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THERMOOSMOSIS THROUGH CHARGED MEMBRANES. THEORETICAL ANALYSIS OF CONCENTRATION DEPENDENCE

Masayasu TASAKA
Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

and

Mitsuru NAGASAWA
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-Ku, Nagoya 464, Japan

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A theoretical equation for thermoosmosis through charged membranes in electrolyte solutions is derived from nonequilibrium thermodynamics. The theory shows that the volume flux through the membrane is proportional to the temperature difference across the membrane. The proportionality constant, i.e., the thermoosmotic coefficient is a function of electrolyte concentration. The electrolyte concentration dependence of the thermoosmotic coefficient calculated is compared with our previous experimental results. Agreement between theory and experiments is satisfactory.

1. Introduction

Theoretical analysis of thermoosmosis through an uncharged membrane in liquids has been carried out by many workers [1–7]. However, less attention has been paid to the theoretical analysis of thermoosmosis through a charged membrane in electrolyte solutions.

In previous papers [8,9], the experimental results of thermoosmosis through collodion, oxidized collodion and collodion-potassium polystyrenesulfonate interpolymer membranes in potassium chloride solutions were reported. It was experimentally shown that if there is no difference in the electrolyte concentration but a difference in the temperature on both sides of a membrane, the volume flux through the membrane J_v is proportional to the effective temperature difference ΔT across the membrane. That is,

$$-J_v = D\Delta T\,, \qquad (1)$$

where D is the thermoosmotic coefficient and is found to vary with the electrolyte concentration. The thermoosmotic coefficient D was found to be composed of three parts as shown in fig. 1. If there are no charges in the membrane and there is no permeation of electrolyte, D for the charged membrane should be constant, as schematically shown in line A of fig. 1. However, since there is permeation of electrolyte which interacts with the water flux in practice, that is, since the permeation of electrolyte accelerates the flow of water, the magnitude of D should increase as seen in curve C. The combination of curves A and C can be found in

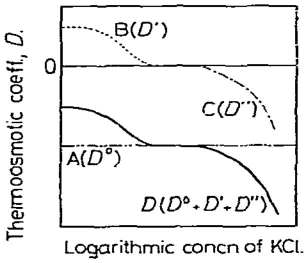

Fig. 1. The schematic electrolyte concentration dependence of the thermoosmotic coefficient D.

the thermoosmosis through an uncharged membrane in electrolyte solutions. The effect of the charges, i.e., the effect of the counterions in the membrane manifests itself in curve B.

2. Theory

Applying nonequilibrium thermodynamics to ion transport processes in electrolyte solution, in mechanical equilibrium, a special form of the entropy production σ is given by the equation [10,11],

$$-T\sigma = J_s \cdot \operatorname{grad} T + \sum_i J_i \cdot \operatorname{grad} \tilde{\mu}_i \,, \tag{2}$$

where

$$\tilde{\mu}_i = \mu_i + v_i P + z_i F \psi \,. \tag{3}$$

In general, the fluxes are written with respect to the mass-fixed frame. However, it is also discussed [11] that eq. (2) holds for the system in the membrane-fixed frame of reference, if the system is in mechanical equilibrium. J_s is the total entropy flux and J_i is the absolute mass flux. In addition, $\tilde{\mu}_i$ is the chemical potential including contributions due to external forces, μ_i the chemical potential depending on temperature and composition, v_i the partial molar volume, z_i the valence of component i, P the pressure, F the Faraday constant, T the temperature, and ψ is the electrostatic potential. Thus, the phenomenological equations for the fluxes relative to membrane are given by

$$-J_s = \bar{L}_{ss} \operatorname{grad} \bar{T} + \sum_i \bar{L}_{si} \operatorname{grad} \bar{\tilde{\mu}}_i \tag{4}$$

$$-J_i = \bar{L}_{is} \operatorname{grad} \bar{T} + \sum_j \bar{L}_{ij} \operatorname{grad} \bar{\tilde{\mu}}_j \tag{5}$$

where the parameters in the membrane phase are denoted by a overbar. In this paper, however, J_s is not discussed. Our discussion is limited to the volume flux under the applied temperature gradient.

