2062 © 1994 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **67**, 2062–2068 (1994) [Vol. 67, No. 8

# Thermal Membrane Potential across Anion-Exchange Membranes in Various Electrolyte Solutions and the Transported Entropy of Ions

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(Received February 21, 1994)

The thermal membrane potential cell with solution inlet channels was constructed from two blocks of poly(methyl methacrylate). Using the cell the thermal membrane potentials across anion-exchange membranes Aciplex A-201, A-211, and A-221, and Neosepta AM-1 were observed in inorganic electrolytes: KF, KCl, KI, $KNO_3$, $KClO_3$, and $KIO_3$, and in organic electrolytes: HCOONa, $CH_3COONa$, $CH_3COOK$, and $C_6H_5COONa$. The thermal membrane potential $\Delta\psi$ across the anion-exchange membrane was always positive at the cold solution side. The temperature coefficient of the thermal membrane potential per unit temperature difference $\Delta\psi/\Delta T$ is proportional to the logarithmic activities of the ions and the slope of this plot was $R/F$ in the range of ideal permselectivity for the counterions except Aciplex A-221. The transported entropies of the counterions in the membrane were estimated by combining data for the thermal membrane potential, thermoosmosis, and electroosmosis. For all types of membranes, both terms of water and ions in the thermal membrane potential increased with the increasing of the friction coefficient of ions.

Thermal membrane phenomena are interesting because the quantities related to the entropy of matters in the membranes can be estimated from experiments. However, systematic studies on the thermal membrane potential have been reported little especially for anion-exchange membranes. This is because the flux of heat is so large that it is difficult to remove the diffusion layers on the membrane surface by stirring and to obtain reproducible results from measurements on thermal membrane phenomena. Then, we used the same cell as that in a previous paper,[1] to carry out systematic measurements of the thermal membrane potential across quaternized ammonium-type anion-exchange membranes in various inorganic and organic electrolyte solutions. The transported entropy of the counterions was estimated from the data of the thermal membrane potential, thermoosmosis, and electroosmosis.[2,3]

## Experimental

**Membranes.** Anion-exchange membranes Aciplex A-201, A-211, and A-221 (Asahi Chemical Ind. Ltd.), and Neosepta AM-1 (Tokuyama Soda Co., Ltd.) were used. These membranes are of the hydrocarbon with quaternized ammonium. The thickness of these membranes ranges from 0.12 to 0.45 mm. The basic properties of these membranes are listed in Table 1. The water content of membranes was measured with $K^+$-form membranes several times and the average of those was described as g $H_2O$ per g dry membrane without counterions. There were small differences in the values of water content between this work and Ref. 1 because of different pieces cut from a membrane.

**Electrolytes.** The reagents used for the preparation of aqueous KF, KCl, KI, $KNO_3$, $KClO_3$, $KIO_3$, HCOONa, $CH_3COONa$, $CH_3COOK$, $C_2H_5COONa$, and $C_6H_5COONa$ solutions were of special grade (Wako Pure Chemical Industries Ltd.) and their molalities ranged from 0.001 to 0.1 $\mathrm{mol\,kg^{-1}}$.

**Thermal Membrane Potential Cell.** The similar thermal membrane potential cell as used in Ref. 1 was employed. The cell was made of poly(methyl methacrylate) and have a narrow solution channel to prevent formation of a diffusion layer on the membrane surface. The cell is similar to the one used by Scatchard et al.[4] for measuring concentration membrane potential. In order to reduce the heat flux across the membrane and to keep the effective temperature difference between both sides of the membrane identical to the temperature difference between the external bulk solutions, we made the cell with a small effective membrane area compared with the old type cell.[2] The effective membrane area was $5\times10$ $\mathrm{mm^2}$. The measurements of the thermal membrane potential were also carried out with 300 $\mathrm{cm^3\,min^{-1}}$ of the flow rate of electrolyte solutions.

**Measurements of Thermal Membrane Potential.** The thermal membrane potential cell was constructed with calomel electrodes as shown in Scheme 1. The thermal membrane potential was measured with a digital electrometer TR-8411 (Advantest Co., Japan), which was carefully electrically shielded from external fields, and with a personal computer PC-9801 DS/U2 (Nippon Electric Co., Ltd.) to record the data obtained. The membranes were equilibrated in solutions at temperature $T$ prior to the experiments. Two controlled solutions with the same concentrations but with different temperatures were flushed on both sides of the membrane; the thermal membrane potential reached a constant value after ca. 10 s. A mean value of $\Delta\psi$ at 30 to 40 s was taken as the value of the steady state.

**Measurements of Electroosmosis.** For KCl solutions the membrane was mounted between two 69.2 $\mathrm{cm^3}$ compartments of a cell made of poly(vinyl chloride) and equipped with magnetic stirrers, silver–silver chloride electrodes, and capillaries for measuring volume flow. Since no reversible electrode is available for the electrolyte solutions except KCl, we employed a four-compartment cell with two Neosepta C66-10F cation-exchange membranes as shown in Scheme 2. A sample anion-exchange membrane was mounted between the middle two 30.8 $\mathrm{cm^3}$ sample electrolyte solution compartments of the cell.[7,8] In order to avoid the edge effect of the membrane area the larger membrane area 6.15 $\mathrm{cm^2}$

