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Membrane Phenomena in Nonisothermal Systems: Part 3. Thermal Membrane Potential across Various Hydrophobic Anion-Exchange Membranes with 10 and 14% Divinylbenzene

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The thermal membrane potential across anion-exchange membranes having various hydrophobic anion-exchange groups was measured for various electrolyte solutions. A good linear relationship between the thermal membrane potential ($\Delta\psi$) and the logarithmic temperature difference ($\Delta\ln T$) was observed. The temperature coefficient of the thermal membrane potential ($\Delta\psi/\Delta\ln T$) was found to be a function of the logarithmic activities of ions with a slope of RT^c/F for 1-1 electrolytes and $RT^c/(2F)$ for 1-2 electrolytes, where T^c is the constant temperature of the solution on one side of the membrane. The absolute value of $\Delta\psi/\Delta\ln T$ decreased with increasing the molality of the external electrolyte solutions. The absolute value of $\Delta\psi/\Delta\ln T$ in KCl solutions was higher than that in KIO_3 solutions. For halide ions the order of the absolute values of the thermal membrane potential ($\Delta\psi$) was $Cl^- > Br^- > I^-$, which corresponds to the order of the values of the *B*-coefficient in the Jones–Dole expression for the viscosity of the solutions, but opposite to that of the conventional partial molar volume. For large oxoanions the order of the absolute values of $\Delta\psi$ was found to be $NO_3^- > IO_3^- > SO_4^{2-}$, which is opposite to the order of the *B*-coefficient as well as to that of the molar volume of these hydrated ions.

In nonisothermal systems mass transport across a membrane depends on the difference in the entropy of the components between the membrane phase and the external solution phase, that is, the difference in the state of components between them.

Nonisothermal membrane phenomena have been fairly studied using various ion-exchange membrane and electrolyte systems.[1—8] However, there have been few studies performed from the standpoint of a systematic view concerning the chemical composition of membranes. Therefore, in the present work the thermal membrane potential was measured with a series of membranes having anion-exchange groups of amines with different alkyl chain lengths. The hydrophobicity of alkylamines directly affects the state of water near to fixed charges of the membrane. In the range of small water content of membranes, the state of counterions would be largely influenced by the change in the hydrophobicity of the fixed charges, because the counterions are restricted near the fixed charges. Therefore, the thermal membrane potential would depend on the change in the hydrophobicity of fixed charges through a change in the state of counterions in the membrane. The purpose of this paper is to compare the theory presented in Part 1[9] with experimental data on the thermal membrane potential.

Equations of the Thermal Membrane Potential

Applying nonequilibrium thermodynamics with a dissipation function, including the product of the energy flux and the coupled force of the difference in logarithmic temperature ($\Delta\ln T$) to nonisothermal systems, a rigorous treatment of the thermal membrane potential ($\Delta\psi$) was presented as[9]

$$-\Delta\psi = \sum_{\mathrm{i}} \tau_i(\overline{e}_i - s_{\mathrm{i}}T_{\mathrm{m}})\Delta\ln T, \tag{1}$$

where T_{m} is the mean temperature ($T_{\mathrm{m}}=\Delta T/\Delta\ln T$), $\overline{e}_i$ the transported energy per mole of component *i* in the membrane, τ_i the reduced transport number, and s_i the partial molar entropy of component *i* in the external solution.

On the other hand, applying a dissipation function including the product of an entropy flux and the coupled force of the difference in temperature (ΔT) and assuming the entropy flux to be nearly constant, a familiar approximate expression was presented as

$$-\Delta\psi = \sum_{\mathrm{i}} \tau_i\left(\overline{\overline{s}}_i - s_i\right)\Delta T, \tag{2}$$

where $\overline{\overline{s}}_i$ is the mean transported entropy of component *i* in the membrane.[8]

The transported energy per mole of component *i* ($\overline{e}_i$) can be approximately written as

$$\bar{e}_i = \bar{\bar{s}}_i T_{\mathrm{m}}. \tag{3}$$

Substitution of Eq. 3 into Eq. 1 also gives Eq. 2. Moreover, Eq. 2 can be rewritten as

$$\begin{aligned} -\Delta\psi &= \tau_0 \left(\bar{\bar{s}}_0 - s_0\right) \Delta T + \sum_{\mathrm{i}}{}' \tau_i \left(\bar{\bar{s}}_i - s_i\right) \Delta T \\ &= -(\Delta\psi)_0 - (\Delta\psi)_{\mathrm{ion}}, \end{aligned} \tag{4}$$

where Σ' means summation without water, and $(\Delta\psi)_0$ and $(\Delta\psi)_{\mathrm{ion}}$ refer to the water term and the ion term in thermal membrane potential, respectively.

If the membrane is ideally perm-selective for anions, Eqs. 1 and 3 become[9)]

$$\begin{aligned} -\left(\frac{\Delta\psi}{\Delta \ln T}\right) &= \left(\frac{RT_{\mathrm{m}}}{z_- F}\right) \ln a_- + \alpha_-^*, \\ \alpha_-^* &= \left(\frac{1}{z_- F}\right) \left(\bar{e}_- - s_-^0 T_m\right) + \tau_0 \left(\bar{e}_0 - s_0 T_{\mathrm{m}}\right), \end{aligned} \tag{5}$$

or

$$\begin{aligned} -\left(\frac{\Delta\psi}{\Delta T}\right) &= \left(\frac{R}{z_- F}\right) \ln a_- + \alpha_-, \\ \alpha_- &= \left(\frac{1}{z_- F}\right) \left(\bar{\bar{s}}_- - s_-^0\right) + \tau_0 \left(\bar{\bar{s}}_0 - s_0\right). \end{aligned} \tag{6}$$

Here, R is the gas constant, F is the Faraday constant, s_-^0 is the standard partial molar entropy, and subscripts $-$ and 0 refer to anion and water, respectively.

