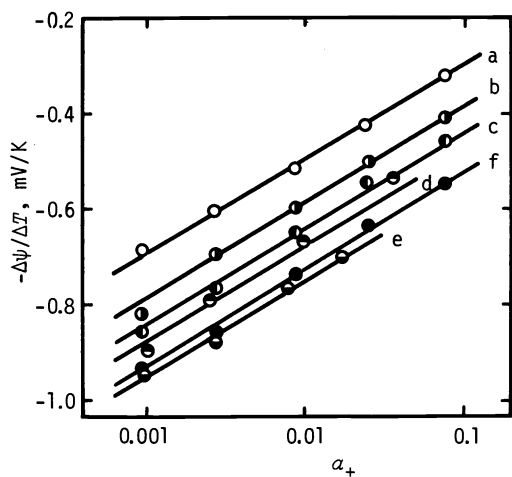exchange membranes, respectively(ref. 6).

Fig. 6. The effect of counterions on the
temperature coefficient of the membrane
potential, $-\Delta\psi/\Delta T$, for cation-exchange mem-
brane M-10/0(ref. 3). Electrolytes: a, Li
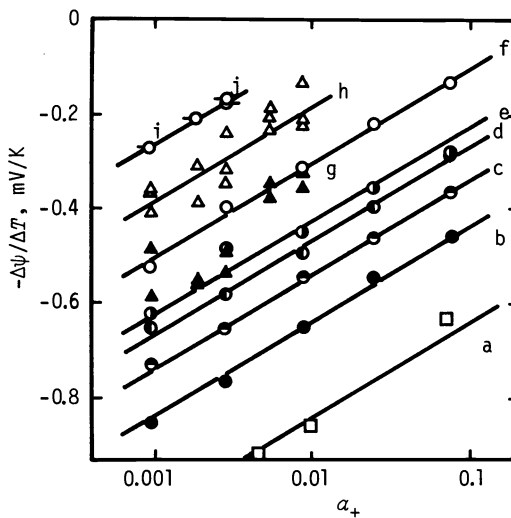Cl; b, NaCl; c, KCl; d, RbCl; e, CsCl; NH₄
Cl.

Fig. 7. Temperature coefficients of the mem-
brane potential, $-\Delta\psi/\Delta T$, for various cation-
exchange membranes: Notations are the same
shown in Table 2(refs. 3,5,40). a, in NaCl
solutions

If the membrane is not ideally permselective,
the transport number t_i lower than unity must
be taken into account. If experimental value
of t_i is introduced into eq.(31), the experi-
mental data for thermal membrane potential
can be explained. In particular, if a mem-
brane is a charge-mosaic membrane which is
composed of ideal   cation- and anion-ex-
change elements, η can be written as the sum
of the combination from two parts:

$$\eta = t_+\eta^c + t_-\eta^a$$

$$= (t_+\bar{\bar{s}}_+^c - t_-\bar{\bar{s}}_-^a)/F + \tau_0^c s_0^c + \tau_0^a s_0^a \tag{36}$$

where the superscripts c and a refer to a
cation permselective element and an anion
permselective element, respectively. Using
the overall transport number, t_i, we have
(ref. 7)

$$-\Delta\psi/\Delta T = (2t_+ - 1)(R/F)\ln a_\pm$$
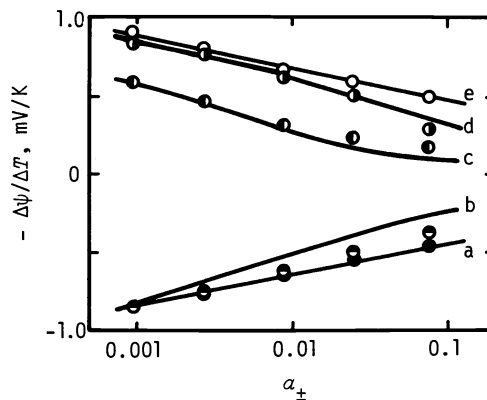
$$+ t_+\alpha_+^c + t_-\alpha_-^a \tag{37}$$

Fig. 8. The dependence of temperature coeffi-
cient, $-\Delta\psi/\Delta T$, on KCl molality(ref. 7).
Membranes: a, M-10/0; b, M-8/2; c, M-4/6; d,
M-3/7; e, M-0/10.

