Chapter IV

TRANSPORT OF ACTINIDES AND LANTHANIDES USING
N,N,N’,N’-TETRA (2-ETHYL HEXYL) DIGLYCOLAMIDE (T2EHDGA)

4.1. Introduction
N,N,N’,N’-tetra (2-ethyl hexyl) diglycolamide (T2EHDGA, Fig. 4.1) is a branched chain homolog of TODGA having identical structure except for a branching on the alkyl substituent in the acyl nitrogen atom of the di-glycolamide. It is reported to favourably extract trivalent actinides similar to TODGA though higher decontamination factor values (with respect to the fission products) are expected due to stereochemical effects [1].

Fig. 4.1. Structure of T2EHDGA where R= (2-ethyl hexyl)

Solvent Extraction and Pilot scale Mixer-Settler studies with T2EHDGA for the separation of trivalent actinides and lanthanides have shown promising results [1]. Supported liquid membrane (SLM) transport studies of actinides and lanthanides using T2EHDGA as carrier have not been reported in literature. Present work was aimed at understanding the transport properties of actinides and lanthanides using T2EHDGA as the carrier across SLM.
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4.2 Studies on the Transport of Trivalent Actinides

The current study was aimed at investigating the transport behavior of trivalent actinides, taking Am(III) as a representative element, from nitric acid medium. Various parameters were studied in detail to understand the different physicochemical factors responsible for Am(III) transport. Some of the parameters studied were feed acid concentration, concentration of T2EHDGA, membrane thickness etc. Understanding the mechanism of transport for Am(III) would help in applying T2EHDGA in Hollow Fiber module for remediation of large volumes of waste solution.

4.2.1. Solvent Extraction Studies

The extraction of Am(III) from nitrate medium with neutral T2EHDGA molecules is usually represented by the following expression:

\[ K_{ex} \]

\[ \text{Am}^{3+} + 3\text{NO}_3^{--} + n\text{T2EHDGA}_{org} \rightleftharpoons \hat{\text{U}}\text{Am(NO}_3^-)_3\cdot n\text{T2EHDGA}_{org} \quad (4.1) \]

The two-phase extraction constant (\( K_{ex} \)) can be expressed by the following equation:

\[ K_{ex} = \frac{[\text{Am(NO}_3^-)_3\cdot n\text{T2EHDGA}]_{org}}{[\text{Am}^{3+}]_{aq} \cdot [\text{NO}_3^-]^3_{aq} \cdot [\text{T2EHDGA}]^n_{org}} \quad (4.2) \]
Since the distribution ratio of Am(III) \( (D_{\text{Am(III)}}) \) can be expressed by the ratio of total Am(III) concentration in the organic phase to that in the aqueous phase, Eqn. 4.2 can be modified as

\[
D_{\text{Am}} = K_{\text{ex}} \left[ \text{NO}_3^- \right]_{(aq)}^3 \cdot [\text{T2EHDGA}]_{(org)}^n
\]  

(4.3)

Taking log of both sides the eqn. becomes

\[
\log D_{\text{Am}} = \log K_{\text{ex}} + 3 \log [\text{NO}_3^-] + n \log [\text{T2EHDGA}]
\]  

(4.4)

---

Fig. 4.2. Plot of \( D_{\text{Am}} \) vs T2EHDGA concentration in \( n \)-dodecane as diluent.

Aqueous phase acidity: 3 M HNO\(_3\)
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The value of ‘n’ has been determined to be close to 3 from the log-log plot of $D_{\text{Am}}$ vs T2EHDGA concentration using $n$-dodecane as diluent at 3 M nitric acid concentration (Fig. 4.2). The value of ‘n’ for TODGA has been reported to be ‘4’ [2]. The difference in number of carrier molecules being attached to Am(III) for TODGA and T2EHDGA may be due to the steric effect expected in the case of T2EHDGA due to its branched structure. From Eqn. (4.3) it is clear that nitric acid/nitrate concentration has a major role in the extraction of Am(III). To understand the effect of nitric acid concentration, solvent extraction studies were carried out at different acidities from 1 M to 6 M using 0.2 M T2EHDGA in $n$-dodecane.

As evident from Table (4.1), the $D_{\text{Am}}$ values increased with increasing nitric acid concentration. This is due to the increase in nitrate ion concentration. Further, solvent extraction studies were carried out at a fixed nitrate ion concentration (using NaNO$_3$) but varying the nitric acid concentration. As evident from the Table (4.1), $D_{\text{Am}}$ values increased with increasing nitric acid concentration. The increase in $D_{\text{Am}}$ values with increasing nitrate concentration may be due to the nitrate ion facilitated extraction as evident from Eqn. (4.1) and also due to salting out effect. But by increasing the acidity at a fixed nitrate ion concentration, the same trend was observed which could not be explained as no significant H$^+$ ion extraction was observed.

4.2.2. Transport studies

4.2.2.1. Effect of Feed Nitric Acid/ Nitrate Concentration
Table 4.1. Distribution data of Am(III) in T2EHDGA / n-dodecane, [T2EHDGA] = 0.2 M at varying acidity and nitrate ion concentration

<table>
<thead>
<tr>
<th>[NO₃⁻] (HNO₃ + NaNO₃) in feed (M)</th>
<th>D_{Am}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.25 + 3.00)</td>
<td>12.8</td>
</tr>
<tr>
<td>(1.25 + 2.00)</td>
<td>41.5</td>
</tr>
<tr>
<td>(2.25 + 1.00)</td>
<td>69.5</td>
</tr>
<tr>
<td>(3.00 + 0.25)</td>
<td>95.7</td>
</tr>
<tr>
<td>(1.00 + 0.00)</td>
<td>3.40</td>
</tr>
<tr>
<td>(2.00 + 0.00)</td>
<td>32.2</td>
</tr>
<tr>
<td>(3.00 + 0.00)</td>
<td>87.1</td>
</tr>
<tr>
<td>(6.00 + 0.00)</td>
<td>141</td>
</tr>
</tbody>
</table>

A detailed study was carried out to understand the role of feed nitric acid concentration on the transport of Am(III). During the experiments, T2EHDGA concentration was kept at 0.2 M and 0.1 M HNO₃ was used as the strippant. Am(III) transport increased with the increase in nitric acid concentration in the feed up to 3 M and decreased thereafter. Near quantitative transport of Am(III) (99.62%) could be achieved in 3 h by using 3M nitric acid in the feed. Fig. (4.3) shows % transport of Am(III) transport at varying concentrations of HNO₃ in the feed. This is partly in agreement with the expected trend.
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since the flux of a cation varies with \( \text{NO}_3^- \) ion concentration according to the relationship [3]:

\[
J_M = \frac{(AT)[\text{NO}_3^-]_{aq}^n [\text{Carrier}]_{org}^n . C_{M,\text{Feed}}}{\eta} \quad (4.5)
\]

Where \( A \) is the area of the membrane (cm\(^2\)), \( T \) is absolute temperature (K), \( \eta \) is viscosity (1\( \times \)10\(^{-3}\) Pa.s ), \([\text{Carrier}]_{org}\) corresponds to concentration of T2EHDGA in the membrane phase and \( C_M \) is concentration of Am(III) in feed (mol/L).

Fig. 4.3. Transport of Am(III) using 0.2 M T2EHDGA/\( n \)-dodecane as carrier from varying feed nitric acid concentration. Strippant- 0.1 M HNO\(_3\); Membrane support: 0.45 \( \mu \)m PTFE
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The increase in transport with increasing nitric acid concentration in THE feed from 1 M to 3 M is due to the increasing tendency of complex formation with increasing nitrate ion concentration while the reduction in transport from 3 M to 6 M is due to the formation of adduct between the extractant T2EH DG A and HNO₃ which decreases the concentration of free T2EH DG A available for complex formation. The strip phase acidity increased with increasing feed acidity (0.15 M for 1 M feed acidity to 0.35 M for 6 M feed acidity after 180 minutes). The increased strip phase acidity also reduced the stripping efficiency in the receiver phase and this could also be another reason for the lower transport rates in case of 6 M feed acidity. The same trend was also observed for the permeability coefficient values. The permeability coefficient value was found to be maximum (2.43×10⁻³ cm/s) at 3 M nitric acid as depicted in Table 4.2. In case of TODGA, maximum transport was found at 2 M HNO₃ [4]. In order to understand the role of H⁺ ion on the transport of Am(III) through FSSLM containing T2EH DG A, experiments were carried out keeping the nitrate ion concentration fixed at 3.25 M and varying the HNO₃ concentration.
Table 4.2. Permeation coefficient data along with percentage transport of Am(III) using 0.2M T2EHDGA/n-dodecane as carrier at varying acidity and nitrate ion concentration of feed

