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# Nonisothermal membrane phenomena across perfluorosulfonic acid-type membranes, Flemion S: part I. Thermoosmosis and transported entropy of water

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*Abstract*: Solvent transports across the perfluorosulfonic acid-type membrane Flemion S were measured for aqueous electrolyte solutions under a temperature difference and under an osmotic pressure difference. $H^+$, $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(n\text{-}C_3H_7)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ were used as counterions. Water flux across the membrane in HCl solution is higher than that in the other electrolyte solutions because hydrogen ions can exchange with the hydrogen of the neighbor water molecules and contribute to the water transport across the membrane as a proton jump in conductivity. The direction of thermoosmosis across the membrane in HCl, NaCl, $(CH_3)_4NCl$ and $(C_2H_5)_4NCl$ solutions was from the cold side to the hot side and that in LiCl, KCl, $NH_4Cl$, $CH_3NH_3Cl$, $(CH_3)_2NH_2Cl$ and $(n\text{-}C_4H_9)_4NBr$ solutions was from the hot side to the cold side, although thermoosmosis across anion-exchange membranes always occurs toward the hot side.

*Key words*: Cation-exchange membranes – osmosis – perfluorosulfonic acid membranes – thermoosmosis – transported entropy

## Introduction

In general, thermoosmosis appears from the hot side to the cold side for hydrophobic membranes and toward the hot side for hydrophilic membranes [1]. For anion-exchange membranes with vairous counterions, the direction of thermoosmosis is all from the cold side to the hot side [2, 3]. However, for cation-exchange membranes, the direction of thermoosmosis changes with the counterions [4, 5]. In this paper, we studied the dependence of the thermoosmotic coefficient on the species of counterions for porous perfluorosulfonic acid-type membranes.

Applying nonequilibrium thermodynamics to ion transport processes [6, 7] gives the phenomenological equations for the fluxes:

$$-J_s = L_{ss}\Delta T + \Sigma_i L_{si}\Delta\tilde{\mu}_i \qquad (1)$$

$$-J_i = L_{is}\Delta T + \Sigma_j L_{ij}\Delta\tilde{\mu}_j\ , \qquad (2)$$

where $J_s$ is the total entropy flux, $J_i$ the absolute mass flux, $T$ the temperature, $\tilde{\mu}_i$ the electrochemical potential, and $L$'s the proportionality constants having units of conductance. Using phenomenological coefficients of generalized resistances ($r$'s), $J_s$ is also expressed as [8, 9]

$$\begin{aligned}-J_s &= (1/r_{ss})\Delta T + \Sigma_i(r_{si}/r_{ss})J_i\\ &= (1/r_{ss})\Delta T + \Sigma_i\bar{\bar{s}}_i J_i\ ,\end{aligned} \qquad (3)$$

where $\bar{\bar{s}}_i = r_{si}/r_{ss}$ is the transported entropy of component i, which means the entropy transported by the transfer of one mole of component i. Therefore, substitution of Eq. (3) into Eq. (1) gives

$$L_{is} = -\Sigma_j L_{ij}\bar{\bar{s}}_j\ , \qquad (4)$$

where Onsager's reciprocal relationship is used.

If cation-exchange membranes are ideally permselective for counterions and a temperature difference ($\Delta T$), and an osmotic pressure difference ($\Delta\pi$) exist across the membranes, the volume flux ($J_v$) can be written as [10]

$$-J_v = D^*\{(\bar{\bar{s}}_0 - s_0)\Delta T - v_0\Delta\pi\}\ , \tag{5}$$

where

$$D^* = (1/\delta)(\bar{c}_0 l_{v0} - \tau_0 F\phi X l_{v+})\ . \tag{6}$$

The subscript 0 refers to water molecules, $\bar{c}_0$ is the concentration of water in the membrane phase, $\tau_0$ the reduced transport number of water, $s_0$ the partial molar entropy of water in the external solution, $\bar{\bar{s}}_0$ the mean molar transported entropy of water in the membrane, $v_0$ the partial molar volume, $\delta$ the thickness of the membrane, $F$ the Faraday constant, and $\phi X$ is the effective concentration of membrane fixed charges. The $l_{v0}$ is a parameter related to the mobility of water in the membrane and $l_{v+}$ is related to the interaction between the cations and water. The $l_{v0}$ and $l_{v+}$ may be expressed by $fl_{v0}^{\circ}$ and $fl_{v+}^{\circ}$ where $f$ is a tortuosity factor depending on the tortuosity and porosity of the membrane [11–13]. Therefore, $D^*$ is rewritten as

