

FABRICATION OF POLYSTYRENE BASED COBALT (II) AND NICKEL (II) PHOSPHATE MEMBRANES: EVALUATION OF MEMBRANE SELECTIVITY OF METAL IONS.***R.B. SHARMA¹, S.K. VERMA, SARITA ARYA AND SHIKHA AGARWAL**

¹Department of Physics,
Department of Physical Chemistry
Bipin Bihari (P.G.) College,
JHANSI (U.P.) INDIA.

*Corresponding Author

Email : rbsharma.jhansi@gmail.com

Received : 26.2.16; **Accepted** : 6.4.16

ABSTRACT

Bi-Ionic potential (BIP) values across both the membranes have been observed experimentally using various combinations of 1:1 electrolytes at different concentrations. On the other hand bionic potential (BIP) values have also been observed experimentally keeping the concentration of one electrolyte constant on one side of the membrane while varying the concentration of other electrolyte on other side of the membrane. The membrane conductance values in contact with single electrolyte at different concentrations have been measured experimentally to evaluate the selectivity of both the membranes. The theory developed by Sandblom and Eisenman based on non equilibrium thermodynamics has been utilized for the evaluation of membrane selectivity. The selectivity sequence of both the membranes was found

$K^+ > Na^+ > Li^+$

Figures : 05

References : 32

Tables : 06

KEY WORDS : β i-ionic potential (BIP), Membrane conductance, Membrane selectivity, Nickel (II) phosphate membranes, Polystyrene based cobalt (II).

Introduction

When two electrolyte solutions having different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena induced the system¹⁴. The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most widely characterized electrochemical and bioelectric phenomena^{1-3,14,16-18,23,27,28}. The fixed charge concept for the charged membranes is a pertinent starting point for the investigation of the actual mechanisms of ionic or molecular processes which occur in membrane phase^{20,30}. For biological membranes the electrical potential difference is usually described in terms

of the equation^{8,14} which are for certain ion exchange membranes permeable solely to species of one sign, is described by generalized Nernst equations. Depending on the transport mechanism, or the assumptions made in the derivation, the permeability ratio has been given various physical meanings as mobility ratio²², ion exchange equilibrium constant²¹, the product of the mobility ratio and Donnan ratio^{20,30}, the product of the mobility ratio and the distribution coefficient ratio¹², the product of the mobility ratio and ion exchange equilibrium constant^{9,13} or the product of the equivalent conductance ratio and the ratio of partition coefficients². However, a number of reviews have appeared dealing with the ion selectivity of membranes^{4,15}.

