Chapter 7

Summary and Conclusions
Ion exchange membrane (IEM) based separation techniques have considerable commercial and technical impact. As the interaction of the cations in a cation exchange membrane is electrostatic in nature, the mutual separation of ions of same valence is difficult using IEM. 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. However, a general problem with IEM is that, the high selectivity always comes at the cost of cationic mobility in the membrane. In the present work, an attempt has been taken to achieve metal ion selectivity (Cs$^+$ over Na$^+$) with significant transport rate using different IEMs like Nafion-117, copper ferrocyanide loaded track etched membrane and polymer inclusion membrane. The novelty of the work is in the use of electrodialysis based transport process instead of the conventional Donnan dialysis based processes. This electromembrane extraction process does not require any counter transport from receiver to feed solution, as in the case of Donnan dialysis based process. The use of electric field, eliminates the need of adding salt or stripping agent in the receiver side. Electric field also helps to enhance the cationic flux in the membrane with subsequent reduction in the transport time.

In the present work, Cs$^+$ has been chosen as the metal ion interest, because, it is one of the most abundant fission products present in nuclear waste. It is of major environmental concern because of the long half-life (30 y) and high gamma energy (662 keV) of its radioisotope $^{137}$Cs. The conventional methods (solvent extraction, precipitation, ion-exchange resin based methods) of Cs separation have associated drawbacks like requirement of large amount of undesirable solvents and macrocyclic carriers, insufficient selectivity and generation of voluminous secondary nuclear waste. Whereas, the membrane based methods are environmentally benign and requires small amount of ligand. Use of different macrocyclic and macromolecular carrier based membranes for facilitated transport of Cs$^+$ are well reported in literature. The major drawback associated with these ligands is the requirement of
anion for charge compensation of the metal ion. Presence of bulk concentration of Na$^+$ in the nuclear waste solution is the major challenge in recovery/ removal of Cs$^+$. This problem has not been addressed by most of the reported membrane based methods.

The work reported in this thesis has relevance in the Cs$^+/\text{Na}^+$ separation using IEM. In the present work, different aspects (effect of mixed cationic environment, activation energy of diffusion) of Cs$^+$ diffusion as well as selective transport of Cs$^+$ over Na$^+$ through different IEM have been studied. Mostly radiotracer based techniques have been used for the measurements of different parameters. Major achievements and conclusions of this work are summarized as follows.

1. The self diffusion coefficient (SDC) of an ion in Nafion-117 membrane is influenced by the ionic composition of the membrane phase, depending upon the path of transport of the two cations within the membrane. Cs$^+$ with low charge density follows a transport pathway through the aqueous side of the interfacial region, while Na$^+$ / Ba$^{+2}$ moves mainly through the water rich micro phase of the membrane. Hence, in Na-Cs and Cs-Ba systems, the ions follow a mutually independent path and do not influence the SDCs of each other. On the other hand, if the two ions are moving through an overlapping path, then depending upon the electrostatic binding of the cation with the fixed charge group of the membrane, the SDCs will be affected. Thus in Na-Ba and Ag-Ba systems, the SDC of Ba$^{+2}$ decreases continuously as the amount of the other cation increases in the membrane. This ionic composition dependent self diffusion behavior of either cation is ultimately reflected in the specific conductivity of the system. Thus, for Na-Cs system, the specific conductance increases linearly, whereas for Na-Ba system, it increases in a parabolic fashion with increase in Na$^+$ content in the membrane.
2. The study of temperature dependence of SDCs of $\text{Cs}^+$ and water in dibenzo-18-crown-6 (DB18C6) modified Nafion membrane indicates high activation energy (~80 kJ/mole) of diffusion. Such a high value of activation energy indicates that there is no continuous water channel in the composite membrane. Experimental results indicated that, the water uptake of Nafion membrane has reduced significantly on introduction of crown ether in the membrane. This shows that complexation of DB18C6 with $\text{Cs}^+$ ion accompanied by the disruption of the water cluster channel network of Nafion-117 has taken place, thereby reducing the SDCs significantly. The stronger binding of $\text{Na}^+$ (than $\text{Cs}^+$) with DB18C6 is reflected in the slower self-diffusion kinetics of $\text{Na}^+$ (than $\text{Cs}^+$) in the composite membrane matrix. The activation energy of diffusion of $\text{Cs}^+$ in diffusion dibenzo-21-crown-7 (DB21C7) has been obtained as $213 \pm 16$ KJ/mole, which is much higher than that in DB18C6 loaded Nafion. The result clearly shows much higher affinity of $\text{Cs}^+$ for DB21C7 than DB18C6. The Differential Scanning Calorimetry (DSC) data corroborates our observations already obtained from equilibrium water uptake measurement and self diffusion measurement of cations and water.