$$D^* = fD^{*\circ}\ , \tag{7}$$

where

$$D^{*\circ} = (1/\delta)(\bar{c}_0 l_{v0}^{\circ} - \tau_0 F\phi X l_{v+}^{\circ})\ . \tag{8}$$

In a capillary model the tortuosity factor $f$ is expressed by [12]

$$f = (A^{\circ}/\delta^{\circ})/(A/\delta)\ , \tag{9}$$

where $A^{\circ}$ and $\delta^{\circ}$ are the effective membrane area and the effective length of the membrane thickness, and $A$ is the membrane area. In general, we may assume that

$$f \propto (\phi^{\circ})^{2/3}/(\phi^{\circ})^{1/3} = (\phi^{\circ})^{1/3}\ , \tag{10}$$

where $\phi^{\circ}$ is the volume fraction of the liquid phase in the membrane.

If the counterion of the membrane is $H^+$ ion, the proton can exchange with the hydrogen of water molecules; therefore, volume flux under a temperature gradient and a pressure gradient may be larger than those with other counterions [4].

If there is no pressure difference, Eq. (5) becomes

$$-J_v = D\Delta T\ , \tag{11}$$

where

$$D = (\bar{\bar{s}}_0 - s_0)D^* = fD^{\circ}\ , \tag{12}$$

$$D^{\circ} = (\bar{\bar{s}}_0 - s_0)D^{*\circ}\ . \tag{13}$$

If the counterions are proton or ammonium-type ions, the ion exchange between a hydrogen of the counterions and a hydrogen of the water molecules in the membrane may occur, and the entropy of water may increase in the membrane.

Moreover, if there is no temperature difference, Eq. (5) becomes

$$-J_v = L_p\Delta\pi\ , \tag{14}$$

where

$$L_p = -v_0 D^*\ . \tag{15}$$

Therefore, if we obtain the values of $D$ and $L_p$, we can estimate the value of the entropy difference $(\bar{\bar{s}}_0 - s_0)$ from Eqs. (12) and (15), and the value of the difference in the molar enthalpy of water between the external solution and the membrane at a steady state, $\Delta h_0 = -T(\bar{\bar{s}}_0 - s_0)$.

$$\begin{aligned}\bar{\bar{s}}_0 - s_0 &= -v_0 D/L_p \\ &= D/D^*\ .\end{aligned} \tag{16}$$

## Experimental

### Membranes

Porous perfluorosulfonic acid-type membranes, Flemion S, were used. The thickness of the membrane was 0.21 mm and the transport number of cations in the membrane was 0.99 for 0.01 mol/kg KCl/membrane/0.02 mol/kg KCl.

### Electrolyte solutions

The reagents used for the preparation of HCl, LiCl, NaCl, KCl, $NH_4Cl$, $CH_3NH_3Cl$, $(CH_3)_2NH_2Cl$, $(CH_3)_4NCl$, $(C_2H_5)_4NCl$, $(n\text{-}C_3H_7)_4NBr$ and $(n\text{-}C_4H_9)_4NBr$ aqueous solutions were special grades and for that of $(CH_3)_3NHCl$ was first grade from Wako Pure Chemical Industries, Ltd. Japan. Thermoosmosis measurements were carried out at 0.01 mol/kg of these electrolyte solutions.

