Chapter V

STUDIES ON SEPARATION OF Y(III) FROM Sr(II) USING SUPPORTED LIQUID MEMBRANE TECHNIQUES
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5.1. Introduction

Membranes are physical / chemical barriers which allow selective permeation of certain species. Membrane technology has contributed significantly for the production of potable water from seawater in the last few decades. In the recent years, membrane processes have been found to be effective in the treatment of industrial effluents and gas purifications [5.1-5.3]. Advantages of membrane based separation techniques are low energy requirements, low capital and operating costs, the possibility of achieving high separation factors and simple modular design [5.4, 5.5].

The use of liquid membranes containing a carrier has been proposed as an alternative to solvent extraction for selective separation and concentration of metal ions from dilute aqueous solutions [5.6, 5.7]. The important feature of liquid membrane is that unlike solvent extraction the extraction and stripping of the metal ions as well as regeneration of the carrier are combined in a single stage.

Liquid membrane usually consists of a water immiscible (organic) layer held on a polymeric support separating a source aqueous phase (feed) containing mixture of metal ions and a receiving aqueous phase (receiver), where the metal ions of interest gets concentrated preferentially. The liquid membrane may be a stirred organic phase separated by aqueous feed and receiver phases (Bulk Liquid Membrane, BLM) or a dispersion of water (strip phase) containing oil droplets in aqueous feed phase (Emulsion Liquid Membrane, ELM). In contrast, supported liquid membrane (SLM) consists of water immiscible organic phase immobilized in the pores of microporous polymeric film (which acts as inert support) separating the two phases, the feed and the receiver phases. Commonly two types of membrane support are used in SLM, a flat sheet (FSSLM) or a hollow fibre (HFSLM). The performance of different types of liquid membranes, viz. BLM, ELM, FSSLM and HFSLM has been reviewed by Izatt, et al. [5.8]. Facilitated transport of metal ions through SLM has been described in a number of papers [5.9 - 5.23]. In such transport systems, the metal ions can be transported across the membrane against their concentration gradient, i.e. “uphill” transport. The driving force in such processes is provided by the chemical potential difference of the chemical species present on the two opposite sides of the membrane. The permeability of the transported species is decided by the parameters
such as membrane thickness, pore structure, aqueous diffusion coefficient of metal ions, aqueous diffusion layer thickness, distribution and diffusion coefficients of the metal bearing species in the organic liquid membrane phase, etc. [5.22 - 5.24]. While diffusion coefficient of the metal bearing species in the carrier solvent depend upon the chosen membrane and the aqueous diffusion coefficient of the metal ions depend on the stirring rate, the transport rates can be controlled through various parameters, viz. feed acidity, solute concentration, carrier concentration, nature of diluent, strip phase composition etc. [5.25]. The preferential extraction of Y(III) as compared to Sr(II) by diglycolamide extractants using solvent extraction studies has been investigated and discussed in Chapter 3. Though the straight chain ligand, N,N,N’,N’-tetra-n-octyl diglycolamide (TODGA) has been found promising, N,N,N’,N’-tetra-2-ethyl-hexyl diglycolamide (T2EHDGA), its branched analog, can also be a candidate for the separation of trivalent Y over Sr (II) in nitric acid medium over a range of acidity (2 - 6 M HNO₃). In Chapter III, we have also discussed the solvent extraction method for the separation of ⁹⁰Y from ⁹⁰Sr using TODGA as the extractant in n-dodecane and T2EHDGA as the extractant in n-dodecane containing 30 % iso-decanol as the phase modifier. The role of iso-decanol is not only to prevent third phase, but also to change the solvent polarity which can seriously affect the aggregation behaviour of these extractants and hence the relative extractability of these metal ions [5.26]. Therefore, it was required to carry out a systematic study on the role of the organic diluent on the extraction behaviour of Y(III) and Sr(III). This behaviour of T2EHDGA can be exploited for the separation of ⁹⁰Y from ⁹⁰Sr.

In view of the growing concern for the environment, it is necessary to evaluate separation methods which dwell on low ligand inventory. In Chapter IV, we have discussed the development of an extraction chromatographic method containing N,N,N’,N’-tetra-n-octyl diglycolamide (TODGA) as the extractant. However, column stability was found to be poor as repetitive column runs indicated fast degrading separation efficiency. In this context, supported liquid membrane based methods are attractive where not only a very small quantity of the extractant was used but also the stability of membrane was found to be good over 20 days of operations [5.27, 5.28]. Other advantages of liquid membrane can be listed as the simultaneous extraction and stripping and generation of carrier [5.29]. Moreover, serious drawbacks of solvent extraction methods such as third phase formation, phase entrainment and phase separation
limitations can be alleviated by the supported liquid membrane methods.

In this Chapter, the studies on the transport of Y(III) and Sr(II) by liquid membrane under various experimental conditions have been described. Two different mineral acids viz., HCl and HNO$_3$ were used as the feed and the separation of Y(III) and Sr(II) was investigated. Acid variation studies have also been carried out. Two extractants (TODGA and T2EH-DGA) have been used as the carrier extractant for the selective transport of Y(III) from mixture containing Y(III) and Sr(II). Role of diluents on the transport behaviour was investigated and the results have been correlated to parameters such as diluents polarity and viscosity. Different diluents and diluent mixtures have been used examined and the findings are presented in this Chapter. Based on these studies a methodology was developed to obtain purified $^{90}$Y from $^{90}$Sr - $^{90}$Y mixture. The purity of product was checked by the half life measurement which has been described in the Chapter IV.