Let us assume that all gradients in the membrane are in the x direction perpendicular to the membrane surfaces and, at steady state, temperature T and chemical potentials $\tilde{\mu}_i$ at points $x = 0$ and $x = \delta$ in the membrane (at opposite surfaces of the membrane) are equal to those in the contiguous solutions. That is,

$$\Delta\tilde{\mu}_i = \tilde{\mu}_i(\delta) - \tilde{\mu}_i(0) = \bar{\tilde{\mu}}_i(\delta) - \bar{\tilde{\mu}}_i(0) = \Delta\bar{\tilde{\mu}}_i \,, \tag{6}$$

$$\Delta T = T(\delta) - T(0) = \bar{T}(\delta) - \bar{T}(0) = \Delta\bar{T} \,, \tag{7}$$

where Δ shows the difference between two fluid phases on either side of the membrane. By solving eqs. (4) and (5) for forces and integrating them from one side of the membrane to the other, keeping the fluxes constant, we have [8,12,13]

$$-J_s = L_{ss}\Delta T + \sum_i L_{si}\Delta\tilde{\mu}_i \tag{8}$$

$$-J_i = L_{is}\Delta T + \sum_j L_{ij}\Delta\tilde{\mu}_j \,, \tag{9}$$

where $L_{\alpha\beta}$ is the permeability coefficient of the membrane of finite thickness.

The membrane potential can be calculated from the condition $I = \Sigma_i z_i F J_i = 0$, as was reported previously [13]. That is,

$$-\Delta\psi = \eta\Delta T + \sum_k \tau_k(\Delta\mu_k + v_k\,\Delta P) \,, \tag{10}$$

where

$$\eta = \sum_j z_j L_{js} \Big/ \sum_k \sum_l z_k z_l L_{kl} F \,, \tag{11}$$

$$\tau_i = \sum_j z_j L_{ji} \Big/ \sum_k \sum_l z_k z_l L_{kl} F \,. \tag{12}$$

The coefficient η is the thermoelectric potential and τ_i is the reduced transport number of species i. If the Onsager reciprocal relationship $L_{kl} = L_{lk}$ is assumed, we have

$$\tau_i = (J_i/I)_{\Delta T=0,\Delta P=0,\Delta\mu_j=0} \,. \tag{13}$$

Moreover, if the transported entropy $\bar{\bar{s}}_j$ is defined in terms of the phenomenological coefficients [10,11,14]

$$L_{is} = \sum_j L_{ij}\bar{\bar{s}}_j \tag{14}$$

and from eq. (11) we have [15]

$$\eta = \sum_j \tau_j \bar{\bar{s}}_j \,. \tag{15}$$

Combination of eqs. (10) and (15) gives

$$-\Delta\psi = \sum_k \tau_k\{(\bar{\bar{s}}_k - s_k)\Delta T + (\Delta\mu_k)_T + v_k\,\Delta P\} \,, \tag{16}$$

where

$$\Delta\mu_k = -s_k\Delta T + (\Delta\mu_k)_T \qquad (17)$$

and s_k is the partial molar entropy of species k. Substituting eqs. (14) and (16) into eq. (9), we have

$$-J_i = \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}}) \times \{(\bar{\bar{s}}_j - s_j)\Delta T + (\Delta\mu_j)_T + v_j\Delta P\}\,, \qquad (18)$$

where L_{E} is the electric permeability: $L_{\mathrm{E}} = \Sigma_i\Sigma_k z_i z_k L_{ik}$ [16,17].

2.1. Thermal hydrostatic pressure difference and hydraulic permeation

At the condition $I = 0$, the volume flux $J_{\mathrm{v}} = \Sigma_i v_i J_i$ may be calculated from eq. (18) as

$$-J_{\mathrm{v}} = \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})(\bar{\bar{s}}_j - s_j)\Delta T + \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})(\Delta\mu_j)_T + \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})v_j\Delta P\,. \qquad (19)$$

That is, the volume flux is determined by three factors: the temperature difference, the electrolyte concentration difference and the pressure difference on both sides of membrane. If the membrane has no charge and $\Delta\psi = 0$, the term $\tau_i\tau_j F^2 L_{\mathrm{E}}$ in eq. (19) vanishes. In this condition eq. (19) corresponds to eq. (24) of ref. [6].

