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Research Article

# **BI-IONIC POTENTIAL STUDIES FOR THALLIUM**

# **CHROMATE PARCHMENT-SUPPORTED MEMBRANE**

# KM. Elsherif<sup>\*</sup>, A. El-Hashani, A. El-Dali and R. El-kailany

Benghazi University, Faculty of Science, Chemistry Department, Benghazi-Libya.

# ABSTRACT

The bi-ionic potential (BIP) values across the parchment supported thallium chromate membrane with various combinations of 1:1 electrolytes at different concentrations have been measured. Theoretical values of BIP have been calculated using the BIP theories developed recently by Toyoshima et al based on principles of non-equilibrium thermo dynamics. Comparison of experimental and theoretical BIP values shows that theoretical equations of BIP are applicable to the parchment supported membrane.

Keywords: Bi-ionic potential, parchment-supported membrane.

# INTRODUCTION

Preparation of membrane with specific properties and study the transport processes which occur across synthetic membranes are of great interest to chemist, chemical engineers, and biologist and large number of works have been published which belong to various fields of science such as surface chemistry, solution theory, colloid chemistry, polymers, electrochemistry, etc. Also, large number of theories has been developed in order to understand the mechanism of transport across the membranes. To test these theories, chemists have synthesized membranes with desired properties to use them as models.

Inorganic precipitate membranes have been used as a model for the study of transport phenomena and to testify the theories of membrane potential and bi-ionic potential<sup>1-8</sup>

In this WORK, we describe the preparation of thallium chromate parchment supported membrane. The recent theory of Toyoshima and Nozaki<sup>9</sup> for bi-ionic potential has been tested.

# MATERIALS AND METHODS

# Preparation of Membrane

All the reagents used were of AR grade (BDH) without further purification and their solutions were prepared in deionized water.

Parchment supported silver thallium chromate was prepared by the method of interaction described by Weiser<sup>10,11</sup> and Siddiqi et al<sup>12-16</sup>. First parchment (Supplied by M/s Baird and Tatlock London Ltd.) was soaked in distilled water for about two hours and then tied to the flat mouth of a beaker containing 0.2 M thallium nitrate solution. This was suspended for 72 hours in a 0.2 M potassium chromate solution at room temperature. The two solutions were interchanged and kept for another 72 hrs. In this way fine deposition of thallium chromate was obtained on the surface of parchment paper. The membrane thus obtained was well washed with deionized water for the removal of free electrolytes. The membrane was clamped between two half cells of an electrochemical cell. The membrane prior to the measurements had been aged by about 24 hrs immersion in 1 M in the testing electrolyte.

# Membrane Potential Measurements (E<sub>m</sub>)

The potential developed by setting up a concentration cell of the type shown in scheme 1 and described by Siddiqi et al.<sup>17</sup>. The membrane potential was obtained by taking the same electrolyte at different concentrations on the two sides of the membrane, such that the concentration ratio  $\sigma = 10$ .

The potentials were monitored by means of Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at  $25 \pm 0.1^{\circ}$ C. The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The uni-univalent electrolytes examined were lithium chloride, sodium chloride, potassium chloride, and ammonium chloride.

Saturated Calomel Electrode	AB	Membrane	AB	Saturated Calomel Electrode
(SCE)	(C <sub>1</sub> )		(C <sub>2</sub> )	(SCE)
		$C_2 = 10 C_1$		

#### Scheme 1

### **Bi-Ionic Potential Measurements (BIP)**

The measurements were recorded by constructing another new cell of the following type:

Saturated Calomel Electrode	AP	Membrane	BP	Saturated Calomel Electrode
(SCE)				(SCE)

### Scheme 2

In this cell, concentrations of both AP and BP electrolytes solutions were equal on both sides of the membrane. The bi-ionic potentials were measured at  $25 \pm 0.1^{\circ}$ C across parchment supported thallium chromate membrane using LiCl-NaCl, LiCl-KCl, LiCl-NH<sub>4</sub>Cl, NaCl-KCl, NaCl- NH<sub>4</sub>Cl, and KCl- NH<sub>4</sub>Cl electrolytes sets in each successive measurement. The solutions were stirred by means of magnetic stirrer in order to be maintained uniform on both sides of the membrane.

At first, the solutions were left as they were for 1 hr at least till the fluxes of the all species reached to steady state, and then we exchanged them for new identical solutions and measured the emf. The measurements were recorded when three changes in the test solutions did not lead to potential variation 0.2 mV. The bi-ionic potentials were measured by means of Knick Digital Potentiometer (No. 646).

# **RESULTS AND DISCUSSION**

The bi-ionic potential (BIP) has been defined as the dynamic membrane potential which arises across a membrane separating the solutions of two electrolytes at the same concentration with different critical ions; which are able to exchange across the membrane, and the same non-critical ions for which the membrane is impermeable<sup>18</sup>. The critical ions in the case of electronegative membranes; such as collodion membranes, are the cations, conversely in the case of electropositive membranes, the critical ions are the anions. The sign and the magnitude of the BIP are determined by the relative ease with which the two critical ions penetrate the membrane<sup>19</sup>.

