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Nonisothermal membrane phenomena across perfluorosulfonic acid-type membranes, Flemion S: Part II. Thermal membrane potential and transported entropy of ions

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Abstract: Thermal membrane potentials across the perfluorosulfonic acid-type membrane, Flemion S, were measured for HCl, alkali metal chlorides, and ammonium and methyl ammonium chlorides. The difference between the mean molar transported entropy of the counterions in the membrane and the partial molar entropy of the counterions in the external solution ($\bar{\bar{s}}_+ - s_+$) was determined from the experimental data on thermal membrane potential, thermoosmosis and electroosmosis. The sign of the thermal membrane potential in HCl solution varies from positive to negative with the concentration. In HCl and alkali metal chloride solutions, the order of their thermal membrane potentials ($-\Delta\psi/\Delta T$) is $H^+ > Li^+ = Na^+ > K^+$ which is roughly the inverse of that of the crystallographic radii of the ions. However, the order of their entropy differences ($\bar{\bar{s}}_+ - s_+$) is $H^+ > Na^+ > K^+ > Li^+$ which is just the inverse of that of their thermoosmotic coefficients (D) or the entropy difference of water ($\bar{\bar{s}}_0 - s_0$) in thermoosmosis. For the ammonium and methyl ammonium ion forms, the orders of both $-\Delta\psi/\Delta T$ and ($\bar{\bar{s}}_+ - s_+$) increase with an increasing number of methyl groups: $(CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2^+ > CH_3NH_3^+ > NH_4^+$, which is also the inverse of that of D or ($\bar{\bar{s}}_0 - s_0$).

Key words: Cation-exchange membrane – electroosmosis – perfluorosulfonic acid membrane – thermal membrane potential – transported entropy

Introduction

Thermal membrane phenomena are interesting because the quantities related to the entropy of matter transported can be estimated from experiments.

The thermal membrane potential per unit of temperature difference ($\Delta\psi/\Delta T$) is predicted as [1, 2]

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

where τ_i, $\bar{\bar{s}}_i$ and s_i refer to the reduced transport number, the mean molar transported entropy in an ion-exchange membrane, and the partial molar entropy in the external solutions of component i, respectively. If the membrane is ideally permselective for a cation, Eq. (1) for 1–1 electrolyte systems becomes [3, 4]

$$\begin{aligned}-\Delta\psi/\Delta T &= (R/F)\ln a_\pm + (\bar{\bar{s}}_+ - s_+^0)/F \\ &\quad + \tau_0(\bar{\bar{s}}_0 - s_0) \\ &= (R/F)\ln a_\pm + \alpha_+ , \end{aligned} \qquad (2)$$

where

$$\alpha_+ = (\bar{\bar{s}}_+ - s_+^0)/F + \tau_0(\bar{\bar{s}}_0 - s_0) , \qquad (3)$$

where R is the gas constant, F the Faraday constant, s^0 the standard molar entropy, and the subscripts + and 0 refer to the cation and water, respectively. The value of $\tau_0(\bar{\bar{s}}_0 - s_0)$ is obtained from the experiments of thermoosmosis, water transport under a pressure difference and electroosmosis. Therefore, if we plot $-F\Delta\psi/\Delta T - F\tau_0(\bar{s}_0 - s_0)$, which means the entropy difference $(\bar{s}_+ - s_+)$ against the logarithmic activity of the cations, we obtain a straight line with a slope of R/F and the value of the entropy difference $(\bar{s}_+ - s_+^0)$ from the intercept at $a_\pm = 1$ when the value of s_+ is constant:

$$
\begin{aligned}
-F\Delta\psi/\Delta T - F\tau_0(\bar{s}_0 - s_0) &= \bar{s}_+ - s_+ \\
&= 2.303R\log a_\pm + (\bar{s}_+ - s_+^0)\,. \qquad (4)
\end{aligned}
$$

The flux of heat is so high that it is difficult to get reproducible experimental results on thermal membrane phenomena because of the thermal diffusion layers on the membrane surfaces. In general, thick membranes are suitable for the measurements of thermal membrane potential. On the other hand, thin, porous membranes are suitable for the measurements of thermoosmosis, hydraulic permeability, and electroosmosis. Moreover, membranes have to be ideally permselective for the counterions in order to estimate their transported entropies. In order to estimate the mean molar transported entropy of the counterions 1) we constructed an improved thermal membrane potential cell, and 2) we selected a porous perfluorosulfonic acid-type membrane Flemion S, having an ideal permselectivity.

