Comparative investigations on electrical conductance of ion-exchange membranes

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The electrochemical transport properties (conductivity and transport number) of cation- and anion-exchange membranes in aqueous solutions of NaCl, KCl and Na₂SO₄ of different concentrations have been investigated. It has been found that the ion-exchange capacity of these membranes decreases while membrane resistance increases with increase in the membrane thickness. The electrolyte concentration corresponding to the iso-conductance point has been determined and it shows that thinner membrane exhibits improved electrical conductivity. On the basis of the micro-heterogeneous model proposed by Nikonenko and Zabolotsky, describing the micro-structure of the membrane material, the counter-ion diffusion coefficient in the membrane phase has been determined. Good relations have been found between the counter-ion diffusion coefficient across the ion-exchange membranes and their ion-exchange capacity value.

The ion-exchange membranes find application in diverse processes (electrodialysis, diffusion dialysis, electro-deionization, membrane electrolysis, fuel cells, storage batteries, electro-chemical synthesis etc) which are energy-, resource- and environment saving. The development of ion-exchange membranes of high chemical, mechanical and thermal stabilities, which meet growing demands of the aforementioned processes, is of great importance. In all the above said electrochemical processes, ion-exchange membrane works as highly conducting medium due to the high internal molality of ionogenic functional group in it. The electrochemical characteristics and thus electrical resistance of ion-exchange membrane depends on the nature of the membrane forming material, structure of the membrane and in a very substantial measure on its interfacial character along with the nature and concentration of the electrolytic solution in which membrane is operated. It is necessary not only to know the main transport characteristics of the membranes, but also predict the behavior of these membranes in relation with their structural properties, thickness and its electrolytic environment. The micro-heterogeneous model derived by Zabolotsky and Nikonenko appeared to be the main factor for relating the membrane transport properties such as electrical conductivity, diffusion permeability and transport number to the ionic concentration of the external aqueous solution.

The cation- and anion-exchange membranes (CEM and AEM respectively) prepared in our laboratory and used in electrodialysis units for versatile applications, have been studied in the present investigation because of their high chemical and thermal stability and ionic conductivity. The ionic conductivity of ion-exchange membranes (IEM) is however adversely affected when its thickness increases due to the decreased ion-exchange capacity and non-uniform distribution of fixed charge sites in the membrane polymer. Membrane conductance value in conjunction with solution conductivity is used for the estimation of iso-conductance points and thus counter-ion diffusion coefficient values at different thicknesses of IEM in equilibration with NaCl, KCl and Na₂SO₄ of varied concentrations. The data of iso-conductance point and corresponding electrolyte concentration are useful to predict the nature and concentration of electrolyte where membranes will be most efficient in electro-driven separation process.

Materials and Methods

The interpolymer ion-exchange membranes used in these investigations were prepared by the procedures reported earlier. The membranes were based on an interpolymer of polyethylene and styrene-divinylbenzene copolymer having sulphonic acid and quaternary ammonium groups as a functional group for cation and anion-exchange membranes respectively. The membranes were conditioned by treatment with 1M HCl and 1M NaOH successively and then thoroughly washed in distilled water, before their equilibration in 1M NaCl solution. Reagent grade sodium chloride, potassium chloride and sodium sulphate obtained from S. d fine chemicals, were used as such.

Measurements

The membrane thickness was determined using
Table 1—Characteristics of cation- and anion-exchange membranes at different thickness

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness capacity (mm)</th>
<th>Water content (%)</th>
<th>Specific weight (Kg/m)</th>
<th>Ion-exchange (equiv/m)</th>
<th>Mean NaCl Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05 M</td>
</tr>
<tr>
<td>CEM</td>
<td>0.130</td>
<td>14.7</td>
<td>476.7</td>
<td>1186.5</td>
<td>0.926</td>
</tr>
<tr>
<td></td>
<td>0.180</td>
<td>12.5</td>
<td>452.3</td>
<td>993.9</td>
<td>0.918</td>
</tr>
<tr>
<td>AEM</td>
<td>0.130</td>
<td>12.6</td>
<td>423.7</td>
<td>680.5</td>
<td>0.906</td>
</tr>
<tr>
<td></td>
<td>0.180</td>
<td>11.4</td>
<td>417.2</td>
<td>613.9</td>
<td>0.894</td>
</tr>
</tbody>
</table>

Fig. 1—Schematic design of the electric resistance cell: 1-Graphite electrode, 2- Equilibrated Ion-exchange membrane, 3-Plexiglass plate and 4 - Driving screw.

