Potentiometric determination of fixed charge density and permselectivity for Thallium Chromate membrane

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Abstract
Membrane potentials have been measured across parchment-supported thallium chromate membrane separating various 1:1 electrolytes at concentrations $C_1$ and $C_2$ such that $C_2 = 10 C_1$. Membrane potential data have been used to calculate transference number of ions, permselectivity, and also to evaluate the effective fixed charge density which is an important characteristic governing the membrane phenomena by utilizing the generally accepted and most widely used theory of the Teorell-Meyer-Sievers method (T.M.S.), Altug and Hair method, the recent theories for membrane potential of Kobatake et al, and Nagasawa et al. The values of charge densities derived from different theories were almost the same, confirming thereby the validity of the recently developed theories of membrane potential.

Keywords: Membrane potential, Fixed Charge density, Potentiometry

1.0 Introduction
Transport processes occurring across artificial membranes separating different salt solutions are of great interest to chemists, chemical engineers, and biologists. Chemists and chemical engineers would like to understand the mechanism of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as models for the physiological membranes in order to understand and establish physicochemical principles and to understand the behavior of complex cell membranes. As a result ion-exchange membranes have emerged as the most advance and economical separation membranes for scientific purpose. 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]. The applicability of ion-exchange membranes may be limited without knowing the transport properties of membranes. Since the transport phenomena validate the performance of the membranes and hence provoked various industrial applications. Several membranes have been prepared using inorganic precipitates salt. However these inorganic membranes have sufficiently low chemical stability in acidic and alkaline medium due to dissolution of inorganic phosphate into inorganic salt [6]. 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 [7–9] 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 the present study, the titration method proved inconvenient and very inaccurate. Consequently, the potentiometric method was used. In this paper, we describe the preparation of thallium chromate 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 membrane potential measurements. In the present work also, an attempt has been done to prepare and study properties of inorganic membrane that is Thallium Chromate membrane.

2.0 Materials and Methods
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 thallium chromate was prepared by the method of interaction described by Siddiqi et al. [14-17]. 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 Thallium nitrate solution. This was suspended for 72 hours in a 0.2 M potassium chromate solution at room temperature. The two solutions were interchanged and kept for another 72 hrs. In this way fine deposition of thallium chromate 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 hrs immersion in 1 M in the testing electrolyte.

Scheme-1

2.2 Membrane Potential Measurements
The potential developed by setting up a concentration cell of the type shown in scheme-1 and described by Siddiqi et al. [18]. 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 $\sigma = 10$. The potentials were monitored by means of Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at $25 \pm 0.1^\circ C$. The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The uni-univalent electrolytes examined were lithium chloride, sodium chloride, potassium chloride, and ammonium chloride.

Nomenclature
$E_m$: Membrane Potential in millivolts
$u_+ \text{ and } u_- $: Moieties of cation and anion, respectively, in the membrane
$C_1 \text{ and } C_2$: Concentrations of the electrolyte solutions on either side of the membrane
$X$: Charge density expressed in equivalents per liter
$aX$: Membrane charge density
$a = 1,1$, depending on the nature of the dissociated sites
$r_1 \text{ and } r_2$: Donnan distribution ratios at the two interfaces
$G$: Concentration in the membrane phase
$a$: External solution activity
$R$: Molar gas constant
$T$: Absolute temperature of the system
$F$: Faraday constant
$\alpha$ and $\beta$: Parameters independent of salt concentration
$\Delta E_m$: Reduced membrane potential
$\sigma = \frac{C_2}{C_1}$
$\sigma_{app}$: Apparent transference number for cation in a negatively charged membrane
$\Delta X$: Thermodynamically effective fixed charge density of the membrane
$\phi$: Fraction of counterions in the unbound form
$\tau$: Mass fixed transference number of cation in the membrane
$P_f$: Permeability of the membrane–electrolyte system
### Table-1: Observed membrane potential (mV) across thallium chromate membrane at 25±0.1°C

