



Bi-ionic potential studies of parchment supported synthetic membrane

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ABSTRACT

Membrane potentials and bi-ionic potentials (BIP) across parchment supported inorganic precipitate lead tungstate synthetic membrane using various 1:1 electrolytes have been reported. Thermodynamically effective fixed charged density, which is an important parameter governing the membrane phenomena has been evaluated by the theory of Nagasawa and co-workers. The magnitude of the BIP depends upon the concentration and nature of the cations. Theories based on the principles of irreversible thermodynamics as proposed by Toyoshima et al. have been compared to obtain a relationship which has been used for the evaluation of theoretical values of bi-ionic potentials. The close agreement between the theoretical and the observed values confirms the applicability of the derived relationship to the membrane-electrolyte system used in these investigations. The membrane is characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA).

Keywords: Membrane potential, bi-ionic potential, lead tungstate membrane, fixed charged density.

INTRODUCTION

Electrochemical characterization of membranes is of vital importance from the point of view of determination of their suitability for many applications of practical interest [1]. A potential difference is observed between the two sides of a membrane when the membrane separates two electrolyte solutions of the same molar concentration with a common co-ion but different counter ions. The membrane potential is called the bi-ionic potential (BIP) [2-4].

In the present paper membrane potentials and bi-ionic potentials observed through parchment supported inorganic precipitate lead tungstate synthetic membrane in contact with various 1:1 electrolytes are reported. The thermodynamically effective fixed charge density has been evaluated by the recently developed fixed charge theory of Nagasawa and co-workers [5]. An effort has been made to examine the validity of recently developed theory of Nozaki and Toyoshima [2] for membrane potential and bi-ionic potential based on the thermodynamics of irreversible processes.

MATERIAL AND METHODS

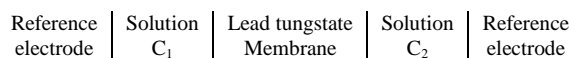
Membrane preparation

Parchment supported inorganic precipitate lead tungstate synthetic membrane has been prepared by the method of interaction as suggested by Ansari and coworkers [6,7]. To precipitate these substances in the interstices of parchment paper, a 0.2M solution of sodium tungstate (S. D. Fine Ltd.) was placed inside glass tube, to one end of which was tied the parchment paper (supplied by Amol group of companies, Mumbai, India) previously soaked in deionised water. The tube was suspended for 72 hours in a 0.2 M solution of lead nitrate (Ranbaxy). The two solutions (fresh solution) were interchanged later and kept for another 72 hours. Thus parchment paper and

inorganic precipitate as a whole acts as a synthetic membrane. The membrane thus prepared was washed with deionized water to remove free electrolytes.

Measurement of membrane potential

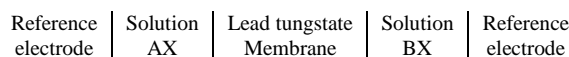
The electrochemical cell of the type



was used for measuring membrane potential (E_m) arising through the membrane by maintaining a tenfold difference in concentration ($C_1 / C_2 = 10$) and using a multimeter (Rishmulti^(R) 4^{3/4} digits 18S).

Measurement of bi-ionic potential

The bi-ionic potentials were determined by setting up electrochemical cell of the type



and taking the same concentration of both the electrolytes AX and BX. The various salt solutions (Chlorides of Li^+ , Na^+ , K^+) were prepared from analytical grade reagents and deionised water. All measurements were carried out using a water thermostat maintained at 25⁰C ($\pm 0.1^0$ C). The solutions on either sides of the membrane were vigorously stirred by a pair of magnetic stirrer.

Characterization of membrane

The expected performance of an ion exchange membrane is its complete characterization, which involves the determination of all those parameters that affect its electrochemical properties. These parameters are the membrane water content, porosity, thickness, swelling etc. and were determined as described elsewhere [8].

Water uptake (% total wet weight)

The membrane was soaked in deionized water for 2 hour. blotted quickly with whatmann filter paper to remove surface moisture and immediately weighted. These were further dried to a constant weight in vacuum over P_2O_5 for 24 hour. The water uptake (total wet weight) was calculated as follows

$$\% \text{ total wet weight} = \left(\frac{W_w - W_d}{W_w} \right) \times 100$$

Where W_w is the weight of the soaked or wet membrane and W_d the weight of the dry membrane.

Porosity

Porosity was determined as the volume of water incorporated in the cavities per unit membrane volume from the water uptake data:

$$\text{Porosity} = \left(\frac{W_w - W_d}{AL\rho_w} \right)$$

Where A is the area of the membrane (cm^2). L the thickness of the membrane (cm) and ρ_w the density of water (g/cm^3).

Thickness

The membrane thickness value was averaged from six measurements different locations on the effective surface region of the membrane using a micrometer.

Swelling

Swelling was measured as the difference between the average thickness of the membrane equilibrated in 1M NaCl for 24 hour and the dry membrane.

Scanning Electron Microscopy (SEM) studies

The surface morphology of parchment supported lead tungstate membrane was analysed with scanning electron microscope (Philips 515 USA). Gold Sputter coatings was carried out on the desired membrane sample at pressure 1 Pa.

Fourier Transformed Infra Red (FTIR) studies

The FTIR spectrum of parchment supported lead tungstate membrane was done by Perkin Elmer instrument (Spectrum BX series, USA). The entrance and exit beam to the sample compartment was sealed with a coated KBr window and these was a hinged cover to seal it from the environment.