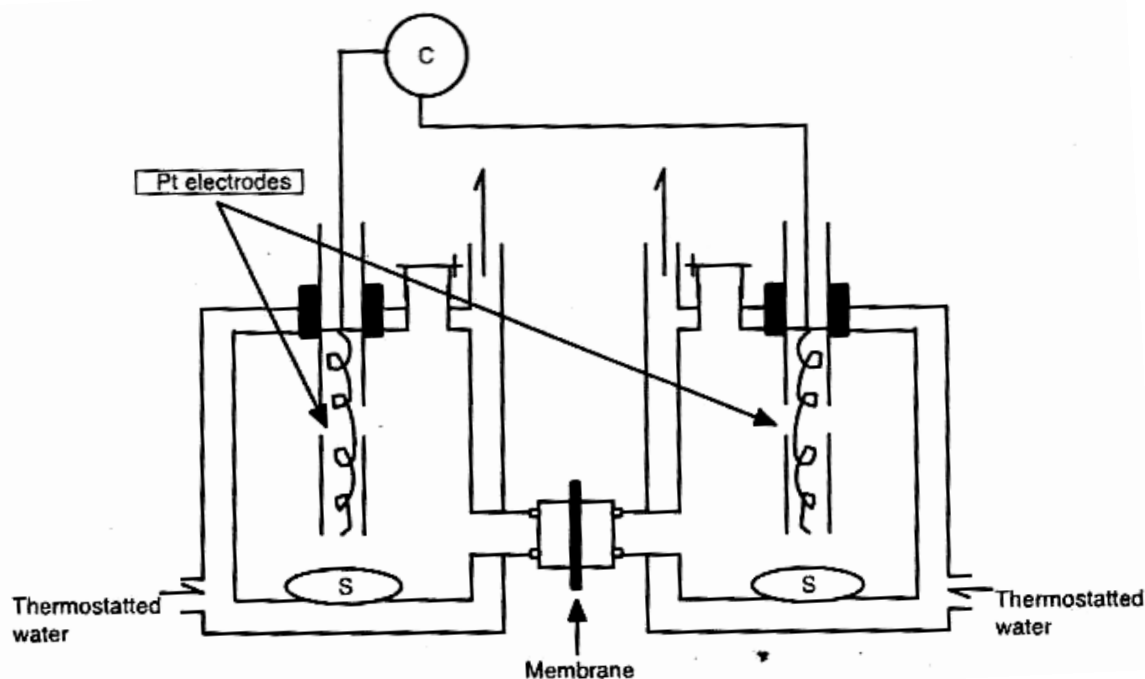


Fig. 1 : Apparatus for membrane conductance measurements: Digital conductivity meter (C),magnetic stirring bar (S).

In this paper initially the preparation of both polystyrene based membranes of cobalt (II) phosphate and nickel (II) phosphate membranes at different pressures have been described. The steady potential developed by introducing the membrane between two solutions of different electrolytes is called biionic potential (BIP)²¹ which is the measure of selectivity³¹ of membrane. Various membrane theories^{5,10,11,24,25,29,30} have been used to evaluate the membrane selectivity of metal ions.

The polystyrene based membranes of cobalt and nickel phosphate are being used here for the evaluation of their selectivity for metal ions. The steady potential developed by interposing the membrane between two solutions is called bi-ionic potential (BIP)³¹ which is measure of selectivity of the membrane²⁹. Membrane conductance values in contact with various 1:1 electrolyte have been determined experimentally to substantiate our findings.

Experimental

1. Preparation of Membrane

Cobalt phosphate precipitate was prepared by mixing a 0.2M solution of cobalt (II) chloride with

0.2M tri-sodium phosphate solution. The precipitate thus obtained was well washed with deionized water to remove free electrolyte and dried at room temperature. The precipitate was ground into fine powder and was sieved through 200 mesh (Granule size 0.07 mm). Pure amorphous polystyrene (cross linked with 1% divinylbenzene obtained from Fluka, product number 81535) was also ground and sieved. The membrane was prepared^{2,17}. Different proportions of polystyrene and cobalt phosphate precipitates were mixed thoroughly using grinder. The mixture was then kept into the cast die having diameter 2.45 cm and placed in an oven maintained at 200°C for about half an hour to equilibrate. The die containing the mixture was then transferred swiftly to a pressure device (Spectra Lab.model SL 89 UK) and various pressures such as 4,5,6,7 and 8 tons were applied. As a result cobalt phosphate membranes of approximate thicknesses 0.10,0.090,0.085,0.075 cm were obtained respectively. Our effort has been to get the membrane of adequate chemical and mechanical stability. Thus the membrane prepared by mixing 25% of polystyrene was found to be mechanically stable and was quite suitable for our

TABLE-1: Experimental values of bi-ionic potential E (mV) across cobalt phosphate membrane at 25±0.1°C

Electrolyte Concentration (Mol/l)	KCl-NaCl	KCl-LiCl	NaCl-LiCl
0.1/0.1	2.4	-4.5	-4.2
0.05/0.05	2.6	-2.5	-2.5
0.02/0.02	6.7	-0.9	0.6
0.01/0.01	6.8	2.6	1.0
0.005/0.005	13.3	5.1	3.5
0.002/0.002	18.9	12.4	8.3
0.00/0.001	19.8	18.5	9.8

studies. Those containing larger amount (>25%) of polystyrene did not give reproducible results, while those containing lesser amount (<25%) were unstable. Similar procedure was adopted for the preparation of nickel phosphate membranes by taking 0.2M-nickel (II) chloride solution and 0.2M tri-sodium phosphate solutions. In all the cases the total amount of the mixture thus utilized for the preparation of the membrane contained 0.125 g. of polystyrene and 0.375 g. of cobalt/nickel phosphate.

