PUBLICATIONS

[1]. Evaluation of effective fixed charge density of egg shell membranes by recently developed theories for membrane potential.


EVALUATION OF EFFECTIVE FIXED CHARGE DENSITY OF EGG SHELL MEMBRANES BY RECENTLY DEVELOPED THEORIES FOR MEMBRANE POTENTIAL

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Effective fixed charge densities of hen and duck egg shell membranes in contact with various uni-univalent electrolyte solutions have been evaluated from membrane potential measurements. The methods used for the estimation of charge densities were: (a) Teorell—Meyer—Sievers method, (b) the methods developed recently by (i) Kobatake et al. and (ii) Nagasawa et al. It was interesting to note that the charge densities evaluated by the methods of Kobatake et al. and Nagasawa et al. gave identical values and that the results were comparable with those obtained by the TMS method.

Introduction

One of the most consistent properties of biological systems is the presence of voltage across cellular surfaces. The mechanism whereby this potential arises is still in dispute. Some consider it to be a diffusion potential while others suggest the voltage to be an adsorption potential [1]. Teorell considered the presence of a net charge on the membrane matrix responsible for the development of potential across it [2, 3]. Based on the fixed charge concept, a number of equations for the membrane potential have been derived and their validity examined [3-18]. In this paper, electrical potentials across hen and duck egg shell membranes have been reported for the evaluation of effective fixed charge density, using the recently developed theories of Kobatake et al. [5] and Nagasawa et al. [8] for membrane potential, based on the thermodynamics of irreversible processes. The theories have been utilized in order to examine the validity of equations developed and their applicability to physiologically important systems.

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Experimental

Material and method

The shell membranes were isolated from the freshly laid hen/duck eggs. The egg was
broken first at one end. Yolk and white of the egg were poured out. The egg membrane was
then separated gently from the hard CaCO₃ covering. The shell membranes consisting of two
layers — a thick outer next to CaCO₃ shell and a thinner next to the albumin [2], were washed
several times with deionized water in order to remove water soluble substances. It was then
clamped between two half cells of an electrochemical cell of the type

<table>
<thead>
<tr>
<th>Reference electrode</th>
<th>Solution $C_2$</th>
<th>Membrane</th>
<th>Solution $C_1$</th>
<th>Reference electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donnan pot.</td>
<td>Diffusion potential</td>
<td>Donnan pot.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

for the measurement of membrane potential. Hg-Hg₂Cl₂—KCl was used as a reference elec-
trode. A tenfold difference in the concentration of alkali chloride solutions (i.e., $C_2/C_1 = 10$)
were maintained and measurements were made using a Pye-precision potentiometer (No.
7568). The whole cell was immersed in a water thermostat maintained at $25 \pm 0.1 \, ^\circ C$. The
solutions were replaced by fresh solutions and when there was no change in potential with the
addition of fresh solutions, with constant vigorous stirring by a pair of magnetic stirrers.
It was taken as the true membrane potential. In both the membranes it could be reproduced
within a few tenths of a mV. The various salt solutions (chlorides of Li⁺, Na⁺ and K⁺) were
prepared from analytical grade reagents and deionized water. In all experiments only freshly
isolated membranes were used.

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 [7]. Membranes in general
have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations. This property is attributed to the
presence of a net charge [9–18] probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly
when dilute solutions are used, is small. This, of course, is dependent on the
porosity of the membrane. If the membrane pores are too wide well defined
potentials can not be obtained. But if the membrane pores are small, a little
charge on it can give ideal potentials according to the Nernst equation

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1}$$

(1)

where $a_1$ and $a_2$ are the activities of the two solutions on either side of the
membrane, $E$ is the membrane potential and $R$, $T$ and $F$ have their usual
meanings.

The commonest substance of which the egg membranes (outer and inner
layers) are composed is keratin, though this protein seems to take many forms.
and to have exactly the same properties in different solutions [19–22]. According to Kitchava et al. [23] the outer layer of the egg vitelline membrane consisted of polypeptides showing mostly z-helix structure, whereas the inner layer mainly contained peptides with random coil structure. Very little is known about the relative proportions of yolk, white and the shell membranes in the eggs of lower animals, although the mineralogical and morphological structure of shells is well understood [21].

