PUBLICATIONS
STUDIES OF MEMBRANE PHENOMENA

I. EFFECT OF TEMPERATURE ON DIFFUSION OF ELECTROLYTES THROUGH A PARCHMENT-SUPPORTED SILVER IODIDE MEMBRANE

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INTRODUCTION

The findings of Teorell that gastric mucosal membrane, in some formal aspects at least, behaved exactly like parchment membrane led us to investigate a very large number of parchment-supported membranes as models for biological membranes. In previous communications the membrane potential \( E \) was related to the permeability \( P \) parameter by a Freundlich adsorption-type equation 
\[
E = aP^n \quad \text{or} \quad E = aP^{1/n},
\]
and the constants \( a \) and \( n \) characterizing the membranes were evaluated. It soon was realized that the electrolytic resistance of the membrane \( R_m \) plays an important role in the diffusion process. This communication deals with the determinations of the membrane resistance \( R_m \), the membrane concentration potential, \( E_m \), and diffusion rate \( D_r \) at various temperatures. The evaluation of the energy and enthalpy of activation of diffusion of biologically important electrolytes and their relationship with various thermodynamic quantities of aqueous ions is also considered. These investigations emphasize the importance of hydration and the energetics of the associated processes in membrane phenomena. The fixed charge theory of Teorell, and Meyer and Sievers as well as the views of Sollner, Gregor, Schmid and Eisenman have been applied to elucidate the electrochemical nature of the membranes investigated.

EQUATION USED FOR DIFFUSION RATE MEASUREMENT

The equations used in these investigations to calculate diffusion rates were modifications of those which apply to the migration of ions under the influence of a potential gradient. The equation:

\[
\frac{dQ_+}{dt} = \frac{1}{Z_+R_mF} \left[ \frac{Z_-}{Z_+ + Z_-} \frac{E_m}{E_{c+}} + \frac{Z_+}{Z_+ + Z_-} \right] \left[ E_{c+} - E_m \right]
\]

where
- \( Q_+ \) = mmoles of cations
- \( Z_+, Z_- \) = valency of cation and anion respectively
- \( E_m \) = membrane concentration potential
- \( E_{c+} \) = potential difference (mV) equivalent to a given difference in cation concentration

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potential difference (mV) equivalent to a given difference in anion concentration

\[ E_{c^-} = \text{potential difference (mV)} \]

Faraday (96,500 C)

\[ F = \text{Faraday (96,500 C)} \]

electrolytic resistance of membrane (Ω)

\[ R_m = \text{electrolytic resistance of membrane (Ω)} \]

diffusion time (s),

which was deduced by Kittleberger\textsuperscript{12}, was employed for the determination of the diffusion rate. For uni-univalent electrolytes, \( Z_+ = Z_- \), eqn. (1) then becomes

\[
\frac{\Delta E}{\Delta t} = \frac{D}{R_m} \left[ \frac{1}{2} \frac{E_m}{E_{c^+}} + \frac{1}{2} \right] (E_{c^+} - E_m)
\]

where \( D \) is the diffusion rate and \( Q \) is mmoles of salt.

EXPERIMENTAL

Preparation of parchment-supported silver iodide membrane

The membrane was prepared by impregnating parchment paper with silver iodide. The paper was first soaked with distilled water and then tied carefully to a glass tube (cylinder). A 0.2 M solution of potassium iodide was put inside the paper container which was then suspended for 72 h in a 0.2 M AgNO\textsubscript{3} solution contained in a beaker. The parchment paper was then taken out and washed repeatedly with distilled water to remove the adsorbed electrolytes. The solutions of potassium iodide and silver nitrate were then interchanged. The paper was then immersed in them for another 72 h. This process was repeated a number of times until a very fine deposit of silver iodide was obtained on the paper. The membrane, yellow in colour, was observed under a microscope; there was a fine deposition over the whole surface.

Apparatus and procedure

The assembly used for the diffusion rate measurement is shown in Fig. 1. It consisted of two half-cells (125-ml capacity) having flanges to fit each other. The vertical female joints, T and T', attached to each half-cell provided introduction for the electrolyte and the conductivity cell electrodes. The test membrane in the form of a disc slightly larger than the cell was installed between the flanges of the half-cells. One Ag/AgCl J-shaped electrode and one Ag/AgCl disc electrode passed through two narrow holes in each half-cell very close to the membrane as shown in Fig. 1. A narrow tube was slipped over the ends of the J-shaped and the disc electrodes and waxed firmly. Some mercury was also placed in each of the tubes to provide connection to the copper wire leads.

The conductivity cell electrodes dipping in the salt solutions in the two half-cells were used to determine the salt concentration of the test solutions. Various salt solutions (KCl, NaCl and LiCl) were prepared from B.D.H. AR-grade chemicals. Initially, they were usually 0.2 M and 0.002 M in the two half-cells. No appreciable change was observed within 5–6 h in 0.2 M electrolyte concentration and we have therefore assumed this concentration to be practically unchanged.

The potential difference between the Ag/AgCl J-shaped electrodes in test solutions on opposite sides of the membrane is the algebraic sum of concentration potential \( E_{c^-} \) and membrane potential \( E_m \). \( E_{c^-} \) was obtained by calculation from the measured concentrations of the two test solutions and \( (E_m + E_{c^-}) \) was obtained.

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directly. The membrane concentration potential $E_m$ was then obtained by subtraction. Under the conditions of the experiment, the dilute side was always positive and $E_m$ was taken with its proper sign.

The electrolytic resistance of the membrane $R_m$ was determined by applying an external e.m.f. to the Ag/AgCl disc electrodes in the solutions on opposite sides of the membrane and measuring the change in the potential difference of the Ag/AgCl J-shaped electrodes. To determine the current in the circuit, the $IR$ drop across a known resistance $R$ (1000 $\Omega$) in series with the cell was also measured. This measuring current was kept as low as possible in order to minimise the transfer of ions during the 2 or 3 min required for each resistance measurement.

![Diagram of apparatus](image)

Fig. 1. Apparatus for diffusion rate measurement and electric circuit for measurement of the membrane resistance $R_m$.

The experimental procedure involved setting up a cell with a membrane and silver–silver chloride electrodes (both J-shaped as well as disc-shaped). Known volumes of the two test solutions (approx. 125 ml of each) were introduced and the conductivity cell electrodes fixed in place. The assembly had magnetic stirrers in each half-cell and was placed in a thermostat maintained at the required temperature. The measurements needed were the determination of (a) the salt concentration of the two test solutions, (b) the membrane concentration potential and (c) the membrane resistance in order to compute the diffusion rate.

Two sets of calibration curves were needed in this experiment, one to obtain the concentration from the measured conductivity and the other to obtain the concentration potential $E_{ce}$. In the first case, the curves were plots of conductance vs. concentration. The curves from which concentration potentials were obtained were plots of e.m.f. vs. log $f_c$ from the equation:

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e.m.f. = \frac{2.303 RT}{F} \log f_c \quad (3)

(for uni-univalent electrolytes)

For all electrolytes, $E_{c^-}$ was equal to the difference between the e.m.f. values of the dilute and concentrated test solutions.