Measurement of bi-ionic potential-

The experimental values of bi-ionic potential

were obtained by setting up an electrochemical cell of the following type.



using Oswa vernier potentiometer (C. No. 30071 UK) and saturated calomel electrode (SCE). The same concentration of both electrolytes ix and jx was taken on either sides of the membrane. The

TABLE-2: Experimental values of bi-ionic potential E (mV) across nickel phosphate membrane at 25±0.1°C

Electrolyte Concentration (Mol/l)	KCl-NaCl	KCl-LiCl	NaCl-LiCl
0.1/0.1	2.3	-3.9	-3.3
0.05/0.05	4.5	-2.7	-2.0
0.02/0.02	6.3	-0.3	2.1
0.01/0.01	8.6	2.6	2.2
0.005/0.005	11.6	3.5	4.2
0.002/0.002	19.1	9.5	10.1
0.00/0.001	19.8	16.0	13.4

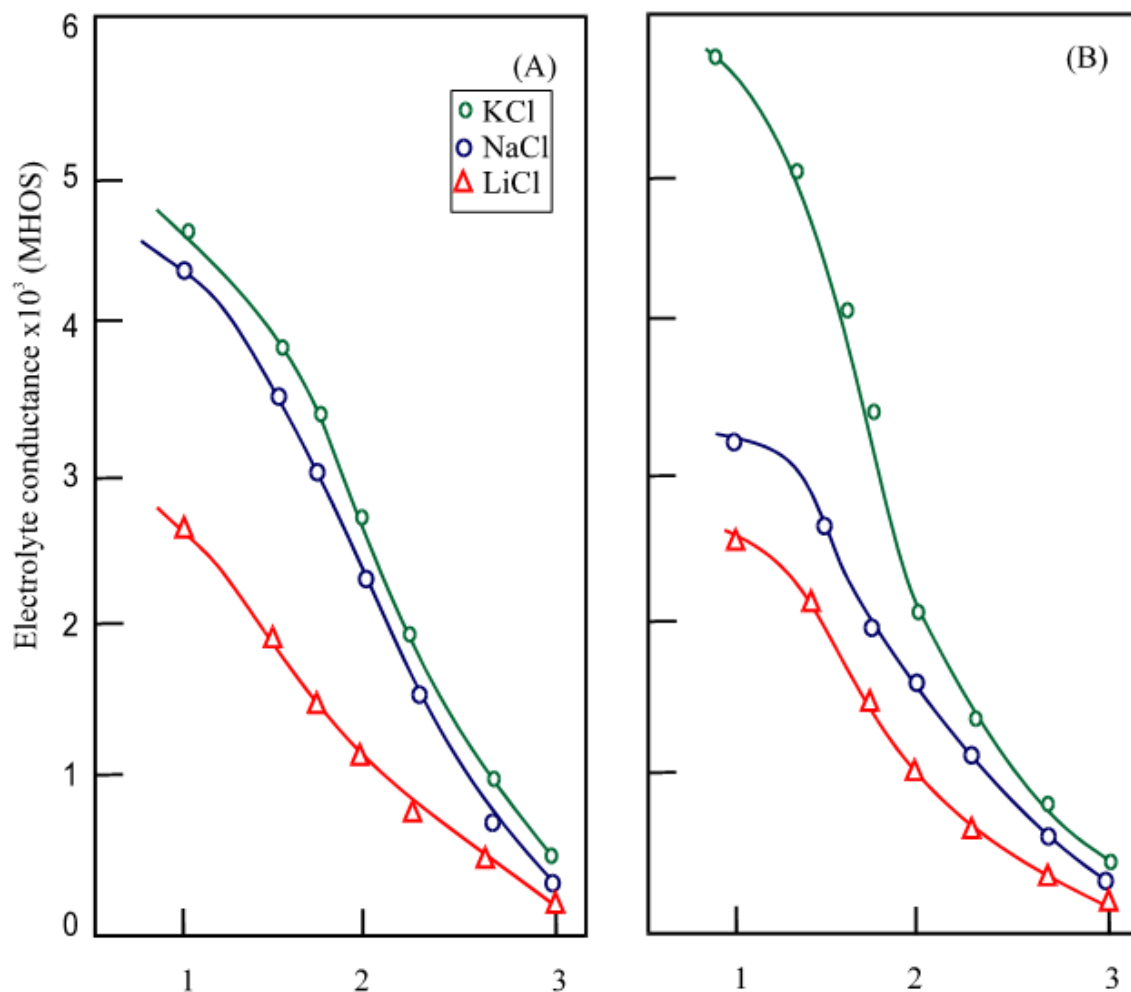


Fig. 2 : Log C

Fig. 3 : Log C

Plots of electrical conductance (MHOS) against - Log C (A)
Cobalt Phosphate and (B) Nickel Phosphate Membranes