X-Ray Diffraction (XRD) studies

X-ray diffraction pattern of the parchment supported lead tungstate membrane was recorded by Miniflex-II X-ray diffractometer (Rigaku Corporation) with CuK α radiation.

Thermogravimetric analysis (TGA) studies

The degradation process and thermal stability of the membrane was investigated using thermogravimetric analyzer (Perkin Elmer, Pyris Diamond), under nitrogen atmosphere (200 ml/min.) using a heating rate of 10 $^{\circ}$ C min $^{-1}$ from 25 $^{\circ}$ C to 1100 $^{\circ}$ C.

RESULTS AND DISCUSSION

The result of water content, Porosity thickness and swelling of parchment supported inorganic precipitate lead tungstate membrane are summarized in Table 1. The water content of a membrane depends on the vapour pressure of the surroundings. In case of most of the transport measurements, only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus low order of water content swelling and porosity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites [9,10].

Table 1. Thickness, water content, Porosity and swelling properties of lead tungstate synthetic membrane

Thickness of the membrane (cm)	0.085
Water content as % weight of wet membrane	0.071
Porosity	0.114
Swelling of % weight wet membrane	0.09

The SEM surface image of parchment supported lead tungstate membrane is presented in Fig. 1. It can be seen that the membrane is heterogeneous in nature as well as dense with no visible cracks. SEM image (Fig. 1) appears to be composed of dense and loose aggregation of small particles and formed pores probably with non-linear channel but not fully inter connected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes.

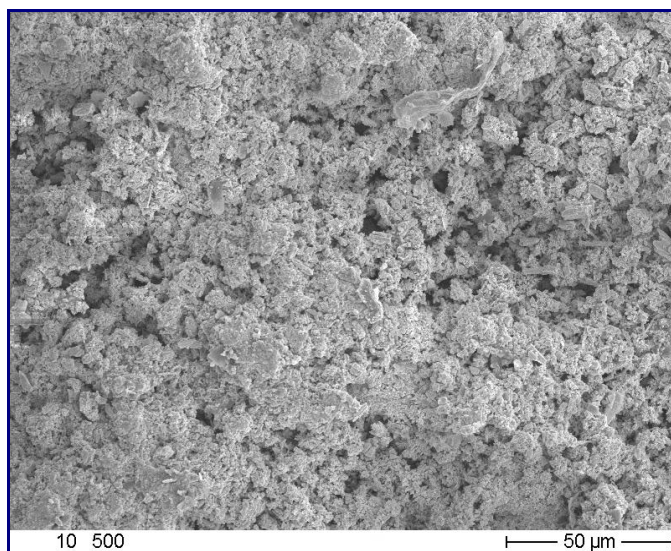


Fig. 1 Scanning electron micrograph (SEM) of parchment supported lead tungstate membrane

The FTIR spectra of the parchment supported membrane has provided in Fig. 2. The membrane contains various characteristic peaks. The spectra exhibits various strong to medium or weak intensity band, such as 3421, 2919, 2851, 2425, 1765, 1383 and 1621 (Cm $^{-1}$) characteristic of the functions present in the inorganic precipitate membrane.

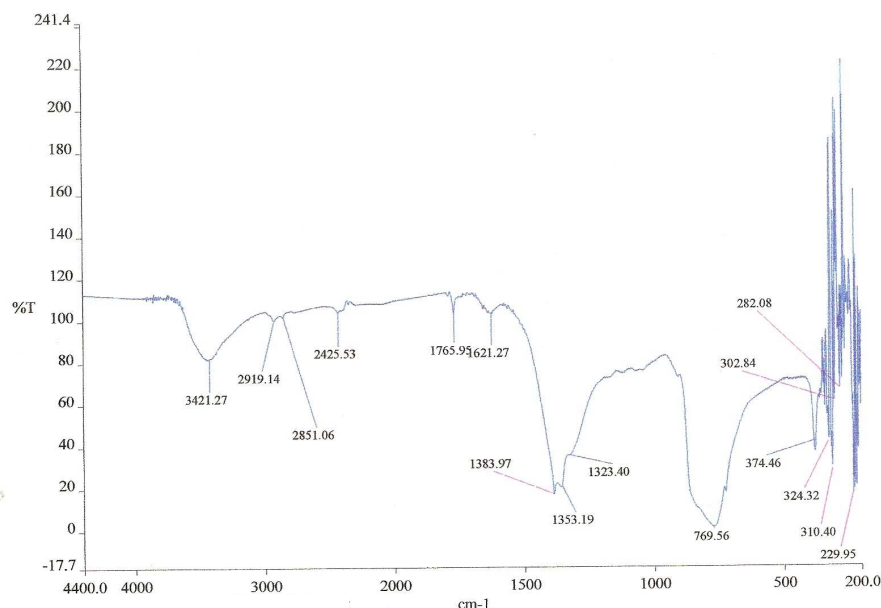


Fig. 2 FTIR Spectra of parchment supported lead tungstate membrane

X-Ray scattering techniques are a family of non-destructive analytical technique which reveal information about the crystallographic structure, chemical composition and physical properties of materials. Fig. 3 shows X-ray diffraction spectrum of the lead tungstate membrane. The material recorded in powdered sample exhibited some sharp peaks in the spectrum shows semi-crystalline nature of the material.

