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THERMAL MEMBRANE POTENTIAL THROUGH CHARGED MEMBRANES IN ELECTROLYTE SOLUTIONS

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Measurements of the thermal membrane potential across cation and anion exchange membranes were carried out by using the same solution of various 1–1 electrolytes on both sides of the membrane. In all cases a good linear relationship was observed between the thermal membrane potential $\Delta\psi$ and the temperature difference ΔT. The slope of the linear plot varied with the concentration of the electrolyte. The value of $\Delta\psi/\Delta T$ versus logarithmic activity of the electrolyte plot was linear with a slope of $\pm R/F$ if the transport number of counterion was unity. The magnitude of $\Delta\psi/\Delta T$ was independent of coion species but dependent on counterions. These experimental results are in agreement with a theory presented previously. The thermal membrane potential caused by the direct effect of temperature difference and that by the indirect effect arising from the changes in ionic and water chemical potentials due to the temperature difference are separately discussed.

1. Introduction

It is well known that an electrostatic potential difference appears if there is a chemical potential or pressure difference across a membrane. They are called the membrane potential and streaming potential, respectively. A similar electrostatic potential difference, which is called the thermal membrane potential, also appears across a membrane if there is a temperature difference on both sides of the membrane [1,2]. That is, the fluxes of ions through a membrane are determined not only by the chemical potential gradient but also by the temperature gradient in the membrane. The membrane potential appearing across the membrane can be calculated from the condition that no current should pass through the membrane. The equation for the potential difference $\Delta\psi$ obtained in a previous paper [3] is

$$\begin{aligned}-\Delta\psi = {} & (2t_+ - 1)(RT/F)\ln[a_\pm(2)/a_\pm(1)] \\ & + (2t_+ - 1)(R\Delta T/F)\ln a_\pm(2) \\ & + \tau_0 RT\ln[a_0(2)/a_0(1)] + \tau_0 R\Delta T\ln a_0(2) \\ & + [t_+(\eta - s_+^0/F - \tau_0 s_0^0) \\ & + t_-(\eta + s_-^0/F - \tau_0 s_0^0)]\,\Delta T, \end{aligned} \quad (1)$$

where $a_\pm(1)$ and $a_0(1)$ are the mean activity of the electrolyte and the activity of water on one side of the membrane, respectively, t_+ is the transport number of cation, s_i^0 is the partial molar entropy which is the partial derivative of the standard chemical potential μ_i^0 with respect to temperature, τ_0 is the reduced transport number of water, and η is the differential thermoelectric potential. The physical meanings of these parameters were discussed in the previous paper in more detail. R, T, and F have the usual physical meanings.

If $c(1) = c(2)$, we may approximately assume $a_\pm(1) = a_\pm(2)$ and $a_0(1) = a_0(2)$ [4]. Then eq. (1) becomes

$$-\Delta\psi/\Delta T = (2t_+ - 1)(R/F)\ln a_\pm(2) + t_+\alpha_+ + t_-\alpha_-, \quad (2)$$

where

$$\alpha_+ = \eta - s_+^0/F - \tau_0 s_0, \quad (3a)$$

$$\alpha_- = \eta + s_-^0/F - \tau_0 s_0, \quad (3b)$$

and

$$s_0 = s_0^0 - R\ln a_0(2). \quad (4)$$

If the membrane is an ideal permselective membrane, i.e., $t_+ = 1$ or $t_- = 1$, from eq. (2) we have

$$-\Delta\psi/\Delta T = (R/F)\ln a_\pm(2) + \alpha_+, \quad (5a)$$

or

$$\Delta\psi/\Delta T = (R/F)\ln a_{\pm}(2) - \alpha_- . \qquad (5b)$$

It was reported in the previous paper that eqs. (2), (5a), and (5b) agree with the experimental results in KCl solutions for various ion exchange membranes. The membrane potential $|\Delta\psi|$ increases linearly with increasing temperature difference and the slope of $\Delta\psi/\Delta T$ versus $\log a_{\pm}(2)$ plot is $2.303R/F$ if the transport number of anion is unity. The intercept at $\log a_{\pm}(2) = 0$ gives α_+ or α_-.

