

LIQUID MEMBRANE POTENTIAL IN NONISOTHERMAL SYSTEMS

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ABSTRACT Electrical membrane potential equations for liquid ion exchange membranes, characterized by the presence of uncharged associated species and by exclusion of co-ions (no electrolyte uptake) have been derived. The irreversible thermodynamic theories already developed for solid membranes with fixed charged site density have been extended to include the different physicochemical aspects of the liquid membranes. To this purpose the dissipation function has been written with reference to the fluxes of all the species present in the membrane. It has been found that the mobile charged site, the counterions, and the uncharged associated species contribute to the electrical membrane potential through their phenomenological coefficients. The electrical membrane potential equations have been integrated in isothermal and nonisothermal conditions for monoionic and biionic systems. The theoretical predictions have been experimentally tested by studying the electrical potential of liquid membranes formed with solutions of tetraheptylammonium salts in *o*-dichlorobenzene.

INTRODUCTION

The mobility of the charged site, the presence of uncharged associated species and the exclusion of co-ions (absence of electrolyte uptake), when solvents of low dielectric constant are used, characterize the liquid ion exchange membrane with respect to the solid membrane of fixed charge density (1). When these liquid membranes are interposed between two aqueous electrolyte solutions of different concentration and temperature electrical potentials can be measured (1). In the case of solid membranes of fixed charge density these electrical potentials have been described by means of irreversible thermodynamics theories. (2, 3). These theories have been obtained by writing the dissipation function with reference to the fluxes of the ions which move through the solid membrane. For the case of liquid membranes a mechanistic theory for isothermal electrical potentials has been developed (4) and experimentally tested (5, 6). The theory is based on the isothermal coupling of ion diffusion (through the membrane) and ion exchange (at the aqueous phase/membrane boundaries) processes. The presence of uncharged associated species, ion pair type, has also been taken into account. In this paper the existing irreversible thermodynamics theories for solid membranes are extended to the case of liquid membranes in nonisothermal conditions. In order to explicitly introduce into the theory the contribution to the electrical potential of the mobile charged site, of the counterions, and of the uncharged associated species

the dissipation function has been written with reference to the fluxes of all the species present in the membrane phase. With this approach the electrical potential equations for isothermal and nonisothermal systems contain, through the phenomenological coefficients, the contribution of all the charged and uncharged species present in the membrane phase. The phenomenological coefficients are dependent on the liquid membrane concentration profiles. Therefore the electrical potential equations cannot be integrated unless the dependence of the L_{ik} coefficients on the concentration is known or restricted conditions are used. In this paper the nonisothermal electrical membrane potential equation has been integrated, and experimentally tested, for monoionic systems and for the case of two counterions (biionic potential) and strongly associated liquid membranes.

Description of the System

The system to be studied (see Fig. 1) is nonisothermal and consists of a liquid membrane separating two homogeneous solution phases (e.g. aqueous phases) whose electrical potentials are ψ'' and ψ' , counterion activities a'_i and a''_i , and temperatures $T' = T$ and $T'' = T + \Delta T$. The membrane is composed of a single liquid phase immiscible with the external solutions. The membrane contains a dissolved salt, IS , which can dissociate through the reaction $IS \rightleftharpoons I + S$. The site S of charge $z_s, \pm 1$ (assumed positive in Fig. 1) is insoluble in the external solutions. In other words the sites are assumed to be completely reflected at the boundaries a and h (as indicated by the arrows) but are free to move within the interior of the membrane. The system also contains a number of permeable univalent counterion species, I , whose charge z_i is opposite to that of the sites, and which are free to cross the membrane solution interfaces. Any number of co-ion species may be present in the external solution phases although they are assumed to be completely excluded from the membrane (absence of

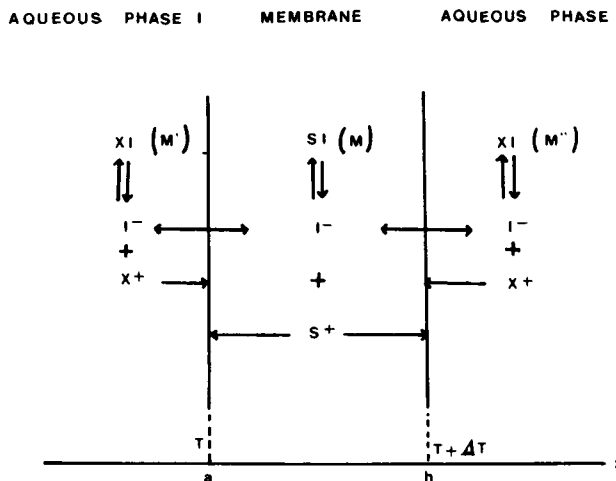


FIGURE 1 Nonisothermal liquid membrane scheme.

electrolyte uptake). Under these circumstances the liquid membrane behaves as a liquid ion (anion in Fig. 1) exchange membrane.

