Chapter V

Evaluation of Malonamides and Ionic Liquid Based Solvent System
Evaluation of Malonamides and Ionic Liquid Based Solvent System

5.1. Introduction

There is a continuing interest for organic/separation chemists to develop environmentally benign solvents/separation processes for the recovery of metal ions from industrial or laboratory waste solutions [1-5]. Malonamide based extraction process (DIAMEX) was proposed for actinide partitioning by French researcher which was mainly based on the use of two malonamides namely, DMDBTDMA and DMDOHEMA (Figure 1.4). Unlike other proposed extractants for actinide partitioning, these diamides do not display any third-phase formation problem under HLW conditions and the addition of phase modifier is avoided [7-12]. However, high ligand inventory is required to perform the actinide partitioning studies in the DIAMEX processes due to the lower extraction coefficients [6]. Therefore, there is a need to look for certain modifications in the solvent system which can enhance the extraction capability of these extractants.

Room temperature ionic liquids (RTILs) are receiving increasing attention for their possible applications as diluents in industrial liquid-liquid extraction processes [13]. It is well recognized that RTILs often display unique extraction behavior of metal ions [14-16]. The RTILs possess many attractive properties such as insignificant vapour pressure, ability to dissolve a wide range of organic and inorganic compounds, wide electrochemical window and tuneability of properties by suitable combination of cation and anion, etc [17,18]. These aspects make the subject of RTILs fascinating and challenging and provide impetus for detailed investigations as alternatives to molecular diluents. RTILs are also being proposed as alternatives to high temperature molten salts in non-aqueous reprocessing applications [19-22]. These striking features of RTILs make them promising for their applications in nuclear fuel cycle to selectively separate target metal ions by suitable manipulation of cation-anion combinations with interesting extraction mechanisms [23-28]. In this context, Dai et. al. reported unprecedented high extraction of metal ions such as Sr(II) by crown ethers in RTILs medium [24]. Dietz et. al. investigated the mechanistic aspects of metal ion extraction in ionic liquid media [25]. Billard et. al. reported a model for the extraction of U(VI) by tri-n-butyl phosphate (TBP) in the ionic liquid 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl) imide (C₄mimTf₂N) medium [27]. In this model, uranyl ion extraction was proposed to proceed via cation exchange at low initial acidities ([UO₂₂⁺(TBP)₅ⁿ]⁺ versus C₄mim⁺ and H⁺) and via anion exchange at high HNO₃ concentrations ([(UO₂(NO₃)₃(TBP)₃m]⁺ versus Tf₂N⁻). By contrast, solvation mechanism is favored during
uranium extraction from nitric acid medium using TBP/n-dodecane as the organic phase. Similarly, dual mechanism was observed during uranium extraction using either dimethyl dibutyl malonamide (DMDBMA) dissolved in \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) (1-methyl,3-butylimidazolium:Tf\(_2\)N) or as a functionalized malonamide on ionic liquid (FIL-MA). At low acidities, the cation exchange mechanism was predominant for UO\(_2^{2+}\) versus 2 H\(^+\) for DMDBMA dissolved in ionic liquid or versus \([\text{C}_4\text{mim}]^+\) and H\(^+\) for FIL-MA. On the other hand, extraction took place through anion exchange of \([\text{UO}_2(\text{NO}_3)_3]^−\) versus Tf\(_2\)N\(^−\) for both ligands at high HNO\(_3\) concentrations. It was also concluded that FIL-MA molecule was more efficient for metal extraction as compared to that of malonamide dissolved in ionic liquids [28]. Recently, Rout et al. have reported the extraction behavior of U(VI), Pu(IV) and Am(III) from nitric acid medium employing DMDOHEMA dissolved in \([\text{C}_4\text{mim}][\text{NTf}_2]\) as the solvent. The separation factors of U(VI) and Pu(IV) were compared with Am(III) and other fission products. The stoichiometry of the metal-solvate was determined to be 1:2 for U(VI) and Pu(IV) and 1:3 for Am(III) [29]. To best of our knowledge, no attempt has been made to compare the extraction behavior of metal ions using DMDBTDMA and DMDOHEMA extractants dissolved in ionic liquids.

Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is one of the reliable techniques to gain an insight about the coordination environment of the metal ions such as Eu(III) and Cm(III) [30,31]. Though the chemistry of trivalent lanthanides and actinides appear similar in aqueous systems, it can be quite different in ionic liquids. This difference in chemical behaviour may provide the opportunity for a separation of lanthanides and actinides with regard to the reprocessing of nuclear fuel [31]. In addition, the radiolytic degradation aspect of malonamides in RTILs (in view of prolonged use of the extractant in processes with recycling options) is of interest for their proposed use in actinide partitioning studies.

This chapter describes the development of malonamides and ionic liquid based extraction system for the actinide partitioning work. It provides insights about extraction mechanism, complexation behavior and stability of malonamides in ionic liquids as the diluents. This chapter is divided in three parts: Part A deals with solvent extraction studies of several actinide ions viz. Am(III), U(VI), Pu(III), Pu(IV), Pu(VI), Np(IV), and Np(VI) from nitric acid medium using DMDBTDMA and DMDOHEMA extractants dissolved in different RTILs. The effects of several experimental parameters such as (a) nature of the RTIL, (b) time of equilibration, (c) aqueous phase acidity, (d) extractant concentration, (e) metal ion oxidation states, etc on the extraction behavior of metal ions have been investigated. In Part B, TRLFS study has been performed to investigate the interaction of both the malonamides
with Eu(III) in RTIL medium. **Part C** describes the gamma radiolytic degradation studies of diamides/RTIL and the identification of degradation products by different techniques has been discussed briefly.
Part A: Actinide Extraction

This part describes extraction studies of actinide metal ions such as Am(III), U(VI), Np(IV), Np(VI), Pu(IV) carried out from nitric acid medium using the two diamides (L) viz. DMDBTDMA and DMDOHEMA dissolved in different room temperature ionic liquids (RTILs). The use of RTILs as the diluent significantly enhances metal ion extraction as compared to that observed in non-polar diluent such as n-dodecane. The effects of parameters such as kinetics, aqueous phase acidity (0.01-3M HNO₃), metal ion oxidation states, diamide concentration on extraction of metal ions were studied. The stoichiometry of the extracted Am (III) species using these diamides varied with ligand. Detailed mechanistic aspects for Np(IV), U(VI), and Pu(IV) were studied. For Pu(IV) extraction, analogues cation exchange mechanism has been proposed.

5.2. Actinide Extraction in Ionic Liquid Medium

5.2.1. Evaluation of different ionic liquids for Am(III) extraction

Different RTILs of general formula \([\text{C}_n\text{mim}][\text{Tf}_2\text{N}]\) viz. 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}], \ 1-\text{Hexyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide \([\text{C}_6\text{mim}][\text{Tf}_2\text{N}], \ 1-\text{Octyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide \([\text{C}_8\text{mim}][\text{Tf}_2\text{N}],\) (Figure 5.1) were evaluated as the diluents for Am(III) extraction from 0.01M HNO₃ while keeping malonamide concentration at 0.01M.

![Figure 5.1](general structural formula of the ionic liquids used in this study)

Figure 5.1: General structural formula of the ionic liquids used in this study

Ionic liquids: \([\text{C}_n\text{mim}][\text{NTf}_2] : 1-\text{Alkyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide, where, } n=4, 6, 8\)

Figure 5.2 showed a decrease in Am(III) extraction with increasing alkyl chain length of the ionic liquid moiety from \(n\)-butyl to \(n\)-octyl group. This has been attributed to the decreased hydrophilicity of imidazolium cation with increased alkyl chain length of the ionic liquid analogues [36]. Similar observations have been reported elsewhere during the extraction of Sr(II), Eu(III), Am(III) and U(VI) from HNO₃ media using crown ethers, CMPO, tripodal
diglycolamide (T-DGA), TBP and TODGA as ligands, respectively [25-27]. It was worth to note that significant lower concentration of diamides (0.01M) offers high extraction of Am(III) compared to 0.5-1M diamide concentration generally used in molecular diluents [32]. Therefore, by fine tuning the cationic substituents of RTIL, it is possible to perform actinide partitioning experiments using much lower concentration of the malonamides. Due to better extraction properties by [C₄mim][NTf₂], it was used for all the subsequent experiments.