As is clear from eqs. (5a) and (5b), the thermal membrane potential is caused by two effects of temperature. One is the direct effect of temperature difference on fluxes, which is expressed by a coefficient η. The other is the indirect effect arising from the changes in ionic and water chemical potential due to temperature change. The purpose of this paper is to report additional experimental data on thermal membrane potential using various charged membranes and various 1–1 electrolytes and to estimate the pure thermoelectric potential coefficient η. That is, if the values of α_+ or α_- can he determined for various ions, we can estimate the pure thermoelectric potential coefficient η using the values of s_+^0, s_-^0, and s_0 in literature. The value of τ_0 used in the above calculation can be determined from electroosmosis experiments.

2. Experimental

2.1. Membranes

The same heterogeneous cation and anion exchange membranes as used in the previous work [3] were employed in the present work. These membranes were prepared from ion exchange resin powder 60% and polyvinyl chloride (a copolymer containing vinyl acetate 5%) 40% as binder. In addition, some cation exchange membranes: homogeneous (C-2, C-3, and C-4), interpolymer (C-5), and liquid type (C-6 and C-7); and also a homogeneous anion exchange membrane (A-2), were employed. The interpolymer cation exchange membrane C-5 was prepared by the method of Neihof [5], by dissolving polystyrenesulfonic acid (43% of dried membrane) into collodion. Liquid membranes C-6 and C-7 were made by placing 14.2% and 4.4% solutions of potassium polystyrenesulfonate (KPSS) between two inert cellophanes. The degree of sulfonation of KPSS was 72.2% per styrene monomer. The changes in transport number of cation t_+ with KCl concentration for liquid membranes C-6 and C-7 are shown in fig. 1, as examples. These transport numbers were calculated from membrane potentials in KCl solutions with concentration ratio $c(2)/c(1) = 2$, using the following equation:

$$-\Delta\psi = (2t_+ - 1)(RT/F)\ln[a_{\pm}(2)/a_{\pm}(1)] . \qquad (6)$$

The transport numbers of counterion of other membranes are higher than 0.95 in 0.1–0.2 M KCl solutions. Therefore, these membranes may be practically treated as ideal permselective membranes.

2.2. Electrolytes

A series of chloride salts (LiCl, NaCl, KCl, RbCl, CsCl, and NH_4Cl) and a series of potassium salts (KF, KCl, KBr, and KI) were used to study the effect of counterion and coion species on thermal membrane potential.

2.3. Membrane potential cell and measurements

The membrane potential cell is similar to that reported previously [3]. That is:

$$\text{Temperature:}\quad \underbrace{\text{Hg/Hg}_2\text{Cl}_2\text{/satd.KCl/MX/}}_{T}\text{membrane/}$$

$$\underbrace{\text{/MX/}}_{T+\Delta T}\underbrace{\text{satd.KCl/Hg}_2\text{Cl}_2\text{/Hg}}_{T}, \qquad (7)$$

where MX is an electrolyte. A membrane was mounted between the half cells. The solution inlet and outlet as well as a mercury thermometer were inserted into each half cell. The electrolyte solution was flowed to remove

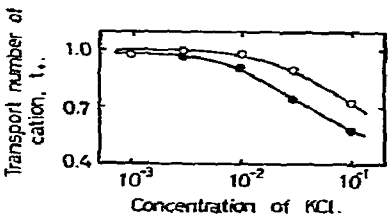

Fig. 1. Examples of the concentration dependence of transport number of cation. Membranes: (○) C-6; (●) C-7.

a diffusion layer on the membrane surfaces. The concentrations on both sides of the membrane were kept equal. The temperature on one side of the membrane, T, was kept at 20°C and the temperature on the other side of the membrane, $T + \Delta T$, was kept at a value between 10 and 30°C. Strictly speaking, the observed potential differences may include not only the electrical potential difference across the membrane but also a small thermal junction potential in solution. In this work, therefore, the temperature gradient is given only in a saturated KCl bridge, so that such a thermal junction potential may be negligible. The temperatures of both calomel electrode compartments were also kept at 20°C.

The thermal membrane potential is very sensitive to changes in membrane structure. That is, if several membrane samples are made from a sheet, they do not always give identical thermal membrane potentials. Thus, the reproducibility of the thermal membrane potential with changing membranes is not as high, as that of concentration membrane potentials. Therefore, when we study the effect of ion species on thermal membrane potential, the same membrane sample was used for all measurements and reproducible experimental data were obtained.