various aqueous salt solutions (Chlorides of Li^+ , Na^+ and K^+) were prepared from AR (BDH) reagents and deionized water. The solutions in both the half cells were vigorously stirred by a pair of electrically operated magnetic stirrers to remove completely or at least to minimize the effect of the film controlled diffusion²³. However, to substantiate the findings of membrane, bi-ionic potential (BIP) values across both the membranes were measured by keeping the concentration of the electrolyte constant on one side of the membrane and varying the concentration

of other electrolyte on other side of it.

(ii) Measurement of Conductance

Electrical conductivity of the membrane was determined by setting up a cell of the type shown in Figure 1 with a conductivity bridge (Cambridge Instrument Co. Ltd., England). All measurements were carried out at $25 \pm 0.1^\circ\text{C}$. The error in measurement of bi-ionic potential was within $\pm 1\%$ whereas, electrical conductivity was measured to better than 99.5% accuracy.

Results and Discussion

Membrane selectivity for metal ions

When an ion exchange membrane is interposed between two solutions of the same electrolyte, but of different concentrations, the potential difference developed is called the concentration potential or membrane potential. The sign and magnitude of this emf gives the selectivity of the membrane towards the ions of the electrolyte. But if the membrane is used to separate solution of two electrolytes of the type ix and jx (or ix and iy), the steady potential developed is called bi-ionic potential (BIP)³¹, which is a measure of selectivity²⁹ of the membrane for the ions of the same sign and has been the subject of many theoretical and experimental studies^{5,10,11,25}. For a general case the bi-ionic potential $\Delta\phi_{BIP}$ for counter ions of equal valencies is given as³².

$$\Delta\phi_{BIP} = \frac{RT}{F} \ln a_i \bar{U}_i / a_j \bar{U}_j \quad \dots(1)$$

where a_i / a_j and \bar{U}_i / \bar{U}_j are the activity ratio of the solutions and mobility ratio of the ions in the membrane phase respectively. The intermembrane mobility ratio²⁷ is expressed as :

$$\bar{U}_i / \bar{U}_j = \bar{t}_i / \bar{t}_j = \bar{M}_i \bar{\lambda}_i / \bar{M}_j \bar{\lambda}_j \quad \dots(2)$$

where \bar{t}_i / \bar{t}_j is the intramembrane transference ratio and \bar{M}_i / \bar{M}_j are the steady state equilibrium concentration of i and j in the respective zones, $\bar{\lambda}_i$ is the conductivity of the membrane when it is wholly in i from and $\bar{\lambda}_j$ is the conductivity of the membrane when it is wholly in j from. Furthermore, it was shown that $\bar{M}_i / \bar{M}_j \approx K_{ji}$ is the selectivity. This on substitution in Eq. (2) gives.

$$\bar{U}_i / \bar{U}_j = K_{ji} (\bar{\lambda}_i / \bar{\lambda}_j) \quad \dots(3)$$

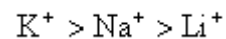
Thus, the ratio of mobilities are related to

the chemical and electrical properties of the membrane.

The values of bi-ionic potential observed experimentally across both polystyrene based cobalt and nickel phosphate membranes given in Tables 1-2, were used to calculate the intramembrane mobility ratio using the Eq. (1). The values thus calculated are given in Tables 3-4. An interesting point with regard to the values of \bar{U}_i / \bar{U}_j is that the mobility ratio undergoes considerable change with the concentration of the each electrolyte pair.