<table>
<thead>
<tr>
<th>[NO₃⁻] (HNO₃ + NaNO₃) in feed (M)</th>
<th>P ×10⁻³ (cm/s)</th>
<th>Transport after 180 min (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.25 + 3.00)</td>
<td>1.2</td>
<td>90.1</td>
</tr>
<tr>
<td>(1.25 + 2.00)</td>
<td>1.86</td>
<td>94.5</td>
</tr>
<tr>
<td>(2.25 + 1.00)</td>
<td>2.4</td>
<td>98.6</td>
</tr>
<tr>
<td>(3.00 + 0.25)</td>
<td>1.93</td>
<td>93.8</td>
</tr>
<tr>
<td>(1.00 + 0.00)</td>
<td>0.48</td>
<td>68.5</td>
</tr>
<tr>
<td>(2.00 + 0.00)</td>
<td>1.51</td>
<td>96.6</td>
</tr>
<tr>
<td>(3.00 + 0.00)</td>
<td>2.43</td>
<td>99.6</td>
</tr>
<tr>
<td>(6.00 + 0.00)</td>
<td>1.46</td>
<td>95.9</td>
</tr>
</tbody>
</table>

Table (4.2) shows the transport of Am(III) at a fixed nitrate ion concentration of 3.25 M but at different H⁺ ion concentration varying from 0.25 M to 3 M. The maximum transport of 98.62% could be achieved when [NaNO₃] = 1 M and [HNO₃] = 2.25 M as can be seen from Table (4.2). The permeability coefficient value was found to be maximum in the above composition (2.4×10⁻³ cm/s, Table 4.2). The further decrease in permeability coefficient with increasing NaNO₃ concentration, is attributed to the competition of Na(I) ion with Am(III) [5].
4.2.2.2. Effect of Carrier Concentration

To understand the effect of T2EHDGA concentration in the membrane phase on the transport rate of Am(III), permeation experiments were carried out using varying concentrations of T2EHDGA (from 0.1 M to 0.3 M in n-dodecane as the diluent) supported on PTFE membranes (0.45 μm PTFE). Feed and strip phase acidities were maintained as 3 M HNO₃ and 0.1 M HNO₃, respectively. % Am(III) transported at varying concentration of carrier (Fig. 4.4) increased up to 0.2 M of carrier concentration and decreased thereafter. The liquid membrane pertraction of metal cations involves a heterogeneous chemical reaction between an organic carrier and the aqueous metal ion and so the metal flux ($J_M$) will be governed by the diffusion rates of the reactants in the presence of fast kinetics of interfacial reaction. The diffusion coefficient of a solute D, across the membrane is defined by the Stokes–Einstein equation (Eqn. 3.2). Generally, an increase in the carrier concentration will produce an increase in the cation flux. However, the concurrent increase in viscosity results in a steady decrease in the diffusivity of the carrier as well as of the metal-carrier complex. The transport of Am(III) should be a function of both the distribution coefficient and diffusion coefficient. In carrier-mediated transport of Am(III) with T2EHDGA, a more complex behavior was seen. Babcock et al. [6] have assigned the dominant effects that cause this “maximal phenomenon” to be due to: (i) the concentration gradient of the carrier-complex species (ii) the viscosity of the membrane phase and (iii) hindered diffusion of metal complex caused by aggregation of the complex.
Fig. 4.4. Effect of carrier (T2EHDGA) concentration on the transport of Am(III).

Feed: Am(III) in 3 M HNO₃; Strippant: 0.1 M HNO₃; Membrane support: PTFE (0.45 µm)

To understand the effect of carrier concentration on the transport of Am(III), various concentrations of T2EHDGA/ n-dodecane solutions, already equilibrated with the feed acidity, were used as carrier. From the results, it was quite clear that there was a significant increase in viscosity with increase in carrier concentration. From Fig. 4.5, it was evident that as the T2EHDGA concentration increased from 0.1 M to 0.3 M the viscosity increased from 1.62 to 2.35 mPa.s whereas the change in density was nominal from 0.758 to 0.779 g/cm³. Since the flux is inversely proportional to the viscosity, an increase in the viscosity should reduce the flux, as was the case in the present study. Evidently, the organic phase viscosity proves to be a controlling parameter in the
optimum carrier concentration for a liquid membrane system. Since an increase in the viscosity of T2EHDGA solutions may lead to decrease of the diffusion coefficient and hence permeability of the diffusing species, these opposing effects resulted in a maximum permeation at about 0.2 M T2EHDGA/ n-dodecane. With further increase in carrier concentration, the permeation decreased. The permeability coefficient was found to reach a maximum value ($2.46 \times 10^{-3}$ cm/s) for 0.2 M T2EHDGA/ n-dodecane as carrier at 3 M HNO$_3$. In case of TODGA, 0.1 M TODGA/ n-dodecane was found to be the optimum carrier concentration [4].

4.2.2.3. Effect of Nature of Strippant

Transport of metal ion across FSSLM is strongly dependent on the nature of the strippants used. Detailed experiments were carried out to understand the role played by stripping solution in the transport of Am(III) using T2EHDGA as the carrier. Different strippant mixtures such as distilled water, a buffer mixture (HFC consisting of 0.4 M hydrazine hydrate, 0.4 M formic acid and 0.1 M citric acid) [7], 0.1 M oxalic acid and 0.1 M nitric acid were studied for Am(III) transport. It was observed that among the strippants, 0.1M nitric acid proved to be the most efficient for stripping of Am(III) from membrane phase. Fig. (4.6) shows that near quantitative recovery of Am(III) was possible at ~3 h with 0.1M nitric acid as also observed in the case of TODGA [4].
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Fig. 4.5. Viscosity and density of varying concentration of T2EHDGA equilibrated with 3 M HNO₃

4.2.2.4. Effect of pore size of membrane support

The transport rate across an FSSLM depends on factors like the amount of carrier held in the pores of the filters, pore structure and pore size, the thickness, porosity and tortuosity of membrane, etc. [8,9]. In order to understand the effect of membrane pore size on the transport rates of Am(III) using T2EHDGA as the carrier, PTFE sheets with varying pore sizes, viz. 0.2, 0.45, 1.2 and 5.0µm were used. Membrane pore size has a very distinct role in the permeation rate of metal cation in the membrane studies. From
Fig. 4.6. Variation of transport rate of Am(III) using varying strippants. Feed: Am(III) in 3 M HNO₃; Carrier: 0.2 M T2EHDA/ n-dodecane; Membrane support: PTFE (0.45 µm)

Stokes–Einstein law (Eqn. 4.5), the diffusion coefficient of the complex is inversely related to the radius of the diffusing complex. Therefore, higher the pore size, lower is the resistance experienced by the complex species which results in higher transport rate for higher pore size membranes. The effect of porosity and tortuosity can be expressed by the equation [10]:

\[
D_m = \frac{D_s \theta}{\tau}
\]

(4.6)
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Where $D_m$ is the diffusion coefficient of the Am-T2EHDGA complex, $\theta$ and $\tau$ are the porosity and tortuosity of the membrane, respectively.

![Graph showing variation of transport rate of Am(III) against varying membrane pore size. Feed: 3 M HNO$_3$; strippant: 0.1 M HNO$_3$; Carrier: 0.2 M T2EHDGA/n-dodecane; Membrane support: PTFE of varying pore size.](image)

Fig. 4.7. Variation of transport rate of Am(III) against varying membrane pore size. Feed: 3 M HNO$_3$; strippant: 0.1 M HNO$_3$; Carrier: 0.2 M T2EHDGA/ n-dodecane; Membrane support: PTFE of varying pore size

With increasing membrane pore size, porosity of the membrane increases where as the tortuosity of the membrane decreases as shown in Table (4.3). So both these effects result an increase in the transport rate of Am with increasing membrane pore size. But for diffusion controlled transport process, transport rate also depends on the effective diffusion path length. This can be very well understood from Eqn. (4.7) which clearly
indicates that $P$ is inversely proportional to the thickness of the membrane support in diffusion controlled process \[5\].

$$P = \frac{D_0 D_M}{\tau \cdot d_0} \quad (4.7)$$

As evident from Table 4.3, membrane thickness increases with increasing membrane pore size which causes an increase in the diffusion path length of Am-T2EHGDA complex. This results in a decrease in the transport rate with increasing membrane pore size. Hence as an optimum condition of these effects mentioned, transport rate increases from 0.2 µm pore size to 0.45 µm pore size and then decreases thereafter up to 5 µm as shown in Fig. 4.7.

