Chapter 4

Cs$^+$ diffusion and transport in Crown Ether - Nafion Composite membrane

Ion gated membrane for selective cation transport

SIMS image

DB21C7-Cs$^+$

Cs$^+$

H$^+$

D= 25 μm

No selectivity

Selective Cs$^+$ transport

D = 175 μm

D = 200 μm

Cs$^+$ & Na$^+$
4.1. General Introduction

Inspite of the wide application in various fields, the ion exchange membranes (IEM) show very poor selectivity between two different metal ions (of same charge) and thus are rarely used in mutual separations of different metal ions. One way to increase the metal ion selectivity is to incorporate some ligand within the membrane matrix having high selectivity for the metal ion of interest. Alkali metal ion selective crown ethers, calixarenes and cryptands are well known in literature and use of these ligands in membrane for development of various ion selective electrodes has been studied [Buhlmann et al. 1998, Xia et al. 1998]. Crown ethers mimic the ability of biological cation transport systems and of some antibiotics, which also bind metal cations selectively [Dobler 1981]. The major drawback associated with the separation of alkali metal ion using these ligands [Talanova et al. 1999, Gokel et al. 2004, Charewicz et al. 1982, Walkowiak et al. 1990] is that they require an equivalent amount of counter ion and the separation factor depends on the anion also [Hankins et al. 1993]. The charge compensation of the metal ions has been achieved by incorporating anionic functional groups either in the crown ether or in the polymer backbone of the membrane. Cation exchange membranes can provide the negative charge required by the metal ion-crown ether complex, obviating the need of additional counter-anions. Significant effect of the crown ethers on the transport selectivity has been observed in the proton driven cation transport experiments [Kimura et al. 1983]. Increase in hydrophilicity of the membrane matrix resulted in higher transport rate indicating the important role of water in the transport mechanism [Sakamoto et al. 1986]. Nafion-117 is a widely used and well studied IEM which consists of polytetrafluoroethylene backbone with pendant side chains containing -SO$_3$H groups. Different attempts have been made to modify the transport properties of Nafion for its use in fuel cell [Choi et al. 2008, Shim et al. 2005, Sen et al. 2008, Gribov et al. 2009], chemical
sensors and ion selective electrodes [Torma et al. 2008] by incorporating suitable crown ethers in the membrane.

In earlier work with Nafion-crown ether system [Bhattacharyya and Goswami 2009], attempt has been made to prepare an alkali metal ion selective membrane by loading Dibenzo-18-crown-6 (DB18C6) in Nafion-117 cation exchange membrane. The structural details of DB18C6 are given in table 4.1. It has been observed that the transport behaviors of the alkali metal ions in those membranes are strongly dependent on the cationic form of the membrane in which the crown ether is loaded. When the crown ether was loaded in Li$^+$ form of the membrane, the entire ion exchange sites are available for counter ion exchange and the membrane showed enhanced selectivity for Cs$^+$ over Li$^+$. Complete ion exchange equilibrium could be reached within practical time scale because of favorable ion exchange kinetics. On the other hand, when the crown ether was loaded in Cs$^+$ form of the membrane, all the ion exchange sites were not available for counter ion exchange due to drastic decrease of the mobility of the alkali metal ions in the membrane. This could be due to strong binding of this crown for Cs$^+$, K$^+$ and Na$^+$ over Li$^+$ as observed in the literature [Takeoka et al 1990]. It has also been observed from the infra-red (IR) studies [Bhattacharyya and Goswami 2009], that the Nafion matrix becomes more hydrophobic on introduction of crown ether. As has been described in the cluster channel network model of Gierke [Hsu and Gierke 1982, Hsu and Gierke 1983], water plays an important role in the transport properties of Nafion-117 membrane. Also, the earlier works on temperature dependence of ion and water diffusion in Nafion matrix [Yeager and Steck 1981, Saito et al. 2005] show that activation energy for water diffusion in Nafion is comparable to that in pure water, indicating very little barrier for water transport in the membrane.
Table 4.1: Structural details of the crown ethers used in the present work.

<table>
<thead>
<tr>
<th>Crown Ether</th>
<th>Dibenzo-18-crown-6 (DB18C6)</th>
<th>Dibenzo-18-crown-6 (DB21C7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C_{20}H_{24}O_6</td>
<td>C_{22}H_{28}O_7</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image" alt="DB18C6 Structure" /></td>
<td><img src="image" alt="DB21C7 Structure" /></td>
</tr>
<tr>
<td>Molecular Weight (g)</td>
<td>360.40</td>
<td>404.45</td>
</tr>
</tbody>
</table>

In the present work, the factors governing the diffusional properties of different cations (Cs\(^+\), Na\(^+\)) in Nafion-crown ether composite membrane have been studied with a view of possible selective transport of Cs\(^+\) through the composite membrane.

4.2. Self-Diffusion Studies

From the earlier work [Bhattacharyya and Goswami 2009] with Nafion-DB18C6 composite system, it is not clear whether the cation driven loading of DB18C6 in the Nafion-117 matrix provides template effect for improving the selectivity for other alkali metal ions, viz. Na\(^+\) or K\(^+\) vis-à-vis Cs\(^+\) because of too slow kinetics of isotopic exchange of these metal ions when DB18C6 has been loaded in those cationic form of Nafion-117. DB18C6 is reported to bind Na\(^+\) more strongly compared to Cs\(^+\) as shown by the higher stability constant [Katsura et al. 2004] in the former case. In the present work, experiments were therefore carried out to see the change in diffusional behavior for Cs\(^+\) and Na\(^+\) when DB18C6 (CR1) is loaded in the respective cationic form of Nafion-117. Since the kinetics of isotopic exchange at room temperature with these membranes (M-Naf-CR1, M = Na/ Cs) are too slow, self diffusion
experiments have been carried out as a function of temperature to understand the mechanism of transport. In the present work, the effect of temperature on the self diffusion coefficients (SDC) of water in Cs-Naf-CR1 and the corresponding equilibrium water uptakes have also been measured. The activation energy for self diffusion of both Cs\(^+\) and water have been calculated and compared with that in Nafion-117 in absence of DB18C6. DSC measurements have also been carried out to supplement the observations obtained from self diffusion measurements. Di-Benzo-21-Crown-7 (DB21C7 i.e., CR2, structural detail given in table 4.1) is reported [Moyer et al. 1997] to be more Cs\(^+\) selective than DB18C6. In order to study the effect of affinity of the crown ether for a particular metal ion on the activation energy of diffusion, the Cs\(^+\) self diffusion studies in DB21C7 loaded Cs-Naf-CR2 has been carried out at different temperature. From the data, an attempt has been made to explain the membrane transport behavior in terms of hydration state of the membrane as well as the affinity of the crown ether for a particular metal ion.

