Chapter 1

Introduction

Ion Exchange Membrane

Counterions → Coions

Nafion

PIM

Track etched membrane
1.1. Membranes

A membrane is a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or may be chemically or physically heterogeneous, for example, containing holes or pores of definite dimensions or consisting of some form of layered structure. With increasing demand for more effective separations in the chemical, pharmaceutical, environmental and food industries, new materials and technologies have been investigated and developed. Over the years, membrane based separation techniques have grown from simple laboratory research scale up to large scale industrial processes that have considerable, technical and commercial impact [Strathmann 1990] due to the following advantages.

(a) Appreciable energy savings

(b) Environmentally benign

(c) Clean technology with operational ease

(d) Replaces the conventional processes like filtration, distillation, ion-exchange and chemical treatment systems

(e) Greater flexibility in designing systems

(f) Possibility of obtaining high enrichment/ separation factors

The driving force for the transport of a species across membrane can be a difference in concentration, pressure, electrical potential, or temperature [Paul and Peinemann 1996, Cheung and Raj 1996]. Table 1.1 summarizes membrane based separation processes with the type of driving force and separation mechanism.
Table 1.1: Membrane based separation processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Driving force</th>
<th>Separation mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion dialysis</td>
<td>ΔC</td>
<td>Diffusion</td>
</tr>
<tr>
<td>Microfiltration</td>
<td>ΔP</td>
<td>Sieving</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>ΔP</td>
<td>Sieving</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>ΔP</td>
<td>Sieving/Solubility</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>ΔP</td>
<td>Sieving/Solubility</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>ΔP</td>
<td>Solubility/Diffusion</td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>ΔP</td>
<td>Solubility/Diffusion</td>
</tr>
<tr>
<td>Gas separation</td>
<td>ΔP</td>
<td>Solubility/Diffusion</td>
</tr>
<tr>
<td>Vapor permeation</td>
<td>ΔP</td>
<td>Solubility/Diffusion</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>ΔE</td>
<td>Electromigration</td>
</tr>
</tbody>
</table>

* ΔC, ΔP and ΔE stand for differences in concentration, pressure, and electrical potential, respectively.

The separation processes can either be pressure driven processes (RO, NF, UF, MF) which are governed by size exclusion principles or charged membranes (ion exchange membrane) based processes, where separation is achieved by the interaction of permeating species (i.e. electrolyte) with the fixed charges of an ion exchange membrane (IEM). Since the work in this thesis has been carried out using different IEMs, in the rest of this chapter, emphasis is given on this type of membrane based separation process only.

1.1.1. Ion Exchange Membrane

An ion exchange membrane consists of a barrier or thin layer, which contains ionogenic (IEM) groups that restrict the transport of various ionic species. A schematic diagram of a cation exchange membrane is shown in figure 1.1. This membrane consists of a cross linked
polymeric matrix with the fixed negative charges, which attract positively charged mobile ions and rejects negatively charged mobile ions. Ion exchange membranes are, in general, finely micro porous, with the pore walls carrying fixed positive or negative charges [Baker 2004]. An ion-exchange material has fixed positive or negative charges which associate with ions of the opposite charge. These ions are called counterions. Ions that have the same sign as the fixed charges of the ion exchange material are called coions. For example, in figure 1.1, the positively charged mobile ions are counterions and the mobile anions are coions.

![Figure 1.1: Schematic structure of a cation-exchange membrane.](image)

Depending upon the type of replaceable group, IEMs can be either cation exchangers or anion exchangers. IEMs are semi-permeable, i.e., they allow only the counter ion to pass through them, excluding the co-ions. In ion exchange membranes the counterions interact with the fixed charged functional groups in the membrane electrostatically. Separation with charged membranes is achieved mainly by exclusion of the same charge as the fixed groups on the membrane backbone, and to a lesser extent by the pore size. Separation techniques based on IEMs are increasingly gaining importance as relatively clean separations with high separation factors are achievable and also they are cost effective. The key parameters for specific applications of these membranes are: (i) selective partitioning of target species from
solution to membrane phase, (ii) diffusion of the species in the membrane matrix and (iii) release of the target species into the receiver phase. Therefore, the interaction of the target species with the functional groups and, physical and chemical architecture of the membrane matrix play an important role in designing target specific membranes. Depending on the method of preparation, IEMs can be classified as

(a) **Homogeneous membranes:** These membranes are prepared by polymerization or condensation of functional monomers or by heating a pre-condensed reaction mixture containing oligomers or mixture of monomers [Helfferich 1962].

(b) **Graft copolymer membranes:** These membranes are prepared by incorporating the polyelectrolyte gel within the pores of a robust microporous host membrane and they are having outstanding mechanical and good electrochemical properties.

(c) **Liquid Membranes (Mobile carrier membranes):** A liquid membrane utilizes a carrier to selectively transport components such as metal ions at relatively high rate across the membrane interface. The membrane types that are commonly studied are Bulk liquid membranes (BLM), Supported Liquid Membranes (SLM), and Polymer Inclusion Membranes (PIM).

In the present study, we have used either homogeneous cation exchange membrane named as Nafion-117 (modified or as it is) or ion exchanger loaded polycarbonate track etched membranes or polymer inclusion membranes. The details about these different types of membrane are given below.

1.1.1.1. **Nafion**

Nafion is a cation exchange membrane developed by E.I. DuPont deNemours and Co. Inc. It finds wide applications in separation science and industry. Its chemical structure (figure 1.2)
consists of a polytetrafluoroethylene (PTFE) backbone with pendent side chain containing –SO₃H group. These materials are synthesized by copolymerization of a fluorinated vinyl ether monomer with tetrafluoroethylene [Mauritz & Moore 2004].

\[
\begin{align*}
&-\left[ (CF - CF_2) - (CF_2 - CF_2)_m \right] - \\
&O - CF_2 - CF - O - CF_2 - CF_2 - SO_3H \\
&CF_3
\end{align*}
\]

**Figure 1.2:** Chemical structure of Nafion membrane.

Nafion can be converted into any cationic form by simple ion-exchange process. Membranes having different equivalent weight can be obtained by varying the m in the above chemical formula. The equivalent weight (EW) of Nafion is the number of grams of dry Nafion per mole of sulfonic acid groups when the membrane is in acidic form [Mauritz & Moore 2004]. This is an average value obtained from the distribution in the comonomer sequence (value of m). The EW is related to m as EW = 100m + 446. For example, if the value of m is 7, then the EW is 1100. In Nafion-117 membrane, the suffix “117” refers to the EW of 1100 g/equivalent of sulfonic acid groups in dry H⁺-form of the membrane, and the membrane sheet thickness of 7 mil (1mil = 25 μm). Nafion has high degree of disorder in physical organization of its matrix. To obtain information on structural morphology of Nafion under different environment, several experimental techniques like small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), small angle neutron scattering (SANS), atomic force microscopy (AFM), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR) spectroscopy have been used over the years [Hsu & Gierke 1982, Hsu & Gierke 1983, Xue et al, 1989, Lee et al. 1992, McLean et al 2000, Rollet et al. 2002,]
Based on these studies, different models describing the self-assembling morphology of Nafion under different physico-chemical environments have been proposed [Mauritz & Moore 2004, Kusoglu et al. 2012, Gebel et al. 2000, Schmidt-Rohr et al. 2008, Rubatat et al. 2002, Rollet et al. 2004, Rubatat et al. 2004, Starkweather et al. 1982, Elliott et al. 2011]. The first important morphological description of Nafion is based on “Cluster-channel network model” proposed by Hsu and Gierke [Hsu and Gierke 1982, Hsu and Gierke 1983]. Gierke and co-workers, using SAXS and wide-angle X-ray diffraction (WAXD), have compared the morphological features of Nafion membranes of different equivalent weights. They concluded that the water-swollen morphology of Nafion was best described by a model of approximately spherical shaped ionic clusters with an inverted micellar structure. It was also proposed that the high ionic permselectivity in Nafion membranes is due to the interconnectivity between the ionic clusters by narrow channels, thus providing a percolation pathway for ionic transport. This morphology referred to as the cluster-channel model is shown in figure 1.3. Theoretical calculations based on this model showed that, for a given equivalent weight, the cluster diameter, the exchange sites per cluster, and the number of water molecules per exchange site increased linearly with water content. It was proposed that the growth of clusters with increasing water content is due to a combination of expansion in cluster size and a redistribution of the sulfonate sites to yield fewer clusters in the fully hydrated material. This original, yet phenomenological, cluster-channel model has received significant acceptance in the literature and has served as the foundation for numerous studies of morphology-property relationships of Nafion. In recent times several other models have also been proposed, some of which are described below.
Rubatat et al. [Rubatat et al. 2002] suggested the “Polymeric bundle model” consisting of fluorocarbon chains surrounded by ionic groups and water. More recently, a unified morphological description of organization of water swollen Nafion has been proposed. This model suggests a bicontinuous network of ionic clusters embedded in a matrix of fluorocarbon chains and accepts the existence of ionic clusters network without need of extended parallel channels. In the present thesis, the observations are discussed based on the cluster channel model of Hsu & Gierke [Hsu and Gierke 1982, Hsu and Gierke 1983]. The other structural and physicochemical properties of Nafion will be discussed in detail in other chapters of this thesis.