From Eqs. 5 and 6 we obtain for 1-1 electrolytes

$$\frac{\Delta\psi}{\Delta \ln T} = \left(\frac{RT_{\mathrm{m}}}{F}\right) \ln a_- - \alpha_-^*, \tag{7}$$

$$\frac{\Delta\psi}{\Delta T} = \left(\frac{R}{F}\right) \ln a_- - \alpha_-, \tag{8}$$

and for 1-2 electrolytes[10)]

$$\frac{\Delta\psi}{\Delta \ln T} = \left(\frac{RT_{\mathrm{m}}}{2F}\right) \ln a_- - \alpha_-^*, \tag{9}$$

$$\frac{\Delta\psi}{\Delta T} = \left(\frac{R}{2F}\right) \ln a_- - \alpha_-. \tag{10}$$

The values of $\bar{e}_i$ and $\bar{\bar{s}}$ were estimated from the thermal membrane potential and thermoosmosis[11)] and nonisothermal membrane phenomena were analyzed using these data. Moreover, the validity of the approximation of Eq. 2 can be confirmed experimentally comparing plots of $\Delta\psi/\Delta \ln T$ and $\Delta\psi/\Delta T$ against $\ln a_-$.

In deriving the above equations the membrane phase is considered to be homogeneous. For heterogeneous membranes the observed value of phenomenological coefficients reflects an average value over the cross-section of the membrane if each one-dimensional flow due to the driving force at a local position in the membrane is small and the interference among their flows is negligibly small.

Experimental

1. Membranes. Two series of strong-base anion-exchange membranes having benzylamines quaternized with various alkyl chains and having 10% and 14% divinylbenzene (DVB) were prepared. The anion-exchange groups were benzyltrimethyl (M-1), benzyltriethyl (M-2), benzyltripropyl (M-3), benzyltributyl (M-4), and benzyltripentylammonium (M-5). Membranes M-1(10) and M-1(14) refer to those membranes having benzyltrimethylammonium and 10% DVB, and benzyltrimethylammonium and 14% DVB, respectively, where the number in the parentheses means the percent of DVB. The details concerning membrane preparation were reported in a previous paper.[12)] The basic properties of these membranes are summarized in Table 1. The transport numbers of counterions in membranes (t_-) were estimated from the concentration membrane potential ($\Delta\psi$) to be 0.03 mol kg^{-1}KCl/membrane/0.06 mol kg^{-1} and 0.1 mol kg^{-1} KCl/membrane/0.2 mol kg^{-1} KCl using

$$\Delta\psi = (2t_- - 1) \frac{RT}{F} \ln \left(\frac{a_\pm^{(2)}}{a_\pm^{(1)}}\right), \tag{11}$$

where $a_\pm$ is the mean activity of ions. In all membranes the transport numbers of anions were 1.00 for 0.03//0.06 mol kg^{-1} KCl and higher than 0.94 for 0.1//0.2 mol kg^{-1} KCl, as shown in Table 1.

2. Electrolytes. The reagents used for the preparations of KCl, KBr, KI, KNO_3, KIO_3, and K_2SO_4 solutions were of special grade from Wako Pure Chemical Industries Ltd.

3. Thermal Membrane Potential Cell. A thermal membrane potential cell was made of poly(vinyl chloride) resin, similar to one used in previous studies.[6,7)] A membrane was mounted between two half cells equipped with a solution inlet and an outlet just as the apparent thickness of the membrane becomes larger than the real thickness, as shown in Fig. 1.[7)] The apparent membrane thickness was about 0.5 mm. At a rate of 280 cm^3 min^{-1}, two solutions were flushed on both surfaces of the membrane through the solution inlet so as to remove the diffusion layers. The thermal membrane potential cell was constructed as

$$\begin{array}{lcc} & \mathrm{Hg/Hg_2Cl_2/satd.KCl/soln(1)} & \mathrm{/membrane/soln(2)/satd.KCl/Hg_2Cl_2/Hg.} \\ & \underbrace{\qquad\qquad}\underbrace{\qquad\qquad} & \underbrace{\qquad\qquad}\underbrace{\qquad\qquad} \\ \text{Temp :} & T \qquad\qquad T & T+\Delta T \qquad\qquad T \\ \text{Potential :} & \psi & \psi + \Delta\psi \end{array} \tag{12}$$

The temperature on one side of the membrane (T) was kept at T^{c}=303.2 K and that on the other side (T+ΔT) was varied from 293.2 to 313.2 K. In this case T_{m} varied with ΔT. We thus used

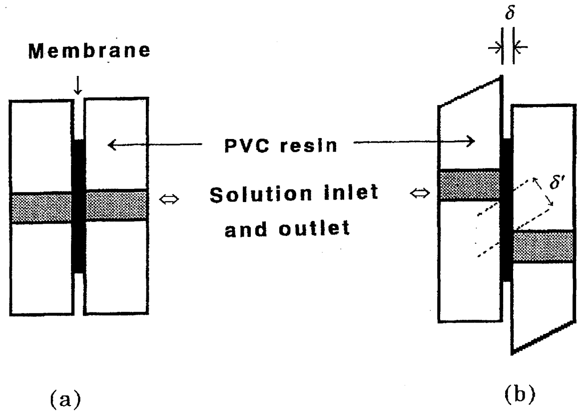

Fig. 1. Schematic diagram of membrane thickness and apparent membrane thickness: (a) projection from the side, and (b) projection from the top: δ is the membrane thickness and δ' is the apparent membrane thickness ($\delta' > \delta$).