5.2. Theory of Facilitated Transport

In the facilitated transport process, the metal ion diffuses through the aqueous feed boundary layer and reacts with the carrier molecule (present in the pores of the solid support) at the aqueous feed-membrane interface resulting into the formation of metal-carrier complex. The metal-carrier complex then diffuses through the liquid membrane to the receiver phase because of its negative concentration gradient. Finally, the metal-carrier complex dissociates and releases the metal ion into the strip solution at the membrane-aqueous strip interface. The quantitative description of the facilitated transport, therefore, requires a detailed knowledge of the processes like (a) diffusion of the metal ions through the aqueous feed boundary layer, (b) reversible chemical reaction at the aqueous feed-membrane interface, (c) diffusion of the ‘metal-carrier complex’ in the membrane phase, and (d) dissociation reaction of the metal-carrier complex at the membrane-aqueous strip interface. The mathematical relationships for the permeation of metal ions in the facilitated transport can be derived by simple assumptions. The model described by Danesi, et al. [5.23] assumes that the chemical reactions (process (b) and (d) in Fig.5.1) between the metal ions and the ligand occur instantaneously (relative to other rate controlling processes (a) and (c) in Fig.5.1) at the aqueous-membrane interface. It implies that the local equilibrium always occurs at the aqueous-membrane interface and the metal ion
The transport rate will be determined by the diffusion rate through the aqueous stagnant layers (Nernst films) and the diffusion rate through the liquid membrane.

To quantify the transport phenomena, one needs to have a detailed knowledge of the following:
- Distribution coefficient of metal ion
- Diffusion coefficient of carrier
- Kinetics of extraction and stripping
- Viscosity of the medium
- Temperature
- Stirring speed

### 5.3. Flux Equations for Permeation

\[
\begin{align*}
\text{Feed} & \quad \text{Membrane} & \quad \text{Strip} \\
Y_{\text{aq,f}} & \quad d_a & \quad Y_{\text{org,f}} \\
Y_{\text{aq,i}} & \quad b & \quad Y_{\text{org,i}} \\
& \quad Y_{\text{org},s} & \quad Y_{\text{aq},s} \\
\end{align*}
\]

- \(a\): Aqueous diffusion; \(b\): Chemical reaction; \(c\): Membrane diffusion

Fig. 5.1: Schematic presentation of the processes controlling the permeation of Y(III) ion through an SLM containing DGA extractant when the distribution ratio at the membrane-receiver solution interface is much lower than that at the feed-membrane solution interface.

The chemical reaction involved during the extraction of metal ions (\(M^{n+}\)) from aqueous nitrate medium by neutral ligand, diglycolamide (L), can be described as,
where, the subscripts (aq) and (org) represent the aqueous and the organic phases, respectively. The term \(\text{M(NO}_3\text{)}_n\cdot x\text{L}\) represents the extracted species in the organic phase. For simplicity, we will represent this term as \([\text{M-L}]\) in this Chapter. The stoichiometry of the extracted species of DGA and various actinide ions are described in Chapter 3. At the aqueous feed-membrane interface, the equilibrium reaction (5.1) is shifted to right and the \([\text{M-L}]\) complex species then moves towards the receiving phase within the membrane as a consequence of concentration gradient. On the other hand, at the membrane-strip interface, the equilibrium reaction (5.1) is shifted to the left because of unfavourable conditions in the strippant phase. This results in the dissociation of the \([\text{M-L}]\) complex leaving behind free ligand molecules in the membrane phase. The free carrier molecules then move towards the feed solution due to negative concentration gradient to complete the cycle. The equations describing flux across the stagnant aqueous diffusion layer and membrane can be derived by applying Fick’s diffusion law with simple assumptions: (a) the composition of the strip solution is such that the complex of Y(III) and DGA (also referred to as L) is completely dissociated at membrane-receiver strip interface, (b) the membrane polarity is low enough to neglect the concentration of charged species in comparison to the uncharged one, and (c) there is no extraction of Y(III) by the pure diluent, (d) the concentration gradients are linear, and (f) feed concentration of \(\text{NO}_3^-\) is constant, the equations describing the flux, \(J_a\) (feed phase) and \(J_o\) (membrane phase) under steady state are given by equations (5.2, 5.3),

\[
J_a = \frac{D_a}{d_a} \left( [M]_{a,fb} - [M]_{a,fi} \right) = \frac{\{[M]_{a,fb} - [M]_{a,fi}\}}{\Delta_a}
\]

\[
J_o = \frac{D_o}{d_o \tau} \left( [M]_{o,fi} - [M]_{o,si} \right) = \frac{\{[M]_{o,fi} - [M]_{o,si}\}}{\Delta_o}
\]
[\text{[M]}_{a,fi} \text{ is the metal concentrations in the bulk aqueous feed phase and at the aqueous feed-membrane interface, respectively, } \tau \text{ is the tortuosity of membrane material. The symbol, } \Delta \text{ represents the mass transfer resistances of respective phases given by } \Delta = d / D. \text{ All these parameters are shown in Fig. 4.1. The symbol, } [\text{M.L}]_{o,fi} \text{ denotes the concentration of metal-ligand complex ion at feed side interface inside the membrane while } [\text{M.L}]_{o,si} \text{ denotes the metal-ligand complex ion concentration at strip side interface inside the membrane. The distribution coefficient (} k_d \text{) of M at the feed-membrane interface is reasonably high under the chosen experimental conditions. However, experimental conditions on the strip side are such that the } k_d \text{ value of the given metal ion at the membrane-receiver interface is very low i.e. } [\text{M.L}]_{o,si} << [\text{M.L}]_{o,fi}. \text{ Therefore, Eq. (5.3) can be rewritten as,}

\begin{equation}
J_o = \frac{[\text{M.L}]_{o,fi}}{\Delta_o} \quad (5.4)
\end{equation}

If we assume that the carrier in the liquid membrane is not saturated with the metal ions, then the concentration terms \([\text{M.L}]_{o,fi}\) and \([\text{M}]_{a,fi}\) are related to the \(k_d\) by the following equation,

\begin{equation}
k_d = \frac{[\text{M.L}]_{o,fi}}{[\text{M}]_{a,fi}} \quad (5.5)
\end{equation}