In a previous paper with respect to thermoosmosis [5], it was found that the direction of thermoosmosis was, unusually, from the hot side to the cold side in a number of ammonium-type electrolytes as well as LiCl, and that both the difference between the mean molar transported entropy of water and the partial molar entropy of water in the external solution was positive, although the entropy difference of water was negative for the usual charged membranes [1, 6, 7]. Then, in this work the thermal membrane potential was measured for various alkali metal chlorides, and ammonium and alkyl ammonium chlorides to analyze the nonisothermal membrane phenomena on the whole. The entropy difference of the counterions $(\bar{s}_+ - s_+)$ was estimated from the experimental results of the thermal membrane potential, thermoosmosis, hydraulic permeability, and electroosmosis measurements.

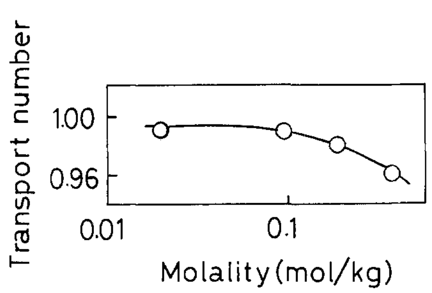

Fig. 1. The dependence of the transport number of cations on KCl molality for Flemion S.

Experimental

Membrane

The perfluorosulfonic acid-type cation-exchange membrane, Flemion S, was used. The thickness of the membrane was 210 μm. The properties of the membrane were shown in the previous paper [5]. Figure 1 shows the dependence of the transport number of K^+ ion (t_+) on its concentration in KCl solutions. The values of t_+ were estimated from the concentration membrane potential with Eq. (4).

$$
-\Delta\psi = (2t_+ - 1)(RT/F)\ln(a''_\pm/a'_\pm)\,, \qquad (5)
$$

where $a''_\pm$ and $a'_\pm$ are the mean activities of the two solutions on the two sides of the membrane. The molality ratio of the two solutions was kept at $m''/m' = 2$.

Electrolytes

The reagents used for the preparation of HCl, LiCl, NaCl, KCl, NH_4Cl, CH_3NH_3Cl, $(CH_3)_2NH_2Cl$ and $(CH_3)_4NCl$ aqueous solutions were of special grade, and that of $(CH_3)_3NHCl$ was first grade (Wako Pure Chemical Industries Ltd.); their molalities ranged from 0.001 to 0.1 mol/kg.

Thermal membrane potential cell

An improved thermal membrane potential cell was used in order to measure reproducible thermal membrane potentials across thin membranes [8]. The cell was made of poly(vinyl chloride) resin and each half cell had a narrow solution channel, as reported previously [4]. The cell is

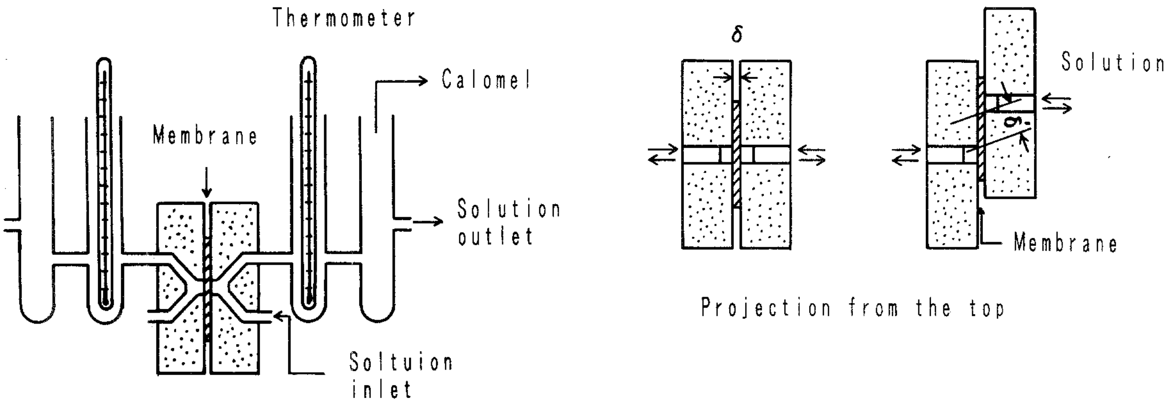

Fig. 2. a) Thermal membrane potential cell. b) Projection from the top. δ is the membrane thickness and δ' is the apparent membrane thickness.