The values of membrane potential, $E_m$ (mV) measured across both hen and duck egg shell membranes are given in Table I. An interesting point with the values of $E_m$ is the fact that these are negative in all the electrolyte concentration ranges. However, the values of $E_m$ decreases algebraically as

Table I

<table>
<thead>
<tr>
<th>Electrolyte Concentration (Normality)</th>
<th>Hen</th>
<th>Duck</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{CI}$</td>
<td>$KCI$</td>
<td>$NaCl$</td>
</tr>
<tr>
<td>0.01/0.001</td>
<td>-19.5</td>
<td>-33.5</td>
</tr>
<tr>
<td>0.05/0.005</td>
<td>-16.2</td>
<td>-29.3</td>
</tr>
<tr>
<td>0.1/0.01</td>
<td>-14.7</td>
<td>-24.0</td>
</tr>
<tr>
<td>0.5/0.05</td>
<td>-8.9</td>
<td>-18.8</td>
</tr>
<tr>
<td>1.0/0.1</td>
<td>-6.5</td>
<td>-16.2</td>
</tr>
</tbody>
</table>

* Dilute solution side taken as +ve.
Deviation = 0.15 mV.

the electrolyte concentration across the membranes is increased. This means that both the membranes in contact with dilute electrolyte solutions are anion selective whereas the anion selectivity decreases as the concentration across the membrane are increased. The stepwise change in membrane potential or the selectivity character of the membrane electrolyte system may radially be explained in terms of the structural changes produced in the electrical double layer at the interfaces. The egg shell membranes are considered to be negatively charged in contact with water. It is quite probable that in these cases the negative charge is due to the firm attachment of hydroxide ions from water and few ionogenic groups of organic fibres [22] constituting the egg shell membrane. An equivalent number of protons and/or cations, some closely held in the fixed part of the double layer and the remainder in the diffused portion, is left in the solution. By the addition of uni-univalent electrolytes, there will be a tendency for cations to accumulate on the solution side of the

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fixed double layer by increasing the positive charge density, the interfacial potential difference changes thereby changing the overall membrane potential and the membrane becomes less selective. If the electrolyte concentrations are further increased the overall membrane potential or the selectivity character of the membrane changes.

The fixed groups present in well-characterized ionexchange membranes can be easily estimated by titration. This procedure was used by Sollner et al. [22] to estimate the end groups present in the collodion material. Lakshmimayanaiah [24] in his studies with thin membranes of parlodion used two methods — the isotopic and the potentiometric to evaluate the apparent fixed charge on the membrane material. Beg and coworkers [9—18] used potentiometric method for the evaluation of effective fixed charge density of a number of parchment supported and polystyrene-based inorganic precipitate membranes. In the present studies the potentiometric method based on fixed charge theory of membrane potential has been used for the evaluation of effective fixed charge density of hen and duck egg shell membranes.

The fixed charge concept of Teorel [2] and Meyer and Sievers [4] 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. The simplest and most popular formulations of the fluxed and potentials across charged membranes which can be used to interpret data on biological systems are still those based on the Teorel—Meyer—Sievers (TMS) fixed charge model. These authors obtained Eqn. (2) for the emf across a charged membrane by integrating the equation for the emf due to diffusion of ions within a membrane and subsequently adding the two phase boundary (Donnan) potentials to the intramembrane diffusion potential.

\[
E_m = 59.2 \left[ \log \frac{C_x \sqrt{4C_x^2 + X^2 + X}}{C_1 \sqrt{4C_1^2 + X^2 + X}} + \bar{U} \log \frac{1}{\sqrt{4C_1^2 + X^2 + XU}} \right]
\]

where \( \bar{U} = \bar{v} - \bar{v}/\mu + \bar{v} \), \( \bar{v} \) and \( \bar{v} \) are the mobilities of cation and anion, respectively, in the membrane phase and \( X \) is the charge on the membrane expressed in equivalent/litre of the imibed solution. In order to evaluate this parameter for a 1 : 1 electrolyte and a membrane carrying a net charge of unity (\( X = -1 \)), theoretical concentration potentials \( E_m \) existing across the membrane were calculated as a function of \( C_x \), the ratio \( (C_x/C_1) \) being kept constant for different mobility ratios \( \bar{v}/\bar{v} \) and plotted as shown in Fig. 1. The observed membrane potentials for both hen and duck egg shell membranes using various electrolytes were plotted in the same graph. The experimental curve for any given membrane was shifted horizontally until it coincided with one of the theoretical curves. The extent of this shift gave
Fig. 1. Plots of membrane potential $E_m$ vs. $\log 1/C_e$ for hen (1) and duck (2) egg shell membranes in contact with NaCl solutions (see text).

