Electrochemical characterization of cation exchange membrane with immobilized anionic and cationic surfactants

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Electrochemical characterization of a cation exchange membrane has been carried out on the basis of membrane potential and membrane conductance measurements to investigate variation in its permselectivity with concentration of sodium chloride solutions. Alteration in the ion selective character of the membrane on immobilization of sodium lauryl sulphate and cetyl pyridinium chloride has been examined with the objective of exploring the possibility of obtaining cation exchange membrane endowed with enhanced permselectivity. Results indicate that it is possible to manipulate permselective character of a cationic membrane upon controlled immobilization of suitable surfactants. Critical micelle concentration of sodium lauryl sulphate and cetyl pyridinium chloride has been determined by surface tension measurements, to correlate it with the coverage of the membrane by immobilization.

Membranes are endowed with electrochemical and dimensional characteristics which depend on the nature of the membrane forming material, structure of the membrane and in a very substantial measure on the electrolytic environment and interfacial character of the membrane. Presence of additives such as surfactants is reported to modify the transmission characteristics of membrane on account of the formation of immobilized structures. Surfactants are amphiphatic compounds composed of both lyophobic and lyophilic segments in the same molecule. When dissolved in aqueous solution at low concentration, it is energetically favourable for the surfactant to migrate to any available hydrophobic interface and orient itself with its hydrophobic portion towards the interface and its hydrophilic portion in the aqueous phase. It has been found that surfactant immobilization depends on many factors such as pH, ionic strength, temperature and surfactant structure in addition to the degree of hydrophobicity and surface charge density of the adsorbing surface.

In the present work we have studied the ion-selective characteristics of cation exchange membrane that has been developed and used in electrodialysis units for versatile applications. The ion-selective character of the cation-exchange membrane is, however, adversely affected when it is operated at higher electrolytic concentrations. We have examined the possibility of circumventing this deterioration in the membrane functional activity upon immobilization of suitable surfactants. For this purpose sodium lauryl sulphate (SLS) an anionic surfactant and cetyl pyridinium chloride (CPC) a cationic surfactant have been used to obtain information about their ability to alter permselectivity of a cation exchange membrane on the basis of membrane potential measurements. Conductance behaviour of the membrane has also been examined under comparable conditions. Considerable improvement in ion selectivity is observed with increase in surfactant concentration upto a certain concentration beyond which increased surfactant concentration does not result in any detectable change in ion-selectivity.

Surface tension measurements also have been carried out to investigate surface active behaviour of the surfactants.

Materials and Methods

Sodium lauryl sulphate (SLS, Loba Chemie, India) and N-cetylpyridinium chloride (CPC, E. Merck, Germany) were used in present investigation without further purification.

The cation exchange membranes used in these studies, containing sulphonated inter-polymer matrix of polystyrene and polyethylene, were prepared by the methods developed in our laboratory. The membrane was conditioned by treatment with 1M HCl and 1M NaOH successively and then equilibrated with...
1M NaCl. Areal resistance (Ω cm²), moisture content (%) and exchange capacity (m. equiv/g) of this membrane were found to be 1.5, 29.8 and 1.80 respectively. The experimental cell used for membrane potential and membrane conductance measurements was made out of Perspex, and had two compartments (inner and outer) separated by the cation exchange membrane, circular in shape, firmly fitted at the lower end of inner compartment. Two large and flat titanium electrodes [supplied by Titanium Tantalum Products Limited (TITAN), Madras] over which a triple (precious metal oxide) coating of 6 μm thickness was applied, placed one above and the other below the membrane, were used to apply a known current across the membrane. For membrane potential measurements, sodium chloride solutions of unequal concentrations containing the surfactant were kept on the two sides of the cation exchange membrane. The developed potential difference across the membrane structure was measured with the help of a digital

Results and Discussion

The variations in surface tension with concentration of SLS and CPC are presented in Fig. 1. The
Table 2—\( t^+ \), \( P^+ \), and \( \phi x \) values at different concentration of NaCl and SLS

<table>
<thead>
<tr>
<th>[SLS] ( (mM) )</th>
<th>Mean [NaCl] ( (M) )</th>
<th>( t^+ )</th>
<th>( P^+ )</th>
<th>( \phi x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.005</td>
<td>0.926</td>
<td>0.896</td>
<td>0.871</td>
</tr>
<tr>
<td>2.0</td>
<td>0.025</td>
<td>0.949</td>
<td>0.902</td>
<td>0.891</td>
</tr>
<tr>
<td>5.0</td>
<td>0.050</td>
<td>0.966</td>
<td>0.923</td>
<td>0.917</td>
</tr>
<tr>
<td>8.0</td>
<td>0.250</td>
<td>0.978</td>
<td>0.939</td>
<td>0.942</td>
</tr>
<tr>
<td>10.0</td>
<td></td>
<td>0.979</td>
<td>0.941</td>
<td>0.946</td>
</tr>
</tbody>
</table>

Table 3—\( t^+ \), \( P^+ \), and \( \phi x \) values at different concentration of NaCl and CPC