To gain knowledge of selectivity K_{ji} from the predetermined values of \bar{U}_i / \bar{U}_j the ratio of

electrical conductivities $\bar{\lambda}_i / \bar{\lambda}_j$ demanded by Eq. (2) must be known. Membrane conductance measurements were carried out when it was wholly in form of i or in form of j . The values of membrane electrical conductance observed experimentally of cobalt and nickel phosphate membranes respectively show in Fig. (2,3) are relatively more dependent on the concentration of electrolyte which implies that the membranes have a relatively high Donnan uptake of anion and a low selectivity constant values. The values of selectivity K_{ji} evaluated using the values of electrical conductivity and the values of intramembrane mobility ratio from Tables 3-4 are given in Tables 5-6. These values of K_{ji} thus evaluated refer to the selectivity sequence of the membrane for the cations.



This order of selectivity on the basis of the Eisenman-Sherry model of membrane selectivity^{6,26} points towards the weak field strength of the charge groups attached to the membrane matrix.

Further, (BIP) has been considered¹¹ in accordance with the concepts of the TMS theory^{28,30}, as being the algebraic sum of two interfacial potentials and an internal diffusion potential. A complete mathematical discussion under conditions: (a) membrane diffusion control, (b) film diffusion control and (c) coupled membrane film diffusion control has been presented^{10,11} for a general case involving complete membrane diffusion control, the (BIP) for counterions is given

by

$$E = \frac{RT}{ZF} \ln \left[\frac{\bar{D}_i a_i' \bar{\gamma}_j K_j}{\bar{D}_j a_j' \bar{\gamma}_i K_j} \right] = \frac{RT}{ZF} \ln \left[K_{ji} \left(\frac{\bar{D}_i a_i' \bar{\gamma}_j}{\bar{D}_j a_j' \bar{\gamma}_i} \right) \right] \quad (4)$$

where a_i' / a_j'' , \bar{D}_i / \bar{D}_j , $\bar{\gamma}_i / \bar{\gamma}_j$ are the ratio of the activities, diffusion coefficients, and the activity coefficients of the counterions i and j respectively, Overbars refer the phenomena in the membrane phase, R, T, Z and F have their usual

meanings. Using the Einstein's relation $D_i = U_i RT$ and the generalized Nernst equation in which the permeability ratios are independent of external electrolyte solution^{7,19,21}, equation (4) reduces to the form

$$E = \frac{RT}{ZF} \ln \left[\frac{a_i' \bar{U}_i}{a_j'' \bar{U}_j} K_{ji} \right] = \frac{RT}{ZF} \ln \left[\frac{a_i' \bar{P}_i}{a_j'' \bar{P}_j} \right] \quad (5)$$

equation (5) gives

$$\bar{P}_i / \bar{P}_j = K_{ji} \frac{\bar{U}_i}{\bar{U}_j} \quad (6)$$

This equation²⁴ has been derived from thermodynamic treatment for fixed site membranes which implies that the permeability ratio is quite generally, related to the ion exchange equilibrium constant K_{ij} and the ratio of mobilities of the critical

ions. Further, using the well known relation $\bar{U}_i / \bar{U}_j = \bar{\lambda}_i / \bar{\lambda}_j$ equation (6) gives

$$\bar{P}_i / \bar{P}_j = K_{ji} \frac{\bar{U}_i}{\bar{U}_j} = K_{ji} \frac{\bar{\lambda}_i}{\bar{\lambda}_j} \quad (7)$$

TABLE-3: Values of the intramembrane permeability ratio of various 1:1 electrolyte ion pairs across cobalt phosphate membrane

Electrolyte (ion pair) Concentration (Mol/l)	$\bar{P}_{K^+} / \bar{P}_{Na^+}$	$\bar{P}_{K^+} / \bar{P}_{Li^+}$	$\bar{P}_{Na^+} / \bar{P}_{Li^+}$
0.1/0.1	1.1	0.8	0.8
0.05/0.05	1.2	0.9	0.9
0.02/0.02	1.3	1.0	1.1
0.01/0.01	1.3	1.1	1.1
0.005/0.005	1.7	1.2	1.2
0.002/0.002	2.1	1.6	1.4
0.001/0.001	2.2	1.9	1.5

where λ_i is the conductivity of the membrane when it is wholly in i form and λ_j is the conductivity of the membrane when it is wholly in the j form.

