Studies with Model Membrane: Determination of Fixed Charge Density of Silver Sulfite Membrane

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Abstract: Parchment-supported silver sulfite membrane has been prepared by the interaction method. The membrane potential across the membrane in contact with different 1:1 electrolytes has been measured. The experimentally measured membrane potential values were used to evaluate the thermodynamically effective fixed charge density of the membrane-electrolyte systems using Teorell, Meyer, and Sievers (T. M. S.), Altug and Hair, and Kobatake et. al. theories. The values of effective charge densities were quite low (they were in order of $10^{-2}$ – $10^{-3}$ eq/l) and hence very difficult to determine by usual exchange methods. The values of effective charge densities by different theories were the same order of magnitude for each membrane-electrolyte system. The theoretical predictions for membrane potential were borne out quite satisfactorily by experimental results obtained with the membranes. Apparent transference numbers of coions and permselectivity values of the membrane-electrolytes have also been calculated. A method based on permselectivity values for determination of charge density was also used. It was interesting to note that the charge densities evaluated from two methods of Kobatake and co-workers gave similar values and that the results were comparable to those derived from the TMS method.

Keywords: Membrane Potential, Fixed Charge Density, Permselectivity, Parchment Supported Membrane

1. Introduction

Large amount of interesting works have been published for developing new membranes with desired properties, on account of their utilization for the economic separation processes. In this regard ion-exchange membranes have emerged as the most advance and economical separation membranes. These membranes are being widely used for the processes like electro dialysis of sea water or brackish water, separation of inorganic toxic metal ions, pharmaceutical products, sugar processing and beverages industries [1–5]. A variety of membranes can be constructed whose structure is well defined and whose permeation mechanisms and particular parameters can be varied in a controlled manner. By correlating structure and ion permeation in such membranes, it should be possible to develop experimental criteria for determining the structure, and hence the mechanism of ion permeation through an unknown membrane. In an attempt to develop these criteria a number of inorganic precipitated membranes [6–9] have been prepared with ion exchange sites and have studied the extent to which their chemical and transport properties depend on various external forces such as different chemical environments, temperature etc. The ionic selectivity of a membrane and the concentration range of the external salt solution in which its cationic behavior is shown both depend strongly on the fixed charge concentration of the membrane. The membrane fixed charge density can be determined using several methods: analytical titration [10], streaming potential measurements [11], and membrane potential measurements [12, 13]. In previous works, we have studied different parchment-supported membranes in order to evaluate the fixed charge density and to study the permeation of different electrolytes [14-20]. In this paper, we describe the preparation of silver sulfite parchment supported membrane. The effective charge density which is considered as the most effective parameter controlling the membrane phenomena, have been determined by the different methods using
2. Experimental

2.1. Preparation of Membrane

All the reagents used were of AR grade (BDH) without further purification and their solutions were prepared in deionized water.

Parchment supported silver sulfite membrane was prepared by the method of interaction described by Siddiqi et al. [21-24]. First parchment (Supplied by M/s Baird and Tatlock London Ltd.) was soaked in distilled water for about two hours and then tied to the flat mouth of a beaker containing 0.2 M silver nitrate solution. This was suspended for 72 h in a 0.2 M sodium sulfite solution at room temperature. The two solutions were interchanged and kept for another 72 h. In this way fine deposition of silver sulfite was obtained on the surface of parchment paper. The membrane thus obtained was well washed with deionized water for the removal of free electrolytes. The membrane was clamped between two half cells of an electrochemical cell. The membrane prior to the measurements had been aged by about 24 h immersion in 1 M in the testing electrolyte.

2.2. Membrane Potential Measurements

The potential developed by setting up a concentration cell of the type in Figure 1 described by Siddiqi et al. [25]. The membrane potential was obtained by taking the same electrolyte at different concentrations on the two sides of the membrane, such that the concentration ratio \( \gamma = 10 \). The potentials were monitored by means of Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at 30 \( \pm 0.1^\circ \)C. The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The 1:1 electrolytes examined were sodium chloride, potassium chloride, ammonium chloride, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium bromide, and sodium acetate.

\[
E = 59.16 \log \frac{C_2}{C_1} \sqrt{\frac{4C_1^2+X^2+x^2}{4C_1^2+X^2}} + U \log \frac{4C_2^2+X^2+u^2}{4C_2^2+X^2+u^2}
\]

Where:

\[
U = \frac{U_a - U_m}{U_i + U_m}
\]

The values of membrane potentials are low when the membrane is used to separate concentrated solutions whereas they increase with dilution and reach a maximum limit. The signs of membrane potentials with different electrolytes are positive. This means that the membrane is negatively charged and cation selective. And the selectivity increases when the concentrations of electrolyte are decreased. The negative charge on the membrane surface may be attributed to adsorption of anions.