similar to that used for measuring concentration membrane potentials by Scatchard et al. [9] as shown in Fig. 2. In order to reduce the heat flux across the membrane and to keep the same temperature difference working effectively on both sides of the membrane as that between the external bulk solutions, we set the effective area of membrane contiguous to the solution to be $2.5 \times 2.5 \times \pi = 19.6\ \text{mm}^2$. Each half cell was assembled by sliding the two inside faces of the half cells 5 to 15 mm to create a temperature difference across the long distance of the membrane (δ') instead of the membrane thickness (δ) as shown in Fig. 2b. That is, the membrane was used as a ribbon with the two contacts to the external solutions on opposite sides and separated by 0 to 10 mm.

Measurements of thermal membrane potential

The thermal membrane potential cell was constructed with calomel electrodes as follows:

$$\begin{array}{lccc} & \underbrace{\text{Hg/Hg}_2\text{Cl}_2\text{. satd. KCl/electrolyte/membr./}} & \underbrace{\text{electrolyte/satd. KCl.}} & \underbrace{\text{Hg}_2\text{Cl}_2\text{/Hg .}} \\ \text{temperature:} & T & T+\Delta T & T \\ & \underbrace{\qquad\qquad\qquad\qquad} & \underbrace{\qquad\qquad\qquad} & \\ \text{electric potential:} & \psi & \psi+\Delta\psi & \end{array}$$

The thermal membrane potential was measured with a digital electrometer TR-8411 (Advantest Co., Japan) which was carefully shielded from the electric field. The membranes were equilibrated in the solutions at the temperature T before being used for the experiments. Two controlled solutions with the same concentration but at different temperatures were flushed on the two surfaces of the membrane. The thermal membrane potentials reached constant values after about 10 s, at a flow rate of 250 cm^3/min.

Measurements of electroosmosis

A membrane was mounted between two 69.2 cm^3 of cells made of poly(vinyl chloride) resin equipped with magnetic stirrers, silver-silver chloride electrodes, and capillaries for measuring volume flow. All experiments were run in 0.1 mol/kg solutions at 2 to 4 mA/cm^2. The reduced transport number of water (τ_0), i.e., the number of moles of water transported through the

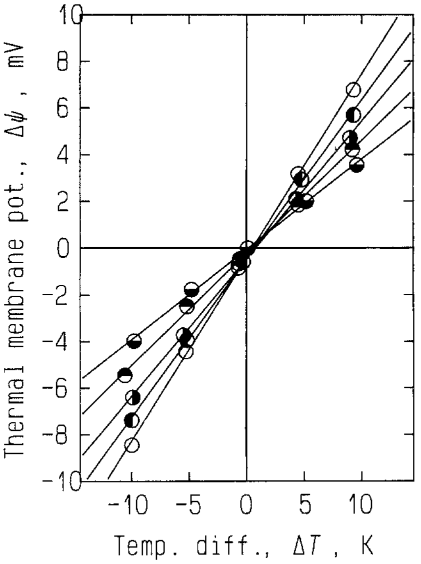

Fig. 3. The thermal membrane potential $\Delta\psi$ across Flemion S against temperature difference ΔT in KCl solution. Molalities (mol/kg): ○, 0.001; ◐, 0.003; ◑, 0.01; ◓, 0.03; ◒, 0.1.