The quantity \bar{P}_i / \bar{P}_j is considered truly a membrane property²⁴. It is independent of the changes made in the activities a_i and a_j of the external solution. Thus it is apparent from eq. (5) that a plot of $\log a_i$ against potential for a constant a_j gave a straight line. Similarly a straight line was obtained as a_i was varied and a_j was kept constant. Both these lines showed potential changes of RT/F or 59.2 at 25°C for each tenfold change in activity when membranes are separating 1:1 electrolytes. Accordingly BIP across cobalt and nickel phosphate membranes were determined for various electrolyte pairs, viz., NaCl-LiCl, KCl-NaCl, and KCl-LiCl, taking the concentration of one of the electrolyte constant (0.05M) and varying the concentration of the other electrolyte between 0.001 M to 0.05M. In the second set of experiment the concentration of the other electrolyte was kept constant (0.05M) and the concentration of the first electrolyte was varied. The bi-ionic potentials thus observed were plotted against logarithm of the mean molal activity. Two sets of straight lines in accordance with the expectation of eq. (5) were obtained (Figs. 4,5). The straight lines confirm the views^{6,21} that the permeability ratios are independent of external solution conditions. In order to derive the values of the permeability ratio, these straight lines were extended to cut the activity axis at zero potential. Thus two sets of a_i and a_j values for which potential E was zero were obtained. At zero potential the ratio a_i/a_j was equal to \bar{P}_i / \bar{P}_j . The values of \bar{P}_i / \bar{P}_j derived in this way for the membrane and different electrolyte pairs are as follows :

$$\bar{P}_{K^+} / \bar{P}_{Na^+} = 1.99, \bar{P}_{K^+} / \bar{P}_{Li^+} = 1.71, \bar{P}_{Na^+} / \bar{P}_{Li^+} = 1.18 \text{ for cobalt phosphate membrane:}$$

$$\bar{P}_{K^+} / \bar{P}_{Na^+} = 1.72, \bar{P}_{K^+} / \bar{P}_{Li^+} = 1.50, \bar{P}_{Na^+} / \bar{P}_{Li^+} = 1.36 \text{ for nickel phosphate membrane:}$$

The values of \bar{P}_i / \bar{P}_j are generally low which point towards the fact that the membranes are relatively more imbided in an equilibrium water content³². The values of the intramembrane permeability ratio also refer to the selectivity sequences of the membrane for the cations as follows :



TABLE-4: Values of the intramembrane permeability ratio of various 1:1 electrolyte ion pairs across nickel phosphate membrane

Electrolyte (ion pair) Concentration (Mol/l)	$\bar{P}_{K^+} / \bar{P}_{Na^+}$	$\bar{P}_{K^+} / \bar{P}_{Li^+}$	$\bar{P}_{Na^+} / \bar{P}_{Li^+}$
0.1/0.1	1.1	0.9	0.8
0.05/0.05	1.2	0.9	0.9
0.02/0.02	1.3	1.0	1.1
0.01/0.01	1.4	1.1	1.1
0.005/0.005	1.6	1.1	1.2
0.002/0.002	2.1	1.5	1.4
0.001/0.001	2.2	1.8	1.7