Heterogeneous cation- and anion-exchange membranes(M-10/0, M-0/10) and three heterogeneous mixed ion-exchange membranes(M-8/2, M-4/6, M-3/7) were prepared from 60% ion-exchange resin (cation-exchange resin: Amberlite XE-69 and anion-exchange resin: Amberlite XE-119 of about 300 mesh) and 40% poly(vinyl chloride) as a binder. The values of α_+^c and α_-^a can be obtained from the experimental data of thermal membrane potential with ideally permselective membranes M-10/0 and M-0/10. If the overall transport numbers of cations and anions in membranes are obtained, the values of $-\Delta\psi/\Delta T$ for membranes M-8/2, M-4/6, and M-3/7 can be calculated from eq.(37). In Fig. 8 the experimental data of thermal membrane potential are compared with the calculated values shown by the solid lines. Considering the experimental error, the agreement is good(ref. 7).

TABLE 1. The values of α_+, τ_0, and η with membrane M-10/0(ref. 3)

Counterion	$\tau_0 F$	α_+, mV/K	η, mV/K
Li^+	6.64	-0.10	4.48
Na^+	6.27	-0.20	4.94
K^+	6.05	-0.24	5.20
Rb^+	5.91	-0.29	5.24
Cs^+	6.04	-0.36	5.40
NH_4^+	5.88	-0.33	5.11

TABLE 2. The properties of charged membranes in KCl solutions(refs. 3,5,40)

	Membrane	Ion-exchange capacity[a]	Water content[b]	$\tau_0 F$ [c]	α_+ mV/K	η mV/K
a	Bilayer: egg yolk phosphatidylcholine[d]	–	–	–	-0.45	–
b	Heterogeneous: sulfonated polystyrene + PVC(40%), M-10/0	1.89	0.37	6.05	-0.24	5.20
c	Homogeneous: sulfonated polystyrene	1.03	0.59	6.63	-0.14	5.72
d	Homogeneous: sulfonated polystyrene (Nepton CR-61)	1.21	0.43	22.6	-0.07	17.36
e	Homogeneous: sulfonated phenol resin (Nepton CR-51)	0.95	0.43	9.61	-0.03	7.72
f	Interpolymer: sulfonated polystyrene + dried collodion(57%)	1.05	0.81	60	0.10	44.6
g	Liquid: sulfonated polystyrene(14.2%)	3.80	6.0	150	0.05	109.7
h	Liquid: sulfonated polystyrene(4.4%)	3.80	21.7	–	0.21	–
i	Oxidized collodion	–	3.3	–	0.26	–
j	Interpolymer: sulfonated polystyrene + dried collodion(95%)	0.25	2.0	550[e]	0.26	400

[a] The units are millimole per gram of dry membrane. [b] Measured as grams of water per gram of dry membrane. [c] In 0.01 M-KCl. [d] Measured in NaCl solutions. [e] Measured in 0.001 M-KCl.

THERMOOSMOSIS

Although the bulk solutions on the two sides of the membrane were fairly strongly stirred in thermoosmotic experiments as shown in Fig. 9, it is nearly impossible to remove the stagnant layers with respect to temperature on the membrane surfaces.

