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Studies on Inorganic Precipitate Membranes: Membrane Potential and Bi-ionic Potential

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Electrical potentials arising across barium(II) phosphate, mercury(II) iodide and cobalt(II) chromate membranes using various 1:1 electrolytes are reported. Thermodynamically effective fixed charge density, which is an important parameter governing the membrane phenomena, has been evaluated by the theory of Toyoshima and Nozaki. Using the values of effective fixed charge density determined, the theory of bi-ionic potentials developed by Toyoshima and Nozaki based on the principles of the irreversible thermodynamics has been examined. Theoretical predictions were borne out quite satisfactorily by our experimental results.

In recent years we have studied a large number of parchment supported inorganic precipitate and polymeric composite membranes.[1-6)] Various transport parameters such as ion migration, self diffusion coefficient, hydrodynamic permeability *etc.* occuring across the membranes have been evaluated in the light of the theory described by Speigler[7)] and by the use of the generalized Stefan-Maxwell equations. The theory of absolute reaction rates,[8)] Eisenman-Sherry theory of membrane selectivity[9)] and the theory of irreversible thermodynamics developed by Kedem and Katchalsky,[10)] Smit and Staverman,[11)] Bearman and Krikwood,[12)] and Kobatake and coworkers[13-16)] have been applied to evaluate apparent fixed charge density as well as to examine the various aspects of membranes.

In this communication a series of membrane potentials and bi-ionic potentials observed across parchment supported barium(II) phosphate, mercury(II) iodide and cobalt(II) chromate membranes using various 1:1 electrolytes are presented. Thermodynamically effective fixed charge density, which is an important parameter governing the membrane phenomena has been evaluated by the recently developed theory of Toyoshima and Nozaki based on the principles of irreversible thermodynamics.[17)] An effort has been made to examine the validity of the theory of Toyoshima and Nozaki[17)] for bi-ionic potential.

Experimental

Preparation of Membranes. Parchment supported barium(II) phosphate, mercury(II) iodide and cobalt(II) chromate membranes were prepared by the method of interaction suggested by Siddiqi, Beg, and coworkers.[1-6)] To precipitate barium(II) phosphate in the interstices of parchment paper, a 0.2 M solution of barium(II) chloride was placed inside a glass tube, to one end of which was tied the parchment paper (supplied by M/s- Baired and Tatlock London Ltd.). The tube was suspended for 72 h in a 0.2 M solution of potassium dihydrogenphosphate. The two solutions were interchanged later and kept for another 72 h. The membrane was taken out and washed with deionized water to remove free electrolyte. Similar procedure was adopted for the preparation of mercury(II) iodide and cobalt(II) chromate membranes by taking 0.2 M solutions of mercury(II) chloride and potassium iodide, cobalt(II) chloride and potassium chromate, respectively.

Measurements of Membrane Potential and Bi-ionic Potential. Membrane potential E_m were obtained by constructing a cell of the following type taking different concentrations C'_N and C''_N of an electrolyte such that $C''_N/C'_N = 10$

SCE	Solution C'_N	Membrane	Solution C''_N	SCE

and the bi-ionic potentials (BIP) were determined by setting up another cell of the type

SCE	Solution AP	Membrane	Solution BP	SCE

and keeping the same concentration of both the electrolytes AP and BP. The various salt solution (chlorides of Li^+, Na^+, K^+) were prepared from analytical grade reagents and deionized water. All measurements were carried out using a water thermostate maintained at 25±0.1 °C. The solutions on either sides of the membrane were vigorously stirred by a pair of magnetic stirrer.

Results and Discussion

When two electrolyte solutions of different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena are induced in the system. The fixed charge theory of Teorell-Meyer-Seivers (TMS) for charged membranes is a pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes which occur in the membrane phase. Based on the fixed charge concept various mathematically rigorous equations for membrane potential and bi-ionic potential have in recent years been derived.[17-22)] Most recently Toyoshima and Nozaki[17)] have derived equations for membrane potential and bi-ionic potential using the principles of non-equilibrium thermodynamics and by utilizing appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase.[17)] The effect of ionic interaction, mass flow and osmotic effect were neglected. For a negatively charged membrane separating two 1:1 electrolytes (common co-ions) of the same concentration, these authors derived following expression for bi-ionic potential, E_{BIP},

$$E_{BIP} = (F/RT)[2\ln K_A/K_B + \ln(JV_A + 1/JV_B + 1)]. \tag{1}$$

Knowing the values of parameters K_A, K_B, V_A, V_B, and the flux J, the values of theoretical E_{BIP} can be

