Chapter 6

Selective transport of Cs\(^+\) using a Polymer Inclusion Membrane of HCCD
6.1. Introduction

Use of different macrocyclic and macromolecular carrier based PIMs [Raut et al. 2012, Mohapatra et al. 2009, Levitskaia et al. 2002, Arena et al. 1998] or SLMs [Raut et al. 2008] for facilitated transport of Cs⁺ are well reported in literature. Raut and co-workers [Raut et al. 2012] have studied recovery of Cs from acidic feed solution using calix[4]-bis-2,3-naphthocrown-6 in PIM, while Mohapatra and co-workers [Mohapatra et al. 2009] have used di-benzo-21-crown-7 and di-tert-butylbenzo-18-crown-6 for selective Cs separation from nuclear waste solution. Arena et al [Arena et al. 1998] have reported selective transport of Cs⁺ from high Na⁺ background using a calixerene derivative in PIM. The major drawback associated with these ligands is the requirement of anion for charge compensation of the metal ion. Literature reports [Kimura et al. 1983, Sakamoto et al. 1986, Sata et al. 2000, Sata et al. 2001, Nemat-Nasser et al. 2006] are available where 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. As described in chapter 4, in order to make Cs⁺ ion selective membranes, cation driven loading of crown ethers within Nafion-117 cation exchange membranes has been done. In this case, however, the Cs⁺ selectivity (from crown ether) and anion for charge compensation (-SO₃⁻ groups in Nafion) are provided by two different moieties.

CCD⁻ is one such anion, which itself is highly selective for Cs⁺ and the two requirements, viz. charge compensation and selectivity can therefore be fulfilled by this single moiety. HCCD is also reported to display good stability towards radiation [Kyrs 1994]. The solvent extraction of Cs⁺ using protonated form of CCD⁻ (HCCD) as extractant and trifluoromethylphenyl sulfone (FS-13) [Scott Herbst et al. 2008] or nitrobenzene [Murali et al. 2012] as the solvent is well reported in literature. Murali and co-workers [Murali et al. 2012] have studied the efficacy of HCCD for the extraction and recovery of Cs from
simulated high-level waste (SHLW) solutions using 20% nitrobenzene in xylene as the solvent. Scott Herbst and co-workers [Scott Herbst et al. 2008] have studied the solvent extraction of Cs\(^+\) using HCCD in FS-13 and reported that the extraction of Cs by HCCD exclusively involves exchange of proton for cesium by formation of ion-paired CsCCD. Mohapatra et al. [Mohapatra et al. 2010] have reported the selective transport of cesium using HCCD in SLM and have reported a decontamination factor (DF, defined as the ratio of product to impurity in the product divided by that in the feed) of ~ 300 over different transition metal ions. One of the major disadvantages of this study is the requirement of 8-9 M HNO\(_3\) for stripping. Moreover, most of these membrane-based studies [Raut et al. 2012, Mohapatra et al. 2009, Levitskaia et al. 2002, Raut et al. 2008, Mohapatra et al. 2010], except the work of Arena and co-workers [Arena et al. 1998], have not addressed the selective separation of Cs\(^+\) from Na\(^+\) ions from nuclear waste solution.

In general, the ionic carrier facilitated membrane-based cation transports requires counter transport of another ion from receiver to feed phase to maintain electrical neutrality. This obviates the need of 8-9 M HNO\(_3\) concentration in the receiver phase, as reported in literature [Mohapatra et al. 2010]. As discussed in chapter 1, it can be avoided if an electric field is applied across the membrane, so that the anion in the feed compartment is oxidized at the anode and the cation moves to the receiver phase without any counter transport. The use of electric field, thus, eliminates the need of adding salt or stripping agent in the receiver side along with the enhancement in the cation transport rate. As described in chapter 4 and chapter 5, the electro-driven Cs\(^+\) transport through inorganic ion exchanger loaded track etched membrane and crown ether modified Nafion membrane has been shown. The DF for Cs\(^+\) over Na\(^+\) in the receiver phase in the two works have been reported to be ~2.0 and ~4.5 respectively. It is also to be mentioned that electro-driven transport is expected to be more
effective with ionic carriers like HCCD as compared to any other chelating or neutral macrocyclic ligands.