To study the thermoosmosis quantitatively, therefore, it is important to know the temperature difference working effectively on both sides of membrane, ΔT, which was always found to be different from the temperature difference in bulk solutions, ΔT_b. Since the relationship between thermal membrane potential and ΔT is already established, ΔT may be estimated by measuring thermal membrane potential. However, the thermal membrane potential in the thermo-osmotic cell cannot be measured while thermoosmosis is being observed. Therefore, the relationship between the temperature difference of bulk solutions, ΔT_b, and the thermal membrane potential is first observed under the same experimental conditions as when thermoosmosis was measured. Since the relationship between ΔT and thermal membrane potential is already known, we can determine the relationship between ΔT and ΔT_b at the experimental conditions for thermoosmosis. An example of the relationship between ΔT and ΔT_b for sulfonated polystyrene -collodion interpolymer membrane i-m-2 is shown in Fig. 10. The value of $\Delta T/\Delta T_b = 0.7$(ref. 6).

Figure 11 shows an example of J_v against ΔT plot. From the slope, we can determine the thermoosmotic coefficient, D. For membrane i-m-2, thermoosmotic coefficient is plotted against potassium chloride molality in Fig.12. The staircase-type behavior of the electrolyte
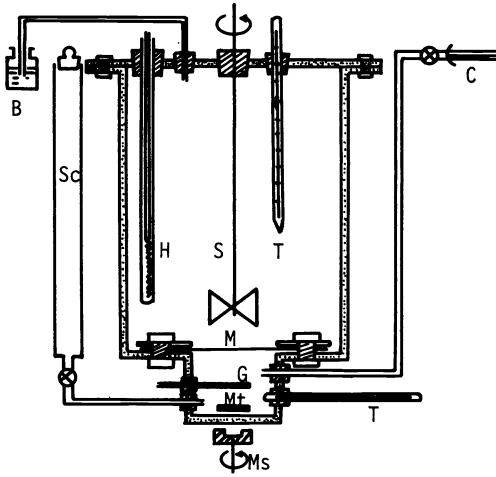
Fig. 9. The apparatus for measurement of thermoosmosis(ref. 5). B, bottle to adjust the solution level; C, capillary tube; G, glass tube for circulating cold water; H, heater; M, membrane; Ms, magnetic stirrer; Mt, magnetic stirrer tip; S, stirrer; Sc, solution container; T, thermometer.
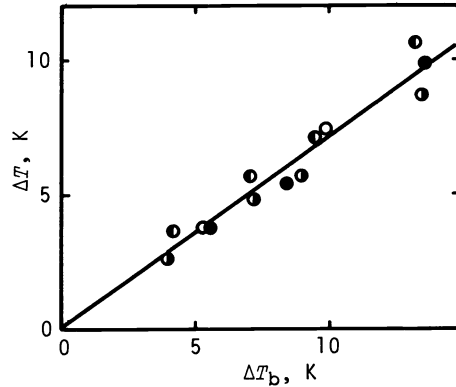
Fig. 10. The relationship between the effective temperature difference, ΔT, and the temperature difference of two bulk solutions, ΔT_b(ref. 5). KCl molalities(mol/kg): ○, 0.003; ◑, 0.01; ◒, 0.03; ●, 0.1.

concentration dependence of D in the figure may be commonly found for charged membranes(refs. 2,5,8,9).

If ions move from the hot side to the cold side across a membrane, the electrical potential of the hot side solution must be negative for cation permselective membranes. However, as mentioned above, it was observed that the electrical potential of the hot side solution was almost positive for cation permselective membranes and negative for anion permselective membranes. This means that the solute is forced to move toward the hot side.

If $\Delta \mu_i = 0$, from eq.(28) we have(refs. 8,9)

$$D = D° + D' + D'' \tag{38}$$

where

$$D° = \bar{c}_0 l_{v0} (\bar{\bar{s}}_0 - s_0)/\delta \tag{39}$$

$$D' = -\bar{c}_0 F\phi X l_{v\pm} (\bar{\bar{s}}_0 - s_0)/\delta \tag{40}$$

$$D'' = (\bar{c}_- + t_-\phi X) l_{v\pm} (\bar{\bar{s}}_s - s_s)/\delta \tag{41}$$

and

$$L_{ij} = \bar{c}_j l_{ij}/\delta \tag{42}$$

$$l_{vi} = \sum_j v_j l_{ji} \tag{43}$$

$$\bar{\bar{s}}_s = \bar{\bar{s}}_+ + \bar{\bar{s}}_- \qquad \text{and} \qquad s_s = s_+ + s_- \tag{44}$$

$$\bar{c}_+ = \bar{c}_- + \phi X \tag{45}$$

We may assume that $l_{v+} = l_{v-} = l_{v\pm}$ because electroosmosis and streaming potential tend to zero at high salt concentrations(ref. 13).