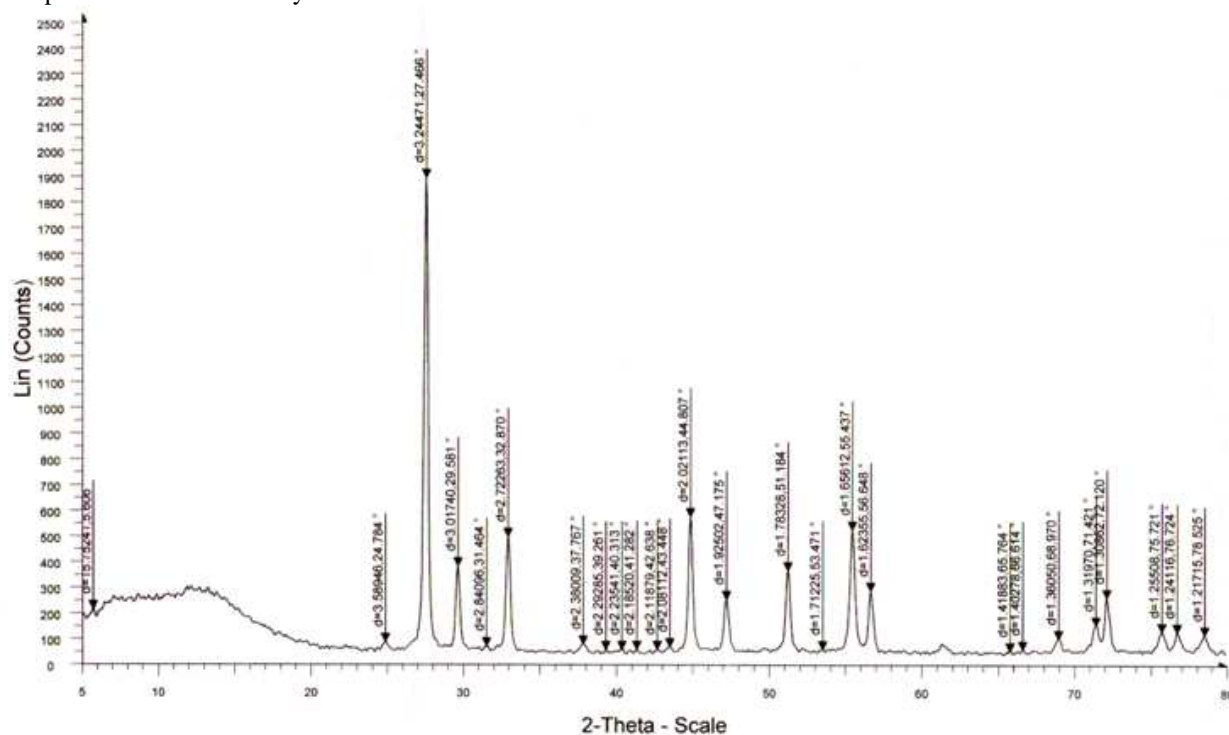


Fig. 3 X-RD pattern of parchment supported lead tungstate membrane

The thermal stability of the lead tungstate membrane was analyzed by TGA. The TGA curve measured under flowing nitrogen is reported in Fig. 4. TGA of the membrane material showed gradual weight loss of a about 3 percent to 11 percent from 400⁰C to 580⁰C which may be due to the removal of external water molecules present at the surface of the membrane material. Further weight loss of 15 percent to 20 percent from 800⁰C to 1000⁰C indicating the start of condensation due to the removal of the lattice water from the material.