<table>
<thead>
<tr>
<th>[CPC] ( (mM) )</th>
<th>Mean [NaCl] ( (M) )</th>
<th>( t^+ )</th>
<th>( P^+ )</th>
<th>( \phi x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.005</td>
<td>0.926</td>
<td>0.896</td>
<td>0.871</td>
</tr>
<tr>
<td>0.3</td>
<td>0.025</td>
<td>0.911</td>
<td>0.865</td>
<td>0.845</td>
</tr>
<tr>
<td>0.6</td>
<td>0.050</td>
<td>0.886</td>
<td>0.832</td>
<td>0.825</td>
</tr>
<tr>
<td>1.0</td>
<td>0.250</td>
<td>0.859</td>
<td>0.806</td>
<td>0.800</td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td>0.857</td>
<td>0.801</td>
<td>0.792</td>
</tr>
</tbody>
</table>

critical micelle concentration (CMC) of SLS is ~8 mM while that for CPC is ~1 mM. These values are in good agreement with the reported values.

When electrolyte solutions of unequal concentration are separated by a membrane, an electrical potential difference develops across the membrane due to the tendency of oppositely charged ions to move with different mobilities. The magnitude of the membrane potential depends on the electrical characteristics of the membrane in addition to the nature and concentration of electrolyte solution used. Membrane potential data obtained using cation exchange membrane and sodium chloride solutions of unequal concentrations in absence and presence of surfactants at different concentrations are presented in Fig. 2. A perusal of these data shows a significant reduction in membrane potential with increase in electrolyte mean concentration inspite of the fact that the magnitude of concentrations ratio was kept constant. Also in the presence of SLS, an anionic surfactant, membrane potential increases with increasing surfactant concentration and attains a limiting value beyond a certain concentration which corresponds to its CMC value, while in the case of CPC it decreases with increasing concentration and attains its limiting value at its CMC. Alteration in membrane potential with concentration can principally arise on account of increased adsorbability of ionic surface-active substances on the membrane surface.

In the case of 1:1 electrolyte, using thermodynamic principles the liquid junction potential \( (E_L) \) is given by:

\[
E_L = (t_+ - t^-) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \ldots (1)
\]

where \( a_1 \) and \( a_2 \) denote activities of sodium chloride solutions, \( t_+ \) and \( t^- \) denote the transport number of anion and cation respectively in the solution phase. A comparison of the membrane potential data with the liquid junction potential values, \( E_L \), estimated using Eq. 1 presented in Table 1, clearly shows that the membrane is endowed with cation selectivity.

For a cation selective membrane, using the T.M.S. approach, the membrane potential \( (E_M) \) may be expressed as:

\[
E_M = (2 t_+ - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \ldots (2)
\]

where \( t_+ \) denotes the transport number of cation in the membrane phase. The transport numbers under different experimental conditions estimated using Eq. (2) are presented in Tables 1 and 2. These results clearly show that the cation selectivity of ion-exchange membrane markedly deteriorates when it is kept in equilibrium with electrolytic solutions of increasing concentration. Moreover, due to the pres-
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Fig. 3—Dependence of membrane conductance on SLS concentration [1-0.005 M, 2-0.025 M, 3-0.050 M and 4-0.250 M NaCl].

Fig. 4—Dependence of membrane conductance on CPC concentration [1-0.005 M, 2-0.025 M, 3-0.050 M and 4-0.250 M NaCl].

Table 4—(1/ΔΦ)ns values at different concentration of NaCl using SLS and CPC

<table>
<thead>
<tr>
<th>[SLS] (mM)</th>
<th>(1/ΔΦ)ns x 10^2 (Ω⁻¹) [NaCl] (M)</th>
<th>[CPC] (mM)</th>
<th>(1/ΔΦ)ns x 10^2 (Ω⁻¹) [NaCl] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.877 4.712 8.210 13.778</td>
<td>0.3</td>
<td>0.780 3.044 6.965 9.133</td>
</tr>
<tr>
<td>5.0</td>
<td>0.772 4.285 7.341 10.985</td>
<td>0.6</td>
<td>0.664 2.600 5.489 7.985</td>
</tr>
<tr>
<td>8.0</td>
<td>0.728 3.846 5.953 8.828</td>
<td>1.0</td>
<td>0.615 2.405 5.389 7.041</td>
</tr>
<tr>
<td>10.0</td>
<td>0.719 3.801 5.857 8.796</td>
<td>1.4</td>
<td>0.609 2.358 5.287 6.458</td>
</tr>
</tbody>
</table>

ence of SLS, counter-ion transport number is enhanced to some extent and practically does not change when concentration of SLS is increased beyond a certain limit. On the other hand, presence of CPC results in the lowering of counter-ion transport number.

An ion selective membrane is endowed with permselectivity P, defined as

\[ P_s = \frac{t_+ - t_-}{1 - t_+} \]  

Permeability is a measure of the extent to which counter-ion migration is facilitated by an ion-exchange membrane. Counter-ion migration is facilitated because of the charge that membrane matrix carries, the so called fixed charge density. Fixed charge density, has been expressed in the terms of permeability in the following manner:

\[ \phi_x = \frac{2 C P_s}{\sqrt{1 - P_s^2}} \]  

where C denotes mean electrolytic concentration.