With $R_m$ in ohms and $E_{c^-}$ and $E_m$ in millivolts, eqn. (2) gives the rate of diffusion of an electrolyte through the membrane in mmol s$^{-1}$.

The potential and conductance measurements were made by means of a Pye precision vernier potentiometer (No. 7568) and Cambridge conductivity bridge (No. L-350140), respectively.

RESULTS AND DISCUSSION

The equation for the diffusion rate for a uni-univalent electrolyte is given by eqn. (2) which clearly shows that $D$ depends mainly upon two main factors, membrane resistance $R_m$ and membrane potential $E_m$. The changes in the diffusion rate over a range of nearly 6 h for the chlorides of alkali metal ions are shown in Fig. 2. The variations in the membrane resistance and membrane potential over the same time range are shown in Figs. 3 and 4 respectively. As the diffusion rate depends markedly

Fig 2 Rates of diffusion ($D_c$) of various electrolytes through silver iodide membrane at different temps LiCl (straight lines) (○) 10°, (■) 18°, (□) 25°, (■) 35°C NaCl the same with a dashed line KCl the same with a dotted line

on temperature, it was thought worthwhile to study the effect of temperature on membrane resistance and membrane potential. The behaviour of membrane resistance and membrane potential for KCl at various temperatures is shown in Figs. 3 and 4 respectively. The effect of temperature on membrane resistance and membrane potential was found to be similar for NaCl and LiCl; representative curves for NaCl and LiCl at 25°C are also shown in the same Figures.

In order to obtain the energy of activation of diffusion of the three electrolytes (viz. KCl, NaCl and LiCl), plots of log $D$, vs. $1/T$ ($T$ is the absolute temperature) were drawn for the three electrolytes and from the slope, the energy of activation $E_A$ was evaluated. As is clear from Figs. 2, 3 and 4, the changes in $D$, $R_m$ and $E_m$ are appreciably lower after 300 min, so these values at 340 min were chosen for each
Fig 5: Plots of log $D_i$ (full line) and log $R_m$ (dashed line) vs $1/T$ (both at 340 min) for different electrolytes ($\square$) (1), KCl, (○) (2), NaCl, (○) (3), LiCl (○) (4), KCl, (■) (5), NaCl, (□) (6), LiCl

Fig 6: Plots of log $E_m$ vs $1/T$ for different electrolytes

TABLE 1
VALUES OF MEMBRANE RESISTANCE $R_m$, MEMBRANE POTENTIAL $E_m$, AND DIFFUSION RATE $D_i$ (AT THE 340TH MINUTE) FOR VARIOUS ELECTROLYTES AT DIFFERENT TEMPERATURES USING PARCHMENT-SUPPORTED SILVER IODIDE MEMBRANE ($C_1/C_2 = 0.2 M/0.002 M$)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temp °C</th>
<th>$R_m$/$\Omega$</th>
<th>$E_m$/mV</th>
<th>$10^9 D_i$/mol s$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>KCl</td>
<td>10</td>
<td>118.0</td>
<td>37.0</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>94.5</td>
<td>34.8</td>
<td>3.37</td>
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<td></td>
<td>25</td>
<td>72.0</td>
<td>29.7</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>48.0</td>
<td>27.0</td>
<td>6.83</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>158.5</td>
<td>29.7</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>111.5</td>
<td>27.9</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>106.0</td>
<td>23.5</td>
<td>3.45</td>
</tr>
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<td></td>
<td>35</td>
<td>61.0</td>
<td>26.0</td>
<td>5.20</td>
</tr>
<tr>
<td>LiCl</td>
<td>10</td>
<td>198.5</td>
<td>24.5</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>160.0</td>
<td>21.6</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>126.0</td>
<td>21.4</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>90.0</td>
<td>20.3</td>
<td>4.18</td>
</tr>
</tbody>
</table>

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...electrolyte to make a comparative study. In order to draw the plots of \( \log D, \log R_m \) and \( \log E_m \) vs. \( 1/T \), the values of \( D, R_m \) and \( E_m \) chosen for each electrolyte at each temperature were those at the 340th minute. The plots of \( \log D \) and \( \log R_m \) vs. \( 1/T \) for different electrolytes are shown in Fig. 5; those of \( \log E_m \) vs. \( 1/T \) are shown in Fig. 6. The values of \( D, R_m \) and \( E_m \) for different electrolytes at different temperatures (at the 340th minute) are summarized in Table 1.

The energies of activation of diffusion for the three electrolytes are in the order: KCl, 6974; NaCl, 6132; LiCl, 5675 cal mol\(^{-1}\).

The enthalpies of activation \( \Delta H^\circ \) (at 25°C) for the three electrolytes are as follows: KCl, 6382; NaCl, 5540; LiCl, 5083 cal mol\(^{-1}\).

A critical evaluation of the experimental results on the diffusion rates has to take into consideration the following factors which are responsible for slowing down the diffusion through the membrane compared to the diffusion in free solution.

1. A part of the cross section of the membrane is occupied by the frame-work (cellular material and silver iodide precipitate).
2. Diffusion of the electrolyte takes place through a tortuous and hence longer path.
3. The frame-work impedes the diffusion of large hydrated ions.
4. Interaction of the fixed ionic groups of the frame-work retards the diffusion.

Moreover, pore geometry also plays a role in explaining the retardation in diffusion rate. In the system investigated, all homogenous membrane elements are taken to be charged, rigid capillary structures or gels which may be adequately described by the classical fixed charge theory of Teorell. The charged membrane is to be viewed as a set of parallel capillaries having a diameter large with respect to the thickness of the electrical double layer at the walls.

The interpretation of the results of the diffusion rate studies can be discussed in terms of ionic sizes, solvation, mobilities, adsorption properties and other thermo-dynamic properties. The theory put forward by Gregor in relation to the ionic selectivity depends largely on the use of hydrated ionic volumes. As our discussion is largely dependent upon ionic hydration, it seems necessary to mention some concept of ionic hydration as applied to membrane phenomena. Levine and Bell have considered the region of water surrounding an ion as a coordinated hydration shell, and call it an ion complex. Its formation and breaking would be accompanied by substantial free energy and entropy changes. Stern and Amis considered that ions may possess solvation sheaths of water molecules "bound" to give distinct molecular species. Stokes and Robinson have given the number of bound molecules \( N_h \) in their hydration shell by the interaction of ions and the surrounded water. This number \( N_h \) is not the same as the conventional number of water molecules in the first layer around the ion, it is rather a number introduced to allow for the average effect of all ion–solvent interaction. The following are the values of \( N_h \) and \( a_0 \) (mean distance of approach in Å units) for the three cations:

<table>
<thead>
<tr>
<th>Cation</th>
<th>( N_h )</th>
<th>( a_0 (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>1.9</td>
<td>3.63</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.5</td>
<td>3.97</td>
</tr>
<tr>
<td>LiCl</td>
<td>7.1</td>
<td>4.32</td>
</tr>
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</table>

*J. Electroanal. Chem.*, 23 (1969) 137–146
Fig. 7. Plots of: (1), $N_\alpha$; (2), hydrated ionic volumes; (3), $E_{\text{eff}}$; (4), $z/a_0$ vs $D_\alpha$, where the $D_\alpha$ values are those at 340 min and 25°C.