In an attempt to make $\text{Cs}^+$ selective membranes, with which $\text{Cs}^+$ can be transported at room temperature, two types of crown ether -Nafion composite membranes have been prepared. In one case, the DB21C7 has been incorporated uniformly in $\text{Cs}^+$ form of Nafion-117 membrane in varying molar ratio with respect to $\text{Cs}^+$ and in the other case, the $\text{Cs}^+$ driven loading of DB21C7 has been confined (ion gating) at one surface of the membrane. The isotopic and the ion exchange studies in the uniformly crown ether loaded membranes has indicated that the decrease in the extent of crown ether loading increases SDC of $\text{Cs}^+$ at the cost of mutual cationic selectivity ($\text{Cs}^+$ over $\text{Na}^+$). This problem has been successfully overcome by confinement of the templating (with crown ether) only at a very small thickness (25 μm) from one of the surfaces of the membrane. At room temperature, under electric field (4V) this ion gated membrane has been found to selectively transport $\text{Cs}^+$ within practical time scale with
an average enrichment factor of 4.5 over Na$^+$. When applied for the simulated nuclear waste solution, selective transport of Cs$^+$ has also been obtained using this gated membrane even in the presence of very high Na$^+$ concentration in aqueous solution.

3. In another attempt, highly Cs$^+$ selective copper ferrocyanide nano-crystals have been synthesized within the pores of track etched membrane. Characterization of the composite membrane (KCFCNm) indicates presence of mixed potassium copper ferrocyanide composition, which has been represented as KCFCN in this work. The conical shaped pores of the membrane are almost uniformly filled with the KCFCN crystals and the rod like structures, as has been observed in the TEM images, are made up of nanosized KCFCN crystals (~40 nm).

Under applied electric field, the KCFCNm has been found to selectively transport Cs$^+$ from acidic feed solution with an average enrichment factor of ~2 over Na$^+$. Study of water transport through the membrane indicates that though KCFCN crystals cause physical blocking of the pores of the membrane but some water channels still exist in the KCFCNm. The self diffusion measurement of Cs$^+$ in the membrane indicates very fast absorption of the cation. Absorption experiments have indicated that the Cs$^+$ exchange capacity of the membrane as well as the distribution coefficients of Cs$^+$ in the membrane are much higher than the best reported in literature till date. The $^{137}$Cs removal efficacy of the membrane has been found to be affected by the activity dilution and more equilibration time is required when the activity is distributed in larger volume of solution. Application of this composite membrane for removal of Cs$^+$ from a simulated nuclear waste has indicated exclusive absorption of $^{137}$Cs inspite of presence of other radionuclides, though the absorption rate is affected due to their presence. This composite membrane shows promising properties for Cs$^+$ removal from nuclear waste solution.
4. For the first time, use of the hexachlorinated derivative of cobalt bis (dicarbollide) (HCCD) as a selective carrier for Cs\textsuperscript{+} transport through cellulose tri acetate (CTA) / poly vinyl chloride (PVC) based polymer inclusion membrane (PIM) is reported in this work. The electrodriven transport study through this PIM indicated excellent selectivity for Cs\textsuperscript{+} over Na\textsuperscript{+}. The working potential of the transport system has been optimized as 3 V. Under applied electric filed, the CTA based membrane has been found to selectively transport Cs\textsuperscript{+} from a neutral feed solution with a decontamination factor (DF) of 51 for Cs\textsuperscript{+} over Na\textsuperscript{+}. Presence of large concentration of H\textsuperscript{+} in the feed solution has been found to slower the cation transport rate and increase the transport selectivity of Cs\textsuperscript{+} over Na\textsuperscript{+}. Thus, for a simulated nuclear waste solution containing 0.1 M NaNO\textsubscript{3} and 3.5 x 10\textsuperscript{-4} M CsNO\textsubscript{3} in 0.4 M HNO\textsubscript{3}, a DF of >400 for Cs\textsuperscript{+} over Na\textsuperscript{+} has been obtained with a much slower transport rate as compared to neutral feed solution. In order to study transport selectively of Cs\textsuperscript{+} from a simulated high level nuclear waste (SHLW) in 3 M HNO\textsubscript{3}, a PVC based membrane, which has higher stability in high acidic medium, has been used. This membrane selectively transported Cs\textsuperscript{+} with a decontamination factor of 80 over Na\textsuperscript{+} and >500 over other metal ions present in the SHLW. The results indicate that HCCD-PIM, inspite of its high selectivity for Cs\textsuperscript{+}, allows the cation to be transported within reasonable time under electric field.

In conclusion, the present study, demonstrates a novel and cleaner method of Cs\textsuperscript{+}-separation of from simulated nuclear waste solution The promising results explore the possibility of using this kind of electrodriven membrane transport methods for nuclear waste treatment. However, further extensive studies for different type of waste solutions need to be pursued to establish it as a standard method.