Table 1. Properties of Anion-Exchange Membranes

Membranes	ϕ–CH$_2$–N≡R$_3$ R:	Transport number[a)] of Cl$^-$	Water content[b)] (g-H$_2$O/g-dry membrane with Cl$^-$-form)	Ratio of water molecules to the ions (mol H$_2$O/mol total ions)	
				Cl$^-$-form	IO$_3$$^-$-form
M-1(10)[c)]	–CH$_3$	0.98	0.33	4.35	5.31
M-2(10)	–C$_2$H$_5$	0.98	0.36	6.76	8.07
M-3(10)	–C$_3$H$_7$	0.98	0.32	7.41	8.56
M-4(10)	–C$_4$H$_9$	0.96	0.25	6.88	8.52
M-5(10)	–C$_5$H$_{11}$	0.95	0.15	4.79	7.98
M-1(14)	–CH$_3$	0.97	0.27	4.08	4.83
M-2(14)	–C$_2$H$_5$	0.97	0.27	6.25	7.17
M-3(14)	–C$_3$H$_7$	0.96	0.23	6.73	7.31
M-4(14)	–C$_4$H$_9$	0.95	0.17	5.62	6.61
M-5(14)	–C$_5$H$_{11}$	0.94	0.12	4.44	5.19

a) Estimated from the membrane potential in 0.1//0.2 mol kg^{-1} KCl solutions. b) g-H$_2$O/g-dry membrane without counterions. c) ( ): % DVB.

a constant temperature (T^c) of 303.2 K as the average value of the mean temperatures. Then, the values of T_m/T^c were 0.983 to 1.016. The thermal membrane potential was measured with a digital electrometer (TR-8411; Advantest Co. Japan) which was carefully electrically shielded from any external field and with a personal computer (PC-9801EX; Nippon Electric Co., Ltd.) to record data.

4. Measurements of Electroosmosis. The membrane was mounted between two compartments made of poly(vinyl chloride) resin and equipped with magnetic stirrers, silver–silver chloride electrodes, and capillaries for measuring the volume flow for KCl solutions, and a four-compartment cell was used for the other solutions.[13,14)] All of the experiments were run in 0.1 mol kg^{-1} solutions of electrolyte at 2, 3, and 4 mA cm^{-2}. The reduced transport number (τ_0), i.e., the number of moles of water flowing through the membrane per 96485 C, was calculated from the data.

Results and Discussion

The membrane potential ($\Delta\psi$) varied linearly with the difference in the logarithmic temperature ($\Delta\ln T$) or the temperature difference (ΔT) at $-10 \leqq \Delta T \leqq 10$ K, as reported in previous papers.[5—7)] Figures 2 and 3 show examples of $\Delta\psi$ against $\Delta\ln T$ or ΔT plots with membranes M-1(10) and M-1(14) in KCl solutions, where T was kept at T^c=303.2 K and $-10 \leqq \Delta T \leqq 10$ K. In all cases the membrane potential ($\Delta\psi$) varied linearly with $\Delta\ln T$ or ΔT, and all straight lines intersected near to the zero point (0,0). The electric potential at the hot-side solution was always negative. This means that the counterions were forced to move from the cold side to the hot side.

The slopes of the temperature coefficient of the thermal membrane potential per unit temperature difference ($\Delta\psi/\Delta\ln T$ or $\Delta\psi/\Delta T$) are plotted in Figs. 4a, 4b, 5a, and 5b as a function of the logarithmic mean activities of the ions ($\log a_\pm$) in KCl solutions for membranes M-1(10) to M-5(10) series and M-1(14) to M-5(14) series, respectively. It has been reported that the contribution of the co-ions on the thermal membrane potential due to a decrease in the transport number is small in experimental errors if the transport number of counterions are more than 0.94, just as in this work.[15)] The value of $(\Delta\psi/\Delta T)T^c$ was nearly equal to that of $\Delta\psi/\Delta\ln T$ in less than 0.5%, as shown in Table 2. This means that Eq. 2 is a good approximate expression.

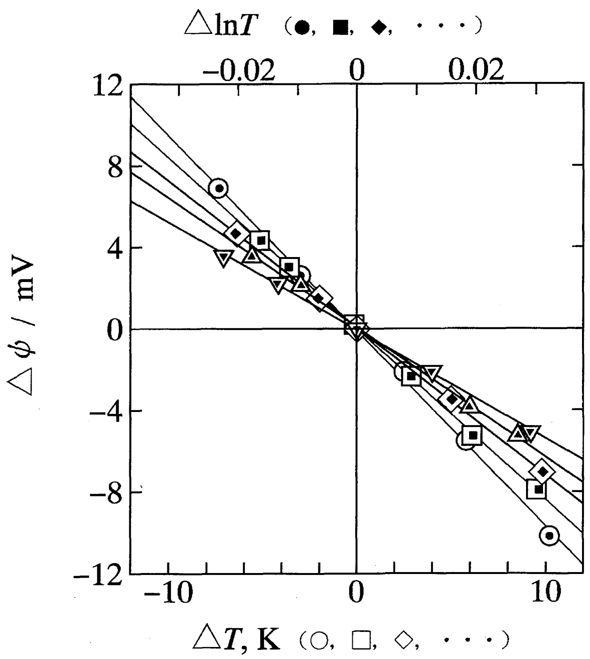

Fig. 2. The dependence of thermal membrane potential, $\Delta\psi$, on logarithmic temperature difference, $\Delta\ln T$, or temperature difference, ΔT, for M-1(10) membrane with the Cl$^-$-form. Molalities of KCl solutions (mol kg^{-1}): (○) 0.001, (□) 0.003, (◇) 0.01, (△) 0.03, and (▽) 0.1.