3.1. Teorell, Meyer, and Sievers (T. M. S.) Method

The graphical method of Teorell, Meyer, and Sievers determines the fixed charge density \( X \) in equivalent per litter and the cation-to-anion mobility ratio \( (u_+/u_-) \) in the membrane phase. Theoretical concentration potentials \( (E_m) \) existing across the membrane carrying a net negative charge of unity \( (X = 1) \) and different mobility ratios are calculated with the help of equation (1) as a function of \( \gamma \). The concentration ratio \( (C_1/C_2) \) being kept at constant value for different mobility ratios.

3. Results and Discussion

Effective fixed charge density of parchment-supported silver sulfite membrane has been estimated from membrane potential data. The potentiometric methods used for estimation were: Teorell-Meyer-Sievers method [26, 27], Altug and Hair method [28] and Kobatake et al. method [29]. The experimentally determined membrane potentials which were generated between both sides of the parchment-supported silver sulfite membrane for various 1:1 electrolytes at different concentrations \( C_1 \) and \( C_2 \) such that \( C_2/C_1 = 10 \) are given in Table 1.

![Figure 1. Concentration cell.](image)
\(E_m\): membrane potential in millivolts

\(u_+\) and \(u_-\): Mobilities of cation and anion respectively in the membrane

\(C_1\) and \(C_2\): Concentrations of the electrolyte solutions on either side of the membrane

\(X\): Charge density expressed in equivalents per liter

The values thus calculated are plotted as a function of \(\log (1/C_2)\) as illustrated in Figure 2. The observed membrane potential values given in Table 1 for each electrolyte solution are also plotted in the same graph as a function of \(\log (1/C_2)\). The experimental curve is shifted horizontally until it coincides with the theoretical curve. The extent of this shift gives \((\log X)\) and coinciding theoretical curve, the value for \((u_+/u_-)\). The values derived in this way are given in Table 2. Some experimental curves do not coincide exactly as demanded by the theoretical method of T.M.S. and very rough approximation has been made. The reason for these discrepancy is low charge density of the membrane. This method gave satisfactory results for the fixed charge density evaluation, the values of which are found to be low and hence very difficult to determine by the usual exchange reaction.

The limitations of this conceptually useful theory which has stimulated both theoretical and experimental work, are applicable only to an idealized system and this should be borne in mind when it is applied to analyze membrane phenomena.

**Figure 2.** Membrane Potential vs. \(\log (1/C_2)\) in contact with different concentrations of NaCl (TMS method).

**Table 2.** Comparison of Charge density values \(X\) (eq.1') by different methods for various electrolytes for silver sulfite membrane.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>T M S</th>
<th>Altug and Hair</th>
<th>Kobatake et al.</th>
<th>Permeability values</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.035</td>
<td>0.050</td>
<td>0.036</td>
<td>0.038</td>
</tr>
<tr>
<td>KCl</td>
<td>0.007</td>
<td>0.008</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>NHCl</td>
<td>0.013</td>
<td>0.010</td>
<td>0.011</td>
<td>0.009</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.010</td>
<td>0.020</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>KNO₃</td>
<td>0.006</td>
<td>0.010</td>
<td>0.009</td>
<td>0.006</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>0.007</td>
<td>0.010</td>
<td>0.009</td>
<td>0.005</td>
</tr>
<tr>
<td>NH₄Br</td>
<td>0.008</td>
<td>0.010</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>CH₃CO₂Na</td>
<td>0.010</td>
<td>0.010</td>
<td>0.010</td>
<td>0.009</td>
</tr>
</tbody>
</table>