2.4. Electro-osmosis

The membrane was mounted between two 50 cm^3 compartments of a cell made of poly(methyl methacrylate) and equipped with magnetic stirrers, silver – silver halide electrodes, and capillaries for measuring volume flow. The silver–silver halide electrodes are reversible in all alkali halide solutions except in KF solution. All experiments were run in 0.01 M solutions of the electrolyte at 1.7 $\mathrm{mA/cm}^2$. At least two runs were made for each experiment, by changing the direction of flow. A DC Precision Current Supply type 2854 (Yokogawa Electric Works Ltd., Tokyo, Japan) was used. Concentration changes during experiments were in no case greater than 10% and volume flows due to concentration changes were assumed to be negligible. The reduced transport number τ_0, i.e., the number of moles of water flowing through the membrane per Faraday, was calculated neglecting the volume change of electrodes [6]. The reproducibility was within ±2%.

Since no reversible electrode is available for F^-, we employed the four-compartments cell [7] with cation exchange membrane C-1 as shown by

$$\mathrm{Ag/AgCl\cdot KCl}\ \underset{\substack{\text{cation}\\ \text{exchange}\\ \text{membrane}\\ \text{C-1}}}{//}\ \mathrm{KF}\ \underset{\substack{\text{sample}\\ \text{membrane}}}{//}\ \mathrm{KF}\ \underset{\substack{\text{cation}\\ \text{exchange}\\ \text{membrane}\\ \text{C-1}}}{//}\ \mathrm{KCl\cdot AgCl/Ag.} \qquad (8)$$

The volume change in the KF compartment is caused by two electro-osmotic flows, that is, by the flow through cation exchange membrane C-1 and by that through the sample (anion exchange) membrane. The former value was independently determined in the ordinary two-compartments cell with membrane C-1.

3. Results and discussion

The membrane potential $\Delta\psi$ for the cation exchange membrane C-1 varies linearly with the temperature difference ΔT between −10°C and 10°C, as was reported for KCl solutions in the previous paper [3]. Similar results were obtained in all electrolyte solutions. Examples of $\Delta\psi$ versus ΔT plots with a membrane in various electrolyte solutions are shown in fig. 2. The slopes, $\Delta\psi/\Delta T$ (mV/deg), determined are plotted as a function of activities of electrolytes. The plot gives a good straight line with the slope of $\pm 2.303R/F$ (0.1984 mV/deg) as shown in figs. 3 to 6. This is also in accord with the previous experimental results.

The effect of counterions on thermal membrane potential with cation exchange membrane C-1 is shown in fig. 3, where the coion is Cl^-. The temperature coefficient of the thermal membrane potential $\Delta\psi/\Delta T$ decreases with increasing ionic radius of hydrated alkali metal ions. The value of $\Delta\psi/\Delta T$ for NH_4^+ ion is intermediate between the values for Rb^+ and Cs^+.

The effect of coions on thermal membrane potential with cation exchange membrane C-1 is shown in fig. 4, where the counterion is K^+. It is evident that the effect of coions on thermal membrane potential is negligible.

The effect of counterions on thermal membrane potential with anion exchange membrane A-1 and K^+ coion is shown in fig. 5. The magnitude of $\Delta\psi/\Delta T$ increases with increasing molecular weight of halogen ions except for F^- ion. The effect of coions on $\Delta\psi/\Delta T$ with anion exchange membrane A-1 is also negligible, as shown in fig. 6. Moreover, the data of $\Delta\psi/\Delta T$ for various KCl solutions are shown in figs. 7 and 8. The variation of

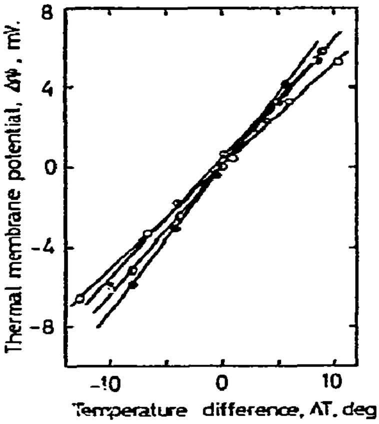

Fig. 2. Examples of thermal membrane potentials. Membrane: C-1. Concentration: 10^{-2} mol/kg of H_2O. Electrolytes: (○), LiCl; (◑), NaCl; (◒), KCl; (●). NH_4CL