THEORY

In the case of an electrolyte whose n constituting ions for m ($m > n$) associated species, the dissipation function for the transport of matter and energy can be alternatively written with reference either to the constituting ions or to all the species present. This latter choice has been already studied for isothermal solutions (7). In nonisothermal condition the dissipation function written with reference to the fluxes of all the present species is given by

$$T = \sum_{i=1}^m J_i X_i + J_u X_u. \quad (1)$$

In Eq. 1 J_i, J_u are the mass and energy fluxes; X_i, X_u are the conjugated forces given by

$$X_i = e_i \nabla(-\psi^o) - T \nabla(\mu_i^o/T^o) = e_i \nabla(-\psi^o) + \nabla(-\mu_i^o) + \mu_i^o \nabla T^o/T^o \quad (2)$$

$$X_u = \nabla(-T^o)/T^o. \quad (3)$$

As a consequence of the chemical coupling between the n constituting ions, the m X_i forces are linear combinations of the n independent X_i^o forces referring to the constituting ions (in matrix notation $X = BX^o$). In order for the dissipation function to be invariant the fluxes and the phenomenological coefficients have to transform according to (8, 9)

$$J^o = B^T J; L^o = B^T L B; (B^T \text{ transposed of } B). \quad (4)$$

With the definition (8)

$$L_{iu}^o = \sum_{k=1}^n u_k^o L_{ik}^o, \quad (5)$$

we obtain

$$J_i^o = \sum_{k=1}^n L_{ik}^o \{ \text{grad}(-\mu_k^o) + e_k \text{grad}(-\psi^o) + S_k \text{grad}(-T^o)/T^o \} \quad (6)$$

with

$$S_k = u_k^o - \mu_k^o, \quad (7)$$

where μ_k^o and u_k^o are the chemical potential and the energy of transfer of the k th ion in the membrane. In steady state the overall flow of any species, J_i , through the aqueous and the membrane phases is constant. Therefore for an ion exchange membrane with the mobile charged site insoluble in the external aqueous solutions the steady-state condition gives $J_n^o = J_n = 0$ (the index n refers to the site). By means of Eq. 6 with $i = n$ the site conjugated force can be then expressed in terms of the other $n - 1$ ion conju-

gated forces. In this way Eq. 6 reduces to

$$J_i^o = \sum_{k=1}^{n-1} [L_{ik}^o - (L_{in}^o L_{nk}^o / L_{nn}^o)] \{ \text{grad}(-\mu_k^o) + e_k \text{grad}(-\psi^o) + S_k \text{grad}(-T^o) / T^o \}. \quad (8)$$

From the steady-state density current condition $I = \sum_i e_i J_i^o = 0$ ($i = 1, \dots, n-1$) with J_i^o from Eq. 8 and by solving for grad^o we obtain

$$\text{grad} \psi^o = \sum_{k=1}^{n-1} R_k \{ -\text{grad} \mu_k^o - S_k \text{grad} T^o / T^o \}, \quad (9)$$

$$R_k = \sum_{i=1}^{n-1} e_i [L_{ik}^o - (L_{in}^o L_{nk}^o / L_{nn}^o)] / \sum_{k,j=1}^{n-1} e_i e_k [L_{ik}^o - (L_{in}^o L_{nk}^o / L_{nn}^o)]. \quad (10)$$

The novel features of the fluxes and of the potential equations (Eqs. 8 and 9) are: (a) the contribution of the charged site through the phenomenological coefficients L_{in}^o, L_{nn}^o ; (b) the L_{ik}^o coefficients which are linear combinations of the L_{ik} phenomenological coefficients of all the charged and uncharged species present in the membrane phase (Eq. 4). Therefore all these species contribute to the i th ion flux and to the electrical membrane potential. By integrating Eq. 9 between the membrane boundaries (a, h) we obtain

$$\Delta \psi^o = [\psi^o(h) - \psi^o(a)] = - \int_a^h \sum_{k=1}^{n-1} R_k d\mu_k^o - \int_a^h \sum_{k=1}^{n-1} R_k S_k dT^o / T^o. \quad (11)$$

In the following section Eq. 11 will be integrated for monoionic ($n = 2$) and biionic ($n = 3$) systems.