Table 1. The Properties of Anion-Exchange Membranes

| Membr. | Thickness<br>mm | Transport number of counterions | Water content[a) (g $H_2O$/g dry membrane) | Ion-exchange capacity[b) (mmol/g dry membrane) | Molality of fixed charges (mmol/g $H_2O$) |
|---|---|---|---|---|---|
| A-201 | 0.218 | 0.98[c) | 0.39 | 1.38 | 3.5 |
| A-211 | 0.454 | 0.86,[c) 0.95[d) | 0.51 | 0.78 | 1.5 |
| A-221 | 0.124 | 0.98[c) | 0.52 | 2.34 | 4.5 |
| AM-1 | 0.132 | 0.98[c) | 0.31 | 1.15 | 3.7 |

a) g-$H_2O$ per g dry membrane without counterions. b) mmol per g dry membrane without the weight of counterions. c) Estimated from the membrane potential in 0.1//0.2 mol kg$^{-1}$ KCl solutions. d) Estimated from the membrane potential in 0.03//0.06 mol kg$^{-1}$ KCl solutions.

$$\mathrm{Hg}/\underbrace{\mathrm{Hg_2Cl_2{\cdot}satd.\ KCl/soln.}}/\mathrm{membr.}/\underbrace{\mathrm{soln./satd.\ KCl}}{\cdot}\underbrace{\mathrm{Hg_2Cl_2/Hg}}$$

temperature: $T$  $T+\Delta T$  $T$

$$\underbrace{\qquad\qquad}\qquad\qquad\underbrace{\qquad\qquad\qquad}$$

electric potential: $\psi$  $\psi+\Delta\psi$

Scheme 1.

Ag/AgCl·KCl//sample soln.//sample soln.//KCl·AgCl/Ag

membranes: C66-10F  sample membr.  C66-10F

Scheme 2.

was adopted compared with that in the previous paper.[1) The volume change in its compartment is caused by two electroosmotic flow, i. e. by the flow through the sample membrane and by that through the cation-exchange membranes. The latter was independently determined in the ordinary two-compartment cell. All experiments were run in 0.1 mol kg$^{-1}$ solutions at 2 to 4 mA cm$^{-2}$. The reduced transport number of water $\tau_0$, i.e. the number of moles of water flowing through the membrane per 96485 C, was calculated neglecting the volume change of the electrodes. For the KCl solutions, the electroosmosis was measured using both the two-compartment cell and the four-compartment cell to check the reliability of the data obtained by the two methods. The experimental error in these methods were within 4%.

## Results and Discussion

Thermal membrane potential per unit temperature difference $\Delta\psi/\Delta T$ is predicted by[2,3)

$$-\Delta\psi/\Delta T = \sum_i \tau_i(\bar{\bar{s}}_i - s_i), \qquad (1)$$

where $\tau_i$, $\bar{\bar{s}}_i$, and $s_i$ refer to the reduced transport number, the mean molar transported entropy in the membrane, and the partial molar entropy in the external solutions of component $i$, respectively. If the membrane is ideally permselective for anions, Eq. 1 becomes

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

where $R$ is the gas constant, $F$ the Faraday constant, $a_{\pm}$ the mean activity of ions, and $\alpha_{-}$ is defined by

$$\alpha_{-} = -(\bar{\bar{s}}_{-} - s_{-})/F + \tau_0(\bar{\bar{s}}_0 - s_0). \qquad (3)$$

Subscripts − and 0 refer to anion and water, respectively.

Figure 1 shows the thermal membrane potential across the membrane A-201 against temperature difference in KF solutions. In all cases, the linear relationship between $\Delta\psi$ and $\Delta T$ was observed, when $\Delta T$ varied from −10 to 10 K. The electric potential at the hot side solution was always negative. The ions are forced to move from the cold side to the hot side solution. The absolute value of the thermal membrane potential decreases with an increase in electrolyte molality.

For membrane A-211, which has a low ion-exchange capacity and a high water content, the thermal membrane potential was measured for electrolyte molalities in the range of 0.001 to 0.01 mol kg$^{-1}$. The transport number of counterions decreased at the higher molalities than 0.01 mol kg$^{-1}$. Similar relationships between thermal membrane potential and temperature difference were also observed in all electrolyte solution systems. In all the cases a good linear relationship between $\Delta\psi$ and $\Delta T$ was observed.

The slopes $\Delta\psi/\Delta T$ of the graphs in (Figs. 2, 3, 4, and 5) are plotted as a function of the activity of the electrolytes in the external solutions, respectively. As expected from Eq. 2 the slope of $\Delta\psi/\Delta T$ against $\log a_{\pm}$

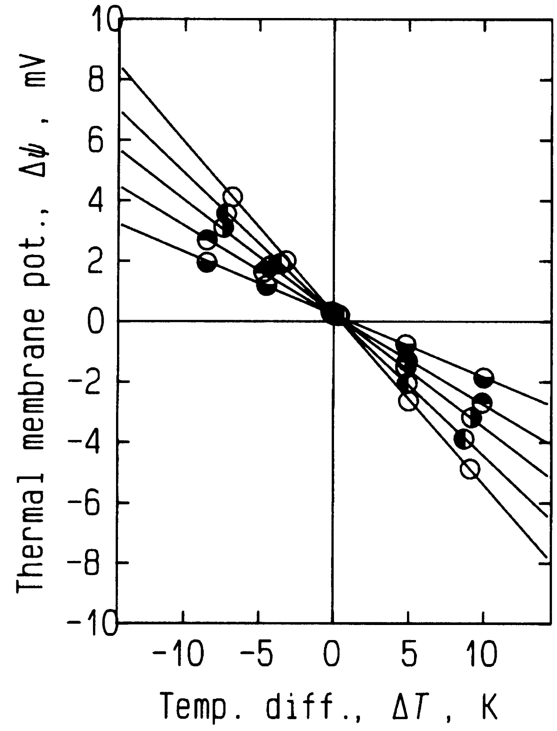

Fig. 1. The thermal membrane potential $\Delta\psi$ across A-201 against temperature difference $\Delta T$ in KF solution. Molalities (mol kg$^{-1}$): (○) 0.001, (◐) 0.003, (◑) 0.01, (◓) 0.03, (◒) 0.1.

