Biophysical Chemistry 4 (1976) 269–274

THERMAL MEMBRANE POTENTIAL ACROSS CHARGED MEMBRANES IN NaCl–NH_4Cl AND LiCl–NH_4Cl SOLUTIONS

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Received 19 January 1976

Measurements of the thermal membrane potential across cation exchange membranes were carried out by using aqueous solutions containing two 1–1 electrolytes, with an anion in common. The same solution was used on both sides of the membrane. In all cases a good linear relationship was observed between the thermal membrane potential $\Delta\psi$ and the temperature difference ΔT (in the range $\Delta T = \pm 10^{\circ}$C). Assuming that the activity of one cation is equal to that of another cation in the solutions and the sum of transport numbers of cations is unity, the plot of $\Delta\psi/\Delta T$ vs logarithmic activity of one cation is linear with a slope of R/F. These experimental results are in agreement with a theory presented previously. From the analysis of thermal membrane potential in mixtures of electrolytes it is obtained that the cross coefficient of cation–cation interaction in membranes is negative and about 6 to 9% of the main coefficient.

1. Introduction

An electrostatic potential difference, which is called thermal membrane potential, appears across a membrane if there is a temperature difference on both sides of the membrane [1,2]. In previous papers [3–5], applying nonequilibrium thermodynamics, a theory of thermal membrane potential has been proposed and experiments in single electrolyte solutions have been carried out. An agreement between the theory and experimental results was observed.

In this paper, the theory is extended to the solution system containing two electrolytes and measured thermal membrane potentials in the solutions are reported. Also the cross coefficients of cation–cation interactions are estimated from these data.

2. Theory

Applying nonequilibrium thermodynamics to ion transport processes in electrolyte solutions, in absence of applied pressure gradient, the fluxes relative to the membrane are given by [4,6]

$$-J_s = L_{ss}\Delta T + \sum_i L_{si}\Delta\tilde{\mu}_i, \tag{1a}$$

$$-J_i = L_{is}\Delta T + \sum_j L_{ij}\Delta\tilde{\mu}_j, \tag{1b}$$

where

$$\tilde{\mu}_i = \mu_i + z_i F\psi, \tag{2}$$

and J_s is the total entropy flux, J_i the absolute mass flux, T the temperature, $\tilde{\mu}_i$ the electrochemical potential, μ_i the chemical potential, z_i the valence of component i, $L_{\alpha\beta}$ the permeability coefficient, F the Faraday constant, ψ the electric potential, and Δ shows the difference between two fluid phases on both sides of the membrane.

The thermal membrane potential can be calculated from the condition of $I = \Sigma_i z_i F J_i = 0$, as was reported previously [3,4].

$$-\Delta\psi = \eta\Delta T + \sum_i \tau_i\Delta\mu_i, \tag{3}$$

where

$$\eta = \sum_i z_i L_{is} / \sum_i \sum_j z_i z_j L_{ij} F, \tag{4}$$

$$\tau_i = \sum_j z_j L_{ji} / \sum_j \sum_k z_j z_k L_{jk} F. \tag{5}$$

The η is the thermoelectric potential coefficient and τ_i is the reduced transport number of the ith species. If the Onsager reciprocal relationship $L_{ij} = L_{ji}$ is assumed [3], we have

$$\tau_i = (J_i/I)_{\Delta T=0,\Delta\mu_i=0}. \tag{6}$$

2.1. Single 1–1 electrolyte solutions

Consider a system consisting of a neutral solvent (water) and a 1–1 electrolyte MX which ionizes as M^+ and X^-. If the electrolyte concentrations on both sides of membrane are the same, eq. (3) gives [3,4]

$$-(\Delta\psi/\Delta T) = (2t_+ - 1)(R/F)\ln a_\pm + (t_+\alpha_+ + t_-\alpha_-), \tag{7}$$

where α_+ and α_- are defined by

$$\alpha_+ = \eta(+-) - [s_+^0/F + \tau_0(s_0^0 - R\ln a_0)], \tag{8a}$$

$$\alpha_- = \eta(+-) - [s_-^0/F - \tau_0(s_0^0 - R\ln a_0)], \tag{8b}$$

and

$$\eta(+-) = (L_{+s} - L_{-s})/(L_{++} + L_{--} - L_{+-} - L_{-+})F, \tag{9}$$

$$\tau_i(+-) = (L_{+i} - L_{-i})/(L_{++} + L_{--} - L_{+-} - L_{-+})F, \tag{10}$$

$$-s_i^0 = \partial\mu_i^0/\partial T, \tag{11}$$

$$t_i = z_i F\tau_i. \tag{12}$$

Moreover, $a_\pm$ and a_0 are the mean activity of ions and the activity of water, respectively, and subscripts +, −, and 0 refer to cation, anion, and water, respectively.