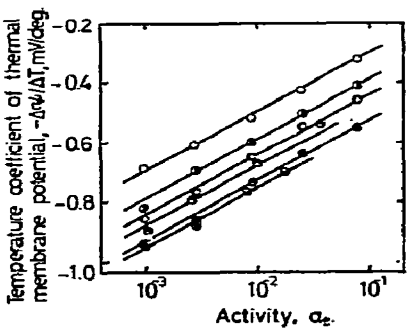

Fig. 3. The effect of counterions on the temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, for cation exchange membrane C-1. Electrolytes: (○) LiCl; (◑) NaCl; (◒) KCl; (◓) RbCl; (◐) CsCl; (●) NH_4CL

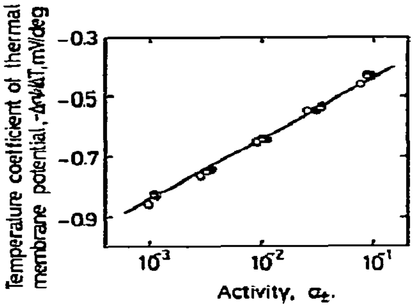

Fig. 4. The effect of coions on the temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, for cation exchange membrane C-1. Electrolytes: (○) KCl; (◑) KBr; (●) KI.

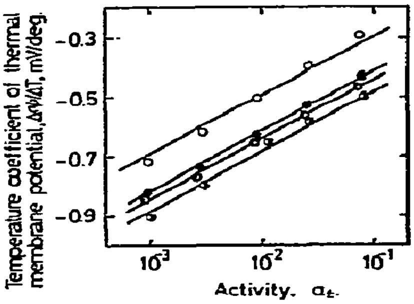

Fig. 5. The effect of counterions on the temperature coefficient of the membrane potential, $\Delta\psi/\Delta T$, for anion exchange membrane A-1. Electrolytes: (○) KF; (◑) KCl; (◒) KBr; (◓) KI.

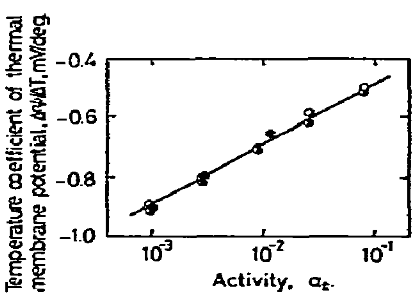

Fig. 6. The effect of coions on the temperature coefficient of the membrane potential, $\Delta\psi/\Delta T$, for anion exchange membrane A-1. Electrolytes: (○) LiCl; (◑) NaCl; (●) KCl.

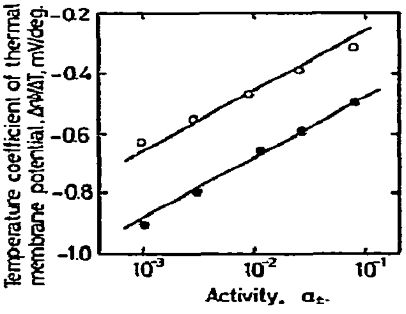

Fig. 7. Temperature coefficients of the membrane potential, $-\Delta\psi/\Delta T$ for various cation exchange membranes. Membranes: (●) C-1; (◐) C-2; (◒) C-3; (◑) C-4; (○) C-5; (●) C-6; (○) C-7.