Integration of the Potential Equation

Monoionic system: $n = 2$. It is evident that for $n = 2$ (one mobile charged site and one counterion) it is $R_1 = (1/e_k)$. In mechanical equilibrium the integrated form of Eq. 11 is given by

$$-e_k \Delta \psi = e_k (\psi'' - \psi') = +RT \ln(a_k''/a_k') + R\Delta T \ln a_k'' + (S_k^*/T) \Delta T \quad (12)$$

with $S_k^* = u_k^o - \mu_k^o - Ts_k; s_k = -(\delta\mu_k/\delta T). \quad (12A)$

To obtain Eq. 12 the boundary conditions $\Delta\mu_k^o = \Delta\mu_k$ and $\Delta T^o = \Delta T$ ($\Delta\mu_k$ and ΔT refer to the aqueous external phases) have been used. It has to be noted that to account for the temperature difference the boundary condition $-\Delta\mu_k^o = \Delta\mu_k$ has been written

$$RT \ln[a_k(h)/a_k(a)] + [R \ln a_k(h) - s_k^o] \Delta T \\ = RT \ln(a_k''/a_k') + (R \ln a_k'' - s_k^o) T + e_k (\Delta \psi - \Delta \psi^o).$$

Further, the second integral of Eq. 11 has been approximated to $(-S_k \Delta T^o / T^o)$ assuming that S_k is temperature independent over small ΔT range.

Biionic system: n = 3. The L_{ik}^o coefficients of Eq. 10 are a function of the concentration profiles in the membrane phase. In order to integrate Eq. 11 it is more convenient to write these L_{ik}^o coefficients in a form that explicitly shows their dependence on the concentration. By means of Eq. 4 each L_{ik}^o coefficient can be written as a linear combination of the L_{ik} coefficients (in the case of $n = 3$ the indexes i and k in L_{ik} range from 1 to 5¹). In these linear combinations all the L_{ik} ($i \neq k$; $i, k = 1, \dots, 5$) coefficients, but L_{12} and L_{13} , refer to ion-dipole interactions. Assuming that the L_{ik} ($i \neq k$) are negligible and that the ion-ion mobility interaction coefficients, L_{12} and L_{13} , can also be neglected since these interactions are fully represented by the ion pair coefficients L_{44} and L_{55} , Eq. 9 becomes

$$-F \text{grad } \psi^o = \frac{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) \sum_{i=2}^3 L_{ii} (\text{grad } \mu_i^o + S_i \text{grad } T^o / T^o)}{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) \sum_{i=2}^3 L_{ii} + L_{11} \sum_{j=4}^5 L_{jj}} + \frac{L_{11} \sum_{j=4}^5 \sum_{i=2}^3 L_{jj} (\text{grad } \mu_i^o + S_i \text{grad } T^o / T^o)}{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) \sum_{i=2}^3 L_{ii} + L_{11} \sum_{j=4}^5 L_{jj}}, \quad (13)$$

where L_{11} , L_{ii} , and L_{jj} refer, respectively, to the mobile charged site, the counterions, and the associated species (ion pairs). To obtain Eq. 13 the identity $e_2 = e_3$ and $e_i = z_i F$, with F the Faraday constant, have been used. In order to explicitly introduce the dependence of the L_{ik} ($i = k$) coefficients on the concentration let us consider the following identities (9): $L_{11} = u_1 c_1 / z_1 F$; $L_{22} = -u_2 c_2 / z_2 F$; $L_{33} = -u_3 c_3 / z_3 F$; $L_{44} = u_4 c_4$; $L_{55} = u_5 c_5$; where u_i and c_i are the ion, ion pair mobilities, and concentrations. The ion pair concentrations, c_4 and c_5 , can be expressed in terms of mobile charged site and counterion concentrations by using the chemical equilibria of the ion pair formation constants: $c_4 = K_{2s} c_s c_2$ and $c_5 = K_{3s} c_s c_3$, where K_{is} ($i = 2, 3$) are the ion pair formation constants and c_s , c_i ($i = 2, 3$) are the membrane concentration of the charged mobile site and of the counterions, respectively. In isothermal condition by using these identities and with $z_1 = +1$ and $z_2 = z_3 = -1$ Eq. 13 becomes

$$-\frac{d\psi^o}{dx} = \frac{RT}{F} \frac{\left(u_s + \sum_{i=2}^3 u_{is} K_{is} c_i \right) \sum_{i=2}^3 u_i dc_i / dx + u_s c_s \left(\sum_{i=2}^3 u_{is} K_{is} dc_i / dx \right)}{\left(u_s + \sum_{i=2}^3 u_{is} K_{is} c_i \right) \sum_{i=2}^3 u_i c_i + u_s c_s \left(\sum_{i=2}^3 u_{is} K_{is} c_i \right)}. \quad (14)$$