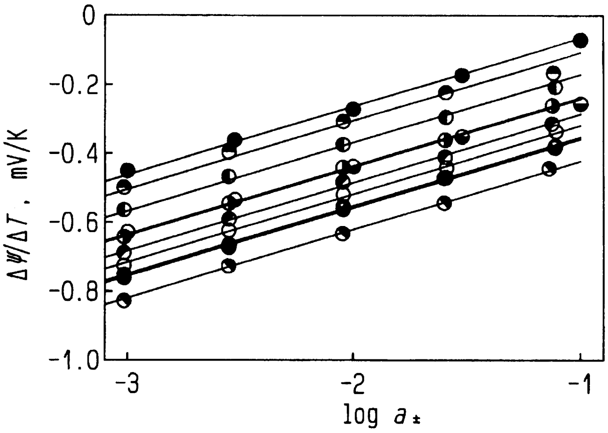

Fig. 2. Temperature coefficients of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_{\pm}$ for A-201. Electrolytes: (●) $C_6H_5COONa$, (◓) $CH_3COOK$, (◐) KF, (◑) $KIO_3$, (◒) $C_2H_5COONa$, (⊘) $KClO_3$, (○) HCOONa, (◕) KI, (◔) KCl, (◗) $KNO_3$.

was nearly equal to 2.3 $R/F$ (0.1984 mV K$^{-1}$). Therefore, all the slopes in the figures except the membrane A-221 are fixed with 2.3 $R/F$. However, for the membrane A-221, the slopes $\Delta\psi/\Delta T$ were in the ranges of 0.111 to 0.132 mV K$^{-1}$ which is fairly small compared with 0.1984 mV K$^{-1}$. When a membrane has high fixed charges, the swelling pressure in the membrane decreases with increasing the external salt concentration. Moreover, if the membrane has hydrophilic flexible polymer chains having fixed charges in the liquid phase and has high water content, the state of the polymer chains and counterions will be susceptible to change with the change in swelling pressure. In general, the abolute value of the thermal membrane potential decreases with an increase of the water content of the membrane.[8] At the low molalities the swelling pressure is high and the water content will be high. The state of liquid phase of the membrane may change with the external salt concentration even if the analytical water content of the membrane does not change. Thus, the slopes $\Delta\psi/\Delta T$ were small for the membrane A-211 having high water content and high fixed charges.

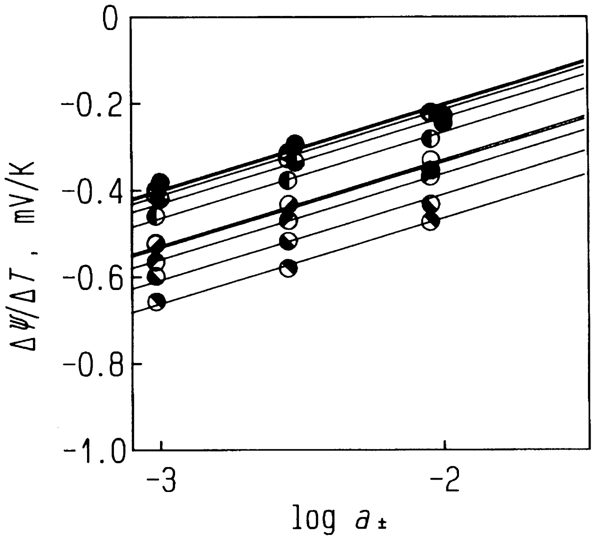

Fig. 3. Temperature coefficients of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_{\pm}$ for A-211. Electrolytes: (●) $C_6H_5COONa$, (◓) $CH_3COOK$, (◐) KF, (◑) $KIO_3$, (◒) $C_2H_5COONa$, (⊘) $KClO_3$, (○) HCOONa, (◕) KI, (◔) KCl, (◗) $KNO_3$.

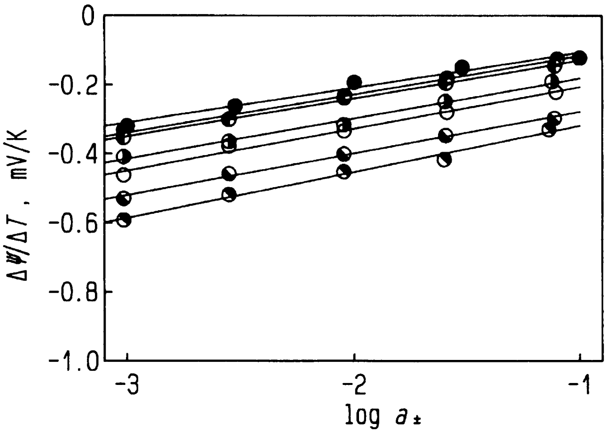

Fig. 4. Temperature coefficients of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_{\pm}$ for A-221. Electrolytes: (●) $C_6H_5COONa$, (◓) $CH_3COONa$, (◐) KF, (◑) $KIO_3$, (○) HCOONa, (◔) KCl, (◗) $NaNO_3$.