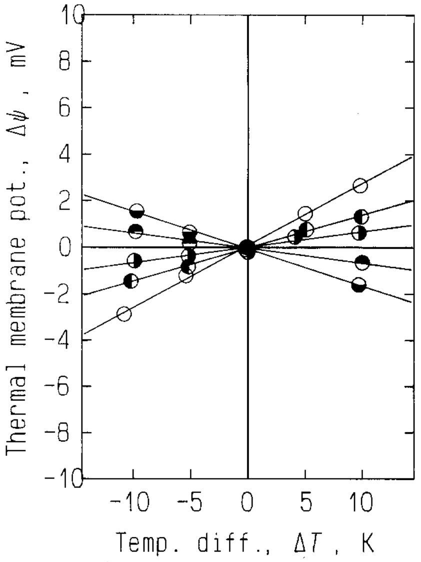

Fig. 5. The thermal membrane potential $\Delta\psi$ across Flemion S against temperature difference ΔT in HCl solution. Molalities (mol/kg): ○, 0.001; ◐, 0.003; ◑, 0.01; ◓, 0.03; ◒, 0.1.

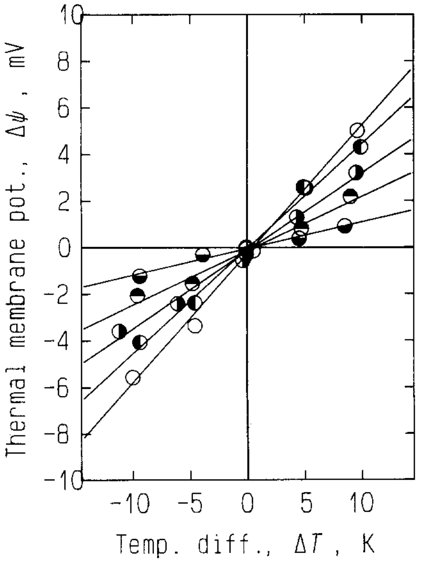

Fig. 4. The thermal membrane potential $\Delta\psi$ across Flemion S against temperature difference ΔT in $(CH_3)_4NCl$ solution. Molalities (mol/kg): ○, 0.001; ◐, 0.003; ◑, 0.01; ◓, 0.03; ◒, 0.1.

membrane per 96485 C, was calculated neglecting the volume change of the electrodes.

Results and discussion

Figures 3 and 4 show the thermal membrane potential difference between the two cells for KCl and $(CH_3)_4NCl$ relative to the temperature difference, respectively. In all cases the potential on the hot side is positive. The positive values of $\Delta\psi$ mean that the counterions in the membranes are forced from the cold side to the hot side just as the concentration membrane potential across a cation-exchange membrane where the electric potential at the low concentration side is positive because cations are forced to move from the high concentration side to the lower concentration side.

Figure 5 also shows the relationship between the thermal membrane potential and the temperature difference for HCl solutions. For HCl solutions, the sign of the potential varies from positive to negative at molalities of 0.03 and 0.1 mol/kg, as observed for hydrocarbonsulfonic acid-type membranes in HCl solutions [3]. In all cases of the other electrolytes, linear relationships between $\Delta\psi$ and ΔT were observed to be similar to that shown in the figures. The correction for the liquid junction potentials was neglected because the difference between the two liquid junction potentials was smaller than 0.1 mV. In all cases except HCl the thermal membrane potential was always positive.

Figure 6 shows the temperature coefficients of thermal membrane potential $(-\Delta\psi/\Delta T)$ against

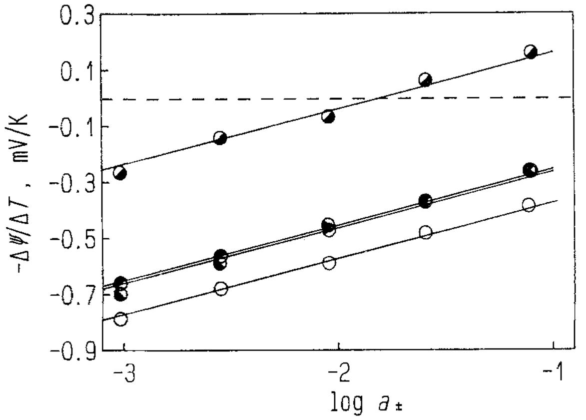

Fig. 6. Temperature coefficient of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_\pm$. Electrolytes: ◒, HCl; ◑, LiCl; ◐, NaCl; ○, KCl.