Electronic Digital Micrometer (Digitrix MarkII, Japan) with ±1μm sensitivity. Measurements were made on five different spots; the mean value was taken as the membrane’s thickness. The specific weights for cation- and anion-exchange membranes separately, were obtained by measuring their dimensions and weights after drying at 50°C for eight hours. The experimental cell containing two compartments separated by an IEM (10.2 cm²) of different thickness was used for membrane potential measurements. Membrane potential data obtained for both type of IEM using sodium chloride solutions of unequal concentrations (C₁/C₂) was kept constant at 10.0 while mean electrolyte concentration was fixed at 0.01 and 0.005 M, used for the estimation of counter-ion transport number and membrane permselectivity.

The electrical resistance measurements for different type of membranes were obtained from Clip-cell. The expanded view of the cell is represented in Fig. 1. This is composed of two black graphite electrodes fixed on plexiglass plates. The active area of electrodes as well of the IEM was 1.0 cm². During the experiments, the wet membrane was tightly sandwiched between both the electrodes and secured in place by means of set of screws. Before introduction into the cell, the membranes were immersed in 1M NaCl for overnight. The membrane resistance was measured with the help of digital conductivity meter (Century, Model CC601). The process was repeated till reproducible values within ±0.01 ohm were obtained.

Iso-concentration (Ciso) and iso-conductance point (Kiso m) were determined from the intercept of curves drawn K m–C (solid line) and K–C (dotted line) in Figs 2–4. The point on x axis corresponding to the intercept is taken as Ciso while the point on y axis corresponding to the intercept is taken as Kiso m.

Results and Discussion
Ion-exchange capacity and water content

The characteristics of the ion-exchange membranes are summarized in Table 1. The water content value decreases with increase in thickness of the membrane, although the specific weight of the membrane material remained constant. When immersed in water, the membranes take up water to different degrees. The membranes having the same degree of cross-linking absorb the same amount of water, in the case when the density of ionizable hydrophilic group is the same throughout the membrane. With increase in membrane thickness the density of functional (hydrophilic) group became less, this may be one of the reasons for less water content for thicker membrane in comparison to the thinner one. The main feature of an ion-exchange membrane is its ion-exchange capacity (IEC). As the specific weight for each type of membrane is same, the IEC should be constant characteristic and independent of the membrane thickness. But, IEC value for each type as presented in Table 1, decreases with increase in membrane thickness. This variation may be attributed to non-uniform chemical composition i.e. extent of ionization in the interfacial zone and the bulk of the membrane film. The water content decreased with decrease in overall (average) ion-exchange capacity of the membrane, as is the case with all other ion-
exchange membranes (i.e., as the ion-exchange capacity of the polymer increases, it becomes more hydrophilic and sorbs more water). The preformed membrane film was subjected to sulphonation in the case of CEM, chloromethylation and subsequent ammination for AEM. However, it should be noted that the extent of ionization at the interfacial zone of the membrane film will be more in comparison to that of the bulk of the film.

**Transport number and membrane permselectivity**

The counter-ion transport numbers for different type of membranes were estimated by membrane potential measurements. For ion-exchange membrane, using TMS approach, the membrane potential \((E_m)\) for uni-univalent electrolyte may be expressed as,

\[ E_m = \frac{RT}{F} \ln \frac{a_1}{a_2} \]

where \(a_1\) and \(a_2\) are activities of electrolyte solutions contacting through membrane and \(i^m\) denotes the counter-ion transport number in the membrane phase. The \(i^m\) values presented in Table 1, reveal that both CEM and AEM are strongly ion-selective in lower NaCl concentration (0.005 \(M\)), while its ion-selectivity markedly deteriorated with increase in membrane thickness and electrolytic concentration.
An ion selective membrane is endowed with permselectivity ($P$), which measures the extent to which counter-ion migration is facilitated by it, and is defined as:

$$P = \frac{t^+ - t^-}{1 - t^-} \quad \ldots \ (2)$$

where $t^+$ denotes the counter-ion transport number in the solution phase. Permselectivity values estimated for CEM and AEM are also included in Table 1 for different membrane thickness. Permselectivity decreases with the increase in the membrane thickness for each type of membrane. Counter-ion migration is facilitated because of the charge that membrane matrix carries, which is proportional to its ion-exchange capacity value\(^{12}\). Examination of the results clearly shows that the thinner membrane behaves as an ideal ion-exchanger as a result of Donnan exclusion of co-ion, and its ion-selectivity declines with the increase in the membrane thickness as a result of invasion of co-ion for thicker membrane. Furthermore, membrane exhibited enhanced permselectivity (Table 1) below the electrolytic concentration corresponding to its iso-conductance point presented in Table 2.