3.2. Altug and Hair Method

In a modification of the type of plot of TMS, Altug and Hair evaluated \(\omega X\) for glass membranes, choosing the solution values \((u_+, u_-)\). In this method, a value of \(\omega X\) was assumed and the distribution ratios \((r_1, r_2)\) were calculated according to equation (3) for the given electrolyte concentrations \(C_1\) and \(C_2\), the theoretical membrane potential was then determined from equation (4) for each electrolyte and concentration range:

\[
r = \frac{C}{a} = \sqrt{1 + \frac{(\omega X)}{2a} - \frac{(\omega X)^2}{2a}}
\]

\[
E_m = \frac{u_+ - u_-}{u_+ + u_-} \frac{RT}{F} \ln \left( \frac{\frac{a_1(r_1u_+ + u_-)}{a_2(r_2u_+ + u_-)}}{r_1} \right) + \frac{RT}{F} \ln \frac{r_2}{r_1}
\]

Where:

\(\omega = \pm 1\), depending on the nature of the dissociated sites \(r_1\) and \(r_2\): Donnan distribution ratios at the two interfaces

\(\omega X\): Membrane charge density

By following the algebraic procedure, a series of theoretical curves were obtained and are shown by the solid lines in Figure 3. The experimental values of membrane potential observed for each electrolyte have been also plotted against concentration in the same figure (3). The theoretical curve which almost nearly coincides with the experimental one gives the value of fixed charge density. The values derived in this way are given in Table 2. The method of Altug and Hair gave effective fixed charge density values somehow different to those given by T. M. S. method. This is because it is not very realistic to use the bulk solution mobility ratios in the calculations. The mobilities undergo a change in the membrane phase, so it is expected that Altug and Hair method overestimate fixed charge density in comparison T. M. S. method.

**Figure 3.** Membrane potential vs. \(\log (1/C_2)\) in contact with different concentrations of NaCl.

3.3. Evaluation of Effective Fixed Charge Density and Apparent Transference Numbers According to Kobatake et al

Equation (5) indicates that a value of \(\beta\) and a relation between \(\alpha\) and \(X\) can be obtained of a plot of \(\Delta E_m\) against \(C_2\) at fixed \(\gamma =10\) (in the region of very low concentration, from 0.05 M to 0.005 M – Figure 4). The values of \(\beta\) and the relation between \(\alpha\) and \(X\) can be determined by evaluating the intercept and initial slope. The value of intercept is equal
The values of $\alpha$, $\beta$, $X_d$ against $1/C_2$ intercept, $\gamma$ may be evaluated.

$$|\Delta E_{mr}| = \frac{1}{\beta} \ln \gamma - \frac{1}{2} \left( 1 + \frac{\alpha}{\gamma} \right)$$

Equation (6) indicates that the intercept of a plot of $1/t_{-app}$ against $1/C_2$ at fixed $\gamma = 10$ allow the values of $\alpha$ to be determined in the region of high salt concentrations (from 1 M to 0.05 M). The values of the apparent transference number of co-ion calculated using equation (7) are given in Table 3. Plots of $1/t_{-app}$ against $1/C_2$ for various 1:1 electrolytes are given in Figure 5. From the value of intercept, $\gamma$ may be evaluated.

$$\Delta E_{mr} = (1 - t_{-app}) \ln \gamma$$

Where:
- $\alpha$ and $\beta$: Parameters independent of salt concentration
- $\Delta E_{mr}$: Reduced membrane potential
- $\gamma = C_2 / C_1$
- $t_{-app}$: Apparent transference number for co-ion in a negatively charged membrane

For the evaluation of $X$, there are two limiting cases: (a) in dilute range from the slope of equation (5). This value of $X$ is designated by $X_s$; (b) in the concentrated range from the slope of equation (6). This value of $X$ is designated by $X_c$. The values of $\alpha$, $\beta$, $X_s$, and $X_c$ derived in this way for membrane and 1:1 electrolytes are given in Table 4.

For the evaluation of effective fixed charge density, the various values of permselectivity $P_s$ were calculated by substituting the values of $\alpha$ and $t_{-app}$ in equation (8), and the values of permselectivity are given in Table 5, and then plotted against $\log [C_1 + C_2]/2$. The results are shown in Figure 6.

$$\frac{1}{P_s} = \frac{1}{\alpha - (2\alpha - 1)(1 - t_{-app})}$$

The term $\zeta$ has already defined as:
\[ \zeta = \frac{C}{\phi X} \]  \hspace{1cm} (9)

When the average concentration \( C \) is equal to the effective fixed charge density \( \phi X \), the value of \( P_s \) must give \( 1/\sqrt{5} = 0.448 \) from left hand side equation (8). The corresponding concentration is obtained from the plot of \( P_s \) versus log \( C \) as given in Figure 6. This value of concentration is equal to the fixed charge density. The values are given for various electrolytes in Table 2.