<table>
<thead>
<tr>
<th>(C₂/C₁), M</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>NH₄Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0/0.1</td>
<td>-10</td>
<td>-1</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>0.5/0.05</td>
<td>-4</td>
<td>3</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>0.2/0.02</td>
<td>4</td>
<td>12</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>0.1/0.01</td>
<td>12</td>
<td>22</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>0.05/0.005</td>
<td>27</td>
<td>33</td>
<td>34</td>
<td>33</td>
</tr>
<tr>
<td>0.02/0.002</td>
<td>35</td>
<td>39</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>0.01/0.001</td>
<td>40</td>
<td>40</td>
<td>43</td>
<td>41</td>
</tr>
<tr>
<td>0.005/0.0005</td>
<td>43</td>
<td>41</td>
<td>44</td>
<td>42</td>
</tr>
</tbody>
</table>

### 3.0 Results and Discussion

**Evaluation of effective fixed charge density by potentiometric methods**

The methods of Teorell-Meyer-Sievers [19-21], Altug and Hair [22], Kobatake et al [23, 24], and the most recent one of Nagasawa and co-workers [25, 26] were used for the evaluation of fixed charge density of membrane. The inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations [27-28]. This property is attributed to the presence of a net charge on the membrane due to absorption of anions or cations. The values of membrane potential measured in contact with different concentrations of various 1:1 electrolytes are given in Table-1.

The values of potentials observed across the membrane under investigation are low when these are used to separate concentrated solutions whereas it increases with dilution and reaches a maximum limit. This means that the membrane is negatively charged and selectivity increases with dilution. The negative charge may be attributed to the preferential absorption of a common anion between inorganic precipitate and the solution used for the preparation of the membrane. Two important factors which control electrolyte permeability through a membrane are charge on the membrane and its porosity. The fixed charged groups present on the membrane can be determined by potentiometric methods.

![Figure-1: Membrane Potential vs. log (1/C₂) in contact with different concentrations of LiCl (TMS method)](image-url)
Table-2: Comparison of charge density (eq. 1\textsuperscript{1}) by different methods for various electrolytes at 25±0.1°C

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>TMS method</th>
<th>Altug &amp; Hair method</th>
<th>Kobatake et al method</th>
<th>Nagasawa et al method</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.022</td>
<td>0.020</td>
<td>0.019</td>
<td>0.032*</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.017</td>
<td>0.020</td>
<td>0.018</td>
<td>0.030*</td>
</tr>
<tr>
<td>KCl</td>
<td>0.028</td>
<td>0.020</td>
<td>0.020</td>
<td>0.028*</td>
</tr>
<tr>
<td>NH\textsubscript{4}Cl</td>
<td>0.027</td>
<td>0.030</td>
<td>0.026</td>
<td>0.032*</td>
</tr>
</tbody>
</table>

* From Permselectivity values

3.1 Teorell, Meyer, and Sievers method (TMS 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 are calculated with the help of equation (1) as a function of \(C_2\), the concentration ratio (\(C_1/C_2\)) being kept at constant value for different mobility ratios.

\[
E_m = 19.16 \log \left[ \frac{C_2^{4C_1^2 + X^2 + X}}{C_1^{4C_2^2 + X^2 + X}} + U \log \frac{\sqrt{4C_2^2 + X^2} + UX}{\sqrt{4C_1^2 + X^2} + UX} \right]
\]

Where:

\[
U = \frac{u_+ - u_-}{u_+ + u_-}
\]

The values thus calculated are plotted (Figure-1). The observed membrane potential values are also plotted in the same graph as a function of log (1/C\textsubscript{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. This method gave satisfactory result 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.

![Figure-2: membrane potential vs. log (1/C\textsubscript{2}) in contact with different concentrations of LiCl (Altug & Hair method)](image-url)

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:
By following the algebraic procedure, a series of theoretical curves were obtained and are shown by the solid lines in Figure-2. The experimental values of membrane potential observed for each electrolyte have been also plotted against concentration in the same Figure-2. 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.