Marshal and Krinbill<sup>20</sup> developed the following equation for the bi-ionic potential:

$$\Delta E_{BIP} = \frac{RT}{F} \ln \left( \frac{a_A u_A}{a_B u_B} \right) \tag{1}$$

, where  $\frac{u_A}{u_B}$  is the mobility ratio in the membrane phase of the two ions

Most recently Toyoshima and Nozaki<sup>9</sup> derived various theoretical equations for membrane potential and bi-ionic potential which are applied and tested with parchment supported thallium chromate membrane. The theoretical equation for bi-ionic potential using variables which contains four

parameters (V<sub>A</sub>, V<sub>B</sub>), 
$$(\frac{\phi X}{K_A})$$
,  $(\frac{\phi X}{K_B})$ , (g<sub>A</sub>, g<sub>B</sub>), and (K<sub>A</sub>, K<sub>B</sub>) is given by:  

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

, where  $\frac{K_{\scriptscriptstyle A}}{K_{\scriptscriptstyle B}}$  is the selectivity constant of a membrane for positive ion species A to B

$$V_{A} = 1 + \frac{u_{A}^{o}}{u_{P}^{o}}$$
 (3)  $V_{A} = 1 + \frac{u_{B}^{o}}{u_{P}^{o}}$  (4)

For the evaluation of flux J of ion species, Toyoshima and Nozaki<sup>9</sup> gave the following equation which also used in the present investigation:

$$(2J+1)\ln\frac{(g_A+2J)}{(g_B+2J)} - \ln\frac{(JV_A+1)}{(JV_B+1)} - \ln\frac{g_A}{g_B} = 0$$
(5)

, where:

$$g_{A} = 1 + \sqrt{1 + (\frac{2K_{A}C}{\phi X})^{2}}$$
 (6)  $g_{B} = 1 + \sqrt{1 + (\frac{2K_{B}C}{\phi X})^{2}}$  (7)

The apparent transference number t.app of anion is defined by:

$$\frac{1}{t_{-app}} = V_N + (V_N - 1)\frac{(\sigma - 1)}{\sigma \ln \sigma} \frac{\phi X}{K_N} \frac{1}{C_2}$$
(8)

The above equation was used for the evaluation of V<sub>N</sub> and  $\frac{\phi X}{K_N}$ , where N = A, B,  $\sigma$  = 10.

The apparent transference number  $t_{app}$  can be calculated using the following equation:

$$\Delta E_{mr} = (1 - 2 t_{-app}) \ln \sigma \tag{9}$$

, where  $\Delta E_{mr}$  is the value of reduced membrane potential defined by:

$$\Delta E_{mr} = \frac{F\Delta E}{RT} \tag{10}$$

The values of membrane potential measured across parchment supported thallium chromate membrane in contact with different concentrations of various 1:1 electrolytes are given in Table 1 Apparent transference numbers for co-ions are calculated using equation (9) and given in Table 2.

Equation (8) predicts a linear relationship between  $\frac{1}{t_{-app}}$  and  $\frac{1}{C_2}$ . The values of V<sub>N</sub> and  $\frac{\phi X}{K_N}$  for a

$$\frac{1}{t_{-app}}$$
 vs  $\frac{1}{C_2}$  [Figure 1]. The values of V<sub>N</sub> and  $\frac{\varphi X}{K_N}$  so obtained are given in Table 3.

The values of bi-ionic potential measured across parchment supported thallium chromate membrane in contact with different set of electrolytes are given in Table 4. The values derived for mobility ratios across the membrane for 1:1 set of electrolytes according to equation (1) are given in Table 5.

These values of V<sub>N</sub> and  $\frac{\phi X}{K_N}$  may now be utilized to give the values for g<sub>N</sub> [Table 6] using equations 6

and 7. Once the membrane parameters V<sub>N</sub>,  $\frac{\phi X}{K_N}$ , and g<sub>N</sub> for a membrane – electrolyte system are

known, one can calculated the theoretical BIP using equations 2 and 5. The values of BIP thus calculated are plotted in Figures 2a, 2b, 2c, 2d, 2e, 2f as a function of electrolyte concentration C. The comparison demonstrates that the theoretical predictions are quite satisfactorily borne by our experimental results, thereby confirming the validity of Toyoshima and Nozaki theory to the system under investigation.

#### CONCLUSION

The approach of TMS is unreliable to evaluate X for ion-exchange membranes which have a high concentration of fixed groups. It is not that unreliable for a membrane which has a low concentration of X, as found in this study, due to the fact the change in the values of the factor  $(u_+/u_-)$  is not as drastic as it is with membranes of high charge density. It is believed that the approach of Altug and Hair overestimated X in comparison to TMS method.