4.2.1. Experimental Section

4.2.1.1. Incorporation of the crown ether

Incorporation of the crown ethers (CR1/CR2) in the membrane samples having desired (Cs\(^+\)/Na\(^+\)) ionic form was done following the method described below. Precisely, the Nafion-117 samples in appropriate cationic form were placed in a saturated solution of either of the crown ether in 200 mL dimethyl formamide for 24 h. The samples were subsequently removed from the solution, and excess solution was wiped out. The samples were washed thoroughly with deionised water and dried under vacuum.
4.2.1.2. Membrane characterization

The weight of dry membrane was obtained by heating the membrane sample in Cs\(^+\) / Na\(^+\) form for 6–8 h at 60°C. The extent of loading of crown ether was confirmed from the change in the dry weight of the sample before and after the loading of crown ether. The loading of DB18C6 was found to be in the molar ratio of 1:1 with respect to Na\(^+\), while it was 0.7:1.0 with respect to Cs\(^+\). In case of DB21C7, the molar ratio was found to be 0.8:1.0 with respect to Cs\(^+\). Infrared spectra of the Cs/Na-Naf-CR1 have also been recorded using a Jasco Fourier transform IR spectrometer model JASCO FTIR4100 (Japan). The spectra obtained were found to be similar to that shown in earlier work [Bhattacharyya and Goswami 2009]. The thicknesses of the membranes were measured using a digital micrometer (Mitutoyo, Japan) which is having an accuracy of 0.001 mm.

4.2.1.3. Differential Scanning Calorimetry (DSC)

DSC measurements for the Cs\(^+\) / Na\(^+\) form of Nafion with and without DB18C6 were done using a Mettler Toledo DSC 822 instrument at a heating rate of 10°C/min within the temperature range of -10°C to 300°C. About 7 - 8.5 mg of membrane samples were used to record the scans. The scans were recorded under inert atmosphere with an empty aluminum pan as the reference. Indium was used as the calibration standard. The DSC traces were analyzed using the software supplied by Mettler Toledo.

4.2.1.4. Self diffusion measurement of cations

The Cs\(^+\) ion self diffusion measurement in Cs-Naf-CR1/ Cs-Naf-CR2, were measured by the method as described in chapter 2. For Cs-Naf-CR1, the measurements were carried out at 4 different temperatures, viz, 50°C, 55°C, 60°C and 65°C, while for Cs-Naf-CR2, measurements were carried out at 3 different temperatures (60°C, 65°C and 70°C). The temperature of the solution has been maintained using a constant temperature bath. During
the course of the experiment, the temperature was monitored constantly using an external thermometer. The experiments at each temperature were repeated to verify the reproducibility of the measurement. The dry weight of the membrane was taken before and after every experiment. It was observed that the weight of the membrane sample remains constant indicating that crown ether did not come out of the membrane during the course of the experiment.

In case of Na-Naf-CR1, the self diffusion study of Na⁺ ion was carried out only at 60 °C since the kinetics was found to be too slow at lower temperatures. Even at 60 °C, it was not possible to reach complete equilibrium after long time period. In order to obtain the fractional attainment of equilibrium as a function of time (t), the amount of radiotracer ions in the membrane at equilibrium (t = ∞) is required. This was found out indirectly, assuming that the amount of radiotracer ion in the membrane at infinite time is governed by the ratio of the amount of sodium ion in the membrane to that in the external solution. Total radioactivity added in the external salt solution was obtained by counting 100 μL of the solution in NaI(Tl) detector connected to a 4k channel analyzer. The number of available ion exchange sites (mili equivalent) in the membrane was obtained from the dry weight of the membrane sample before incorporation of the crown ether. The equilibrium radioactivity in the membrane was obtained from the product of the ratio of Na⁺ in the membrane to that in the external salt solution and the total activity present in the external salt solution. It is assumed that the uptake of radiotracer in the membrane did not alter the radioactivity concentration in the external salt solution.

4.2.1.5. Self diffusion measurement of water in Cs-Naf-CR1

In order to study the self diffusion behavior of water in Cs-Naf-CR1, the membrane sample (2 cm X 2 cm) was equilibrated in water spiked with ³H (HTO) at a constant temperature
with stirring for 2 h. After equilibration, the membrane was taken out and gently wiped with a filter paper to remove the water droplets attached to the surface. Then the sample was placed in 25 mL deionised water which is kept at the same temperature at which equilibration of the membrane with HTO has been carried out. The water was continuously stirred (~52 rad/s) during the course of the desorption experiment to minimize the film diffusion. The water diffusion rate in the membrane sample was measured by pipetting out 50 μL of the equilibrating solution after regular time intervals. The β activity of ³H has been measured by mixing the sample in a vial with 5 mL of scintillation cocktail-w (2, 5-diphenyl oxazole (PPO) = 0.7%, 1,4-di-2-(5-phenyloxazolyl benzene (POPOP) = 0.03%, naphthalene= 10%, and tri-noctyl phosphine oxide (TOPO) = 1% in 1,4-dioxane solvent), and counting the samples with a liquid scintillation analyzer. The water diffusion experiments were carried out at 27 °C, 38 °C, 45 °C, 51 °C and 56 °C.