As expected from Eqs. 7 and 8, the slopes of the plot $\Delta\psi/\Delta\ln T$ or $\Delta\psi/\Delta T$ against $\log a_\pm$ are about $2.3RT^c/F$ or $2.3R/F$, where the straight lines were drawn with the value of $2.3RT^c/F$ or $2.3R/F$; that is, the average value of T_m was assumed to be equal to T^c=303.2 K. The slopes $2.3RT_m/F$ or $2.3R/F$ are mainly due to the equilibrium electric potentials between the external electrolyte solutions and the membrane on both sides of the membrane, that is, the Donnan potentials on both sides of the membrane surface.[9)]

Figure 6 shows that the relationship of $\Delta\psi/\Delta\ln T$ against

Table 2. The Values of $F\tau_0$, $(\bar{s}_0-s_0)$, $(\Delta\psi/\Delta\ln T)$, $(\Delta\psi/\Delta T)T^c$, $(\Delta\psi/\Delta T)$, $(\Delta\psi/\Delta T)_0$, and $(\Delta\psi/\Delta T)_-$ at 0.01 mol kg^{-1} KCl Solution for Various Anion-Exchange Membranes

Membranes	$-F\tau_0$	$(\bar{s}_0-s_0)^{a)}$ J K^{-1} mol^{-1}	$-(\Delta\psi/\Delta\ln T)$ mV	$-(\Delta\psi/\Delta T)T^c$ mV	$-(\Delta\psi/\Delta T)$ mV K^{-1}	$-(\Delta\psi/\Delta T)_0$ mV K^{-1}	$-(\Delta\psi/\Delta T)_-$ mV K^{-1}
M-1(10)	7.6	−0.81	221±3	221	0.73	0.06	0.67
M-2(10)	7.9	−0.72	187±5	187	0.62	0.06	0.56
M-3(10)	7.7	−0.68	205±5	205	0.68	0.05	0.62
M-4(10)	6.2	−0.49	199±7	199	0.66	0.03	0.63
M-5(10)	5.8	1.76	127±9	126	0.42	−0.11	0.52
M-1(14)	8.1	−0.96	174±2	174	0.57	0.08	0.49
M-2(14)	7.4	−0.75	145±3	145	0.47	0.06	0.42
M-3(14)	5.9	−0.75	133±6	133	0.44	0.05	0.40
M-4(14)	5.8	0.50	145±3	145	0.48	−0.03	0.51
M-5(14)	5.7	2.25	128±2	128	0.42	−0.13	0.55

a) From Ref. 11.

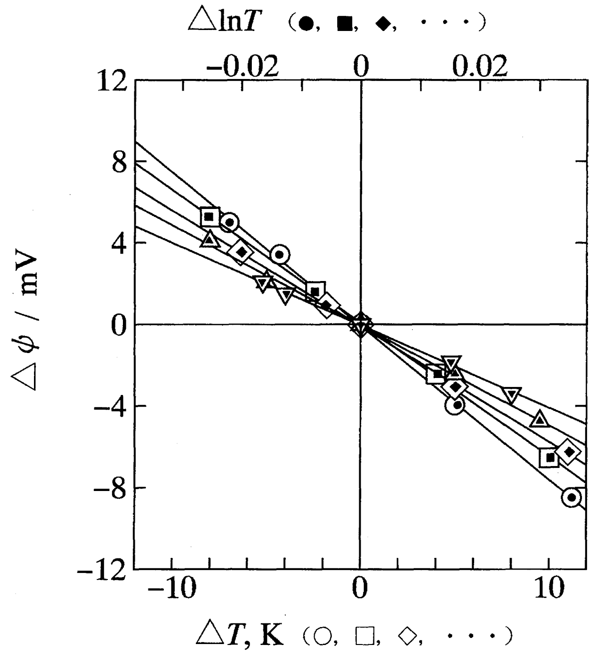

Fig. 3. The dependence of thermal membrane potential, $\Delta\psi$, on logarithmic temperature difference, $\Delta\ln T$, or temperature difference, ΔT, for M-1(14) membrane with the Cl$^-$-form. Molalities of KCl solutions (mol kg^{-1}): (○) 0.001, (□) 0.003, (◇) 0.01, (△) 0.03, and (▽) 0.1.

$\log a_\pm$ in KIO_3 for membranes M-1(10) to M-5(10) series. The relationship was similar to that observed in KCl solutions. In all cases the absolute values of $\Delta\psi/\Delta\ln T$ in KCl solutions were larger than those in the KIO_3 solutions, even if we considered the experimental errors. In general, the absolute values of $\Delta\psi/\Delta\ln T$ in both KCl and KIO_3 solutions decreased with increasing carbon number of the alkyl chain of fixed charges.

In electroosmosis, generally, the direction of water flow through anion-exchange membranes is opposite to the electric current. Therefore, the values of τ_0 estimated from the measurements of electroosmosis were negative, as shown in Table 2. The values of $(\bar{s}_0-s_0)$ and $\bar{s}_0$ increased with increasing the alkyl chain length bonded to the ammonium groups.[11]

Using the values of $(\bar{s}_0-s_0)$ in Ref. 11, the thermal membrane potential per unit temperature difference $(\Delta\psi/\Delta T)$ can be divided into two terms by Eq. 4: a water term, $(\Delta\psi/\Delta T)_0$, and an anion term, $(\Delta\psi/\Delta T)_-$. For membranes M-1(10)—M-5(10) the contribution of the absolute values of the water term to the total thermal membrane potential could not be neglected, and was 5 to 24% at 0.01 mol kg^{-1} of a KCl solution, as shown in Table 2.