Table 4.3. Various physical parameters of the membrane

<table>
<thead>
<tr>
<th>Pore size (µm)</th>
<th>Thickness (µm)$^a$</th>
<th>Porosity, $\theta^b$</th>
<th>Tortuosity, $\tau^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>65</td>
<td>0.51</td>
<td>2.15</td>
</tr>
<tr>
<td>0.45</td>
<td>80</td>
<td>0.64</td>
<td>1.44</td>
</tr>
<tr>
<td>1.20</td>
<td>90</td>
<td>0.74</td>
<td>1.22</td>
</tr>
<tr>
<td>5.00</td>
<td>100</td>
<td>0.84</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^a$: Data from Catalogue of Sartorious AG Germany. $^b$: From Ref. \[5\].
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4.2.2.5. Selectivity over Fission Products

In order to determine the selectivity of T2EHDGA for actinides and lanthanides over different fission products, we carried out transport studies taking a feed solution containing different fission products, e.g., Ru(multivalent), Cs(I), Zr(IV), Nb(IV), Ce(III) at 3 M HNO$_3$ using 0.2 M T2EHDGA/n-dodecane taking 0.1 M HNO$_3$ as the strippant. As evident from Fig. (4.8) only Ce being a trivalent lanthanide got transported ~90% in 240min. Among the other fission products only Cs got transported ~8% and all other fission products got transported insignificantly (~1%). Ru inspite of being multivalent did not get transported in significant amount. Fe(III) too got transported to a much lower extent (~4%) though it existed in the trivalent state. This is probably because the rate constant for exchange of inner sphere water molecules of the hydrated Fe(III) ions is about five orders of magnitude lower as compared to trivalent lanthanides which may be taken as analogues of Am(III) [5]. Hence T2EHDGA can be used selectively to separate trivalent actinides and lanthanides from fission products with high selectivity.
Fig. 4.8. Transport of various fission products across T2EHDGA/ n-dodecane FSSLM. Feed: Major F.Ps. in 3 M HNO$_3$; strippant: 0.1 M HNO$_3$; Carrier: 0.2 M T2EHDGA/dodecane; Membrane support: PTFE (0.45 µm)

4.2.2.6. Stability of Supported Liquid Membrane

The polymer supports used in supported liquid membranes are generally having pores which adsorb the organic solution or carrier within its moieties. This organic solution is held within its pores by the capillary forces of these pores. After prolong use, these membranes start to degrade. The degradation of the membranes can be because of the one or accumulative effect of chemical degradation, loss of carrier and/or solvent by dissolving in adjacent aqueous phases, leaching out of the membrane carrier by an osmotic or hydrostatic pressure gradient, formation of emulsion or reverse micelles, etc.
Sometimes stability of these membranes may be affected due to the chemical degradation of the support material. Hence studies were performed to see the stability of these membranes as a carrier leaching out of the support and integrity of the support material point of view. The chemical resistance of PTFE membranes against T2EHDGA/dodecane was periodically tested over a period of 30 days by keeping it dipped in 0.2 M carrier solution. Experiments carried out using 3 M HNO$_3$ as feed, 0.2 M T2EHDGA in n-dodecane as carrier and 0.1 M HNO$_3$ as the strippant showed that there was no significant change in the transport of Am(III) over a period of 30 days, thereby suggesting that the integrity of the support was not affected during this period. The stability of membrane, with respect to carrier leaching out, was checked by operating the same membrane over the period of 22 days continuously and it was found that there was no significant decrease in percentage transport of Am(III) over the first fourteen days of operations and then marginal decrease in percentage transport of Am(III) was observed (Fig. 4.9). Hence the stability of the membrane was found to be quite satisfactory over the time period studied.

4.3. Eu(III) Transport

Transport behavior of trivalent actinides using T2EHDGA as carrier across FSSLM has been described in detail in the previous section. However, in view of the large concentration of the trivalent lanthanides present in the high level waste (about 2-3 g/L in HLLW of fuel with a burn up of 33 GWD/te), it was required to understand the
Fig. 4.9. Stability of PTFE membrane for Am(III)-T2EHDGA for carrier leaching. Feed: Am(III) in 3 M HNO₃; Strippant: 0.1 M HNO₃; Carrier: 0.2 M T2EHDGA/dodecane; Membrane support: PTFE (0.45 µm)

extraction and transport behavior of Eu³⁺ (surrogate for all the trivalent lanthanides) under acidic feed conditions similar to the HLLW.

The present study involves the extraction and transport studies involving Eu³⁺ using T2EHDGA in n-dodecane as the carrier solvent which also contained iso-decanol as the phase modifier. The SLM transport studies involved the effect of membrane pore size, feed acidity, Eu concentration in the feed, phase modifier composition etc on the transport rate of Eu³⁺. Diffusion parameters have also been calculated and compared with the Am³⁺ - T2EHDGA transport system reported above.
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4.3.1. Solvent Extraction Studies

4.3.1.1. Nature of the Extracted Species

Extraction of Eu(III) by T2EHDGA in n-dodecane can be represented by the following equilibrium reaction:

$$\text{Eu}^{3+} + 3\text{NO}_3^- + n\text{T2EHDGA}_{(o)} \rightleftharpoons \text{Eu(NO}_3)_3.n(\text{T2EHDGA})_{(o)}$$  \hspace{1cm} (4.8)

Where the species with the subscript ‘(o)’ indicate those in the organic phase and those without any subscript indicate the species in the aqueous phase. The number of extractant molecules associated with the extracted species was reported to be 3 for the analogous Am(III)-T2EHDGA extraction system while n was reported to be 4 for the Am(III) – TODGA extraction system [4] which was ascribed to reverse micelle formation involving 4 TODGA molecules [10]. Eu(III) extraction studies carried out at varying T2EHDGA concentration indicated extraction of species of the type Eu(NO$_3$)$_3.3$(T2EHDGA)$_{(o)}$ (Fig. 4.10) suggesting participation of three T2EHDGA molecules similar to the Am(III)-T2EHDGA extraction studies reported above. It appears that the branched structure of T2EHDGA restricts the number of extractant molecules in the extracted species to 3 instead of 4 due to steric factors.
Fig. 4.10. Dependence of $K_{d,Eu}$ on T2EHDGA concentration. Aqueous phase acidity: 3 M HNO$_3$

4.3.1.2. Effect of the Feed Acidity

The extraction of Eu$^{3+}$ by T2EHDGA takes place by nitrate ion assisted complexation as shown in Eqn. (4.8). With increasing nitric acid concentration in the aqueous phase, the D value of Eu increases from 0.76 at 0.5 M HNO$_3$ to 164 at 3 M HNO$_3$. On further increasing the aqueous phase acidity to 6 M HNO$_3$ third phase formation was observed. It was required, therefore, to use a phase modifier to prevent the formation of the third phase. The data on distribution ratio against different concentration of HNO$_3$ using 0.2 M T2EHDGA in the absence and the presence of $iso$-decanol is given in Table (4.4).
Table 4.4. Distribution data of Eu(III) using 0.2M T2EHDGA in the absence and the presence of 30% iso-decanol as extractant against varying concentration of HNO₃

<table>
<thead>
<tr>
<th>[HNO₃], M</th>
<th>$K_{d,\text{Eu(III)}}$ (0.2 M T2EHDGA)</th>
<th>$K_{d,\text{Eu(III)}}$ (0.2M T2EHDGA + 30% iso-decanol)</th>
<th>$P \times 10^4$(cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.76</td>
<td>0.64</td>
<td>0.76</td>
</tr>
<tr>
<td>1</td>
<td>4.36</td>
<td>4.15</td>
<td>3.54</td>
</tr>
<tr>
<td>2</td>
<td>67.87</td>
<td>36.1</td>
<td>10.02</td>
</tr>
<tr>
<td>3</td>
<td>164.75</td>
<td>114</td>
<td>6.19</td>
</tr>
<tr>
<td>6</td>
<td>Third phase</td>
<td>166</td>
<td>2.77</td>
</tr>
</tbody>
</table>

4.3.1.3. Effect of Phase Modifier

Earlier studies on the effect of phase modifier on the prevention of third phase with T2EHDGA have suggested iso-decanol as the most promising [11]. Therefore, 30% iso-decanol was chosen as the phase modifier for 0.2 M T2EHDGA and the distribution ratio data is presented in Table 4.4. Though the third phase problem was alleviated with the addition of the phase modifier, the $D_{\text{Eu}}$ values were found to decrease in its presence which was attributed to the change in polarity of the solvent system. Studies were also carried out at varying percentage of the phase modifier. Table 4.5 shows that with
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Increasing iso-decanol concentration from 0 to 40%, the $D_{Eu}$ for Eu(III) value decreased which was ascribed to the increasing polarity of the organic phase which is not favorable for the extraction of the solvated species as given in Eqn. (4.8).