Permselectivity and fixed charge density values obtained under different experimental conditions are presented in Tables 2 and 3. Examination of the results clearly shows that at lower electrolytic concentration, membrane behaves as an ideal cation exchanger as a result of Donnan exclusion of co-ion, and its cation selectivity declines with increase in electrolyte concentration as a result of invasion of co-ions at higher electrolyte concentration. In spite of this, cation selective character of the membrane in the higher electrolyte concentration region increases substantially and approaches almost ideal cation selectivity due to immobilization of SLS upon membrane matrix. With ion exchange membranes, ion selectivity is known to diminish with increase in concentration of the electrolyte solution because of lowered co-
ion exclusion. On the other hand, CPC immobilization, reduces the charge density of the membrane surface as well as co-ion exclusion, which is responsible for the reduction in cation selectivity of the membrane. SLS is an anionic surfactant and membrane is cation selective in nature because it bears negative charge, and exhibits coulombic and non-coulombic interactions when kept in contact with polymeric surfaces. Their interactions are influenced mainly by (1) coulombic forces between the ionic sites of surfactant and polymer and (2) hydrophobic interactions between surfactant alkyl chain and polymer backbone. The immobilization of surfactant molecules on the charged surface depends upon which of the above fact or is dominant. It has been suggested in the past that electrostatic repulsions between the anionic head groups of the surfactant and charged surfaces, cause the surfactant molecules to adsorb in a more extended conformation, thus allowing more molecules to contact the surface. Thus attachment of SLS to the supporting cation exchanger membrane leads to the development of negative charge which increases with increase in SLS concentration and is responsible for the observed enhancement of the cation selectivity. The presence of cationic CPC molecules at the membrane surface on the other hand reduces the negative charge with increasing concentration and is responsible for the lowering of cation selectivity of the cationic membrane.

Further information concerning immobilization of a surfactant can be had on the basis of examination of the conductance behaviour of the supporting substrate. Variation of membrane conductance with surfactant concentration in solution, depicted in Figs 3 and 4, shows progressive immobilization of SLS and CPC. Beyond a certain concentration, interfacial resistance tends to attain a limiting value in each case, and these concentrations corresponds to their critical micelle concentration values. These observations are in conformity with the expectation that a completely formed immobilized layer of the surfactant molecules in the interfacial region exists at concentrations beyond their CMC.

The overall conductance may be expressed as

\[
\frac{1}{(1/\Delta \phi)_e} = \frac{1}{(1/\Delta \phi)_s} + \frac{1}{(1/\Delta \phi)_r} \quad \ldots \quad (5)
\]

where \((1/\Delta \phi)_e\) is the conductance of the composite membrane system, \((1/\Delta \phi)_s\) is the conductance of the clean membrane and \((1/\Delta \phi)_r\) is the conductance of the immobilized surfactant layer. The values of \((1/\Delta \phi)_s\) for 0.005 \(M\), 0.025 \(M\), 0.050 \(M\) and 0.250 \(M\) NaCl were found to be \(0.183 \times 10^{-2}\ \Omega^{-1}\), \(1.007 \times 10^{-3}\ \Omega^{-1}\), \(2.439 \times 10^{-2}\ \Omega^{-1}\) and \(4.100 \times 10^{-2}\ \Omega^{-1}\) respectively. The values of \((1/\Delta \phi)_r\) estimated using Eq. 5 are presented in Table 4. With increasing sodium chloride concentration, membrane conductance increases in both the cases. It, however, decreases with increase in surfactant concentration. Furthermore, SLS immobilized layer is more conductive in comparison to CPC immobilized layer. Immobilization of SLS, which bears negatively charged sulphonate group, on the negatively charged polymeric membrane increases the charge density on the membrane surface which facilitates the cation transport. While immobilization of cationic CPC reduces the charge density on the membrane surface which obstructs the movement of ion in comparison to SLS immobilization and thus it forms a uniform hydrophobic layer on the cation exchanger membrane.

Thus it is possible to manipulate the ion-selective character of an ion-exchanger membrane by the immobilization of a suitable surfactant. In the presence of SLS, the cationic membrane does not exhibit any significant reduction in ion selectivity even on fifty-fold increase in concentration of sodium chloride solution. While on CPC immobilization on the cationic membrane, its ion selectivity is adversely affected due to the reduction of fixed charge density on the membrane matrix. On the basis of these observations, one can think of chemically bonding suitable surfactant molecules on the surface of ion exchange membrane to enhance charge density to extend its application over a large range of electrolyte concentration without losing permselectivity. Secondly, depending upon the nature of feed solutions, one can identify potential foulants and remove them by suitable pre-treatment to preserve permselectivity. One can also think of fouling protective layers in terms of appropriate choice of hydrophobic and hydrophilic segments.

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