The value of α_-^* is expressed by the sum of the ionic term containing the energy difference of counterions $(\bar{e}_- - s_-^0 T^c)$ and the water term containing the energy difference of water $(\bar{e}_0 - s_0 T^c)$, as can be seen in Eq. 5. The values of $(\bar{e}_- - s_-^0 T^c)$ were obtained by substituting the data of α_-^*, $F\tau_0$, and $(\bar{e}_0 - s_0 T^c)$ into Eq. 5. The values of $\bar{e}_0$ were estimated using $\bar{e}_0 = \bar{s}_0 T^c$, and the values of $\bar{e}_-$ were estimated from the values of s_-^0 based on $s_H^0=0$.[16] They are summarized with the value of α_-^* in Tables 3, 4, and 5.

On the other hand, the value of α_- is expressed by the sum of the ionic term containing the entropy difference of counterions $(\bar{\bar{s}}_- - s_-^0)$ and the water term containing the entropy difference of water $(\bar{s}_0 - s_0)$, as can be seen in Eq. 6. The value of the difference between the mean molar transported entropy and the standard partial molar entropy of anions $(\bar{\bar{s}}_- - s_-^0)$ was obtained by substituting the data of α_-, $F\tau_0$, and $(\bar{s}_0 - s_0)$ into Eq. 6. The values of $\bar{\bar{s}}_-$ and $\bar{\bar{s}}_- T^c$ were estimated from the value of $\bar{s}_-^0$ based on $s_H^0=0$.[16] They are also summarized along with the values of α_- in Tables 3, 4, and 5.

The difference between the value of $\bar{e}_-$ and the value of $\bar{\bar{s}}_- T^c$ was less than 1%. The agreement between them was satisfactory in experimental errors. It was confirmed that Eq. 2 is a good approximate expression under the condition of such small temperature differences as $-10\ \mathrm{K} < \Delta T < 10\ \mathrm{K}$.

In a previous paper[11] it was observed that the transport entropy of water increases with increasing hydrophobicity of the fixed charged groups for both series of membranes. However, an explicit relationship could not be found between the transport entropy of counterions and the hydrophobicity in this experiment. This would be because thermoosmosis is influenced by a direct interaction between the hydrophobic alkyl groups and water molecules; however, the thermal mem-

Table 3. The Values of α_-^*, $(\bar{e}_- - s_-^0 T^c)$, $\bar{e}_-$, α_-, $(\bar{\bar{s}}_0 - s_-^0)$, $\bar{\bar{s}}_-$, and $\bar{\bar{s}}_- T^c$ at 0.01 mol kg^{-1} KCl Solution for Various Anion-Exchange Membranes

Membranes	α_-^* / mV	$(\bar{e}_- - s_-^0 T^c)$[a] / kJ mol^{-1}	$\bar{e}_-$ / kJ mol^{-1}	α_- / mV K^{-1}	$(\bar{\bar{s}} - s_-^0)$[a] / J K^{-1} mol^{-1}	$\bar{\bar{s}}_-$[b] / J K^{-1} mol^{-1}	$\bar{\bar{s}}_- T^c$ / kJ mol^{-1}
M-1(10)	100	−7.7	9.0	0.33	−25	30	9.0
M-2(10)	65	−4.6	12.2	0.21	−15	40	12.2
M-3(10)	84	−6.5	10.2	0.28	−21	34	10.2
M-4(10)	74	−6.2	10.5	0.24	−20	35	10.5
M-5(10)	4	−3.5	13.2	0.01	−12	44	13.2
M-1(14)	51	−2.7	14.0	0.17	−9	46	14.1
M-2(14)	16	0.1	16.8	0.05	0	56	16.9
M-3(14)	12	0.2	16.9	0.04	1	56	17.0
M-4(14)	25	−3.3	13.4	0.08	−11	44	13.5
M-5(14)	4	−4.3	12.4	0.01	−14	41	12.5

a) At $\log a_{\pm} = -1$. b) Calculated from the values of s_-^0 based on $\bar{\bar{s}}_H^0 = 0$.[16]

Table 4. The Values of α_-, $F\tau_0$, $(\bar{\bar{s}}_0 - s_0)$, Water Content, and Other Parameters for Membrane M-1(10)

Counter ions	Water content[a]	α_- / mV K^{-1}	$-F\tau_0$	$(\bar{\bar{s}}_0 - s_0)$ / J K^{-1} mol^{-1}	Viscosity B-coefficient[b] / dm^3 mol^{-1}	Stokes radius[c] / pm
Cl^-	0.32	0.33	7.6	−0.81[d]	−0.007	121
Br^-	0.31	0.08	7.9	−0.36	−0.042	118
I^-	0.34	−0.02	10.5	0.18	−0.068	119
$NO_3{}^-$	0.27	0.34	8.2	−0.72	−0.046	129
$IO_3{}^-$	0.39	0.11	11.7	−2.05[d]	0.140	222
$SO_4{}^{2-}$	0.36	−0.17	13.0	−2.64	0.208	230

a) g-H_2/O/g-dry membrane without counterions. b) From Ref. 21. c) From Ref. 18. d) From Ref. 11.