In all membranes, the values of $\Delta\psi/\Delta T$ for organic anions roughly decrease in the order of $C_6H_5COO^- <$

Table 2. The Values of $\alpha_-$, $F(\Delta\psi/\Delta T)$, $F\tau_0$, $-(\bar{\bar{s}}_0-s_0)$, $(\bar{\bar{s}}_- - s_-)$, $(\bar{\bar{s}}_- - s^\circ_-)$, $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$, $\bar{\bar{s}}_-$, and Water Content for Anion-Exchange Membrane Aciplex A-201

| Counterion | $\alpha_-$ | $F(\Delta\psi/\Delta T)$ a) | $F\tau_0$ | $-(\bar{\bar{s}}_0-s_0)$ b) | $(\bar{\bar{s}}_- - s_-)$ a) | $(\bar{\bar{s}}_- - s^\circ_-)$ | $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$ e) | $\bar{\bar{s}}_-$ c) | Water content d) |
|---|---|---|---|---|---|---|---|---|---|
| | mV K$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | | J K$^{-1}$ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | |
| $F^-$ | 0.028 | −35.5 | −45.7 | 1.61 | 38.1 | 73.6 | 26.6 | 64.0 | 0.52 |
| $Cl^-$ | −0.160 | −53.6 | −29.3 | 1.08 | −22.0 | −2.9 | −22.0 | 52.2 | 0.40 |
| $I^-$ | −0.154 | −53.2 | — | — | — | — | — | — | — |
| $NO_3{}^-$ | −0.250 | −101 | −37.1 | 1.05 | −62.0 | −42.6 | −65.8 | 104 | 0.32 |
| $ClO_3{}^-$ | −0.087 | −46.6 | — | — | — | — | — | — | — |
| $IO_3{}^-$ | −0.030 | −41.1 | −35.0 | 3.11 | 67.9 | 86.9 | 55.6 | 204 | 0.47 |
| $HCOO^-$ | −0.120 | −49.8 | −44.2 | 1.40 | 12.1 | 31.2 | | | 0.42 |
| $CH_3COO^-$ | 0.092 | −29.4 | −58.8 | 2.00 | 88.6 | 107 | 73.4 | — | 0.46 |
| $C_2H_5COO^-$ | −0.043 | −42.4 | — | — | — | — | — | — | — |
| $C_6H_5COO^-$ | 0.133 | −25.4 | −62.0 | 2.54 | 132 | 151 | — | — | 0.46 |

a) At $\log a_\pm = -2$. b) From Ref. 9. c) Calculated from the values of $s^\circ_-$ based on $s^\circ_{H^+} = 0$.[12] d) g $H_2O$ per g dry membrane without counterions. e) Calculated from the values of $(\bar{\bar{s}}_- - s_-)$ and Eastman entropy.[14]

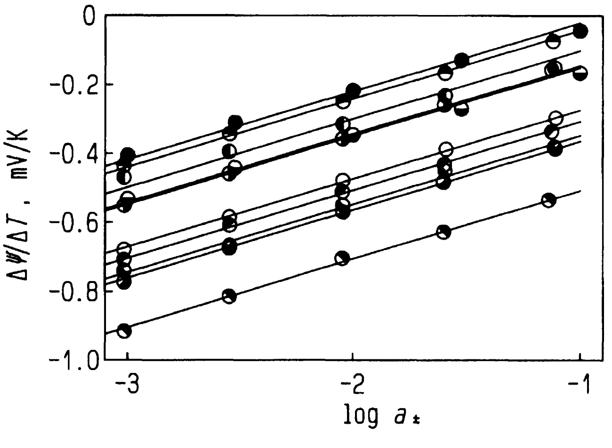

Fig. 5. Temperature coefficients of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_\pm$ for AM-1. Electrolytes: (●) $C_6H_5COONa$, (◓) $CH_3COOK$, (◐) KF, (◑) $KIO_3$, (◒) $C_2H_5COONa$, (◩) $KClO_3$, (○) HCOONa, (◪) KI, (⬕) KCl, (⬔) $KNO_3$.

