Thermoosmosis Across Hydrophobic and Hydrophilic Polymer Membranes

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Solvent transport across a hydrophobic PTFE membrane and the modified PTFE membranes was measured in water under a temperature difference. Moreover, thermoosmosis across the anion-exchange membrane, Neosepta AM-1, was measured for poly(acrylamide) and urea solutions. The direction of thermoosmosis across the PTFE and the modified PTFE membranes was from the hot side to the cold side, whereas that across anion-exchange membrane was from the cold side to the hot side. Thermoosmosis across the modified PTFE membranes decreased with increasing the hydrophilic groups in the membrane. For poly(acrylamide) and urea solutions the absolute values of volume fluxes decreased with increasing the concentration of the external solution, because of the decrease of the entropy difference of water between the membrane and the external solution.

Key Words : Anion-exchange membrane, PTFE membrane, Thermoosmosis, Transported entropy.

1. Introduction

For uncharged or low charged membranes, it was observed that the direction of thermoosmosis in water or aqueous solutions changes with wettability (hydrophobicity or hydrophilicity) of membranes¹⁾, temperature of external solutions^{2, 3)}, pore size of membranes^{4, 5)}, and solvent⁶⁾. In recent studies, for hydrophobic membranes thermoosmosis always occurs from the hot side to the cold side^{1, 7, 8)}. For charged membranes the direction of thermoosmosis is from the cold side to the hot side in anion-exchange membranes^{9, 10)}, and in cation-exchange membranes the direction of ther-

moosmosis depends on the nature of the counterions¹¹⁻¹⁵⁾.

According to the theory based on nonequilibrium thermodynamics^{16, 17)}, the volume flux, J_v , across an anion-exchange membrane for aqueous 1-1 electrolyte solutions is given by

$$-J_v = (D^0 + D' + D'')\Delta T, \quad (1)$$

where

$$D^0 = \bar{c}_0 l_{v0} (\bar{s}_0 - s_0) / \delta, \quad (1-1)$$

$$D' = \tau_0 F \phi X l_{v-} (\bar{s}_0 - s_0) / \delta, \quad (1-2)$$

$$D'' = (\bar{c}_+ + t_+ X) l_{v-} (\bar{s}_s - s_s) / \delta. \quad (1-3)$$

The ΔT is the temperature difference across the membrane, F the Faraday constant, ϕX the effective concentration of fixed charges, t_+ the transport number of cations in the membrane, δ the thickness of the membrane, and τ_0 is the reduced transport number of water. The $\bar{c}_0$ and $\bar{c}_+$ are the concentration of water and cations in the membrane phase, s_0 and s_s the partial molar entropies of water and solute in the external solution, $\bar{s}_0$ and $\bar{s}_s$ the mean molar transported entropies of water and solute in the membrane, respectively. The parameters l_{v0} and l_{v-} are related to the mobility of water in the membrane and related to the interaction between water and the anions, respectively.

If pure water is separated by an uncharged membrane, D' and D'' disappear and Eq. (1) reduces to

$$-J_v = \bar{c}_0 l_{v0} (\bar{s}_0 - s_0) (1/\delta) \Delta T. \quad (2)$$

Therefore, the direction and magnitude of thermosmosis across hydrophilic and/or hydrophobic membranes mainly depends on the difference between the transported entropy of water in the membrane, $\bar{s}_0$, and the partial molar entropy of water in the external solution, s_0 , whether the state of water in the membrane is liquid or not¹⁾. Although both $\bar{s}_0$ and s_0 are dependent on the temperature, the entropy difference of water at the hotter side interface, $\bar{s}_0(T+\Delta T) - s_0(T+\Delta T)$, will be approximately equal to that at the colder side interface of the membrane, $\bar{s}_0(T) - s_0(T)$. That is, the entropy difference between the membrane and the external solution at various temperatures, $\bar{s}_0 - s_0$, can be considered as constant: $\bar{s}_0 - s_0 = \bar{s}_0(T+\Delta T) - s_0(T+\Delta T) = \bar{s}_0(T) - s_0(T)$. If $\bar{s}_0$ is higher than s_0 , the transfer of water molecules from the external solution into the mem-

brane is endothermic and apt to occur at the hotter side interface, and the process of the water transfer from the membrane to the external solution is exothermic and apt to occur at the colder side. The direction of thermosmosis is toward the cold side ($J_v < 0$). But, if $\bar{s}_0$ is lower than s_0 , the direction is toward the hot side ($J_v > 0$). For hydrophilic collodion membranes it was observed that the absolute value of thermosmosis decreases with increasing the water content of the membranes, because the difference in the state of water between the membrane phase and the external solution phase decreases with increasing the water content¹⁾.