Equation (5.5) can be rearranged as,

\begin{equation}
[\text{M.L}]_{o,fi} = [\text{M}]_{a,fi} k_d \quad (5.6)
\end{equation}

Substituting equation (5.6) in equation (5.4) we get,

\begin{equation}
J_o = \frac{1}{\Delta_o} k_d [\text{M}]_{a,fi} \quad (5.7)
\end{equation}
Rearranging equation (5.7) we get,

$$[M]_{a,fi} = J_o \frac{\Delta_o}{k_{d,f}}$$  \hspace{1cm} (5.8)

From equation (5.2)

$$J_a \Delta_a = [M]_{a,fb} - [M]_{a,fi}$$  \hspace{1cm} (5.9)

From equations (5.8) and (5.9), we get,

$$[M]_{a,fi} = J_a \Delta_a + J_o \frac{\Delta_o}{k_{d,f}}$$  \hspace{1cm} (5.10)

If the chemical reaction between ligand and the metal nitrate is assumed to be fast compared to the diffusion rate, a local equilibrium at the interface is reached. Thus, at steady state,

$$J_a = J_o = J$$  \hspace{1cm} (5.11)

Using equation (5.11) in equation (5.10), we get,

$$[M]_{a,fi} = J \left( \Delta_a + \frac{\Delta_o}{k_{d,f}} \right)$$  \hspace{1cm} (5.12)

Rearranging equation (5.12) we get,

$$J = \frac{k_{d,f} [M]_{a,fb}}{k_{d,f} \Delta_a + \Delta_o}$$  \hspace{1cm} (5.13)
or, \[ J = \frac{k_{d,f}[M]_{a,fb}}{k_{d,f}\left(\frac{d_a}{D_a}\right) + \left(\frac{d_o\tau}{D_o}\right)} \] (5.14)

where, \( \tau \) is the tortuosity factor of the membrane. Here the value of membrane thickness \( (d_o) \) can be assumed to be equal to the nominal thickness of the membrane support. Membrane permeability coefficient \((P)\) is written as,

\[
P = \frac{J}{[M]_{a,fb}} \quad (5.15)
\]

Substituting equation (5.14) in equation (5.15), we get,

\[
P = \frac{k_{d,f}}{k_{d,f}\left(\frac{d_a}{D_a}\right) + \left(\frac{d_o\tau}{D_o}\right)} \quad (5.16)
\]

Above equation can be used for calculating \( P \) using \( k_{d,f} \) and diffusion coefficient data. The membrane diffusion coefficient \( (D_o) \) can be calculated from the knowledge of permeability coefficient \( (P) \) and the distribution ratio of the metal ions \( (k_{d,f}) \) as per the above equation (5.16). Assuming that the rate determining step is diffusion of the bulky complex across the membrane, the first term in the denominator of equation (5.16) (which refers to the transport of hydrated metal ions across aqueous diffusion layer) can be ignored. Therefore, Eq. (5.16) can be rearranged as follows,

\[
P = \frac{D_o \cdot k_{d,f}}{\tau d_o} \quad (5.17)
\]

In the present studies, PTFE membranes of 85 \( \mu \)m thickness \( (d_o) \) were employed and the tortuosity factor \( (\tau) \) for the membrane is reported as 2.4 [5.30]. Thus, from the knowledge of \( P \)
and $D_M$, the value of $D_o$ of the metal-ligand complex in the membrane can be obtained. Alternatively, $D_o$ can also be obtained experimentally by determining the $P$ value of metal ions for varying thickness of the membrane ($d_o$). A plot of $P$ vs $1/d_o$ would be a straight line and the value of $D_o$ can be obtained from the slope of the linear fit.

Permeability is described as amount of metal ion (in terms of concentration) transported through membrane per unit area per unit time and related to membrane flux as per following equation (5.18) and (5.19).

$$J = \left( - \frac{V}{Q} \frac{d[M]_{a,fb}}{dt} \right)$$  \hspace{1cm} (5.18)

$$J = P[M]_{a,fb}$$  \hspace{1cm} (5.19)

Rearranging above equations (5.18) and (5.19) we get,

$$\left( \frac{d[M]_{a,fb}}{dt} \right) = - \frac{Q}{V} P[M]_{a,fb}$$  \hspace{1cm} (5.20)

Integrating above equation we get,

$$\int_{C_a}^{C_t} \frac{d[M]_{a,fb}}{dt} \, dt = - \frac{Q}{V} \int_0^t P[M]_{a,fb} \, dt$$  \hspace{1cm} (5.21)

$C_t$ and $C_o$ are the concentration of metal ion in the aqueous feed solution at time $t$ and initial concentration ($t = 0$), respectively.

$$\ln \left( \frac{[M]_t}{[M]_o} \right) = - P \left( \frac{Q}{V} \right) t$$  \hspace{1cm} (5.22)
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In general, \( P \) is obtained experimentally using above equation (5.22). Here, \( Q \) is the effective membrane area obtained from the total exposed membrane surface area \( A \) and the porosity \( \varepsilon \) \( (Q = A \cdot \varepsilon) \), \( V \) is the volume of the feed solution in \( \text{cm}^3 \), and \( t \) is the permeation time (seconds). A plot of \( \ln([M]_t / [M]_0) \) versus time allows one to calculate the \( P \) value from the slope of the linear fit. It should be noted that the above equation is valid only when the carrier is not saturated and the flux decreases linearly with time. In the present work, since all the experiments were carried out at tracer concentration of the metal ion, Eq. (5.22) was applied for the calculation of \( P \). The cumulative \( \% T \) at a given time was determined by the following equation (5.23).

\[
\% \text{ Transport} = \frac{([M]_0 - [M]_t)}{[M]_0} \times 100
\]  

(5.23)