**Membrane resistance**

Electric resistance were measured for CEM and AEM having varying thickness from 0.130 to 0.180 mm, equilibrated with the different electrolytic solutions i.e. NaCl, KCl and Na\(_2\)SO\(_4\). The concentration of the equilibrating electrolyte solution varied from 10 \(mM \) to 50 \(mM \). The membrane resistance data presented in Table 2 reveal that resistance of AEM is slightly higher than that of CEM under similar experimental conditions, although crosslinking of basic polymeric matrix of both type of membranes are the same. However, it should be noted that ion-exchange capacity in Na\(^+\) form is about one-half time smaller in the case of AEM in comparison to that of CEM. In electrolytic solution the membrane takes up water and electrolyte. The concentration of sorbed electrolyte is dependent upon the nature of polymeric matrix as well as the concentration and nature of electrolyte\(^{12}\). Membrane resistance measured for different electrolyte concentration is also presented in Table 2. The membrane resistance decreases rapidly with the increase in concentration for each type of electrolyte solution. This variation may be attributed to (i) increased sorbtion of co-ions and (ii) deswelling of the membrane matrix with increase in electrolytic concentration. Factor (ii) will result in the increase of fractional volume of the polymer matrix due to lowering of matrix swelling at higher concentration. Furthermore, the membrane resistance of thinner membrane (0.130 mm) is less than that of the thicker (0.180 mm) one. It is obvious from the Table 1, that water content or in other word void volume of the membranes having thickness of 0.130 mm is about 10% more in comparison with the membranes having thickness 0.180 mm, which may be one of the factors responsible for the observed variation of membrane resistance with its thickness.

**Table 3**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Thickness (mm)</th>
<th>CEM</th>
<th>AEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{iso}$ (M)</td>
<td>$K_{iso}$ (S/m)</td>
<td>$D_m^X \times 10^{11}$ (m(^2)/sec)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.130</td>
<td>0.065</td>
<td>0.625</td>
</tr>
<tr>
<td>KCl</td>
<td>0.130</td>
<td>0.036</td>
<td>0.355</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>0.130</td>
<td>0.045</td>
<td>0.555</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.180</td>
<td>0.030</td>
<td>0.340</td>
</tr>
<tr>
<td>KCl</td>
<td>0.180</td>
<td>0.018</td>
<td>0.285</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>0.180</td>
<td>0.015</td>
<td>0.225</td>
</tr>
</tbody>
</table>

**Fig. 3**

Electro-conductivity of the (A) CEMs and (B) AEMs of different thickness (--- 0.130 mm —— 0.180 mm) in contact with the KCl solutions; solid curves: membrane specific conductivity; and dotted line: solution specific conductivity.
The choice of electrolytes has been made in such a way that for each type of membrane there are two different types of counter-ions. In the case of CEM where Na\(^+\) and K\(^+\) are the counter-ions, the membrane resistance in Na\(^+\) is high in comparison to that of the K\(^+\) form. Generally, according to the cation hydration energy the swelling of the membrane increases K\(^+\) form to Na\(^+\) form\(^{13}\). Also such a difference can be caused by a better access of the K\(^+\) to the sulphonic acid group attached with the polymer matrix in the case of CEM. The electrolytes sorbed in the order NaCl < KCl, which is in accordance with the order of hydration energies of counter-ions (Na\(^+\)> K\(^+\))\(^{13}\). The lower the hydration energy stronger the electrostatic interactions of counter-ions with the charged group, which results in reduced membrane resistance. When AEM was equilibrated in different types of electrolytic solution of the same concentration, the membrane resistance values exhibit the sequence Na\(_2\)SO\(_4\) > KCl > NaCl with respect to the nature of the electrolyte. This is also in accordance with the hydration energies of its counter-ions (SO\(_4^{2-}\)> Cl\(^-\)). In aqueous solutions the anionic mobility varied in the order NaCl > KCl > Na\(_2\)SO\(_4\). Similar to the counter-ion mobility, the AEM’s resistance in NaCl solution is very less in comparison to the other two electrolytic solutions of same concentration.