¹In this section on biionic systems the indexes will be either letters or numbers; the choice between them will be a matter of convenience. The indexing is as follows: (a) index 1 or s for the mobile charged site; (b) indexes $i = 2, 3$ for the two counterions; (c) indexes $i = 4, 5$ or $2s, 3s$ for the two ion pairs.

With the condition $(u_s c_s / \sum_i u_{is} c_{is}) \ll 1$ (with $c_{is} = K_{is} c_s c_i$) that characterizes strongly associated membranes Eq. 14 has been already integrated (ref. 4, Eq. 32).²

In nonisothermal condition Eq. 13 can be written as

$$-F \text{grad } \psi^o = G_2 \text{grad } \mu_2^o + G_3 \text{grad } \mu_3^o + (G_2 S_2 + G_3 S_3) \text{grad } T^o / T^o \quad (15)$$

with

$$G_2 = \frac{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) L_{22} + L_{11} \sum_{j=4}^5 L_{jj}}{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) \sum_{i=2}^3 L_{ii} + L_{11} \sum_{j=4}^5 L_{jj}}, \quad (16)$$

$$G_3 = \frac{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) L_{33} + L_{11} \sum_{j=4}^5 L_{jj}}{\left(L_{11} + \sum_{j=4}^5 L_{jj} \right) \sum_{i=2}^3 L_{ii} + L_{11} \sum_{j=4}^5 L_{jj}}. \quad (17)$$

G_2 and G_3 are not absolute constants for the membrane electrolyte system but as first approximation they can be treated as constant (3). Therefore by assuming: (a) G_2 and G_3 constants over a small concentration difference range; (b) G_2 , G_3 , S_2 , and S_3 constants over small ΔT range; and by using the same boundary conditions as already done to obtain Eq. 12 we have

$$\begin{aligned} -F \Delta \psi &= -F(\psi'' - \psi') \\ &= G_2 \Delta \mu_2^c + G_3 \Delta \mu_3^c + G_2 (R \ln a_2 + S_2^*/T) \Delta T + G_3 (R \ln a_3 + S_3^*/T) \Delta T. \end{aligned} \quad (18)$$

($\Delta \mu_i^c$ refers to the concentration part of the chemical potential). In the case of strongly associated membranes $(u_s c_s / \sum_i u_{is} c_{is}) \ll 1$ and in isochemical conditions ($\Delta \mu_2^c = \Delta \mu_3^c$), by expressing the L_{ii} and L_{jj} coefficients of Eqs. 16 and 17 in terms of mobilities and concentrations, as previously done for Eq. 14, Eq. 18 becomes

$$-F \Delta \psi / \Delta T = t_s N, \quad (19)$$

$$t_s = \frac{u_s (K c_2' / c_3' + 1)}{(u_s + u_2) K c_2' / c_3' + (u_s + u_3)}, \quad \text{with } K = K_{32}^{-1} (K_{3s} / K_{2s}), \quad (20)$$

²Eq. 32, ref. 4:

$$(F/RT)(\psi'' - \psi') = (1 - \tau) \ln \frac{\sum_{i=1}^2 (u_i + u_s) k_i a_i'}{\sum_{i=1}^2 (u_i + u_s) k_i a_i''} + \tau \ln \frac{\sum_{i=1}^2 (u_{is}/K_i) k_i a_i'}{\sum_{i=1}^2 (u_{is}/K_i) k_i a_i''},$$

$$\tau = u_s [(u_{2s}/K_2) - (u_{1s}/K_1)] / [(u_1 + u_s)(u_{2s}/K_2) - (u_2 + u_s)(u_{1s}/K_1)].$$

$$N = D + 0, \quad (21)$$

$$D = \frac{(u_2/u_3) K_{32}^{-1}(c_2'/c_3')(R\ln a_2'' + S_2^*/T) + (R\ln a_3'' + S_3^*/T)}{(u_2/u_3) K_{32}^{-1}(c_2'/c_3') + 1}, \quad (22)$$

$$0 = \frac{(u_2/u_3) K(c_2'/c_3')(R\ln a_2'' + S_2^*/T) + (u_3/u_2)(R\ln a_3'' + S_3^*/T)}{K(c_2'/c_3') + 1}. \quad (23)$$