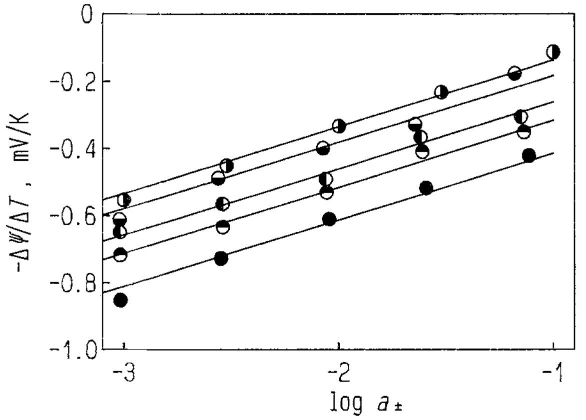

Fig. 7. Temperature coefficient of the membrane potential $-\Delta\psi/\Delta T$ against $\log a_\pm$. Electrolytes: ●, NH_4Cl; ◓, CH_3NH_3Cl; ◐, $(CH_3)_2NH_2Cl$; ◒, $(CH_3)_3NHCl$; ◑, $(CH_3)_4NCl$.

$\log a_\pm$ for HCl and alkali metal chlorides, where the mean activities of the ions [10] were used instead of the activities of the single cations. In the figure, the slope was fixed at a theoretical value, $2.303R/F = 0.1984$ mV/K, because all the observed values have nearly the same slope as the theoretical value predicted by Eq. (2). The values of $-\Delta\psi/\Delta T$ increase in the order of $H^+ > Li^+ = Na^+ > K^+$, which is roughly the inverse of that of the crystallographic radii of the ions. Figure 7 also shows $(\Delta\psi/\Delta T)$ against $\log a_\pm$ for ammonium and methyl ammonium chlorides. The mean activities of these salts were estimated from the data in the literature [10, 11]. The molality was used instead of the activity for tetramethylammonium chloride at low molalities because of the lack of data. The slopes in the figure are also fixed at $2.303R/F$. The values of $-\Delta\psi/\Delta T$ increase with an increasing number of methyl groups, that is, the absolute values of the thermal membrane potential increase with a decreasing number of methyl groups. The molar entropies of water and ions are dependent on the temperature [12]. However, Figs. 6 and 7 show that the values of $(\bar{\bar{s}}_+ - s_+^0)/F$ and $\tau_0(\bar{\bar{s}}_0 - s_0)$ are constant and nearly independent of the temperature in the range of the experiments.

The values of $F\tau_0$ were obtained by measurements of electroosmosis and are listed in Table 1. The value of τ_0 increases with increasing radii of the hydrated ions and with increasing membrane water content for the alkali metal ions, where the water content was expressed by the unit: g H_2O per g of dry membrane without the weight of the counterions. The value of τ_0 for H^+ is smaller than that for Li^+ because the proton jump mechanism may occur in the membrane in electroosmosis. For ammonium and alkyl ammonium ions, the water contents are nearly constant without NH_4^+ ion. The values of τ_0 increase with an increase in the number of bulky methyl groups. Similar relationships were observed for hydrocarbonsulfonic acid-type membranes [13].

Substituting the data on both electroosmosis and thermoosmosis [5] into Eq. (3) gives relationships between $-F\Delta\psi/\Delta T - F\tau_0(\bar{\bar{s}}_0 - s_0)$ and $\log a_\pm$. The value of $-F\Delta\psi/\Delta T - F\tau_0(\bar{\bar{s}}_0 - s_0)$ means the value of the entropy difference of the counterions, $(\bar{\bar{s}}_+ - s_+)$. The order of $(\bar{\bar{s}}_+ - s_+)$ for HCl and alkali metal ions is $H^+ > Na^+ > K^+ > Li^+$, which is the same as for the conventional ionic heats of transport (Q^*) and is just the inverse of that of D or $(\bar{\bar{s}}_0 - s_0)$ in thermoosmosis. The values of the entropy difference of H^+ $(\bar{\bar{s}}_H - s_H)$ are negative at 0.001 mol/kg of HCl solution, that is, the difference in the molar enthalpy of H^+ ions transferring from the external solution into the membrane, $\Delta h_H = -T(\bar{\bar{s}}_H - s_H)$, is positive. This exothermic process is more apt to occur at the cold solution side than at the hot side. Thus, H^+ ions are forced to move from the cold side to the hot side. However, in the range of 0.003 or greater molalities, H^+ ions are inversely forced to move toward the cold side. The H^+ is so small that the difference in the ionic states may be small between the membrane phase and the external

Table 1. The values of α_+, $F\tau_0$, $(\bar{s}_0 - s_0)$, $(\bar{s}_+ - s_+^0)$, $\bar{s}_+$ and water content for Flemion S.