Table 5. The Values of $(\Delta\psi/\Delta T)$, $(\Delta\psi/\Delta T)_0$, and $(\Delta\psi/\Delta T)_-$ at 0.01 mol kg^{-1} Electrolytes, and $(\bar{s}_0 - s_-^0)$, $\bar{s}_-$, and $\bar{e}_-$ for Membrane M-1(10)

Counterions	$-(\Delta\psi/\Delta T)$ / mV K^{-1}	$-(\Delta\psi/\Delta Tr)_0$ / mV K^{-1}	$-(\Delta\psi/\Delta T)_-$ / mV K^{-1}	$(\bar{\bar{s}}_- - s_-^0)$[a] / J K^{-1} mol^{-1}	$\bar{\bar{s}}_-$ / J K^{-1} mol^{-1}	$\bar{e}_-$ / kJ mol^{-1}
Cl^-	0.73	0.06	0.67	−25	30	9.0
Br^-	0.48	0.03	0.45	−5	76	23.1
I^-	0.38	−0.02	0.40	−1	109	33.0
$NO_3{}^-$	0.75	0.06	0.69	−27	120	36.3
$IO_3{}^-$	0.53	0.25	0.28	14	131	39.6
$SO_4{}^{2-}$	0.07	0.36	−0.29	51	69	20.9

a) At $\log a_{\pm} = -1$. b) Calculated from the values of s_-^0 based on $\bar{\bar{s}}_H^0 = 0$.[16]

brane potential is a phenomenon which appears as the result of an indirect interaction between the alkyl groups and the ions through intervening water molecules. It is necessary to measure many other series of membranes to discuss the effect of hydrophobicity on the thermal membrane potential in detail.

The effect of counterions on the thermal membrane potential for anion-exchange membrane M-1(10) is shown in Fig. 7. The slopes of the plots of $\Delta\psi/\Delta\ln T$ against $\log a_{\pm}$ are about $2.3RT_m/F$ for monovalent ion-form membranes and about $2.3RT_m/(2F)$ for divalent ion-form membrane, as expected from Eq. 7 and 9. For halide ions the absolute value of $\Delta\psi/\Delta\ln T$ decreases along with increasing molecular weight of halide ions, $Cl^- > Br^- > I^-$, although the Stokes or hydrated ion radii of hydrated halide ions are nearly equal to each other.[17,18] This order of thermal membrane potential is the same as that reported previously.[14]

The water content for these ion-form membranes was nearly constant, as shown in Table 4. The order of the conventional partial molar volume of ions is $Cl^- < Br^- < I^-$.[19,20] Moreover, the values of the B-coefficient in the Jones–Dole expression for the viscosity of the solutions are negative, and their order is Cl^- (−0.007 dm^3 mol^{-1})> Br^-(−0.042 dm^3 mol^{-1})>I^-(−0.068 dm^3 mol^{-1}).[21] The values of the activation energy of the ionic components are also negative, and their order is the same as the B-coefficient.[21] Similarly, the values of the difference in the activation energy of water between the water neighboring

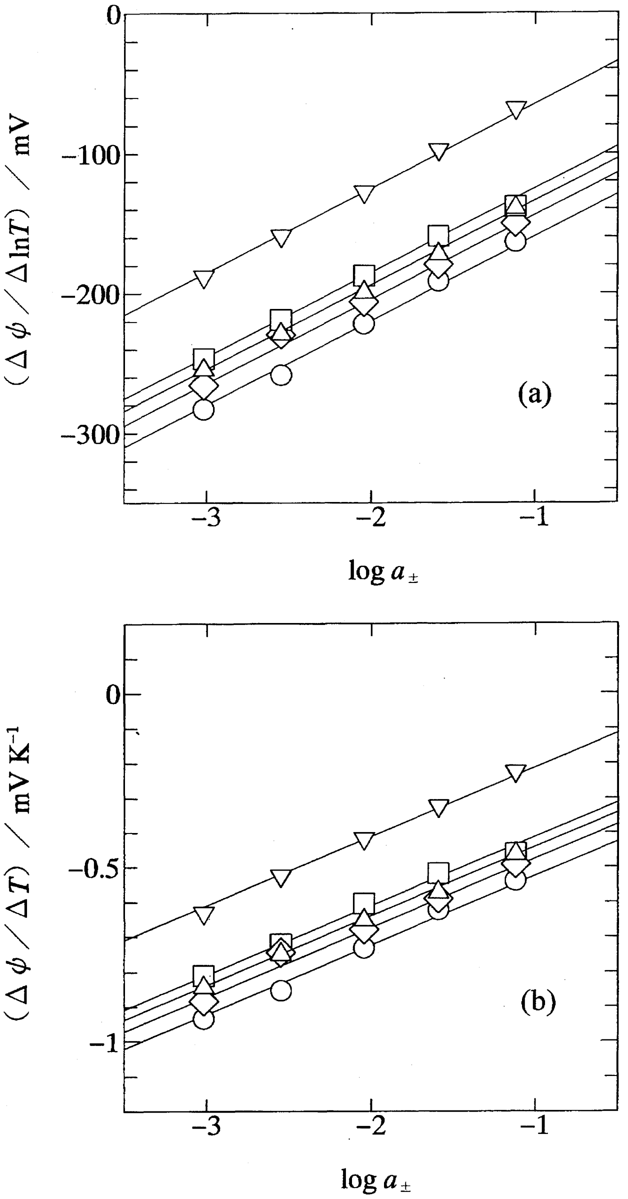

Fig. 4. (a) Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta\ln T$, plotted against $\log a_\pm$ in KCl solutions. Membranes: (○) M-1(10), (□) M-2(10), (◇) M-3(10), (△) M-4(10), and (▽) M-5(10). (b) Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta T$, plotted against $\log a_\pm$ in KCl solutions. Membranes: (○) M-1(10), (□) M-2(10), (◇) M-3(10), (△) M-4(10), and (▽) M-5(10).