1.1.1.2. Track etched membrane

Irradiation of polymer foil (polycarbonate, polyethylene terephthalate) with accelerated heavy ions (that must have enough energy to penetrate) creates latent tracks in the bulk of polymer foil. These on subsequent chemical (using NaOH) etching produces homogeneously distributed track etched membranes [Fischer and Spohr 1983, Bieth et al. 1991, Lueck et al. 1990]. Figure 1.4 shows the atomic force microscopy (AFM) image of the surface of a track etched membrane having ~0.2 µm pore size. The use of nuclear tracks for the production of porous membranes was proposed almost immediately after the discovery of particle track etching in thin sheets of materials [Bayley and Martin 2000]. Track-etch membranes offer

Figure 1.3: Cluster-network model for the morphology of hydrated Nafion.
distinct advantages over conventional membranes due to their precisely determined structure. The geometrical parameters (pore size, shape and density) of these membranes can be varied in a controlled manner in different stages of the production process by controlling the ion beam parameters (ions energy, ions density) and physicochemical treatment (sensitization, etching process parameters). Track etched membranes because of their homogeneous and nanoporous structures have various applications in analytical chemistry, specifically in membrane based bioseparations, in electroanalytical chemistry and in the development of new approaches to design biosensor. Use of these membranes for the synthesis of different nanostructures is also well established. In the present work, polycarbonate based track etched membrane has been used for the synthesis of nanosized copper ferrocyanide crystals. This inorganic ion exchanger loaded track etched membranes have further been used for the treatment of Cs$^+$.  

![Figure 1.4. AFM image of the surface of a track etched membrane.](image)

1.1.1.3. Polymer Inclusion Membrane  Among different types of membranes, the liquid membranes (bulk liquid membrane, supported liquid membrane-SLM and polymer inclusion membranes-PIM) have drawn considerable attention because of selective carrier mediated transport of molecules of interest. The problem of solvent leaching from the porous support in SLM can be overcome by
incorporating the ligand in the polymer matrix, i.e, PIM, resulting in higher lifetime of the membrane [Nghiem et al. 2006]. These membranes are prepared by physical immobilization of the extractant in a plasticized cellulose tri acetate (CTA) or poly vinyl chloride (PVC) matrix. The surface roughness profiles of a cellulose tri acetate based PIM sample with nitro phenyl octyl ether (NPOE) the plasticizer, as obtained from AFM is shown in figure 1.5 [Sodaye 2007]. The properties of these membranes can be tuned by appropriate selection of the matrix forming polymer, plasticizer and extractant. These membranes have been used as potentiometric sensors as Ion Selective Electrodes and Field Effect Transistors [Bakker et al. 1997, Pretsch et al. 1998, Ngheim et al. 2006].

Figure 1.5. AFM image of CTA based PIM surface containing NPOE as plasticizer [Sodaye 2007].

1.1.2. Properties of Ion-Exchange Membrane

Ion-exchange membranes show physico-chemical and electrochemical properties very similar to the conventional ion-exchangers. The final application of these membranes for various separation and analytical processes hinges on the manifestation of some of the following physico-chemical properties, which are briefly described below.
1.1.2.1. Ion Exchange Capacity

IEMs are characterized quantitatively by their ion-exchange capacity, which is defined as the number of equivalents of counterions in a specified amount of the material [Helfferich 1962]. The capacity data, primarily used in the numerical calculations of ion-exchange operations, is a characteristic constant of the material and is independent of the experimental condition. The ion-exchange capacity of these membranes can be determined by pH titration or equilibrating with counterion solutions tagged with radiotracer or using radioanalytical techniques like neutron activation analysis.

1.1.2.2. Swelling/ Solvent Uptake Capacity

IEMs are able to sorb water or polar solvents in which they are placed [Helfferich 1962]. While taking up solvent, the IEMs usually expand or “swell”. This swelling is only up to a limited degree, as swelling does not proceed after equilibrium is attained between the two media. IEMs have ionizable functional groups in their matrix. These groups, as well as the ions they dissociate into, tend to surround themselves with the polar solvent molecules. The swelling equilibrium is a balance of opposing forces. The tendency of the polar and ionic constituents to surround themselves with solvent molecules and thus to stretch the matrix is counterbalanced by an increasing resistance by the matrix. The resistance of the matrix is due to network elasticity arising from the cross-linked polymer chains in the membrane. Equilibrium is attained when the elastic forces of the matrix balance the dissolution or solvation tendency. The extent of swelling depends on:

(a) Nature of the solvent
(b) Nature of fixed ionic groups
(c) Degree of cross-linking (if it is there)
(d) Nature of counterion 
(e) Concentration of the external solution 
(f) Ion-pair formation and association

1.1.2.3. Perm-selectivity

When an IEM is in contact with electrolyte solutions of low or moderate concentrations, there exist considerable concentration differences between the two phases, the counterion concentration being large in the membrane whereas the solution has a large concentration of the mobile coions [Helfferich 1962]. This process disturbs the electro-neutrality as both the type of ions carry electric charge. The migration of counterions into the solution and of coions into the membrane results in building up of an electric potential difference between the two phases. This potential is called the Donnan Potential and is of opposite sign for cation and anion exchange membranes. This potential repels the coion from the membrane and thus prevents the internal coion concentration from rising beyond an equilibrium value, which is usually much smaller than the concentration of the external solution. The higher is the Donnan potential value, the stronger is the exclusion, i.e., the smaller is the electrolyte uptake by the membrane. Mathematically, Donnan potential ($E_{Don}$) is written as the difference of potential at the interface and is given by,

$$E_{Don} = \overline{\phi} - \phi = \frac{RT}{z_iF} \ln \frac{\overline{a_i}}{a_i}$$

(1.1)

where $\Phi$ is the electric potential, $R$ is the gas constant, $T$ is the absolute temperature, $F$ is the Faraday constant, $z_i$ is the valence and $a_i$ is the activity of the species $i$. The terms with overbar represent the membrane values. For a given monovalent ionic species at activity ratio ($\frac{a_i}{a_i}$) of 1:10, the Donnan potential is 59 mV. This relation holds for any mobile ionic species
present in the system. When applied to the counterions, it reflects the dependence of the Donnan potential on the concentration (or activity) difference between the two phases and on the counter-ion valence. When applied to the coion, it shows the dependence of coion exclusion on Donnan potential and the coion valence. As the value of the activity of the species in the two phases become equal (at high concentrations in solution), $E_{Don}$ approaches zero, the potential breaks down and there is a free flow of electrolyte through the membrane. This property of exclusion of coions by the IEMs is called Donnan exclusion and is shown in figure 1.6. The membrane is said to be perm-selective or semi-permeable to counterions. The perm-selectivity is reflected not only in differences in permeability but also in the membrane potential. However, when the concentration of the solution is increased, the Donnan exclusion becomes less effective and thus perm-selectivity is reduced.