4.2.1.6. Membrane water content measurement
The water content (cm³) of the membrane was obtained from the uptake of ³H β activity at equilibrium in the membrane and the radioactivity concentration of the ³H labeled water (HTO) used for equilibration. Assuming the density of water to be 1 g cm⁻³ in the membrane phase, and using the dry weight of the membrane after incorporation of the crown ether, the membrane water content (water to exchange site mole ratio = λ = n_{H₂O} / n_{SO₃⁻}) was obtained. In Cs-Naf-CR1 the water content has been measured at 27 °C, 38 °C, 45 °C, 51 °C and 56 °C while that for Na-Naf-CR1 has been carried out only at 56 °C.
4.2.2. Results and Discussion

4.2.2.1. Temperature dependence of self diffusion of cations in Cs/Na-Naf-CR1 and Cs-Naf-CR2

The temperature dependences of Cs\(^+\) self diffusion profiles in Cs-Naf-CR1 and Cs-Naf-CR2 are shown in figure 4.1(a) and figure 4.1 (b) respectively. As seen from the figure, there is a steady increase in isotopic exchange rate with increase in temperature, indicative of existence of barrier for diffusion. Along with the experimental points, the fitted lines to these self diffusion profiles in Cs-Naf-CR1 are also shown in the figure 4.1a.

Figure 4.1: Self diffusion profile of Cs\(^+\) ion in (a) Cs-Naf-CR1 and (b) Cs-Naf-CR2 at different temperatures. The symbols are the experimental points and the lines are the fitted line to those experimental points.

The SDCs for Cs\(^+\) (\(D_{Cs^+}^m\)) ion in these membranes at each temperature have been obtained from these profiles using eq 1.8 [Goswami et al. 2001] and are listed in table 4.2. The Arhenius plot of the \(D_{Cs^+}^m\) data in Cs-Naf-CR1 and Cs-Naf-CR2 are shown in figure 4.2a and 4.2b respectively. From the slope of this linear plot, the activation energy for diffusion of Cs\(^+\)
has been obtained which is given in table 4.3 along with the literature [Yeager and Steck 1981] reported activation energy for Cs-Naf (Nafion-120). The value of activation energy ($E_a$) is seen to have increased by a factor of ~ 2.2 in Cs-Naf-CR1 compared to Cs-Naf, accounting for the very slow diffusion rate of Cs$^+$ ion in Cs-Naf-CR at room temperature, as observed in our earlier work [Bhattacharyya and Goswami 2009].

**Table 4.2:** Variation of $D_{Cs^+}^m$ in Cs-Naf-CR1 and Cs-Naf-CR2 at different temperatures

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Cs^+}^m \times 10^6$ (cm$^2$/Sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs-Naf-CR1</td>
<td>3.50E-03</td>
<td>5.13E-03</td>
<td>1.32E-02</td>
<td>1.32E-02</td>
<td>--</td>
</tr>
<tr>
<td>Cs-Naf-CR2</td>
<td>--</td>
<td>--</td>
<td>7.40E-04</td>
<td>2.00E-03</td>
<td>7.02E-03</td>
</tr>
</tbody>
</table>

In Cs-Naf-CR2, $E_a$ for Cs$^+$ diffusion has been calculated as 213 ±16 KJ/mole, which is much higher than that in Cs-Naf-CR1. The result clearly shows much higher affinity of Cs$^+$ for DB21C7 than DB18C6 as expected. Such a large value of activation energy is typical of ionic diffusion in ionic crystal lattice rather than in swollen polymers [Yeager and Steck 1981]. This is indicative of significant change in the morphology and different mechanism of Cs$^+$ ion diffusion in the crown ether modified Cs-Naf compared to Cs-Naf.
Figure 4.2: Variation of logarithm of SDCs of Cs⁺ (ln $D_{{}^{m}C_{S}^{+}}$) in (a) Cs-Naf-CR1 and (b) Cs⁺ in Cs-Naf-CR2 as a function of inverse of temperature. The solid points are the experimental points while the lines are the fitted line.

Table 4.3: Activation barrier for Cs⁺ ion and water in pure [Yeager and Steck 1981] and crown ether modified Cs-Naf

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Activation Energy (Cs⁺) (kJ/mol)</th>
<th>Activation Energy (H₂O) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs-Naf</td>
<td>35.9</td>
<td>22.0</td>
</tr>
<tr>
<td>Cs-Naf-CR1</td>
<td>80.1 ± 4.0</td>
<td>79.8 ± 5.0</td>
</tr>
<tr>
<td>Cs-Naf-CR2</td>
<td>213.0 ± 16.0</td>
<td>--</td>
</tr>
</tbody>
</table>
Attempt to carry out similar self diffusion experiments with Na-Naf-CR has not been possible at lower temperature as the isotopic exchange kinetics was too slow to reach complete equilibrium within reasonable time scale. Figure 4.3 shows the comparison between the isotopic exchange kinetics for Cs$^+$ and Na$^+$ with Cs-Naf-CR1 and Na-Naf-CR1 respectively at 60 °C.

![Comparison between Cs$^+$ and Na$^+$ self diffusion profile at 60 °C in Cs-Naf-CR1 and Na-Naf-CR1 respectively.](image)

**Figure 4.3**: Comparison between Cs$^+$ and Na$^+$ self diffusion profile at 60 °C in Cs-Naf-CR1 and Na-Naf-CR1 respectively.

As can be seen from this figure, the Cs$^+$ isotopic exchange is complete within ~ 20000 sec, while the Na$^+$ isotopic exchange is not complete even at 50000 sec. The lower mobility of Na$^+$ in Na-Naf-CR1 indicates higher activation energy for diffusion of Na$^+$ in this membrane. This may reflect the stronger binding of Na$^+$ with the DB18C6 in membrane matrix, retarding the mobility of the Na$^+$ ion [Katsura et al. 2004]. There are literature reports [Muraviev et al. 1995, Zagorodni et al. 1997, Cerjan-Stefanovic et al. 1984, Zahran et al. 2010], where selectivity of ion exchange resins and ion selective electrode have been enhanced by carrying out the measurement at elevated temperatures. It will be of interest to see whether the
selectivity of this crown ether loaded membrane could be tuned by carrying out the transport study at higher temperature.