$CH_3COO^- < C_2H_5COO^- < HCOO^-$. On the other hand, $\Delta\psi/\Delta T$ for halide ions decrease in the order of $F^- < I^- < Cl^-$, and that of the other anions in the order of $IO_3{}^- < ClO_3{}^- < NO_3{}^-$. For all types of membranes, these orders are identical to those of the friction coefficient of ions except $C_2H_5COO^-$. In all the membranes of hydrocarbon with quaternized ammonium, the value of $\Delta\psi/\Delta T$ is small if the water content of the membranes is high and the molality of the fixed charges is low. The values of $(\bar{\bar{s}}_0 - s_0)$ for water are given in Ref. 9; these values were determined from experiments of solvent transport under a temperature difference and under an osmotic pressure difference in 0.01 mol kg$^{-1}$ electrolytes. These values are also listed in Tables 2, 3, and 4. The experimental data of thermoosmosis have not been obtained for the membrane A-221. The values of $(\bar{\bar{s}}_0 - s_0)$ are almost constant where the transport number of the counterions in the membrane is unity.[10] The values of $F\tau_0$ increase roughly in the order of $C_6H_5COO^- > CH_3COO^- > HCOO^-$; $IO_3{}^- > NO_3{}^-$; and $F^- > Cl^-$. The values of $F\tau_0$ increase as the ion becomes bulkier. Similar results were also reported by Breslau et al.[7] If the water content of the membranes increases, the influence of the fixed charges and the membrane matrix on the state of water in the membranes decreases.[11] Therefore, the transported entropy of water in the membrane tends to the partial molar entropy of water in the external solution, and the entropy difference of water $(\bar{\bar{s}}_0 - s_0)$ becomes small when the water content is high. Substituting the values of $\alpha_-$, $F\tau_0$ and $(\bar{\bar{s}}_0 - s_0)$ into Eq. 4, we estimated the values of $(\bar{\bar{s}}_- - s_-)$, which are also listed in Tables 2, 3, and 4. If we adopt the values of $s^\circ_-$ based on $s^\circ_H = 0$,[12] the values of $\bar{\bar{s}}_-$ can be estimated from $(\bar{\bar{s}}_- - s^\circ_-)$ as shown in Tables 2, 3, and 4. Equation 2 can be rewritten as

$$\Delta\psi/\Delta T = (\Delta\psi/\Delta T)_0 + (\Delta\psi/\Delta T)_-, \tag{4}$$

where

$$(\Delta\psi/\Delta T)_0 = \tau_0(\bar{\bar{s}}_0 - s_0), \tag{5}$$

$$(\Delta\psi/\Delta T)_- = -(\bar{\bar{s}}_- - s_-)/F, \tag{6}$$

and

$$s_- = s^\circ_- - R \ln a_\pm. \tag{7}$$

$(\Delta\psi/\Delta T)_0$ and $(\Delta\psi/\Delta T)_-$ are terms due to water and anion, respectively.

Using the data in Tables 2, 3, and 4, the values of $(\Delta\psi/\Delta T)_0$ and $(\Delta\psi/\Delta T)_-$ were estimated at $\log a_\pm = -1$ and are shown in Table 5. The fractions of the water term in the thermal membrane potential $|(\Delta\psi/\Delta T)_0|/|(\Delta\psi/\Delta T)|$ were 0.3 to 210 for the membranes A-201, A-221, and AM-1 at $\log a_\pm = -1$ for all electrolytes. It is clear from the above analysis that the water term $(\Delta\psi/\Delta T)_0$ plays a very important role in thermal membrane potential.[1] On the other hand, the value of $(\bar{\bar{s}}_- - s_-)$ becomes very small at high molalities of all solutions. We have not observed a reversal in sign of the thermal membrane potential for anion-exchange

Table 3. The Values of $\alpha_-$, $F(\Delta\psi/\Delta T)$, $F\tau_0$, $-(\bar{\bar{s}}_0-s_0)$, $(\bar{\bar{s}}_- - s_-)$, $(\bar{\bar{s}}_- - s^\circ_-)$, $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$, $\bar{\bar{s}}_-$, and Water Content for Anion-Exchange Membrane Aciplex A-221

| Counterion | $\alpha_-$ | $F(\Delta\psi/\Delta T)$[a] | $F\tau_0$ | $-(\bar{\bar{s}}_0-s_0)$[b] | $(\bar{\bar{s}}_- - s_-)$[a] | $(\bar{\bar{s}}_- - s^\circ_-)$ | $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$[e] | $\bar{\bar{s}}_-$[c] | Water |
|---|---|---|---|---|---|---|---|---|---|
| | $\mathrm{mV\,K^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | content[d] |
| $F^-$ | 0.163 | −15.7 | −49.0 | 1.38 | 51.9 | 64.2 | 40.4 | 54.6 | 0.99 |
| $Cl^-$ | −0.033 | −41.4 | −32.9 | 0.44 | −26.9 | −7.8 | −26.9 | 47.3 | 0.66 |
| $I^-$ | — | — | — | 4.21 | — | — | — | — | 0.35 |
| $NO_3{}^-$ | −0.051 | −43.1 | −40.2 | 0.47 | −24.2 | −5.1 | −28.0 | 141 | 0.51 |
| $ClO_3{}^-$ | | — | — | — | — | — | — | — | — |
| $IO_3{}^-$ | −0.105 | −28.1 | −39.2 | 3.89 | 124 | 143 | 112 | 260 | 0.83 |
| $HCOO^-$ | −0.074 | −31.1 | −54.7 | 0.59 | −12.0 | 20.3 | — | — | 0.79 |
| $CH_3COO^-$ | 0.184 | −20.5 | −65.5 | 1.35 | 67.9 | 86.9 | 50.6 | — | 0.88 |
| $C_2H_5COO^-$ | | — | — | — | — | — | — | — | — |
| $C_6H_5COO^-$ | 0.190 | −18.3 | −62.0 | 2.54 | 162 | 181 | — | — | 0.62 |

a) At $\log a_\pm=-2$. b) From Ref. 9. c) Calculated from the values of $s^\circ_-$ based on $s^\circ_{H^+}=0$.[12] d) g $H_2O$ per g dry membrane without counterions. e) Calculated from the values of $(\bar{\bar{s}}_- - s_-)$ and Eastman entropy.[14]

