Biophysical Chemistry 7 (1978) 279–283

THERMAL MEMBRANE POTENTIAL ACROSS CHARGED MEMBRANES IN 2-1 AND 1-2 ELECTROLYTE SOLUTIONS

Masayasu TASAKA, Kuniichi OGAWA and Takayoshi YAMAZAKI
Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

Received 18 October 1976
Revised manuscript received 9 May 1977

Measurements of thermal membrane potential across cation exchange membranes in $MgCl_2$, $CaCl_2$ and $BaCl_2$ solutions and across anion exchange membranes in K_2SO_4, Na_2SO_4 and K_2CO_3 solutions were carried out. The magnitude of the thermal membrane potential for divalent counterions is lower than that for monovalent counterions. If the transport number of counterions in the membrane phase is unity, the slopes of the temperature coefficient of thermal membrane potential against logarithmic activities of counterion in the external solution are predicted to be $-R/2F$ for 2-1 electrolytes with cation exchange membranes and $R/2F$ for 1-2 electrolytes with anion exchange membranes, respectively.

1. Introduction

Work on thermal membrane potential has been carried out for 1-1 valence type electrolytes [1–7]. In previous papers [5–7], we proposed a theory of thermal membrane potential and found good agreement between the theory and experimental data for various 1-1 electrolytes with various ionic membranes. The purpose of this paper is to extend the theory to systems containing higher valence type electrolytes and to test the reliability of the theory with new experimental data.

2. Basic equations

The phenomenological equations for the total entropy flux J_s and the absolute mass fluxes J_i across the membrane are written as follows if there is no pressure difference across the membrane [8,9]:

$$-J_s = L_{ss}\Delta T + \sum_j L_{sj}\Delta\tilde{\mu}_j, \tag{1}$$

$$-J_i = L_{is}\Delta T + \sum_j L_{ij}\Delta\tilde{\mu}_j, \tag{2}$$

where

$$\Delta\tilde{\mu}_j = \Delta\mu_j + z_j F\Delta\psi. \tag{3}$$

Δ shows the small difference between two fluid phases on both sides of the membrane and T is the thermodynamic temperature, ψ the electric potential, $\tilde{\mu}_j$ the electrochemical potential, μ_j the chemical potential, z_j the valence of species j, F the Faraday constant and $L_{\alpha\beta}$ are the phenomenological coefficients. $L_{\alpha\beta}$ are not absolute constants for membrane-electrolyte systems but can practically be treated as constant [5].

The thermal membrane potential can be calculated from the condition of $I = \Sigma_i z_i F J_i = 0$. That is [5,9],

$$-\Delta\psi = \eta\Delta T + \sum_i \tau_i \Delta\mu_i, \tag{4}$$

where

$$\eta = \sum_j z_j L_{js} \Big/ \sum_j \sum_k z_j z_k L_{jk} F, \tag{5}$$

$$\tau_i = \sum_j z_j L_{ji} \Big/ \sum_j \sum_k z_j z_k L_{jk} F. \tag{6}$$

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

Fig. 1. Illustration of a membrane bathed by different solutions of an electrolyte.

$$\tau_i = (J_i/I)_{\Delta T=0,\ \Delta\mu_j=0}. \tag{7}$$

Moreover, for the system illustrated in fig. 1 $\Delta\mu_i$ is written as

$$\Delta\mu_i = (\Delta\mu_i)_T - s_i \Delta T, \tag{8}$$

where

$$s_i(T) = s_i^0 - R \ln a_i(T) - RT(\partial \ln a_i/\partial T)_T. \tag{9}$$

The s_i is the partial molar entropy, s_i^0 the standard partial molar entropy and a_i the activity of species i.

Substituting eq. (8) into eq. (4), we have

$$-\Delta\psi = \sum_i \tau_i RT \ln \frac{a_i[m_i(2), T]}{a_i[m_i(1), T]} + \left\{\eta - \sum_i \tau_i s_i\right\} \Delta T. \tag{10}$$

Eq. (10) is equivalent to eq. (10) of ref. [5].