![Figure 1.6: Donnan exclusion in a cation-exchange membrane.](image)
1.1.3. Physical properties Important for Membrane based Separation Process

Other than the properties mentioned above, IEMs exhibit many physical properties, which are important in governing the separation processes based on ion-exchange membranes. Some of those properties, that have been studied and are reported in the present thesis, are described below.

1.1.3.1. Diffusion

Diffusion is a process in which matter is transported from one part of the system to another as a result of random molecular motion [Crank 1964]. In the absence of any external force, concentration gradient is the driving force for diffusion. In the context of ion-exchange membranes, diffusion is the process of transport of ionic species across the membrane [Helfferich 1962]. The ionic flux involves a transfer of electric charge. In the absence of electric current, this charge transfer must be balanced by one or more ionic fluxes. The compensation of the fluxes is brought about by the electric potential gradient, called the diffusion potential, built up by the diffusion process. Thus, diffusion of ionic species in membrane is not an independent phenomenon. In certain cases, the overall diffusion rate from bulk solution on one side to bulk solution on the other side may be controlled by diffusion in either the membrane (membrane diffusion control) or the liquid films, which adhere to the membrane surface (film diffusion control). To avoid film diffusion control, the concentrations in the bulk solutions are kept uniform by stirring.

Diffusion process in any isotropic substance, including IEMs, can be expressed mathematically by Fick’s laws [Crank 1964]. According to Fick’s first law (equation 1.2) of
diffusion, the rate of transfer of diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section

$$J = -D \frac{dC}{dx}$$  \hspace{1cm} (1.2)

where, $D$ is the diffusion coefficient of the species (unit cm$^2$/s) and $J$ is the flux in unit of moles/cm$^2$/s. The negative sign shows that diffusion occurs in the opposite direction to that of increasing concentration. $D$ is a matrix parameter governing the mobility of the ionic species and hence, the transport rate. The change in concentration with time is given by Fick’s second law as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (1.3)

Self-diffusion is diffusion of a species in a medium or between two media having no concentration gradient. In such a case, the diffusion constant, called the self-diffusion coefficient (SDC), gives the true mobility of any species in the matrix. The entropy of mixing is the driving force for self-diffusion. This is characteristic for a particular type of cation in a particular medium and depends on the nature and composition of that particular phase and on temperature. Self-diffusion of ions in a membrane matrix is governed by two important factors, the physical and chemical architecture of the polymer matrix through which the counterions are moving and the nature of interaction of the counterions with the functional group on the polymer backbone.

It has been generally observed that the SDCs of the ions of same valence in a particular medium decrease with increasing ionic size. Also, the SDCs of monovalent ions are distinctly higher than the divalent ions except for Cs$^+$, which has a low SDC. This behavior has been explained on the basis of hydration characteristics of the ions and their electrostatic interactions with the fixed charged groups in the membrane. The distinctly different
behaviors of the mono and divalent ions can be used to identify the valence state of the diffusing ions in the membrane. Radiotracers are extensively used for measuring self-diffusion coefficient of ions in membranes. Other methods like conductivity measurements and pulse field gradient NMR also have been used for the same. The detail of different methods for SDC determination are given below

**a) Radiotracer permeation method**

This method involves exchange of two isotopic counterions in a system, which is in equilibrium except for isotopic distribution [Helfferich 1962]. In practice, self-diffusion is measured by monitoring the transport of a cation through the membrane from one compartment to another compartment. In one of the compartment, the cation is tagged with an carrier free radiotracer. The two solutions on either side otherwise have the same concentration. The steady state self-diffusion ionic flux is given by [Lopez et al. 1977]

\[
J = \frac{-\overline{D} \overline{C}}{d \left(1 + 2 \frac{\overline{D} \overline{C} \delta}{D \overline{C} d}\right)}
\]  

(1.4)

where, D is the diffusion coefficient, C is the molar concentration, d is the thickness of the membrane and \(\delta\) is the thickness of the unstirred liquid film at the membrane surface. The over bar terms refers to values in the context of the membrane. The second term in the parenthesis of the denominator is significant only when the diffusion through the unstirred liquid film begins to limit the overall ionic flux. If well-stirred solutions are used, then the equation 1.4 reduces to

\[
J = \frac{-\overline{D} \overline{C}}{d}
\]

(1.5)
Thus $\overline{D}$ can be calculated from measured $J$ and known $\overline{C}$. This method has been extensively used for determining SDC using radiotracers [Lopez et al. 1977, Yeager and Kipling 1979, Yeager et al. 1980, Yeager & Steck 1981, Yeager 1982 (a), Verbrugge & Hill 1990, Verbrugge et al. 1992, Pourcelly et al. 1996, Rollet et al. 2000].

**b) Non-Stationary Radiotracer Method (Transient Method)**

This method of measuring self-diffusion coefficient of ions and water in IEMs is essentially based on the analysis of kinetics of isotopic exchange in the membrane using an analytical solution of Fick’s second law. This transient method of SDC determination is simple, does not require stringent control over hydrodynamics near the membrane, and is faster because a single measurement can yield the SDCs of the ions [Goswami et al. 2001]. The method is based on the assumptions that (i) it is a membrane controlled diffusion process, (ii) the SDC of any species within the membrane is constant, and (iii) diffusion process is one dimensional. The first assumption is valid only if the concentrations of the radiotracer ions at both the boundaries are same as that in the bulk solution. In the case of radiotracer sorption experiment, the membrane free of radiotracer is kept in contact with an equilibrating salt solution containing radiotracer ions. With the initial conditions $t=0$, $0<x<L$, $c=0$ and boundary conditions $t>0$, $c=c^*$, $x=0$, and $x=L$, the solution of equation 1.3 is

$$c(x,t) = c^* + \frac{2c^*}{\pi} \sum_{n=1}^{\infty} \frac{(\cos n\pi - 1)}{n} \sin \frac{n\pi x}{L} \exp \left( -D \frac{n^2 \pi^2 t}{L^2} \right)$$  \hspace{1cm} (1.6)$$

where, $L$ is the thickness of the membrane. For a fixed time ($t=t_k$), the amount of radiotracer sorbed by the membrane of area $A$ is given by

$$n(t_k) = A \int_{0}^{L} c(x,t) dx$$  \hspace{1cm} (1.7)$$

which on integration gives
\[ n(t_k) = n^* \left[ 1 - \left( \frac{8}{\pi^2} \right) \exp\left( -\frac{D \pi^2 t_k}{L^2} \right) + \left( \frac{1}{9} \right) \exp\left( -\frac{9D \pi^2 t_k}{L^2} \right) + \ldots \right] \]  

(1.8)

where, \( n^* \) is the total amount of the radiotracer ions in the membrane at equilibrium (\( t=\infty \)). In the case of reverse experiment, that is, radiotracer diffusing out of the membrane, \( n^* \) represents the total radiotracer ions in the salt solution at equilibrium (\( t=\infty \)). \( D \) is deduced by a non-linear least-squared fit of equation 1.8 with both \( n^* \) and \( D \) as free parameters.