With this in view, in the present work, for the first time, HCCD has been used as a carrier in 2-nitro-phenyl-octyl ether (NPOE) plasticized cellulose tri acetate (CTA) / Poly Vinyl Chloride (PVC) based PIM. The present work describes the electro-driven transport studies of Cs\(^+\) and Na\(^+\) using these membranes, which includes the optimization of the working potential and determination of the current efficiency for the transport process. In view of the different possible compositions of the nuclear waste solutions, experiments have also been carried out for different feed compositions. The suitability of this membrane for selective removal of \(^{137}\text{Cs}\) from a simulated nuclear waste solution has been studied. The membrane has been characterized to study its stability. PVC based PIM of HCCD has been used to demonstrate the transport selectivity of Cs\(^+\) from a simulated high level nuclear waste (SHLW) solution containing 3 M  HNO\(_3\). The uniqueness of the method in terms of cation transport rate vis-à-vis selectivity is discussed.

6.2. Experimental

6.2.1. Preparation of membrane

A mixture of 0.08 g cellulose triacetate (CTA), 5 mg HCCD and 0.2 mL NPOE was dissolved in dichloromethane and homogenized by sonication. The solution was poured into a flat petridish and allowed to evaporate at room temperature. The resulting PIM was peeled out by spreading few mL of water on it and subsequently used for the transport studies. The carrier concentration in the membrane matrix is limited by the solubility of HCCD in the plasticizer NPOE. In 0.2 mL NPOE, 5 mg (0.01 mmoles) HCCD can be dissolved i.e the weight percentage of the carrier is 1.71. Increase in the amount of the NPOE resulted in over-plasticization of the membrane.
The PVC based membrane was prepared using 0.28 g PVC, 5 mg HCCD and 0.2 mL NPOE. 10 mL tetra hydro furan was used as the solvent for this preparation. Thickness of the membranes was measured using digimatic micrometer (Mitutoyo Corporation, Japan). The thickness of the synthesized CTA and PVC based membrane were 41 μm and 48 μm respectively.

6.2.2. Transport Studies with CTA based PIM

Electrodriven two compartment permeation experiments using CTA based membranes for different feed (32 mL) compositions were carried out. Electric field was applied across the membrane using two Pt electrodes and the current was monitored using a digital multimeter. The active surface area of the membrane was 1.77 cm². Deionized water (3.2 mL) spiked with NaOH (0.004 mmol) was used in the receiver compartment. In order to achieve volume reduction in the receiver compartment, the volume ratio of feed to receiver compartment has been kept at 10. The solutions in both the compartments were stirred continuously to avoid any film controlled diffusion at the membrane interface. The cations (Na⁺/ Cs⁺) in the feed compartment were tagged with ²²Na and ¹³⁷Cs tracer. The amount of Na⁺ and Cs⁺ transferred from the feed to the receiver side was monitored by taking out 200 μL of aliquots from both the compartments at regular time intervals and counting the ²²Na and ¹³⁷Cs activity in high purity germanium (HPGe) detector.

In order to optimize the applied electric field, the permeation experiments were carried out at different applied potentials (1 V-7 V). A mixture (32 mL) of 0.0025 M NaCl and 0.0025 M CsCl (tagged with ²²Na and ¹³⁷Cs tracer) was used in the feed compartment. The cation transport was monitored by counting the radiotracers. For the rest of the experiments (at the optimized potential) involving CTA based membranes, described in the work, only feed compositions were varied and all other experimental conditions were kept same (as mentioned in previous section).
In order to study the transport selectivity at different neutral feed compositions, two compartment permeation experiments at the optimized potential were also carried out with varying proportions (1:1 or 1:25) of Cs\(^+\) and Na\(^+\) in the feed. For these experiments the CsCl concentration (0.0025 M) was kept fixed and the NaCl concentration (0.0025 M / 0.0625 M) has been varied. In order to obtain the transport profiles of the cations (Na\(^+\)/Cs\(^+\)), they were tagged with their corresponding radiotracers in the feed compartment. Experiments were also carried out at 3V with either 0.0025 M NaCl or 0.0025 M CsCl in the feed compartment (other experimental conditions remaining same) and tagging the cation with respective radiotracers.

Transport experiment with the CTA based PIM was also carried out for a solution having the same Cs\(^+\) to Na\(^+\) ratio as that in the effluent solution (SRELW) of Resorcinol Formaldehyde Polycondensate Resin (Intermediate Level Nuclear Waste treated with RFPR) [Banerjee et al. 2013]. The feed composition was kept as 0.1 M NaNO\(_3\) and 3.5 x 10\(^{-4}\) M CsNO\(_3\) in 0.4 M HNO\(_3\), while the receiver compartment contained 3.2 mL deionized water spiked with NaOH (0.004 mmol). The transport rates of the cations (Cs\(^+\)/Na\(^+\)) were monitored by the same method as described in the previous section and the proton transport was monitored by acid-base titration method. In order to obtain the transport profile of salt and HNO\(_3\), the same experiment was repeated at zero applied potential. The salt transport was monitored by measuring the gamma activity of \(^{137}\)Cs and \(^{22}\)Na in the receiver compartment. The stability of the CTA based membrane was studied using UV-visible spectrophotometry.