At equal molalities $-\Delta\psi/\Delta T$ is given by

$$-\frac{\Delta\psi}{\Delta T} = \eta - \sum_i \tau_i \left\{s_i^0 - R \ln a_i(T) - RT\left(\frac{\partial \ln a_i}{\partial T}\right)_T\right\}$$
$$\approx \eta - \sum_i \tau_i \{s_i^0 - R \ln a_i(T)\}. \tag{11}$$

The transported entropies $\bar{\bar{s}}_j$ (the symbol s_j^* which is called "the entropy of transport" is used by De Groot and Mazur [10] and Katchalsky and Curran [8]) may be defined in terms of the phenomenological coefficients [11]:

$$L_{is} = \sum_j L_{ij} \bar{\bar{s}}_j. \tag{12}$$

Substituting eq. (12) into eq. (5), we have

$$\eta = \sum_j \tau_j \bar{\bar{s}}_j. \tag{13}$$

Combining eqs. (11) and (13), $-\Delta\psi/\Delta T$ is also given by

$$-\frac{\Delta\psi}{\Delta T} \approx \sum_i \tau_i \{\bar{\bar{s}}_i - s_i^0 + R \ln a_i(T)\}. \tag{14}$$

If the transport number of the counterions is unity and there is no molality difference across the membrane, from eq. (11) or (14) we have for 2-1 electrolytes with a cation exchange membrane

$$-\frac{\Delta\psi}{\Delta T} = \frac{R}{2F} \ln a_+(T) + \alpha_+ \tag{15}$$

and for 1-2 electrolytes with an anion exchange membrane

$$\frac{\Delta\psi}{\Delta T} = \frac{R}{2F} \ln a_-(T) - \alpha_-. \tag{16}$$

Here, the following abbrevation is used.

$$\alpha_i = \eta - \frac{s_i^0}{z_i F} - \tau_0 s_0 = \frac{1}{z_i F}(\bar{\bar{s}}_i - s_i^0) + \tau_0(\bar{\bar{s}}_0 - s_0). \tag{17}$$

From eqs. (15) and (16) the slope of $\mp \Delta\psi/\Delta T$ plotted against logarithmic counterion activities is expected to be $R/2F$.

3. Experimental

3.1. Membranes

The same homogeneous cation exchange membrane C-2 used in previous work [7] was employed. Membrane C-2 has sulfonic groups. Three samples made of a sheet of membrane C-2 were used in $MgCl_2$, $CaCl_2$ and $BaCl_2$ solutions, because it is very difficult to change perfectly the type of divalent counterion species in the membrane. In order to confirm that the properties of three samples of C-2 were the same measurements of thermal membrane potential in KCl solutions with these samples were carried out.

The same heterogeneous anion exchange membrane A-1 used in previous work [7] was also employed. This membrane was prepared from anion exchange resin powder 60 wt% and polyvinyl chloride (a copolymer containing vinyl acetate 5 wt%) 40 wt% as binder.

In all cases the transport numbers of counterions in these membranes are higher than 0.95 in 0.1–0.2 mol/kg electrolyte solutions. The transport numbers of counterions in membranes were calculated from membrane potentials at $\Delta T = 0$ using the approximate equation:

$$-\Delta\psi \approx \left(\frac{t_+}{z_+} + \frac{t_-}{z_-}\right)\frac{RT}{F}\ln\left(\frac{a_\pm(2)}{a_\pm(1)}\right). \tag{18}$$

Therefore, these membranes will be treated here in a first approximation as perfectly selective in the whole range of molality.

3.2. Electrolytes

Aqueous solutions of $MgCl_2$, $CaCl_2$ and $BaCl_2$ were used with cation exchange membranes and aqueous solutions of K_2SO_4, Na_2SO_4 and K_2CO_3 were used with anion exchange membranes.

3.3. Membrane potential cell and measurements

The thermal membrane potential cell was constructed as shown schematically in eq. (19).

$$\underbrace{\mathrm{Hg/Hg_2Cl_2/satd.KCl/soln.(1)}}_{T}\mathrm{/membrane/}$$

Temperature:

$$\underbrace{\mathrm{/soln.(2)/}}_{T+\Delta T}\underbrace{\mathrm{satd.KCl/Hg_2Cl_2/Hg}}_{T}. \tag{19}$$

The molalities of electrolyte on both sides of the membrane were equal. The temperature on one side of the membrane, T, was kept at 293 ± 0.1 K. The difference of temperature across the membrane, ΔT, was systematically varied from −10 to +10 K. The experimental method was similar to the one reported previously [5,6].

3.4. Electro-osmosis

The membrane was mounted between two 50-cm^3 compartments of a cell made of poly(methyl methacrylate) and equipped with magnetic stirrers, silver–silver chloride electrodes and capillaries for measuring volume flow. All experiments were run in 0.01 mol/kg solutions of the electrolyte at 1.7 mA/cm^2.