Table 4.5. Distribution data for Eu(III) at 3 M HNO$_3$ using 0.2 M T2EHDGA as extractant in presence of varying concentration of iso-decanol

<table>
<thead>
<tr>
<th>% iso-Decanol (0.2 M T2EHDGA)</th>
<th>$D_{Eu(III)}$ (3 M HNO$_3$)</th>
<th>P (cm/s) $\times 10^4$ (3M HNO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>164.75</td>
<td>6.19</td>
</tr>
<tr>
<td>10</td>
<td>149.52</td>
<td>4.72</td>
</tr>
<tr>
<td>20</td>
<td>135.45</td>
<td>2.89</td>
</tr>
<tr>
<td>30</td>
<td>113.95</td>
<td>2.65</td>
</tr>
<tr>
<td>40</td>
<td>91.77</td>
<td>2.60</td>
</tr>
</tbody>
</table>

4.3.2. Transport Studies

4.3.2.1. Effect of the Feed Acidity

As the metal ion pertraction is a consequence of its extraction at the feed–membrane interface, the transport of Eu(III) from nitric acid medium takes place via nitrate ion assisted extraction suggesting feed nitric acid concentration should play a major role in the transport rate of Eu(III). A continuous increase in the Eu pertraction with feed acidity was observed up to 3 M HNO$_3$ beyond which a
significant decrease was seen for 6 M HNO₃. This observation was similar to our report on Am³⁺-T2EHDGA supported liquid membrane work. On the other hand, maximum transport rate for the Am³⁺-TODGA system was observed at 2 M HNO₃ which decreased considerably at 6 M HNO₃ [4]. In the present study, the transport rate was found to increase up to 2 M HNO₃ and then there was significant decrease at 6 M HNO₃ (Fig. 4.11). The permeability coefficient values are also calculated and are listed in Table (4.4). This trend was followed to be similar to that of Am³⁺-T2EHDGA system except that maximum transport was observed at 3 M HNO₃.

Fig. 4.11. Effect of feed acid concentration on the transport of Eu³⁺ ion. Receiver: 0.01 M HNO₃; Carrier: 0.2 M T2EHDGA; Membrane Support: 0.45 micron PTFE
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The reason behind the increase in transport rate with increasing feed acidity is partly due to the increase in D with nitric acid concentration as indicated in Table (4.4). However, T2EHDGA being acidic in nature ($K_H = 2.1$) has tendency to form adduct with HNO$_3$ itself and this trend increases with increasing feed HNO$_3$ concentration. The formation of adduct with HNO$_3$ causes a decrease in the free T2EHDGA concentration in the membrane phase which can result in lower D of Eu$^{3+}$ at higher acidities. This is the possible reason for the transport rate to decrease at higher feed acidity. Another reason behind the decrease in transport rate at higher acidity could be due to increasing acidity of the receiver phase which can lead to inefficient stripping of the metal ion. It may be mentioned here that the acidity of the receiver phase increases from 0.25 M at 1 M HNO$_3$ to 0.5 M at 6 M HNO$_3$ in ~5 h time.

4.3.2.2. Effect of T2EHDGA Concentration

Facilitated transport of a metal ion across a SLM takes place through complexation of metal ion with the carrier molecule at the feed – membrane interface followed by its release at the membrane – receiver interface. Therefore, the concentration of the carrier molecule in the membrane phase plays a very important role in the overall transport process. Generally, it is observed that there is a maximum concentration of carrier which gives highest transport rate of any metal ion. This “maximal phenomenon” has been assigned by Babcock et al., [6] due to factors such as: i) concentration gradient of the metal-carryer complex ii) viscosity of the complex iii) hindered diffusion of the
metal complex due to the aggregation of the carrier. With increasing carrier concentration the first parameter becomes dominant causing transport rate to increase. But after a certain concentration of the carrier, viscosity and aggregation of the carrier molecule increase. Both these effects cause the transport to decrease. These facts have been investigated in detail in the experiments where concentration of T2EHDGA has been varied from 0.1 M to 0.3 M keeping all the other parameters fixed. As can be seen from Fig. (4.12), the transport rate increased up to 0.15 M T2EHDGA beyond which the transport rate was found to decrease. In about 360 minutes ~99.95% Eu(III) got transported to the receiver phase for 0.15 M T2EHDGA which got reduced to ~ 95.3% at the same time frame when 0.2 M T2EHDGA was used as the carrier solvent. As seen from Table (4.6), the permeability co-efficient value for 0.1 M T2EHDGA was $5.07 \times 10^{-4}$ cm/s which increased to a maximum value of $11.2 \times 10^{-4}$ cm/s for 0.15 M T2EHDGA. When Am(III) transport behavior using T2EHDGA as the carrier was compared, 0.2 M was found to be the optimum concentration where the permeability-coefficient value was $24.6 \times 10^{-4}$ cm/s (Table 4.6). In view of this, 0.2 M T2EHDGA was chosen as the optimum carrier concentration for all other studies.

4.3.2.3. Effect of the Phase Modifier Concentration

The solvent extraction studies have indicated that 30% iso-decanol, when used as the phase modifier, prevented third phase at higher acidities and also in the presence of higher concentration of metal ion. Very few studies have been carried out to see the behavior of phase modifier on the transport rate of metal ions. We have investigated the
effect of varying concentration of *iso*-decanol with 0.2 M T2EHDGA on the transport rate of U(VI) and found that the transport rate decreased with increasing concentration of the phase modifier [12]. Same trend was observed for Eu$^{3+}$-T2EHDGA system in the present studies. Transport rates for this system are shown in Fig. (4.13) while the permeability coefficient values are listed in Table 4.6.

Fig. 4.12. Effect of T2EHDGA concentration on the transport of Eu$^{3+}$ ion. Feed: 3.0 M HNO$_3$; Receiver: 0.01 M HNO$_3$; Support: 0.45 micron PTFE

It was observed that in the absence of any phase modifier about 95% Eu(III) got transported in 5 h when the feed acidity was 3 M HNO$_3$ while 0.01 M HNO$_3$ was used as the receiving phase. This rate was found to decrease continuously from 0 to 40% *iso*-
Table 4.6: Comparative permeability coefficient data for Eu(III) and Am(III) using different concentration of T2EHDGA/ n-dodecane from 3 M HNO₃

<table>
<thead>
<tr>
<th>[T2EHDGA], M</th>
<th>Pₑₓ × 10⁴(cm/s)</th>
<th>Pₐₓ × 10⁴(cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>5.07</td>
<td>20.8</td>
</tr>
<tr>
<td>0.15</td>
<td>11.2</td>
<td>18.7</td>
</tr>
<tr>
<td>0.20</td>
<td>6.19</td>
<td>24.6</td>
</tr>
<tr>
<td>0.30</td>
<td>4.84</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Fig. 4.13. Effect of phase modifier composition on the transport of Eu³⁺ ion. Feed: 3 M HNO₃, Receiver: 0.01 M HNO₃, Support: 0.45 micron PTFE
decanol and about 72% Eu(III) got transported in the presence of 40% iso-decanol after 5 h and are attributed to the increased polarity of the medium.

4.3.2.4. Effect of Membrane Pore Size

The effect of membrane pore size in SLM on the transport of a metal ion for a particular carrier molecule is given by the Eqn. (3.12). This equation clearly shows that with increasing membrane pore size, the diffusing complex of metal-carrier faces less resistance and consequently the transport rate is higher. However, the Laplace’s equation tells us that the pore size can not be increased infinitely to get higher transport as very high pore size means easy displacement of the carrier from the pores. This is shown by th Eqn. (3.13) based on which the transport rate should decrease with increasing pore size of the membrane. However for the Am(III)-T2EHDGA system, there was an initial increase in transport rate followed by a decrease. The plot of P vs membrane pore size for the present system is depicted in Fig. (4.14) and follows a decreasing trend with increasing membrane pore size. This signifies that for the system studied here increasing membrane pore size plays a destabilizing effect.