Fig. 8. Plots of: (1), $D_\alpha$; (2) $\Delta H^\circ$ vs heats of hydration. $D_\alpha$-values are those at the 340th min and 25°C, $\Delta H^\circ$-values are those at 25°C.

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According to Gregor’s theory of ion selectivity, of two exchangeable cations the one with the smaller hydrated radius will be preferred by the exchanger. Depending on the size and electrical charge pattern of a pore, it may either admit or repel a solute particle. This is the basis of ion selectivity and applies equally to the material in a thin sheet (a membrane) or in bulk (an ion exchanger). It has been proposed by Mullins that the hydration of the materials of the pores themselves may provide a favourable water environment for particular ions or molecules, so that they slip into the pore away from their previous water molecules. According to the Mullins argument this could result in selection of a particular size with discrimination against both smaller and larger hydrated ions. However it is more general to regard the state of hydration as being in a dynamic condition so that a fraction $f$ of the number of a given kind of particles in the solution has a reduced hydration corresponding to excess energy $\Delta E$/mole, according to the Boltzmann distribution $f = \exp (-\Delta E/RT)$. Thus, it can be said that those ions that have lost sufficient water of hydration to become smaller than the pore, can enter the material.

To obtain a quantitative relation between the ease of penetration and the ion size (hydrated) it will be necessary to know the electrostatic force that acts between the ions and the material of the membrane, since this force provides energy equal to $\Delta E$ to displace water of hydration. Eisenman has pointed out that the order of the ease of penetration of univalent cations will depend upon the energy for the ion-fixed charge interaction. The values of the activation energies as determined for a silver iodide membrane for the three electrolytes are found to lie between 5.6 and 7.0 kcal mole$^{-1}$. It is quite probable that the pores of the membrane may have such a size that they allow some of the hydrated sheaths along with the ions to pass through. However in Fig. 7, plots of the hydration numbers and the hydrated ionic volumes vs. $D_i$ show that Li$^+$ having the highest value has the lowest $D_i$ value. The plots of $D_i$ and enthalpy of activation $\Delta H^*$ vs. heats of hydration (Fig. 8) of the individual ions show that Li$^+$ having the lowest value of heat of hydration has the lowest values of $D_i$ and $\Delta H^*$.

Noyes while dealing with the thermodynamics of ion hydration as a measure of the effective dielectric properties of water, has regarded the thermodynamic changes during hydration as a measure of the effective dielectric properties of solvent and shows that $\epsilon_{\text{effective}}$ is primarily a function of the size (crystallographic radii) of such a cation and is virtually independent of charge on it. As, during the diffusion process, adsorbability and polarizability play an important part which will certainly influence and thereby diminish the effective hydration (the higher adsorbability of Li$^+$, Na$^+$, K$^+$ are linked closely with their stepwise stronger polarizabilities and, hence, effective hydration is diminished to a larger extent) it would be quite logical to relate the effective dielectric constant with $D_i$. The plots of $\epsilon_{\text{eff}}$ vs. $D_i$ are shown in Fig. 7, the highest values of $\epsilon_{\text{eff}}$ of K$^+$ giving the largest value of $D_i$.

ACKNOWLEDGEMENT

The authors are grateful to Dr. S. M. F. Rahman, Head of the Chemistry Department, for providing facilities for carrying out these investigations.

SUMMARY

The diffusion of LiCl, NaCl and KCl through parchment-supported silver
iodide membrane has been studied at various temperatures. The diffusion rate is in the order $K\text{Cl} > Na\text{Cl} > Li\text{Cl}$. The membrane resistance $R_m$ and the membrane potential $E_m$ are found to decrease with increase in temperature. The membrane resistance is in the order $R_m(\text{LiCl}) > R_m(\text{NaCl}) > R_m(\text{KCl})$ whereas the membrane potential is in the order $E_m(\text{KCl}) > E_m(\text{NaCl}) > E_m(\text{LiCl})$. The results have been discussed in the light of TMS theory and the views of Sollner, Gregor and Eisenman. The diffusion rate and the enthalpy of activation of diffusion have been related to the number of hydration, heats of hydration and other ionic quantities.

REFERENCES


INTRODUCTION

For the characterisation of the selectivity of ionic membranes, the electrical potentials arising across the ionic membrane have been measured by constructing a cell of the type

Ref. electrode | Solution | Membrane | Solution | Ref. electrode
1 2

the reference electrodes being the saturated calomels connected to the solutions by means of a KCl-agar bridge. The cell potential in this method gives directly the membrane potential. The calculation of the membrane potential and the theoretical approaches for it have been classified into three main groups: (a) the idealised theory of Teorell, Meyer and Sievers (TMS) and its refinements; (b) the pseudo-thermodynamic approach and the treatment based on thermodynamics of irreversible processes and (c) the kinetic approach.

In part I of these investigations, the electrochemical behaviour of the membrane was treated on the basis of TMS theory. In this communication the evaluation of Donnan potentials, diffusion potentials, membrane fixed charge density and perm-selectivity has been carried out on the basis of the TMS model of an ionic membrane.

EXPERIMENTAL

Preparation of the silver iodide membrane
The membrane was prepared as described in Part I.

Measurement of the membrane potential
The potential developed by setting up the concentration cell of the type described by Michaelis

SCE | Solution | Membrane | Solution | SCE
$a_1$ | $a_2$

$a_1 = 10a_2$

was taken as a measure of the membrane potential. The measurements were carried out using a Pye precision vernier potentiometer (No. 7568).

RESULTS AND DISCUSSION

The results of the membrane potential measurements may be discussed in terms of the theories put forward by Michaelis, Meyer and Sievers and also by Teorell. Michaelis held the view that the selective permeability and potential of the collodion membranes were due to preferential adsorption modifying the differential diffusion rates. Willis extended this theory to cupric ferrocyanide, and Malik and Siddiqi applied it to a large number of parchment-supported metal ferro- and ferricyanide membranes thus confirming the earlier view of Sollner that the behaviour of collodion membrane is due to the surface charges fixed on the membrane matrix.

For the evaluation of membrane fixed charge density \( \omega \) by the potentiometric method, Teorell and Meyer have given a method which has been developed and reviewed by Lakshminarayanan. Recently, Altug and Hair have given an ingenious and indirect method, which has also been developed on the lines of Teorell's model, for the evaluation of \( \omega \).