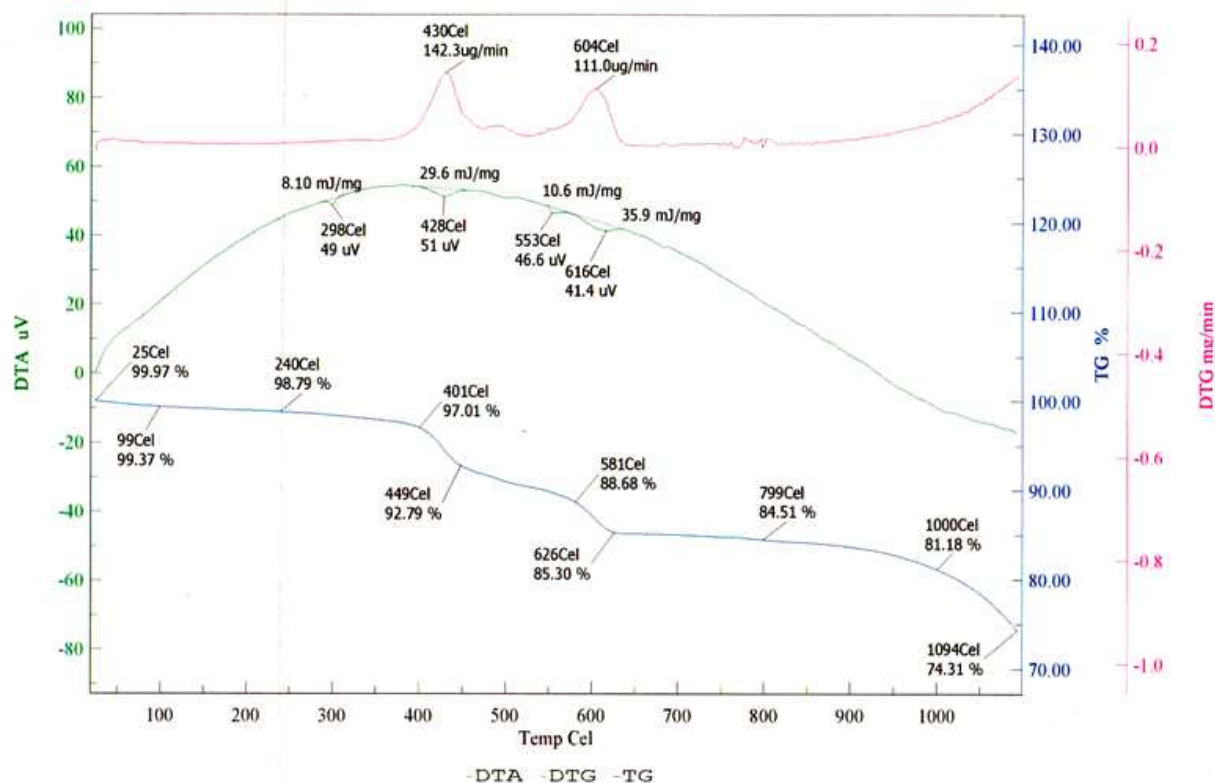


Fig. 4 TG, DTA and DTG curves of the parchment supported lead tungstate membrane

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-Sievers (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.

Tasaka and co-workers [11] based on the fixed charge concept developed a theory for membrane potential and used it for the evaluation of effective fixed charge density of membranes. The total membrane potential (E_m) was considered as algebraic sum of diffusion potential (E_d) inside the membrane and electrostatic potential difference (E_e) between the membrane-solution interfaces on either side of the membrane. E_d was obtained by integrating the basic flow equation for diffusion while E_e was calculated from Donnan's theory. These authors derived the following approximate equation (eq. 1) for membrane potential [11] when negatively charge membrane was used to separate two concentrated solutions of an electrolyte.

$$-E_m = \frac{RT}{F} \left(\frac{\gamma-1}{\gamma} \right) \left(\frac{\bar{X}}{2} \right) 1/C_2 \dots \dots \quad (1)$$

where $\gamma = C_1/C_2 = 10$; \bar{X} is the charge density of the membrane and other symbols have their usual significance.

Equation 1 predicts a linear relationship between E_m and $1/C_2$. The linear plots in Fig. 5 support the validity of eq. (1). The values of \bar{X} derived from the slopes of the linear plots are given in Table 2. The low values of charge densities are in full agreement with earlier findings on inorganic precipitated membranes [12-14] and solid nanocrystalline thin films [15-19].