The effective membrane resistance determined experimentally as a function of solution concentration in equilibrium with the membrane, may in principle, be used for estimation of membrane specific conductivity. The specific conductivity \(K^m\) of the membrane is given by the relation,

\[
K^m = \frac{e}{AR}
\]  

where \(e\) is the thickness of the wet membrane, \(A\) its area and \(R\) its electrical resistance. The variation of membrane specific conductivity with electrolyte concentration is shown in Figs 2-4 for CEMs and AEMs equilibrated with NaCl, KCl and Na\(_2\)SO\(_4\), respectively. The dotted lines represent the specific conductivity of the solution (\(K\)) in contact with the membrane. As seen in Figs 2-4, the \(K^m\) value initially increases with the solution concentration and attains limiting point at higher electrolytic concentration.

Iso-conductance point

An ion-exchange membrane has to be considered as a micro-heterogeneous system. Among the models described in the literature, we have chosen one, which has been previously proposed by Gnusin et al.\(^{14}\) and more recently developed by Zabolotsky and Nikonenko\(^{5}\). The membrane may be considered as a combination of a ‘gel-phase’ with a relatively uniform distribution of ionogenic groups and hydrophilic parts of the polymer matrix chains, on the one hand, and an electro-neutral solution filling the interstices between the elements of the gel phase named the “inter-gel phase”, on the other. Inter-gel phases are inner parts of pores, channels and cavities. They again used the two-phase model by combining the gel-phase and the inert phase into a coherent region which can be considered as quasi-homogeneous and named the “joint-gel phase” or membrane phase. It was shown\(^{5}\) that the micro-heterogeneous structure of the membrane material is the main factor determining the concentration dependence of membrane transport properties such as electrical conductivity, diffusion permeability and transport numbers. It was shown that, near iso-conductance point the conductivity of the membrane phase (\(K^m\)) and solution phase (\(K\)) became equal. The iso-conductance point (\(K_{iso}^m\)) is obtained from the intercept of the curves drawn in \(K^m-C\) (solid line) and \(K-C\) (dotted line) coordinates in Figs 2-4 (A&B). Analysis of concentration dependence of the conductivities shows that the membranes having thickness 0.130 mm exhibit higher conductivities than the membranes with 0.180 mm thickness for the same type of the counter-ion. For a given CEM, the membrane conductivity follows the sequence KCl > NaCl > Na\(_2\)SO\(_4\), while for AEM, the same data follows the sequence NaCl > KCl > Na\(_2\)SO\(_4\). Comparison of iso-conductivity values (\(K_{iso}^m\)) presented in Table 2, shows the trend, for CEM: K\(^+\)> Na\(^+\); and for AEM: Cl\(^-\)> SO\(_4^{2-}\). The sequence of ionic mobilities in aqueous solution also follows the above trend. It is also interesting to note
that for the CEM with the common counter-ion, $K_{\text{so}}$ values for NaCl is significantly higher than that of Na$_2$SO$_4$, due to the high ionic mobility of Na$^+$ in the former one.

**Counter-ion diffusion coefficients**

The diffusion coefficients ($D^{m}$) of the counter-ions in the membrane phase can also be calculated from the magnitude of the membrane conductivity at the iso-conductance point using Eq. (4):

$$D^{m} = \frac{RT K^{m}}{F^2 Q}$$

where $Q$ is the ion-exchange capacity of the membrane in equiv./m$^3$. The calculated values of diffusion coefficients of the counter-ions in the membrane phase for CEM and AEM are also included in Table 3 at different thicknesses. The thinner membranes are more permeable to the counter-ions than the thicker ones, similar to membrane conductivity. For different types of counter-ions, as expected the counter-ion diffusion coefficient values follow the sequence Na$^+ > K^+$ and Cl$^- > $SO$_4^{2-}$ for CEM and AEM respectively. Thus IEC of IEM is a function of membrane thickness and the counter-ion diffusion coefficient is a function of IEC. For complete co-ion rejection, a high average membrane resistance and enhanced transport properties for each type of electrolyte, the thinner membrane is more suitable for electrochemical processing. The electric resistance measurement of ion-exchange membranes and the determination of counter-ion diffusion coefficient value for each type of membrane allow a better characterization of these membranes. Below the electrolytic concentration corresponding to the iso-conductance point ($C_{\text{iso}}$), the membranes exhibit enhanced permselectivity while above the $C_{\text{iso}}$ the permselectivity of ion-exchange membranes markedly deteriorated. Thus iso-conductance point and corresponding electrolyte concentration allow to predict the concentration range where the membranes will be most efficient in the electro-driven separation process.

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**References**