The essential feature of the original fixed charged theory of Teorell was the assumption that the overall membrane potential was composed of three potential jumps: two Donnan potentials at each solution-membrane interface (denoted by \( \pi_1 \) and \( \pi_2 \)), and one residing inside the membrane, the internal potential or driving potential being denoted by \( \phi_2 - \phi_1 \). The overall total membrane potential \( E_{\text{calc}} \) is thus given by:

\[
E_{\text{calc}} = (\pi_1 + \pi_2) + (\phi_2 - \phi_1)
\]

\( \pi_1 \) and \( \pi_2 \) have been calculated according to the equation:

\[
\pi_1 = -\frac{RT}{F} \ln r_1
\]

and

\[
\pi_2 = \frac{RT}{F} \ln r_2 \quad \text{(for uni-univalent electrolytes)}
\]

where \( r_1 \) and \( r_2 \), the Donnan distribution ratios, are determined with the help of the equation

\[
r = \left\{ 1 + \left( \frac{\omega \bar{x}}{2a} \right)^2 \right\}^{\frac{1}{2}} - \left( \frac{\omega \bar{x}}{2a} \right)
\]

where \( a \) is the external solution concentration. The diffusion potential \( \phi_2 - \phi_1 \) for uni-univalent electrolyte is given by:

\[
\phi_2 - \phi_1 = \frac{u-v}{u+v} \frac{RT}{F} \ln \left( \frac{a_1 (r_1 u + v/r_1)}{a_2 (r_2 u + v/r_2)} \right)
\]

\( u \) and \( v \) being the cation and anion mobilities in the membrane. However, in the present calculations, these are assumed to be the same as in solution. Owing to the practical difficulty of measuring ionic activity in the membrane phase, concentrations have

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been used in place of activities, as suggested by Altug and Hair\textsuperscript{12}.

In order to determine the fixed charge density of a parchment-supported silver iodide membrane, various values (e.g., -0.4 N, -0.1 N, etc.) were given to $\omega \bar{x}$ and for each value the total membrane potential was calculated for different concentrations of KCl using the above equations. The curves of total membrane potential vs. concentration were plotted for various $\omega \bar{x}$-values. At the same time, a curve was plotted between the experimentally determined membrane potential values for KCl and the concentrations of KCl (the concentration range being the same in the two cases). The fixed charge density $\omega \bar{x}$ is then the same as that of the theoretical curve which overlaps the experimental curve.

The values of the Donnan potential ($\pi_1 + \pi_2$), the diffusion potential $(\phi_2 - \phi_1)$, and the total membrane potential $E_{calc}$ for various concentrations of KCl (for various values of $\omega \bar{x}$) are given in Table 1A. The values of the observed membrane potential $E_{obs}$ across the silver iodide membrane for various concentrations of KCl are given in Table 1B, (Fig. 1).

### Table 1A

<table>
<thead>
<tr>
<th>$\omega \bar{x}$/N</th>
<th>Cons. $a_1/a_2$/M</th>
<th>($\pi_1 + \pi_2$)/mV</th>
<th>$(\phi_2 - \phi_1)$/mV</th>
<th>$E_{calc}$/mV</th>
</tr>
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<tr>
<td>-0.4</td>
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<td>31.4</td>
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<td>0.1/0.01</td>
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<td>-0.05</td>
<td>56.53</td>
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<tr>
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<td>0.00</td>
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<td>0.00</td>
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<td>-0.02</td>
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<td>2.27</td>
<td>-1.12</td>
<td>1.15</td>
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<td>0.1/0.01</td>
<td>19.7</td>
<td>-0.96</td>
<td>18.74</td>
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<td>31.2</td>
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<td>19.68</td>
<td>-0.95</td>
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<tr>
<td></td>
<td>0.001/0.0001</td>
<td>57.85</td>
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<td>57.85</td>
</tr>
</tbody>
</table>

\textsuperscript{12}J. Electroanal. Chem., 23 (1969) 147-156
TABLE IB

<table>
<thead>
<tr>
<th>Concentration</th>
<th>1 M/0 1 M</th>
<th>0.1 M/0.01 M</th>
<th>0.05 M/0.005 M</th>
<th>0.01 M/0.001 M</th>
<th>0.001 M/0.0001 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed membrane potential $E_{\text{obs}}$ (mV)</td>
<td>0.4</td>
<td>13.9</td>
<td>23.0</td>
<td>41.0</td>
<td>51.67</td>
</tr>
</tbody>
</table>

The fixed charge density of the silver iodide membrane was thus found to be $-0.01 \, \text{N}$. Assuming the same value for fixed charge density, the values of Donnan potentials, diffusion potentials and total membrane potentials were calculated for NaCl, LiCl and NH₄Cl at various concentrations. The calculated and observed values are given in Table 2 and shown in Figs. 2, 3 and 4.

A very good agreement between the observed and calculated values of membrane potential is observed in the case of KCl and NH₄Cl, thus showing that the behaviour of the silver iodide membrane is closely allied to Teorell's model. The agreement is only fair for NaCl but in the case of LiCl the deviation is quite marked. It should be noted that in our calculations we have assumed that the ionic mobilities in the membrane are the same as those in the free solution. The diffusion data in the literature show that the ion mobilities go through a considerable change in a charged phase, and hence apparent anionic mobilities (assuming cationic mobilities to be constant) were calculated as suggested by Willis².

The electrochemical nature of the membrane and its influence on the mobilities

---

TABLE 2
CALCULATED VALUES OF DONNAN POTENTIAL ($\pi_1 + \pi_2$), DIFFUSION POTENTIAL ($\phi_2 - \phi_1$) AND TOTAL MEMBRANE POTENTIAL $E_{\text{m}}$ (ASSUMING $\omega x = -0.01$ N), AND THE OBSERVED VALUES OF MEMBRANE POTENTIAL $E_{\text{obs}}$ ACROSS THE SILVER IODIDE MEMBRANE IN NaCl, LiCl AND NH$_4$Cl OF VARIOUS CONCENTRATIONS (AT 20°C)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concns $a_1/a_2/M$</th>
<th>($\pi_1 + \pi_2)/mV$</th>
<th>($\phi_2 - \phi_1)/mV$</th>
<th>$E_{\text{m}}/mV$</th>
<th>$E_{\text{obs}}/mV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1/0 1</td>
<td>112</td>
<td>-12.12</td>
<td>-11.0</td>
<td>-0.9</td>
</tr>
<tr>
<td></td>
<td>0.1/0.01</td>
<td>10.89</td>
<td>-11.96</td>
<td>-1.07</td>
<td>8.20</td>
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<td></td>
<td>0.05/0.005</td>
<td>19.68</td>
<td>-10.99</td>
<td>8.69</td>
<td>20.11</td>
</tr>
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<td>0.01/0.001</td>
<td>46.25</td>
<td>-4.8</td>
<td>41.45</td>
<td>40.75</td>
</tr>
<tr>
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<td>0.001/0.0001</td>
<td>57.85</td>
<td>-0.1</td>
<td>57.73</td>
<td>48.7</td>
</tr>
<tr>
<td>LiCl</td>
<td>1/0 1</td>
<td>112</td>
<td>-19.1</td>
<td>-17.98</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1/0.01</td>
<td>10.89</td>
<td>-19.22</td>
<td>-8.33</td>
<td>13.1</td>
</tr>
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<td>0.05/0.005</td>
<td>19.68</td>
<td>-18.08</td>
<td>1.6</td>
<td>18.34</td>
</tr>
<tr>
<td></td>
<td>0.01/0.001</td>
<td>46.25</td>
<td>-8.38</td>
<td>37.87</td>
<td>40.57</td>
</tr>
<tr>
<td></td>
<td>0.001/0.0001</td>
<td>57.85</td>
<td>-0.22</td>
<td>57.63</td>
<td>47.75</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>1/0 1</td>
<td>112</td>
<td>-1.16</td>
<td>-0.04</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>0.1/0.01</td>
<td>10.89</td>
<td>-1.1</td>
<td>9.79</td>
<td>15.45</td>
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<tr>
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<td>0.05/0.005</td>
<td>19.68</td>
<td>-0.99</td>
<td>18.69</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>0.01/0.001</td>
<td>46.25</td>
<td>-0.39</td>
<td>45.86</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
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<td>57.85</td>
<td>0.00</td>
<td>57.85</td>
<td>45.0</td>
</tr>
</tbody>
</table>