### *Ion-exchange capacity and water content*

Ion-exchange capacities were measured by immersing the $H^+$ form membrane in NaCl solution and titrating the amount of $H^+$ ions released. The counterions of the membranes were changed by boiling the membranes in 1 mol/kg of the electrolyte solution for 30 min. The electrolyte absorbed in the membrane was repeatedly rinsed out in pure water four to five times at room temperature. Moreover, the membrane was boiled in pure water for 30 min to remove the free electrolyte. The ion-exchange capacity is expressed by the unit: mmol of ion-exchange groups per g of the dry membrane without the weight of the counterions.

The water contents of membranes equilibrated with ion exchanged water and 0.01 mol/kg electrolyte solutions were measured. However, the difference in the water contents between them was not observed in experimental errors. Moreover, the water content was independent of temperature in the range of the experiments. The water content ($w_0$) is also expressed by the unit: g of water per g of the dry membrane without the weight of the counterions.

### *Measurements of membrane resistance*

Membranes were equilibrated at 0.01 mol/kg of the ammonium and the alkyl ammonium halide solutions. Two flat, impervious carbon electrodes were directly connected to both sides of the membrane equilibrated with the solution and the membrane resistance was measured at 25 °C with 10 kHz using an LF Impedance Analyzer 4192A (Yokogawa-Hewlett-Packard, Ltd., Japan).

### *Measurements of thermoosmosis*

The cell for measuring mass transport under a temperature gradient was similar to the thermoosmosis cell described in the previous paper [3]. The upper section, which is a hot chamber (1500 $cm^3$), was larger than the lower, a cold chamber (96 $cm^3$). All measurements of thermoosmosis were carried out at 308.2 K, the mean temperature of the two chambers. The effective area of the membrane was 28 $cm^2$. The relationship between the effective temperature difference across the membrane ($\Delta T$) and the temperature difference of two bulk solutions ($\Delta T_b$) was estimated by measuring the thermal membrane potential. The value of $\Delta T/\Delta T_b$ was about 0.7 for all membranes [1].

### *Measurements of osmotic volume flux*

Volume flux under an osmotic pressure difference was measured using the same cell as that described in the previous paper [3]. The effective area of the membrane was 2.54 $cm^2$. The cell was placed in an air thermostat and the temperature was kept at $298.16 \pm 0.05$ K. The concentration of the external salt solution on one side of the membrane was fixed at 0.001 mol/$dm^3$, and that on the other side was varied in the range of 0.025 to 0.2 mol/$dm^3$. The osmotic pressure difference between the two chambers was estimated from the concentration difference and osmotic coefficients in the literature [14,15]. However, the osmotic coefficients for $CH_3NH_3Cl$, $(CH_3)_2NH_2Cl$ and $(CH_3)_3NHCl$ were assumed to be 0.9 because of the lack of data. When the volume flux was plotted against the osmotic pressure difference, deviation of the volume flux from a straight line was sometimes observed. In those cases, we estimated the hydraulic coefficient ($L_p$) or the coefficient ($D^*$) from the initial slopes.

## Results and discussion

Figures 1 and 2 show examples of the movement of the liquid meniscus against time ($t$) for Flemion S with the $H^+$ form in 0.01 mol/kg of HCl solution and the $NH_4^+$ form in 0.01 mol/kg of $NH_4Cl$ solution, respectively, where the mean temperature was kept at 308.2 K and the temperature differences of the bulk solutions ($\Delta T_b$) were 3 to 12 K. For the $H^+$ form, the direction of thermoosmosis is from the cold side to the hot side; whereas, for the $NH_4^+$ form that is from the hot side to the cold side. Thermoosmotic volume fluxes were calculated from the slopes of these figures.

Figure 3 shows the linear relationships between the volume flux and the temperature difference of the bulk solutions in 0.01 mol/kg of HCl, LiCl, NaCl and KCl solutions. The linear relationship means that $(\bar{s}_0 - s_0)$ is independent of the temperature in the range of the experiments, although