4.3.2.5. Effect of Eu Concentration

In actual HLW the concentration of lanthanides depends on the burn up of the fuel and can be as high as 3-4 g/L. Taking Eu as a surrogate of the rare earth elements the effect
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of Eu carrier concentration on the transport rate of Eu$^{3+}$ was investigated using T2EH-DGA as the carrier extractant. Eu carrier concentration was varied from 0.1 g/L to 10 g/L keeping 3 M HNO$_3$ as feed acidity while maintaining all other parameters identical. The transport rate against varying Eu carrier concentration is plotted in Fig. (4.15) which indicated that the transport rate decreased significantly

![Graph showing effect of membrane pore size on Eu$^{3+}$ ion permeability coefficients. Feed phase: 3.0 M HNO$_3$; Carrier: 0.2 M T2EH-DGA; Receiver: 0.01 M HNO$_3$](image)

with increasing Eu concentration in the feed. This is in the expected line due to the limited availability of carrier molecule in the membrane phase for complexation. Similar trend was observed by Nakamura et al., [13] for Eu loading using a phosphinic acid extractant. The flux values were calculated to be $3.44 \times 10^{-7}$ mol cm$^{-2}$ s$^{-1}$ for 0.1
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g/L Eu which increased to $5.79 \times 10^{-6}$ mol cm$^{-2}$ s$^{-1}$ for 10 g/L Eu (Fig. 4.16). For feed containing 3-4 g/L Eu carrier, the flux appears to be reasonable suggesting the feasibility of application of the supported liquid membrane system for the separation of rare earth element from acidic radioactive wastes such as the high level waste.

4.3.2.6. Thermodynamics study

Transport studies were carried out at varying temperatures to evaluate the activation energy of the transport of Eu$^{3+}$ using T2EHDGA as the carrier extractant. Transport

![Graph](image)

**Fig. 4.15.** Effect of Eu concentration on Eu$^{3+}$ ion transport. Feed: 3.0 M HNO$_3$; Receiver: 0.01 M HNO$_3$; Carrier: 0.2 M T2EHDGA
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rates measured at four different temperatures viz. 23, 30, 40 and 50°C (Fig. 4.17) suggested that the transport becomes significantly faster at higher temperatures which are reasonable as the viscosity of the medium decreases with temperature thereby leading to more facile diffusion of the complex species as indicated from the Stokes–Einstein equation. The thermodynamic parameters were calculated from the van’t Hoff plots as well as the Gibbs–Helmholtz equation as follows. Free energy change for the extraction equilibria can be expressed as

\[ \Delta G^\circ = -2.303 \text{RT} \ln P \]  
\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

![Graph showing the relationship between Eu concentration and flux](image)

**Fig. 4.16.** Effect of Eu concentration on Eu³⁺ ion flux. Feed: 3.0 M HNO₃; Receiver: 0.01 M HNO₃; Carrier: 0.2 M T2EHDGA
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From Eqns. (9) and (10),

\[
\ln P = - \frac{(\Delta H^0)}{R} \left( \frac{1000}{T} \right) + \frac{(\Delta S^0)}{R}
\]  

(4.11)

where \( R \, \text{(8.314 JK}^{-1}\text{mol}^{-1}) \) is the universal gas constant. \( \Delta H^0 \) (in kJ.mol\(^{-1}\)) and \( \Delta S^0 \) (in J.K\(^{-1}\).mol\(^{-1}\)) were therefore calculated from the slope \((-\Delta H^0 / R)\) and intercept

Fig. 4.17. Effect of temperature on Eu\(^{3+}\) ion transport. Feed: 3.0 M HNO\(_3\); Receiver: 0.01 M HNO\(_3\); Carrier: 0.2 M T2EHDGA
(ΔS° / R) of the plot of ln P vs 1000/T (Fig. 4.18). The ΔH° and ΔS° values were calculated to be 26.5±2.4 kJ.mol⁻¹ and 28.6±7.7 J.K⁻¹.mol⁻¹, respectively.

### 4.3.2.7. Calculation of diffusion parameters

The diffusion coefficient $D_o$ can be calculated as per the empirical Wilke–Chang equation [14] (Eqn. 3.17). The association parameters for the diluents are taken as unity [14]. The molar volume of T2EHDGA was calculated to be 909.42 cm³.mol⁻¹ [15]. Using the dynamic viscosity value for 0.2 M T2EHDGA as 2.001 mPa.s, and assuming that the extracted species contained the diffusion coefficient ($D_o$) was calculated from eqn. (4.12) to be 4.25×10⁻⁶ cm²/s which is higher than the value reported for Am³⁺ in an identical transport system for a feed containing 3 M HNO₃. The higher diffusion coefficient value is attributed to the approximations made in the Wilke – Chang model where the molar volume of the complex was calculated by taking three T2EHDGA molecules and three nitrate ions and the molar volume of Eu³⁺ ion has been ignored.

### 4.4. Hexavalent actinide [U(VI)] transport

#### 4.4.1. Introduction

Uranium along with the trivalent actinides and lanthanides constitute a major part of High Level Waste (HLW). The concentration of U in HLW can be more than 10g/L. Actinide partitioning strategists have proposed two different procedures: one is U removal prior to Actinide partitioning step and in another there is no prior removal of U. U removal is not a part of actinide partitioning using T2EHDGA as it does not suffer
Fig. 4.18. Arrhenius plot of Eu$^{3+}$ transport. Feed : 3.0 M HNO$_3$; Receiver: 0.01 M HNO$_3$; Carrier: 0.2 M T2EHDGA

the problem of third phase problem as encountered for the reagent N,N-isobutyl carbamoyl methyl phosphine oxide (CMPO) when used along with phase modifier(30% iso-decyl alcohol) even in presence of 10-12 g/L of U [16].

So it is very important to understand the transport behavior of U from HNO$_3$ medium using T2EHDGA as carrier prior to testing the reagent for actinide partitioning in Hollow Fiber module using actual HLW. Hence an attempt was made to carry out the transport behavior of U(VI) from HNO$_3$ medium and understand the effect of various parameters that effect the transport it using T2EHDGA as carrier in FSSLM mode. Feed acidity, carrier concentration, membrane pore size, membrane thickness, concentration
of phase modifier, U concentration etc was varied and optimized for maximum permeation of the metal. Mechanism of membrane transport was established and membrane transport data like permeability coefficient, diffusion coefficient etc were calculated and compared with TODGA, a straight chain homologue of T2EHDGA.

4.4.2. Solvent Extraction studies

4.4.2.1. Effect of Phase Modifier Concentration

T2EHDGA was found to form third phase at higher acidities and under loading conditions and a phase modifier was required to mitigate this problem [1]. Out of the various reagents used as phase modifier, iso-decanol was found to be the most suitable due to its lower acid uptake [1]. The composition of the solvent, proposed for actinide partitioning, was 0.2 M T2EHDGA / n-dodecane with 30% iso-decanol [11]. In the present study, the distribution behaviour of U(VI) was investigated at varying concentrations of nitric acid with as well as without the phase modifier (30% iso-decanol). For comparison purpose, the solvent extraction data with 0.1 M TODGA in n-dodecane are also reported (Table 4.7). It is clear from the Table that the extraction efficiency of T2EHDGA decreased in the presence of 30% iso-decanol. This behavior is analogous to those obtained with other diglycolamide extractants, such as TODGA, which also show lower extraction efficiency in the presence of phase modifiers [17]. It is expected that the diglycolamides form reverse micelle aggregates in non-polar mediums such as n-dodecane [10]. By adding a polar phase modifier such as iso-decanol the aggregate formation is seriously affected. Though the polarity increase
helps in increasing the limiting organic concentration (LOC) of the extracted complex (thereby suppressing the third phase formation), the D values show a decreasing trend, probably as a result of the deaggregation of the reverse micelles.

4.4.2.2. Effect of Feed HNO$_3$ Concentration

The solvent extraction data presented in Table 4.7 also show that increasing the nitric acid concentration increases the D value of U. This is expected as solvated species are extracted as will be discussed below. However, the D values of T2EHDGA increased more sharply with nitric acid concentration as compared to TODGA. When NaNO$_3$ was used in the feed in the absence of nitric acid, the D values were significantly enhanced and the enhancement was more prominent at lower NaNO$_3$ concentration. On the other hand, in TODGA system, an entirely opposite trend was observed, i.e., the D values were lower in the presence of NaNO$_3$ as compared to those in the presence of HNO$_3$. These results suggest that the presence of NaNO$_3$ may be responsible for breaking the TODGA aggregates thereby causing the drastic decrease in the $D_U$ values. On the other hand, an entirely opposite trend was observed with T2EHDGA, i.e., the $D_U$ values increased in the presence of NaNO$_3$, the reason for which is yet to be understood.