$log X$ and the parallel theoretical curve gave the value for $u/v$. The values of $X$ and $u/v$ derived in this way for both the membranes with various 1:1 electrolyte combinations are given in Tables II and III. It is, however, noted

Table II

Values of the effective fixed charge density calculated from different methods using various 1:1 electrolytes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hen</th>
<th>Duck</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>$\overline{X} \times 10^4$</td>
<td>$\phi \overline{X} \times 10^4$</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>LiCl</td>
<td>4.9</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table II

Values of membrane parameters $a$, $\beta$ and $u/v$ for hen and duck egg shell membranes using various 1:1 electrolytes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hen</th>
<th>Duck</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Parameter</td>
<td>$a$</td>
</tr>
<tr>
<td>KCl</td>
<td>0.589</td>
<td>3.07</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.627</td>
<td>1.70</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.666</td>
<td>1.64</td>
</tr>
</tbody>
</table>

that the experimental curves for both hen and duck egg shell membranes after shifting horizontally did not overlap completely with any of the theoretical curves in all the electrolyte concentration ranges studied. This discrepancy is not peculiar for these systems [3, 9–18].

Recently, Kobatake et al. [5] derived the following equation for the electrical potential $E_m$ which arises when a negatively charged membrane separates two solutions of a 1:1 electrolyte of concentration $C_2$ and $C_1$ ($C_2 > C_1$)

$$E_m = -\frac{RT}{F} \left[ \frac{1}{\beta} \ln \frac{C_2}{C_1} - \left( 1 + \frac{1}{\beta} - 2\alpha \right) \ln \left( \frac{C_2 + x\beta X}{C_1 + x\beta X} \right) \right]$$

(3)

where $\alpha = u/(u + v)$

$$\beta = 1 + KFX/u$$

$F$ and $K$ represent, respectively, the Faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed, $u$ and $v$ are the mobilities of cation and anion in the membrane phase. In order to evaluate the membrane parameters $\alpha$, $\beta$ and $X$, two limiting forms of the above equation were derived:

(a) when the salt concentration $C$ is sufficiently small,

$$|E_m^x| = \frac{1}{\beta} \ln \gamma - \frac{\gamma - 1}{\alpha\beta\gamma} \left( 1 + \frac{1}{\beta} - 2\alpha \right) \left( \frac{C_2}{X} \right) +$$

(4)

where $|E_m^x| = FE_m/RT$ and $\gamma = C_2/C_1$

(b) when the salt concentration $C$ is high

$$\frac{1}{t_-} = \frac{1}{(1 - \alpha)} + \frac{(1 + \beta - 2\alpha\beta)(\gamma - 1)}{2(1 - \alpha)(1 - \alpha) \ln \gamma} \left( \frac{X}{C_2} \right) +$$

(5)

where $t_-$ is the apparent transference number of cations (anions) in a negatively charged membrane defined by

$$|E_m^x| = (1 - 2t_-) \ln \gamma$$

(6)

The values of $t_-$ calculated from observed membrane potentials using Eqn. (6) are given in Table IV. Eqn. (4) was used to give the value of $\beta$ and a relation between $\alpha$ and $X$ by evaluating the intercept and the initial slope of the plot of $|E_m^x|$ versus $C_2$ (Fig. 2), while Eqn. (5) was used to evaluate $\alpha$ from the intercept of a plot of $1/t_-$ versus $1/C_2$ (Fig. 3). The value of $X$ was then determined by inserting the value of $\alpha$ in the relation of $\alpha$ and $X$ obtained earlier. Once $\alpha$, $\beta$ and $X$ for the membrane-electrolyte systems are known, in the manner described, $E_m$ can be calculated using Eqn. (3). The values of membrane parameters $\alpha$, $\beta$ and $X$ thus derived are given in Tables II and III.
Table IV

<table>
<thead>
<tr>
<th>Electrolyte Concentrations (Normality)</th>
<th>Hen egg shell</th>
<th>Duck egg shell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KCl</td>
<td>NaCl</td>
</tr>
<tr>
<td>0.01/0.001</td>
<td>0.34</td>
<td>0.22</td>
</tr>
<tr>
<td>0.05/0.005</td>
<td>0.36</td>
<td>0.25</td>
</tr>
<tr>
<td>0.1/0.01</td>
<td>0.38</td>
<td>0.30</td>
</tr>
<tr>
<td>0.5/0.05</td>
<td>0.43</td>
<td>0.34</td>
</tr>
<tr>
<td>1.0/0.1</td>
<td>0.45</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Fig. 2. Plots of reduced potential $|E_m|$ vs. $C_2$ for hen (1) and duck (2) egg shell membranes using various 1:1 electrolytes