5.4. Effect of the Nature of the Diluent in Solvent Extraction Studies with T2EHDGA as Extractants

From equation (5.1), we can write,

\[
Y^{3+} + 3 NO_3^- + n \text{T2EHDGA}_{(o)} \rightleftharpoons Y(NO_3)_3 \cdot n \text{T2EHDGA}_{(o)}
\]  

(5.24)

where, the subscript ‘(o)’ indicates species in the organic phase and those without any subscript indicate species in the aqueous phase. It is expected that the extractability of the \( Y \)-T2EHDGA complex depend on the nature of the extracted species (stoichiometry including number of T2EHDGA and water molecules) and the polarity of the medium. It is well known that the nature of the extracted species change depending on the organic phase characteristics. While non-polar diluents like n-dodecane can favor the extraction of charge neutralized species, polar diluents like nitrobenzene stabilize charge separated or ion-pair species. Solvent extraction studies were carried out using several commonly used diluents namely 1-decanol, xylene, MIBK, chloroform, carbon tetrachloride along with T2EHDGA as extractant.

In this study, solutions of the desired concentration of T2EHDGA (0.2 M) prepared in the desired diluents were agitated with an equal volume of the aqueous phase (containing the requisite quantity of \(^{90}\text{Y} \) and \(^{85,89}\text{Sr} \) tracer) in a rotary thermostated water bath for
Table 5.1: Effect of diluents on the distribution behaviour of Sr(II) and Y(III) by T2EHDGA; Org. phase: 0.2 M T2EHDGA; Aq. phase: 6 M HNO₃

<table>
<thead>
<tr>
<th>Diluent</th>
<th>K_{d,Y}</th>
<th>K_{d,Sr}</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBK (Hexone)</td>
<td>26</td>
<td>0.03</td>
<td>866</td>
</tr>
<tr>
<td>CCl₄</td>
<td>60</td>
<td>0.24</td>
<td>250</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>50</td>
<td>0.01</td>
<td>5000</td>
</tr>
<tr>
<td>1-decanol</td>
<td>2.56</td>
<td>0.01</td>
<td>256</td>
</tr>
<tr>
<td>Xylene</td>
<td>29</td>
<td>0.05</td>
<td>580</td>
</tr>
<tr>
<td>n-dodecane + 30 %-iso-decanol</td>
<td>20</td>
<td>0.04</td>
<td>500</td>
</tr>
</tbody>
</table>

An hour at 25.0 ± 0.1°C. The two phases were then centrifuged and assayed by taking suitable aliquots from both the phases. The distribution ratios (K_d) of Sr(II) and Y(III) which is the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase, were determined. As shown in Table 5.1, chloroform gave the best results with K_{d,Y} and K_{d,Sr} values of 50 and 0.01, respectively with a separation factor value of ~5000. Solvent extraction studies using 30% iso-decanol in n-dodecane also yielded encouraging results. The effect of diluent parameter on the separation factor SF_{Sr/Y} is shown as Fig. 5.2.

![Fig. 5.2: Effect of Diluents on Separation Factor (SF = K_{d,Y} / K_{d,Sr}); Org. phase: 0.2 M T2EHDGA; Aq. phase: 6 M HNO₃](image)
5.5. Flat Sheet Supported Liquid Membrane Studies

5.5.1. Role of the Nature of the Diluents in SLM Studies With T2EHDGA as Extractant

The diluent property has a major role in the transport of the metal-extractant complex. The diluent polarity helps in stabilizing the extracted species in the organic phase which can lead to higher extraction and hence higher transport rates. Further, the viscosity of the diluent decides the diffusivity of the complex as per the Stokes-Einstein equation:

\[ D_o = \frac{kT}{6\pi R \eta} \]  

(5.25)

where, \( D_o \) is the membrane diffusion coefficient, \( R \), the radius of the diffusing species and \( \eta \), the dynamic viscosity of the extractant solution, \( k \) is the Boltzmann constant and \( T \) is absolute temperature.

![Graph showing the role of organic diluent on Y(III) transport using 0.2 M T2EHDGA. Feed: 6 M HNO₃; Receiver: 0.01 M HNO₃.](image-url)

Fig. 5.3: Role of organic diluent on Y(III) transport using 0.2 M T2EHDGA. Feed: 6 M HNO₃; Receiver: 0.01 M HNO₃,
Table 5.2: Correlation of physical parameters with Y(III) transport data. Extractant concentration: 0.2 M T2EHDGA. Feed: 6 M HNO₃; Receiver: 0.01 M HNO₃

<table>
<thead>
<tr>
<th>Diluent system</th>
<th>Viscosityᵃ (mPa.s⁻¹)</th>
<th>Densityᵃ (g.cm⁻³)</th>
<th>Dielectric constantᵇ</th>
<th>% Y transport (1 hr)</th>
<th>P x 10³ (cm.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>0.9043</td>
<td>0.8705</td>
<td>2.57</td>
<td>95.9</td>
<td>1.58 ± 0.08</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.8648</td>
<td>1.3876</td>
<td>4.81</td>
<td>68.5</td>
<td>1.84 ± 0.05</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1.4633</td>
<td>1.4868</td>
<td>2.24</td>
<td>53.1</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>Hexone</td>
<td>0.8198</td>
<td>0.8142</td>
<td>13.1</td>
<td>91.9</td>
<td>1.60 ± 0.02</td>
</tr>
<tr>
<td>n-dodecane + 30 % iso-decanol</td>
<td>3.5382</td>
<td>0.7938</td>
<td>3.26</td>
<td>45</td>
<td>1.09 ± 0.03</td>
</tr>
</tbody>
</table>

Note: “ᵃ”: The viscosity and density values are for 0.2 M solution of T2EHDGA in the diluent; “ᵇ”: The dielectric constant values are for the diluents or their mixture as indicated in the table.