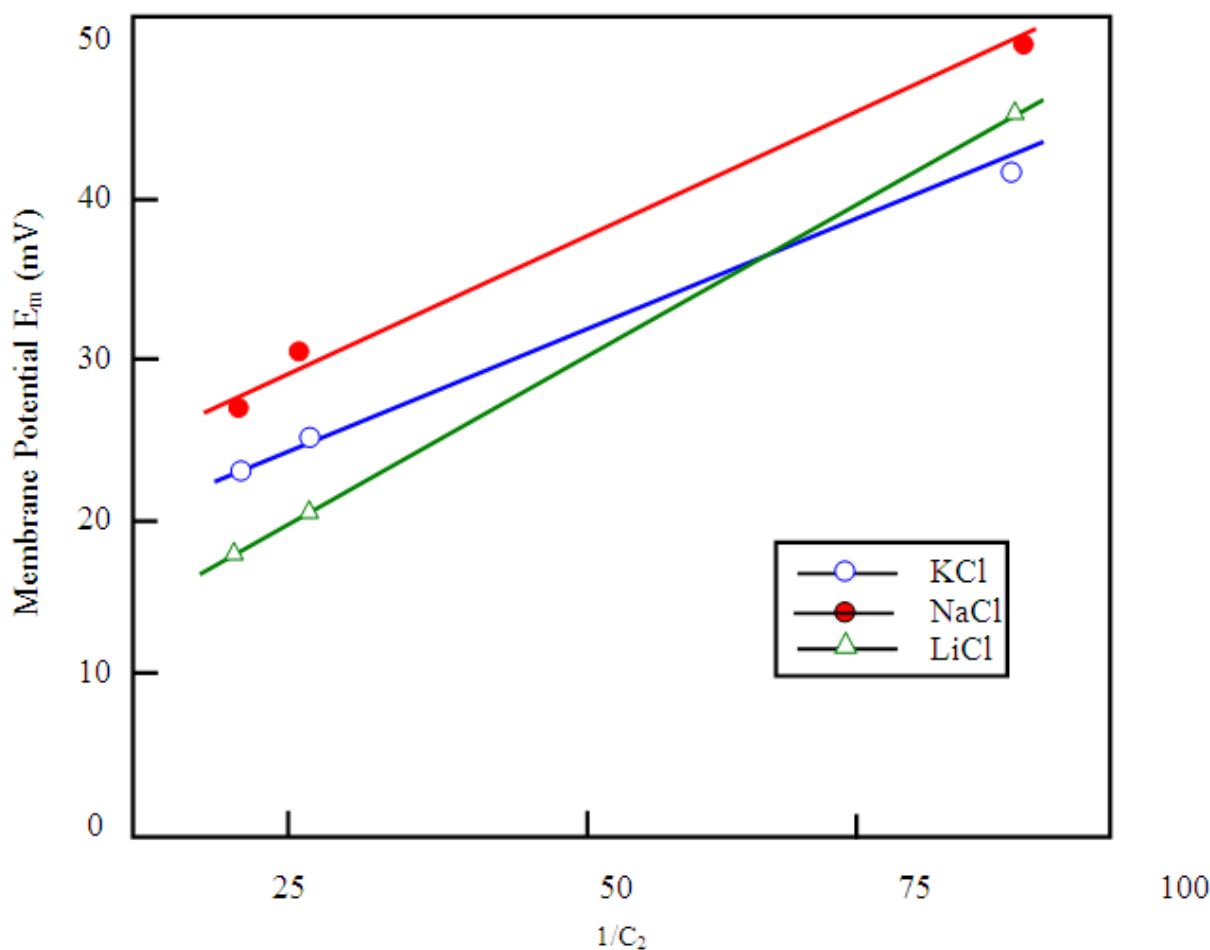


Fig. 5 Plots of membrane potential E_m against $1/C_2$ for various 1:1 electrolytes through parchment supported lead tungstate membrane

Table-2 Values of the thermodynamically effective fixed charge density of the parchment supported lead tungstate membrane

Membrane	Fixed charge density (eq.1)		
	KCl	NaCl	LiCl
Lead tungstate	0.0160	0.0180	0.0088

Nozaki and Toyoshima[2] have derived equations for membrane potential E_m and bi-ionic potential E_{BIP} using the principles of non-equilibrium thermodynamics and certain appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase[2]. The effects of ionic interaction, mass flow and osmotic effect were neglected. For a negatively charge membrane separating two 1:1 electrolytes (Common co-ions) of the same concentration, Toyoshima and Nozaki derived expression (2) for bi-ionic potential, E_{BIP} .

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

Equation 2 can be used to give the value of bi-ionic potentials provided the membrane parameters K_A , K_B , V_A , V_B and the ionic flux J are known. For the evaluation of these parameters following equations have also been forwarded [2].

$$(2J + 1) \ln (g_A + 2J / g_B + 2J) - \ln (JV_A + 1 / JV_B + 1) - \ln (g_A / g_B) = 0 \tag{3}$$

$$V_N = 1 + U_N^0 / U_P^0 \tag{4}$$

$$g_N = 1 + \left[1 + (2K_N C_N / \bar{X})^2 \right]^{1/2} \tag{5}$$

$$1 / K_N = \exp (\mu_N - \mu_N + \mu_P - \mu_P) / 2RT \tag{6}$$

where μ_N is the standard chemical potential of cation N in the membrane phase and μ_N is that in the external bulk solution and μ_P and μ_P are the corresponding values of anion P. U_N^0 and U_P^0 are the mobilities of cation and anion respectively and other symbols have their usual significance.