Fig. 3. Plots $1/t$ -- vs. $1/C_2$ for hen (1) and duck (2) egg shell membranes using various 1:1 electrolytes

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More recently, Nagasawa et al. [8] derived Eqn. (8) for membrane potential existing across a charged membrane. The total membrane potential $E_m$ was considered as the sum of diffusion potential $E_d$ inside the membrane and the electrostatic potential difference $E_e$ between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential $E_d$ was obtained by integrating the basic flow equation for diffusion while the electrostatic potential difference was calculated from Donnan theory, stated mathematically,

$$E_m = E_d + E_e$$  \hspace{1cm} (7a)

where

$$
-E_d = - \int_1^2 \left( \frac{J_0}{FC_0} \right) \frac{\Phi \bar{X}}{(C_+ + \Phi \bar{X})u + C_- v} \, dx + \frac{RT}{F} \int_1^2 \frac{(C_+ + \Phi \bar{X}) u}{(C_- + \Phi \bar{X}) u C_- v} \, d
$$

$$\ln \bar{a} + - \frac{RT}{F} \int_1^2 \frac{C_- v}{(C_+ + \Phi \bar{X}) u + C_- v} \, d \ln \bar{a}$$  \hspace{1cm} (7b)

$$-E_e = - \frac{RT}{F} \ln \left[ \frac{\bar{a}^1 - a^1}{a^1_\infty - a^2_\infty} \right]$$  \hspace{1cm} (7c)

where $C_0$ is the effective concentration of anions in the solution phase (mol/L), $a^1$ and $a^2$ are the activities of the electrolyte on two sides of the membrane, overbar refers to the activity in the membrane phase, $J_0$ is the flow of electrolyte in the absence of external electric field, $\Phi \bar{X}$ is effective fixed charge density, and other symbols have their usual meaning. Equation (7) on integrating and putting the limit of high electrolyte concentrations across the membrane, following equation for membrane potential was obtained,

$$
-E_m = \frac{RT}{F} \left( \frac{\Phi \bar{X}}{2} \right) \frac{(\gamma - 1)}{C_1} + \frac{RT}{F} \left( \frac{u - v}{u + v} \right) \left[ 1 - \frac{\Phi \bar{X} J_0}{RT C_0 (u - v) K} \right]
$$

$$\ln \gamma + \frac{RT \Phi \bar{X}}{2F \, uv \, \left( RT C_0 K \right)} \left[ 1 - \frac{\Phi \bar{X} J_0 (u + v)}{4RT C_0 uv K} \right] \frac{1}{\left( 1 - \frac{\Phi \bar{X} J_0}{2RT C_0 v K} \right)^2} (\gamma - 1) C_1.$$  \hspace{1cm} (8)

In order to evaluate $\Phi \bar{X}$, Eqn. (8) was put in the following approximate form,

$$-E_m = \frac{RT}{F} \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{\Phi \bar{X}}{2} \right) \frac{1}{C_1} + \ldots.$$  \hspace{1cm} (9)

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This equation predicts a linear relationship between $E_m\left(\frac{\gamma - 1}{\gamma}\right)$ and $1/C_1$.

The plot of $E_m\left(\frac{\gamma - 1}{\gamma}\right)$ versus $1/C_1$ (Fig. 4) gives straight lines in consistent with Eqn. (9). The values of $\Phi X$ derived from the slope of the lines are given in Table II.

![Graph showing plots of membrane potential versus $1/C_1$](image)

*Fig. 4. Plots of membrane potential $E_m\left(\frac{\gamma - 1}{\gamma}\right)$ vs. $1/C_1$ for hen (1) and duck (2) egg shell membranes in contact with various 1:1 electrolytes*

The values of fixed charge densities evaluated from the two recently developed theories of Kobatake et al. and Nagasawa et al., are closer to those derived from the TMS theory — the theory most widely used to interpret data on biological systems. The values obtained vary somewhat depending on the different methods used. It can be concluded that the methods developed recently by Kobatake et al. and Nagasawa et al. based on the principles of irreversible thermodynamics are valid for the evaluation of effective fixed charge densities of the egg shell membranes.