Fig. 5.4: Role of organic diluent on Sr(II) transport using 0.2 M T2EHDGA. Feed: 6 M HNO₃; Receiver: 0.01 M HNO₃
Fig. 5.3 gives the relative Y(III) transport profiles with several diluents used in the present study. With the exception of xylene, which showed highest transport rate in the five diluents used, the transport rates were mainly governed by the polarity of the diluent. The n-dodecane + 30% iso-decanol solvent system has a dielectric constant of 3.26 (calculated using [5.31]) and hence was seen to yield relatively poor transport rate which was compared to that with carbon tetrachloride as the diluent. The permeability coefficient values for Y(III) transport using T2EHDGA as the carrier extractant were computed with different diluent systems and are listed in Table 5.2. The Y(III) transport trend was found to be xylene ~ hexone > chloroform > carbon tetrachloride > n-dodecane + 30% iso-decanol. The transport rates of Sr(II) was also investigated and the results are presented in Fig. 5.4. Though the solvent extraction data indicated poor Sr(II) extraction as compared to Y(III) extraction, the transport rates of Sr(II) was surprisingly large for diluents and the trend for 6 M HNO₃ as the feed was carbon tetrachloride > hexone > xylene > chloroform >> n-dodecane + 30% iso-decanol mixture. It was noticed, however, that the % Sr transported was negligible for n-dodecane + 30% iso-decanol mixture while relatively lower transport was seen with chloroform and subsequent studies were carried out with these diluents and not with carbon tetrachloride, hexone and xylene which were found to be not suitable for the subsequent studies aimed at the separation of carrier free $^{90}$Y from $^{90}$Sr.

### 5.5.2. Role of Feed Acidity

The acidity of the feed has been reported to have a major influence on the transport of metal ions in analogous systems [5.27, 5.32 - 5.34]. Though % Y transported was higher with chloroform as the diluent as compared to the n-dodecane + 30% iso-decanol mixture at 6 M HNO₃ up to 150 minutes, a reversal was seen subsequently. It was required to carry out transport studies at lower acidities. Results obtained with 3 M HNO₃ are presented in Fig. 5.5. Chloroform was clearly seen as the superior diluent system so far as the Y(III) transport rates were concerned. A close look at the transport profiles indicate that they are comparable up to 50 minutes while after that Y(III) transport increased significantly for chloroform as the diluents. However, it was required to see the relative transport rate at this feed condition (3 M HNO₃). The plot of ln($C_t/C_0$) vs time is presented in Fig. 5.6 and indicates that the transport of Sr(II) though much lower as compared to that of Y(III) cannot be ignored and is going to decide the purity of the product.
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Fig. 5.5: Relative transport behaviour of Y(III) using 0.2 M T2EHDGA in CHCl$_3$ and n-dodecane. Feed: 3 M HNO$_3$; Receiver: 0.01 M HNO$_3$; Temp.: 24 ± 1°C

Fig. 5.6: Plot of ln($C_t/C_0$) vs time for 0.2 M T2EHDGA in CHCl$_3$ and n-dodecane. Feed: 3 M HNO$_3$; Receiver: 0.01 M HNO$_3$; Temp.: 25 ± 1°C
Fig. 5.7: Effect of acidity on the transport of Y(III) by T2EHDGA-SLM; Carrier: 0.2 M T2EHDGA in CHCl₃; Strip phase: 0.01 M HNO₃.

Fig. 5.8: Effect of acidity on the transport of Sr(II) by T2EHDGA-SLM; Carrier: 0.2 M T2EHDGA in CHCl₃; Strip phase: 0.01 M HNO₃.
Fig. 5.7 shows the effect of feed acidity, in the range of 1-6 M HNO$_3$, on the transport of Y using 0.2 M T2EHDGA in chloroform as the carrier solvent. It was found that the transport rate of Y(III) increased with feed acidity from 1 M HNO$_3$ to 2 M HNO$_3$ and beyond which a decrease was observed. However, the trend was found to change with transport time. For example, after 30 minutes the trend was 6 M > 3 M > 2 M > 1 M which changes after 2 hrs to 3 M > 2 M > 6 M > 1 M which further changed after 3 hrs to 2 M > 3 M > 6 M > 1 M. After 3 hrs, the Y transport was 65 %, > 99.99 %, 95 % and 80 % at 1 M, 2 M, 3 M and 6 M HNO$_3$, respectively. At the same time, the transport of Sr was 43 %, 58 %, 10 % and 6 %, respectively (Fig. 5.8). This observation is quite interesting as increasing acid concentration usually enhances the metal ion transport [5.27, 5.32-5.34]. The possible reason could be due to 18-crown-6 type cavity formation by two T2EHDGA molecules with 6 ‘O’ donor atoms which is stabilized at lower acidity [5.35]. It is proposed that due to possible reverse micelle formation similar to that in case of TODGA destabilizes the 18-crown-6 type dimeric structure leading to lower Sr(II) transport at higher acidities. The separation factor (SF, defined as the concentration of Y(III) over concentration of Sr(II) in the strip solution which was taken from the % transport data) was found to increase with increased feed acidity from 2.09 (at 1 M HNO$_3$) to 51.9 (at 6 M HNO$_3$) after 1 hour of transport (Table 5.3). Similar observations have been reported in a solvent extraction study using TODGA as the extractant [5.36]. The separation factor values decreased further with time suggesting that Sr contamination in the product would increase making it unsuitable for pharmaceutical applications.