![Figure 5.2:](image)

**Figure 5.2:** Effect of different ionic liquids on Am(III) extraction from 0.01 M HNO₃ solution; Time of equilibration: 3 h; T: 298 K

### 5.2.2. Extraction kinetics in RTIL

Hydrodynamic processes (extraction kinetics) are significantly influenced by the viscosity and density of the extracting medium [26]. Thus, to evaluate Am(III) extraction kinetics using malonamides in the ionic liquid ([C₄mim][NTf₂]) media and the studies showed that 30 minutes were sufficient for achieving equilibrium Am(III) extraction from 0.01M HNO₃ (Figure 5.3) suggesting that the kinetics of extraction was relatively fast in the RTIL medium.
Ionic Liquid based Extraction System

Figure 5.3: Effect of time of equilibration on Am(III) extraction
Aq. Phase: 0.01 M HNO₃ solution; Ionic liquid:[C₄mim][NTf₂]

5.2.3. Different factors influencing Am (III) extraction

5.2.3.1. Effect of aqueous phase acidity

Figure 5.4 showed a decrease in $D_{\text{Am}}$ values with increased nitric acid concentration. This observation can be explained as,

(1) At higher acidities, H⁺ ion competes with the metal cations as per the ion exchange mechanism in [C₄mim] [Tf₂N] RTIL as shown in equation (5.1) [25].

(2) At higher acidities, it is noted by the Dietz et. al. that NO₃⁻ replaces the NTf₂⁻ of ionic liquids after continuous contacts with higher nitric acid concentration resulting in gradual decrease in organic phase [25].

(3) At higher acidities, Patil et. al. reported that DMDOHEMA forms adducts with HNO₃. Therefore free ligand concentration available for extraction is decreases [32].

\[
\text{Am}^{3+}_{(aq)} + xL_{(IL)} + 3[C_{n}\text{mim}]^{+}_{(IL)} \rightarrow [\text{Am}L_x]^{3+}_{(IL)} + 3[C_{n}\text{mim}]^{+}_{(aq)} \quad (5.1)
\]

where, L = DMDOHEMA/ DMDBTDMA, and subscripts ‘aq’ and ‘IL’ refer to aqueous and ionic liquid phases, respectively.
In contrast, $D_{Am}$ increased with nitric acid concentration in nonpolar medium and suggested solvation mechanism during the extraction process. Rout et al. also showed similar trend for Am(III) extraction which was attributed to the interaction of DMDOHEMA with nitric acid concentration [29].

5.2.3.2. Nature of Am(III) extracted species

Both DMDBTDMA and DMDOHEMA were reported to form disolvated extracted species in nonpolar $n$-dodecane medium [32]. It was of interest to evaluate the number of diamides ligands involved in extracted species in RTIL $[C_{4}mim][TF_{2}N]$ medium. The malonamide concentration was varied from 0.005-0.1 M in $[C_{4}mim][TF_{2}N]$. Under the experimental conditions, it was noticed that two different extracted species were present for both the malonamides. The log-log plot of $D_{Am}$ against diamides concentration (from 0.005-0.02 M) showed slopes of 3.00±0.10, and 3.05±0.17 for DMDBTDMA and DMDOHEMA, respectively. However, at higher ligand concentration 0.05-0.1 M, the slope values were 1.75±0.29, 2.52±0.03 for DMDBTDMA and DMDOHEMA respectively (Figure 5.5).
This observation indicated the presence of mixed trisolvated and disolvated extracted species at lower and higher diamides concentrations, respectively. From Figure 5.5, it is seen that the slope value decreases when ligand concentration increases. This behavior is attributed to aggregation behavior of diamide ligands at higher concentrations. This tendency is influenced by the nature of ligand, diluent as well as nitric acid concentration [43,44]. The formation of mixed species has also been reported for other proposed solvents for actinide partitioning such as CMPO and TODGA [22]. However, Rout et al., have reported the formation of trisolvated species in the ligand concentration range 0.05 – 0.5M [29]. On the other hand, the authors tend to conclude the formation of mixed species (disolvated/trisolvated) in view of slope = 2.52±0.03.

Table 5.1 compares the conditional extraction constants of Am(III) (K_{Am(III)}) for these malonamides in different diluents and at different nitric acid concentrations. K_{Am(III)} can be defined as, $K_{Am(III)} = D_{Am}/[L]^n$ (in ionic liquid medium) and $K_{Am(III)} = D_{Am}/[1+β_n[NO_3^-]]/a^{3NO_3^-}\cdot[L]^n$ (in n-dodecane medium)

Where, L = diamide extractant,
n = number of ligands in extracted species, and
$a^{3NO_3^-} = activity of nitrate anion.$
**Table 5.1:** Comparison of malonamide extractant (L) and diluent compositions for Am(III) extraction; T: 298 K