To obtain Eqs. 19–21 the ion exchange equilibrium constant, K_{32} , for the reaction $\bar{2}s + 3 \rightleftharpoons \bar{3}s + 2$ (bar indicates membrane phase) and the electroneutrality condition $c_s = c_2 + c_3$ have been used. In order to test Eq. 19 we have studied the nonisothermal (thermal) biionic (chloride and nitrate couple with indexes 2 and 3, respectively) electrical membrane potential of liquid anion exchange membranes formed by solutions of tetraheptylammonium nitrate in *o*-dichlorobenzene.

EXPERIMENTAL

Reagents and Electrodes

KCl, KNO₃, and *o*-dichlorobenzene were Carlo Erba purity grade reagents. Tetraheptylammonium chloride (THACl) was an Eastman Kodak product. Tetraheptylammonium nitrate (THANO₃) was prepared as reported in ref. 10. Silver-silver chloride electrodes and standard calomel electrodes (SCE), prepared according to ref. 11, were used. Care was taken to use electrodes having an asymmetry less than 0.05 mV.

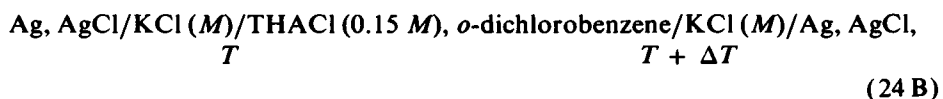
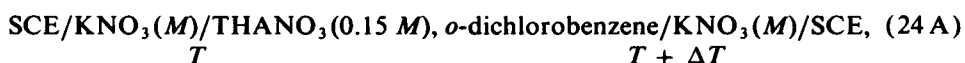
Equipment

A Cary vibrating reed electrometer model 31V was used to measure the potentials (Cary Instrument Co., Fairfield, N.J.). Since the thermal emf values were small and the total cell resistance very high ($10^6 - 10^7 \Omega$), great care was taken not to introduce stray emf values. To the purpose the measurements were performed into a Faraday cage. The temperature differences were measured by means of two calibrated thermometers.

Thermal Cell and Procedure

Experimental thermal potential values were obtained using the apparatus schematically shown in Fig. 2: *E* represents the two sets of the electrodes and *T* the two thermometers. Section B of the apparatus was kept at the desired temperature by circulating oil supplied by a thermostat. Section A was kept at 21°C. The cell shown in Fig. 2 can be schematized as follows:

Monoionic Potentials



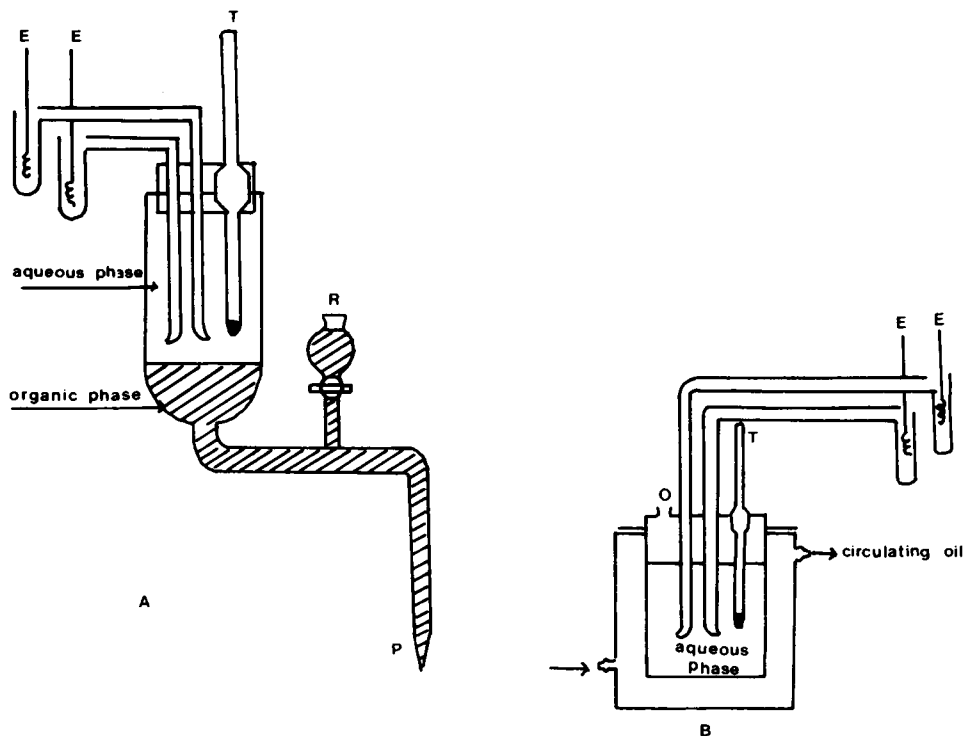


FIGURE 2 Thermal membrane potential experimental apparatus: E are standard calomel electrodes (monoionic systems) or Ag/AgCl electrodes; T = thermometers; R = reservoir containing the liquid ion exchanger.

with $M = 10^{-3}, 10^{-2}, 10^{-1}$, mol · liter⁻¹ for KNO₃ and $M = 10^{-3}, 10^{-2}, 1$ mol · liter⁻¹ for KCl.

Bionic Potentials

Ag, AgCl/KCl (M_2), KNO₃ (M_3)/THANO₃ (0.15 M),
 T

o-dichlorobenzene/KCl (M_2), KNO₃ (M_3)/AgCl, Ag, (25)
 $T + \Delta T$

with the following aqueous solution compositions (isochemical system): $M_2 + M_3 = 0.1$ mol · liter⁻¹; $M_2/M_3 = (c'_2/c'_3) = \text{variable}$.

The measurements were performed according to the following procedure. First thermal equilibrium in the separated A and B sections of the apparatus was obtained. Then the P tube was inserted into the section B through the opening O. At this moment the electrical circuit (externally closed on the electrometer) was not any longer open and the instantaneous emf value was registered for any desired T . To avoid any temperature difference between the organic phase in the bulk and in the P tube the liquid membrane was renewed after each measurement by using the solution contained

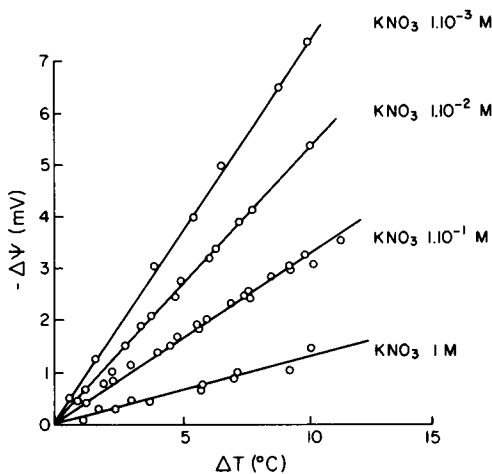


FIGURE 3

FIGURE 3 $\Delta\psi$ vs. ΔT plots at different KNO_3 concentrations (monoionic membrane, THANO_3 0.15 M in *o*-dichlorobenzene).

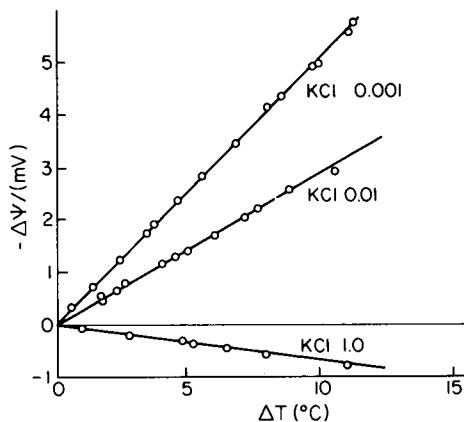


FIGURE 4

FIGURE 4 $\Delta\psi$ vs. ΔT plots at different KCl concentrations (monoionic membrane, THACL 0.15 M in *o*-dichlorobenzene).

in reservoir R. The influence of time on the thermal potential values was investigated by following the emf readings for several hours. No significant variations were observed. This fact indicates that no appreciable concentration gradient, both in organic and aqueous phases, was set up during the experiment. The potential of the electrode dipped into the compartment having the higher temperature was found negative with respect to the other. Measurements with $dT/dz > 0$ and $dt/dz < 0$ (z being the vertical axis of the cell) gave the same results indicating that there was no contribution of convection to the thermal potential values at time $t = 0$.

