Studies of inorganic precipitate membrane: Evaluation of membrane selectivity from bi-ionic potential and conductivity measurements

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Received 23 September 1991; revised and accepted 15 January 1992

Bi-ionic and multi-ionic potential across parchment supported mercuric sulphide membrane with various combinations of 1 : 1 electrolytes at different concentrations have been measured. Membrane conductivity in contact with a single electrolyte has been experimentally determined to evaluate the selectivity of the membrane with the predetermined values of the intra-membrane mobility ratio. The selectivity sequence of the membrane has been found as K⁺ > Na⁺ > Li⁺ which on the basis of the Eisenman-Sherry model of membrane selectivity, points towards the weak field strength of the charge groups attached to the membrane matrix.

Effective fixed charge density of parchment supported membranes1-7 and duck and hen egg shell membranes8 has already been demonstrated using Eisenman-Sherry model9-10 of membrane selectivity and the theories of membrane potential based on non-equilibrium thermodynamics. In this paper bi-ionic potential measurements across a parchment supported mercuric sulphide membrane have been carried out for the evaluation of membrane selectivity of ions. Membrane conductance in contact with various 1 : 1 electrolytes has also been experimentally determined to substantiate our findings.

Experimental

The membrane was prepared by the method of interaction described in part XI of this series2. The bi-ionic and multi-ionic potentials were measured by constructing an electro-chemical cell of the following type with a pye precision vernier potentiometer:

[AQ + BK] | Membrane |
---|---|
KCl-agar | solution AX, or (AX + BX)
Saturated | electrolyte
Hg-Hg₂Cl₂ | Hg₂Cl₂-Hg

Aqueous solutions of sodium, potassium and lithium chlorides (BDH, AR grade) were used on the two sides of the membrane and were vigorously stirred with a pair of electrically operated magnetic stirrers to remove completely or at least to minimize the effect of the film controlled diffusion11.

Electrical conductivity of the membrane was determined by setting up a cell of the type shown in Fig. 1 with a conductivity bridge (Cambridge Instrument, England). All measurements were carried out at 25 ± 0.1°C. The error in measurement of membrane potential was within ± 1% whereas electrical conductivity could be measured to better than 99.5% accuracy.

Results and discussion

When an ion exchange membrane of different concentrations is interposed between two solutions of an electrolyte the mobile species penetrate the membrane and various transport phenomena are introduced into the system12. If the membrane is used to separate the solutions of the type AX and BX (or AX and AY) electrolytes the steady potential developed is called bi-ionic13 which is a measure of the selectivity of the membrane for ions of the same sign. Bi-ionic potential has been considered by Helfferich14, according to the concepts of the TMS theory15,16 as being the algebraic sum of two interfacial potentials and an internal diffusion potential. For a general case the total bi-ionic potential E for counterions of equal valencies by Wyllie and Kanaan17 is given by Eq. (1)

\[ E = \frac{RT}{F} \ln \frac{a_i \bar{U}_j}{a_j \bar{U}_i} \]  

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 mem-

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brane phase respectively. Wyllie\textsuperscript{18} expressed the intramembrane mobility ratio as:

\[
\frac{U_j}{U_i} = \frac{\bar{m}_i}{\bar{m}_j} \frac{\bar{\lambda}_i}{\bar{\lambda}_j} \quad \ldots (2)
\]

where \(t_i/t_j\) is the intramembrane transference ratio and \(\bar{m}_i\) and \(\bar{m}_j\) are the steady state equilibrium concentration of i and j in the respective zone; \(\bar{\lambda}_i\) is the conductivity of the membrane when it is wholly in i form and \(\bar{\lambda}_j\) is the conductivity of the membrane when it is wholly in j form. Furthermore, it was shown that \(\bar{m}_i/\bar{m}_j = K_{ji}\) is the selectivity. This, on substitution into Eq. (2) gives

\[
\frac{U_j}{U_i} = K_{ji} \left( \frac{\bar{\lambda}_i}{\bar{\lambda}_j} \right) \quad \ldots (3)
\]

Thus, the ratios of mobilities were related to the chemical and electrical properties of the membrane.

Bi-ionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The values of bi-ionic potential across parchment supported mercuric sulphide membrane with various 1:1 electrolyte combinations at different concentrations are shown in Fig. 2. The values of intramobility ratio \(U_j/U_i\), calculated using Eq. (1) are given in Table 1. An interesting point with regard to the value of \(U_j/U_i\) is that the mobility ratio undergoes considerable change with the concentration of the electrolyte pair.

To gain knowledge of selectivity \(K_{ji}\) from the predetermined values of \(U_j/U_i\), the ratio of electrical conductivities \(\bar{\lambda}_i/\bar{\lambda}_j\), demanded by Eq. (3), must be known. Membrane conductance measurements were carried out when it was wholly in form i or from j. The values of membrane conductance (Fig. 3) were relatively more dependent on the concentration of the electrolytes which implies that the membrane has 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 intramembrane mobility ratio from Table 1 are given in Table 2. The intramembrane mobility ratio values also refer to the selectivity sequence of the membrane for the cations \(K^+ > Na^+ > Li^+\). This order of selectivity on the basis of the Eisemman-Sherry model of membrane selectivity\textsuperscript{9,10} points towards the weak field strength of the charge groups attached to the membrane matrix. Further, it is well known that the bi-ionic potential is a measure of selectivity\textsuperscript{19} of a membrane for ions of the same sign. Equation (4) has been found to predict the values of bi-ionic potential reasonably well.

\[
\text{Bi-ionic potential E}_{\text{BiP}} (\text{mV}) = - \frac{R T}{z F} \ln \left( \frac{C_i}{C_j} \right)
\]

<table>
<thead>
<tr>
<th>Table 1 — Values of the intramembrane mobility ratios of various 1:1 electrolyte ions pairs</th>
</tr>
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<tbody>
<tr>
<td>Membrane</td>
</tr>
<tr>
<td>Electrolyte ion pair</td>
</tr>
<tr>
<td>Concentration (M)</td>
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<tr>
<td>0.1/0.1</td>
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<tr>
<td>0.05/0.05</td>
</tr>
<tr>
<td>0.02/0.02</td>
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<tr>
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<td>0.005/0.005</td>
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<tr>
<td>0.002/0.002</td>
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Fig. 2—Plots of bi-ionic potential \(E_{\text{BiP}} (\text{mV})\) versus log C across mercuric sulphide membrane with 1:1 electrolytes

Fig. 3—Plots of conductance \(\times 10^2\) (MHOS) versus log C for mercuric sulphide membrane with 1:1 electrolytes
Table 2—Values of the selectivity $K_{ij}$ ($1/K_{ji}$) evaluated from the intramembrane mobility ratio and the ratio of electrical conductivities at various electrolyte concentrations

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Concentrations (M)</th>
<th>Mercuric sulphide</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.1/0.1</td>
<td>0.005/0.05</td>
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<tr>
<td>$K_{NaK}$</td>
<td>0.83</td>
<td>0.89</td>
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<tr>
<td>$K_{LiK}$</td>
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<tr>
<td>$K_{LiNa}$</td>
<td>1.09</td>
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</table>

Acknowledgement

The authors are grateful to Prof. R.P. Khandelwal, Head, Department of Chemistry, for providing necessary facilities.

References