![Figure 6. Plot of \( P_s \) against log \([C_1 + C_2]/2\) in contact with different concentrations for various electrolytes.](image)

### Table 5. Values of permselectivity \( P_s \) for various electrolytes at different concentrations at 30°C.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>NaCl</th>
<th>KCl</th>
<th>NH₄Cl</th>
<th>NaNO₃</th>
<th>KNO₃</th>
<th>NH₄NO₃</th>
<th>HBr</th>
<th>CH₃O₂Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.034</td>
<td>0.012</td>
<td>0.017</td>
<td>0.020</td>
<td>0.018</td>
<td>0.008</td>
<td>0.013</td>
<td>0.021</td>
</tr>
<tr>
<td>0.5</td>
<td>0.148</td>
<td>0.036</td>
<td>0.044</td>
<td>0.042</td>
<td>0.035</td>
<td>0.035</td>
<td>0.043</td>
<td>0.040</td>
</tr>
<tr>
<td>0.2</td>
<td>0.273</td>
<td>0.087</td>
<td>0.105</td>
<td>0.084</td>
<td>0.070</td>
<td>0.083</td>
<td>0.074</td>
<td>0.073</td>
</tr>
<tr>
<td>0.1</td>
<td>0.416</td>
<td>0.148</td>
<td>0.182</td>
<td>0.165</td>
<td>0.141</td>
<td>0.135</td>
<td>0.148</td>
<td>0.154</td>
</tr>
<tr>
<td>0.05</td>
<td>0.498</td>
<td>0.256</td>
<td>0.275</td>
<td>0.332</td>
<td>0.209</td>
<td>0.217</td>
<td>0.307</td>
<td>0.314</td>
</tr>
<tr>
<td>0.02</td>
<td>0.560</td>
<td>0.401</td>
<td>0.443</td>
<td>0.449</td>
<td>0.394</td>
<td>0.356</td>
<td>0.421</td>
<td>0.438</td>
</tr>
<tr>
<td>0.01</td>
<td>0.600</td>
<td>0.489</td>
<td>0.520</td>
<td>0.535</td>
<td>0.481</td>
<td>0.460</td>
<td>0.512</td>
<td>0.516</td>
</tr>
<tr>
<td>0.005</td>
<td>0.610</td>
<td>0.571</td>
<td>0.583</td>
<td>0.580</td>
<td>0.555</td>
<td>0.504</td>
<td>0.548</td>
<td>0.548</td>
</tr>
</tbody>
</table>

Further, the plots of \( P_s \) against \( 1/(1 + 4\zeta)^{1/2} \) were drawn for silver sulfate membrane with each electrolyte and shown in Figure 7. It is evident that the line nearly passes through the origin with unit slope, confirming the applicability of Kobatake's equation to the membrane.

The values of fixed charge density obtained by using the different equations of Kobatake are found to be closer to that obtained by T. M. S. Also the test achieved to analyze the obtained values revealed the correctness of the results and the suitability of the method. The theoretical predictions based on Kobatake's membrane potential expression are borne quite satisfactorily by our experimental results on parchment-supported membrane.

![Figure 7. Plots of \( P_s \) against \( 1/(1 + 4\zeta)^{1/2} \) for various 1:1 electrolyte solutions with silver sulfate membrane.](image)

### 4. Conclusions

The comparison of these results shows that the effective fixed charge density of silver sulfate membrane is not constant quantity and depends upon the type of the electrolyte in contact with it.

The values of fixed charge density determined using different methods are to be of the same magnitude, and the little differences between them are broadly well accepted considering the fact that they are in order of \( 10^{-2} \) to \( 10^{-3} \) eq/l, so quite low to determined exactly.

The analytical methods based on Teorell, Meyer, and Sievers [26, 27], Altug and Hair [28], and Kobatake [29] equations for membrane potential gave satisfactory values for effective charge densities evaluations, the values of which are quite low and hence very difficult to determine by the usual exchange methods, confirming thereby the validity of the above different theories for our membrane.

The values of fixed charge density obtained by using the different equations of Kobatake for diverse membrane-electrolyte system are found to be closer to that obtained by T.M.S.

### References


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