In the present thesis, SDCs of different ions in different types IEMs have been measured using the non-stationary radiotracer method.

c) Conductivity Measurement

SDC of different ions in the membrane can also be determined by measuring the ionic conductivity [Millet 1990, Gavach et al. 1989, Canas et al. 2001, Bouzek et al. 2003]. The electrochemical mobility \( u_i \) of an ion is related to the individual diffusion coefficient of the species by Einstein relation

\[ u_i = \frac{F}{RT} D_i \]  

(1.9)

where, \( F \) is the Faraday constant, \( R \) is the universal gas constant and \( T \) is the absolute temperature (K). The diffusion coefficient \( (D_i) \) of an univalent cation present inside the membrane, can be evaluated from the membrane conductivity \( (\sigma) \) or resistivity \( (\rho = \sigma^{-1}) \) measurement as

\[ D_i = \frac{kT}{z_i^2 \rho c_i F e} \]  

(1.10)

where, \( k \) is the Boltzmann constant, \( z_i \) is the charge of the ionic species \( i \), \( e \) is the charge of the electron \( (1.6 \times 10^{-19} \text{ C}) \) and \( c_i \) is the mobile ion concentration in the membrane given by
\[ c_i = \frac{dC}{1 + dN V_{M,H_2O} C} \]  

where, \( d \) is the density of the dry membrane, \( N \) is the molar ratio of water to ion exchange site, \( V_{M,H_2O} \) is the partial molar volume of water (18 cm\(^3\)/mole) and \( C \) is the membrane ion exchange capacity.

d) Pulsed Field Gradient Spin-Echo NMR (PFGSE-NMR)

The pulsed-gradient spin-echo sequence permits to measure the diffusion coefficient and is used primarily for studying translational diffusion [Hornak 1998]. In PFGSE-NMR, two gradient pulses are applied. These two gradient pulses are identical in amplitude, \( G \), and width (\( \delta \)). The two gradient pulses are separated by a time \( \Delta \) and are placed symmetrically about the 180\(^0\) pulse. By applying a gradient to the magnetic field, the top of the sample experiences a slightly different magnetic field as compared to the bottom of the sample. Since the magnets precess at different rates in different fields, after a 90\(^0\) pulse and a PFG of a few milliseconds, it is possible to have the magnetization vectors along the length of the tube pointing in all directions instead of properly aligned along one axis of the rotating frame. Hence, if the magnetization vectors are pointing in all the directions, there is no net signal. The vectors are said to be dephased. When a PFG of opposite sign is applied for the same time, the magnetization will rephase, a signal is obtained as a measure of the extent of rephasing. So the function of the gradient pulses is to dephase magnetization from spins, which have diffused to a new location in the period \( \Delta \). These pulses have no effect on stationary spins. A reference spin is the one, which experiences no gradient pulse. The stationary spin does not diffuse during that time and its signal will be in phase with the reference spin, indicating a positive contribution to the echo. The diffusing spin does not come back into phase with the reference spin so it diminishes the echo height. The
relationship between the signal (S) obtained in the presence of a gradient amplitude G_i in the i direction and the diffusion coefficient (D) in the same direction is given by the following equation

\[ S = S_0 \left[ -\left( G\gamma\delta \right)^2 D (\Delta - \delta/3) \right] \] (1.12)

where \( S_0 \) is the signal at zero gradient. The diffusion coefficient is typically calculated from a plot of \( \ln(S/S_0) \) versus \( (G\gamma\delta)^2 (\Delta - \delta/3) \). Diffusion in the X, Y or Z direction may be measured by applying the gradient respectively in the X, Y or Z direction. This method has been extensively used for measuring ion and water diffusion coefficients in ion exchange membrane [Zawodzinski et al. 1991, Gong et al. 2001, Jayakody et al. 2004, Rollet et al. 2003, Saito et al. 2005, Tsushima et al. 2005].

1.1.3.2. Ion Exchange Isotherm

The ion exchange isotherm of an IEM shows the distribution of a particular type of ion between the solution and the membrane at equilibrium. In this, the equivalent fraction of the counter ion A in the membrane is plotted as a function of the equivalent fraction in the solution. The equivalent ionic fraction is defined as

\[ x_A = \frac{z_i m_A}{\sum z_i m_i} \] (1.13)

where the summation is carried out over all counter ion species. Here, \( m_i \) is the moles of the \( i^{th} \) component. A representative ion exchange isotherm for a bi-ionic system under different preferential conditions is given in figure 1.7.
**Figure 1.7**: The ion exchange isotherm for a A-B system under different preferential conditions in IEM.

If the membrane has no preference for A or B, then the equivalent ionic fractions in the membrane are same as those in the solution, which results in linear plot. On the other hand, if the ion A is preferred in the ion exchange membrane, then, the isotherm is negatively curved and lies above the diagonal, and if B is preferred, the isotherm is positively curved and lies below the diagonal. The nature of the ion exchange isotherm indicates selectivity of a particular ion in mixed ionic system. The equilibrium composition of the IEM at any solution composition can also be read from the isotherm plot.

**1.1.3.3. Selectivity**

When an IEM is placed in a electrolyte solution containing a counter ion different from that present in the membrane, ion-exchange equilibrium is attained following exchange of ions between the two phases [Helfferich 1962]. The concentration ratio of the two counterions in the IEM is different from that in the solution. The membrane selects one counterion in preference to the other. The ion-exchange equilibrium and the selectivity towards one ion over the other are explained by the selectivity coefficient [Marcus & Kertes 1969]. The
selectivity coefficient \( K_A^B \) for exchange of monovalent ions \( B \) with \( A \) ions bound to the ion exchanger \( R^- \) in the membrane samples.

\[
R-A + B \rightleftharpoons R-B + A
\]

at a given composition of the equilibrating solution is given by:

\[
K_A^B = \frac{x_A x_B}{x_B x_A}
\]  \hspace{1cm} (1.14)

where \( x_i \) is the ionic fraction of \( i \)th type of ion in the equilibrating solution and \( \overline{x} \) denotes the ionic fraction of the same ion in the membrane phase. The selectivity of polymer systems towards metal ion varies with the experimental conditions and is governed by various physico-chemical parameters. Some of them are

(a) Valence of the counterion.

(b) Ionic solvation of the counterions.

(c) Nature of the functional group on the polymer backbone.

(d) Swelling characteristics of the matrix.

(e) Concentration of the equilibrating solution.

(f) Specific interactions in the ion exchanger like electrostatic interactions, ion-pair formations and ion association.

(g) Association and complex formation of the counterion in solution, that is, the nature of the co-ion.

(h) Dielectric constant and hydrophobicity of the matrix.
1.1.3.4. Permeability

Permeability of a species through a membrane is a practical quantity that governs the rate of transport of the species. The self-diffusion flux of a species across a membrane can be used as a quantitative measure of the permeability of that species [Helfferich 1962]. Frequently, the diffusion across a membrane is described in terms of permeation coefficient. The permeability coefficient \( P \) (cm /sec) for any diffusing species is a phenomenological quantity defined by the relation

\[
J = P(\Delta C) \\
\therefore P = \frac{DK}{l}
\]

(1.15)

where, \( J \) is the flux, \( K \) is the distribution coefficient or solubility of the species in the membrane phase and the outside solution and \( \Delta C \) is the difference in concentration of the diffusing species in the two solutions separated by the membrane of thickness \( l \). If \( C_0^s \) and \( C_m^s \) are the concentration of the species in the solution and the membrane on the feed side (figure 1.8), respectively, and \( C_i^s \) and \( C_i^m \) are respectively the concentration in the solution and membrane on the receiver/strip side separated by a membrane, then \( J \) and \( K \) will be given by

\[
J = \frac{D}{l} \left( C_o^m - C_i^m \right) \\
J = \frac{DK}{l} \left( C_o^s - C_i^s \right) \quad (1.16) \\
K = \left( \frac{C_o^m}{C_o^s} \right) = \left( \frac{C_i^m}{C_i^s} \right)
\]

The large difference in permeability coefficient of the counter-ion and the co-ion is manifested as the perm-selectivity of the IEMs.
Chapter 1

1.1.4. Ion Exchange membrane based Separation processes

The most important IEM based separation processes are diffusion dialysis, Donnan dialysis and electrodialysis. The first two processes are driven by the concentration gradient, while the last one is driven by the applied electric potential across the membrane. The details of these three different processes are given below.