### 6.2.3. Transport Studies with PVC based PIM

The transport selectivity of Cs\(^+\) from a SHLW was studied at optimized potential using HCCD as carrier in a PVC based PIM. The composition of the SHLW, as obtained from inductively coupled plasma-atomic emission spectroscopic (ICP-AES) measurement, is
shown in table 6.1. The metal ions were present in 3 M HNO₃. It can be seen from the table that apart from cesium, the initial feed solution contains high amount of sodium, manganese, potassium and iron. For this study, a two compartment (each of 25 ml) glass cell with the membrane active surface area of 5.3 cm² was used. In this case, the receiver compartment contains 25 ml deionized water spiked with NaOH (0.004 mmol). The transport of the Cs⁺ ion was monitored using radiotracer technique, while the transport of other cations were monitored by atomic emission spectroscopy using Jobin–Yvon Ultima high resolution ICP-AES. The H⁺ transport was monitored by acid-base titration method.

**Table 6.1:** Elemental composition of the SHLW feed solution used for the transport study.

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. (mg/ L)</th>
<th>Element</th>
<th>Conc. (mg/ L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>220</td>
<td>Mo</td>
<td>62</td>
</tr>
<tr>
<td>Na</td>
<td>4620</td>
<td>Ba</td>
<td>23</td>
</tr>
<tr>
<td>K</td>
<td>220</td>
<td>Y</td>
<td>60</td>
</tr>
<tr>
<td>Cr</td>
<td>112</td>
<td>La</td>
<td>168</td>
</tr>
<tr>
<td>Mn</td>
<td>480</td>
<td>Ce</td>
<td>55</td>
</tr>
<tr>
<td>Fe</td>
<td>690</td>
<td>Pr</td>
<td>76</td>
</tr>
<tr>
<td>Sr</td>
<td>28</td>
<td>Nd</td>
<td>92</td>
</tr>
<tr>
<td>Zr</td>
<td>84</td>
<td>Sm</td>
<td>45</td>
</tr>
</tbody>
</table>
6.3. Results and discussion

6.3.1. CTA based PIM for Cs\(^+\) transport from low acidic/neutral feed solution

The basic principle of electrodriven cation transport is shown in figure 1.10. In presence of Cl\(^-\) ion in the feed solution, the anodic reaction involves oxidation of Cl\(^-\) (2Cl\(^-\) → Cl\(_2\) + 2e\(^-\)) [Strathman 1990], whereas for the experiments with NO\(_3^-\) in the feed solution, water is oxidized (2H\(_2\)O → 4H\(^+\) + O\(_2\) + 4e\(^-\)) at the anode in preference to NO\(_3^-\) at a potential greater than 1.48 V.

The Cs\(^+\) transport profiles with the CTA based membrane for a fixed feed composition (0.0025 M NaCl + 0.0025 M CsCl) at different applied potentials are shown in figure 6.1. It can be seen from the figure that at 1 V, Cs\(^+\) transport does not take place. This can be understood from the fact that oxidation of Cl\(^-\) at anode is required for the onset of transport process and the standard electrode potential for Cl\(^-\) oxidation is 1.36 V. At 2 V, transport of Cs\(^+\) takes place at a very slow rate. The transport profiles at 3 V, 5 V and 7 V indicate that initially there is a continuous increase in the cation transport with increase in potential. However, no significant difference exists at higher percentage (~85 %) of cation transport. It is observed that the DF for Cs\(^+\) over Na\(^+\) is 51 at 3 V, which decreases to 24 at 5V. This indicates that, increase in potential has resulted in loss of selectivity while there is no significant gain in time for ~100% cation transport. Thus, the rest of the experiments were carried out at a working potential of 3 V.

The cation (Cs\(^+\)/Na\(^+\)) transport profiles (obtained using radiotracer technique) for CTA based PIM at 3 V for different Cs\(^+\) to Na\(^+\) ratio (1:1 or 1:25) in the neutral feed solution are shown in figure 6.2. The selectivity of the membrane for Cs\(^+\) over Na\(^+\) is indicated from the figure, where >90 % Cs\(^+\) is transported within ~14 h, with negligible Na\(^+\) transport (1.8 %) throughout the experiment., resulting in a DF of 51. The figure also shows that, the cation
transport rate is unaffected by the change in feed composition in this range. As shown in Table 6.2, the DF for 1:1/1:25 Cs\(^+\)/Na\(^+\) feed compositions are obtained as 51 and 52 respectively.

