Chronopotentiometric studies of bipolar membrane in sodium chloride solution

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The electrical properties of bipolar membrane (BPM), have been examined in sodium chloride solution by chronopotentiometry. In this method, the membrane is placed between the two current carrying electrodes while its potential is recorded against the electrolysis time using two SCE electrodes closely placed on either sides. An inflection is observed in the membrane potential at the transition time, \( r \). The inflection which is fairly sharp in milli-molar concentrations of NaCl and becomes ill-defined as the concentration of the latter is increased to 0.05 \( M \), and is not obtained in 0.1 \( M \) or higher concentration of NaCl.

Bipolar membranes consisting of two distinct layers of the cation- and anion-exchange resins have been the subject of several studies for the past several years because of their utility in the manufacture of acids and alkalis from the respective salt solutions. The transport of electrolyte within the films during the acid and alkali production is an undesirable phenomenon because it suppresses the purity of the products. Therefore, the examination of bipolar membranes is essential before their use.

In the present note, we examined the chronopotentiometric behaviour of bipolar membrane (BPM) which has been developed and used in our laboratory for the production of sulphuric acid and sodium hydroxide from sodium sulphate by chronopotentiometric method.

Theory

Consider an ideal bipolar membrane (Fig. 1) consisting of the cation- and anion-exchange films. Assume that these films are in contact with an electrolyte solution of same strength (C) on either side containing monovalent ions. Let the concentration of the counterions be \([\text{An}]\) in the anion and \([\text{Cat}]\) in cation films. Then,

\[ [\text{An}]_{x=0} = [\text{Cat}]_{x=0}, \quad \ldots \quad (1) \]

According to the Fick's law for linear diffusion, the transport of the ions are given by,

\[ \frac{\partial [\text{An}]}{\partial t} = D_{\text{An}} \frac{\partial^2 [\text{An}]}{\partial x^2}, \quad \ldots \quad (2) \]

and

\[ \frac{\partial [\text{Cat}]}{\partial t} = D_{\text{Cat}} \frac{\partial^2 [\text{Cat}]}{\partial x^2}, \quad \ldots \quad (3) \]

where \( D \) is the diffusion coefficient of the corresponding cation/anion in the film, \( x \) is the distance from the cation-anion film interfacial zone and \( t \) is the experimental time.

When a constant current (\( i \) mA/cm\(^2\)) is applied across the titanium electrodes (Fig. 1), the concentration of the ions, \([\text{Cat}]\) and \([\text{An}]\) is altered in the course of experimental time, due to the migration of ions away from the film interface. Then the concentration profiles for the ions in the membrane would look like that shown in Fig. 2. Then, the limits of the each ion concentration at the film interfacial zone \( (x = 0) \) would be,

\[ \frac{-i}{F}(t_{\text{Cat}} - t_{\text{An}}) = D_{\text{An}} \left( \frac{\partial [\text{An}]}{\partial x} \right)_{x=0} - D_{\text{Cat}} \left( \frac{\partial [\text{Cat}]}{\partial x} \right)_{x=0}, \quad \ldots \quad (4) \]

\[ [\text{An}]_{x=0,t} = [\text{Cat}]_{x=0,t}, \quad \ldots \quad (5) \]
Fig. 2—Imaginary concentration profiles of [An] and [Cat] at the vicinity of film interface at \( t = 0 \) and \( t > \tau \)

\[
\lim_{x \to \infty} [\text{Cat}]_{x, t} = \lim_{x \to \infty} [\text{An}]_{x, t} = \bar{C} \quad \cdots (6)
\]

Eqs (1-6) are similar to those given by Sand\textsuperscript{12} for solution-electrode equilibrium and can be solved\textsuperscript{13} to obtain Eq. (7).

\[
\tau^{1/2} = \frac{\bar{C}F \pi^{1/2} (D_{\text{Cat}}^{1/2} - D_{\text{An}}^{1/2})}{2 \bar{I} (t_{\text{Cat}} - t_{\text{An}})} \quad \cdots (7)
\]

where \( \tau \) is called the transition time at which [An] and [Cat] at the film's interfacial zone becomes negligible.