In this paper, we studied the dependence of thermosmosis on the entropy difference of water, $\bar{s}_0 - s_0$. In order to study the effect of the entropy difference, $\bar{s}_0 - s_0$, on thermosmosis we employed three methods: 1) to decrease $\bar{s}_0$ various modified PTFE membranes were prepared by introducing hydrophilic groups on the surface of a porous PTFE film membrane with radical reactions, 2) to decrease s_0 poly(acrylamide) (PAAm) solutions were used as the external solution, and 3) to change both $\bar{s}_0$ and s_0 aqueous urea solutions were used as the external solution, because both urea and water can enter the membrane phase.

2. Experimental

2.1 Membranes

The hydrocarbon quaternized amine-type anion-exchange membrane, Neosepta AM-1 (Tokuyama Soda Co., Ltd.); the hydrophobic PTFE membrane, Gore-Tex film (Japan Gore-Tex Inc.); and the modified PTFE membrane, WPW-045 (Sumitomo Denko Co., Ltd.), which has OH-groups on the

Table 1. The properties of various membranes.

Membrane	Membrane thickness (μm)	Pore diameter (μm)	Porosity (%)	Apparent water content ($\text{g}\cdot\text{H}_2\text{O}/\text{g}\cdot\text{dry membr.}$)
Gore-Tex film	120	0.20	73	—
WPW-045	188	0.45	86	1.14

Membrane	Membrane thickness (μm)	Ion-exchange capacity ($\text{mmol}/\text{g}\cdot\text{dry membr.}$)	Transport number	Water content ($\text{g}\cdot\text{H}_2\text{O}/\text{g}\cdot\text{dry membr. without conterions}$)
Neosepta AM-1	123	1.15* ¹	0.98* ²	0.35* ¹

*¹ : Cl form.*² : Calculated from the membrane potential in 0.1/0.2 mol kg⁻¹ of KCl solutions.

surface, were used. Moreover, the Gore-Tex films were treated by the agent, Tetra-Etch II (Junkosha Co., Ltd.), to introduce hydrophilic groups. Thus, the modified PTFE Gore-Tex film membranes, GT-TE, were also prepared. The GT-TE membranes will have partially hydrophilic groups on the surface. The properties of these membranes are listed in Table 1. The PTFE-based membranes were used for experiments after boiling in pure water for 1 h in order to remove the gas in the membrane.

2. 2. Preparation of the modified PTFE membranes

In order to introduce hydrophilic groups some pieces of the Gore-Tex film were immersed in viscous solutions with various ratios of the agent, Tetra-Etch II, to the diluent C₂H₅OH for 1 min. The films were pulled up and immediately immersed again in C₂H₅OH in order to stop the reaction. Then, the film membranes were repeatedly rinsed out in pure water and dried completely. Thus, the modified PTFE film membranes, GT-TE, were prepared. The ratios of the Tetra-Etch II to C₂H₅OH were 0, 0.2, 0.5 and 1.0. It was very difficult to carry out the reaction

to introduce hydrophilic groups with high reproducibility, because the mixture of the Tetra-Etch II and C₂H₅OH had high viscosity and the radical reactions on the film were not uniform. However, the degree of the hydrophilicity of the GT-TE membranes will be roughly proportional to the concentration of the Tetra-Etch II used for the same reaction time.

2. 3. Measurements of water content

For hydrophilic charged membranes the water content was measured by the usual method of blotting the water on the membrane surface with filter paper. Measuring the water content of hydrophobic membranes is very difficult. However, in order to know a measure for hydrophobicity of the hydrophobic membranes, we adopted the similar method for measuring water content as used for hydrophilic charged membranes and obtained an apparent water content. The apparent water content was measured : 1) a hydrophobic membrane was boiled for 1 h in pure water and cooled down to room temperature. 2) the weight of the wet membrane was measured for some times by blotting the water on the membrane surface with fil-

Fig. 1. The apparatus for measurement of thermoosmosis.