Fig. 2 Membrane potentials across silver iodide membrane in NaCl of varying concns (○) Calcd values assuming $\omega x = -0.01$ N, (●) observed values.

of anions were also studied by calculating the mobility from the equation

$$u = \frac{z_+ z_2}{u + v} \times \frac{RT}{nF} \ln \frac{f_1 c_1}{f_2 c_2}$$

$E_m$ is the membrane potential) (5)

where the various terms have their usual meanings. This procedure has been used by Willis\(^7\) in the case of a cupric ferrocyanide membrane, and Malik and Siddiqi\(^8\) in the case of a large number of metal ferrocyanide and ferricyanide membranes. The apparent anionic mobilities were calculated over the concentration range 1 — 0.0001
\( M \), keeping \( a_1/a_2 = 10 \). The values of the mobility \( u \) for \( \text{NH}_4^+, \text{K}^+, \text{Na}^+, \text{and Li}^+ \) were taken to be those in free solution. The plots of \( \log 1/a_1 \) (where \( a_1 \) is the higher concentration) vs. apparent anion mobility for all the four electrolytes are shown in Fig. 6. The values of the transport numbers of cations \( t^+ \) were calculated from the equation:

\[
t^+ = \frac{z_+ z_-}{z_+ + z_-} \left( \frac{E_m F}{RT \ln \frac{f_1 c_1}{f_2 c_2}} \right) + \frac{z_+}{z_+ + z_-}
\]

for different electrolytes at various concentrations. The transport numbers of chloride

![Fig. 5. Plots of \( P \) vs. \( \log 1/a_1 \) for various electrolytes. (\( \square \)) \text{NH}_4\text{Cl}, (\( \bullet \)) \text{KCl}, (\( \square \)) \text{NaCl}, (\( \blacksquare \)) \text{LiCl.}](image)

![Fig. 6. Plots of apparent an ion mobility vs. \( \log 1/a_1 \) for various electrolytes. Designations as Fig. 5.](image)
ion in an anionic membrane such as permionic ARX-44 were investigated by Clark et al. They plotted $t_-$ against $\bar{n}$ where $\bar{n}$ is the geometric mean of the concentrations of two solutions across the membrane. A similar procedure was adopted in the case of the membrane under investigation and $\log \bar{n}$ was plotted against $t_+$ for different cations; the plots are shown in Fig. 7. From the Figure it is quite clear that the values of the transport numbers of cations continue to decrease with increase in concentration. Jacobs while using membranes of polymethacrylic acid in KOH solution over a wide concentration range found similar behaviour, i.e. $t_+$ decreased with increasing concentration of the electrolyte.

The permselectivity $P_x$ of the membrane is given by

$$P_x = \frac{t_+ - t_-}{1 - t_+}$$

(7)

where $t_+$ is the transport number in the membrane phase under highly idealized conditions of the TMS model 1 and is given by:

$$t_+ = \frac{E_m}{2E_{\text{max}}} + 0.5$$

(8)

According to Spiegler et al., the permselective materials are defined as the media which transfer certain types of ion in preference to others. Toliday et al. have reported that cupric ferrocyanide membrane behaves similarly in some respects to the electronegative membrane of Sollner. The values of $P_x$ calculated from the above equations are plotted vs. log $1/a_1$ (see Fig. 5). The permselectivity $P_x$ increases abruptly in the region log $1/a_1 \rightarrow 1.5-2.5$. The values of $t_+$, $t_-$, $P_x$ and apparent anion mobility for various concentrations of different electrolytes are summarized in Table 3.

The chief results of all these investigations show that the membrane potential can be determined with reasonable accuracy, and that in the case of a dilute solution it is somewhat closer to the maximum value (highest value of $t_+$ and therefore greatest
TABLE 3

VALUES OF $t_+$, $l_+$, $P$, AND APPARENT ANION MOBILITY FOR VARIOUS ELECTROLYTES AT DIFFERENT CONCENTRATIONS FOR SILVER IODIDE MEMBRANE (AT 20°C)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration</th>
<th>$t_+$</th>
<th>$l_+$</th>
<th>$P$</th>
<th>Apparent anion mobility* ($\text{cm}^2 \text{Ω}^{-1} \text{equiv}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl</td>
<td>1/0.1</td>
<td>0.498</td>
<td>0.498</td>
<td>0</td>
<td>73.7</td>
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<tr>
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<td>0.1/0.01</td>
<td>0.643</td>
<td>0.671</td>
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<td>40.7</td>
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<td>0.05/0.005</td>
<td>0.698</td>
<td>0.74</td>
<td>0.139</td>
<td>31.6</td>
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<tr>
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<td>0.01/0.001</td>
<td>0.887</td>
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<td>0.84</td>
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<tr>
<td></td>
<td>0.001/0.0001</td>
<td>0.893</td>
<td>1</td>
<td>1</td>
<td>8.8</td>
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<tr>
<td>KCl</td>
<td>1/0.1</td>
<td>0.5038</td>
<td>0.504</td>
<td>0.0004</td>
<td>72.3</td>
</tr>
<tr>
<td></td>
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<td>0.634</td>
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<td>1</td>
<td>1</td>
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<tr>
<td>NaCl</td>
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<td>0.491</td>
<td>0.491</td>
<td>0.00</td>
<td>51.6</td>
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<tr>
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<td>0.505</td>
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<td>0.917</td>
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<td>1</td>
<td>3.5</td>
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</table>

* Relative to free solution mobility of K$^+$ being taken as 73.5

value of $P_\text{S}$). With more concentrated solutions this is not so, the membrane potential is progressively smaller than the maximum value. This is readily explained in terms of a decrease in membrane selectivity with increasing concentration of co-ions and diffusion of electrolyte through the membrane. All ion exchange membranes lose permselectivity with increase in concentrations of the solutions they separate. The parchment-supported silver iodide membrane shows high selectivity in the dilute range. In some ways this membrane is similar to an anion exchange membrane. This view is further confirmed by the observation of Heymann and Rabinov18 that, like purified cellulose, parchment also contains exchangeable cations (and therefore acid groups) as part of its structure which may account for its negative charge. The exchangeable cations of this structure will be free to move in the pores and give an apparent increase in the cation mobility and therefore a decrease in the anion mobility (Fig. 6). Within the pores there will be a diffuse ionic atmosphere from the charged wall. The thickness of this atmosphere depends upon electrolyte concentration; in very dilute solutions of the electrolyte which are in contact with the membrane, the thickness becomes so great that only cations are present in the pores and the membrane is cation-permeable only (high value of $P_\text{S}$). As the concentration increases, the thickness of the ionic atmosphere decreases and anions will also be present; at high enough concentrations the ionic atmosphere will be negligible in comparison to the pore radius and the effect of the membrane vanishes.