1.1.4. Diffusion Dialysis

This process is mainly used for the recovery of acids and bases from a mixture of salts. The process is based on the permselective property of the IEM. Exceptions are protons and hydroxide ions which can permeate through both cation and anion exchange membranes. The principle of this process is illustrated in figure 1.9. The cation exchange membrane allows only the cations (Na\(^+\)) and rejects the anions (other than OH\(^-\)). On the other hand, an anion exchange membrane allows only the anions (SO\(_4^{2-}\)) and rejects the cations (other than H\(^+\)), leading to recovery of acid from a salt-acid mixture.

**Fig. 1.8:** Schematic representation of counterion concentration profile in steady state isotopic diffusion across an IEM.
Figure 1.9: Schematic representation of the principle of Diffusion dialysis for base recovery using cation exchange membrane and acid recovery using anion exchange membrane.

1.1.4.2. Donnan Dialysis

In this separation process, ions of the same electrical charge are exchanged between two solutions through an IEM. For the electroneutrality requirement, the fluxes of the ions are coupled, i.e. the flux of a counterion through an IEM, caused by a concentration difference between the two solutions separated by the membrane, leads to a counterion transport in opposite direction. For two different cations A and B, this transport occurs till Donnan equilibrium between the feed and the strip solution is reached. The equilibrium is governed by the following relation.

$$\left( \frac{(C_A)_{\text{feed}}}{(C_A)_{\text{strip}}} \right)^{1/z_A} = \left( \frac{(C_B)_{\text{feed}}}{(C_B)_{\text{strip}}} \right)^{1/z_B}$$

(1.17)
Chapter 1

Where, \( (C_i)_{\text{feed/stripped}} \) = Concentration of the \( i^{th} \) species either in feed or in strip solution and \( z_i \) are the corresponding valencies. The exchange of monovalent and divalent ions through an IEM for water softening is one of the envisioned applications of Donnan dialysis. The principle of this process is illustrated in figure 1.10. In strip solution, the conc. of NaCl is much higher than that of CaCl\(_2\). The CaCl\(_2\) solution has much lower conc. and is referred as the feed solution. Due to the concentration difference in the two compartments, Na\(^+\) moves from strip to feed solution. In order to maintain electroneutrality, equivalent amount of Ca\(^{+2}\) ions moves from feed to strip solution till the electrochemical potential of Na\(^+\) and Ca\(^{+2}\) ions are equal in both the solutions. Due to high concentration difference of Na\(^+\) in the two compartments, at Donnan equilibrium, practically all Ca\(^{+2}\) is transported to the strip solution. This process can also be used for recovery of valuable ions from a very dilute solution. Sarkar et al. [Sarkar et al. 2010] have reported several interesting separations based on Donnan dialysis, like, separation of alum from water treatment residuals and separation of citric acid and its salts from a fermentation broth.

**Figure 1.10:** Schematic representation of the principle of Donnan dialysis with NaCl in the strip and CaCl\(_2\) in the feed solution

\[ \]
1.1.4.3. Electrodialysis

The principle of this process is illustrated in figure 1.11. It consists of a series of alternating cation and anion exchange membranes. On application of electric potential across the two electrodes, the cations migrate towards the negative cathode and the anions move towards the positive anode. The cations can easily permeate the cation exchange membranes but are retained by the anion exchange membranes, while the opposite is true for the anions. The overall result is an increase in ion concentration in alternating compartments.

![Figure 1.11: Schematic representation of the principle of Electrodialysis](image)

The basic principle of electrodialysis has been applied in some of the experiments described in this thesis. In these works, cation (Cs⁺ / Na⁺) transport through different cation exchange membrane has been studied under application of electric field. In Chlor-alkali industry (production of NaOH and Cl₂ from electrolysis of NaCl), this same principle is followed. The working principle of present set of separation experiment is shown in figure 1.12. A mixture
of NaCl and CsCl has been used in the feed compartment and deionized water spiked with NaOH (0.04 mili mole) has been used in the receiver compartment.

![Diagram](image)

**Figure 1.12:** Working principle of electric field driven cation transport through cation exchange membrane.

In the present set of experiments, on application of an electric field across the membrane, the anion in the feed compartment is oxidized at the anode, subsequently forcing the cation to move to the receiver phase without requiring any counter transport. The use of electric field, thus, 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. This can be understood from the following relations. Without any applied potential, the flux ($J_i$) for $i^{th}$ cationic species (valency $z_i$, concentration $C_i$ and diffusion coefficient $D_i$) is governed by the concentration gradient of the species and is given by the Fick’s 1st law (eq. 1.2)

Under electric field, the enhanced flux of the species is given by the Nernst Planck equation

$$J_i = (J_i)_{diff} + (J_i)_{el} = -D_i \left( \frac{\partial C_i}{\partial x} + z_i C_i \frac{F}{RT} \frac{\partial \Phi}{\partial x} \right)$$  \hspace{1cm} (1.18)
where, $\Phi$ = electric potential, $F = \text{Faraday constant}$, $R = \text{gas constant}$ and $T = \text{absolute temperature}$. This equation applies whenever an electric field exists. The field may be generated by an external source or by diffusion within the system. Nernst Planck equation does not include the effect of pressure gradient and convection.

This kind of membrane based analyte preconcentration method under the influence of electric field (called as electro-membrane extraction) is currently receiving attention [Pedersen et al. 2008, See and Hauser 2011, Kuban et al. 2010, Morales-cid et al. 2010]. This type of extraction process, being electric field driven, more than 50 % cation transport is expected, which otherwise is not possible in other type of dialysis processes.

In the present work, attempt has been made to understand the effect of membrane ionic composition on the SDC of $\text{Cs}^+$ and to prepare $\text{Cs}^+$ selective IEMs for electrodriven selective transport of $\text{Cs}^+$ over $\text{Na}^+$ with emphasis on $\text{Cs}^+$ removal from simulated nuclear waste solution.

1.2. Nuclear Waste

In India, Nuclear power is the 4th largest source of electricity and there are 21 nuclear power plants (in 2014) in operating condition, generating 5,780 MWe. In nuclear reactor, nuclear fission chain reaction is sustained in a controlled manner and the thermal energy released during the burning of fissile material is utilized for the generation of electricity. This involves the disintegration of the fissile material such as $^{235}\text{U}$ into two fragments and evolution of large amount of energy. A typical fission reaction is presented as:

$$ ^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{95}_{42}\text{Mo} + ^{139}_{57}\text{La} + 2^{1}_{0}\text{n} $$
In India, a closed nuclear fuel cycle is followed, where, U and Pu are recovered from spent nuclear fuel solutions using hydrometallurgical processes. The raffinate of these processes contain several long lived fission products like $^{99}$Tc, $^{129}$I, $^{135}$Cs and $^{97}$Zr along with relatively shorter half life fission products such as $^{137}$Cs, $^{90}$Sr and trans-uranium elements. Because of health hazards associated with the nuclear radiations, nuclear waste disposal needs to be given special attention compared to any other types of industrial wastes. Radioactive wastes are generated at every stage of nuclear cycle and their disposal depends upon the nature of the waste.