4.2.2.2. Temperature dependence of self diffusion behavior of water

![Image of diffusion profile](image.jpg)

**Figure 4.4:** Self diffusion profile of water in Cs-Naf-CR1 at five different temperatures.

Figure 4.4 shows the self diffusion behavior of water in Cs-Naf-CR1 studied with tritium labeled water at five different temperatures. Here again, the rate of HTO(m) ⇌ H₂O(aq) exchange increases with the rise in temperature. The SDCs of water (\(D_{H₂O}^m\)), calculated from a fit of the experimental data with equation 1.8 are given in table 4.4. The \(D_{H₂O}^m\) values at a given temperature are ~ 30 - 40 times higher than the \(D_{Cs⁺}^m\). It indicates that, as in the case of Cs-Naf, water diffusion in Cs-Naf-CR1 faces less hindrance than the diffusion of Cs⁺ ion. However, all the values are substantially lower than the \(D_{H₂O}^m\) in Cs-Naf, showing that the mobility of the water in Cs-Naf-CR1 is considerably hindered compared to that in Cs-Naf. The value of the activation energy, obtained from the Arhenius plot (figure 4.5) is also given.
in the table 4.3 along with the activation energy for Cs-Naf [Yeager and Steck 1981]. It is seen that the activation energy increases by a factor of ~ 4 and is comparable to the activation energy for Cs\(^+\) diffusion in Cs-Naf-CR1. Such a high value of activation energy indicates that there is no continuous water channel in the Cs-Naf-CR1.

Equilibrium uptake of water as a function of temperature in Cs-Naf-CR1 has also been measured and the corresponding \(n_{H_2O} / n_{SO_3^-}\) values are given in table 4.4. As seen from the data, the water uptake has reduced significantly in Cs-Naf-CR1 over Cs-Naf (\(n_{H_2O} / n_{SO_3^-} = 5.01\), at room temperature) showing that dehydration of Cs\(^+\) in Cs-Naf-CR1 has occurred.

![Graph](image)

**Figure 4.5:** Variation of logarithm of self diffusion coefficient of water (\(\ln D_{H_2O}^m\)) in Cs-Naf-CR1 as a function of inverse of temperature. The solid points are the experimental points while the lines are the fitted line.
Table 4.4: Variation of $D_{H_2O}^m$ and water content in Cs-Naf-CR1 as a function of different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>27</th>
<th>38</th>
<th>45</th>
<th>51</th>
<th>56</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{H_2O}^m \times 10^6$(cm$^2$/Sec)</td>
<td>8.88E-03</td>
<td>3.43E-02</td>
<td>7.74E-02</td>
<td>1.02E-01</td>
<td>1.85E-01</td>
</tr>
<tr>
<td>$n_{H_2O} / n_{SO_3^-}$</td>
<td>1.02</td>
<td>1.09</td>
<td>1.12</td>
<td>1.36</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Reduction in water signal as observed from IR data [Bhattacharyya and Goswami 2009] in Cs-Naf-CR1 as compared to Cs-Naf also confirms the increased hydrophobicity of the Nafion sample after incorporation of DB18C6 in the membrane matrix. This shows that complexation of DB18C6 with Cs$^+$ ion accompanied by the disruption of the water cluster channel network of Nafion-117 has taken place, thereby reducing the $D_{H_2O}^m$ significantly. The effect of water content in Nafion-117 on the self diffusion coefficient of water was extensively studied by Zhao et al. [Zhao et al. 2011] and it has been concluded that the diffusivity changes significantly when $n_{H_2O} / n_{SO_3^-}$ becomes less than 4. At the $n_{H_2O} / n_{SO_3^-}$ values close to that in the present experiment (~ 1), values of diffusion constants reported at different temperature are comparable to the values observed in the present experiments. This shows, apart from the crown ether, water content in the membrane also plays an important role in the cation transport property of the membrane. These results explain why incorporation of hydrophilic species in the membrane increases the cation diffusion rate in the crown ether loaded membrane matrix [Sakamoto et al. 1986].

The cause of enhancement in the activation energy of Cs$^+$ ion in the crown ether loaded Nafion membrane compared to pure Nafion-117 could be due to enhancement in binding of
the ion with the crown ether in the membrane matrix and also due to the reduction in water content in the membrane matrix due to loading of the crown ether, destroying water clusters in Cs-Naf.

In the case of Na-Naf-CR1, equilibrium uptake of water was measured and the corresponding \( n_{H_2O} / n_{SO_3^-} \) value was found to be 1.07. As can be seen from table 4.4, the value is slightly lower than that of Cs-Naf-CR1, indicating higher degree of dehydration of Na\(^+\) in Na-Naf-CR1 as compared to Na-Naf which again reflects that DB18C6 binds more strongly with Na\(^+\) ion in the membrane matrix. Higher \( D^0_{Cs} \) as observed in our earlier work [Bhattacharyya et al 2009], when DB18C6 was loaded in the Nafion-117 membrane in Li\(^+\) form could be due to at least partial retention of the water channels in Li-Naf-CR1. This is due to the lower binding of DB18C6 with Li\(^+\), thereby failing to completely dehydrate the Li\(^+\) ion in the membrane matrix unlike Cs-Naf-CR1 and Na-Naf-CR1.