Even if the concentrations of electrolyte on either side of the membrane are the same at the initial state, a difference in the electrolyte concentration should be set up after a certain time. However, in experiments with the condition $(\Delta\mu_i)_T = 0$ at the initial time, no change in concentration in the external solutions could be detected after a thermoosmosis experiment was carried out. In that sense, our experiments were not experiments at a stationary state but only at a quasi-stationary state, and $(\Delta\mu_i)_T$ may be assumed to be zero.

If a quasi-stationary state $J_{\mathrm{v}} = 0$ is reached after a certain time, the pressure difference at the state is given by

$$\Delta P = -\frac{\sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})(\bar{\bar{s}}_j - s_j)}{\sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})v_j}\,\Delta T\,. \qquad (20)$$

This is called the thermal hydrostatic pressure difference. It was experimentally confirmed [9] that the thermal hydrostatic pressure is proportional to the temperature difference ΔT, as shown by eq. (20).

If a pressure difference is applied across the membrane at a constant temperature, i.e., in the hydraulic permeation, from eq. (19) we have

$$-J_{\mathrm{v}} = \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})v_j\Delta P\,. \qquad (21)$$

2.2. Thermal volume flow

If $(\Delta\mu_i)_T = 0$ and $\Delta P = 0$, from eq. (19) we have

$$-J_{\mathrm{v}} = \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})(\bar{\bar{s}}_j - s_j)\Delta T\,. \qquad (22)$$

Eq. (22) shows that thermal volume flow rate can be proportional to temperature difference if the coefficient of ΔT is independent of T, in agreement with our experimental results (fig. 9 of ref. [8] and fig. 8 of ref. [9]). Moreover, the ratio of the coefficients in eqs. (20) and (21) gives the coefficient in eq. (22). This conclusion agrees with our experimental results that the combination of the data in figs. 5 and 6 of ref. [9] gives a relationship between J_{v} and ΔT similar to fig. 8 of ref. [9]. Thus, the thermoosmotic coefficient D in eq. (1) is given by

$$D = \sum_i v_i \sum_j (L_{ij} - \tau_i\tau_j F^2 L_{\mathrm{E}})(\bar{\bar{s}}_j - s_j)\,. \qquad (23)$$

2.3. Thermoosmotic coefficient

If we can express the phenomenological coefficient L_{ij} by analytical quantities such as electrolyte concentrations, mobilities, membrane charges etc. inside the membrane, D may be given as a function of those analytical quantities. Then, the values of D may be calculated and compared with experimental results. The coefficient L_{ij} may be assumed to be proportional to the concentration of jth species inside the membrane $\bar{c}_j$. That is,

$$L_{ij} = \overline{c}_j l_{ij}/\delta \; , \tag{24}$$

where l_{ij} is a coefficient expressing the interaction between ith and jth species and δ is the thickness of the membrane. For cation exchange membrane-electrolyte solution systems the concentration of ions inside membrane $\overline{c}_j$ may be calculated from the concentration of electrolyte outside the membrane c using the theory of the Donnan membrane equilibrium

$$(y_\pm c)^2 = \overline{y}_\pm \overline{c}_- (\overline{y}_\pm \overline{c}_- + \overline{y}_\mathrm{p} X) = \overline{y}_\pm^2 \overline{c}_- (\overline{c}_- + \phi X) \tag{25}$$

and $\overline{c}_+ = \overline{c}_- + \phi X$; $y_\pm$ is the mean activity coefficient of the electrolyte, $\overline{y}_\pm$ is the value in the pure aqueous solution having the same concentration as the solution inside the membrane and $\overline{y}_\mathrm{p}$ is the activity coefficient of counterion in the charged membrane. The X is the concentration of fixed charges and ϕ is a parameter expressing the nonideality of the solution and denoted by $\phi = \overline{y}_\mathrm{p}/\overline{y}_\pm$, as was discussed in detail in a previous paper [18]. That is, ϕX is the effective concentration of fixed charges of the membrane and $\overline{y}_\mathrm{p}$ or ϕ may be treated as a constant [18].