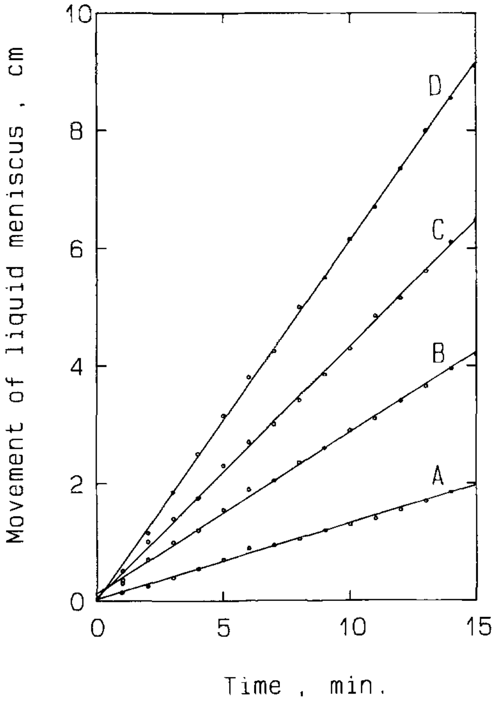

Fig. 1. Examples of the movement of liquid meniscus under temperature differences for the $H^+$ form Flemion S. Temperature differences (K): A, 3; B, 6; C, 9; D, 12.

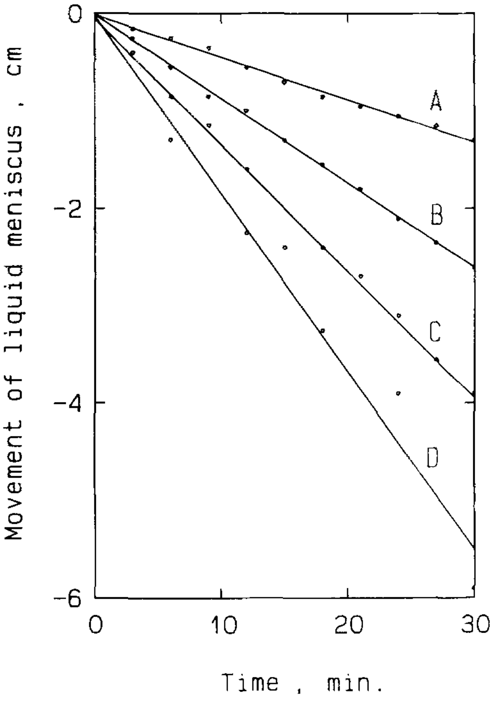

Fig. 2. Examples of the movement of liquid meniscus under temperature difference for the $NH_4^+$ form Flemion S. Temperature differences (K): A, 3; B, 6; C, 9; D, 12.

the molar entropy of water is dependent on the temperature [16]. The direction of thermoosmosis is from the cold side to the hot side when the counterions are $H^+$ or $Na^+$ ions and from the hot side to the cold side when the counterions are $Li^+$ or $K^+$ ions.

Figure 4 shows the linear relationships between the volume flux and the temperature difference in the ammonium and the alkyl ammonium halide solutions. In the $NH_4Cl$, $(CH_3)NH_3Cl$ and $(CH_3)_2NH_2Cl$ solutions, the direction of thermoosmosis is clearly toward the cold side. For $(CH_3)_3NHCl$ solution, the value of thermoosmosis is almost zero. Moreover, for the $(CH_3)_4NCl$ solution the direction of thermoosmosis becomes inverse toward the hot side. The value of thermoosmosis in the $(C_2H_5)_4NCl$ solution is larger than that in the $(CH_3)_4NCl$ solution and toward the hot side because the $(C_2H_5)_4N^+$ ion is bulkier than $(CH_3)_4N^+$. The value of thermoosmosis in the $(n\text{-}C_3H_7)_4NBr$ solution is almost zero. Finally, for the $(n\text{-}C_4H_9)_4NBr$ solution, the direction of thermoosmosis changes again toward the cold side, because the state of water is unstable in the hydrophobic membranes, and the entropy of water in the membrane is larger than the partial molar entropy of the external solution [1]. Thus, the volume flux increases with a decreasing number of hydrogens combining with the nitrogen of the counterions. The highest value of thermoosmosis was observed for the $(C_2H_5)_4NCl$ solution, and after that thermoosmosis decreased with increasing hydrophobicity of the counterions.