4.4.2.3. Nature of the Extracted Species
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Extraction of U was also studied with varying concentration of T2EHDGA in \( n \)-dodecane and 30% iso-decanol as the phase modifier. In a previous report, Zhu et al. have suggested extraction of solvated species of the type \( \text{UO}_2(\text{NO}_3)_2 \cdot n\text{L} \) where L represented the diglycolamide extractant [18]. The extracted species conform to the following extraction equilibrium:

\[
\text{UO}_2^{2+} + 2(\text{NO}_3^-) + n\text{L}_{(o)} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot n\text{L}_{(o)} \quad (4.13)
\]

where the species with the subscript ‘(o)’ indicate those in the organic phase and those without any subscript indicate species in the aqueous phase. The T2EHDGA concentration variation experiments indicated a dependence of \( \sim 1 \) when \( \log D \) was plotted against \( \log [\text{T2EHDGA}] \) (Fig. 4.19) suggesting that the extracted species is \( \text{UO}_2(\text{NO}_3)_2 \cdot \text{T2EHDGA}_{(o)} \). Similar species was reported by us for the extraction studies involving TODGA [19]. However, Sharma et al., reported a species of the type \( \text{UO}_2(\text{NO}_3)_2 \cdot \text{T2EHDGA}_{(o)} \) which is in sharp contrast to the species reported by us [20]. On the other hand, a recent structural analysis of a uranyl diglycolamide extract from nitrate medium conform to the presence of a single tridentate diglycolamide unit which is in conformity with our observation [21].
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Table 4.7. $D_U$ with varying feed nitrate concentration in the absence and presence of the phase modifier for T2EHDGA as extractant

<table>
<thead>
<tr>
<th>[HNO$_3$/NaNO$_3$] in the feed</th>
<th>$D_U$(VI) 0.2 M T2EHDGA</th>
<th>$D_U$(VI) 0.2 M T2EHDGA + 30% iso-decanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M NaNO$_3$</td>
<td>12.17</td>
<td>3.17</td>
</tr>
<tr>
<td>2 M NaNO$_3$</td>
<td>13.89</td>
<td>5.49</td>
</tr>
<tr>
<td>3 M NaNO$_3$</td>
<td>16.37</td>
<td>10.18</td>
</tr>
<tr>
<td>4 M NaNO$_3$</td>
<td>22.45</td>
<td>13.85</td>
</tr>
<tr>
<td>6 M NaNO$_3$</td>
<td>33.62</td>
<td>21.14</td>
</tr>
<tr>
<td>1 M HNO$_3$</td>
<td>0.82 (1.01)$^a$</td>
<td>0.19</td>
</tr>
<tr>
<td>2 M HNO$_3$</td>
<td>2.74 (2.08)$^a$</td>
<td>--</td>
</tr>
<tr>
<td>3 M HNO$_3$</td>
<td>7.63 (4.99)$^a$</td>
<td>2.51</td>
</tr>
<tr>
<td>4 M HNO$_3$</td>
<td>12.25 (5.92)$^a$</td>
<td>--</td>
</tr>
<tr>
<td>6 M HNO$_3$</td>
<td>--$^b$ (7.31)$^a$</td>
<td>9.56</td>
</tr>
</tbody>
</table>
Fig. 4.19. Dependence of $D_U$ on the concentration of [$T2EHDGA$]. Aqueous phase: 3 M HNO$_3$

4.4.3. Transport Studies

4.4.3.1. Effect of the Phase Modifier Concentration

The effect of the modifier ($iso$-decanol) concentration on the U extraction is already discussed above. However, the role of the modifier on the diffusion of the extracted complex across the membrane is not clearly known. Therefore, the transport behaviour of U(VI) was investigated for 0.2 M T2EHDGA as the carrier extractant in $n$-dodecane containing 0% to 40% $iso$-decanol as the phase modifier. Feed acidity was maintained at 3 M HNO$_3$ and 0.01 M HNO$_3$ was used as the strippant in the receiver compartment, in all the experiments. As shown in Fig. (4.20), the transport rates decreased with increasing concentration of $iso$-decanol. We found that after 300
minutes ~81% U was transported when 0.2 M T2EHDGA was used as carrier without any iso-decanol. This was found to decrease to ~ 64 % when 40% iso-decanol was used as the phase modifier after same transport time. The permeability coefficients are calculated and are listed in Table (4.8).

The acid transport from the feed to the receiver side was estimated by volumetric method using standard alkali and phenolphthalein indicator. As indicated in Table 4.8, the acid transport was close to 6% in the absence of any phase modifier. On the other hand, in the presence of phase modifier the acid transport increased only marginally and was 7% even in the presence of 40% iso-decanol. This was probably beneficial in the
transport of uranyl ion and in spite of significant decrease in the $D_U$ values (about 4 times in the presence of 40% iso-decanol as compared to in the absence of the phase modifier) the decrease in the $P$ was only by a factor of two. The dynamic viscosity, on the other hand, showed a significant increase with increasing iso-decanol fraction and might be responsible in the decrease in the transport rates. These results indicated that the diffusion of the metal – carrier complex is more important in deciding transport rates as compared to the $D_U$ values. This also suggests that the transport is a diffusion controlled process similar to various SLM systems studied earlier [4,19].

Table 4.8. Transport data as a function of the phase modifier fraction in the carrier extractant. Support: 0.45 micron PTFE; Extractant: 0.2 M T2EHDGA; Feed: 3 M HNO₃; Receiver: 0.01 M HNO₃

<table>
<thead>
<tr>
<th>Modifier concentration</th>
<th>$P \times 10^4$ (cm/s)</th>
<th>% T (5 h)</th>
<th>% Acid transport (5 h)</th>
<th>Dynamic viscosity (mPa.s)</th>
<th>$D_U$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>(3.80±0.32)</td>
<td>81.7</td>
<td>5.67</td>
<td>2.0010</td>
<td>7.63</td>
</tr>
<tr>
<td>10%</td>
<td>(3.41±0.25)</td>
<td>78.1</td>
<td>6.33</td>
<td>2.3329</td>
<td>3.79</td>
</tr>
<tr>
<td>20%</td>
<td>(3.23±0.06)</td>
<td>71.5</td>
<td>6.67</td>
<td>2.9141</td>
<td>3.54</td>
</tr>
<tr>
<td>30%</td>
<td>(3.20±0.13)</td>
<td>70.7</td>
<td>6.33</td>
<td>3.8501</td>
<td>2.51</td>
</tr>
<tr>
<td>40%</td>
<td>(2.04±0.09)</td>
<td>63.5</td>
<td>7.00</td>
<td>4.8625</td>
<td>1.90</td>
</tr>
</tbody>
</table>
4.4.3.2. Effect of the Feed Acidity

Acidity of the feed solution plays an important role in the carrier facilitated metal ion transport by several factors. Firstly, the acid provides the counter anion in the solvated extraction mechanism, such as the present case. In such case, the transport rate should increase with increasing feed acidity. Secondly, if the acid interacts with the carrier extractant, then with increasing feed acid concentration, a decrease in the free ligand concentration is resulted leading to a decrease in U transport rate. Finally, if there is a co-transport of acid, then the receiver phase acidity can increase resulting in inefficient stripping. The transport profiles of U as a function of the feed nitric acid concentration are presented in Fig. 4.21. As indicated in the figure, the transport of U(VI) increased from 0.5 M HNO$_3$ to 3 M HNO$_3$ for 0.2 M T2EHDGA as the carrier. As per Eqn.(4.15), the transport of U(VI) takes place via nitrate assisted complexation of U(VI) with T2EHDGA. In other words, higher the feed acidity, higher will be the complexation and hence the transport rate. However, the possibility of the formation of T2EHDGA·HNO$_3$ complex can result in lower free T2EHDGA concentration which can lead to lower transport rates. T2EHDGA is expected to form adducts such as T2EHDGA·HNO$_3$ and the equilibrium constant ($K_H$) is given as:

\[
K_H = \frac{[T2EHDGA\cdot HNO_3]}{[H^+] [NO_3^-] [T2EHDGA_{(o)}]} \quad \text{(4.14)}
\]
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The value of $K_H$ is reported as $1.8 \pm 0.3$ as compared $4.1 \pm 0.4$ for TODGA [22]. Therefore, though there is a decrease in the availability of free T2EHDGA for complex formation with U(VI), it is to a much lower extent as compared to TODGA, as reported earlier. This effect causes the transport rate to decrease after certain acidity similar to the transport studies involving TODGA. This is clear from Fig. 4.21 that when the feed acidity increases from 3 M to 6 M HNO$_3$, the transport rate is found to decrease. On the other hand, increasing the feed acidity to 8 M HNO$_3$, the transport rate is found to increase further. This unusual behaviour is probably due to a change in the extraction mechanism at higher acidities. It is clear from the above discussion that there is a possibility of higher transport of acid for higher feed acidity which may lead to an increase in the acidity of the receiving phase. It was observed that the acidity of the strip phase increased from 0.2 M for 1 M HNO$_3$ feed to 0.4 M for 6 M HNO$_3$ feed acidity after 5 h. As a consequence of increasing acidity in the receiving side stripping efficiency decreased and this led to lower transport rate at higher acidity. For trivalent and tetravalent ions we found that when the acidity of the feed phase increased from 3 M HNO$_3$ to 6 M HNO$_3$ transport rate decreased quite significantly for both T2EHDGA and TODGA. However, for the hexavalent ions, there is a consistency in the transport rate when feed acidity increased from 3 M HNO$_3$ to 6 M HNO$_3$ (Table 4.9). This is due to the fact that only two nitrate ions are required to form an extractable complex for
hexavalent ions whereas for trivalent and tetravalent ions this number is three and four respectively. The transport of U with varying nitric acid concentration in the feed can be summarized as follows: 1) with increasing nitric acid concentration U extraction is expected to increase due to the availability of nitrate ion for complexation and formation of the extracted species (eqn. (4.15)); 2) with increasing nitric acid concentration (beyond 3 M) the T2EHDGA-HNO$_3$ adduct formation becomes predominant and this leads to a decrease in extraction and hence transport rates; 3) with increasing nitric acid concentration the extraction mechanism may change (beyond 6 M HNO$_3$) and this can result in higher extraction of U and hence higher transport rates. The net result of this three processes is an initial increase in transport up to 3 M HNO$_3$, slight decrease up to 6 M HNO$_3$ and further increase at 8 M HNO$_3$.

In order to discount the effect of nitric acid on the decrease in transport rates at higher acidities while trying to understand the effect of nitrate ion, transport experiments were carried out from feed solutions having varying nitrate ion concentration at a fixed H$^+$ ion concentration (0.1 M). The results, as shown in Fig. 4.22, clearly proved the effect of acid transport on the transport rate of U(VI). There was continuous increase in transport rate with increasing nitrate ion concentration from 1 M to 6 M. This is reflected in the permeability data (Table 4.9). Here neither was any adduct formation for T2EHDGA nor any transport of acid causing acidity of the receiver phase to increase. As a result, the transport rates increased with the nitrate ion
concentration in the feed. However, though the transport rates were steep in the initial phase (up to 2 h) for 6 M NaNO$_3$ as the feed, a plateau was observed afterwards. On the other hand, a continuous increase in the transport rate was observed with 6 M HNO$_3$ and marginally higher transport (79%) as compared to 6 M NaNO$_3$ (74%) was observed after 5 h.

Fig. 4.21. Transport of U (VI) using varying concentration nitric acid in the feed. Carrier: 0.2 M T2EHDGA in $n$-dodecane containing 30% iso-decanol; Receiver: 0.01 M HNO$_3$

4.4.3.3. Nature of the Feed Acid
Table 4.9: Transport parameters as a function of the nitrate ion concentration in the feed. Support: 0.45 micron PTFE; Extractant: 0.2 M T2EHDGA; Receiver: 0.01 M HNO₃

<table>
<thead>
<tr>
<th>[HNO₃], M</th>
<th>P x10⁴ (cm/s)</th>
<th>[NaNO₃], M</th>
<th>P x10⁴ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.11±0.01</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.0</td>
<td>0.36±0.02</td>
<td>1.0</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>2.0</td>
<td>1.94±0.08</td>
<td>2.0</td>
<td>0.80±0.11</td>
</tr>
<tr>
<td>3.0</td>
<td>3.37±0.29</td>
<td>3.0</td>
<td>0.93±0.06</td>
</tr>
<tr>
<td>6.0</td>
<td>3.86±0.23</td>
<td>6.0</td>
<td>2.70±0.30</td>
</tr>
<tr>
<td>8.0</td>
<td>4.16±0.33</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

It was also required to investigate the effect of various mineral acid types such as HCl and HClO₄ on the U transport rates. Fig. 4.23 gives the transport profiles under these feed conditions at 3.0 M acidity. The transport rates followed the trend: HNO₃ >> HCl ~ HClO₄. This was in sharp contrast to the extraction of Am³⁺ reported with these acids which was explained on the basis of the reverse micelle formation ability of these acids as indicated by the metal ion extraction ability which followed the trend HClO₄ > HNO₃ > HCl. Increasing the acid concentration from 3.0 M to 6.0 M indicated spectacular increase in the transport rate with HCl while there was no significant change in case of HNO₃. This is, of course, in line with the extraction behaviour of the metal ions observed with HCl and HNO₃ [2]. The permeability coefficient values are listed in
Fig. 4.22. Transport of U (VI) using varying concentration sodium nitrate in the feed. Carrier: 0.2 M T2EHDGA in n-dodecane containing 30% iso-decanol; Receiver: 0.01 M HNO₃

Table 4.10. In order to discount the effect of co-transport of hydrogen ion which adversely affected the transport of U, several experiments were carried out using the respective sodium salts in the feed. The results are presented in Fig. 4.23 while the permeability coefficients are listed in Table 4.10. The permeability data indicated that while the permeability coefficient for uranyl ion decreased significantly when the feed condition was changed from 3 M HNO₃ to 3 M NaNO₃ an entirely opposite effect was observed with 3 M HCl and 3 M NaCl. On the other hand, the transport rate became negligible when 3 M NaClO₄ was used as the feed. This behaviour is rather intriguing
and need a more detailed investigation. The significant increase in the P value, while changing the feed from 3 M NaNO₃ to 6 M NaNO₃, was ascribed to the increased tendency to form the extractable species with increased nitrate ion. On the other hand, a sharp decline in the transport rate and P value was seen when the feed concentration of NaCl was increased from 3 M to 6 M which may be attributed to the formation of non-extractable anionic species such as UO₂Cl₃⁻ and UO₂Cl₄²⁻.

Fig. 4.23. Transport profile of U(VI) using different mineral acid types in the feed. Receiver: pH 2.0 solution; Carrier: 0.2 M T2EHDEGA in n-dodecane. Pore size: 0.45 micron
Fig. 4.24. Transport profile of U(VI) using different sodium salts of different mineral acids as the feed. Receiver: pH 2.0 solution; Carrier: 0.2 M T2EHDGA in n-dodecane. Pore size: 0.45 micron

Table 4.10: Permeability data of UO$_2^{2+}$ under varying feed conditions using 0.2 M T2EHDGA in n-dodecane + 30% iso-decanol as the carrier solvent

<table>
<thead>
<tr>
<th>Feed</th>
<th>P x10$^4$(cm/s)</th>
<th>Feed</th>
<th>P x10$^4$(cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 M HNO$_3$</td>
<td>3.37±0.29</td>
<td>3.0 M NaNO$_3$</td>
<td>0.67±0.03</td>
</tr>
<tr>
<td>3.0 M HCl</td>
<td>0.86±0.12</td>
<td>3.0 M NaCl</td>
<td>1.12±0.03</td>
</tr>
<tr>
<td>3.0 M HClO$_4$</td>
<td>0.73±0.04</td>
<td>3.0 M NaClO$_4$</td>
<td>(4.22±0.23)x10$^{-2}$</td>
</tr>
<tr>
<td>6.0 M HNO$_3$</td>
<td>3.86±0.23$^a$</td>
<td>6.0 M NaNO$_3$</td>
<td>2.70±0.30$^a$</td>
</tr>
<tr>
<td>6.0 M HCl</td>
<td>2.27±0.11</td>
<td>6.0 M NaCl</td>
<td>0.28±0.02</td>
</tr>
</tbody>
</table>

Note: $^a$: Data taken from Ref [12]
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4.4.3.4. Comparison with PuO$_2^{2+}$ ion transport

As mentioned earlier HLW usually contains small amount of Pu due to the losses from the PUREX cycle. In view of the large number of metal ions present in the HLW and the oxidizing conditions prevailing, it was of interest to compare the transport behaviour of Pu in the +6 oxidation state. The transport profile of PuO$_2^{2+}$ is presented in Fig. 4.25 along with that for UO$_2^{2+}$ for comparison purpose. The transport rate for the PuO$_2^{2+}$ ion was significantly lower as compared to that for UO$_2^{2+}$ ion. This may be due to either the higher complex formation and hence extraction constants for the uranyl ion compared to the plutonyl ion [23] or due to formation of extracted species with different stoichiometry than that for the uranyl ion. Similar observation was made in the TODGA system reported earlier [19]. TODGA is found to be a far superior extractant as compared to T2EHDGA as the P values for both UO$_2^{2+}$ and PuO$_2^{2+}$ are significantly higher even with 0.1 M TODGA as compared that of 0.2 M T2EHDGA as the carrier extractant.