1 J Electroanal Chem, 23(1969) 147-156
Spiegler et al. working with ion-exchange resin systems have explained the loss in permselectivity as due to increasing penetration of anions and cations into cation and anion exchange resins, respectively, and to the water transport. If the solutions are concentrated, the membrane acts as an inert material and the potential difference between the two solutions approaches the liquid junction potential value.

ACKNOWLEDGEMENT

The authors are grateful to Dr. S. M. F. Rahman, Head of the Chemistry Department, for providing facilities for carrying out these investigations.

SUMMARY

Membrane potentials across parchment-supported silver iodide membrane in NH₄Cl, KCl, NaCl and LiCl solutions of various concentrations have been determined to evaluate fixed charge density \( (\omega \bar{x}) \) and permselectivity of the membrane. \( \omega \bar{x} \) of silver iodide membrane has been found to be \(-0.01\ N\). The effect of concentration on transport numbers, apparent anion mobility and permselectivity has been studied. The results have been discussed in the light of the TMS theory.

REFERENCES

STUDIES ON MEMBRANE CONCENTRATION POTENTIALS ACROSS PARCHMENT-SUPPORTED SILVER IODIDE MEMBRANE IN SOLUTIONS OF SOME ALKALINE EARTH CHLORIDES

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(Received 27th April 1971, in revised form 16th September 1971)

INTRODUCTION

Membrane potentials have been regarded for a long time as a measure of the membrane selectivity. Moreover, studies of membrane potentials constitute one of the various approaches to understanding the mechanism of membrane behaviour. Various factors have been considered as governing membrane potentials. Among these the membrane fixed charge density, pore size and geometry, adsorption, ionic size and ionic mobilities are of key importance. Teorell, Meyer and Sievers, Sollner and Michaelis have discussed these factors critically. Willis studied the membrane concentration potentials across a parchment and a copper ferrocyanide membrane in solutions of various electrolytes and examined the effect of anionic adsorption, ion valency and electrolyte concentration, etc. Malik et al. extended these studies to a number of other ferrocyanide membranes. The fixed charge density of a parchment-supported silver iodide membrane and its permselectivity in solutions of some alkali metal chlorides have already been reported. Little work has, so far, been done on membrane potentials in solutions of 2:1 electrolytes. Willis has reported the concentration effect on membrane potentials across a parchment membrane in solutions of BaCl₂. We have studied membrane concentration potentials across a parchment-supported silver iodide membrane in solutions of BaCl₂, CaCl₂ and MgCl₂ of varying concentrations and the effect of electrolyte concentration on the membrane permselectivity, cationic transport numbers and apparent anionic mobilities for these electrolytes.

EXPERIMENTAL

The membrane was prepared as described earlier. Membrane potentials were measured by constructing a cell of the type:

\[ \text{SCE} | \text{Solution (c₁)} | \text{Membrane} | \text{Solution (c₂)} | \text{SCE} \]

The same electrolyte was used on both sides of the membrane and the concentration ratio \( c₁/c₂ \) was kept equal to 10 throughout. The membrane potential in some cases increased with time whereas in other cases (usually at higher concentrations)...
it decreased with time. The solutions on the two sides of the membrane were changed a number of times until the membrane potential commenced from the same value. This value was taken as the membrane potential at that concentration ratio.

The membrane potentials were measured at 20 ± 1°C with the help of a Pye precision potentiometer.

RESULTS AND DISCUSSION

Membrane potentials across a parchment-supported silver iodide membrane in solutions of BaCl₂, CaCl₂ and MgCl₂ of various concentrations are given in Table 1. The sign of the membrane potential refers to that of the dilute solution.

The cationic transport numbers inside the membrane, $t_+$, have been calculated using Kittelberger's equation:

$$ t_+ = \frac{2}{3} \frac{E_m F}{R T \ln \left( \frac{c_1}{c_2} \right)} + \frac{2}{3} \quad \text{(for a 2:1 electrolyte)} $$

$E_m$ is the membrane potential and the other terms have their usual significance. Concentrations are expressed in equivalents per litre. Permselectivity of the membrane, $P_+$, which is the measure of the membrane selectivity for the counterions over co-ions, was then calculated using the relation

$$ P_+ = \frac{t_+ - t_+}{(1 - t_+)} $$
given by Winger et al., $t_+$ is the transport number of the cation in the free solution.

### Table 1

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration $c_1/c_2$</th>
<th>Membrane potential $E_m$/mV</th>
<th>$t_+$</th>
<th>$P_+$</th>
<th>Apparent anionic mobility $\mu_{aq}$/cm²·s⁻¹·equiv⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCl₂</td>
<td>0.001N/0.001N</td>
<td>24.25</td>
<td>0.9533</td>
<td>0.915</td>
<td>3.12</td>
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<tr>
<td></td>
<td>0.01N/0.001N</td>
<td>20.10</td>
<td>0.9142</td>
<td>0.847</td>
<td>5.97</td>
</tr>
<tr>
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<td>0.05N/0.005N</td>
<td>-3 84</td>
<td>0.6168</td>
<td>0.326</td>
<td>39.53</td>
</tr>
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<td>0.1N/0.01N</td>
<td>-15.07</td>
<td>0.4639</td>
<td>0.067</td>
<td>73.52</td>
</tr>
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<td>1N/0.1N</td>
<td>-26.66</td>
<td>0.3040</td>
<td>-0.121</td>
<td>145.6</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.001N/0.001N</td>
<td>23.40</td>
<td>0.9432</td>
<td>0.889</td>
<td>3.58</td>
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<td>0.01N/0.01N</td>
<td>13.95</td>
<td>0.8383</td>
<td>0.718</td>
<td>11.47</td>
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<td>0.05N/0.005N</td>
<td>-1.60</td>
<td>0.6460</td>
<td>0.396</td>
<td>32.60</td>
</tr>
<tr>
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<td>-12.75</td>
<td>0.4988</td>
<td>0.156</td>
<td>59.75</td>
</tr>
<tr>
<td></td>
<td>1N/0.1N</td>
<td>-23.99</td>
<td>0.3584</td>
<td>—</td>
<td>106.5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.001N/0.001N</td>
<td>20.04</td>
<td>0.9034</td>
<td>0.837</td>
<td>5.67</td>
</tr>
<tr>
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<td>0.8137</td>
<td>0.690</td>
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<td>31.34</td>
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<td>0.4603</td>
<td>0.137</td>
<td>62.20</td>
</tr>
<tr>
<td></td>
<td>1N/0.1N</td>
<td>-27.15</td>
<td>0.3286</td>
<td>0.054</td>
<td>108.3</td>
</tr>
</tbody>
</table>