In order to estimate the difference between the mean molar transported entropy of water in the membrane phase ($\bar{s}_0$) and the molar entropy of water in the external solutions ($s_0$), the volume flux ($J_v$) was measured under an osmotic pressure difference. Figures 5 shows the relationship between the volume flux and osmotic pressure difference in electrolyte solutions. Water contents for Flemion S with various counterion forms are listed in Table 1. The volume flux is abnormally higher in HCl solutions than in the other electrolyte solutions, even if we take the highest water content in HCl solution into consideration. The volume flux could not be observed for $(n\text{-}C_3H_7)_4NBr$ and $(n\text{-}C_4H_9)_4NBr$ solutions. The

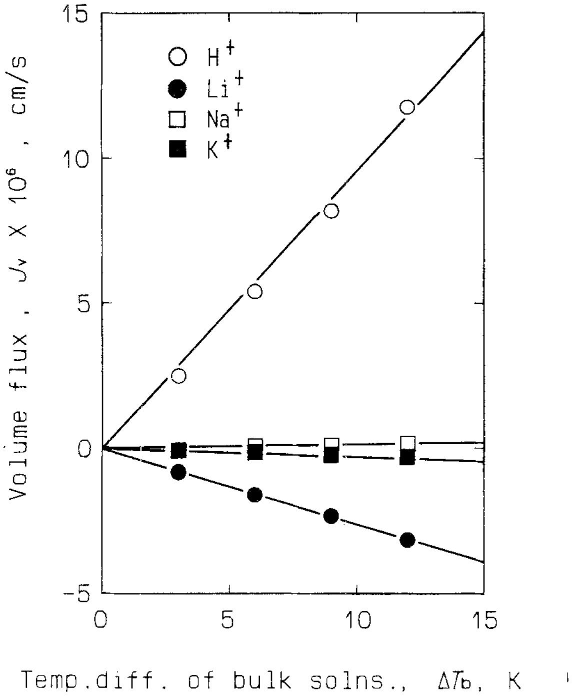

Fig. 3. The dependence of thermoosmotic volume flux ($J_v$) on the temperature difference of bulk solutions ($\Delta T_b$) for Flemion S with the $H^+$, $Li^+$, $Na^+$, and $K^+$ forms at the mean temperature 308.2 K.

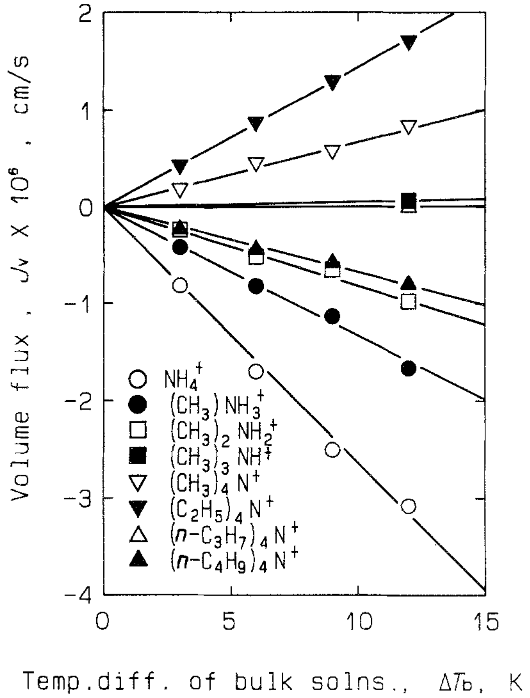

Fig. 4. The dependence of thermoosmotic volume flux ($J_v$) on the temperature difference of bulk solutions ($\Delta T_b$) for Flemion S with the various ammonium ion forms at the mean temperature 308.2 K.