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Diluent</th>
<th>Extracted species</th>
<th>Log $K_{\text{Am(III)}}$</th>
<th>[HNO₃]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMDBTDMA</td>
<td>n-dodecane</td>
<td>Am(NO₃)₃•3L</td>
<td>1.31 ± 0.06</td>
<td>3 M</td>
<td>[11]</td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>n-dodecane</td>
<td>Am(NO₃)₃•2L</td>
<td>1.98 ± 0.12</td>
<td>3 M</td>
<td>[32]</td>
</tr>
<tr>
<td>DMDBTDMA</td>
<td>[C₄mim][NTf₂]</td>
<td>Am•3L⁺⁺</td>
<td>6.98 ± 0.04</td>
<td>0.01 M</td>
<td>Present work [32]</td>
</tr>
<tr>
<td>DMDBTDMA</td>
<td>[C₄mim][NTf₂]</td>
<td>Am•2L⁺⁺</td>
<td>5.00 ± 0.06</td>
<td>0.01 M</td>
<td>Present work [32]</td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>[C₄mim][NTf₂]</td>
<td>Am•3L⁺⁺</td>
<td>2.38 ± 0.11</td>
<td>1 M</td>
<td>[29]</td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>[C₄mim][NTf₂]</td>
<td>Am•3L⁺⁺</td>
<td>6.4 ± 0.06</td>
<td>0.01 M</td>
<td>Present work [32]</td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>[C₄mim][NTf₂]</td>
<td>Am•2.5L⁺⁺</td>
<td>5.44 ± 0.01</td>
<td>0.01 M</td>
<td>Present work [32]</td>
</tr>
</tbody>
</table>

It is evident that the use of RTIL as the extraction media enhances the extraction of Am(III) multifold which is reflected in high $K_{\text{Am(III)}}$ values. However, the $K_{\text{Am(III)}}$ values from the present work and that reported in literature [29] are significantly different. This may be probably due to the nitric acid concentration used in these studies. These studies suggest that it may be possible to reduce the ligand inventory for desired Am(III) extraction in ionic liquid medium.

5.2.4. Extraction of other actinide ions

5.2.4.1. U (VI) extraction

The dissolution of uranium salts and their extraction mechanism in different RTIL media has been reported recently [27,28]. However, its extraction properties with the malonamides in ionic liquids need to be studied further. Both DMDBTDMA and DMDOHEMA (0.02 M) has been studied as a function of nitric acid concentration (Figure 5.6). At lower acidities (0.001-0.1 M HNO₃), there was the enhancement in $D_{U}$. However, there was a gradual decrease in U(VI) extraction beyond 0.1 M HNO₃. This decrease in $D_{U}$ was similar to those observed for other metal ions at higher acidities [18]. The larger $D_{U}$ values for DMDOHEMA than DMDBTDMA are contradictory to those observed in nonpolar n-dodecane medium [1,32]. The increase in U(VI) extraction with increasing acidity can be attributed partly to solvation mechanism and partly to the salting out effects.
Figure 5.6: U(VI) extraction as a function of nitric acid concentration
Ionic liquid: [C₄mim][Tf₂N]; Time of equilibration: 2 h; T: 298 K

Bonnaffee-Moity et al. [28] have reported an entirely opposite trend, where a decrease in the metal ion was seen at lower acidities followed by an increasing trend beyond 2M HNO₃. The extraction mechanism of U(VI) by malonamide ligands was investigated using UV-visible spectrophotometry from both RTIL as well as n-dodecane as diluents.

Figure 5.7: UV visible spectra of UO₂ extracted by malonamides
Aqueous phase: 8.4 mM U(VI) in 0.01M HNO₃ (for RTIL) and 1M HNO₃ (for n-dodecane)
The experimental data suggests that uranyl cation solvated by diamide is extracted in the ionic liquid medium via the exchange of its cationic moiety (Figure 5.7). This was independently proved by performing uranium extraction studies from nitric acid to ionic liquid medium, while in nonpolar medium, the trend observed was complexation which is dissimilar to RTIL. The detailed mechanistic aspects with the different malonamide analogues were discussed in some recent literatures indicating the cation exchange of $\text{UO}_2^{2+}$ with $2\text{H}^+$ or $[\text{C}_4\text{mim}]^+$ from HNO$_3$ media [28,29].