![DSC thermograms](image)

**Figure 4.6:** DSC thermograms of (a) Cs\(^+\) form and (b) Na\(^+\) form of Nafion membrane with and without DB18C6.
Figure 4.6a and 4.6b depicts the DSC traces of pure and DB18C6 modified Cs⁺/ Na⁺ form of Nafion respectively. In the case of Cs-Naf, one sharp endothermic peak at 128 °C and another broad endothermic peak at 242 °C have been observed while for Na-Naf only one sharp endothermic peak at 136 °C has been observed. This behavior of Cs⁺/ Na⁺ form of Nafion is well explained in the literature [Almeida and Kawano 1999, Stefanithis and Mauritz 1990]. Thus the transition at ~ 130 °C (T₁) has been associated with the transition into the ionic clusters and that at ~ 245 °C (T₂) has been associated with the region of crystallite melting of the ionomers. The comparison of the DSC traces of Cs-Naf and Cs-Naf-CR1 shows that the sharp endothermic peak at 128 °C in Cs-Naf has almost disappeared in Cs-Naf-CR1. As can be seen from figure 4.6b, the same is true for Na-Naf-CR1 also. This change in DSC traces could be attributed to the absence of regions of water cluster channels after incorporation of DB18C6 in the Nafion-117 matrix. This corroborates our observations already obtained from equilibrium water uptake measurement and self diffusion measurement of cations and water.

4.3. Selective Transport

A general problem with the IEM is that the enhanced selectivity of an ion is usually accompanied by reduction in mobility of the ion. Enhancement in the permeability retaining the selectivity, therefore, is a challenge for use of IEM in separating ions of similar charge. Possible solutions can be the partial incorporation of the ligand (<1 mole ratio with respect to no. of ion exchange sites), so that the ion exchange sites free of ligand can provide faster transport pathway for the cations while the ligand occupied sites can provide selectivity. Alternatively, the crown ether can be loaded in a membrane where only a thin surface layer is occupied by the desired ion (templating only at the surface layer). Such an ion templated crown ether loaded thin layer may prevent the transport of undesirable ions, allowing the desired cations to selectively pass through a thin surface barrier in shorter time. Also,
permeation of ion from feed to receiver phase through IEM requires counter transport of another ion from receiver to feed phase to maintain electrical neutrality. This however, can be avoided if an electric field is used as a driving force for cation transport.

With this in view, in the present work, a Cs\(^+\) selective Dibenzo-21-crown-7 (DB21C7=CR), has been incorporated uniformly in Cs\(^+\) form of Nafion-117 membrane in varying molar ratio \((N = n_{CR}/n_{Cs^+})\) with respect to Cs\(^+\) in the membrane. The Cs\(^+\)\(_{sol}\) ⇌ Cs\(^+\)\(_{mem}\) (sol = solution and mem = membrane) isotope exchange kinetics and Na\(^+\)\(_{sol}\) ⇌ Cs\(^+\)\(_{mem}\) ion exchange kinetics in these homogeneously crown ether loaded membranes (Cs-Naf-CR\(_h\)) have been studied to assess the transport rate of the ions in these membranes. A crown ether-Nafion composite membrane has also been prepared by incorporating DB21C7 in a thin surface layer (few \(\mu\)m) of Nafion-117 membrane (ion gating). The surface confinement of Cs\(^+\) in this ion gated membrane (Cs-H-Naf-CR) has been studied using Energy Dispersive X-ray spectroscopy (EDS) and Time of Flight Secondary Ion Mass Spectrometry (ToFSIMS). A comparative account of these 2 types of membranes (Cs-Naf-CR\(_h\) and Cs-H-Naf-CR) for electro-driven selective transport of Cs\(^+\) from Na\(^+\) is also presented. The suitability of this ion gated membrane for selective removal of \(^{137}\)Cs from a simulated nuclear waste solution has also been studied. The results have been discussed in terms of cationic diffusivity and selectivity.

4.3.1. Experimental Section

4.3.1.1. Incorporation and Quantification of the crown ether in Cs-Naf-CR\(_h\)

The loading of DB21C7 in Cs-Naf was done by the method mentioned in section 4.2. The extent of loading in the membrane was controlled by varying the dissolved amount of DB21C7 in Dimethyl formamide (DMF), so that the mole ratio of Cs\(^+\) in the membrane and
dissolved DB21C7 in solution varies from 1:1 to 4:1. The quantification of the crown ether in the membrane matrix was done by gravimetric method as well as by UV-visible spectrophotometry, where, the spectra of the left over DB21C7 in DMF solution (after crown ether loading in the membrane) were used for the quantification. A representative UV-visible spectrum for 2.0 \times 10^{-4} \text{ M} solution of DB21C7 in DMF is shown in figure 4.7a. Using very dilute solution (\mu M/ L) of DB21C7in DMF, a linear calibration plot of absorbance vs. concentration of DB21C7 (figure 4.7b) is obtained at \lambda_{\text{max}} =281 \text{ nm}. For solutions of higher concentration, nonlinear behavior is observed. In gravimetric method, the dry weights of the membranes before and after loading of the DB21C7 were used to calculate N. The weight of dry membrane was obtained by heating the membrane sample for 6–8 h at 70\degree \text{C}.

![Figure 4.7](image)

**Figure 4.7**: (a) UV-visible spectrum acquired for 2.0 \times 10^{-4} \text{ M} DB21C7 solution in DMF. (b) Calibration plot of absorbance vs concentration of DB21C7.

### 4.3.1.2. Preparation and Characterization of Cs-H-Naf-CR

The Cs\(^+\) gated membrane (Cs-H-Naf-CR) was prepared by first exposing H-Naf (pure Nafion-117) membrane to 0.1 M CsCl solution from one surface for 15 seconds. The exposure time was decided from the Cs\(^+\)-H\(^+\) ion exchange kinetics as given by [Suresh et al. 2004]. This partially Cs\(^+\) loaded membrane is immediately placed in a DB21C7-DMF
solution so that the motion of Cs\(^+\) ions is arrested by DB21C7 in DMF medium. The amount of crown ether in the DMF solution was in a stoichiometric ratio of 1:1 to the total ion exchange sites in the membrane. The annealing of the crown ether loaded membrane was done by the method described in section 4.2. As calculated from gravimetric measurement, the value of \( \frac{n_{CR}}{n_{IES}} \) (\(n_{IES}\) = no. of ion exchange site in the membrane) in the Cs-H-Naf-CR membrane was found to be 0.32.