RESULTS AND DISCUSSION

The theory has been tested by verifying the adequacy of Eq. 19 to predict experimental $\Delta\psi/\Delta T$ values at different c_2/c_1 aqueous concentration ratios for an isochemical (the same composition in both aqueous phases) biionic system. For this test we must: (a) obtain all the parameters present in Eqs. 20, 22, 23; (b) obtain experimental $\Delta\psi/\Delta T$ vs. c_2/c_1 values; calculate a theoretical $\Delta\psi/\Delta T$ vs. c_2/c_1 curve in order to compare experimental and calculated results. All the experimental values of the parameters appearing in Eqs. 20, 22, 23 but the S_2^*/TF and S_3^*/TF values, have been obtained in a previous work (6) by means of conductometric (mobilities and association constants) and ion exchange (K_{32}) measurements.³ The experimental S_2^*/TF and S_3^*/TF values have

³The data at 25°C are: $Fu_1 = 9.50$; $Fu_2 = 36.0$; $Fu_3 = 15.0$; $Fu_{2s} = 45.0$; $Fu_{3s} = 25.0$ (all of them in equivalent or molar conductivity units; F is the Faraday constant). $K_{2s} = 6.25 \times 10^5$; $K_{3s} = 6.67 \times 10^4$; $K_{32} = 14$.

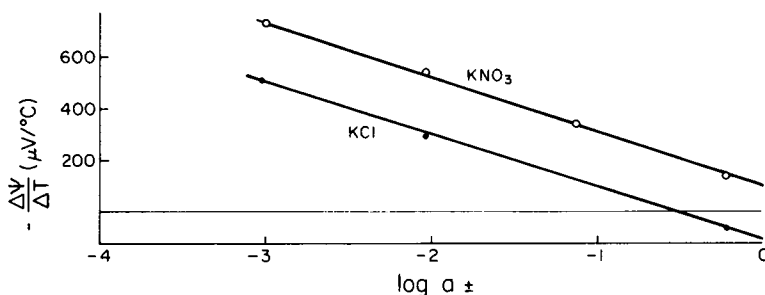


FIGURE 5 $\Delta\psi/\Delta T$ vs. $\log a_{\pm}$ plots for monoionic membranes.

been obtained measuring the $\Delta\psi$ (millivolts) vs. ΔT values for monoionic KCl and KNO_3 (cells 24A and 24B) systems. The experimental data are shown in Figs. 3 and 4 ($\Delta\psi$ vs. ΔT for different KNO_3 and KCl molarities) and in Fig. 5 ($\Delta\psi/\Delta T$ vs. $\log a_{\pm}$ with a_{\pm} the mean activity of the electrolyte). As predicted by the theory for monoionic systems (Eq. 12) all the data of Figs. 3 and 4 lay on a straight line of slope $+200 \mu\text{V}/^\circ\text{C}$. The intercepts at $a_{\pm} = 1 \text{ M}$ (both for Cl^- and NO_3^-) give the values $S_2^*/TF = +100 \mu\text{V}/^\circ\text{C}$ and $S_3^*/TF = -135 \mu\text{V}/^\circ\text{C}$, respectively. It has to be noted that Eq. 19 was obtained assuming t_i and N as temperature independent. For $\Delta T = 10^\circ\text{C}$ variation in the mobility ratios, ion pair association constant ratios and ion exchange constant, is small and may be ignored. The experimental biionic $\Delta\psi$ vs. ΔT data at different c'_2/c'_3 ratios have been obtained by using the isochemical biionic system previously described. In Fig. 6 an example of a $\Delta\psi$ vs. ΔT curve is reported. Similar plots have been obtained for 14 different c'_2/c'_3 ratios ranging from 0.031 to 999. The $\Delta\psi/\Delta T$ values for these concentration ratios are reported in Table I and, as experimental

TABLE I
THERMAL BIIONIC POTENTIAL VALUES FOR THE LIQUID
MEMBRANE SYSTEM SHOWN IN CELL 25

$c'_{\text{Cl}}/c'_{\text{NO}_3}$	c'_{KCl}	c'_{KNO_3}	$(\Delta\psi/\Delta T)_{\text{exp}}$
	<i>mol · liter⁻¹</i>	<i>mol · liter⁻¹</i>	<i>μV/°C</i>
0.031	0.003	0.097	-344 ± 16
0.053	0.005	0.095	-340 ± 23
0.111	0.010	0.090	-350 ± 23
0.250	0.020	0.080	-350 ± 19
0.429	0.030	0.070	-355 ± 18
0.667	0.040	0.060	-365 ± 20
1.000	0.050	0.050	-390 ± 30
1.500	0.060	0.040	-413 ± 12
2.333	0.070	0.030	-410 ± 25
4.000	0.080	0.020	-445 ± 20
9.000	0.090	0.010	-430 ± 20
19.00	0.095	0.005	-345 ± 30
99.00	0.099	0.001	-245 ± 15
999.0	0.0999	0.0001	-130 ± 5