*Thanks are due to Professor M. S. Ahmad, Chairman, Department of Chemistry for providing the necessary facilities and to UGC and CSIR (India) for financial support.*

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REFERENCES

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

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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 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 membranes\(^{1,2}\) and duck and hen egg shell membranes\(^8\) has already been demonstrated using Eisenman-Sherry model\(^9,10\) 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 series\(^2\). 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:

\[
\begin{array}{c|c|c|c|c}
\text{Saturated} & \text{electrolyte} & \text{solution AX} & \text{Membrane} & \text{solution BX} \\
\text{Hg-Hg}_2\text{Cl}_2 & \text{KCl-agar} & \text{(AX + BX)} & \text{Hg}_2\text{Cl}_2-\text{Hg} \\
\text{electrolyte} & \text{Saturated} & \text{KCl-agar} & \text{Hg}_2\text{Cl}_2-\text{Hg} \\
\text{solution BX} & \text{solution AX} & \text{(AX + BX)} & \text{Hg}_2\text{Cl}_2-\text{Hg} \\
\end{array}
\]

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 diffusion\(^{11}\).

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 system\(^{12}\). If the membrane is used to separate the solutions of the type AX and BX (or AX and BY) electrolytes the steady potential developed is called bi-ionic\(^{13}\) which is a measure of the selectivity of the membrane for ions of the same sign. Bi-ionic potential has been considered by Helfferich\(^{14}\), according to the concepts of the EMS theory\(^{15,16}\), 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 valency by Wyllie and Kanaan\(^{17}\) is given by Eq. (1)

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

... (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 mem-

Fig. 1—Experimental cell
brane phase respectively. Wyllie expressed the intramembrane mobility ratio as:

\[ \frac{\bar{U}_i}{\bar{U}_j} = \frac{\bar{n}_i}{\bar{n}_j} \times \left( \frac{\bar{x}_i}{\bar{x}_j} \right) \]  (2)

where \( \bar{n}_i/\bar{n}_j \) is the intramembrane transference ratio and \( \bar{x}_i \) and \( \bar{x}_j \) are the conductivity of the membrane when it is wholly in i form and \( \bar{x}_j \) 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 substituting \( n \) into Eq. (2) gives

\[ \frac{\bar{U}_i}{\bar{U}_j} = K_{ji} \left( \frac{\bar{x}_i}{\bar{x}_j} \right) \]  (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 \( \bar{U}_i/\bar{U}_j \) calculated using Eq. (1) are given in Table 1. An interesting point with regard to the value 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 \( \bar{x}_i/\bar{x}_j \), demanded by Eq. (3), must be known. Membrane conductance measurements were carried out when it was wholly in i form 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 conductivity 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 Eismann-Sherry model of membrane selectivity 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 of a membrane for ions of the same sign. Equation (4) has been found to predict the values of bi-ionic potential reasonably well.

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**Table 1**: Values of the intramembrane mobility ratios of various 1:1 electrolyte ions pairs

<table>
<thead>
<tr>
<th>Electrolyte ion pair</th>
<th>( \bar{U}<em>{K^+}/\bar{U}</em>{Na^+} )</th>
<th>( \bar{U}<em>{K^+}/\bar{U}</em>{Li^+} )</th>
<th>( \bar{U}<em>{Na^+}/\bar{U}</em>{Li^+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1/0.1</td>
<td>1.01</td>
<td>1.32</td>
<td>1.17</td>
</tr>
<tr>
<td>0.05/0.05</td>
<td>1.04</td>
<td>1.34</td>
<td>1.22</td>
</tr>
<tr>
<td>0.02/0.02</td>
<td>1.10</td>
<td>1.53</td>
<td>1.42</td>
</tr>
<tr>
<td>0.01/0.01</td>
<td>1.21</td>
<td>1.74</td>
<td>1.75</td>
</tr>
<tr>
<td>0.005/0.005</td>
<td>1.27</td>
<td>1.99</td>
<td>1.83</td>
</tr>
<tr>
<td>0.002/0.002</td>
<td>1.38</td>
<td>2.21</td>
<td>1.94</td>
</tr>
<tr>
<td>0.001/0.001</td>
<td>1.52</td>
<td>2.39</td>
<td>1.97</td>
</tr>
</tbody>
</table>
Table 2—Values of the selectivity $K_{A} (1/K_{B})$ 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>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1/0.1</td>
<td>0.005/0.05</td>
</tr>
<tr>
<td>Selectivity</td>
<td>$K_{Na}$</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>$K_{Li}$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>$K_{LiNa}$</td>
<td>1.09</td>
</tr>
</tbody>
</table>

provided $\gamma_{B}/\gamma_{A}$ remains constant.