**Fig.1.13:** Schematic presentation of nuclear fuel cycle. In open fuel cycle storage is followed by disposal (indicated by violet color path) while in closed fuel cycle it follows the steps indicated prior to disposal.
The Nuclear fuel cycle, as shown in Fig. 1.13, begins with mining of uranium and ends with disposal of the wastes generated. The front end of the cycle includes mining, milling, extraction, purification, fuel fabrication and use of uranium in the reactor, while the back end covers the removal of used fuel from the reactor core, its subsequent reprocessing to recover valuables radionuclides, and finally the disposal of the wastes. In closed fuel cycle strategy, the spent nuclear fuel rods, after sufficient cooling period, are dissolved in nitric acid medium (PUREX- Plutonium Uranium Reduced Extraction process) for the recovery of Pu and depleted uranium for their subsequent use as fuels. The raffinate of PUREX process contains a large number of fission products, which are the main contributors for the heat output and are the major source of radiation. Table 1.2 shows the major radioactive nuclides (fission / activation products) that are present in the spent fuel after a cooling period of 50 days [Holder 1978].

**Table 1.2**: Major contributors to the radioactivity in the spent fuel after a cooling period of 50 days.

<table>
<thead>
<tr>
<th>Nuclides</th>
<th>Half life</th>
<th>Nuclides</th>
<th>Half life</th>
<th>Nuclides</th>
<th>Half life</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>12.3 y</td>
<td>$^{95}$Nb</td>
<td>35 d</td>
<td>$^{140}$La</td>
<td>40.2 d</td>
</tr>
<tr>
<td>$^{85}$Kr</td>
<td>10.8 y</td>
<td>$^{103}$Ru</td>
<td>39.6 d</td>
<td>$^{141}$Ce</td>
<td>32.4 d</td>
</tr>
<tr>
<td>$^{89}$Sr</td>
<td>50.6 d</td>
<td>$^{106}$Ru</td>
<td>367 d</td>
<td>$^{145}$Pr</td>
<td>13.6 d</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>28.5 y</td>
<td>$^{129m}$Te</td>
<td>34 d</td>
<td>$^{134}$Ce</td>
<td>285 d</td>
</tr>
<tr>
<td>$^{90}$Y</td>
<td>64.1 h</td>
<td>$^{131}$I</td>
<td>8.05 d</td>
<td>$^{148}$Pr</td>
<td>17.3 min</td>
</tr>
<tr>
<td>$^{91}$Y</td>
<td>58.8 d</td>
<td>$^{137}$Cs</td>
<td>30.07 y</td>
<td>$^{147}$Nb</td>
<td>11.1 d</td>
</tr>
<tr>
<td>$^{95}$Zr</td>
<td>65 d</td>
<td>$^{140}$Ba</td>
<td>12.8 d</td>
<td>$^{147}$Pm</td>
<td>2.62 yr</td>
</tr>
</tbody>
</table>
Depending upon the radioactivity concentration, the radioactive waste can be classified as low level, intermediate level and high level. In low level waste (LLW), the radioactivity concentration is less than mci/l. It is generated from the hospitals, laboratories and industry as well as from various stages in the nuclear fuel cycle. Usually, it is buried in shallow landfill sites. Before disposal, its volume reduction is done by either compaction or incineration (in closed containers). When the radioactivity concentration in the waste ranges from mci-ci/l, it is referred to as intermediate level waste (ILW). The ILW typically comprises of the resins, chemical sludge and reactor components. It may be solidified in concrete or bitumen for disposal. The activity concentration in the high level waste (HLW) is greater than ci/l. It is conceptualized as the waste consisting of the spent fuel and the liquid effluent arising from the reprocessing of the spent fuel. As indicated, the HLW contains the long lived fission products, minor actinides and unrecovered U and Pu along with the structural materials and process chemicals. This type of waste requires proper cooling as well as special shielding during handling and transport. Major challenge in the final disposal of HLW is due to the radio toxicity and health hazards of the long lived minor actinides and the two heat emitting radionuclides viz.; $^{137}$Cs and $^{90}$Sr. Before disposal, this type of waste requires special treatment to remove certain nuclides and the prescribed treatment depends on the nature of radionuclide, particularly the half life, which range from fractions of second to millions of years.

1.2.1. Sources of Radio-Cesium

Cesium (Cs), being one of the major fission product of U and Pu, is of major environmental concern due to its radaiotoxicity and has four major isotopes present in the radioactive waste, $^{133}$Cs (stable), $^{134}$Cs, $^{135}$Cs and $^{137}$Cs. $^{135}$Cs has a half life in the range of few million years while that of the other cesium isotopes are much lower. Due to very high fission yield (6% from thermal neutron fission of $^{235}$U) and high gamma output (at 662 keV), even after 30
years (half life = 30.2 yr), a major portion of the heat and the gamma radiation in HLW is contributed by $^{137}$Cs. In terms of weight, it is estimated that about 240 g of $^{137}$Cs is produced from 1 tonne of fuel irradiated in Pressurized Heavy Water Reactor at the rate of 6,700 MWD/tonne. Separation and recovery of this radionuclide from nuclear waste will not only solve the problem of personnel exposure, but also will facilitate waste management and make this isotope available for further beneficial use.

![Pie chart showing distribution of radionuclides](image)

**Figure 1.14**: Typical distribution of $^{137}$Cs in different waste available for recovery at Trombay.

Among the different types of wastes generated, three waste streams are important with respect to Cs recovery point of view. These waste streams are (i) Acidic HLW (ii) Alkaline ILW and (iii) Alkaline declad waste. The acidic HLW generated from reprocessing plants in India have gross $\beta$ activity in the range of 10-30 Ci/L which is due to the presence of major radionuclides $^{137}$Cs (3-10 Ci/L), $^{90}$Sr (3-10 Ci/L), fission products and several actinides [Kaushik et al. 2000]. The ILW generated at the back end of nuclear fuel cycle is alkaline in nature and has high salt loads. The waste has gross $\beta$ activity in the range of 4-50 mCi/L with $^{137}$Cs as the major radionuclide and traces of $^{90}$Sr, $^{106}$Ru etc. The declad waste, generated
from the chemical dissolution of aluminium cladded natural uranium fuel irradiated in research reactors, is characterized by much higher concentration of NaOH, Al and Na-salts. However, with respect to activity content, it is similar to that of ILW. It is worth mentioning here that, although $^{137}$Cs concentration in both the alkaline streams are quite low, total inventory of $^{137}$Cs in these waste streams are quite significant because of high waste volumes. A typical distribution scheme of this radioisotope in the waste streams is shown in figure 1.14. It can be seen that the acidic HLW generated from reprocessing plants is the main source for $^{137}$Cs.