4.4.3.5. Effect of membrane pore size

Membrane pore size plays an important role in the transport of metal ions across an SLM. This has been shown by various workers for various metal ions and various extractants [24,25]. In diffusion controlled transport, as in the present case, the permeability coefficient of a diffusing species across a polymeric matrix is given by Eqn. (3.12). This equation clearly indicates that with increasing pore size, the resistance...
Fig. 4.25. Transport profile of U(VI) and Pu(VI) with 0.45 micron PTFE flat sheet membranes. Feed: 3 M HNO₃; Receiver: pH 2.0 solution; Carrier: 0.2 M T2EHDGA in n-dodecane

resistance felt by the diffusing complex decreases and as a result, the transport rate increases. But at the same time, from the Laplace’s eqn., (3.13) it is quite clear that the trans-membrane pressure (p) required to displace the carrier from the membrane pore is inversely proportional to the pore size (rₚ) of the membrane. So when the pore size increases, the trans-membrane pressure also decreases and hence the stability of the membrane due to release of the organic carrier molecule from the pores also decreases. Both these factors play an opposing role on the transport of any metal ion across an SLM of varying pore size. Keeping these factors in consideration, the transport studies of U were carried out from 3 M HNO₃ feed using PTFE membranes of varying pore
sizes, viz. 0.2 μm, 0.45 μm, 1.20 μm and 5.0 μm. As reported earlier, for different metal ions the variation in transport rate is affected differently with membrane pore size variation [24-26]. It is clear from Fig. (4.26) that for U(VI)-T2EHDGA system, transport rate increases up to 0.45μm and decreased thereafter similar to the Am(III)-T2EHDGA system reported earlier. This signifies that up to 0.45 μm the increase in transport due to less hindrance of U(VI)-T2EHDGA complex and thereafter the loss of carrier molecule due to lower trans-membrane pressure becomes dominant causing in decrease in transport rate. Due to this reason, 0.45 μm PTFE have been used as membrane filters throughout the present study.

4.4.3.6. Thermodynamics Study

As mentioned above, the transport process is a combination of extraction, diffusion and stripping steps. As diffusion is the rate determining step, the transport rates are decided by the diffusion coefficients or the permeability coefficients. It was decided to carry out transport studies as a function of temperature and the thermodynamic parameters were determined from the Van’t Hoff equation and Gibb’s Helmholtz equation given by Eqns. 4.9, 4.10 and 4.11. The plot of log P vs 1000/T is illustrated in Fig. 4.27 and from the slope and intercept the $\Delta H^o$ and $\Delta S^o$ values were calculated as 10.24±0.79 kJ/mol and $-31.82±2.55$ J/oK/mol, respectively. Endothermicity of the transport process suggests that with increasing temperature the diffusion is facilitated by the decreasing viscosity of the membrane phase which favours the mobility of the complex and
T2EHDGA molecules alike. At the same time, the complexed molecules indicate a decrease in their entropy values resulting in a reasonably high negative entropy term.

4.4.3.7. Effect of U concentration

Concentration of U in the feed plays an important role in the transport rate of U(VI) ion. It is clear from eqn. (4.13) that the complexation and the transport rate increases with increasing U concentration in the feed. However, due to limitation in the carrier concentration in the membrane phase, the U transport rate may actually decrease. Transport studies were carried out using U concentration from 0.1g/L to 20g/L and the results are shown in Fig. 4.28. As expected, the transport rates decreased with increasing U concentration. The permeability coefficients also decreased with increasing U concentration (Table 4.12). On the other hand, analysis of the flux vs U concentration data indicates an initial increase was observed with a plateau approaching at higher U concentrations (Table 4.12). When the U concentration was
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Fig. 4.26. Transport of U(VI) using 0.2 M T2EHDGA / n-dodecane from 3 M HNO₃ with varying membrane pore sizes

Fig. 4.27. Temperature dependence of permeability coefficient of U(VI) transport from 3 M HNO₃ using 0.2 M T2EHDGA as the carrier extractant
0.1 g/L flux value was \( 2.09 \times 10^{-7} \) mol cm\(^2\) s\(^{-1}\) which increased to \( 80.3 \times 10^{-7} \) mol cm\(^2\) s\(^{-1}\) for 20 g/L of U concentration.

### 4.4.3.8. Mathematical Modeling

The membrane transport was modeled using a computer software discussed in Chapter I. The membrane phase diffusivity (\( \Delta o \)) and aqueous phase diffusivity (\( \Delta a \)) were calculated by a plot of \( 1/P \) vs \( 1/Kd \) (Fig. 4.29) where the slope and the intercept values were found to be 8950 and 1105, respectively. Hence, the organic and aqueous phase mass transfer co-efficient were found out to be \( 9.04 \times 10^{-4} \) and \( 1.12 \times 10^{-4} \) cm/s, respectively. These values were used to predict the transport data. Based on the mathematical model and the known transport parameters, simulation of

![Fig. 4.28. Transport of U(VI) using 0.2 M T2EHDA against different concentration of U from 3 M HNO\(_3\). Feed: 3 M HNO\(_3\); Receiver: pH 2.0 solution; Carrier: 0.2 M T2EHDA in \( n \)-dodecane](image)
Table 4.11: Permeability coefficients and flux values as a function of the U concentration in the feed

<table>
<thead>
<tr>
<th>U Concentration (g/L)</th>
<th>P x10^4(cm/s)</th>
<th>Flux x10^9(mol.cm^-2.s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.27±0.19</td>
<td>0.14±0.01</td>
</tr>
<tr>
<td>0.5</td>
<td>2.21±0.17</td>
<td>0.47±0.03</td>
</tr>
<tr>
<td>1</td>
<td>1.88±0.08</td>
<td>0.79±0.02</td>
</tr>
<tr>
<td>5</td>
<td>1.61±0.12</td>
<td>3.38±0.21</td>
</tr>
<tr>
<td>10</td>
<td>1.45±0.06</td>
<td>6.01±0.23</td>
</tr>
<tr>
<td>20</td>
<td>0.69±0.05</td>
<td>5.81±0.03</td>
</tr>
</tbody>
</table>

the transport process was carried out for the three different feed acidity viz.; 2 M HNO₃, 3 M HNO₃ and 6 M HNO₃ for 0.2 M T2EHDGA as carrier and is presented in Fig 4.30. In another fitting, simulation of the transport process was carried out for four different T2EHDGA concentration viz.; 0.05 M, 0.1 M, 0.15 M and 0.2 M at 3 M HNO₃ and is presented in Fig 4.31. The lines indicated the transport profile as predicted by the mathematical model (computed data) while symbols represented the experimental data in each figure. The predicted data found to be fitted with the 8% error limit to that obtained U(VI) transport rate. The data fitting was excellent up to 0.2 M T2EHDGA as the carrier concentration. The membrane parameters such as diffusivity and flux were optimized at this carrier concentration. However, at higher T2EHDGA concentration (0.3 M), the predicted transport profile was found to be in
variance to the experimentally obtained transport profile. At higher T2EHDGA concentrations, the viscosity and aggregation of the carrier molecule causes the experimental data to differ greatly from that of predicted value as the factors mentioned above are not considered in the program.

Fig. 4.29: Plot of 1/P vs 1/Kd for U(VI). Carrier: 0.2 M T2EHDGA in n-dodecane (30% iso-decanol as phase modifier). Feed: 3 M HNO₃; Receiver: 0.01 M HNO₃
Fig. 4.30: Prediction of U(VI) transport rate (indicated by the lines in the fig.) for the varying feed acidity in SLM using 0.2 M T2EHDA as carrier and actual (indicated by the symbols in the fig.) transport rate observed, □ 2M HNO₃, ♦ 3M HNO₃, ▲ 6M HNO₃
Fig. 4.31: Prediction of U(VI) transport rate (indicated by the lines in the fig.) in SLM at 3M HNO₃ using different concentration of T2EHDGA as carrier and actual (indicated by the symbols in the fig.) transport rate observed, ■ 0.05 M T2EHDGA, ♦ 0.1 M T2EHDGA, ▲ 0.15 M T2EHDGA, ◆ 0.2 M T2EHDGA
4.5. Conclusions

In conclusion T2EHDGA based support liquid membrane was found to be effective for transport of actinides and lanthanides from nitric acid medium. Various factors like feed acidity, membrane pore size, carrier concentration, phase modifier concentration were found to affect the transport rate significantly and were studied in detail.
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4.4.5. REFERENCES


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