*J Electroanal Chem* 36 (1972)
Apparent anionic mobility, \( v \) (which not only refers to the relative speed of the anions in the membrane but also to the probability of the anion entering the membrane pore), was calculated relative to the cationic mobility using the equation:

\[
E_m = \frac{u/Z_+ - v/Z_-}{u + v} \frac{RT}{F} \ln \frac{f_1 c_1}{f_2 c_2}
\]

The cationic mobility in the membrane, \( u \), is assumed to be equal to that in the free solution (for \( \text{Ba}^{2+}, \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \), \( u \) has been taken to be 63.64, 59.5 and 53.06 \( \Omega^{-1} \text{cm}^2 \text{equiv}^{-1} \) respectively).

Cationic transport numbers inside the membrane \( i_+ \), permselectivity, \( P_v \), and the apparent anionic mobilities for the three electrolytes are also given in Table 1.

The membrane potential, permselectivity, cationic transport number \( i_+ \) and apparent anionic mobility are shown as functions of \( \log c_1 \) in Figs. 1, 2, 3 and 4 respectively.

In all cases the membrane potential falls with increasing concentration because with increase in external electrolyte concentration more and more co-ions enter the membrane pores and the membrane thus loses its selectivity. Permselectivity and cationic transport number in the membrane also fall with increasing external electrolyte concentrations, for the same reason.

In the case of \( \text{BaCl}_2 \) at the concentration ratio \( 1 \, N/0.1 \, N \), the membrane potential falls even below the liquid junction potential thus indicating that membrane charge reversal (from electronegative to electropositive) has taken place. Furthermore, at the concentration ratio \( 1 \, N/0.1 \, N \), \( i_+ \) becomes less than \( i_- \) and \( P_v \) becomes negative showing thereby the attainment of a positive charge by the membrane.

In the case of \( \text{MgCl}_2 \) the membrane potential does not fall below the liquid junction potential even at the concentration ratio \( 1 \, N/0.1 \, N \).
junction potential, $P$, remains positive and $t_+^*$ remains greater than $t_+$ throughout indicating that adsorption of cations may not be strong enough to reverse completely the membrane charge.

In the case of CaCl$_2$ the membrane potentials are less negative than those for BaCl$_2$ at higher concentrations ($c_1 > 0.05$ N) and at these concentrations, $t_+^*$ values for CaCl$_2$ are greater than those for BaCl$_2$ indicating that the reduction of the membrane charge has taken place to a lesser extent than for BaCl$_2$. However as $t_+$ is not known at 1 N concentration, it has not been possible to determine the permselectivity of the membrane or whether the membrane reverses its charge or not for CaCl$_2$ at 1 N/0.1 N concentration ratio.

In all the cases reported apparent anionic mobility increases with increasing concentration of the external electrolytes thus showing that more and more anions enter the membrane pores and also that their speed inside the membrane pores increases relative to that of the cations. In the higher concentration range, the increase in the apparent anionic mobility is more pronounced in the case of BaCl$_2$ because the charge reversal of the membrane results in the reduction of the cationic mobility inside the membrane.

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MEMBRANE POTENTIALS ACROSS PARCHMENT

(S.P.) is also grateful to the Ministry of Defence, Government of India for the grant of a leave for study.

SUMMARY

Membrane concentration potentials across a parchment-supported silver iodide membrane in solutions of BaCl₂, CaCl₂ and MgCl₂ of different concentrations have been measured. The effect of the external electrolyte concentration on the membrane potential, membrane permselectivity \( P_m \), cationic transport number in the membrane \( t^+ \) and apparent anionic mobility have been studied. Membrane potential, \( P_m \) and \( E_+ \) fall, whereas apparent anionic mobility increases, with increase in external electrolyte concentration. This behaviour has been attributed to the loss of membrane selectivity with increase in external electrolyte concentration as well as to the reduction in the membrane fixed charge density due to adsorption of cations at higher electrolyte concentrations. In the case of BaCl₂ at a concentration ratio of 1N/0.1 N the membrane charge reverses its sign from electronegative to electropositive.

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J Electroanal Chem, 36 (1972)
DIFFUSION OF ALKALI AND ALKALINE EARTH CHLORIDES THROUGH PARCHMENT SUPPORTED SILVER IODIDE MEMBRANE

By

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ABSTRACT

Diffusion rates of KCl, NaCl, LiCl, BaCl₂, and MgCl₂ through a parchment supported silver iodide membrane have been measured at various temperatures using a constant flow method. Activation energies and various Eyring activation parameters for the diffusion of these electrolytes have also been evaluated. The diffusion rate sequences obtained are KCl > NaCl > LiCl and BaCl₂ > CaCl₂ > MgCl₂ and they point towards the weak field strength of the membrane fixed charged groups. Diffusion coefficients and the various Eyring activation parameters have been related to the ionic hydrated sizes and the various thermodynamic quantities of ionic hydration thus emphasizing the importance of ion hydration in diffusion across the membrane.

INTRODUCTION

Permeability of inorganic precipitate membranes to electrolytes has been the subject of investigation of a number of workers. Various factors have been considered as governing the diffusion process across membranes. According to Teorell, Meyer, and Sievers the walls of the membrane pores carry a number of fixed charges due either to adsorption or ionization. A Donnan type of equilibrium excludes the cations from the membrane pores (the exclusion being complete in case of the membranes in contact with dilute solutions) whereas the counter-

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ions are free to move in the pores. The membrane, thus, behaves like an ion exchanger.

The basis for the counterion selectivity of ion exchangers (tendency to show preference for one counterion over the other) has been worked out by Gregor\(^5\), Eisenman\(^6\) and Sherry\(^7\). Whereas Gregor emphasized the importance of hydrated ionic size, Eisenman and Sherry regarded the energetics of hydration and ion-site interaction as of key importance. It was, therefore, thought worth while to measure the diffusion rates of various alkali and alkaline earth chlorides (KCl, NaCl, LiCl, BaCl\(_2\), CaCl\(_2\), and MgCl\(_2\)) through a parchment supported silver iodide membrane and to investigate the relationships between the diffusion rates of electrolytes and the energetics of diffusion on the one hand and the hydrated ionic size and the energetics of ionic hydration on the other. The results are presented in this paper.

EXPERIMENTAL

Preparation of Silver Iodide Membrane

Parchment supported silver iodide membrane was prepared as described earlier\(^3\). The area of cross section of the membrane and the average thickness of the membrane were 24.62 cm\(^2\) and 0.026 cm respectively.