<table>
<thead>
<tr>
<th>[HNO$_3$], M</th>
<th>% Transport (1 hr)</th>
<th>Permeability coefficient (cm/s)</th>
<th>S.F. (%T$_Y$/%T$_Sr$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(III)</td>
<td>Sr(II)</td>
<td>Y(III)</td>
<td>Sr(II)</td>
</tr>
<tr>
<td>1.0</td>
<td>19.6</td>
<td>9.36</td>
<td>(0.53 ± 0.02) x 10$^{-3}$</td>
</tr>
<tr>
<td>2.0</td>
<td>51.7</td>
<td>28.2</td>
<td>(1.79 ± 0.06) x 10$^{-3}$</td>
</tr>
<tr>
<td>3.0</td>
<td>71.3</td>
<td>4.26</td>
<td>(1.87 ± 0.07) x 10$^{-3}$</td>
</tr>
<tr>
<td>6.0</td>
<td>68.5</td>
<td>1.32</td>
<td>(1.84 ± 0.05) x 10$^{-3}$</td>
</tr>
</tbody>
</table>
Table 5.4: Comparative acid transport data with 0.2 M T2EHDGA in chloroform / n-dodecane + 30% iso-decanol as the carrier solvent systems; Feed: 3 M HNO₃; Receiver: 0.01 M HNO₃

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>% Acid transport in the following solvent systems</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 M T2EHDGA in n-dodecane + 30% iso-decanol</td>
</tr>
<tr>
<td>10</td>
<td>0.38</td>
</tr>
<tr>
<td>20</td>
<td>0.49</td>
</tr>
<tr>
<td>30</td>
<td>0.56</td>
</tr>
<tr>
<td>60</td>
<td>1.03</td>
</tr>
<tr>
<td>120</td>
<td>1.85</td>
</tr>
<tr>
<td>300</td>
<td>4.09</td>
</tr>
</tbody>
</table>

The low SF values are due to saturation in Y transport data (at lower acidities) and increase in Sr transport data with time. Relative acid transport data is presented in Table 5.4 which suggested that relatively lower acid transport rate was seen with n-dodecane + 30% iso-decanol diluent mixture as compared to chloroform as the diluent.

5.5.3. Separation of ⁹⁰Y from ⁹⁰Sr Using T2EHDGA as Extractant

Keeping these observations in mind, viz. Y(III) transport rates, Sr(II) transport rates and acid transport rates two separate experiments were carried out using a mixture of ⁹⁰Y + ⁹⁰Sr in the feed, and the product was monitored for ⁹⁰Y purity by the half life method.

The radioactive decay equation is given by:

\[ N_t = N_0 e^{-\lambda t} \]  \hspace{1cm} (5.26)

where, \( N_0 \) and \( N_t \) are the initial activity and the activity at a time ‘t’ and \( \lambda \) is the decay constant. Therefore, from semi-log plot of ln \( N(t) \) vs time, the half-life of the radioisotope can be calculated. One set of experiment involved 0.2 M T2EHDGA in n-dodecane + iso-decanol as the carrier solvent and ⁹⁰Y + ⁹⁰Sr in 6 M HNO₃ as the feed while the second experiment involved
0.2 M T2EHDGA in chloroform as the carrier solvent and $^{90}\text{Y} + ^{90}\text{Sr}$ in 3 M HNO$_3$ as the feed. The product in the receiver phase was assayed after 0.5, 1.0 and 2.0 h and the half-lives were measured from the semi-log plots as mentioned before (*vide supra*) and the data are presented in Table 5. Apparently, $^{90}\text{Sr}$ in the product increases with time when chloroform was used as the diluent. As the half-life of $^{90}\text{Y}$ is 64.1 hrs, higher half-life of the product obtained in the receiver phase was indicative of contamination due to the presence of traces of $^{90}\text{Sr}$. It is interesting to note that the half-life of the product decreases with transport time for the system with n-dodecane + *iso* decanol as the diluent while an opposite trend was seen for the chloroform system. The samples were kept aside for 100 days to enable the $^{90}\text{Y}$ to decay completely and were counted for the residual $^{90}\text{Sr}$ (and $^{90}\text{Y}$ generated out of it as its daughter product).

Decontamination factor (DF) values in the range of 98 to 120 were obtained with the products obtained in the present study (all the three fractions from the n-dodecane + *iso*-decanol system and the first fraction from the chloroform system as shown in Table 5.5) indicating that the products obtained by both the systems may not be suitable for radiopharmaceutical use (recommended DF: $10^6$) and purification using other method is recommended as discussed in Chapter III. We have reported product with better purity using solvent extraction using TODGA.

### Table 5.5: Purity test data of the samples taken from the receiver phase as checked by the half-life method

<table>
<thead>
<tr>
<th>Carrier solvent</th>
<th>Assaying time</th>
<th>Half-life (h)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 M T2EHDGA in n-dodecane + <em>iso</em> decanol$^a$</td>
<td>0.5 h</td>
<td>67.7</td>
<td>DF = 98.2 (Reasonably pure$^d$)</td>
</tr>
<tr>
<td></td>
<td>1.0 h</td>
<td>67.3</td>
<td>DF = 114 (Reasonably pure$^e$)</td>
</tr>
<tr>
<td></td>
<td>2.0 h</td>
<td>67.0</td>
<td>DF = 120 (Reasonably pure$^f$)</td>
</tr>
<tr>
<td>0.2 M T2EHDGA in Chloroform$^b$</td>
<td>0.5 h</td>
<td>67.5</td>
<td>DF = 103 (Reasonably pure$^d$)</td>
</tr>
<tr>
<td></td>
<td>1.0 h</td>
<td>73.2</td>
<td>Contaminated$^d$</td>
</tr>
</tbody>
</table>

*Note:* $^a$: *Feed: 6 M HNO$_3*$; $^b$: *Feed: 3 M HNO$_3*$; $^c$: 100 µL samples taken from the receiver phase; $^d$: Contaminated with small traces of $^{90}\text{Sr}$.
in Chapter III and extraction chromatographic separation methods with DF values in the range of $10^3$ - $10^4$ as discussed in Chapter IV. The poor decontamination of the product in the present case is attributed to the co-transport of Sr(II). However, coupling to another separation method may result in the product with the required purity.