If a membrane has no fixed charges and the solution does not contain electrolyte, D' and D'' disappear and we have $D = D°$. If the membrane has fixed charges, the additional frictional interaction between fixed charges and water flow must be considered. The charge effect is predicted by D' of eq.(40). At the low concentration D' is large because τ_0 increases with decreasing concentration of electrolyte, while at high concentrations D' tends to zero. On the other hand, D'' is zero at low electrolyte concentrations. Since the transport number of coions increases with increasing concentration of electrolyte, the absolute value of D'' would monotonically increase with concentration.
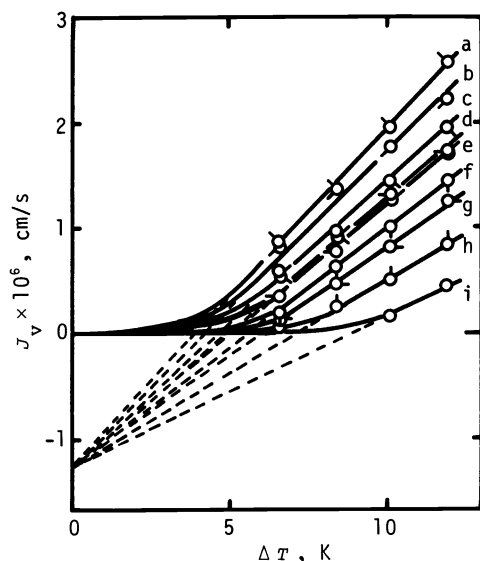
Fig. 11. The dependence of thermoosmotic flow on effective temperature difference with i-m-2(ref. 5). KCl molalities(mol/kg): a, 0.001; b, 0.003; c, 0.01; d, 0.02; e, 0.05; f, 0.1; g, 0.2; h, 0.5; i, 0.93.
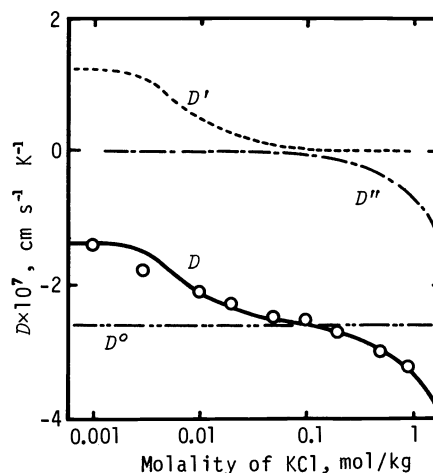
Fig. 12. The dependence of thermoosmotic coefficient, D, on KCl molality for membrane i-m-2(ref. 8).

The quantitative features of salt concentration dependence of D' and D'' are shown by broken lines in Fig. 12. Combination of three terms $D°$, D', and D'' can qualitatively reproduce the experimental salt concentration dependence of D in Fig. 12.

For noncharged membranes $D' = D'' = 0$ so that we have $D = D°$. Since $D° \propto (\bar{\bar{s}}_0 - s_0)$ which is the difference between the transported entropy in membrane and the entropy in external solution, the direction of thermoosmosis may be sensitive to the membrane materials. In hydrophobic membranes we speculate that $(\bar{\bar{s}}_0 - s_0)$ would be positive, so that the direction of thermoosmosis may be toward the cold side. In practice it was found that thermoosmosis occurred clearly toward the cold side when polytetrafluoroethylene membranes were used.

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