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TABLE 1. THE VALUES OF MEMBRANE POTENTIALS, E_m (mV) OBSERVED ACROSS PARCHMENT SUPPORTED BARIUM(II) PHOSPHATE, MERCURY(II) IODIDE AND COBALT(II) CHROMATE MEMBRANES AT 25±0.1 °C

Membrane concentration (M)	Barium(II) phosphate			Mercury(II) iodide			Cobalt(II) chromate		
	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
1/0.1	1.51	−4.39	−4.98	6.68	−1.35	−13.40	−5.30	−7.90	−14.32
0.5/0.05	2.90	−3.89	−4.01	10.03	2.24	−8.27	−3.20	−5.50	−11.50
0.1/0.01	9.82	2.10	1.96	31.11	23.59	14.77	4.50	−1.23	−5.50
0.05/0.005	16.34	7.95	2.50	39.58	34.35	25.22	8.80	2.63	−1.00
0.01/0.001	33.78	22.05	20.15	49.86	46.32	40.63	21.20	16.83	13.80

Dilute solution side taken as positive.

TABLE 2. THE VALUES OF THE MEMBRANE PARAMETERS V_N AND $(\bar{X}/K_N)$ DERIVED FROM THE TOYOSHIMA AND NOZAKI THEORY FOR PARCHMENT SUPPORTED MEMBRANE

Membrane parameters	Mercury(II) iodide		Barium(II) phosphate		Cobalt(II) chromate	
	V_N	$\bar{X}/K_N$	V_N	$\bar{X}/K_N$	V_N	$\bar{X}/K_N$
KCl	2.05	0.438	2.00	0.092	1.75	0.012
NaCl	1.73	0.474	1.88	0.066	1.75	0.013
LiCl	1.53	0.490	1.86	0.026	1.55	0.010

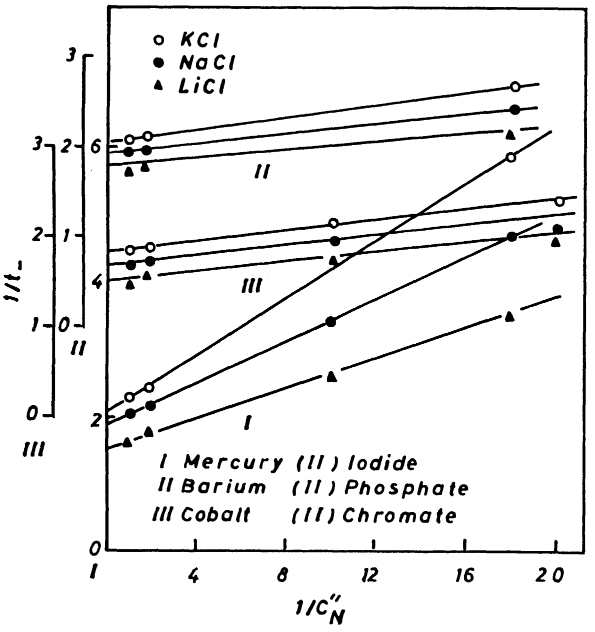

Fig. 1. Plots of $1/t$ against $1/C$ for various electrolytes across (i) mercury(II) iodide, (ii) barium(II) phosphate and (iii) cobalt(II) chromate membranes.

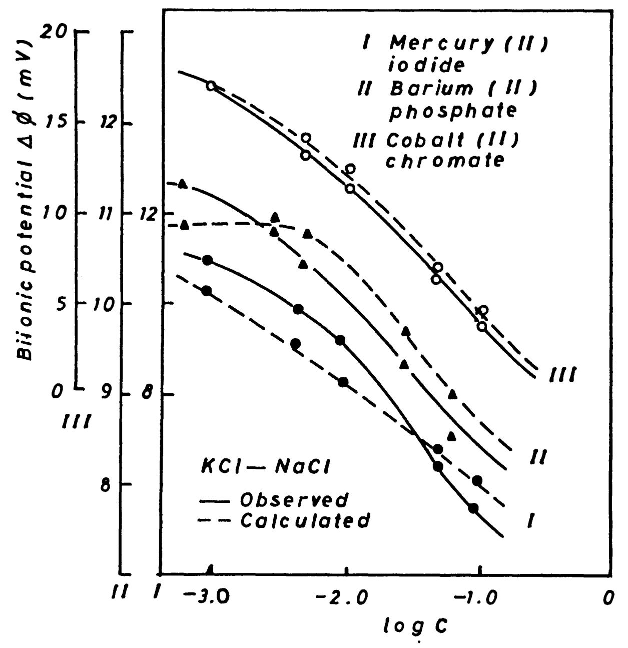

Fig. 2. Plots of bi-ionic potentials against log C for KCl–NaCl pair of electrolytes across (i) mercury(II) iodide, (ii) barium(II) phosphate and (iii) cobalt(II) chromate membranes.