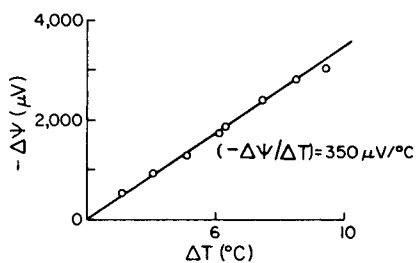


FIGURE 6

FIGURE 6 $\Delta\psi$ vs. ΔT plot for $c_2^+/c_3^+ = 0.003/0.097$ (KCl 0.003 M, KNO₃ 0.097 M). Similar curves for 14 different aqueous concentration ratios have been obtained (Table I).

FIGURE 7 $\Delta\psi/\Delta T$ vs. $\log c_2^+$ plot; Φ experimental points (Table I). The continuous line shows the calculated curve (Eq. 19).

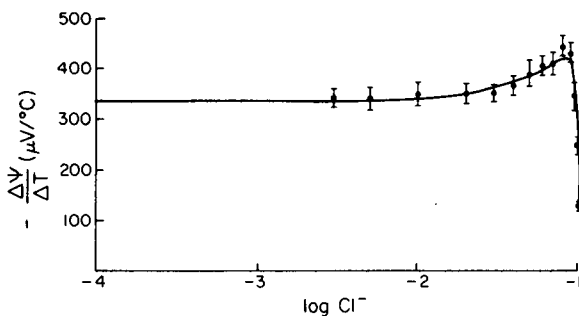


FIGURE 7

points, in Fig. 7 ($\Delta\psi/\Delta T$ vs. $\log c_2^+$). The theoretical $\Delta\psi/\Delta T$ vs. $\log c_2^+$ curve calculated by using Eq. 19 and the parameters already reported is shown in Fig. 7 as a continuous line. The experimental $\Delta\psi/\Delta T$ values are also reported. The agreement between the experimental and calculated $\Delta\psi/\Delta T$ is rather good.

CONCLUSIONS

The electrical membrane potential equation (Eq. 11) has been obtained by writing the dissipation function with reference to all the charged and uncharged species present in the membrane phase and assuming a complete co-ion exclusion (absence of electrolyte uptake) as well as the insolubility of the charged mobile site in the external aqueous solutions. As consequence of this approach the mobile charged site, the counterions and the associated species contribute to the electrical membrane potential through their phenomenological coefficients (Eq. 13). These contributions become important in the multiionic potential case. In fact, in the monoionic case the R_k terms (Eq. 10) disappear ($R_k = 1/e_k$) (Eq. 12) and, as expected, the electrical membrane potential equation is equivalent to that of the solid membrane. For biionic systems the R_k terms (Eq. 10) are dependent on the membrane concentration profiles. The membrane potential equation has been then integrated under restricted conditions: (a) the membrane is characterized by a large degree of association; (b) the t_s and N parameters (Eqs. 20, 22, 23) are constants over small ΔT range (this assumption is not so restrictive by considering that in the equations the ion exchange constant does not change appreciably for systems with small ion exchange enthalpies and that the ion pair mobilities are under the form of ratios); (c) the L_{ik} ($i \neq k$) coefficients are negligible. This last assumption is valid for systems where the phenomenological coefficients due to the ion-dipole interaction mobilities are negligible and those due to the ion-ion interaction mobilities (L_{12} , L_{13}) are of second order with respect to the ion pair phenomenological coefficients (L_{44} , L_{55}). These approximations seem to

apply to our experimental systems. In fact the analysis of the conductivity-concentration curves of our membranes (6) has evidenced the presence of the ion pairs but no influence of triple ions (ion-dipole) has been detected. Further the good agreement between our experimental and calculated thermal biionic membrane potentials shows that the theory does work very well, under the restricted condition we have used, to describe the nonisothermal electrical potential behavior of our membranes.

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