![Graph showing Cs\(^+\) transport profiles](image)

**Figure 6.1:** Cs\(^+\) transport profiles obtained using CTA based PIM at different applied potential for the same feed composition of 0.0025 M NaCl + 0.0025 M CsCl.

**Table 6.2:** Decontamination factors (DF) of Cs\(^+\) over Na\(^+\) in electrodriven (3V) transport experiments using PIMs.

<table>
<thead>
<tr>
<th>No</th>
<th>Base polymer</th>
<th>Feed Composition</th>
<th>DF (at &gt;90% Cs transport)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CTA</td>
<td>Cs: Na= 1:1 (Neutral)</td>
<td>51</td>
</tr>
<tr>
<td>II</td>
<td>CTA</td>
<td>Cs: Na= 1:25 (Neutral)</td>
<td>52</td>
</tr>
<tr>
<td>III</td>
<td>CTA</td>
<td>SRELW (0.4 M HNO(_3))</td>
<td>410</td>
</tr>
<tr>
<td>IV</td>
<td>PVC</td>
<td>SHLW (3M HNO(_3))</td>
<td>80</td>
</tr>
</tbody>
</table>
Figure 6.2: Cation (Cs⁺/Na⁺) transport profiles obtained using CTA based PIM at 3 V for different Cs⁺ to Na⁺ ratio in the neutral feed solution. The ratios indicate the Cs⁺:Na⁺ ratio in the initial feed solution.

In order to study the possibilities of loss of current due to any unwanted process, the current efficiencies was calculated by measuring the current along with the cation transport at different time intervals. The current profiles, obtained for CTA based PIM at 3 V for different neutral feed compositions are shown in figure 6.3. The current efficiency (I_{eff}) for different feed compositions have been calculated using the following equation and are given in table 6.3.

\[
I_{\text{eff}} = \frac{\text{Total current carried by cation}}{\text{Integrated Current}} = \frac{m_c e N_A}{\int_0^t I(t) dt}
\]

(6.1)

Where, \(m_c\) = moles of cation transported, \(e=1.6 \times 10^{-19}\) Coulomb and \(N_A=\text{Avogadro’s number.}\)
Figure 6.3: Current profiles obtained for CTA based PIM at 3 V for different neutral feed compositions.

As shown in the table, the current efficiency for Cs\(^+\) (0.0025 M CsCl) and Na\(^+\) (0.0025 M NaCl) in the feed compartment is obtained as 95% and 100% respectively. This indicates that cation transport alone can account for the integrated current. The current efficiency for Cs\(^+\) transport from the feed containing 1:1 Cs\(^+\) to Na\(^+\) (0.0025 M NaCl + 0.0025 M CsCl) is obtained as 90%. Of the remaining, 1.8% is accounted for the Na\(^+\) transport.

Table 6.3: Current efficiencies obtained using CTA based PIM at 3 V for different neutral feed compositions.

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Current efficiency for cation transport at the end of transport process</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0025 M NaCl + 0.0025 M CsCl</td>
<td>90%</td>
</tr>
<tr>
<td>0.0025 M NaCl</td>
<td>100%</td>
</tr>
<tr>
<td>0.0025 M CsCl</td>
<td>95%</td>
</tr>
</tbody>
</table>
The electrodriven selective transport of Cs\(^+\) from SRELW has been attempted using the CTA based PIM of HCCD and the results are summarized in figure 6.4. The gamma spectra (for a fixed counting time) of the initial and final feed solution as well as final receiver solution are shown in figure 6.4 a, b and c, respectively. As seen in figure 6.4c, the quantitative transport of \(^{137}\text{Cs}\) as well as the negligible transport of \(^{22}\text{Na}\) in the receiver spectra indicates excellent selectivity for Cs\(^+\) over Na\(^+\). The corresponding DF, as shown in table 6.2, is calculated to be 410.