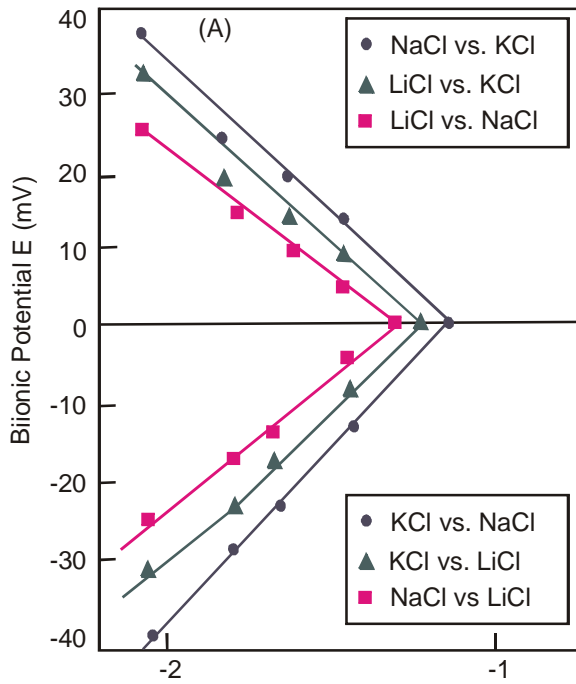


Fig. 4

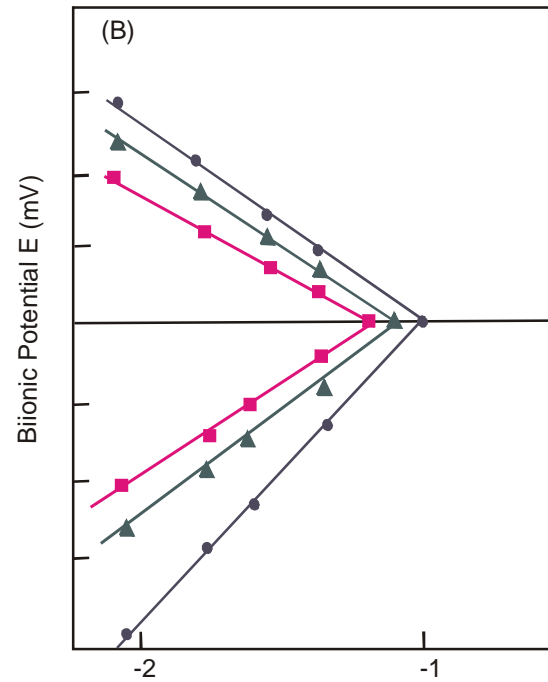


Fig. 5

log (mean malal activity)

Plots of bi-ionic potential E (mV) against logarithm of mean malal activity for (A) cobalt phosphate and (B) nickel phosphate membrane

TABLE-5: Values of the selectivity K_{ji} ($\approx 1/K_{ij}$) evaluated from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentrations for cobalt phosphate membrane

Electrolyte (ion pair) Concentration (Mol/l)	K_{NaK}	K_{LiK}	K_{LiNa}
0.1/0.1	1.06	0.57	0.60
0.05/0.05	1.10	0.58	0.65
0.02/0.02	1.24	0.71	0.72
0.01/0.01	1.25	0.73	0.72
0.005/0.005	1.60	0.76	0.74
0.002/0.002	2.08	0.13	0.99
0.001/0.001	2.09	1.25	1.05

TABLE-6: Values of the selectivity K_{ji} ($\approx 1/K_{ij}$) evaluated from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentrations for cobalt phosphate membrane

Electrolyte (ion pair) Concentration (Mol/l)	K_{NaK}	K_{LiK}	K_{LiNa}
0.1/0.1	0.90	0.65	0.88
0.05/0.05	0.95	0.62	0.92
0.02/0.02	1.00	0.66	0.98
0.01/0.01	1.10	0.71	0.99
0.005/0.005	1.12	0.72	1.00
0.002/0.002	1.24	0.73	1.44
0.001/0.001	1.25	0.97	1.16

This order of selectivity is also based on the membrane selectivity^{6,26} point towards the weak field strength of the charge groups attached to the membrane matrix. This is in accordance of earlier findings^{16,17} of charge density (charge density 10^{-3} eq/l) determinizations of membranes.

Conclusion

The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most widely characterized electrochemical and bioelectric phenomena.

The steady electromotive force of a bi-ionic cell containing two electrolytes separated by a membrane is also called the bi-ionic potential (BIP) which is a measure of selectivity of the membrane for the ions of the same sign. Moreover, electrical membrane conductance also equally contribute in

the evaluation of membrane selectivity for metal ions. Therefore, after having evaluated the mobility ratio of ions in the membrane phase and using these values with electrical conductivity measured experimentally of the cobalt and nickel phosphate membranes found the selectivity sequence of the respective membranes for the cations as



However, to confirm the selectivity sequence of the membrane, the bi-ionic potential across the membrane was also measured by keeping the concentration of the electrolyte on one side constant and varying the concentration of other electrolyte on other side of the membrane. The selectivity sequence of both the membranes obtained using the membrane theories for such experimentally observed bi-ionic potential values is also same. In this way these findings again test the membrane theories, stability and the utility of the membranes.