### 1.2.2. Health Hazards of Radio-Cesium

Radio cesium if released into the atmosphere, gets sorbed by the moisture and return to the earth’s crust as a consequence of radioactive fallout. Once, it enters ground water, it is deposited on sediment surfaces and removed from the landscape primarily by the transport processes. The accident at the Chernobyl nuclear power plant resulted in the release of an estimated $5.4 \times 10^5 \text{Ci (2.0 x10}^{16} \text{ Bq)}$ of $^{134}$Cs and $1.1 \times 10^6 \text{ Ci (4.0 x10}^{16} \text{ Bq)}$ of $^{137}$Cs into the atmosphere over Europe. Once released, the radioactive cesium isotopes persist in the environment, with the potential to cause adverse health effects. Radiation exposure can be external or internal through ingestion of radioactive cesium-contaminated food. The hazards of external exposure to $^{134}$Cs and $^{137}$Cs are similar to those of other beta- gamma emitting radionuclides. Workers can get exposed to cesium through oral, dermal, and inhalation routes. Energy released by radioactive isotopes can result in significant damage to the living cells. Signs and symptoms of acute toxicity from external and internal exposure to high levels of radiation from $^{134}$Cs or $^{137}$Cs are typical of those observed in cases of high exposure to ionizing radiation [Sokolov 2001].
1.2.3. Applications of $^{137}$Cs

The decay scheme of $^{137}$Cs is shown in figure 1.15. Due to the reasonably high gamma energy (661.6 KeV) and long half-life, $^{137}$Cs has potential application as a radiation source in gamma irradiators in place of $^{60}$Co for a variety of purposes as listed below. The use of $^{137}$Cs in place of $^{60}$Co ($t_{1/2} = 5.2$ years, 1173 KeV, and 1332 KeV) will also reduce shielding requirements and frequency of source replenishment. Various uses of $^{137}$Cs based gamma irradiator are listed below [Sadat 1994].

a. Food preservation: Irradiation of food samples kills the harmful microorganisms and bacteria resulting in increased shelf life of the food without affecting the taste and flavour.

b. Sewage sludge treatment: Disinfection of sewage sludge by gamma radiation is done in order to render it suitable as a fertilizer or soil conditioner in the urban environment. The gamma irradiation of sewage sludge does not cause any coagulation in the waste.

c. Sterilization of medical accessories: Different medical products and accessories can be sterilized by the use of gamma irradiation.

d. $^{137}$Cs irradiators are also used in brachytherapy which is an effective treatment for cancer.
f. $^{137}\text{Cs}$ is widely used throughout the construction industry for level, moisture, and thickness gauging applications. Cesium is also commonly used in medical research & treatment and oil well drilling.

### 1.2.4. Separation/recovery methods for $^{137}\text{Cs}$

The scientific principles that govern the separation of Cs from waste solutions are similar to those of other metal ions and are based on chemical reactions, equilibrium kinetics, fluid mechanics and mass transfer from one phase to another. A number of methods have been developed for the recovery of this radionuclide from acidic and alkaline waste solutions. However, few of them have been tested at plant scale [Orth et al. 1994, Schulz 1987]. Literature reports on separation of Cs from acidic waste solutions include the use of number of techniques viz., precipitation, ion exchange and solvent extraction. A brief discussion of these techniques is given below.

#### 1.2.4.1. Precipitation Method

Sodium phosphotungstic acid {Na$_3$[P(W$_3$O$_{10}$)].4H$_2$O} used for Cs recovery from the acidic waste. Phosphotungstate anion, reacts with Cs(I) ion in acidic (0.5 to 5M HNO$_3$) medium to form insoluble precipitate. Further, it can be dissolved in NaOH solution to recover Cs. Similar chemistry has been used for recovery of Cs from the PUREX waste at Hanford site, U.S.A. [Singh 1983].

#### 1.2.4.2. Ion Exchange Methods

Ion exchange methods have been widely used for the Cs recovery from the waste solutions. The use of inorganic ion exchangers (IIX) offers many advantages over the use of regenerable organic ion exchangers. The IIX are much more resistant to chemical, thermal and radiation degradation. Three groups of exchangers have potential use in the removal of
cesium from acid wastes: ferrocyanides, phosphates and oxides. Cu-ferrocyanide (CuFC, K$_2$-xCu$_{x/2}$[CuFe(CN)$_6$]•nH$_2$O, x=1.22), heteropolyacids (Ammonium molybdophosphate (AMP), Ammonium tungstophosphate $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$$\cdot$$3\text{H}_2\text{O}$ (AWP)) and zeolites (modernite, clinoptilolite) were used for the uptake of the Cs [Mimura et al. 2002]. Use of metal ferrocyanides for Cs removal has been discussed in details in the later part of the thesis.

(a) Titanates

Crystalline silicotitanates, (CSTs) are a class of ion exchangers that were jointly invented by researchers at Sandia National Laboratories and Texas A & M University [Miller et al. 1997, Walker 2000]. In alkaline media, cesium is strongly sorbed by CST’s. Cesium cannot be easily removed from CST and, therefore, the exchanger becomes part of the final waste form. Major drawbacks such as inefficient elution of the loaded cesium and long term stability are issues which need to be addressed.

(b) Ammonium Molybdophosphate (AMP)

Ammonium molybdophosphate $[(\text{NH}_4)_3\text{Mo}_{12}\text{O}_{40}$$\cdot$$3\text{H}_2\text{O}]$ is a dark yellow crystalline inorganic compound that has been shown to have the requisite selectivity for Cs and stability. Due to its microcrystalline nature it has been always a challenge to the researchers to load it on to a support material. Poly acrylo nitrate (PAN) is commonly used support material for AMP. The performance of the AMP coated PAN has been extensively studied [Sebesta et al. 1996]. The Cs loading in all cases has been found to be related directly to the AMP content of the material and no adverse effect on Cs loading due to support material was reported. However, the elution of the loaded Cs from AMP is not easy task and cesium cannot be quantitatively eluted from this material. The study on radiation stability of AMP [Rao et al. 1995] revealed no effect on the uptake capacity even upto 1 MGy dose. In general, the advantages of AMP are,
• High distribution coefficient in acidic media
• High loading capacity
• High selectivity for Cs ion in complex mixture
• Rapid uptake
• Soluble in alkaline solution

While the disadvantages include,
• Difficulty of elution of the absorbed Cs
• Microcrystalline nature making it unfavorable for column use
• The high loading in the AMP results in high radiation doses in and hot spots on column, requiring cooling solution
• Heat generation can affect the support material.

(c) Resorcinol Formaldehyde Polycondensate Resin (RFPR)

The resin is an alkali catalyzed polycondensation product of resorcinol and formaldehyde, in which the phenolic OH group of resorcinol ionizes under alkaline conditions and functions as cation exchanger. It is noteworthy that the RFPR has extensively been used for the separation of $^{137}$Cs from low and medium active alkaline waste solutions [Samanta et al. 1995, Hassan et al. 2004, Fiskum et al. 2008]. The main reasons behind the selection of the ion exchanger are (i) high selectivity for Cs (ii) high ion exchange capacity (iii) high radiation stability and (iii) ease of availability. Further, the weakly acidic nature of the functional groups facilitates the recovery of Cs$^+$ ions from loaded resin by elution in small volumes of dilute acid. The ion exchange cycle for the separation of $^{137}$Cs by RFPR can be represented as follows (figure 1.16). As the resin can only process alkaline solution, it is considered that the acidic eluate will be neutralized prior to Cs separation.
1.2.4.3. Solvent Extraction Methods

Solvent extraction technique is attractive due to large throughput, continuous nature and ease of operations. A number of methods were developed using various reagents so far to recover Cs from the waste solution. These methods primarily dwell on the use of chlorinated cobalt dicarbollide (CCD') and macrocyclic ionophores as the extractants.

(a) Dicarbollides

Cobalt Dicarbollide is an organometallic complex of cobalt with two boron cluster compound. The structure of CCD' is shown in figure 1.17. The protonated form of CCD' (HCCD) has first been prepared by Hawthorne in 1965 and then extensively studied by Czech scientists [Kyrs 1994, Hawthorne 1997]. The process, based on the use of CCD' in polar diluent (metanitrobenzotrifluoride-FS13), has been developed at the Nuclear Research Institute in Czechoslovakia and successfully adopted in the commercial separation plant at Mayak PA in Russia [Ramonovsky 2003]. The loaded Cs on CCD' can be stripped using 5-6 M HNO₃. Poorly hydrated dicarbollide anions associate with the cations to form neutral compounds. Though dicarbollides display good stability towards radiation [Kyrs 1994], main drawback is the large scale use of nitrobenzene as the diluent. Also the halides present in the chlorinated cobalt dicarbollide can get released in the solution, which may lead to corrosion.

