The transport phenomena occurring across parchment supported and polystyrene moulded membranes have been thoroughly investigated by taking into account the following aspects, namely (i) ionic transport, (ii) membrane potential, (iii) electrical conductivity, (iv) ionic distribution equilibria and (v) spatial distribution of ions and the potential within the membrane. Fick's diffusion law and Nernst-Planck flux equations were applied for the determination of diffusion rates of a number of 1:1, 2:1 and 3:1 type of electrolytes. The equations used for the evaluation of diffusion rate involves values of membrane potential $E_m$, membrane resistance $R_m$, cationic and anionic potentials $E_{C_+}$ and $E_{C_-}$ etc., which have been determined purely by electrometric methods. Diffusion rates of the chlorides of $\text{NH}_4^+$, $K^+$, $\text{Na}^+$, $\text{Li}^+$, $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{Al}^{3+}$ at various temperatures have been evaluated with the help of following equations.

For 1:1 type electrolyte,

$$\frac{dC}{dt} = \frac{1}{RT_m} \left[ 59.16 \log \frac{C_2}{C_1} \frac{\gamma_2}{\gamma_1} - E_m \right] \left[ \frac{E_m}{59.16 \log \frac{C_2}{C_1} \frac{\gamma_2}{\gamma_1}} + 1 \right]$$

For 2:1 type electrolyte,

$$\frac{dC}{dt} = \frac{1}{RT_m} \left[ 59.16 \log \frac{C_2}{C_1} \frac{\gamma_2}{\gamma_1} - E_m \right] \left[ \frac{E_m}{59.16 \log \frac{C_2}{C_1} \frac{\gamma_2}{\gamma_1}} + 1 \right]$$
For 3:1 type electrolyte,

\[
\frac{dc}{dt} = \frac{1}{4 \pi R_m} \left[ 19.73 \log \frac{c_2 \gamma_2}{c_1 \gamma_1} - E_m \right] \left[ \frac{E_m}{59.16 \log \frac{c_2 \gamma_2}{c_1 \gamma_1} + 1} \right]
\]

where \( C \) and \( \gamma \) stand for concentration and activity coefficients respectively.

The applicability of the above equations has been tested by comparing the "observed" and "computed" diffusion rates. It was found that these equations are valid for the study of diffusion of electrolytes through parchment supported membranes.

The values of membrane resistance \( R_m \) for each membrane with different electrolytes vary in the following order

\[ \text{LiCl} > \text{NaCl} > \text{KCl} > \text{NH}_4\text{Cl} \]

and

\[ \text{AlCl}_3 > \text{MgCl}_2 > \text{CaCl}_2 > \text{BaCl}_2 \]

The order of diffusion rates \( D_x \) for various electrolytes through each of the membranes is as follows

\[ \text{NH}_4\text{Cl} > \text{KCl} > \text{NaCl} > \text{LiCl} \]

and

\[ \text{BaCl}_2 > \text{CaCl}_2 > \text{MgCl}_2 > \text{AlCl}_3 \]

The membrane potential \( E_m \) values for the various electrolytes display very interesting phenomena. In the case of 1:1
electrolyte the values are all positive (dilute side taken as +ve) indicating that the membrane is cation selective. In the case of 2:1 and 3:1 electrolytes $E_m$ changes sign indicating that the membrane has become anion selective. The selectivity of the membrane has been discussed in the light of the role played by multivalent cations which are responsible for the charge reversal of each of the membranes.

The various membrane parameters were also evaluated at different temperature and energy of activation $E_a$ for diffusion of electrolytes were calculated. It was found that the values of $E_a$ for diffusion through the membranes are higher as compared to those found for free diffusion in solution. The diffusion rate sequence and selectivity of the membranes for various uni, bi and trivalent cations were found to be primarily dependent on the differences in hydration energies of counter ions in the external solution. On the basis of Eisenman-Sherry theory the diffusion rate sequence of alkali metal cations point towards the weak field strength of the fixed charge groups.

The theory of absolute reaction rates has been applied to the diffusion process and the various activation parameters namely enthalpy of activation $\Delta H^\circ$, free energy of activation $\Delta F^\circ$ and entropy of activation $\Delta S^\circ$ have been evaluated. The values of $\Delta S^\circ$ are found to be negative indicating that
the diffusion takes place with partial immobilization in the membrane phase. The relative partial immobility was found to increase with increase in the valence of the ions constituting the electrolyte. A formal relationship between 
\[ \Delta H_{\text{hydration}}, \Delta F_{\text{hydration}} \text{ and } \Delta S_{\text{hydration}} \] of cations with the corresponding values of \( \Delta H^0, \Delta F^0 \text{ and } \Delta S^0 \) for diffusion was also found to exist for these membranes.

For the evaluation of membrane fixed charge density various methods have been employed. The values of Donnan potential, diffusion potential and total membrane potential for KCl of various concentrations have been calculated according to the theory of Teorell-Meyer-Sievers and its modified form by Altabeg and Hair. Various theories of membrane potential, namely Kobatake's and Nagasawa's based on the thermodynamics of irreversible processes have been applied to these parchment supported membranes. The most crucial point in these theories is the assumption that the activities, \( a_+ \) and \( a_- \) of small ions in the membrane phase can be represented by \( a_+ = c_+ \) and \( a_- = c_- \) where \( c_+ \) is the concentration of the co-ions in the membrane phase. This assumption implies that in the direction of membrane thickness, the gradients of the chemical potential of positive and negative ions in the membrane are the same i.e., \( \text{grad } a_+ = \text{grad } a_- \). Kobatake's membrane potential equation contains various parameters, namely \( \alpha, \beta \) and \( \sigma \) which have been evaluated for these system
of parchment supported membranes. These parameters were used for comparison of theory with experiment and confirmed the applicability of Kobatake's equation of membrane potential to these systems of membranes. Another equation representing the degree of permselectivity of membrane-electrolyte system was also applied to these membranes. This equation uses empirical expressions for the activity coefficients and mobilities of small ions in charged membrane. Based on permselectivity $P_s$, a simple method for the determination of the effective fixed charge density $\sigma_X$ was also applied.

Most recently Nagasawa has derived an expression based on thermodynamics of irreversible processes for the determination of thermodynamically effective fixed charge density by taking various assumptions. This theory was also applied to these systems of membranes and thermodynamically effective fixed charge density was evaluated. The results of all these investigations show that the membrane potential data are fitted accurately by the equations derived by Kobatake and Nagasawa.

The theoretical equations, based on thermodynamics of irreversible processes, for bi-ionic potentials (BIP) and membrane potential, derived by Toyoshima & Nakanishi, have also been applied and tested with polystyrene moulded membrane. All the parameters of the equations have been determined and
it was found that the theoretically determined bi-ionic potentials agree well with the experimentally observed bi-ionic potential values. The main assumption of Mozeaki's equation that activity coefficients and mobilities of small ions are given by the expressions proposed from the expanded "additivity rule", are found to be applicable to these system of membranes. The mobility ratios and potentiometric selectivity coefficients have also been evaluated.