References

1. ANSARI, M.A., KUMAR, M., SINGH, N., DADORIYA, K.S., KUSHWAHA, R.S. AND AYUB, S. (2012) *Advance in Applied Science Research*, **3** (1), 251.
2. BEG, M.N., SIDDIQUI, AND SHYAM, R. (1977) *Can. J. Chem.* **55**, 1680.
3. BEG, M.N., SIDDIQUI, F.A., SHYAM, R. AND ARSHAD, M. (1977) *J. Memb. Sci.*, **2**, 365.
4. BUCK, R.P. (1976) *J. Anal. Chem.*, **48**, 23R.

5. DERGSMAN, F. AND STAVARMAN, A. (1956) *J. Discuss Faraday Soc.*, **21**, 61.
6. EISENMAN, G. (1962) Membrane transport and Metabolism, edited by Kleinger, A. & Kotyk, A. (Academic Press New York) (1961) 163, *Biophys. J. Suppl.* **2**, 259.
7. EISENMAN, G. (1961) "Membrane Transport and Metabolism", Academic Press, New York, 163; (1962) *Biophys. J. Suppl.* **2**, 259.
8. GOLDMAN, D. (1962) *J. Physiol.*, **27**, 37.
9. HELFFERICH, F. (1962) Ion exchange, McGraw-Hill, New York,.
10. HELFFERICH, F. (1956) *Discuss Faraday Soc.*, **21**, 83.
11. HELFFERICH, F. (1962) Ion exchange, (McGraw Hill, New York) 378.
12. HODGKIN, A.L. AND KATZ, B. (1949) *J. Physiol.* **108**, 37.
13. KARREMAN, G. AND EISENMAN, G. (1962) *Bull Math. Biophys.* **24**, 413.
14. KOBATAKE, Y. AND KAMO, N. (1973) *Progr. Polymer Sci. Jap.*, **5**, 257.
15. KORYTA, J. (1977) *Anal. Chim. Acta.*, **91**, 1.
16. KUSHWAHA, R.S., ANSARI, M.A., AKHTAR, N. AND SINGH, P. (1992) *Indian J. Chem.* **31A**, 439.
17. KUSHWAHA, R.S., ANSARI, M.A. AND TIWARI, R. (2001) *Indian J. Chem.* **90A**, 270.
18. KUSHWAHA, R.S., ANSARI, M.A., SINGH, N., KUMAR, M., VERMA, S.K. AND BEG, M.N. (2010) *J. Indian Chem. Soc.*, **87**, 472.
19. LAKSHMINARAGANAIH, N. (1969) Transport phenomena in membranes (Academic Press, New York) 170.
20. MEYER, K.H. AND SIEVERS, J.F. (1936) *Helv. Chim. Acta.* **19**, 649, 665, 987.
21. NICOLSKY, B.P. (1937) *Acta Physio-chim, USSR*, **7**, 592.
22. PLANCK, M. (1890) *Ann. Phys. Chem.*, **40**, 561.
23. SANDBLOM, J. AND ORME, F. (1972) in G. Eisenman (Ed.), Vol. 1, Marcel Dekker, New York, 125.
24. SANDBLOM, J.P. AND EISENMAN, G. (1967) *Biophys.J.* **7** 217.
25. SCATCHARD, G. AND HELFFERICH, F. (1958) *Discuss Faraday Soc.* **21**, 70.
26. SHERRY, H. (1968) in Ion exchange, edited by J.A. Marinsky (Dekker New York) 2.
27. SIDDIQI, F.A., LAKSHMINARAYANAIH N., BEG M.N. (1971) *J. Polymer. Sci.*, **9**, 2853, 2869.
28. SIDDIQI, F.A., BEG M.N. AND SINGH S.P. (1977) *J. Polymer Sci.*, **15**, 959.
29. TASAKA, M., IKOWA, S. AND IKEDA, Y. (1985) *J. Memb. Sci.*, **24**, 29.
30. TEORELL, T. (1951) *Proc. Soc. Expt. Bio. Med.* **33** (1935) 282.
31. WILLSON, J.R. (1960) De-mineralisation by electrodialysis, (Butterworths, London) 84.
32. WYLLIE, M.R.J. AND KANNAN, S.L. (1994) *J. Phy. Chem.*, **58**, 73.