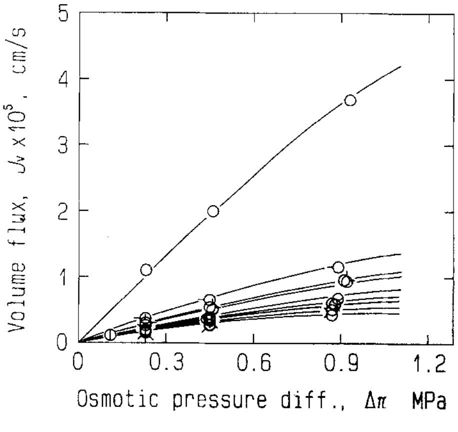

Fig. 5. The dependence of osmotic volume flow ($J_v$) on the osmotic pressure difference of the external salt solutions ($\Delta\pi$) for Flemion S at 298.15 K. ○, HCl; ȯ, LiCl; ○—, NaCl; ọ, KCl; -○, $NH_4Cl$; ○́, $CH_3NH_3Cl$; ○, $(CH_3)_2NH_2Cl$; ○, $(CH_3)_3NHCl$; ○, $(CH_3)_4NCl$; ⦶, $(C_2H_5)_4NCl$.

volume flux under osmotic pressure difference in $NH_4Cl$ solutions is fairly higher than those in alkylammonium chloride solutions, because the water content in the former is higher than those in the latter.

The thermoosmotic coefficient ($D$) obtained from the slopes in Figs. 3 and 4, coefficient ($D^*$) obtained from the initial slopes in Fig. 5, and the entropy difference, $(\bar{\bar{s}}_0 - s_0)$, (estimated from $D$ and $D^*$) are listed in Table 1. In order to study the dependence of $D^\circ$ on the counterions, $f_{Li}D^\circ$ which means the thermoosmotic coefficient at the same water content as that with the $Li^+$ form was calculated and also listed in Table 1, where the volume fraction $\phi^\circ$ was approximately evaluated by the assumption $\phi^\circ = w_0/(1 + w_0)$. The order of $D^\circ$ is the same as that of $D$ because the variation in the water contents was comparatively small.

The values of $-(\bar{\bar{s}}_0 - s_0)$ are from $-0.59\ J\,K^{-1}mol^{-1}$ for the $Li^+$ form to $0.55\ J\,K^{-1}mol^{-1}$ for the $H^+$ form in HCl and alkali metal chloride solutions. The values of $-(\bar{\bar{s}}_0 - s_0)$ are from $-0.39\ J\,K^{-1}mol^{-1}$ for the $NH_4^+$ form to $0.43\ J\,K^{-1}mol^{-1}$ for the $(C_2H_5)_4N^+$ form in ammonium and alkylammonium chloride solutions. On the whole, the

Table 1. The values of water content, $D, f_{\mathrm{Li}}D^{\circ}$, $D^*$ and $-(\bar{s}_0 - s_0)$ for Flemion S.

| Counterions | Water content, $w_0$ (g-$H_2O$/g-dry membr. without counterions) | $-D \times 10^7$ $\mathrm{cm \cdot s^{-1} \cdot K^{-1}}$ | $-f_{\mathrm{Li}}D^{\circ} \times 10^7$ $\mathrm{cm \cdot s^{-1} \cdot K^{-1}}$ | $D^* \times 10^7$ $\mathrm{cm \cdot mol \cdot J^{-1} \cdot s^{-1}}$ | $-(\bar{s}_0 - s_0)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ |
|---|---|---|---|---|---|
| $H^+$ | 0.59 | 14.6 | 14.5 | 26.7 | 0.55 |
| $Li^+$ | 0.56 | −3.7 | −3.7 | 6.2 | −0.59 |
| $Na^+$ | 0.46 | 0.2 | 0.2 | 6.7 | (0.03) |
| $K^+$ | 0.26 | −0.4 | −0.5 | 4.7 | (−0.08) |
| $NH_4^+$ | 0.37 | −3.6 | −4.0 | 9.4 | −0.39 |
| $CH_3NH_3^+$ | 0.28 | −1.9 | −2.2 | 4.9 | −0.39 |
| $(CH_3)_2NH_2^+$ | 0.27 | −1.1 | −1.3 | 3.9 | −0.28 |
| $(CH_3)_3NH^+$ | 0.29 | 0.1 | 0.1 | 4.1 | (0.02) |
| $(CH_3)_4N^+$ | 0.28 | 1.0 | 1.2 | 4.0 | 0.25 |
| $(C_2H_5)_4N^+$ | 0.33 | 2.0 | 2.3 | 4.8 | 0.43 |
| $(n\text{-}C_3H_7)_4N^+$ | 0.14 | 0.0 | 0.0 | 0.0 | – |
| $(n\text{-}C_4H_9)_4N^+$ | 0.47 | −0.9 | −0.9 | 0.0 | $-\infty$ |