$$E_{BIP} = \frac{RT}{F} \ln \frac{\bar{U}_{A}a_{A}^{-1} \gamma_{B}}{\bar{U}_{B}a_{B}^{-1} \gamma_{A}} \quad \cdots (4)$$

Equation (4) can be written as

$$E_{BIP} = \frac{RT}{F} \ln \frac{\bar{U}_{A}a_{A}^{-1}}{\bar{U}_{B}a_{B}^{-1}} \quad \text{(if } \gamma_{A} = \gamma_{B}) \quad \cdots (5)$$

and

$$E_{BIP} = \frac{RT}{F} \ln \frac{I_{A}}{I_{B}} \quad \cdots (6)$$

where

$$I_{A} = \frac{\bar{U}_{A} \bar{a}_{A} \gamma_{B}}{\bar{U}_{B} \bar{a}_{B} \gamma_{A}}$$

provided that the Donnan relation $\bar{a}_{A}/\bar{a}_{B} = a_{A}'/a_{B}'$ is established.

The bi-ionic potentials generated across mercuric sulphide membrane were also measured by keeping the concentration of AX constant and by varying the concentration of BX, and again by keeping [BX] constant and varying [AX]. These measurements were extended to three solutions, i.e. KCl-NaCl, KCl-LiCl and NaCl-LiCl. The bi-ionic potential values thus measured were plotted in Fig. 4 as a function of log $a_{AX}/a_{BX}$. Good linear plots as demanded by Eq. (5) were obtained. The point of intersection of the two linear plots at the same activity, i.e., $a_{AX}/a_{BX} = 1$, gives the value of the transport ratio using Eq. (6). The transport ratio thus obtained for different 1:1 electrolyte pairs are

$$I_{K+}/I_{Na^+} = 1.12, I_{K+}/I_{Li^+} = 1.08, I_{Na^+}/I_{Li^+} = 1.06.$$  

These results also point towards the order of selectivity of cations transporting through the membrane as: $K^+ > Na^+ > Li^+$.  

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Head, Department of Chemistry, for providing necessary facilities.

References


TITLE: EVALUATION OF EFFECTIVE FIXED CHARGE DENSITY AND SELECTIVITY OF MEMBRANES FROM ELECTRICAL POTENTIAL MEASUREMENTS.

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KEY WORDS: Hen and duck egg shell membranes; Membrane potential; Charge density and selectivity.

ABSTRACT

Membrane potential measurements across hen and duck shell membranes in contact with 1:1 electrolytes have been carried out in order to evaluate the effective fixed charge density of the membranes by various methods: (a) Teorell-Meyer-Sievers method, (b) The methods developed recently by (I) Kobatake et al. and Nagasama et al. It was interesting to note that the charge densities evaluated by the methods of Kobatake et al. and Nagasama et al. gave identical values and that the results were comparable with those obtained by the TNS method. Effective fixed charge densities have been used to calculate biionic potential values to estimate the selectivity of the membranes for cation. The order for selectivity of cations transporting through the membranes have been found as K > Na > Li.
Abstract of the paper presented in the symposium of Indian Science Congress Association held at Cochin in Feb. 1990.

TITLE : STUDIES WITH EGG SHELL MEMBRANES : EVALUATION OF EFFECTIVE FIXED CHARGE DENSITY OF MEMBRANES BY RECENTLY DEVELOPED THEORIES FOR MEMBRANE POTENTIAL.


KEY WORDS : Hen and Duck egg shell membranes, electrical membrane potential, fixed charge density and transference number.

ABSTRACT

Membrane potential measurements across hen and duck egg shell membranes in contact with various 1:1 electrolyte solutions have been carried out in order to evaluate the effective fixed charge density of membranes. The methods used for the estimation of charge densities were : (a) Teorell-Meyer-Sievers method, (b) The methods developed recently by (i) Kobatake et al and (ii) Tasaka et al. It was interesting to note that the charge densities evaluated by the methods of Kobatake et al and Tasaka et al gave identical values and that the results were comparable with those obtained by the T.M.S. method.