If the selectivity of the cation exchange membrane is ideal, i.e., $t_+ = 1$, moreover, eqs. (7), (9), and (10) give

$$-\Delta\psi/\Delta T = (R/F)\ln a_\pm + \alpha_+, \tag{13}$$

$$\eta(+-) = \eta(+) = L_{+s}/FL_{++}, \tag{14}$$

$$\tau_i(+-) = \tau_i(+) = L_{+i}/FL_{++}. \tag{15}$$

The slope of the $\Delta\psi/\Delta T$ vs $\log a_\pm$ plot must be 2.303 R/F (0.1984 mV/deg) and its intercept at the $\log a_\pm$ axis gives α_+.

2.2. Solutions containing two 1–1 electrolytes

Consider two 1–1 electrolytes, MX and M′X, with the anion X in common, which ionize as M^+, $M'^{\ominus}$, and X^-. If the electrolyte concentrations on both sides of membrane are the same for each electrolyte, eq. (3) gives

$$-(\Delta\psi/\Delta T) = \sum_{i=+,\ominus,-} (t_i/F)(-s_i^0 + R\ln a_i) + \tau_0(+\ominus-)(-s_0^0 + R\ln a_0) + \eta(+\ominus-), \tag{16}$$

where

$$\eta(+\ominus-) = (L_{+s} + L_{\ominus s} - L_{-s})/(L_{++} + L_{\ominus\ominus} + L_{--} + L_{+\ominus} + L_{\ominus+} - L_{+-} - L_{\ominus-} - L_{-+} - L_{-\ominus})F, \tag{17}$$

$$\tau_i(+\ominus-) = (L_{+i} + L_{\ominus i} - L_{-i})/(L_{++} + L_{\ominus\ominus} + L_{--} + L_{+\ominus} + L_{\ominus+} - L_{+-} - L_{\ominus-} - L_{-+} - L_{-\ominus})F. \tag{18}$$

If the selectivity of the cation exchange membrane is ideal, i.e., $t_+ + t_\ominus = 1$, eqs. (16), (17), and (18) give

$$\begin{aligned}-(\Delta\psi/\Delta T) &= \sum_{i=+,\ominus} (t_i/F)(-s_i^0 + R\ln a_i) + \tau_0(+\ominus)(-s_0^0 + R\ln a_0) + \eta(+\ominus)\\ &= \sum_{i=+,\ominus} [(t_i/F)(-s_i^0 + R\ln a_i) + t_i\alpha_i + \delta_i(\alpha_i + s_i^0/F)],\end{aligned} \tag{19}$$

$$\begin{aligned}\eta(+\ominus-) = \eta(+\ominus) &= (L_{+s} + L_{\ominus s})/(L_{++} + L_{\ominus\ominus} + L_{+\ominus} + L_{\ominus+})F\\ &= \eta(+)(t_+ + \delta_+) + \eta(\ominus)(t_\ominus + \delta_\ominus),\end{aligned} \tag{20}$$

$$\begin{aligned}\tau_0(+\ominus-) = \tau_0(+\ominus) &= (L_{+0} + L_{\ominus 0})/(L_{++} + L_{\ominus\ominus} + L_{+\ominus} + L_{\ominus+})F\\ &= \tau_0(+)(t_+ + \delta_+) + \tau_0(\ominus)(t_\ominus + \delta_\ominus),\end{aligned} \tag{21}$$

where

$$t_i = (L_{+i} + L_{\ominus i})/(L_{++} + L_{\ominus\ominus} + L_{+\ominus} + L_{\ominus+}), \qquad (i = +,\ominus) \tag{22}$$

$$\delta_+ = -L_{\ominus+}/(L_{++} + L_{\ominus\ominus} + L_{+\ominus} + L_{\ominus+}), \tag{23a}$$

$$\delta_\ominus = -L_{+\ominus}/(L_{++} + L_{\ominus\ominus} + L_{+\ominus} + L_{\ominus+}). \tag{23b}$$

If the activity of one cation is equal to that of another cation in mixtures, $a_+ = a_\ominus \equiv a$, eq. (19) gives

$$-(\Delta\psi/\Delta T) = (R/F)\ln a + \sum_{i=+,\ominus} [t_i\alpha_i + \delta_i(\alpha_i + s_i^0/F)]. \tag{24}$$