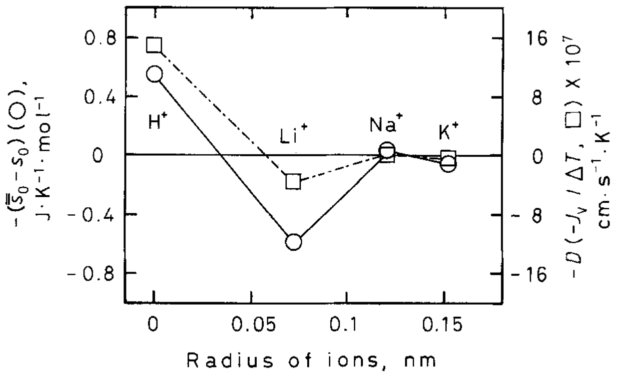

Fig. 6. The dependence of the entropy difference $-(\bar{s}_0 - s_0)$ and thermoosmotic coefficient $(-D)$ on the radius of counterions for Flemion S with the alkali metal ion forms.

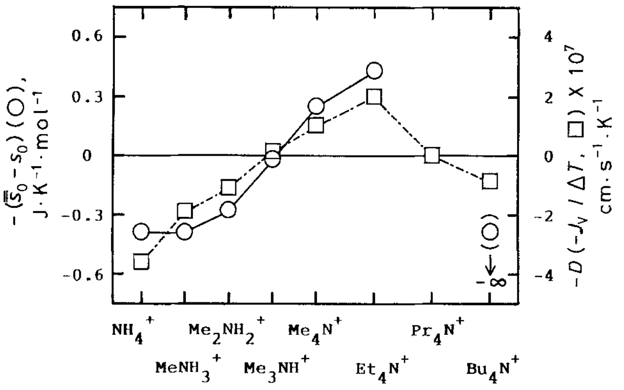

Fig. 7. The dependence of the entropy difference $-(\bar{s}_0 - s_0)$ and thermoosmotic coefficient $(-D)$ on the species of counterions for Flemion S with the various ammonium ion forms.

enthalpy differences $\Delta h_0 = -T(\bar{s}_0 - s_0)$ are from $-0.18$ to $0.17\ \mathrm{kJ\,mol^{-1}}$ when one mole of water is transported from the external solution phase into the membrane phase at $T = 308.2$ K.

The thermoosmotic coefficients $(D)$ are plotted against the ionic radii for hydrogen and alkali metal ions in Fig. 6, and against the species of the ammonium ions in Fig. 7. The order of the thermoosmotic coefficients in the hydrogen and alkali metal chloride solutions $(-D)$ is $H^+ > Na^+ > K^+ > Li^+$, which is the same for conventional ionic heats of transport in aqueous solutions $(Q^*)$ [17, 18]. Similar phenomena were reported for hydrocarbonsulfonic acid-type membranes [4, 5]. For ammonium and the alkyl ammonium ions, the order of $-D$ is $(C_2H_5)_4N^+ > (CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2^+ > CH_3NH_3^+ > NH_4^+$, which is also the same as that for the values of $Q^*$ [17, 18]. However, for bulkier alkyl ammonium ions, the order of $-D$ for the $(n\text{-}C_3H_7)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ forms is not the same as that for $Q^*$. The value of $-D$ for the $(n\text{-}C_4H_9)_4N^+$ form is negative and lower than that of the other methyl ammonium and ethyl ammonium ion forms, although the conventional ionic heat of transport of $(n\text{-}C_4H_9)_4N^+$ is higher than those of the other methyl ammonium and the ethyl ammonium ions [18]. Similarly, for anion-exchange membranes, it is known that there is no simple relationship between thermoosmotic coefficients and conventional ionic heats of transport in aqueous solutions [2, 3].