Counterions	α_+ (mV·K^{-1})	$F\tau_0$	$(\bar{s}_0 - s_0)^a$ (J·K^{-1}·mol^{-1})	$(\bar{s}_+ - s_+^0)$ (J·K^{-1}·mol^{-1})	$\bar{s}_+{}^b$ (J·K^{-1}·mol^{-1})	Water content^{a,c}
H^+	0.403	26.6	−0.548	53.5	53.5	0.59
Li^+	−0.011	51.5	0.594	−31.7	−35.1	0.56
Na^+	−0.036	37.0	−0.030	−2.36	−16.8	0.46
K^+	−0.151	15.4	0.077	−15.8	−40.3	0.26
NH_4^+	−0.159	31.9	0.387	−27.6	−54.0	0.37
$CH_3NH_3^+$	−0.105	39.5	0.393	−25.6	–	0.28
$(CH_3)_2NH_2^+$	−0.08	39.6	0.285	−19.0	–	0.27
$(CH_3)_3NH^+$	0.07	47.3	−0.020	7.7	–	0.29
$(CH_3)_4N^+$	0.105	60	−0.249	25.0	–	0.28

[a] from ref. [5].

[b] calculated from the values of s_+^0 based on $s_H^0 = 0$ [10].

[b] g-H_2O/g-dry membrane without counterions.

Table 2. The values of $-\Delta\psi/\Delta T$, $-(\Delta\psi/\Delta T)_0$, and $-(\Delta\psi/\Delta T)_+$ at 0.001 and 0.1 (mol/kg) for Flemion S.

Counterions	$-\Delta\psi/\Delta T$ mV·K^{-1}		$-(\Delta\psi/\Delta T)_0$ mV·K^{-1}	$-(\Delta\psi/\Delta T)_+$ mV·K^{-1}	
	0.001 (mol/kg)	0.1 (mol/kg)		0.001 (mol/kg)	0.1 (mol/kg)
H^+	0.266	−0.16	0.151	−0.115	0.311
Li^+	0.698	0.263	−0.317	−1.02	−0.58
Na^+	0.66	0.261	0.012	−0.648	−0.249
K^+	0.786	0.386	−0.012	−0.798	−0.398
NH_4^+	0.852	0.452	−0.127	−0.979	−0.579
$CH_3NH_3^+$	0.719	0.351	−0.161	−0.88	−0.512
$(CH_3)_2NH_2^+$	0.649	0.305	−0.117	−0.766	−0.422
$(CH_3)_3NH^+$	0.611	0.175	0.010	−0.601	−0.165
$(CH_3)_4N^+$	0.553	0.113	0.154	−0.399	0.041

solution phase, and the entropy difference is also small. Therefore, the sign of $(\bar{s}_H - s_H)$ varies with the molality.

We can rewrite Eq. (1) for an ideal cation permselective membrane and 1 − 1 electrolyte systems as follows

$$-\Delta\psi/\Delta T = -\left[(\Delta\psi/\Delta T)_+ + (\Delta\psi/\Delta T)_0\right] , \quad (6)$$

where

$$-(\Delta\psi/\Delta T)_+ = (\bar{s}_+ - s_+) , \quad (7)$$

$$-(\Delta\psi/\Delta T)_0 = \tau_0(\bar{s}_0 - s_0) . \quad (8)$$

As shown in Table 2, at 0.1 mol/kg of HCl solution the value of $-(\Delta\psi/\Delta T)_+$ is − 0.33 mV/K and the value of $-(\Delta\psi/\Delta T)_0$ is −0.10 mV/K. In the thermoosmotic experiments [5], the direction of water for the HCl solution is toward the hot side: $(\bar{s}_0 - s_0)$ is negative. Therefore, the thermal membrane potential due to the interaction between water and ions $-(\Delta\psi/\Delta T)_0$ is negative. However, the value of $-(\Delta\psi/\Delta T)_+$ at 0.001 mol/kg is positive 0.10 mV/K against $-(\Delta\psi/\Delta T)_0$.