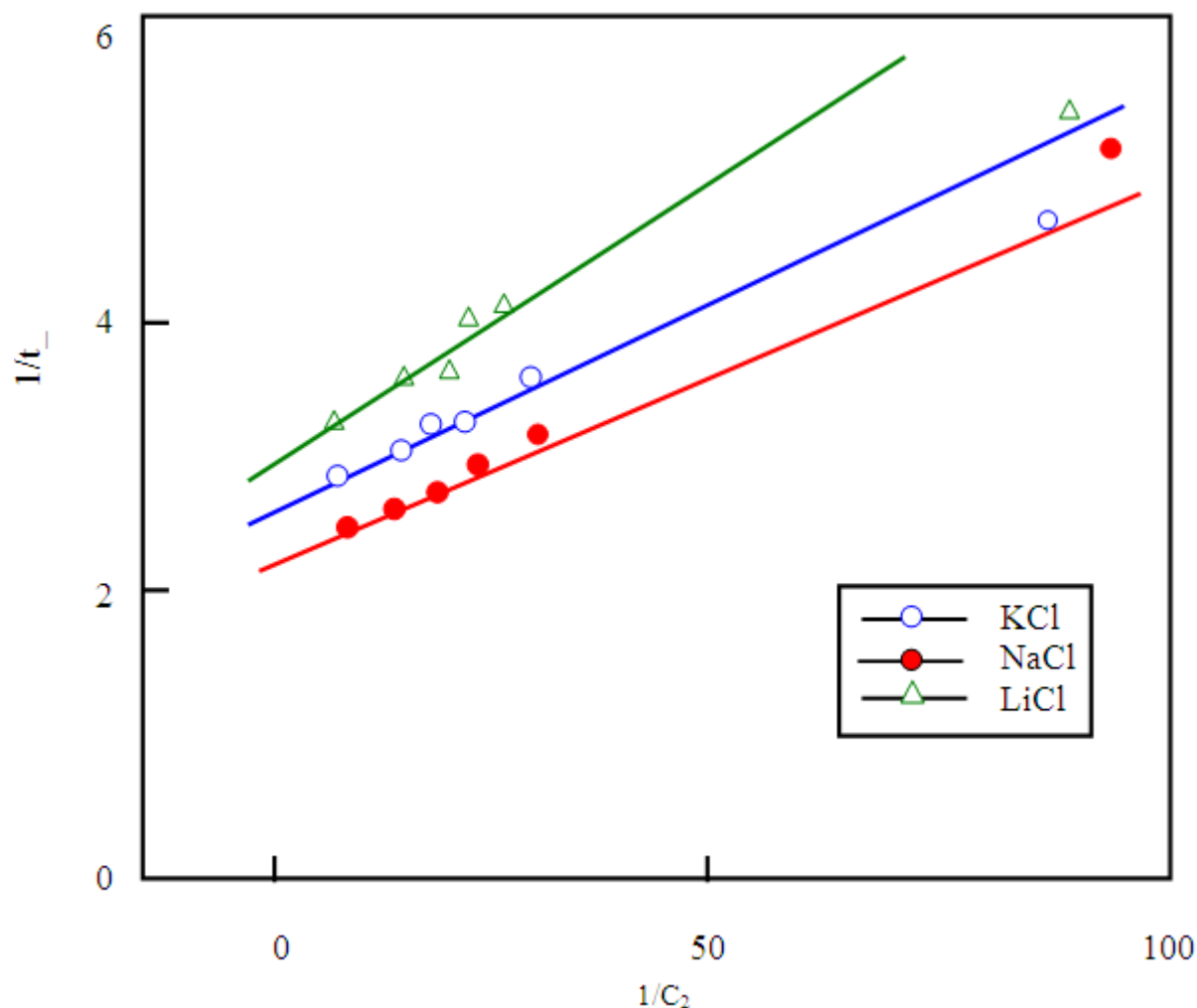


Fig. 6 Plots of $1/t_-$ against $1/C_2$ through parchment supported lead tungstate membrane with various 1:1 electrolyte

In order to derive the values of the parameters V_N and \bar{X} according to eqs. (4) and (5) Toyoshima and Nozaki [2] derived another eq. (7) for E_m arising across a membrane when it is used to separate two solutions of an electrolyte at different concentrations C_1 and C_2 .

$$(F/RT)E_m = -\ln \gamma - (1 - 2/V_N) \ln \frac{\sqrt{1 + (2C_2 K_N / \bar{X})^2} + (1 - 2/V_N)}{\sqrt{1 + (2C_1 K_N / \bar{X})^2} + (1 - 2/V_N)} + \ln \frac{\sqrt{1 + (2C_2 K_N / \bar{X})^2} + 1}{\sqrt{1 + (2C_1 K_N / \bar{X})^2} + 1} \quad (7)$$

Equation (7) on expression in powers of concentration, ratio $\gamma=10$ being kept constant, yields

$$(F/RT)E_m = -(1 \times 2/V_N) \ln \gamma - 2(1 - 1/V_N)(1/V_N)(1 - 1/\gamma)(\bar{X}/K_N)(1/C_2) + \dots \quad (8)$$

The apparent transference number t_- for co-ions is defined by the Nernst equation

$$-(F/RT)E_m = (1 - 2t_-) \ln \gamma \quad (9)$$

Combining eqs. (8) and (9) and expanding $1/t_-$ as a power of series of $1/C_2$ expression (10) is obtained

$$1/t_- = V_N + (V_N - 1) \left[\frac{\gamma - 1}{\gamma \ln \gamma} \right] \frac{\bar{X}}{K_N} \frac{1}{C_2} + \dots \quad (10)$$

Equation 10 predicts a linear relationship between $1/t_-$ and $1/C_2$. The values of V_N and (\bar{X}/K_N) can be determined from the ordinate intercept and initial slope of a plot for $1/t_-$ against $1/C_2$. The values of V_N and (\bar{X}/K_N) thus derived for the membrane and various 1:1 electrolyte systems using Fig. 6 are given in Table 3.