B : bottle for adjusting the head difference, C : cooler, Ct : capillary tube, E : carbon electrode, H : heater, M : membrane, Ms : magnetic stirrer, R : regulator, S : stirrer, Sc : solution container, St : magnetic stirrer tip, T : thermometer.

ter paper. 3) the membrane was dried completely and its weight was measured. The apparent water content was expressed by the unit : g-H₂O/g-dry membrane. The apparent water content of the GT-TE membranes was very little, because GT-TE membrane still remained a lot of hydrophobic part and water in the membrane was removed easily with filter paper. Therefore, we could not find out the relationship between the apparent water content and the ratio of the Tetra-Etch II to C₂H₅OH.

2. 4. External solutions

The reagents used for the preparation of aqueous KCl and urea solutions were special grades of Wako Pure Chemical Industries, Ltd. Japan. Poly(acrylamide) ($M_v = 8.2 \times 10^6$) fractionated from Diafloc (sup-

Fig. 2. Examples of the movement of liquid meniscus against time under temperature differences for Gore-Tex film membrane in water.
Temperature differences (K) : (A) 16 ; (B) 12 ; (C) 8 ; (D) 4.

plied by Nitto Chemical Industry Co., Ltd.) was also used to prepare the aqueous PAAM solutions.

2. 5. Measurements of thermoosmosis

The volume flux under a temperature difference was measured using two thermoosmosis cells as shown in Fig. 1. The upper hot chamber was larger than the lower cold chamber. The effective area of the membrane was 28 cm² or 19 cm². The two temperatures in the cold side and the hot side were controlled to fix the mean temperature at 308.2 K. The relationship between the effective temperature difference across the membrane, ΔT , and the temperature difference of two bulk solutions, T_b , has already been known and $\Delta T/\Delta T_b$ was 0.70 to 0.73 for usual various

Fig. 3. Examples of the movement of liquid meniscus against time under temperature differences for Neosepta AM-1 with the Cl^- form in 10 wt% of urea solution
Temperature differences (K) : (A) 12 ; (B) 9 ; (C) 6 ; (D) 3.

membranes⁹⁾. Therefore, we also assumed that $\Delta T = 0.7 \Delta T_b$ in this work.

3. Results and discussion

Figures 2 and 3 show examples of the movement of the liquid meniscus against time for the Gore-Tex film in water and for Neosepta AM-1 with the Cl^- form in 10 wt% of urea solution, respectively. The mean temperature was kept at 308.2 K and the temperature differences of the bulk solutions, ΔT_b , were 4 to 16 K for the Gore-Tex films and 3 to 12 K for Neosepta AM-1. For the Gore-Tex films the direction of thermoosmosis was from the hot side to the cold side whereas for Neosepta AM-1 with the Cl^- form that

Fig. 4. The dependence of thermoosmotic volume flux, J_v , on the temperature difference of bulk solutions, ΔT_b , for Neosepta AM-1 with the Cl^- form in poly(acrylamide) solutions at the mean temperature 308.2 K. Concentrations (wt%) : (○) 0.007 ; (□) 0.036 ; (△) 0.071.

was from the cold side to the hot side. The plots of the data for Neosepta AM-1 scattered, because the absolute values of thermoosmosis for Neosepta AM-1 were very smaller than those for the Gore-Tex film. In general, for hydrophobic membranes the state of water in the membrane is considerably different from that in the external solution compared to the case for hydrophilic membranes. Moreover, the hydraulic permeability of the hydrophobic membranes used was considerably larger than that of Neosepta AM-1. Thus, the absolute values of thermoosmosis across the hydrophobic membranes were very larger than that across the hydrophilic membranes. Thermoosmotic volume fluxes, J_v , were calculated from the slopes of these figures.

Fig. 5. The relationship between the thermosmotic coefficient, $-D$, and ratio of Tetra-Etch II to $\text{C}_2\text{H}_5\text{OH}$ for GT-TE membranes.