![Diagram](image_url)

**Figure 1.16:** Ion exchange cycle for RFPR.
Figure 1.17: Structure of Chlorinated Cobalt Dicarbollide anion.

(b) Macro cyclic Ionophores

Macro cyclic ionophores are relatively large cyclic compounds containing donor atoms to bind metal ions. These compounds, in general have hydrophilic interior and hydrophobic exterior which enable them to extract metal ions efficiently. Macro cyclic ionophores such as crown ethers and calix crowns have also been proposed for selective extraction of cesium.

(i) Crown Ethers

Depending upon the similarities between the cavity size of the ionophores and the ionic size, different crown ethers are known to be selective for different metal ions. Blasius et al. [Blasius et al. 1984-p 173, Blasius et al. 1984-p 207] used DB21C7, out of several crown ethers, to extract cesium from two medium active wastes mainly containing sodium nitrate and nitric acid. Only DB21C7, used in high dielectric constant diluents such as nitromethane and nitrobenzene, showed reasonably good extraction of cesium. However, the distribution
coefficients are too low for practical applications. A way to increase cesium extraction is the addition of voluminous and polarizable anions such as molybdophosphate, tetra phenyl borate, hexachloro antimonite etc. Gerow et al. [Gerow et al. 1979, Gerow et al. 1981] developed extraction method for cesium from high active acidic liquid waste using substituted crown ethers. Cesium can be stripped from the aqueous phase by 1M nitric acid. Dietz [Dietz et al. 1996] evaluated several crown ethers, viz.; dicyclohexano-18-crown-6, di-tert-butyl-benzo-18-crown-6, di-tert-butyl-benzo-21-crown-7 and di-tert-butyl-benzo-24-crown-8 for cesium extraction from 4 M HNO₃. However, none of the tested compounds provided the ideal combination of extraction efficiency, selectivity, stability and solubility and thus were employed for actual plant scale use.

(ii) Calixerens

Different types of Calixarenes are found to be selective for different metal ion due to favorable conformations. For example, the cone conformation was found to be highly effective in selective extraction. Arnaud et al. [Arnaud-Neu et al. 1991] reported that calix[4]arenes bearing ester or ketone groups displayed higher affinity for alkali cations, especially for sodium. The introduction of the p-tert-butyl groups on the calix[6]arenes strongly increases the complexation of the Cs(I). Izatt et al. [Izatt et al. 1985] reported selective transport of Cs⁺ by using calixarene in a mixture of dichloromethane and CCl₄. The selectivity was found to increase as the size of the calixarenes decreased. The major advantages of calixarenes are,

- Negligible carrier loss due to low water solubility.
- Irradiation stability.
- High selectivity

that due to low water solubility, carrier loss is negligible besides its selective nature and irradiation stability.
(iii) Calix crowns

In search of better extractants than crown ethers and calixarenes, efforts were made to include crown ether moieties into the calixarene framework. This led to the synthesis of compounds known as the calixcrown. It has been found that in spite of the presence of two cavities, the stoichiometry of the metal-ligand complex was 1:1 with calix-bis-crown-6 [Haverlock et al. 2000]. The selectivity of this calixcrown-6 is very high for Cs in the presence of Na (29000 in nitro phenyl hexyl ether), which has been attributed to the stabilization of the Cs-calix-crown complexes by the four benzene units. The presence of the ‘benzo’ or ‘naptho’ group enhances the organophilicity and selectivity. Even the presence of second benzene group on the crown moiety has shown high distribution coefficient for the Cs(I) at higher acidity ( \sim 4 \text{ M}). Wipff and Lauterbach [Wipff and Lauterbach 1995] concluded that this selectivity for cesium is related to solvation effects rather than to interactions with the \textit{pi} electrons of benzene units. Though several solvents have been developed world wide for cesium recovery, calix-crown based reagents are amongst the most promising for the selective recovery of Cs from acidic waste solutions. However, high cost of reagents necessitates the need for development of methods with low ligand inventory.

1.3. Scope and Aim of Work

The aim of this thesis work is to study the different aspects of Cs\(^+\) diffusion and transport through different IEMs. Attempt has been made to understand the effect of membrane ionic composition on the SDC of Cs\(^+\) and to prepare Cs\(^+\) selective IEMs for electrodriven selective transport of Cs\(^+\) over Na\(^+\) with emphasis on Cs\(^+\) removal from simulated nuclear waste solution. In order to have a clean separation of Cs\(^+\), a novel method of electromembrane extraction has been attempted. The work presented in the thesis can be broadly summarized as follows
1. In order to understand the transport behavior of Cs$^+$ in Nafion membrane, the self-diffusion coefficient (SDC) of cations (Na$^+$/ Cs$^+$/ Ba$^{+2}$) have been measured in mixed cationic compositions of the membrane.

2. In general, separating (with high degree of selectivity) ions of similar charge using IEM alone is difficult. The selectivity can be imparted by incorporating some macrocyclic ionophores within the membrane matrix. However, high degree of selectivity is achieved only at the cost of cationic mobility within the membrane. In this work, attempt has been taken to enhance the transport selectivity of Cs$^+$, by templating Nafion membrane with Cs$^+$ selective crown ether. This composite membrane system has been chosen because the crown ether can impart the selectivity for the desired metal ion and the polymeric backbone of the membrane can compensate for the charge requirement of the metal ion-crown ether complex. In order to explore the possibilities of tuning the metal ion selectivity at higher temperature, the temperature dependence of the SDCs of cation (Cs$^+$/ Na$^+$) and water diffusion within this composite membrane matrix has been studied. In an attempt to achieve selective transport of Cs$^+$ over Na$^+$ at room temperature, two types of Cs$^+$ ion selective crown ether-Nafion composite membranes have been prepared. In one case, DB21C7 has been incorporated uniformly in Cs$^+$ form of Nafion-117 membrane in varying molar ratio with respect to Cs$^+$ and in the other case, Cs$^+$ driven loading of DB21C7 has been confined to a very small thickness (25 $\mu$m) from one of the surfaces of the Nafion-117 membrane (ion gating). Electrodriven (4 V) transport experiments using these membranes have been carried out to study the transport selectivity of Cs$^+$ over Na$^+$. The suitability of the gated membrane for selective removal of $^{137}$Cs from a simulated nuclear waste solution has also been studied.

3. In another attempt to prepare Cs$^+$ selective membrane, copper ferrocyanide crystals (KCFCN) have been synthesized within the pores of track etched membrane. The synthesis of the KCFCN crystals have been done by two compartment permeation method using CuSO$_4$
and K₄Fe(CN)₆. The composite membrane (KCFCNm) has been characterized using different techniques like X-ray Diffraction (XRD), Small Angle X-ray Scatttering (SAXS), Energy Dispersive X-ray Fluorescence (EDXRF) and Transmission Electron Microscopy (TEM). The transport selectivity of this composite membrane for Cs⁺ over Na⁺ has also been studied under electric field. Attempt has been taken to systematically study the properties of the KCFCNm for removal of Cs⁺ from neutral aqueous solution. The composite membrane has also been used to remove Cs⁺ from a 1 L simulated nuclear waste solution.

4. A highly Cs⁺ selective IEM has been prepared by using HCCD as a carrier in CTA/PVC based PIM. Attempt has been taken to study electrodriven selective transport of Cs⁺ over Na⁺ using these membranes. Experiments have been carried out to optimize the working potential of the transport system involving CTA based membrane. 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 ¹³⁷Cs from a simulated nuclear waste solution has been studied. Transport selectivity of Cs⁺ from a simulated high level nuclear waste (SHLW) solution using HCCD as carrier in PVC based PIM has also been studied.