5.6. Effect of the Nature of the Diluents in Solvent Extraction Studies with TODGA as Extractants

In the previous section (Section 5.4), we have seen the effect of the nature of diluents on the solvent extraction and supported liquid transport of Y(III) and Sr(II) with T2EHDGA as the extractant. Similar studies were carried out with TODGA as extractant. In this study, solutions of desired concentration of TODGA (0.1 M) were prepared in several diluents viz. 1-decanol, xylene, MIBK, chloroform and carbon tetrachloride, and solvent extraction experiments were carried out in the same manner as described in the previous section. Distribution ratio values of $^{90}$Y and $^{85-89}$Sr were measured using 0.1 M TODGA in different diluents as organic phase at three different feed conditions viz., 6 M and 3 M HNO$_3$ and 6 M HCl. The $D_Y$ and $D_{Sr}$ values are listed in Table 5.6 - 5.8 along with the separation factors (SF). Comparing the data given in Table 5.6 and Table 5.7, it can be stated that in the case 6 M HNO$_3$, with the exception of xylene, for all other diluents the SF values are 10-1000 fold higher as compared to 3 M HNO$_3$. Hence the Supported Liquid Membrane (SLM) studies were carried out with 0.1M TODGA as carrier ligand in the above mentioned diluents (except xylene), 6 M HNO$_3$ as feed phase spiked with $^{90}$Y.

<table>
<thead>
<tr>
<th>Diluents</th>
<th>$K_{d,Y}$</th>
<th>$K_{d,Sr}$</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>181</td>
<td>0.08</td>
<td>2.26x10$^3$</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>178</td>
<td>0.003</td>
<td>5.9x10$^5$</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>229</td>
<td>0.104</td>
<td>2.2x10$^3$</td>
</tr>
<tr>
<td>MIBK (Hexone)</td>
<td>161</td>
<td>0.031</td>
<td>5.3x10$^3$</td>
</tr>
<tr>
<td>n-Decanol</td>
<td>89</td>
<td>0.02</td>
<td>4.4x10$^3$</td>
</tr>
</tbody>
</table>
### Table 5.7: Variation of Diluents on the solvent extraction of $^{90}\text{Y}$ and $^{85-89}\text{Sr}$ with 0.1 M TODGA as extractant from 6 M HNO$_3$

<table>
<thead>
<tr>
<th>Diluents</th>
<th>$K_{d,Y}$</th>
<th>$K_{d,Sr}$</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>44.8</td>
<td>0.006</td>
<td>$7.4 \times 10^3$</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>2188</td>
<td>0.00004</td>
<td>$5.4 \times 10^6$</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>6319.2</td>
<td>0.025</td>
<td>$2.5 \times 10^5$</td>
</tr>
<tr>
<td>MIBK(Hexone)</td>
<td>101.3</td>
<td>0.0005</td>
<td>$2.0 \times 10^5$</td>
</tr>
<tr>
<td>$n$-Decanol</td>
<td>35.5</td>
<td>0.0005</td>
<td>$7.1 \times 10^4$</td>
</tr>
</tbody>
</table>

### Table 5.8: Variation of Diluents on the solvent extraction of $^{90}\text{Y}$ and $^{85-89}\text{Sr}$ with 0.1 M TODGA as extractant from 6M HCl

<table>
<thead>
<tr>
<th>Diluents</th>
<th>$K_{d,Y}$</th>
<th>$K_{d,Sr}$</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>67.3</td>
<td>0.0013</td>
<td>51546</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>2.62</td>
<td>0.0014</td>
<td>1907</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>49.4</td>
<td>0.0019</td>
<td>26013</td>
</tr>
<tr>
<td>MIBK(Hexone)</td>
<td>4.6</td>
<td>0.0158</td>
<td>291</td>
</tr>
<tr>
<td>$n$-Decanol</td>
<td>229</td>
<td>0.0146</td>
<td>15667</td>
</tr>
</tbody>
</table>

### Table 5.9: Transport behavior of $^{90}\text{Y}$ in SLM studies with 0.1 M TODGA in different diluents; Feed: 6 M HNO$_3$ and strip: pH 2

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$%Y_{\text{CCl}_4}$ Feed</th>
<th>$%Y_{\text{CCl}_4}$ Strip</th>
<th>$%Y_{\text{CHCl}_3}$ Feed</th>
<th>$%Y_{\text{CHCl}_3}$ Strip</th>
<th>$%Y_{\text{Hexone}}$ Feed</th>
<th>$%Y_{\text{Hexone}}$ Strip</th>
<th>$%Y_{\text{1-decanol}}$ Feed</th>
<th>$%Y_{\text{1-decanol}}$ Strip</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>42.26</td>
<td>18.36</td>
<td>56.13</td>
<td>3.43</td>
<td>53.34</td>
<td>0.49</td>
<td>84.02</td>
<td>1.04</td>
</tr>
<tr>
<td>30</td>
<td>22.71</td>
<td>27.94</td>
<td>36.48</td>
<td>4.66</td>
<td>33.12</td>
<td>0.52</td>
<td>70.71</td>
<td>2.12</td>
</tr>
<tr>
<td>45</td>
<td>14.07</td>
<td>41.84</td>
<td>24.22</td>
<td>6.86</td>
<td>19.03</td>
<td>0.60</td>
<td>57.49</td>
<td>3.15</td>
</tr>
<tr>
<td>60</td>
<td>12.04</td>
<td>58.18</td>
<td>15.35</td>
<td>7.77</td>
<td>4.94</td>
<td>0.50</td>
<td>54.98</td>
<td>4.55</td>
</tr>
<tr>
<td>90</td>
<td>11.43</td>
<td>59.28</td>
<td>5.49</td>
<td>10.12</td>
<td>2.23</td>
<td>0.42</td>
<td>48.65</td>
<td>5.29</td>
</tr>
<tr>
<td>120</td>
<td>9.15</td>
<td>61.52</td>
<td>1.28</td>
<td>11.05</td>
<td>2.15</td>
<td>0.48</td>
<td>43.16</td>
<td>6.54</td>
</tr>
</tbody>
</table>
Fig. 5.9: Transport profiles of Y(III) from 6 M HNO$_3$ feed solutions. Receiver: 0.01 M HNO$_3$. Carrier: 0.1 M TODGA. Square: CCl$_4$; Circle: CHCl$_3$; Triangle: Hexone; Diamond: 1-decanol. Closed symbol: As observed in feed phase; Open symbol: As observed in receiver phase.