Figure 4 shows an example of linear relationships between the volume flux and the temperature differences of the bulk solutions for Neosepta AM-1 with the Cl^- form in PAAm solutions. The positive sign of J_v means the directions of thermosmosis toward the hot solution side. The thermosmotic coefficient, D , can be obtained from the slopes of this figure. In order to examine the influence of sorbed PAAm in the membrane on the volume flux, measurements of thermosmosis were carried out in pure water before and after the experiments in the PAAm solutions. The difference between the values of D obtained in pure water was within 6.7%. This means that the sorption of polymer substance on the surface of the membrane will be weak and the effect of the sorption on thermosmosis can be neglected.

Figure 5 shows the relationship between the thermosmotic coefficient and the ratio of the Tetra-Etch II to $\text{C}_2\text{H}_5\text{OH}$ for the modified PTFE membranes. In general, for a hydrophobic membrane the entropy of water in the membrane will be higher than that in the external solution, because the membrane has less affinity for the water mole-

Fig. 6. The relationship between thermosmotic coefficient, $-D$, and concentration of poly(acrylamide) in the external solution for Neosepta AM-1 with the Cl^- form.

cules, and thermosmosis occurs from the hot side to the cold side¹⁾. The absolute value of the thermosmotic coefficient decreased with increasing the concentration of the treating agent. The treating agent, Tetra-Etch II, can introduce hydrophilic groups on the porous PTFE membrane surface. The hydrophilic groups of GT-TE membranes will increase the affinity of the membrane matrix for water molecules, and the state of water in the membrane approaches to that of the external free water. The increase of the ratio of the Tetra-Etch II to $\text{C}_2\text{H}_5\text{OH}$ will act as the increase of the hydrophilic groups introduced in the GT-TE membranes and the entropy difference of water, $\bar{s}_0 - s_0$, will decrease. Thus, thermosmosis decreased with increasing the ratio of the Tetra-Etch II to $\text{C}_2\text{H}_5\text{OH}$. The volume flux across WPW-045, which was modified by introducing a lot of OH^- groups on a porous PTFE membrane, was not observed. This means that $\bar{s}_0$ in this highly modified membrane WPW-045 is nearly equal to s_0 . Moreover, thermosmosis was not observed when we used the GT-TE membranes containing a small amount of $\text{C}_2\text{H}_5\text{OH}$. A small amount of

Fig. 7. The relationship between the thermoosmotic coefficient, $-D$, and concentration of urea in the external solutions for Neosepta AM-1 with the Cl^- form.

$\text{C}_2\text{H}_5\text{OH}$ sorbed in the membrane will act just like as hydrophilic groups of highly modified membranes.

Figure 6 shows the relationship between the thermoosmotic coefficient for Neosepta AM-1 with the Cl^- form and the concentration of PAAM solutions. In general, for anion-exchange membranes the entropy of water in the membranes will be lower than that in the external solutions, because both the membrane matrix and the fixed charges of quaternized ammonium act to order the structure of water¹⁸⁾, and thermoosmosis occurs from the cold side to the hot side^{9, 10)}. The absolute value of the thermoosmotic coefficient decreased with increasing the concentration of PAAM. The value of $\bar{s}_0$ is constant regardless of the change in the concentration of PAAM, because PAAM cannot enter the membrane phase. Since PAAM molecules act to order the structure of water, the state of water in the external solution will tend to be similar to that in the membrane at high concentrations. Therefore, $(\bar{s}_0 - s_0)$ decreases with increasing the concentration of the external solution and $-D$ also decreases with increasing the con-

centration. The decrease of the activity of water with the concentration of PAAM will also cause the decrease of the volume flux. However, the 55% decrease of $-D$ from $9.6 \times 10^{-8} \text{ cm K}^{-1} \text{ s}^{-1}$ (at 0 wt%) to $4.2 \times 10^{-8} \text{ cm K}^{-1} \text{ s}^{-1}$ (at 0.071 wt%) cannot be explained only by the decrease of the water activity. The decrease of thermoosmosis will be mainly dependent on the decrease of the entropy difference of water between the membrane and the external solution.