The theoretical predictions from the Kobatake membrane potential equation is borne out quite satisfactorily by our experimental results and hence it may safely be concluded that Kobatake approach for charge density evaluation is the best among the existing of membrane potential.

thallium chromate membrane at 25±0.1°C							
	Observed membrane potential (mV)						
$(C_2/C_1), W$	LiCI	NaCl	KCI	NH₄CI			
1.0/0.1	-10	-1	5	6			
0.5/0.05	-4	3	9	10			
0.2/0.02	4	12	16	18			
0.1/0.01	12	22	25	26			
0.05/0.005	27	33	34	33			
0.02/0.002	35	39	42	39			
0.01/0.001	40	40	43	41			
0.005/0.0005	43	41	44	42			

# Table 1: Observed membrane potential (mV) across thallium chromate membrane at 25±0.1°C

Tab	le 2: Apparer	nt transference number of co-ior	າຣ
	for vario	us electrolytes at 25±0.1°C	
Г			

	t <sub>-app</sub>						
(C <sub>2</sub> /C <sub>1</sub> ) W	LiCI	NaCl	KCI	NH₄CI			
1.0/0.1	1.709	1.969	2.183	2.227			
0.5/0.05	1.872	2.105	2.358	2.410			
0.2/0.02	2.145	2.506	2.740	2.874			
0.1/0.01	2.506	3.185	3.460	3.571			
0.05/0.005	3.676	4.525	4.695	4.525			
0.02/0.002	4.902	5.882	6.897	5.882			
0.01/0.001	5.102	6.172	7.299	6.536			
0.005/0.0005	7.299	6.536	7.812	6.896			

Table 3: $V_N$ and $\frac{\phi X}{K_N}$ for the membrane in conta	act
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with various 1:1 electrolyte solutions

Electrolyte	V <sub>N</sub>	φX/K <sub>N</sub>
LiCl	1.618	0.418
NaCl	1.836	0.410
KCI	2.086	0.311
NH₄CI	2.206	0.255

Table 4: Measured bi-ionic potentials (BIP) in mV obtained across
thallium chromate membrane for various sets of electrolytes
at different concentrations

					-					
с м	E <sub>BIP</sub> , mV									
С, М	LiCI-NaCl	LiCI-KCI	LiCI-NH₄CI	NaCI-KCI	NaCl-NH₄Cl	KCI-NH₄CI				
1.0	4.00	14.00	24.2	12.80	20.30	7.30				
0.5	5.10	18.80	26.70	13.80	24.40	8.40				
0.2	6.50	23.30	32.20	16.60	27.90	10.50				
0.1	7.30	27.20	37.90	18.90	31.20	11.60				
0.05	8.00	28.20	41.70	19.50	33.60	12.10				
0.02	8.30	29.20	41.90	19.90	33.90	12.90				
0.01	8.60	29.30	42.10	20.20	34.10	13.10				
0.005	8.70	29.50	42.40	20.30	34.20	13.20				
0.002	8.80	29.60	42.50	20.50	34.30	13.30				

СМ			u	<sub>A</sub> /u <sub>B</sub>		
С, М	LiCI-NaCI	LiCI-KCI	LiCI-NH₄CI	NaCl-KCl	NaCl-NH₄Cl	KCI-NH₄CI
1.0	1.169	1.725	2.567	1.646	2.205	1.329
0.5	1.220	2.080	2.829	1.712	2.587	1.387
0.2	1.288	2.478	3.505	1.909	2.964	1.505
0.1	1.329	2.885	4.376	2.088	3.371	1.571
0.05	1.366	2.976	5.074	2.137	3.701	1.602
0.02	1.382	3.118	5.114	2.171	3.745	1.653
0.01	1.398	3.131	5.215	2.196	3.774	1.666
0.005	1.403	3.151	5.235	2.205	3.789	1.672
0.002	1 409	3 167	5 247	2 222	3 804	1 679

Table 5: Mobility ratios across thallium chromate membrane for various sets of electrolytes at different concentrations

Table 6:  $g_N$  values for thallium chromate membrane in contact with various 1:1 electrolyte solutions at different concentrations

electrolyte	g <sub>N</sub> at different concentrations given in M								
	1.0	0.5	0.2	0.1	0.05	0.02	0.01	0.005	0.002
LiCI	5.888	3.593	2.384	2.109	2.028	2.005	2.001	2.000	2.000
NaCl	5.979	3.636	2.397	2.113	2.029	2.005	2.001	2.000	2.000
KCI	7.508	4.367	2.629	2.189	2.050	2.008	2.002	2.001	2.000
NH₄CI	8.907	5.047	2.860	2.271	2.074	2.012	2.003	2.001	2.000



a. LiCI-NaCI





Fig/ 2: Plots of observed and theoretically calculated BIP for different electrolyte systems

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