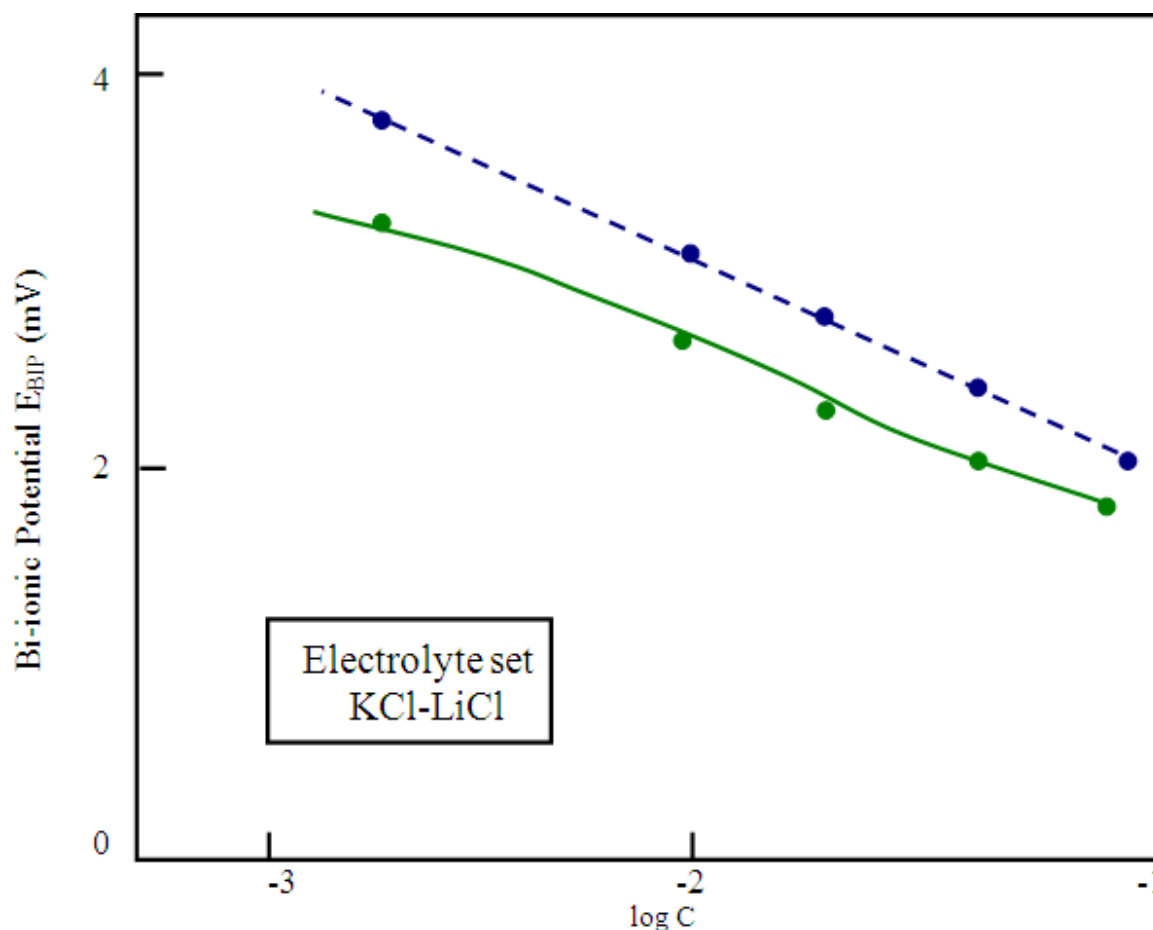


Fig. 7 Plots of observed (____) and calculated (-----) bi-ionic potentials E_{BIP} Vs. $\log C$ for KCl-LiCl set with parchment supported lead tungstate membrane

Table-3 Values of membrane parameters V_N and \bar{X}/K_N derived from the Toyoshima and Nozaki theory for parchment supported lead tungstate membrane

Electrolyte	V_N	$(\bar{X}/K_N) 10^2$ (eq. 1)
KCl	1.98	2.4
NaCl	1.87	2.1
LiCl	1.74	1.7

These values of V_N and (\bar{X}/K_N) are then used to calculate J and g_N using eqs. (3) and (4). Once the membrane parameters V_N , g_N , J and (\bar{X}/K_N) are known for the membrane electrolyte system, one can calculate theoretical bi-ionic potential using eq. (2). The bi-ionic potential thus obtained are plotted as a function of $\log C$ in Figs. [7-9] (shown by dotted line). For comparison the experimentally observed bi-ionic potentials are also plotted in the same graph (shown by solid line). Figs. [7-9] demonstrates that the theoretical predictions are borne out quite satisfactorily by our experimental results on parchment supported membrane. However, a slight deviation in the values may be accounted due to various reasons, most notably due to the low fixed charge density.