The distribution of Cs\(^+\) ion along the thickness of this membrane was studied by EDS and ToFSIMS methods. The EDS analysis was carried out using a Cam Scan made spectrometric unit (model no 3100) with 20 kV voltage and 150 \( \mu \text{A} \) beam current. The scanning was done along the thickness of the membrane in 20 steps (each step covered 10 \( \mu \text{m} \) length). At each step, data was acquired for 1 minute. For comparison purpose, this analysis was also carried out for Cs-Naf-CRh\(_h\) (\(N=0.8\), uniform Cs\(^+\) ion distribution throughout the membrane thickness).

**Figure 4.8:** (a) Microscopic image of the cross section of Cs-Naf-CRh\(_h\) (\(N = 0.8\)) along which EDS analysis has been carried out. (b) Atom % ratio of Cs to S (as obtained from EDS analysis) in Cs-Naf-CRh\(_h\) (\(N = 0.8\)) and Cs-H-Naf-CR.
Figure 4.8 (a) shows the cross sectional view of the Cs-Naf-CR2 membrane (N = 0.8) under scanning electron microscope. The number of steps that has been taken to cover the full thickness of the membrane for EDS analysis is also marked in the image. The Cs to S (each S atom corresponds to one ion exchange site in the membrane) atom % ratio (as obtained from EDS analysis) in Cs-Naf-CR<sub>h</sub> (N = 0.8) and Cs-H-Naf-CR are shown in figure 4.8 (b). The constant Cs to S atom % ratio in Cs-Naf-CR<sub>h</sub> indicates homogeneous distribution of Cs<sup>+</sup> throughout the membrane thickness. The sharp fall in Cs/S ratio in Cs-H-Naf-CR in the first few micron (25 μm) indicates that Cs<sup>+</sup> is loaded only in the initial ~25μm thickness. The EDS analysis shows that Cs<sup>+</sup> is confined only within 25 μm from the surface.

ToFSIMS data was acquired with 30 KeV Au<sup>+</sup> ion source as the primary beam, using a TRIFT V time of flight instrument, manufactured by ULVAC-Physical Electronics, Mn, USA. The Cs<sup>+</sup> distribution along the membrane (Cs-H-Naf-CR) thickness as obtained from ToFSIMS analysis is shown in figure 4.9. The first part of the figure (4.9a) shows the variation of Cs<sup>+</sup> counts at two different locations along the length. The similar nature of the Cs<sup>+</sup> distribution in both the locations indicates uniform distribution of this cation along the length of the membrane. The second part of the figure (4.9b) shows the overlay spectrum of Cs<sup>+</sup> ion (green coloured) distribution over total ion (red coloured) along the thickness of Cs-H-Naf-CR. The presence of Cs<sup>+</sup> only in the initial 25 μm of the membrane thickness is again obvious form both this figure.
Figure 4.9: ToFSIMS spectra showing (a) Variation of Cs\(^+\) counts and (b) Overlay of Cs\(^+\) ion (green) distribution over total ion (red) along the thickness of Cs-H-Naf-CR membrane.

4.3.1.3. Self diffusion and ion exchange measurement in Cs-Naf-CR\(_h\)

The Cs\(^+\) self diffusion measurements in the partially crown ether loaded Cs-Naf-CR\(_h\) membranes were carried out at room temperature following the standard radiotracer method as described in chapter 2. For the cases, where complete attainment of equilibrium was not possible, the fractional attainment of equilibrium (F\(_t\)) as a function of time (t) was found out indirectly using the following equation

\[
F_t = \frac{C_t}{(C_{mem})_\infty}
\]

Where, C\(_t\) is the radiotracer count in the membrane at time t and (C\(_{mem}\))\(_\infty\) is the expected radiotracer count in the membrane at equilibrium.

The amount of radiotracer ion in the membrane at equilibrium ((C\(_{mem}\))\(_\infty\)) is governed by the ratio of the amount of Cs\(^+\) ion in the membrane to that in the external solution. This quantity is calculated from the following relation
\[(C_{\text{mem}})_{x} = \frac{I_{\text{mem}} C_{\text{sol}}}{I_{\text{sol}}} \quad (4.2)\]

Where, \(I_{\text{mem}}\) is the number of available ion exchange sites in the membrane, \(C_{\text{sol}}\) is the total radioactivity added in the external salt solution and \(I_{\text{sol}}\) is the mili-equivalence of Cs\(^{+}\) in the external solution.

\(C_{\text{sol}}\) has been obtained by counting 100 \(\mu\)L of the solution in NaI(Tl) detector connected to a 4k channel analyzer. \(I_{\text{mem}}\) has been obtained from the dry weight of the membrane sample before incorporation of the crown ether.

For \(Na^{+}_{\text{sol}} \rightleftharpoons Cs^{+}_{\text{mem}}\) ion exchange kinetics measurement, the Cs-Naf-CR\(_{h}\) membrane sample (1 cm X 2 cm) was placed in 30 ml of 0.1 N NaCl solution. The solution was tagged with \(^{22}\)Na radiotracer. The kinetics of exchange between Cs\(^{+}\) ion the membrane and Na\(^{+}\) ions in the solution was monitored by the same method as described in the previous section. The 511 keV peak of \(^{22}\)Na was monitored. The fractional attainment of equilibrium (\(F_t\)) as a function of time (\(t\)) was found out indirectly following the same method as described in the previous section.