Table 1
The properties of charged membranes in KCl solutions

Membrane	Type	Polyelectrolyte	Trade mark	Ion exchange capacity (meq/g of dry membrane)	Water content (g/g of dry membrane)	Reduced water transport number in 0.01 M solution, τ_0 (mol/F)	α_+ or α_- (mV/deg)	η (mV/deg)
Cation exchange membranes								
C-1	heterogeneous (binder: polyvinylchloride 40%)	polystyrenesulfonate	(ion exchanger: Amberlite XE-69)	1.89	0.37	6.05	−0.24	5.20
C-2	homogeneous	polystyrenesulfonate		1.03	0.59	6.63	−0.14	5.72
C-3	homogeneous	polystyrenesulfonate	Nepton CR-61	1.21	0.43	22.6	−0.07	17.36
C-4	homogeneous	phenolsulfonate resin	Nepton CR-51	0.95	0.43	9.61	−0.03	7.72
C-5	interpolymer (with dried Collodion 57%)	polystyrenesulfonate		1.05	0.81	60	0.10	44.6
C-6	liquid (polyelectrolyte 14.2%)	polystyrenesulfonate (degree of sulfonation: 72%)		3.80	6.0	150	0.05	109.7
C-7	liquid (polyelectrolyte 4.4%)	polystyrenesulfonate (degree of sulfonation: 72%)		3.80	21.7	–	0.21	–
Anion exchange membranes								
A-1	heterogeneous (binder: polyvinylchloride 40%)	polystyrene with quarternary ammonium	(ion exchanger: Amberlite XE-119)	1.53	0.47	−5.15	0.28	−4.02
A-2	homogeneous	polystyrene with quarternary ammonium	Nepton AR-111	0.79	0.36	−13.1	0.08	−9.95

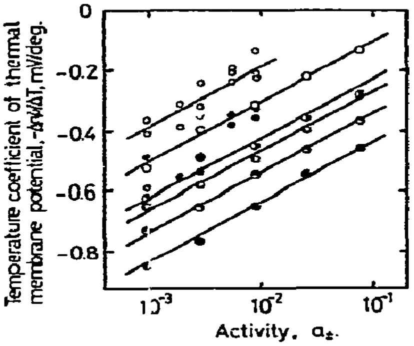

Fig. 8. The effect of anion exchange membranes on temperature coefficient of membrane potential, $\Delta\psi/\Delta T$. Membranes: (●) A-1; (○) A-2.

$\Delta\psi/\Delta T$ with changing membranes is as large as that with changing counterion species.

These experimental results are in agreement with the theoretical predictions. From eqs. (5a) and (5b) it is reasonable to admit that the temperature coefficient of thermal membrane potential is determined only by the counterions if those membranes are ideal.

As shown by eqs. (3a) and (3b), $\alpha_\pm$ is made of three terms, η, $s^0_\pm/F$, and $\tau_0 s_0$. The values of $s^0_\pm$ are known as the molar entropy of ions referred to that of H^+ ion and the value of s_0 may be approximated by the molar entropy of pure water, i.e., $s_0 \approx 16.7$ cal deg^{-1} mol^{-1}, neglecting the effect of the hydration of ions on the molar entropy of water [8]. The values of τ_0 are obtained by the measurement of electro-osmosis in tables 1 and 2. The direction of water flow through anion exchange membranes is opposite and that through cation exchange membranes is in the same direction as the electric current. Hence, the values of τ_0 with anion exchange membranes is negative, while that with cation exchange membranes is positive.

Thus, using eqs. (3a) and (3b) we can calculate values of the pure thermoelectric potential coefficient η for various membranes. These values are also shown in tables 1 and 2. The values of η, positive for cation exchange membranes and negative for anion exchange membranes, thus estimated are not the absolute but merely relative values since the conventional molar entropy of ions s^0_i are used in eqs. (3a) and (3b). However, it may be concluded that the pure thermal membrane potential due to temperature difference (η-term) is fairly large, though its effect is cancelled by the other effects arising from the changes in ionic and water chemical potentials with changing temperature in the observed thermal membrane potential. The values of η as shown in table 2 are found to be only slightly dependent on ionic species with an anion exchange membrane. In both cases, the value of η appears to be determined by ionic size. In the experimental range of this work, η may be treated as a constant independent of salt concentration since t_+ or $t_- = 1$.

Table 2
The values of $\alpha_\pm$, τ_0, and η with membranes C-1 and A-1

Counterion	α_+ or α_- (mV/deg)	τ_0 (mol/F)	η (mV/deg)
Membrane C-1			
Li^+	−0.10	6.64	4.82
Na^+	−0.20	6.27	4.96
K^+	−0.24	6.05	5.20
Rb^+	−0.29	5.91	5.24
Cs^+	−0.36	6.04	5.40
NH_4^+	−0.33	5.88	5.11
Membrane A-1			
F^-	0.06	−3.18	−2.14
Cl^-	0.28	−5.15	−4.02
Br^-	0.24	−6.48	−5.29
I^-	0.21	−10.36	−8.42

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