Figure 7 shows the relationship between the thermoosmotic coefficient for Neosepta AM-1 with the Cl^- form and the concentration of urea solutions. If an aqueous solution does not contain an electrolyte but contains an uncharged organic solute, Eq. (1) can be rewritten as

$$\begin{aligned} -J_v &= (D^0 + D') \Delta T \\ &= \{ (D_0^0 + D_0') + (D_u^0 + D_u') \} \Delta T, \end{aligned} \quad (3)$$

where

$$D_0 = D_0^0 + D_u^0, D' = D_0' + D_u', \quad (3-1)$$

$$\begin{aligned} D_0^0 &= \bar{c}_0 l_{v0} (\bar{s}_0 - s_0) / \delta, \\ D_u^0 &= \bar{c}_u l_{vu} (\bar{s}_u - s_u) / \delta, \end{aligned} \quad (3-2)$$

$$\begin{aligned} D_0' &= \tau_0 F \phi X l_{v-} (\bar{s}_0 - s_0) / \delta, \\ D_u' &= \tau_u F \phi X l_{v-} (\bar{s}_u - s_u) / \delta. \end{aligned} \quad (3-3)$$

The subscripts 0 and u refer to water solvent and an uncharged organic solute, respectively. In Fig. 7, the absolute value of the thermoosmotic coefficient decreased with increasing the concentration of urea solutions. It is known that the activity coefficient of aromatic electrolytes decreases with increasing the concentration of urea because of the change in the state of water^{19, 20)}. If we use aqueous urea solutions as the external solu-

tion for anion-exchange membranes, urea can enter the membrane phase because of its small molecular weight. The state of water in the membrane is influenced by both the membrane matrix containing fixed charges and the sorbed urea. If the effect of urea on the water structure larger than that of the membrane matrix at high concentrations, the entropy difference, $\bar{s}_0 - s_0$, becomes small and $-D$ decreases with increasing the concentration. The value of $-D$ may also decrease with increasing the concentration due to the increase in the viscosity of urea solutions and shrinkage of the membrane. However, the reciprocal of the relative viscosity in 20 wt% of urea solution is about $0.8^{21)}$. Moreover, the decrease of the water content of Neosepta AM-1 in about 2 mol kg^{-1} of NaCl and KCl solutions, which are isotonic electrolyte solutions for 20 wt% of urea solution at $298.2 \text{ K}^{22)}$, was approximately 5%. Thus, the change of $-D$, $1.0 \times 10^{-7} \text{ cm K}^{-1} \text{ s}^{-1}$ (at 0 wt%) to $3.8 \times 10^{-8} \text{ cm K}^{-1} \text{ s}^{-1}$ (at 20 wt%), cannot be explained only by the change in the viscosity of urea solutions and shrinkage of the membrane. The change in the entropy difference, $\bar{s}_0 - s_0$, will play an important role on the decrease of $-D$.

If the entropy difference of urea, $\bar{s}_u - s_u$, is negative similarly to that of water, the signs of D_0^0 , D_u^0 , D_0' and D_u' are all negative. D_u^0 and D_u' increase with increasing the concentration of urea, whereas D_0^0 and D_0' decrease with that because of the decrease in the entropy difference of water, $\bar{s}_0 - s_0$. Since the concentration and mobility of water are considerably higher than those of urea, D^0 and D' will mainly depend on D_0^0 and D_0' , respectively. Therefore, $-D$ [$=(D^0 + D')$] decreased with increasing the concentration of urea.

4. Conclusions

1) For the modified PTFE membranes the absolute value of the thermoosmotic coefficient decreased with increasing the ratio of the Tetra-Etch II to $\text{C}_2\text{H}_5\text{OH}$ in the treating mixture, because the introduced hydrophilic groups increase the affinity of the membrane matrix for the water molecules, thus, the transported entropy of water in the membrane, $\bar{s}_0$, decreases to the partial molar entropy of water in the external solution, s_0 .

2) For the anion-exchange membrane, Neosepta AM-1, the absolute value of the thermoosmotic coefficient in PAAM solutions decreased with increasing the concentration of the external solution, because PAAM molecules act to order the structure of water in the external solution and s_0 decreases to $\bar{s}_0$.

3) For Neosepta AM-1 the absolute value of the thermoosmotic coefficient in urea solutions decreased with increasing the concentration of the external solution, because the effect of urea molecules on the water structure in the membrane larger than that of the membrane matrix at the high concentrations and the entropy difference of water, $\bar{s}_0 - s_0$, becomes small.

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