### 4.3.1.4. Transport study

In order to study the selective transport of Cs\(^{+}\) over Na\(^{+}\) (using Cs-Naf/ Cs-Naf-CR\(_{h}/\) Cs-H-Naf-CR membranes), two compartment permeation experiments were carried out at room temperature. During the experiment, electric field (4V) was applied across the membrane using two Pt electrodes. The membrane active surface area was 1.7 cm\(^2\). A schematic diagram of the experimental arrangement is shown in figure 4.10. In order to achieve volume reduction along with selective transport, the volume ratio of feed to receiver compartment was kept to be 10. A mixture (32 ml) of NaCl and CsCl was used in the feed and deionized water (3.2 ml) spiked with NaOH (0.004 mmol) has been used in the receiver compartment.
Two different mole ratios of CsCl and NaCl (1:1 or 1:4) were used in the feed compartment. The Cs\(^+\)-gated surface of the membrane was exposed to the feed solution which is tagged with \(^{22}\text{Na}\) and \(^{137}\text{Cs}\) tracer. The solutions in both the compartments were stirred continuously to avoid any film controlled diffusion at the membrane interface. Amount of Na\(^+\) and Cs\(^+\) transferred from the feed to the receiver side were monitored by taking out 200 \(\mu\)L of aliquots from both the compartments at regular time intervals and counting the \(^{22}\text{Na}\) and \(^{137}\text{Cs}\) activity in HPGe detector. For comparison of the results, one of the transport experiment (Cs\(^+\) : Na\(^+\) = 1:1 in feed solution) was repeated with Cs-Naf, keeping other conditions unaltered.

\[\text{Figure 4.10: Experimental arrangement for transport studies under applied electric field.}\]

Transport experiment was also carried out for the simulated effluent solution of Resorcinol Formaldehyde Polycondensate Resin (Intermediate Level Nuclear Waste treated with RFPR) with the feed composition being 0.1 M NaNO\(_3\) and 3.5 \(\times\) 10\(^{-4}\) M CsNO\(_3\) in 0.4 M HNO\(_3\) [Banerjee et al. 2014]. During the course of the experiment it was observed that, the crown ether was leaching out from the membrane possibly due to the strong interaction between HNO\(_3\) and DB21C7. The feed solution was thus neutralized with NaOH (pH ~ 7) before the
experiment was carried out. The final feed composition for this simulated waste was 0.5 M NaNO₃ and 3.5 X 10⁻⁴ M CsNO₃.

4.3.2. Results and Discussion

4.3.2.1. Cs-Naf-CRh

Four Cs-Naf-CRh membranes were prepared containing different mole ratio (N= 0.80, 0.66, 0.36, 0.21) of DB21C7 with respect to Cs⁺. The Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem isotopic exchange in Cs-Naf-CRh membrane (N = 0.8) is too slow to be observed at room temperature. However, for other Cs-Naf-CR membranes with lower (< 0.8) N, the Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem isotopic exchange takes place at room temperature. The Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem isotopic exchange profiles and the Na⁺ₜₚsol ⇔ Cs⁺ₜₚmem ion exchange profiles in these partially DB21C7 loaded Cs-Naf-CRh membranes are shown in figure 4.11a and 4.11b respectively. The arrows in the figures show the extent of sites available for isotopic/ ion exchange. The results show that, the mobility of Cs⁺ in Cs-Naf-CRh membrane decreases with increase in N and also the fraction of isotopic exchange sites available for Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem exchange decreases. It is also seen from the figures that the Na⁺ₜₚsol ⇔ Cs⁺ₜₚmem exchange profiles are faster than the corresponding Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem exchange. However, Na⁺ₜₚsol ⇔ Cs⁺ₜₚmem exchange proceeds to the extent that can be expected from the fraction of sites free of crown ether (1-N). This shows that there are two different types of Cs⁺ ionic sites in these Cs-Naf-CRh membranes, one associated with crown ether and the other free of crown ether. As seen from the profiles in figure 4.11a, with increasing N, the crown ether associated sites are increasingly difficult for Cs⁺ₜₚsol ⇔ Cs⁺ₜₚmem exchange due to change in membrane morphology.
Figure 4.11: Room temperature (a) $\text{Cs}^+_{\text{sol}} \leftrightarrow \text{Cs}^+_{\text{mem}}$ isotopic exchange profiles and (b) $\text{Na}^+_{\text{sol}} \leftrightarrow \text{Cs}^+_{\text{mem}}$ ion exchange profiles in Cs-Naf-CRh membranes with different N. The arrows indicate the fraction of exchangeable sites in the membrane at room temperature.

The time dependent relative cation transport (% Cs⁺/ %Na⁺) for different membranes [Cs-Naf, Cs-Naf-CRh (N= 0.36) and Cs-H-Naf-CR] are shown in table 4.5. The data shown in the table are for the experiments that have been carried out at 4 V with the feed solution having 5 milimoles Cs⁺ and 5 milimoles Na⁺. As can be seen from this table, transport selectivity of Cs⁺ over Na⁺ has not been observed in the two compartment transport experiments for the Cs-Naf and Cs-Naf-CRh (N=0.36) membranes. The absence of selective transport in Cs-Naf-CRh membranes can be understood on the basis of presence of two types of ion exchange sites in these membranes as explained earlier. The sites free of crown ether provide transport pathways like pure Nafion-117 with lower activation barrier (Ea) and lower selectivity. On the other hand, the diffusion involving crown ether associated ion exchange sites have very high activation barrier (templating effect) for diffusion and high selectivity. These two transport pathways in Cs-Naf-CRh membrane are represented schematically in figure 4.12a. Since both the ion exchange sites are randomly distributed throughout the membrane,
transport of most of the ions occurs involving the lower activation barrier sites, resulting in transport behavior (no selectivity) similar to that of pure Nafion-117.

**Table 4.5:** The time dependent relative cation transport (% $\text{Cs}^+/\%\text{Na}^+$) for different membranes. The experiments have been carried out at 4 V with the feed solution having 5 milimoles $\text{Cs}^+$ and 5 milimoles $\text{Na}^+$.