**Figure 6.4:** Gamma spectra of the initial (SRELW) and final feed solution as well as final receiver (93% Cs transport) solution, showing the selective transport of \(^{137}\text{Cs}\) over \(^{22}\text{Na}\) through CTA based PIM. The spectra have been normalized for the same counting time.
It is also to be mentioned that, due to presence of large amount of Na\(^+\) as well as H\(^+\) (0.4 M HNO\(_3\)), the cation transport rate is very slow i.e. long time (59 h) is required for significant (93 \%) Cs\(^+\) transport, which is associated with 2.3 \% H\(^+\) transport. This can be explained only if there is a leakage of HNO\(_3\) through the membrane. Otherwise, in case of electrodriven H\(^+\) transport, the pH of the receiver phase would not have decreased as the OH\(^-\) generated at the cathode neutralizes the transported H\(^+\). This is confirmed when the same experiment has been repeated at zero applied potential. In this case, the possible transport is driven by only concentration gradient i.e., HNO\(_3\) is transported (from feed to receiver) as a neutral molecule. The transport profiles of HNO\(_3\) along with that of CsNO\(_3\)/NaNO\(_3\) are shown in figure 6.5. The experimental result indicates that after 59 h, 2.4 \% of initial HNO\(_3\) in the feed has been transported to the receiver compartment, whereas no \(^{137}\text{Cs} / ^{22}\text{Na}\) radioactivity is observed in the receiver compartment (below the detection limit of gamma spectrometry), i.e., the salt transport remains zero throughout the experiment.

The faster cation transport rate and lower DF in neutral feed solution as compared to that in the SRELW can be explained on the basis of presence of large amount of H\(^+\) in SRELW. In case of SRELW, the feed compartment contains 3.2 mmol of Na\(^+\) (Cs\(^+\):Na\(^+\) = 1:286) along with 12.8 mmol of H\(^+\). Proton transport through HCCD-PIM can compete with other cation transport (Cs\(^+\) or Na\(^+\)) transport, which leads to slower transport rate of both Cs\(^+\) and Na\(^+\). Because of the inherent selectivity of the membrane for Cs\(^+\), in presence of large proton concentration, Na\(^+\) transport is more suppressed as compared to Cs\(^+\) transport through the membrane. This explains the higher DF in the SRELW as compared to that in the case of neutral feed solution.
From UV-visible calibration of the CTA based PIMs, it is observed that there is a 12% decrease in the carrier concentration of the membrane after 48 h of continuous use. This indicates moderate stability of the CTA based PIM of HCCD and its stability can be further enhanced by grafting.

6.3.2. PVC based PIM for Cs\(^+\) transport from high level waste solution

Separation of Cs\(^+\) from SHLW is important from waste management aspect. The SHLW contains a large number of metal ions (table 6.1) in a high HNO\(_3\) (3M) concentration, where CTA based PIM can’t be used due to the acid hydrolysis of the CTA matrix. PVC based membrane has thus been prepared for Cs\(^+\) transport from SHLW. The results obtained for the transport study with SHLW using HCCD as carrier in PVC based PIM are summarized in figure 6.6. The Cs\(^+\) concentrations in feed and receiver compartments were measured using radiotracer technique, whereas those of the other metal ions were determined using ICP-AES technique. The bar diagrams given in figure 6.6, clearly indicates that, the membrane
exclusively transports Cs$^+$ from a SHLW solution. The results show that, inspite of presence of large quantity of Na$^+$, only 1.2 % of the initial Na$^+$ is transported to the receiver side at the end of the transport process. The compositions of other elements in the final feed solution remain unaltered as those in the final receiver solution are below 0.1 mg/L. In this case, the DF (as shown in table 6.2) for Cs$^+$ is calculated to be 80 over Na$^+$ and in the range of $\sim$500-5000 over other metal ions. Quantitative (>99%) Cs$^+$ transport takes place in $\sim$42 h. This is accompanied with only 3.3% (of initial feed proton conc.) HNO$_3$ transport to the receiver phase.

Figure 6.6: Relative concentrations of different metal ions in the (a) initial feed solution (b) final feed solution and (c) final receiver solution for the treatment of SHLW using PVC based PIM.
In general, enhancement in the permeability retaining its selectivity is a challenge for use of ion-exchange membrane in separating ions of similar charge. In our works with Nafion-Crown ether composite membrane, it has been observed that high selectivity is achieved only at the cost of cationic mobility in the membrane. On the other hand, the results described in the present work indicate that HCCD-PIM is a highly Cs\(^+\) selective membrane with which the cation can be transported within reasonable time under electric field. From this aspect, this is indeed a unique approach of separation of Cs\(^+\) from nuclear waste solution.

6.4. Conclusion

The present study, for the first time, demonstrates a novel and cleaner method of Cs\(^+\)-separation of from simulated nuclear waste solution using HCCD as a carrier in PIM. HCCD, being a highly selective ionic carrier for Cs\(^+\), a very high DF has been obtained in the electro-driven transport study. The work addresses the decontamination of Cs\(^+\) over Na\(^+\), which is the major challenge in nuclear waste treatment and has not been addressed in any membrane based separation methods. The use of stripping agent (8 M HNO\(_3\)), as described in previous literatures, has been avoided by using electric field in the present study. This makes this separation process more safe and environment friendly.