### 3.3 Kobatake et al Method

Equation (5) indicates that a value of $\beta$ and a relation between $\alpha$ and $X$ can be obtained of a plot of $|\Delta E_{mr}|$ against $C_2$ at fixed $\sigma = 10$ [in the region of very low concentration – Figure-3]. The value of intercept is equal to $(1/\beta) \ln \sigma$, from which $\beta$ may be evaluated.

\[
|\Delta E_{mr}| = \left(\frac{1}{\beta}\right) \ln \sigma - \left(\frac{\sigma - 1}{\alpha \beta \sigma}\right) (1 + \frac{1}{\beta} - 2\alpha) \left(\frac{C_2}{X}\right)
\]  

………………..(5)

Figure-3: $|E_{mr}|$ vs $C_2$ in contact with different electrolytes (at low concentrations)

Equation (6) indicates that the intercept of a plot of $(1/t_{app})$ against $(1/C_2)$ at fixed $\sigma = 10$ allow the values of $\alpha$ to be determined. 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-4. From the value of intercept, $\alpha$ may be evaluated.

\[
\frac{1}{t_{app}} = \frac{1}{1 - \alpha} \left[ \frac{(1 + \beta - 2\alpha) (\sigma - 1) \alpha}{2 (1 - \alpha)^2 \ln \sigma} \right] \left(\frac{X}{C_2}\right)
\]

………………..(6)

\[
\Delta E_{mr} = (1 - 2/t_{app}) \ln \sigma
\]

………………..(7)

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 $X_d$; (b) in the concentrated range from the slope of equation (6). This value of $X$ is designated by $X_c$. The values of $\alpha$, $\beta$, $X_d$, and $X_c$ derived in this way for membrane and 1:1 electrolytes are given in Table 4.
Figure 4: $1/t_{app}$ vs. $1/C_2$ in contact with different electrolytes (at high concentrations)

Table 3: Apparent transference number of co-ions for various electrolytes at $25\pm0.1^\circ C$

<table>
<thead>
<tr>
<th>(C_2/C_1) M</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>NH_4Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0/0.1</td>
<td>1.709</td>
<td>1.969</td>
<td>2.183</td>
<td>2.227</td>
</tr>
<tr>
<td>0.5/0.05</td>
<td>1.872</td>
<td>2.105</td>
<td>2.358</td>
<td>2.410</td>
</tr>
<tr>
<td>0.2/0.02</td>
<td>2.145</td>
<td>2.506</td>
<td>2.740</td>
<td>2.874</td>
</tr>
<tr>
<td>0.1/0.01</td>
<td>2.506</td>
<td>3.185</td>
<td>3.460</td>
<td>3.571</td>
</tr>
<tr>
<td>0.05/0.005</td>
<td>3.676</td>
<td>4.525</td>
<td>4.695</td>
<td>4.525</td>
</tr>
<tr>
<td>0.02/0.002</td>
<td>4.902</td>
<td>5.882</td>
<td>6.897</td>
<td>5.882</td>
</tr>
<tr>
<td>0.01/0.001</td>
<td>5.102</td>
<td>6.172</td>
<td>7.299</td>
<td>6.536</td>
</tr>
<tr>
<td>0.005/0.005</td>
<td>7.299</td>
<td>6.536</td>
<td>7.812</td>
<td>6.896</td>
</tr>
</tbody>
</table>

In the present investigation with parchment-supported membranes, the $X_d$ values are found to be higher than $X_c$ values. It is also noted that the lower values of $X$ ($X_c$) are closer to the charge density values determined by TMS method.