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Relative cation transport ($%\text{Cs}^+/%\text{Na}^+$)</th>
<th>Time (Minutes)</th>
<th>Relative cation transport ($%\text{Cs}^+/%\text{Na}^+$)</th>
<th>Time (Minutes)</th>
<th>Relative cation transport ($%\text{Cs}^+/%\text{Na}^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.91</td>
<td>60</td>
<td>0.87</td>
<td>210</td>
<td>4.08</td>
</tr>
<tr>
<td>210</td>
<td>1.12</td>
<td>150</td>
<td>0.99</td>
<td>420</td>
<td>4.49</td>
</tr>
<tr>
<td>330</td>
<td>0.87</td>
<td>210</td>
<td>1.05</td>
<td>1380</td>
<td>4.39</td>
</tr>
<tr>
<td>450</td>
<td>1.03</td>
<td>360</td>
<td>1.06</td>
<td>1635</td>
<td>4.03</td>
</tr>
<tr>
<td>1410</td>
<td>1.05</td>
<td>435</td>
<td>1.03</td>
<td>1860</td>
<td>3.91</td>
</tr>
</tbody>
</table>

**Figure 4.12:** Cation transport paths in (a) Uniformly crown ether loaded Cs-Naf-CRh membrane and (b) Ion gated Cs-H-Naf-CR membrane.
4.3.2. Ion Gated membrane (Cs-H-Naf-CR)

Transport experiments have been carried out with the membrane having one of the surface layers (~ 25 μm) loaded with DB21C7 templated Cs⁺. It is based on the conjecture, that a very thin selective layer, inspite of having high barrier for transport, may allow only Cs⁺ to pass through, leading to Cs⁺ ion gated membrane.

The results of the experiments carried out using different feed compositions are given in table 4.6. The different experiments carried out are identified with the corresponding experiment numbers in this table. The higher enrichment factor (ε >1) in this table indicates higher selectivity in transport of Cs⁺ over Na⁺ to the receiver side. The errors shown on the enrichment factors are the corresponding absolute errors on the measured data and have been calculated from the radioactivity counting statistics.

Table 4.6: The details of the two compartment transport experiments carried out at 4V along with corresponding enrichment factor of Cs⁺ over Na⁺ and Permeability coefficient of Cs⁺.

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Feed Composition (milimoles)</th>
<th>Membrane</th>
<th>Enrichment Factor (ε)</th>
<th>Permeability Coefficient of Cs⁺ (cm/ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cs⁺</td>
<td>Na⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
<td>Cs-Naf</td>
<td>1.0 ±0.1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>Cs-Naf-CRₙ (N=0.36)</td>
<td>1.0 ±0.1</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>Cs-H-Naf-CR</td>
<td>4.5±0.1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>8</td>
<td>Cs-H-Naf-CR</td>
<td>4.3±0.1</td>
</tr>
<tr>
<td>5</td>
<td>0.0084</td>
<td>12</td>
<td>Cs-H-Naf-CR</td>
<td>2.3±0.1</td>
</tr>
</tbody>
</table>
The cation transport profiles for different feed compositions are shown in figure 4.13. With Cs\(^+\) form of Nafion-117 membrane (Cs-Naf), after 7 h 24% Cs\(^+\) and 23% Na\(^+\) has been transported to the receiver side without any enrichment (ε=1.0). For the experiments with Cs-H-Naf-CR (exp 3 and exp 4), at the same time scale (7 h), the percentage Cs\(^+\)/ Na\(^+\) transported are 3/0.6 and 5.5/1.6 respectively, which shows the effect of crown ether on the cationic mobility. The percentages, as shown in figure 4.12, are with respect to the initial amount of cations in the feed side which are available for transport. Along with a volume reduction factor of 10, the observed enrichment factor of Cs\(^+\) over Na\(^+\) for third and fourth experiment are 4.5 ± 0.1 and 4.3 ± 0.1 respectively. The results indicate that, ion gating of the membrane with crown ether has imparted enhanced selectivity over pure Nafion-117 and enhanced transport rate over fully crown ether loaded membrane. It is also to be noted that, in the present set of experiments, as the cation transport is not solely driven by the concentration gradient due to presence of electric field, so more than 50% transport, as seen from figure 4.13 (92% in 3rd experiment), has therefore been observed.

The results of the transport experiment (exp 5) carried out for simulated effluent solution of Resorcinol Formaldehyde Polycondensate Resin (RFPR) [Banerjee et al. 2013] is also shown in table 4.6. It can be seen from the data that here also an enrichment factor of 2.3 ± 0.1 has been observed for Cs\(^+\) over Na\(^+\). This indicates that the selective transport of Cs\(^+\) in this ion gated membrane is possible inspite of such a high (Cs\(^+\)/ Na\(^+\)= 1:1428) Na\(^+\) concentration in aqueous solution.
**4.4. Conclusion**

The mobility of ions (Cs⁺ / Na⁺) and water is found to reduce drastically in Cs-Naf-CR1/CR2 and Na-Naf-CR1 compared to corresponding cationic form of pure Nafion-117. The temperature dependence of isotopic exchange of Cs⁺ and Na⁺ ion in Cs-Naf-CR1/CR2 and Na-Naf-CR1 respectively shows that there is a significant increase in the exchange rate with rise in temperature. The activation energies for diffusion of Cs⁺ and water in Cs-Naf-CR1 are comparable and are much higher than that in case of pure Nafion. On account of the higher affinity of DB21C7 for Cs⁺ than that of DB18C6, the activation barrier for Cs⁺ diffusion in Cs-Naf-CR2 is higher than that of Cs-Naf-CR1. This high value of activation barrier is comparable to that of ionic diffusion in ionic crystal lattice. Loading of crown ether in Nafion-117 enhances the hydrophobicity of the membrane matrix, thereby reducing the water uptake in the membranes. The DSC data shows disruption of water clusters in the membrane, and the attendant loss of plasticity, which lowers the SDCs.

**Figure 4.13:** Cation (Cs⁺/ Na⁺) transport profiles under different experimental conditions.
It is also inferred from the results that homogeneous loading of DB21C7 in the bulk of the membrane at different N (<1) enhance the cationic mobility with reduced selectivity. The problem of enhanced selectivity at the cost of mobility has been successfully overcome by confinement of the templating (with crown ether) only at the surface ion exchange sites. In this ion gated membrane, the combined effect of selectivity due to the templating effect of the surface screening layer and the significant mobility of the cation in the bulk under applied electric potential results in selective and quantitative transport of Cs\(^+\) over Na\(^+\) at practical time scale. Further enhancement in transport selectivity is expected with more selective crown ether or calix crown ligand and subsequent tuning of the screening layer thickness.