Eq. (24) states that the plot of the temperature coefficient of thermal membrane potential, $\Delta\psi/\Delta T$, vs logarithmic activity of one counterion is linear with a slope of R/F. If the Onsager reciprocal relationship is assumed, i.e., $L_{+\ominus} = L_{\ominus+}$, moreover, eq. (24) gives

$$-(\Delta\psi/\Delta T)=(R/F)\ln a+\sum_{i=+,\ominus}t_i\alpha_i$$

$$+\delta_{+}\sum_{i=+,\ominus}(\alpha_i+s_i^0/F). \tag{25}$$

Using the data of the thermal membrane potential in mixtures, we can estimate from eq. (25) the ratio of the cross (or coupling) coefficient of cation–cation interaction to the main (or straight) coefficients, $L_{+\ominus}/(L_{++}+L_{\ominus\ominus})=-\delta_{+}/(1+2\delta_{+})$.

If the cross coefficients of cation–cation interaction are negligible compared with the main coefficients, eq. (23) or (24) is simplified to

$$-(\Delta\psi/\Delta T)=(R/F)\ln a+\sum_{i=+,\ominus}t_i\alpha_i. \tag{26}$$

3. Experimental

3.1. Membranes

The same heterogeneous cation exchange membrane (C-1) as used in the previous works [3,5] was employed. This membrane was prepared from ion exchange resin powder 60% and polyvinyl chloride (a copolymer containing vinyl acetate 5%) 40% as binder. In addition, a homogeneous cation exchange membrane (C-2) with sulfonic acid group was kindly furnished by Asahi Chemical Industry Co., Ltd. Membranes C-2a and C-2b were made from a sheet of membrane C-2. The properties of these membranes are listed in table 1. The transport numbers of cation in membranes were calculated from membrane potentials at $\Delta T=0$ using the approximate equation:

$$-\Delta\psi=(2t_{+}-1)(RT/F)\ln[a_{\pm}(2)/a_{\pm}(1)]. \tag{27}$$

Table 1
The properties of cation exchange membranes

Membrane	Ion exchange capacity (meq/g of dry membrane)	Water content (g/g of dry membrane)	Transport number of cation in 0.1–0.2 M KCl	Thickness (mm)
C-1	1.89	0.37	0.98	1.25
C-2	0.79	0.29	0.99	0.99

3.2. Electrolytes

Two pairs of NaCl–NH_4Cl and LiCl–NH_4Cl were used to study the thermal membrane potential in mixtures because the difference between thermal membrane potentials in their single electrolyte solutions is large [5]. Each single electrolyte was also used to analyse the systems of solutions containing two 1–1 electrolytes.

3.3. Thermal membrane cell and measurements

The membrane potential cell is similar to that reported previously [3–5]. It is constructed of two sections of poly(methyl methacrylate) resin, and a calomel electrode is connected to each section. That is,

$$\text{Temp.:}\quad\underbrace{\mathrm{Hg/Hg_2Cl_2/satd.\ KCl}}_{T}\underbrace{\mathrm{/soln./}}_{T}\mathrm{membrane}$$

$$\underbrace{\mathrm{/soln}}_{T+\Delta T}\underbrace{\mathrm{/satd.\ KCl/Hg_2Cl_2/Hg}}_{T} \tag{28}$$

A membrane is mounted between the half cells. The solution inlet and outlet, as well as a mercury thermometer, are inserted in each half cell, and the solutions are flowed into the cell to remove a diffusion layer on the membrane surface [7]. A constant membrane potential is observed if the flow rate of solution is higher than a certain value and the thick membrane of about 1 mm is used [3].

4. Results and discussion

The membrane potential $\Delta\psi$ varies linearly with the temperature difference ΔT for $-10\leqslant\Delta T\leqslant 10^\circ$C, as was reported in previous papers [3–5]. Examples of $\Delta\psi$ vs ΔT plots with membrane C-1 in NaCl–NH_4Cl solutions are shown in fig. 1. Similar results were obtained in all experiments. The slopes, $\Delta\psi/\Delta T$ (mV/deg), determined are plotted as a function of activity of one counterion, $a\ (\equiv a_{\mathrm{Na}^+}=a_{\mathrm{NH}_4^+})$. The activity coefficient of one cation in the mixture may be approximately assumed to be the same as the value in the single electrolyte solution at the total electrolyte concentration. It is a good approximation in the case of the analysis