In KCl solutions where we may assume $\Sigma_i v_i l_{i+} = \Sigma_i v_i l_{i-}$, eq. (23) is symplified as

$$\begin{aligned} D = \{ & (\overline{c}_0 l_{\mathrm{v}0} - \tau_0 F \phi X l_{\mathrm{v}\pm})(\bar{\bar{s}}_0 - s_0) \\ & + (\overline{c}_- + t_- \phi X) l_{\mathrm{v}\pm} (\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s})\}/\delta \; , \end{aligned} \tag{26}$$

where $l_{\mathrm{v}0}$ and $l_{\mathrm{v}\pm}$ are coefficients defined by

$$l_{\mathrm{v}0} = \sum_i v_i l_{\mathrm{i}0} \; , \tag{27}$$

$$l_{\mathrm{v}\pm} \equiv l_{\mathrm{v}+} = \sum_i v_i l_{\mathrm{i}+} = \sum_i v_i l_{i-} = l_{\mathrm{v}-} \tag{28}$$

and

$$\bar{\bar{s}}_\mathrm{s} \equiv \bar{\bar{s}}_+ + \bar{\bar{s}}_- \; , \tag{29}$$

$$s_\mathrm{s} \equiv s_+ + s_- \; . \tag{30}$$

The t_- is the transport number of anion, $t_- = z_- F \tau_-$. Eq. (28) is valid for KCl since both cation and anion have the same hydrodynamic radius in aqueous solution.

If the membrane has no fixed charges and there is no electrolyte in the solution, i.e., if $X = 0$ and $\overline{c}_- = 0$, eq. (26) becomes

$$D = \overline{c}_0 l_{\mathrm{v}0} (\bar{\bar{s}}_0 - s_0)/\delta \quad (\equiv D^0) \tag{31}$$

which is a coefficient depending on membrane structure. Thus, eq. (26) can be written as

$$D \equiv D^0 + D' + D'' \; , \tag{32}$$

where

$$D' = -\tau_0 F \phi X l_{\mathrm{v}\pm} (\bar{\bar{s}}_0 - s_0)/\delta \; , \tag{33}$$

$$D'' = (\overline{c}_- + t_- \phi X) l_{\mathrm{v}\pm} (\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s})/\delta \; . \tag{34}$$

If the phenomenological equations (4) and (5) are defined relative to solvent, that is, in a closed system where the Soret equilibrium is observed, $\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s} (\equiv \overline{s}_\mathrm{s}^*)$ is called Eastman's entropy of transfer and has been well studied [14,19]. $\overline{s}_\mathrm{s}^*$ is found to depend on electrolyte concentration in such cases. In this work, however, $\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s}$ is defined relative to membrane. It may be enough for the purpose of this paper to assume that $\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s}$ is independent of electrolyte concentration.

3. Comparison between the theory and experimental results

If the membrane has no fixed charges and the solution does not contain electrolyte, both D' and D'' disappear and we have eq. (31). The effects of membrane charges and electrolyte on D arise from D' and D''.

As was reported in the previous paper, both electrolyte and water move from the cold side to the hot side. This is consistent with the fact that the electrical potential in the hot side solution is positive for cation exchange membranes and negative for anion exchange membranes [13,15,20]. All these facts imply that both $\bar{\bar{s}}_0 - s_0$ and $\bar{\bar{s}}_\mathrm{s} - s_\mathrm{s}$ are negative (see eqs. (16) and (18)), i.e., D' is positive and D'' is negative.

The qualitative feature of the concentration dependence of D' is schematically shown in fig. 1. At low concentrations D' is large because τ_0 increases with decreasing concentration of electrolyte, while at high concentrations D' tends to zero. Thus, the schematic electrolyte concentration dependence of D' may be shown as in fig. 1. On the other hand, D'' is zero at low electrolyte concentrations, since both $\overline{c}_-$ and t_- are negligible if the membrane has negative charges. Since t_- increases with increasing concentration of electrolyte as was already shown (fig. 1 of ref. [9]), the absolute value of D'' would monotonically increase with concentration as is also schematically shown in fig. 1.

The qualitative feature of the concentration dependence of D can thus be speculated to be as shown in fig. 1. This staircase-type behavior of the electrolyte concentration dependence of D is in accord with the experimental results for membranes o-m-2, o-m-3 and i-m-2 in fig. 9 of ref. [9].

Moreover, if the membrane has no fixed charges and the solution contains an electrolyte, we have

$$D = D^0 + D'' = D^0 + \bar{c}_- l_{v\pm}(\bar{\bar{s}}_s - s_s)/\delta . \qquad (35)$$

In this case, D may monotonically decrease with increasing concentration of electrolyte. The experimental data for membrane c-m in fig. 9 of ref. [9] show this feature.