Since no reversible electrode is available for SO_4^{2-} and CO_3^{2-}, we employed the four-compartment cell [6,14] with cation exchange membranes as shown by

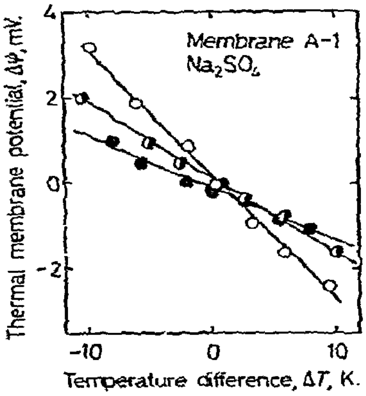

Fig. 2. Examples of thermal membrane potentials in Na_2SO_4 solutions for membrane A-1. Molalities(mol/kg): (○) 0.001; (◐) 0.01; (●) 0.1.

$$\mathrm{Ag/AgCl\cdot KCl}\underset{\substack{\text{cation}\\ \text{exchange}\\ \text{membrane}}}{//}\mathrm{soln.}\underset{\substack{\text{sample}\\ \text{membrane}}}{//}\mathrm{soln.}\underset{\substack{\text{cation}\\ \text{exchange}\\ \text{membrane}}}{//}\mathrm{KCl\cdot AgCl/Ag.} \tag{20}$$

4. Results and discussion

The membrane potential $\Delta\psi$ for ion exchange membranes varies linearly with the temperature difference in the range of ΔT examined (−10 to +10 K). The slope is however different from those reported with 1-1 electrolytes [5,6]. Examples of $\Delta\psi$ versus ΔT plots with an anion exchange membrane in Na_2SO_4 solutions are shown in fig. 2. In fig. 2 all lines must go through the (0,0) point. In practice, the deviation due to an asymmetric membrane potential was observed as shown in fig. 2. The asymmetric membrane potential observed for divalent counterion was generally larger than that for monovalent counterions. However, the asymmetric membrane potential did not change before and after the measurement of thermal membrane potentials at a given electrolyte concentration. Similar $\Delta\psi$ versus ΔT plots were obtained with other 2-1 and 1-2 electrolyte solutions. The slopes, $\Delta\psi/\Delta T$ (mV/K), are plotted in figs. 3 and 4 as a function of the activities of the counterions. The activity coefficients of single ions were calculated using the Debye–Hückel theory shown by eq. (9.7) of ref. [15]. The lines are drawn with the slope of 2.303 $R/2F$, 0.0992 mV/K, as expected from eqs. (15) and (16) (see figs. 3 and 4).

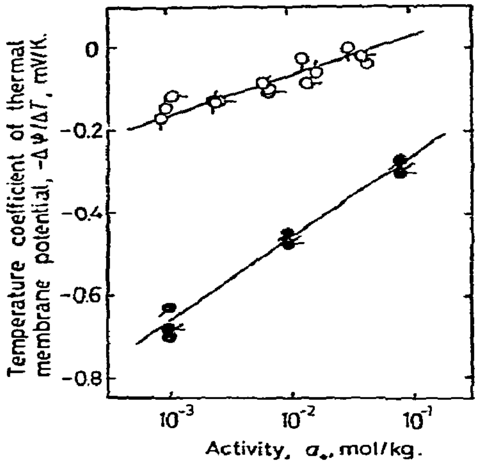

Fig. 3. The effect of counterions on the temperature coefficient of the thermal membrane potential, $-\Delta\psi/\Delta T$, for cation exchange membrane C-2. Electrolytes: (ò) $MgCl_2$; (o-) $CaCl_2$; (♀) $BaCl_2$; (●) KCl with the membrane used for $MgCl_2$; (●-) KCl with the membrane used for $CaCl_2$; (●) KCl with the membrane used for $BaCl_2$.

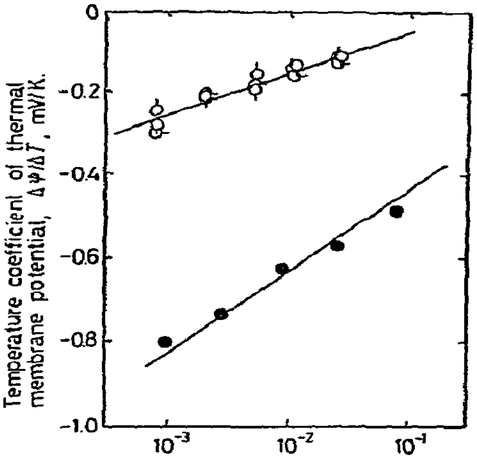

Fig. 4. The effect of counterions on the temperature coefficient of the thermal membrane potential, $\Delta\psi/\Delta T$, for anion exchange membrane A-1. Electrolytes: (ò) K_2SO_4; (o-) Na_2SO_4; (♀) K_2CO_3; (●) KCl.

The thermal membrane potential is almost independent of the type of divalent counterions both with cation exchange membranes and with anion exchange membranes, although in 1-1 electrolyte solutions the thermal membrane potential significantly depends on the species of ion [6].