Table 4. The Values of $\alpha_-$, $F(\Delta\psi/\Delta T)$, $F\tau_0$, $-(\bar{\bar{s}}_0-s_0)$, $(\bar{\bar{s}}_- - s_-)$, $(\bar{\bar{s}}_- - s^\circ_-)$, $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$, $\bar{\bar{s}}_-$, and Water Content for Anion-Exchange Membrane Neosepta AM-1

| Counterion | $\alpha_-$ | $F(\Delta\psi/\Delta T)$[a] | $F\tau_0$ | $-(\bar{\bar{s}}_0-s_0)$[b] | $(\bar{\bar{s}}_- - s_-)$[a] | $(\bar{\bar{s}}_- - s^\circ_-)$ | $(\bar{\bar{s}}_- - \bar{\bar{s}}_-{}^*)$[e] | $\bar{\bar{s}}_-$[c] | Water |
|---|---|---|---|---|---|---|---|---|---|
| | $\mathrm{mV\,K^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | $\mathrm{J\,K^{-1}\,mol^{-1}}$ | content[d] |
| $F^-$ | 0.098 | −28.8 | −34.5 | 2.16 | 45.7 | 64.8 | 34.2 | 54.2 | 0.49 |
| $Cl^-$ | −0.150 | −52.7 | −25.0 | 1.25 | −15.2 | −2.4 | −15.2 | 52.7 | 0.36 |
| $I^-$ | −0.166 | −54.2 | — | — | — | — | — | — | — |
| $NO_3{}^-$ | −0.308 | −68.0 | −24.8 | 0.71 | −50.4 | −31.3 | −54.2 | 115 | 0.31 |
| $ClO_3{}^-$ | −0.109 | −48.7 | — | — | — | — | — | — | — |
| $IO_3{}^-$ | −0.054 | −33.0 | −31.6 | 3.50 | 78.0 | 96.9 | 65.7 | 214 | 0.42 |
| $HCOO^-$ | −0.076 | −45.6 | −47.6 | — | — | — | — | — | 0.43 |
| $CH_3COO^-$ | 0.156 | −23.2 | −51.4 | 2.71 | 116 | 135 | 98.7 | — | 0.45 |
| $C_2H_5COO^-$ | −0.048 | −33.6 | −33.6 | — | — | — | — | — | — |
| $C_6H_5COO^-$ | 0.178 | −21.1 | −49.6 | 2.80 | 116 | 137 | — | — | 0.34 |

a) At $\log a_\pm=-2$. b) From Ref. 9. c) Calculated from the values of $s^\circ_-$ based on $s^\circ_{H^+}=0$.[12] d) g $H_2O$ per g dry membrane without counterions. e) Calculated from the values of $(\bar{\bar{s}}_- - s_-)$ and Eastman entropy.[14]

Table 5. The Values of $-(\Delta\psi/\Delta T)$, $-(\Delta\psi/\Delta T)_0$, and $(\Delta\psi/\Delta T)_-$ at $\log a_\pm=-1$

| Membrane | Counterion | $-(\Delta\psi/\Delta T)$ | $-(\Delta\psi/\Delta T)_0$ | $(\Delta\psi/\Delta T)_-$ |
|---|---|---|---|---|
| | | $\mathrm{mV\,K^{-1}}$ | $\mathrm{mV\,K^{-1}}$ | $\mathrm{mV\,K^{-1}}$ |
| A-201 | $F^-$ | 0.170 | 0.762 | 0.592 |
| | $Cl^-$ | 0.358 | 0.328 | −0.030 |
| | $NO_3{}^-$ | 0.448 | 0.404 | −0.044 |
| | $IO_3{}^-$ | 0.228 | 1.128 | 0.900 |
| | $HCOO^-$ | 0.318 | 0.641 | 0.323 |
| | $CH_3COO^-$ | 0.107 | 1.219 | 1.112 |
| | $C_6H_5COO^-$ | 0.065 | 1.632 | 1.567 |
| A-221 | $F^-$ | 0.035 | 0.701 | 0.665 |
| | $Cl^-$ | 0.231 | 0.150 | −0.081 |
| | $NO_3{}^-$ | 0.249 | 0.417 | 0.167 |
| | $IO_3{}^-$ | 0.094 | 1.580 | 1.487 |
| | $HCOO^-$ | 0.124 | 0.335 | 0.210 |
| | $CH_3COO^-$ | 0.015 | 0.917 | 0.902 |
| | $C_6H_5COO^-$ | 0.009 | 1.867 | 1.858 |
| AM-1 | $F^-$ | 0.101 | 0.772 | 0.672 |
| | $Cl^-$ | 0.348 | 0.324 | −0.024 |
| | $NO_3{}^-$ | 0.507 | 0.183 | −0.324 |
| | $IO_3{}^-$ | 0.144 | 1.146 | 1.002 |
| | $CH_3COO^-$ | 0.042 | 1.444 | 1.402 |
| | $C_6H_5COO^-$ | 0.021 | 1.439 | 1.489 |