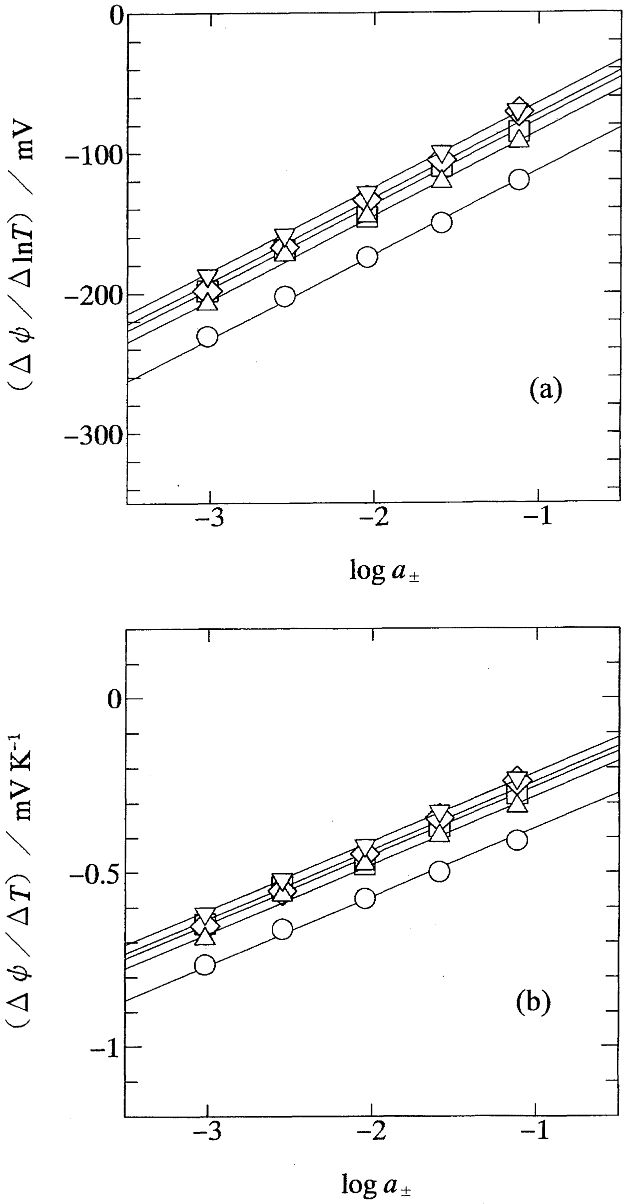

Fig. 5. (a) Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta\ln T$, plotted against $\log a_\pm$ in KCl solutions. Membranes: (○) M-1(14), (□) M-2(14), (◇) M-3(14), (△) M-4(14), and (▽) M-5(14). (b) Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta T$, plotted against $\log a_\pm$ in KCl solutions. Membranes: (○) M-1(14), (□) M-2(14), (◇) M-3(14), (△) M-4(14), and (▽) M-5(14).

the ion and pure water are also negative, and their order is the same as the *B*-coefficient.[22] In general, the negative value of the *B*-coefficient means that the ion breaks the structure of water neighboring the ion. For halide ions of Cl^-, Br^-, and I^- the coordination number of the water molecules surrounding the ions is known to be 4 to 9, although the values are different depending on the experimental methods.[22,23] As shown in Table 1, the ratio of the moles of water molecules to the moles of the total ions (fixed ionic groups and counterions) in the membrane was 4.1 to 7.4. Thus, free water molecules, just as the state of pure water, were few in the membrane on the whole. Therefore, all of the water molecules surrounding the ions in the membrane are directly affected by a change in the chain length of the alkyl groups of fixed chargs, and the mean transported entropy of the ions changes.

The values of $(\bar{\bar{s}}_- - \bar{\bar{s}}^0_-)$, $\bar{\bar{s}}_-$, and $\bar{e}_-$ were estimated by substituting the values of $(\bar{\bar{s}}_0 - s_0)$ and $F\tau_0$ into Eq. 5, and are tabulated in Table 5. The entropy difference of anions $(\bar{\bar{s}}_- - s^0_-)$ is completely negative, and the order of the absolute values of $(\bar{\bar{s}}_- - s^0_-)$ was also $Cl^- > Br^- > I^-$. Considering the fact that the mean transported entropy of water in the

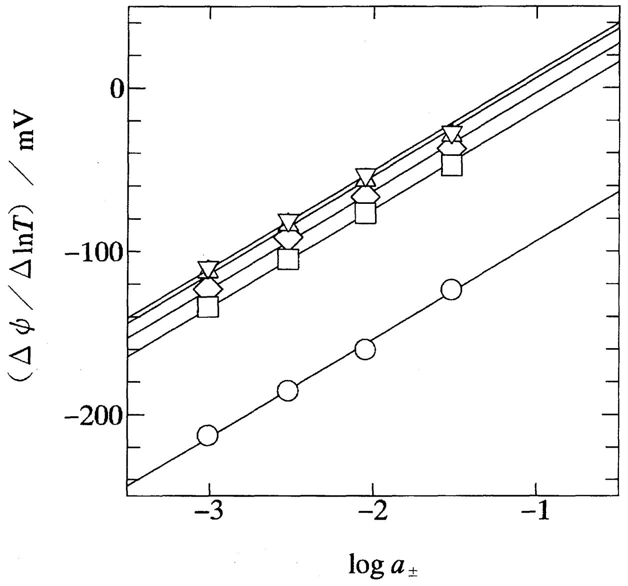

Fig. 6. Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta\ln T$, plotted against $\log a_{\pm}$ in KIO$_3$ solutions. Membranes: (○) M-1(10), (□) M-2(10), (◇) M-3(10), (△) M-4(10), and (▽) M-5(10).