As shown by eq. (17), α_i is made up of three terms, η, s_i^0/z_iF and $\tau_0 s_0$. The values of s_i^0 are the molar entropies of ions referred to that of H^+ ion and the value of s_0 may be approximated by the molar entropy of pure water, i.e., $s_0 \approx 69.9$ J/K mol, neglecting the effect of the hydration of ions on the molar entropy of water [16]. The values of τ_0 estimated by the measurements of electro-osmosis are shown in table 1. The direction of water flow through anion exchange membranes is opposite to that of the electric current.

Table 1
The values of α_i, τ_0 and η for membranes C-2 and A-1

Counterion	α_i (mV/K)	τ_0 (mol/96484 C)	η (mV/K)
membrane C-2			
	$\alpha_+ = (1/2F)(\bar{\bar{s}}_+ - s_+^0) + \tau_0(\bar{\bar{s}}_0 - s_0)$		$\eta = \bar{\bar{s}}_+/2F + \tau_0\bar{\bar{s}}_0$
Mg^{2+}	0.135 ± 0.020	15.9	11.0
Ca^{2+}		12.8	9.1
Ba^{2+}		11.2	8.3
membrane A-1			
	$\alpha_- = -(1/2F)(\bar{\bar{s}}_- - s_-^0) + \tau_0(\bar{\bar{s}}_0 - s_0)$		$\eta = -\bar{\bar{s}}_-/2F + \tau_0\bar{\bar{s}}_0$
SO_4^{2-}	−0.05 ± 0.015	−4.8	−3.6
CO_3^{2-}		−4.5	−3.0

Hence, the value of τ_0 with anion exchange membranes is negative. Thus, using eq. (17) we can calculate values of the pure thermoelectric potential coefficient η. From eq. (13) the values of η can be expressed by $\bar{\bar{\bar{s}}}_+/2F + \tau_0\bar{\bar{\bar{s}}}_0$ for a cation exchange membrane and $-\bar{\bar{\bar{s}}}_-/2F + \tau_0\bar{\bar{\bar{s}}}_0$ for an anion exchange membrane if the transport number of counterions is unity. As shown in table 1 the values of η are positive for cation exchange membranes and negative for anion exchange membranes, respectively, as found for 1 - 1 electrolytes.

Acknowledgement

The authors thank Asahi Chemical Industry Co., Ltd. for supplying the membrane (C-2).

References

[1] H.J.V. Tyrrell, D.A. Taylor and C.M. Williams, Nature 177 (1956) 668.
[2] T. Ikeda, J. Chem. Phys. 28 (1958) 166.
[3] T. Ikeda, M. Tsuchiya and M. Nakano, Bull. Chem. Soc. Japan 37 (1964) 1482.
[4] N. Lakshminarayanaiah, Chem. Rev. 65 (1965) 491.
[5] M. Tasaka, S. Morita and M. Nagasawa, J. Phys. Chem. 69 (1965) 4191.
[6] M. Tasaka, K. Hanaoka, Y. Kurosawa and C. Wada, Biophys. Chem. 3 (1975) 331; 4 (1976) 214.
[7] M. Tasaka, N. Ichijo, S. Kobayashi and H. Kobayashi, Biophys. Chem. 4 (1976) 269.
[8] A. Katchalsky and P.F. Curran, Nonequilibrium thermodynamics in biophysics (Harvard Univ. Press, Cambridge, Massachusetts, 1965) chs. 7 and 13.
[9] M. Tasaka and M. Nagasawa, J. Polymer Sci. Symp. 49 (1975) 31.
[10] S.R. de Groot and P. Mazur, Non-equilibrium thermodynamics (North-Holland, Amsterdam, 1962) ch. 11.
[11] H.J.V. Tyrrell, Diffusion and heat flow in liquids (Butterworths, London, 1961) ch. 2.
[12] H.J.V. Tyrrell, Diffusion and heat flow in liquids (Butterworths, London) ch. 10.
[13] H.S. Harned and B.B. Owen, The physical chemistry of electrolytic solutions, 3rd Ed. (Reinhold, New York, 1950) ch. 12.
[14] B.R. Breslau and I.F. Miller, Ind. Eng. Chem. Fundamentals 10 (1971) 554.
[15] R.A. Robinson and R.H. Stokes, Electrolyte solutions, 2nd Ed. (Butterworths, London, 1959).
[16] G.N. Lewis and M. Randall, revised by K.S. Pitzer and L. Brewer, Thermodynamics, 2nd Ed. (McGraw-Hill, New York, 1961) chs. 12 and 32.