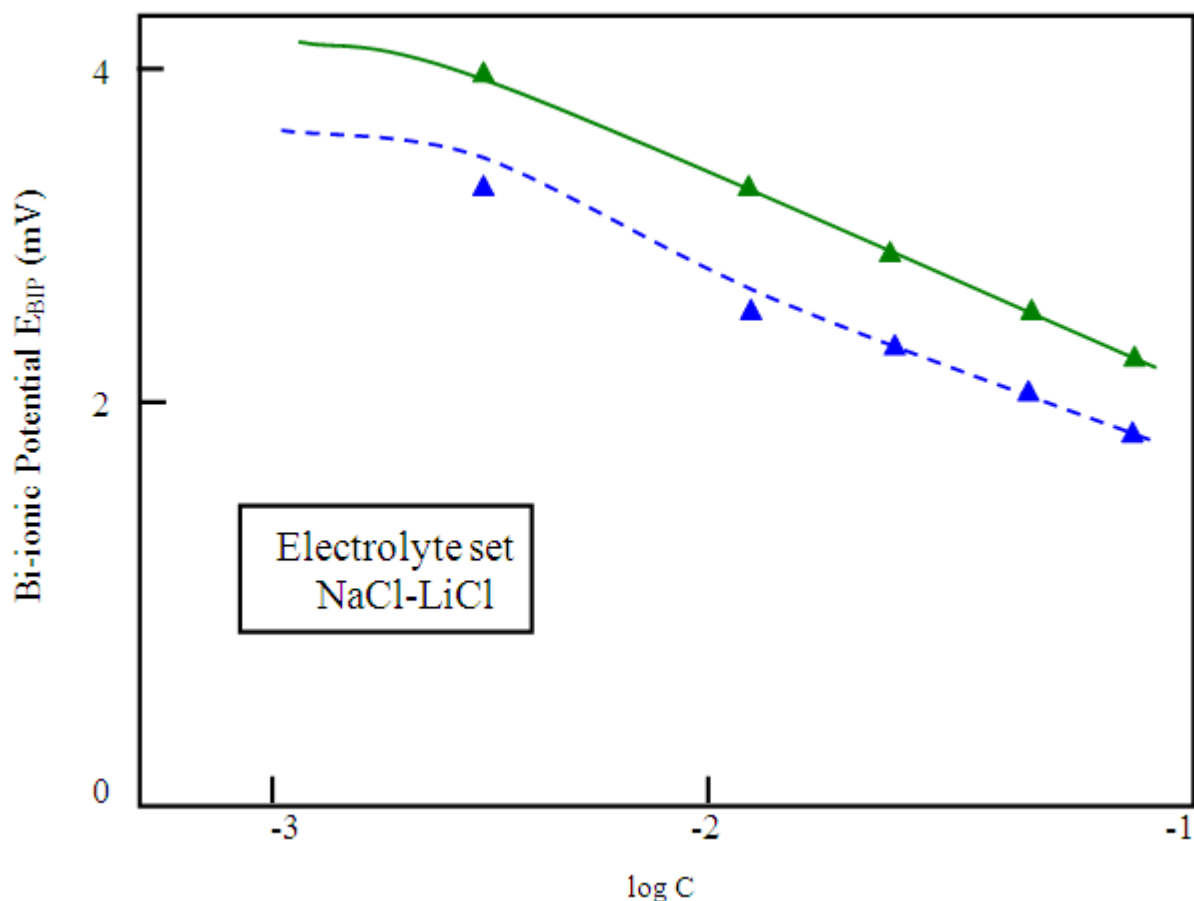


Fig. 8 Plots of observed (____) and calculated (-----) bi-ionic potentials E_{BIP} Vs. log C for NaCl-LiCl set with parchment supported lead tungstate membrane

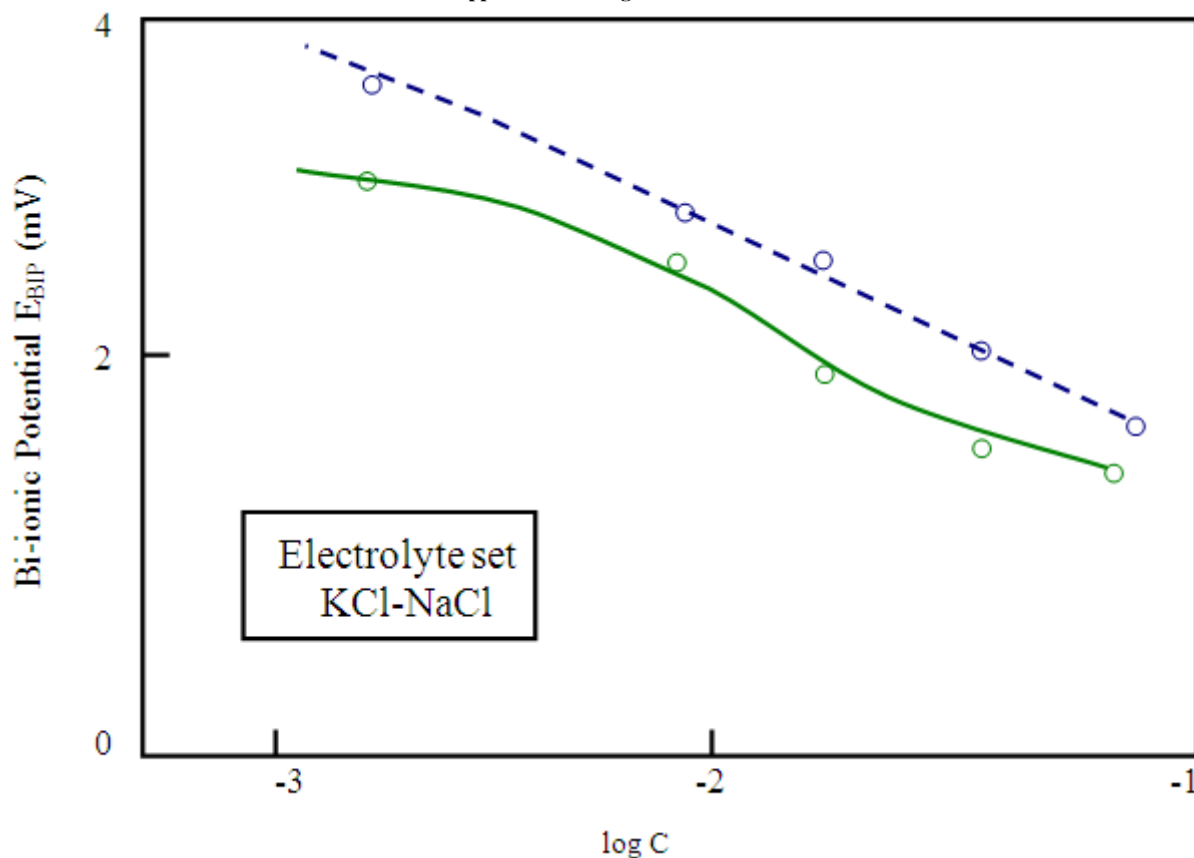


Fig. 9 Plots of observed (____) and calculated (-----) bi-ionic potentials E_{BIP} Vs. log C for KCl-NaCl set with parchment supported lead tungstate membrane

CONCLUSION

Electrical potential arising through parchment supported inorganic precipitate lead tungstate membrane using various 1:1 salt solutions of chlorides of Lithium, Sodium & Potassium are reported and the thermodynamically effective fixed charged density of the membrane has been evaluated by applying the theory of Tyoshima and Nozaki and with the help of determined values of effective fixed charge density. The theory of bi-ionic potential developed by Tyoshima et al. based on the thermodynamics of irreversible processes has been examined. The closed agreements between the theoretical and the observed values confirms the applicability of the derived relationship to the membrane electrolyte systems used in these investigations.

Acknowledgement

The authors are thankful to the Principal of the college for providing necessary research facilities. The authors are also grateful to ACBR, New Delhi (for SEM, FTIR techniques) and to IIT Roorkee (for XRD and TGA techniques).

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