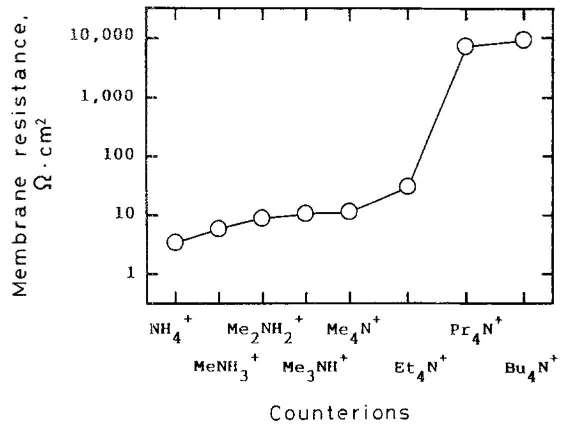

Fig. 8. The dependence of membrane resistance on the species of ammonium and alkyl ammonium ions.

The dependence of $(\bar{\bar{s}}_0 - s_0)$ on the counterions is similar as that of $D$ as shown in Figs. 6 and 7. This means that the dependence of $D^*(=-L_p/v_0)$ on the counterions is small compared with that of $(\bar{\bar{s}}_0 - s_0)$. Figure 8 shows the membrane resistance in the ammonium and the alkyl ammonium halide solutions. For the $(n\text{-}C_3H_7)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ forms, the resistance becomes very high and the appearance of the membrane changed into a stiffer state. This suggests that the hydrophobic interaction between the counterions and the membrane matrix is very strong and the influence of the alkyl group of the counterions on the state of water in the membrane also becomes very strong. Therefore, the value of $-(\bar{\bar{s}}_0 - s_0)$ is negative for the $(n\text{-}C_4H_9)_4N^+$ form as observed for polytetrafluoroethylene and polyethylene membranes [1].

In this work the value of $-D$ was negative with the $Li^+$, $K^+$, $NH_4^+$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$ and $(n\text{-}C_4H_9)_4N^+$ forms. The absolute value of $-D$ for the $NH_4^+$ form is 10 times greater than that for the $K^+$ form although their Stokes and crystallographic radii are similar. The entropy of water in the membranes with ammonium and alkyl ammonium ions will be large, because the hydrogen of ammonium ions may exchange with that of water. The molality of fixed charges of the membrane is about 2 mol/kg in LiCl solutions. Therefore, the bonding or association of the first and subsequent layers of water about the counterions in the membrane would be more strongly affected by the surrounding membrane matrix than those in free solutions. Thus, the difference in the states of water between the membrane and the external solution would be reflected in the entropy difference $(\bar{\bar{s}}_0 - s_0)$. An anomalous strong interaction between lithium ions and water in the membranes might cause the increase in transported entropy of water.

## Conclusions

1) Water flux across a Flemion S membrane with the $H^+$ form is higher than that with the other cation forms, because the hydrogen ions can exchange with the hydrogen of the neighboring water molecules and contribute to the water transport across the membrane as a proton jump in conductivity.

2) The direction of thermoosmosis across Flemion S with the $H^+$, $Na^+$, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ forms was from the cold side to the hot side and their entropy differences between the membranes and the external solutions $(\bar{\bar{s}}_0 - s_0)$ were negative.

3) The direction of thermoosmosis across Flemion S with the $Li^+$, $K^+$, $NH_4^+$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$ and $(n\text{-}C_4H_9)_4N^+$ forms was from the hot side to the cold side and their entropy differences $(\bar{\bar{s}}_0 - s_0)$ were positive.

4) The orders of the entropy difference $-(\bar{\bar{s}}_0 - s_0)$ are $H^+ > Na^+ > K^+ > Li^+$ for the hydrogen and alkali metal ion forms and $(C_2H_5)_4N^+ > (CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2^+ > CH_3NH_3^+ > NH_4^+$ for the ammonium and alkyl ammonium ion forms, respectively.

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