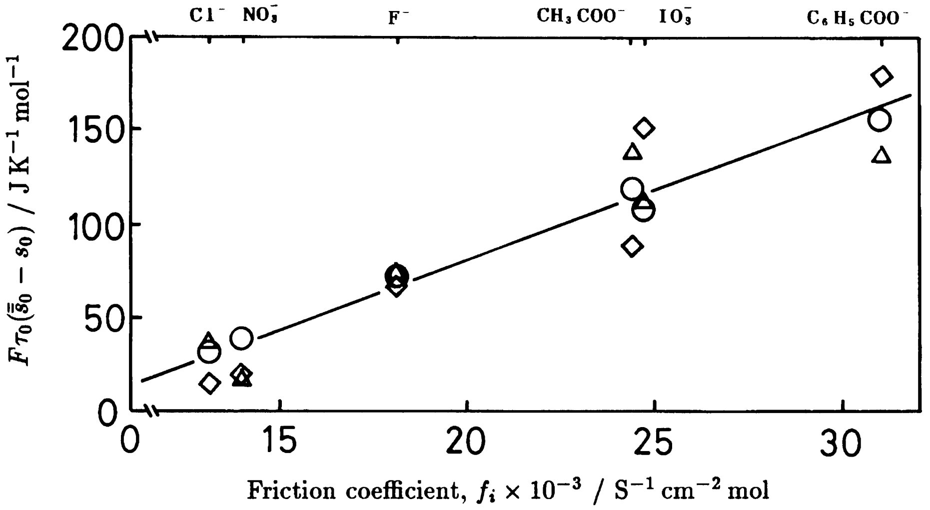

Fig. 6. The relationship between $F\tau_0(\bar{\bar{s}}_0 - s_0)$ and the friction coefficients of the ions. Membranes: (○) A-201, (◇) A-221, (△) AM-1.

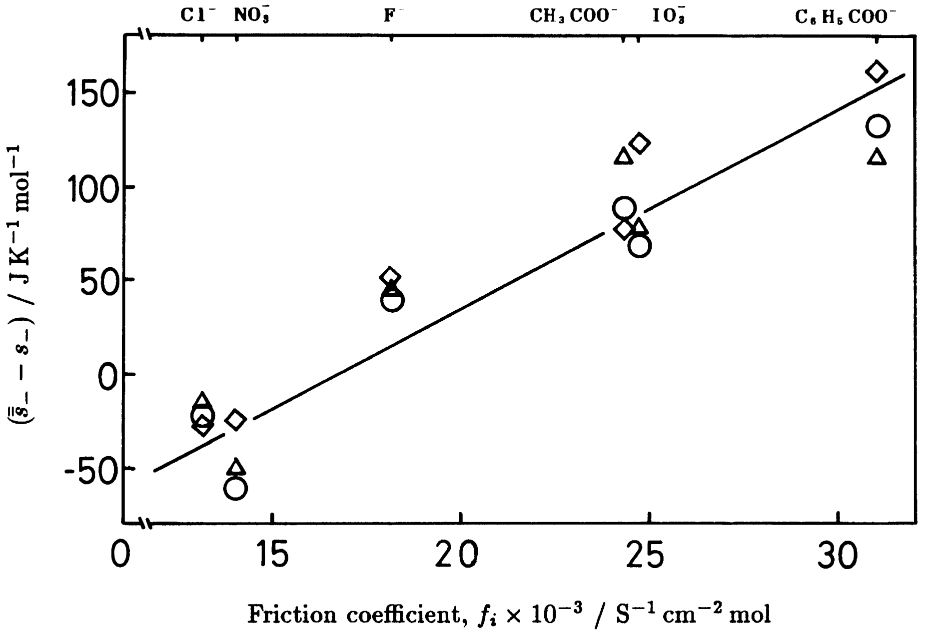

Fig. 7. The relationship between $(\bar{\bar{s}}_- - s_-)$ and the friction coefficients of the ions. Membranes: (○) A-201, (◇) A-221, (△) AM-1.

membranes. In the membranes A-201, A-221, and AM-1, the values of $(\bar{\bar{s}}_- - s_-)$ of the Cl⁻ and $NO_3^-$ forms are negative. Therefore, it suggests that the counterions in the membranes are more stable than those in the external solutions. If the water content of the membrane is lower and the molality of the fixed charges is higher, the counterions surrounding the fixed charges in the membrane may be strongly restricted and become more stable than those in the external solutions.1,5,6) As shown in Table 5, the values of $(\Delta\psi/\Delta T)_-$ of the Cl⁻ and $NO_3^-$ forms are negative in the membranes A-201 and AM-1. Therefore, the counterions are forced to move toward the hot side. However, the other counterions are forced to move toward the cold side because the values of $(\bar{\bar{s}}_- - s_-)$ are positive. On the other hand, for the membrane A-221, the value of $(\Delta\psi/\Delta T)_-$ for the Cl⁻ form is positive.

Figures 6 and 7 show the plots of $F\tau_0(\bar{\bar{s}}_0 - s_0)$ and the friction coefficients of the ions,13) and $(\bar{\bar{s}}_- - s_-)$ against the friction coefficients of the ions for the membranes A-201, A-221, and AM-1. In all the membranes, $F\tau_0(\bar{\bar{s}}_0 - s_0)$ and $(\bar{\bar{s}}_- - s_-)$ roughly increase with the increase of the friction coefficient in the order of $C_6H_5COO^- > IO_3^- \approx CH_3COO^- > F^- > NO_3^- > Cl^-$. The reciprocals of the mobilities of ions are the friction coefficients of ions. If the ions are spherical, the reciprocals of the mobilities are proportional to the radii of the ions. The entropy difference $(\bar{\bar{s}}_- - s_-)$ in the anion-exchange mem-