On the other hand, the transported entropy of Li^+ $(\bar{s}_{Li})$ is much smaller than s_{Li}. For LiCl solutions, $(\bar{s}_0 - s_0)$ is positive, that is, the process of water transferring into the membrane is endothermic.

For ammonium and methyl ammonium ions, the order of $(\bar{s}_+ - s_+)$: $(CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2 > CH_3NH_3^+ > NH_4^+$ is the same as that for $-\Delta\psi/\Delta T$. This order is also the inverse of that of D or $(\bar{s}_0 - s_0)$ obtained in thermoosmosis. It is interesting that the absolute value of $-\Delta\psi/\Delta T$ in the NH_4Cl solution is the highest among the ammonium and methyl ammonium halide solutions and also the value of the thermoosmosis toward the cold solution side is the highest in the NH_4Cl solution. $(\bar{s}_+ - s_+)/F$ in Eq. (1) which is the thermal membrane potential due to the counterions $-(\Delta\psi/\Delta T)_+$ is negative. The counterions are forced to move toward the hot side. On the other hand, $\tau_0(\bar{s}_0 - s_0)/F$ is positive for NH_4^+, $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$. In thermoosmosis, water moves toward the cold side, and the thermal membrane potential due to the interaction between water and ions $-(\Delta\psi/\Delta T)_0$ is positive against $-(\Delta\psi/\Delta T)_+$.

The values of α_+ and $\bar{s}_+$ are also tabulated in Table 1 where the values of s_+^0 based on $s_H^0 = 0$ are used [10].

Conclusions

1) The sign of the thermal membrane potential across a perfluorosulfonic acid-type membrane in the HCl solution varies from positive to negative with the concentration.

2) The difference between the mean molar transported entropy of the counterions in the membrane and the partial molar entropy of the counterions in the external solution $(\bar{s}_+ - s_+)$ was determined from the experimental data on thermal membrane potential, thermoosmosis and electroosmosis.

3) In the HCl and alkali metal chloride solutions, the order of the thermal membrane potential $(-\Delta\psi/\Delta T)$ is $H^+ > Li^+ = Na^+ > K^+$. However, the order of the entropy difference $(\bar{s}_+ - s_+)$ is $H^+ > Na^+ > K^+ > Li^+$, which is just the inverse of that of the thermoosmotic coefficient (D) or the entropy difference of water $(\bar{s}_0 - s_0)$ in thermoosmosis.

4) For the ammonium and methyl ammonium ion forms, the orders of $-\Delta\psi/\Delta T$ and $(\bar{s}_+ - s_+)$ are $(CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2^+ > CH_3NH_3^+ > NH_4^+$, which is also the inverse of that of D or $(\bar{s}_0 - s_0)$.

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References

1. Tasaka M (1986) Pure Appl Chem 58:1637–1646
2. Tasaka M, Morita S, Nagasawa M (1965) J Phys Chem 69:4191–4197
3. Kiyono R, Tanaka Y, Sekiguchi S, Tasaka M (1993) Colloid Polym Sci 271:1183–1190
4. Hanaoka K, Kiyono R, Tasaka M (1993) J Membrane Sci 82:255–263
5. Suzuki T, Kiyono R, Tasaka M (1993) submitted to Colloid Polym Sci
6. Tasaka M, Urata T, Kiyono R, Aki Y (1992) J Membrane Sci 67:83–91
7. Tasaka M, Hirai T, Kiyono R, Aki Y (1992) J Membrane Sci 71:151–159
8. Hanaoka K, Kiyono R, Tasaka M (1993) The 65th Annual Meeting of Chem Soc Japan 4-D4-35
9. Scatchard G, Orttung (1966) J Colloid Sci 22:12–18
10. Parsons R (1959) Handbook of electrochemical constants, Butterworths Sci. Publ., London
11. Jones JH, Spuhler FJ, Felsing WA (1942) J Amer Chem Soc 64:965–968
12. Lentz BR, Hagler AT, Scheraga HA (1974) J Phys Chem 78:1531–1550
13. Breslau BR, Miller IF (1971) I&EC Fundamentals 10:554–565

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