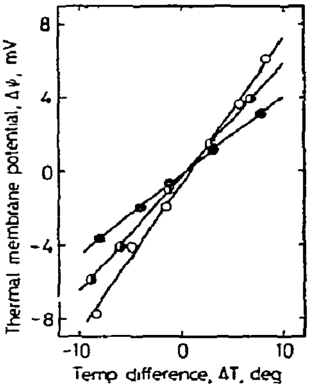

Fig. 1. Examples of thermal membrane potentials in NaCl–NH_4Cl solutions for membrane C-1. Concentrations of one counterion, c (= $c_{Na^+} = c_{NH_4^+}$): (○) 10^{-3}; (◐) 10^{-2}; (●) 10^{-1} mol/kg of H_2O.

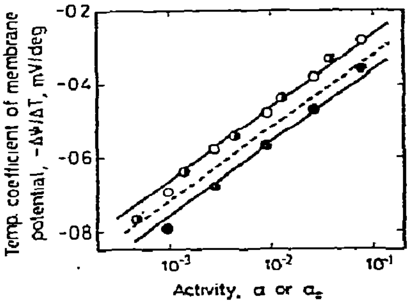

Fig. 3. The temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, for membrane C-2a. Electrolytes: (○) NaCl; (●) NH_4Cl; (◐) NaCl–NH_4Cl. The dotted line is calculated from eq. (26).

for the experiments which are carried out in such wide electrolyte concentrations as shown by logarithmic values. If the activities of cations in the mixtures are equal to each other, the plot of $\Delta\psi/\Delta T$ vs $\log a$ gives a straight line with a slope of $2.303\ R/F$ (0.1984 mV/deg), as expected from eq. (24) or (25) (figs. 2 to 4). The values of $\Delta\psi/\Delta T$ in single electrolyte solutions are also measured and plotted in figs. 1 to 4.

Although membranes C-2a and C-2b were made from one sheet, they did not give identical thermal membrane potential in NH_4Cl solutions as shown in figs. 3 and 4 because the thermal membrane potential is very sensitive to change in membrane structure. However, reproducible experimental data were obtained if the same membrane sample was used.

The values of $\Delta\psi/\Delta T$ in NaCl–NH_4Cl solutions are identical with those in NaCl solutions for membrane C-2a. It seems as if there were no effect of NH_4Cl on the thermal membrane potential in NaCl–NH_4Cl solutions as shown in fig. 3. Fig. 5 shows the temperature coefficient of the membrane potential, $\Delta\psi/\Delta T$, in NaCl–NH_4Cl solutions as a function of NH_4Cl concentration, where the concentration of NaCl is fixed at 10^{-2} mol/kg of H_2O. This figure clearly shows the effect of NH_4Cl concentration on the thermal membrane potential. At low concentrations of NH_4Cl the effect of NH_4Cl on $\Delta\psi/\Delta T$ is small and the thermal

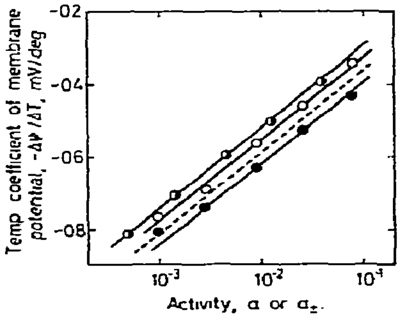

Fig. 2. The temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, for membrane C-1. Electrolytes: (○) NaCl; (●) NH_4Cl; (◐) NaCl–NH_4Cl. The dotted line is calculated from eq. (26).

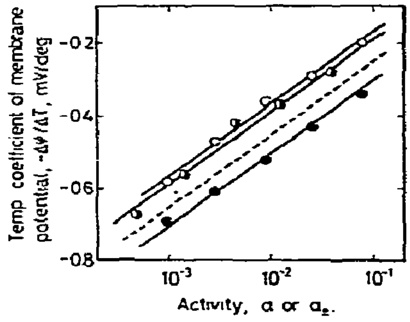

Fig. 4. The temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, for membrane C-2b. Electrolytes: (○) LiCl; (●) NH_4Cl; (◐) LiCl–NH_4Cl. The dotted line is calculated from eq. (26).