Table 4: Values of $\alpha$, $\beta$, $X_d$, and $X_c$ for various electrolytes at $\sigma = 10$ by Kobatake et al method at $25\pm0.1^\circ C$

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$X_d$ (eq. l$^1$)</th>
<th>$X_c$ (eq. l$^1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.459</td>
<td>1.418</td>
<td>0.092</td>
<td>0.019</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.543</td>
<td>1.395</td>
<td>0.096</td>
<td>0.018</td>
</tr>
<tr>
<td>KCl</td>
<td>0.569</td>
<td>1.299</td>
<td>0.088</td>
<td>0.020</td>
</tr>
<tr>
<td>NH_4Cl</td>
<td>0.547</td>
<td>1.375</td>
<td>0.097</td>
<td>0.026</td>
</tr>
</tbody>
</table>

For the evaluation of effective fixed charge density, the various values of permselectivity $P_e$ were calculated by substituting the values of $\alpha$ and $t_{app}$ in equation (8), the values of permselectivity are given in Table 4, and then plotted against $\log [C_1+C_2/2]$. The results are shown in Figure 5.

$$\frac{1}{\sqrt{4\xi^2} + 1} = \frac{1 - t_{app} - \alpha}{\alpha - (2\alpha - 1)(1 - t_{app})} = P_e \quad \text{..........................(8)}$$
Table-4: Values of permselectivity $P_s$ for various electrolytes at different concentrations at 25±0.1°C

<table>
<thead>
<tr>
<th>Concentrations (M)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>NH₄Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.089</td>
<td>-0.102</td>
<td>-0.055</td>
<td>0.008</td>
</tr>
<tr>
<td>0.5</td>
<td>0.014</td>
<td>-0.036</td>
<td>0.014</td>
<td>0.077</td>
</tr>
<tr>
<td>0.2</td>
<td>0.149</td>
<td>0.118</td>
<td>0.137</td>
<td>0.216</td>
</tr>
<tr>
<td>0.1</td>
<td>0.279</td>
<td>0.295</td>
<td>0.302</td>
<td>0.361</td>
</tr>
<tr>
<td>0.05</td>
<td>0.519</td>
<td>0.496</td>
<td>0.474</td>
<td>0.490</td>
</tr>
<tr>
<td>0.02</td>
<td>0.643</td>
<td>0.609</td>
<td>0.634</td>
<td>0.603</td>
</tr>
<tr>
<td>0.01</td>
<td>0.657</td>
<td>0.626</td>
<td>0.653</td>
<td>0.642</td>
</tr>
<tr>
<td>0.005</td>
<td>0.763</td>
<td>0.647</td>
<td>0.675</td>
<td>0.660</td>
</tr>
</tbody>
</table>

The term ζ has already defined as

$$\zeta = \frac{C}{\phi X}$$ .....................................(9)

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

3.4 Evaluation of effective fixed charge density from the Permselectivity values

![Figure-5: Plot of $P_s$ against log $[C_1+C_2/2]$ in contact with different concentrations for various electrolytes](image)

3.5 Nagasawa et al method

Equation (10) predicts a linear relationship between $\Delta E_m$ and $1/C_2$ from which $\phi X$ can be calculated.

$$-\Delta E = \left(\frac{RT}{F}\right) \left(\frac{\phi X}{2}\right) \left(\frac{\sigma - 1}{\sigma}\right) \left(\frac{1}{C_2}\right)$$ .....................................(10)
The values of $\Delta E_m$ were plotted against $1/C^2$ and a set of straight lines in Figure 6 point towards the correctness of the theory. The values of $\phi X$ were calculated from the slope of the lines and are given in Table-2.

![Figure 6: Plot of $E_m$ against $1/C^2$ in contact with different concentrations for various electrolytes](image)

**4.0 Conclusion**

The approach of TMS is unreliable to evaluate X for ion-exchange membranes which have a high concentration of fixed groups. It is not that unreliable for a membrane which has a low concentration of X, as found in this study, due to the fact the change in the values of the factor $(u_u/u_\cdot)$ is not as drastic as it is with membranes of high charge density. It is believed that the approach of Altug and Hair overestimated X in comparison to TMS method. The theoretical predictions from the Kobatake membrane potential equation is borne out quite satisfactorily by our experimental results and hence it may safely be concluded that Kobatake approach for charge density evaluation is the best among the existing of membrane potential.

**References**