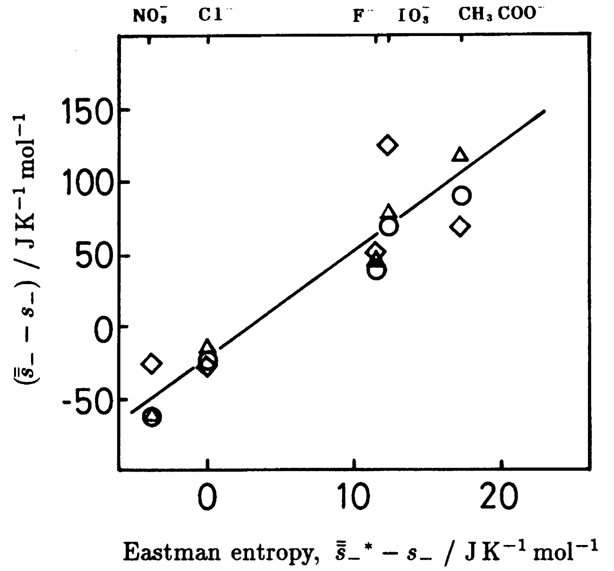

Fig. 8. The relationship between $(\bar{\bar{s}}_- - s_-)$ and Eastman entropy of the ions. Membranes: (○) A-201, (◇) A-221, (△) AM-1.

branes is smaller as the radii of ions are smaller.

Figure 8 shows the relationship between $(\bar{\bar{s}}_- - s_-)$ and Eastman entropy of transport shown in $(\bar{s}_-^* - s_-)$ where $\bar{s}_-^*$ is the mean molar transported entropy of anion in the external free solutions.[14] The values of $(\bar{s}_-^* - s_-)$ can be calculated from the conventional heats of transport $\hat{Q}$ assuming $\hat{Q}_{Cl}=0$ by Ref. 14. As shown in Tables 2, 3, and 4, the values of $(\bar{\bar{s}}_- - \bar{s}_-^*)$ which are estimated from $(\bar{\bar{s}}_- - s_-)$ and $(\bar{s}_-^* - s_-)$ increase with the increasing of $F\tau_0(\bar{s}_0 - s_0)$ and $(\bar{\bar{s}}_- - s_-)$ for membranes A-201 and AM-1. The value of $(\bar{\bar{s}}_- - \bar{s}_-^*)$ will reflect the effect of the membrane structure on the state of anions. If the membrane has high water content and low fixed charges, the values of $(\bar{\bar{s}}_- - \bar{s}_-^*)$ will tend to zero. In general, the value of $(\bar{\bar{s}}_- - s_-)$ increases with increasing $(\bar{s}_-^* - s_-)$. However, the order of $(\bar{\bar{s}}_- - \bar{s}_-^*)$ for membrane A-221 is different from those for membranes A-201 and AM-1 maybe because of the high concentration of fixed charges.

## Conclusion

(1) The thermal membrane potentials across anion-exchange membranes Aciplex A-201, A-211, and A-221, and Neosepta AM-1 were measured in KF, KCl, KI, $KNO_3$, $KClO_3$, $KIO_3$, HCOONa, $CH_3COONa$, $CH_3COOK$, $C_2H_5COONa$, and $C_6H_5COONa$ solutions.

(2) For membranes A-201, A-221, and AM-1, the values of $F\tau_0(\bar{s}_0 - s_0)$ and $(\bar{\bar{s}}_- - s_-)$ roughly increased with the increase of the friction coefficients.

(3) For membranes A-201, A-221, and AM-1, the values of $(\bar{\bar{s}}_- - s_-)$ and $(\bar{\bar{s}}_- - s_-^*)$ roughly increased with the increase of Eastman entropies of transport.

### References

1) K. Hanaoka, R. Kiyono, and M. Tasaka, *J. Membrane Sci.*, **82**, 255 (1993).

2) M. Tasaka, S. Morita, and M. Nagasawa, *J. Phys. Chem.*, **69**, 4191 (1965).

3) M. Tasaka, *Pure Appl. Chem.*, **58**, 1686 (1986).

4) G. Scatchard and W. H. Orttung, *J. Colloid Interface Sci.*, **22**, 12 (1966).

5) K. Hanaoka, R. Kiyono, M. Tasaka, M. Hamada, and K. Yoshie, *Membrane* (*Maku*), **18**, 363 (1993).

6) K. Hanaoka, R. Kiyono, and M. Tasaka, *J. Colloid Polym. Sci.*, in press.

7) B. R. Breslau and I. F. Miller, *Ind. Eng. Chem. Fundam.*, **10**, 554 (1971).

8) M. Tasaka, K. Hanaoka, Y. Kurosawa, and C. Wada, *Biophys. Chem.*, **3**, 331 (1975).

9) T. Suzuki, R. Kiyono, and M. Tasaka, *J. Membrane Sci.*, in press.

10) M. Tasaka, T. Urata, R. Kiyono, and Y. Aki, *J. Membrane Sci.*, **67**, 83 (1992).

11) M. Tasaka, T. Mizuta, and O. Sekiguchi, *J. Membrane Sci.*, **54**, 191 (1990).

12) R. Parsons, "Handbook of Electrochemical Constants," Butterworths Sci. Publ., London (1959), p. 66.

13) B. E. Conway, "Ionic Hydration in Chemistry and Biophysics," Elsevier Sci. Publ. Co., Amsterdam, Oxford, and New York (1981), p. 73.

14) J. N. Agar, "Advances in Electrochemistry and Electrochemical Engineering," in "Electrochemistry," ed by P. Delahay, Interscience Publ., New York and London (1963), Vol. 3, p. 96.