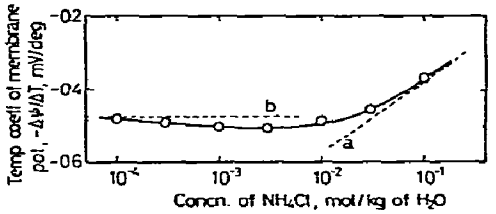

Fig. 5. The effect of NH_4Cl concentration on the temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, in 10^{-2} (mol/kg of H_2O) NaCl solutions for membrane C-2a. (a) The values of $-\Delta\psi/\Delta T$ for the single NH_4Cl solutions. (b) The value of $-\Delta\psi/\Delta T$ for the single NaCl solution at 10^{-2} mol/kg of H_2O.

membrane potential reduces to that in 10^{-2} (mol/kg of H_2O) NaCl, but at high concentrations of NH_4Cl the effect of NH_4Cl on $\Delta\psi/\Delta T$ is dominant. Also, fig. 6 shows the temperature coefficient of the membrane potential in NaCl–NH_4Cl solutions as a function of NaCl concentration, where the concentration of NH_4Cl is fixed at 10^{-2} mol/kg of H_2O. The effect of NaCl concetration on $\Delta\psi/\Delta T$ is clear in this case, too.

From the intercept at the log $a_{\pm}$ axis in single electrolyte solutions in fig. 2 the values of α_{Na^+} and $\alpha_{NH_4^+}$ for membrane C-1 are −0.125 and −0.19 mV/deg, respectively. If the distribution of Na^+ and NH_4^+ ions in the membrane is assumed to be equal to that in the free electrolyte solutions outside the membrane, we may express the transport numbers of cations for ideal cation selective membranes as follow:

$$t_+ = 1 - t_\ominus = l_+/(l_+ + l_\ominus), \qquad (29)$$

where l_i is the limiting ionic mobility in aqueous solutions which is given in tables [8]. If the cross coefficient of cation–cation interaction is negligible, the slope, $\Delta\psi/\Delta T$, of NaCl–NH_4Cl solutions is given by eq. (26). Thus, the values calculated from eq. (26) are shown by the dotted line with $\Sigma_i t_i \alpha_i = -0.164$ in fig. 2. In figs. 3 and 4 dotted lines show also the values calculated from eq. (26).

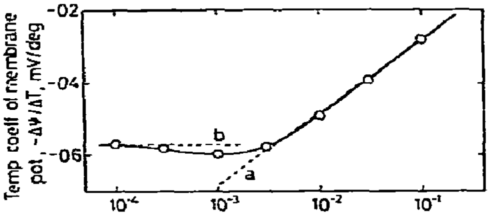

Fig. 6. The effect of NaCl concentration on the temperature coefficient of the membrane potential, $-\Delta\psi/\Delta T$, in 10^{-2} (mol/kg of H_2O) NH_4Cl solutions for membrane C-2a. (a) The values of $-\Delta\psi/\Delta T$ for the single NaCl solutions. (b) The value of $-\Delta\psi/\Delta T$ for the single NH_4Cl solution at 10^{-2} mol/kg of H_2O.

The difference between the dotted line and the observed values shows the effect of cation–cation interaction. In eq. (25) the values of s_i^0 are known as the molar entropy of ions referred to that of H^+ ion [9]. Assuming the Onsager reciprocal relationship, the values of δ_+ [or $-L_{+\ominus}/(L_{++} + L_{\ominus\ominus})$] estimated from eq. (25) are 0.050 (or 0.045) for NaCl–NH_4Cl with membrane C-1, 0.034 (or 0.032) for NaCl–NH_4Cl with membrane C-2a, and 0.051 (or 0.046) for LiCl–NH_4Cl with membrane C-2b, respectively. Therefore, the value of the cross coefficient of cation–cation interaction, $L_{+\ominus}$ or $L_{\ominus+}$, in membranes is negative and about 6 to 9% of the main coefficient. This result agrees with the cross coefficient of cation–cation interaction in free electrolyte solutions reported by many workers [10–14].

The above results emphasize the importance of the cross terms in membranes in an analysis of the thermal membrane potential in solutions containing many electrolytes.

In the above discussion we assumed that the distribution of counterions in the membrane is equal to that in the free electrolyte solutions outside the membrane. However, in practice, the transport number of NH_4^+ ion in the membrane may slightly increase over the value calculated from eq. (29) because the ion exchange membrane tends to prefer the counterion with the smaller hydrated volume [15]. Therefore, the dotted lines calculated from eq. (26) in figs. 2, 3, and 4 may come closer to the line of NH_4Cl and the value of δ_+ may slightly increase. Nevertheless, the above conclusions do not change.

Acknowledgement

The authors thank Asahi Chemical Industry Co., Ltd. for supplying the membrane.

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