radiotracer and nitric acid of pH 2 as the strip phase. The results are given in Table 5.9 and the graphical presentation is shown in Fig. 5.9. Except in the case of CCl$_4$, where ~61%Y(III) transport was observed in 120 minutes, in all the other cases, even though the feed activity was decreasing with time, the strip was not increasing proportionately. The possible reason for such anomalous behavior could attributed to inefficient stripping, slow diffusion of the Y-TODGA complex or both.

From the experiments on the solvent extraction of $^{90}$Y and $^{85-89}$Sr with 0.1 M TODGA as extractant from 6 M HCl using different diluents (Table 5.8), xylene was found to be most efficient diluent (SF = 5.15 x 10$^4$) and hence further separation studies were carried out using xylene as the diluent.
Table 5.10: Impurity analysis of $^{90}$Y product obtained by solvent extraction; Feed: 6 M HCl. Organic phase: 0.1 M TODGA in xylene.

<table>
<thead>
<tr>
<th>Source of Product</th>
<th>Half life (hrs)</th>
<th>Source of Product</th>
<th>Half life (h)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strip 1</td>
<td>64.17</td>
<td>Strip 4</td>
<td>64.47</td>
<td>Reasonably pure</td>
</tr>
<tr>
<td>Strip 2</td>
<td>64.35</td>
<td>Strip 5</td>
<td>64.42</td>
<td>Reasonably pure</td>
</tr>
<tr>
<td>Strip 3</td>
<td>64.41</td>
<td>Extract 1</td>
<td>66.89</td>
<td>Contaminated with $^{90}$Sr</td>
</tr>
</tbody>
</table>

Based on this, a separation method was developed for the recovery of pure $^{90}$Y from a mixture of $^{90}$Y + $^{90}$Sr. The method involved preferential extraction of $^{90}$Y by 0.1 M TODGA in xylene from 6 M HCl followed by its stripping using 0.01 M HCl. The purity of the product was ascertained from its half-life measurements. Several products samples of $^{90}$Y such as: i) after extraction from 6 M HCl, ii) after extraction from 6 M HCl followed by stripping with distilled water and iii) after several cycles consisting of the extraction and stripping steps were obtained. The half-lives of the products from the strip fractions were calculated from the slope of the semi-log plot and were found to be in the range 64.17 hrs to 64.47 hrs suggesting reasonably high purity of the product (Table 5.10). On the other hand, the $^{90}$Y containing extract resulted in much higher half-life suggesting partial $^{90}$Sr contamination.

Based on the promising solvent extraction result, the SLM studies were carried out with 0.1 M TODGA / xylene using a microporous PTFE membrane as a polymeric support. The transport of Sr and Y by TODGA-SLM for a feed phase containing 6 M HCl and receiver phase containing 0.01 M HCl suggested >99% transport of $^{90}$Y in 2 h while $^{85,89}$Sr transport was almost negligible. The results of the transport experiments indicated the feasibility of the separation of $^{90}$Y from $^{90}$Sr using a simple transport cell (Fig.5.10).

$^{90}$Y samples were removed from the receiver phase after different time intervals (after 40, 60 and 120 minutes) from an SLM experiment carried out using $^{90}$Sr and $^{90}$Y mixture and the purity of the product was ascertained as a function of time by the half-life method as indicated above under the solvent extraction studies. The half lives were found to be in the range of 64 hrs to 70 hrs(Fig. 5.11) suggesting that the product was contaminated small quantity of $^{90}$Sr with increasing sampling time (from receiver phase). This is due to permeation of increasing quantity.
Fig. 5.10: Transport of Y(III) and Sr(II) through SLM, carrier ligand: 0.1 M TODGA xylene, feed solution: 6 M HCl, receiver solution: 0.01 M HCl support: PTFE, dip time: 30 min.

Fig. 5.11: $^{90}$Y half life variation in SLM studies as a function of the sampling time.
of $^{90}$Sr from the feed side to the receiver side. The product can be purified by passing through a crown ether column as mentioned in previous report [5.37].

5.7. Conclusions

Solvent extraction studies suggested chloroform as the most suitable diluent of those used in the present study as a large separation factor value of 5000 was obtained. On the other hand, the transport studies indicated relatively high Y(III) transport rates with xylene and hexone which also facilitated significant Sr(II) transport making these diluents unusable from separation point of view. The studies on the effect of feed acidity though indicated increased Y transport with increasing feed acidity, an entirely opposite trend was observed with respect to Sr(II) transport suggesting 3 M HNO$_3$ should be the optimum feed to be used for the separation studies. The present studies suggested that T2EHDGA-SLM though do not appear promising, may be used for the separation of Sr and Y only at lower transport times. The product gets contaminated with $^{90}$Sr as time increases. Similarly solvent extraction studies on extraction of yttrium and strontium employing carrier extractant TODGA in different diluents from two mineral acids namely nitric acid and hydrochloric acid suggested xylene to be promising diluents in case of 6 M HCl as aqueous phase having separation factor (SF$^{Y/Sr}$ $\sim$ 50,000). The SLM studies using TODGA in xylene in separation Sr-Y suggested solvent extraction method was more promising as compared to the supported liquid membrane based separation method. The product obtained from the SLM method can be purified further by passing through a crown ether column for possible applications.

5.8. References

Chapter V