Except l_{v0}, $l_{v\pm}$, $\bar{\bar{s}}_0$ and $\bar{\bar{s}}_s$, all parameters in eq. (26) for membrane i-m-2 are known. Therefore, a quantitative comparison between the theory and experiments is possible. The value of $\bar{y}_p X$ is 1.6×10^{-5} eq/cm^3 [18]. The values of t_- as a function of KCl concentration can be determined from the concentration membrane potential at a constant temperature and are shown in fig. 1 of ref. [9]. The values of τ_0 can be determined from the electroosmotic experiments and are shown in fig. 9 of ref. [21]. The values of $\bar{c}_-$ can be determined from the Donnan membrane equilibrium, using eq. (25).

As KCl concentration increases, the value of τ_0 decreases to zero and eq. (26) may be approximated as

$$D = D^0 + (\bar{c}_- + t_-\phi X) l_{v\pm}(\bar{\bar{s}}_s - s_s)/\delta \qquad (36)$$

at high concentrations of KCl. Eq. (36) predicts that if we plot D against $(\bar{c}_- + t_-\phi X)$ at high concentrations we can determine $l_{v\pm}(\bar{\bar{s}}_s - s_s)/\delta$ from the slope and D^0 from the intercept. The plot of D versus $(\bar{c}_- + t_-\phi X)$ for membrane i-m-2 is shown in fig. 2.

Since both $\bar{c}_-$ and t_- are negligible at low concentrations of KCl, eq. (26) may be approximated as

$$D = D^0 - \tau_0 F \phi X l_{v\pm}(\bar{\bar{s}}_0 - s_0)/\delta . \qquad (37)$$

If we plot D against $\tau_0 F\phi X$ at low concentrations, we can determine $l_{v\pm}(\bar{\bar{s}}_0 - s_0)/\delta$ from the slope and D^0 also from the intercept. The plot of D versus $\tau_0 F\phi X$ for membrane i-m-2 is also shown in fig. 2. The intercepts of two lines in fig. 2 give the same D^0. From the figure we have $D^0 = 2.6 \times 10^{-7}$ cm s^{-1} K^{-1}, $l_{v\pm}(\bar{\bar{s}}_s - s_s)/\delta = -7.3 \times 10^{-5}$ cm^4 mol^{-1} s^{-1} K^{-1} and $l_{v\pm}(\bar{\bar{s}}_0 - s_0)/\delta = -1.42 \times 10^{-5}$ cm^4 mol^{-1} s^{-1} K^{-1}.

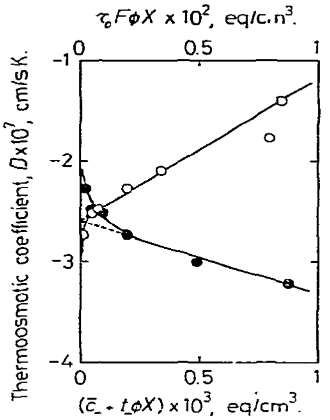

Fig. 2. The relationships of D versus $(\bar{c}_- + t_-\phi X)$ at the limit of high concentrations (●) and D versus $\tau_0 F$ at the limit of low concentrations (○) for membrane i-m-2.

Using the data obtained above, the curve of D can be calculated from eq. (32) to be compared with experimental data of membrane i-m-2 in fig. 3. The calculated values of D' and D'', respectively, are also shown by chain lines in fig. 3. The agreement between theory and experiments is satisfactory.

Unfortunately, since the values of $\bar{y}_p X$ and τ_0 were not obtained for the other membranes o-m-2 and o-m-3, the experimental results for these membranes can not

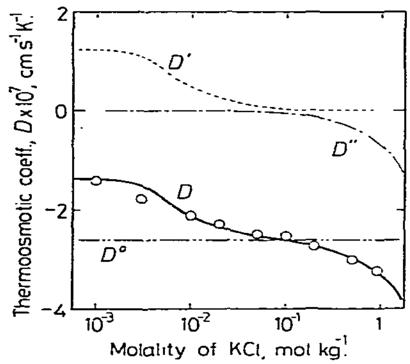

Fig. 3. The dependence of thermoosmotic coefficient, D, on KCl concentration for membrane i-m-2.

be compared with the theory. However, the characteristic staircase-type behavior of the electrolyte concentration dependence of D predicted in fig. 1 was more clearly observed for o-m-2 and o-m-3.

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