**Experimental**

**Bipolar membrane**

The membrane, BPM was prepared according to the method developed in this institute\textsuperscript{11} using a cation-(Indion 225) and anion-(Indion FFIP) exchange resin powders, from Ion-Exchange, India Ltd., with polyvinyl chloride binder. The aerial resistance, ion-exchange capacity and burst strength of this membrane are 20-25 ohm cm\(^{-2}\); 1.1 meq/g (cation film) and 1.0 meq/g (anion film) and 4 Kg/cm\(^2\), respectively.

**Membrane cell**

The membrane cell, used for recording the membrane responses was made out of Perspex and is shown in Fig. 3. It had two compartments (inner and outer) separated by the circular membrane firmly fixed at the lower end of inner container by a threaded cork. Two large surfaced platinitized titanium electrodes placed one above and another below BPM were used as the current carrying electrodes. Two large surfaced platinitized titanium electrodes placed one above and another below BPM were used as the current carrying electrodes. A solution of \((0.001-0.05 \ M)\) NaCl (100 ml in the inner and 400 ml in the outer) was placed in the two compartments. The effective area of the BPM (12.5 cm\(^2\)) facing the electrodes was used in the calculation of current density at the electrodes. Two saturated calomel electrodes (SCE) were used to measure the potential difference across the BPM during the experiment. These two probe electrodes were kept one each above and below the membrane surface through glass tubes filled with saturated KCl solution separated by a G4-glass frit. A mechanical stirrer in the inner compartment and a magnetic stirrer in the outer compartment were employed between two measurements to establish the equilibrium conditions at the membrane-solution interface. The cell temperature was maintained at room temperature (25\(^{\circ}\)).

Chronopotentiograms (E-t plots) were recorded with PAR 175 universal programmer connected to PAR 173 potentiostat through an interface model PAR 306 along with a current-voltage converter model PAR 176. The E-t plots were obtained on a high precision X-Y recorder in conjunction with PAR 174 A.

The membrane of 5.8 cm in diameter was pre-treated with 0.1 M HCl, washed with distilled water and then kept overnight in 1 M NaCl for equilibrium. This pre-treated membrane was washed with distilled water and fitted in the cell. The cell was filled with a known concentration of NaCl solution and kept for 1 h for equilibrium under constant stirring. The E-t plots of the membrane were then recorded under steady state conditions by the current densities between 0.1 to 4 mA/cm\(^2\) and [NaCl] between 0.001 to 0.05 M.

**Results and discussion**

The data indicated two potential zones for the membrane separated by an inflection at the transition time, \( \tau \). Figure 4(a-d) shows the typical chronopotentiograms obtained at four different applied current densities in 0.001 M NaCl. The small changes in the membrane potential before reaching the transition time, is explained for the small changes in [An] and [Cat] at the film interface, which might have not affected the overall
membrane resistance. The potential jump between the potential zones is explained for the fall in [An] and [Cat] to zero near the interface (Fig. 3) which substantially enhances the overall ohmic resistance of the membrane-solution boundary layer. The second potential zone, which is the limiting potential zone after the fall in potential, could be due to transportation of H+ and OH− ions existing in Eq. (8) at the film interfacial zone. Transportation of H+ and OH− ions is feasible if the concentration of counterions at the film-interface fall below the concentration range of $10^{-7}$ M. Absence of sharp inflection is accounted for the net effect due to diffusion of electrolyte ions towards the film interface and the quick transportation of H+ and OH− ions.

\[ \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \]  \hspace{1cm} (8)

The values of $iT^{1/2}$ were plotted against the applied current density, $i$, and [NaCl] and the results are shown in Figs 5 and 6, respectively. The data revealed that the $iT^{1/2}$ value are almost constant and independent of $i$ at a given concentration of NaCl (Fig. 5) but it linearly changed with the increase in concentration of NaCl (Fig. 6), thus verifying the validity of the Eq. (7).

The electrical performance of bipolar membrane which has been developed and used in the manufacture of sulphuric acid and sodium hydroxide from sodium sulphate in our institute was examined in different sodium chloride concentrations by chronopotentiometry. The membrane potential was found to linearly change with the time, under galvanostatic conditions giving an inflection at the transition time, $\tau$. The inflection was fairly sharp in lower NaCl concentrations and it became less and less sharp as concentrations of the latter increased. The observed values of $iT^{1/2}$ are independent of the applied current density, $i$ in a given NaCl concentration, but linearly increased as the concentration of the latter increased. No inflection in the membrane potential was observed in 0.1 M and above NaCl solutions.

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References