Measurement of Diffusion Rate

The diffusion rates were measured using the constant flow method suggested by Hartung et al.\(^1\). In this method the electrolyte (0.2M) and double-distilled water were allowed to flow at known rates through the upper and lower half-cells, respectively, of a cell having the membrane fixed horizontally in between the two half-cells. The concentration of the effluent coming out from the lower
half cell was measured conductometrically. After some time it reached a steady value. From this steady concentration value and the flow rate the diffusion rate was calculated.

The conductivity measurements were carried out with the help of a WTW type LBE/8 conductivity bridge. (This conductivity meter uses a Wheatstone bridge and measures resistance only.)

RESULTS AND DISCUSSION

Diffusion rates, \( D_T \), for the electrolytes have been measured at five temperatures \( (10^\circ, 15^\circ, 20^\circ, 25^\circ, \text{ and } 30^\circ \text{ C.}) \). From these diffusion rates corresponding diffusion coefficients, \( D_C \), have been calculated using the expression

\[
D_T = D_C \left( \frac{A}{t} \right) \Delta C \quad \ldots \quad (1)
\]

where \( A \) and \( t \) are the area of cross section and average thickness of the membrane respectively, and \( \Delta C \) is the concentration difference across the membrane at the steady state.

From the plots of \( \log D_C \) against \( 1/T \) (\( T \) is the absolute temperature), shown in Figure 1, energies of activation, \( E_A \), for the diffusion of these electrolytes have been calculated. The enthalpy of activation \( \Delta H^\pm \), entropy of activation \( \Delta S^\pm \), and the free energy of activation \( \Delta G^\pm \), have then been calculated using the following relations

\[
\Delta H^\pm = E_A - RT \quad \ldots \quad (2)
\]

\[
D_C = \frac{1}{\sqrt{\pi}} \left( kT/h \right) \exp \left( \frac{\Delta S^\pm}{R} \right) \exp \left( -\frac{\Delta H^\pm}{RT} \right) \ldots (3)
\]

\[
\Delta G^\pm = \Delta H^\pm - T \Delta S^\pm \quad \ldots \quad (4)
\]
Here $k$ is the Boltzmann constant, $h$ is Planck's constant, and $\lambda$, the mean distance between successive equilibrium positions, has been assumed to be 3 Å for alkali chlorides and 5 Å for alkaline earth chlorides. The values of $\lambda$ chosen for the alkali and alkaline earth chlorides are of the order of the mean distance of approach of ions for these electrolytes as has also been done by Tien and Ting. Diffusion coefficients, activation energies, and various Eyring parameters for various electrolytes are given in Table 1.

From equations (3) and (4) it follows that $D_C$, the diffusion coefficient, and $\Delta G^\ddagger$, the free energy of activation, should vary in opposite directions, and this is in agreement with our data. However, the diffusion coefficient of an electrolyte is not solely governed by the activation energy as the entropy of activation, $\Delta S^\ddagger$, has also to be considered. Thus KCl may diffuse faster than NaCl if $\Delta S^\ddagger$ for KCl is greater than that for NaCl even though the activation energy for KCl may be greater than that for NaCl as reported in Table 1. Larger $\Delta S^\ddagger$ for KCl implies a greater probability of the formation of activated complex. Variation of permeability and activation energy in similar directions have also been reported by Gregor et al. and Hogg et al.

The diffusion of an electrolyte through a membrane is slower than its diffusion in free solution. This is due to a number of factors such as the pore size of the membrane, fixed charges attached to the membrane pores, pore geometry, etc. The membrane may show preference
### Table I

VALUES OF DIFFUSION COEFFICIENTS, $D_{0}$, AT VARIOUS TEMPERATURES, ACTIVATION ENERGIES, $E_A$, AND VARIOUS EYRING ACTIVATION PARAMETERS (at 25°C) FOR THE DIFFUSION OF VARIOUS ELECTROLYTES ACROSS A SILVER IODIDE MEMBRANE

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temp. (°C)</th>
<th>$10^5 D_{0}$ (cm²-s⁻¹)</th>
<th>$E_A$ (cal mol⁻¹)</th>
<th>$\Delta H^\ddagger$ (cal mol⁻¹)</th>
<th>$\Delta S^\ddagger$ (cal K⁻¹mol⁻¹)</th>
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to one counterion over the other. This results in selective ion exchange and in different diffusion rates of the electrolytes having the same cation but different counterions. According to Gregor\(^5\), an ion exchanger discriminates amongst various counterions on the basis of their hydrated size. However, Gregor's theory fails to account for a number of actually observed reversed affinity sequences.

According to Eisenman, the selectivity depends upon the energetics of hydration and the ionsite interaction. For ion exchangers with fixed charged groupings having weak field strength the selectivity sequence is governed by the differences in the hydration energies of counterions. In such cases the normal selectivity sequence \(K > Na > Li\) should result. On the other hand for the ion exchangers with charged groupings having high field strength the selectivity sequence is governed by crystallographic radii of counterions. In such cases the selectivity sequence \(Li > Na > K\) should result.

Eisenman predicted a number of intermediate selectivity sequences for alkali metal ions for ion exchangers with charged groups of intermediate field strengths. Sherry\(^7\) working on the lines of Eisenman predicted a number of selectivity sequences for alkaline earth ions, the two extreme ones being \(Ba > Ca > Mg\) (for low field strength groups) and \(Mg > Ca > Ba\) (for high field strength groups). On the basis of the Eisenman - Sherry theory, the diffusion rate sequences obtained in our case, viz., \(KCl > NaCl > LiCl\) and \(BaCl_2 > CaCl_2 > MgCl_2\) point towards the weak field strength of the charged groups of the silver iodide membrane. The diffusion coefficients of these electrolytes and the free energies of activation for diffusion of these electrolytes may, therefore, be closely related to the free energies
of hydration of cations. Plots of diffusion coefficients (at 25°C) of various electrolytes against $\Delta H_{\text{hyd}}$ and $\Delta S_{\text{hyd}}$ values (also at 25°C) for the corresponding cations (Fig. 2) and the plots of $\Delta H_f$, $\Delta G_f$, and $\Delta S_f$ values (at 25°C) for the diffusion of various electrolytes against $\Delta H_{\text{hyd}}$, $\Delta S_{\text{hyd}}$, and $\Delta S_{\text{hyd}}$ values respectively for the corresponding cations (Fig. 3-5) show that such a relationship exists. The thermodynamic values for the hydration of various cations are taken from Noyes's data.\(^3\)

As the selectivity sequences predicted by Gregor are the same as those predicted by Eisenman and Sherry for the membranes with charges having weak field strength, the diffusion rates obtained in our cases should show dependence upon hydrated cation sizes in the way suggested by Gregor. This is quite clear from the observed diffusion rate sequences; $\text{K}^+$ and $\text{Ba}^{2+}$ having the smallest hydration sizes have the largest diffusion coefficients amongst alkali and alkaline earth chlorides respectively.

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