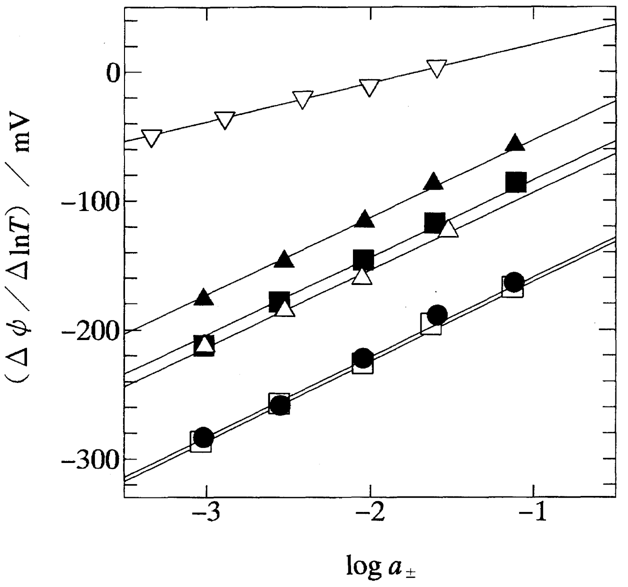

Fig. 7. Temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta\ln T$, on $\log a_{\pm}$, across membrane M-1(10) in various electrolytes. Electrolytes: (●) KCl, (■) KBr, (▲) KI, (□) KNO$_3$, (△) KIO$_3$, and (▽) (1/2)K$_2$SO$_4$.

membrane increased with increasing the hydrophobicity of the ion-exchange groups,[11] the hydrophobic ion-exchange groups act to break the structure of the water neighboring the hydrophobic membrane matrix. Since the viscosity B-coefficient of Cl$^-$ ions is nearly zero, the water molecules surrounding the Cl$^-$ ion in the external solution is scarcely influenced by the electrostatic effect. However, in the membrane phase the water molecules surrounding the Cl$^-$ ion are greatly influenced by any change in the hydrophobicity. On the other hand, for Br$^-$ and I$^-$ ions, breaking the structure of the water molecules, since the state of the water molecules surrounding the ions in the external solutions are already fairly different from that of pure water compared with that of the Cl$^-$ ion, in the membrane phase the effect of the change in hydrophobicity on the state of water molecules is smaller. If the activation energy of the water molecules surrounding the ion becomes larger due to a change in the hydrophobicity of fixed charges, the change in the transported entropy of ions would also become larger. The order of the absolute values of $(\bar{\bar{s}}_{-}-s_{-}^{0})$ (i.e. Cl$^-$>Br$^-$>I$^-$) can be explained by these changes in the water structure due to the hydrophobic ion-exchange groups.

The relationship between the viscosity B-coefficient and the ionic entropy for large polyatomic ions containing oxygen is different from that for small ions.[24] For large ions the order of the absolute values of the thermal membrane potentials was $\mathrm{NO}_3^- > \mathrm{IO}_3^- > \mathrm{SO}_4{}^{2-}$. This order is just opposite to those of the molar volume of these hydrated ions and/or hydration number of oxoanions (NO$_3{}^-$, IO$_3{}^-$, SO$_4{}^{2-}$).[18] The B-coefficients of IO$_3{}^-$ and SO$_4{}^{2-}$ ions have large positive values, which means that these ions strengthen the structure of the water neighboring the ions, although it is negative for NO$_3{}^-$ ions. The values of the entropy difference of these ions $(\bar{\bar{s}}_{-}-s_{-}^{0})$ are listed in Table 5; they are negative for NO$_3{}^-$ and positive for IO$_3{}^-$ and SO$_4{}^{2-}$. The positive values of $(\bar{\bar{s}}_{-}-s_{-}^{0})$ show that the degree of the ordering structure of the water molecules is weakened by the hydrophobic ion-exchange groups in the membranes.

As shown in Table 5, the ionic term of the thermal membrane potential $(-(\Delta\psi/\Delta T)_-)$ is dominant at 0.01 mol kg^{-1} for halide ions. On the other hand, for oxoanions the water term of the thermal membrane potential $(-(\Delta\psi/\Delta T)_0)$ plays a very important role. For SO$_4{}^{2-}$ ions the value of the ion term in the thermal membrane potential $(-(\Delta\psi/\Delta T)_-)$ was negative at 0.01 mol kg^{-1}, though the value of the water term $(-(\Delta\psi/\Delta T)_0)$ was largely positive. Therefore, the total thermal membrane potential $(-(\Delta\psi/\Delta T))$ was positive. This means that SO$_4{}^{2-}$ ions are forced to move toward the cold side in the straight term due to the driving force of the ions, itself. However, the SO$_4{}^{2-}$ ions are largely forced to move toward the hot side by the interaction between the counterions and water due to thermoosmosis. On the whole, the SO$_4{}^{2-}$ ions are forced to move toward the hot side. Thus, the absolute value of $\Delta\psi/\Delta T$ is lower for strongly hydrated SO$_4{}^{2-}$ ion-form membranes, just as those for a cation-exchange membrane with a strongly hydrated Li$^+$ ion-form.[8]

Conclusions

1. An approximate equation derived from a dissipation function including the product of the entropy flux and the coupled force of the temperature difference was a good expression for a thermal membrane potential in the range of small temperature differences: $-10\ \mathrm{K}<\Delta T<10\ \mathrm{K}$.

2. The absolute values of $\Delta\psi/\Delta\ln T$ or $\Delta\psi/\Delta T$ in KCl solutions are higher than those in KIO$_3$ solutions.

3. For oxoanion-form membranes the water term of thermal membrane potential played a very important role.

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