calculated using Eq. 1. For the evaluation of these parameters, following equations have been forwarded[17)]

$$(2J+1)\ln(g_A+2J/g_B+2J) - \ln(JV_A+1/JV_B+1) - \ln(g_A/g_B) = 0 \quad (2)$$

where

$$V_N = 1 + V_N^\circ/V_P^\circ \quad (N=A,\ B) \quad (3a)$$

and

$$g_N = 1 + [1+(2K_N C/\bar{X})^2]^{1/2} \quad (N=A,\ B) \quad (3b)$$

In Eq. 3a, V_N° and V_P° are the mobilities of cation N and anion P, respectively in bulk solution. In Eq. 3b, $\bar{X}$ is the effective charge density of the membrane and K_N is defined by

$$1/K_N = \exp[(\mu_N^{\circ m} - \mu_N^{\circ b} + \mu_P^{\circ m} - \mu_P^{\circ b})/2RT] \quad (3c)$$

where $\mu_N^{\circ m}$ is the standard chemical potential of cation N ion in the membrane phase and $\mu_N^{\circ b}$ is that in bulk solution and $\mu_P^{\circ m}$ and $\mu_P^{\circ b}$ are the corresponding values of anion P. In order to derive the values of the parameters V_N and $\bar{X}$ occuring in Eq. 3a and 3b Toyoshima and Nozaki[17)] derived another equation for membrane potential E_m arising across a membrane when it is used to separate two solutions of an electrolyte at different concentrations C'_N and C''_N

$$(F/RT)E_m = -\ln\gamma - (1-2/V_N)X \ln\frac{\sqrt{1+(2C''_N K_N/\overline{X})^2}+(1-2/V_N)}{\sqrt{1+(2C'_N K_N/\overline{X})^2}+(1-2/V_N)} + \ln\frac{\sqrt{1+(2C''_N K_N/\overline{X})^2}+1}{\sqrt{1+(2C'_N K_N/\overline{X})^2}+1} \tag{4}$$

where $\gamma = C''_N/C'_N$.

Equation 4 on expansion in powers of concentration ratio=10 being kept constant yield

$$(F/RT)E_m = -(1-2/V_N)\ln\gamma - 2(1-1/V_N)X (1/V_N)(1-1/\gamma)(\overline{X}/K_N)(1/C''_N) + \cdots \tag{5}$$

The apparent transference number t_- for co-ion was defined by the Nernst equation

$$-(F/RT)E_m = (1-2t_-)\ln\gamma. \tag{6}$$

Combining Eqs. 5 and 6 and expanding $1/t_-$ as a power of series of $1/C''_N$, following expression was obtained

$$1/t_- = V_N + (V_N-1)\left[\frac{\gamma-1}{\gamma\ln\gamma}\right]\left(\frac{\overline{X}}{K_N}\right)\left(\frac{1}{C''_N}\right) + \cdots \tag{7}$$

Equation 7 predicts a linear relationship between $1/t_-$ and $1/C''_N$. The values of V_N and $(\overline{X}/K_N)$ can be determined from the ordinate intercept and initial slope of a plot for $1/t_-$ against $1/C''_N$. The apparent transference number t_- was calculated from membrane potential data (Table 1) using Eq. 6. The values of V_N and $\overline{X}/K_N$ thus derived for the membrane and various 1:1 electrolyte systems using Fig. 1 are given in Table 2. The values of V_N and $(\overline{X}/K_N)$ were then used to calculate J and g_N using Eqs. 2 and 3. Once the membrane parameters V_N, g_N, J and $(\overline{X}/K_N)$ are known for the membrane electrolyte systems, one can calculate theoretical bi-ionic potential using Eq. 1. The bi-ionic potential thus obtained were plotted as a function of log C in Fig. 2 (shown by dotted lines). In order to compare theoretical bi-ionic potential values, the observed bi-ionic potentials were also plotted in the same graph (shown by solid lines). Figure 2 demonstrates that the theoretical predictions are borne out quite satisfactorily by our experimental results on parchment supported membranes. However, a slight deviation in the values may be accounted due to various reasons, most notably due to the various degree of interaction of ions with the membranes of low fixed charge site.

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