5.2.4.2. Plutonium extraction

Both DMDBTDMA and DMDOHEMA have shown favorable Pu(IV) extraction from dilute HNO$_3$ medium. With both the malonamides dissolved in RTIL ($[\text{C}_4\text{mim}]\text{[Tf}_2\text{N}]$), the extraction of Pu(VI) showed decreasing extraction with increasing acidities (Figures 5.8 and 5.9). It was interesting to observe the opposite trend to that of the extraction of the other actinides such as Am and U. Rout et al. have reported extraction of Pu(IV) from higher concentration of HNO$_3$ (>4M) which involved anion exchange mechanism without participation of the malonamide in the extracted species [29].

By contrast, we noticed no extraction of Pu(IV) in the absence of the ligand in the acidity range investigated. Bonnaffe-Moity et al. have reported that anionic species of U(VI) with malonamide get extracted by anion exchange mechanism with NTf$_2$ [28].

![Figure 5.8: Pu extraction as a function of nitric acid concentration; Extractant: 0.02M DMDBTDMA; Ionic liquid: [C$_4$mim][Tf$_2$N]; Time of equilibration: 2 h; T: 298 K](image-url)
However, similar mechanism is ruled out in the present case due to very low possibility of anionic complexes of Pu(IV) at the acidity range chosen. The increase in $D_{Pu}$ can only be explained by an analogous cation exchange mechanism as given in equation 5.2.

$$\text{Pu}^{4+}_{(aq)} + x\text{NO}_3^{-}_{(aq)} + y\text{L}_{IL} + (4-x)\text{C}_4\text{mim}^{+}_{IL} \rightleftharpoons [\text{Pu(NO}_3]_{y}^{(4-x)+}_{IL} + (4-x)\text{C}_4\text{mim}^{+} \quad (5.2)$$

![Figure 5.9: Pu extraction as a function of nitric acid concentration; Extractant: 0.02M DMDOHEMA; Ionic liquid: [C₄mim] [Tf₂N]; Time of equilibration: 2 h; T: 298 K](image)

### 5.2.4.3. Neptunium extraction

Np is one of the major long-lived radionuclides present in HLW and contributes significantly to its long term radiotoxicity [1]. Hence, it is important to study the extraction behavior of Np in RTIL media. The Np extraction by malonamide in RTIL medium shows the trend of decrease in $D_{Np}$ with increasing acidity. Np(VI) and Np(IV) show the more extraction in 0.02M DMDBTDMA (Figures 5.10 and 5.11). This trend is similar to that of U(VI) extraction indicating identical extraction mechanism. The extraction of Np(VI) increases up to 0.5M HNO₃ and decreases with further increase in HNO₃ concentration, while Np(IV) shows decrease in extraction with increasing acidity. The Np(IV) shows different extraction behavior than Pu(IV) because of the presence of analogues cationic species of Pu(IV) at lower acidities as mentioned above.
Figure 5.10: Np(VI) extraction as a function of nitric acid concentration
Ionic liquid: [C₄mim][Tf₂N]; Time of equilibration: 2 h; T: 298 K

Figure 5.11: Np(IV) extraction as a function of nitric acid concentration
Ionic liquid: [C₄mim][Tf₂N]; Time of equilibration: 2 h; T: 298 K

Table 5.2 compares the distribution data of different actinides showing very interesting and unusual extraction profiles in the RTIL medium from nitric acid medium. It shows that the hexavalent metal ions are extracted better than trivalent and tetravalent ions in RTIL media. It is also evident that DMDBTDMA is a better extractant than DMDOHEMA. This observation is contradictory to that observed in nonpolar medium such as n-dodecane, where
DMDOHEMA shows the better extracting behavior [10,11]. This is because in nonpolar medium and at higher acidities, the basicity of the extractant plays the vital role along with its lipophilic nature [32].

**Table 5.2:** Comparison of different metal ions extraction profile by malonamides in RTILs extractants: 0.02M DMDBTDMA, 0.02M DMDOHEMA; Acidity: 0.5M HNO₃; Ionic liquid: [C₄mim][NTf₂]; T: 298 K

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>0.02M DMDBTDMA</th>
<th>0.02M DMDOHEMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Am(III)</td>
<td>18.7±1.5</td>
<td>6.6±1.3</td>
</tr>
<tr>
<td>U(VI)</td>
<td>13.4±0.17</td>
<td>6.6±0.11</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>3.0±0.1</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>2.5±0.1</td>
<td>2.5±0.1</td>
</tr>
<tr>
<td>Pu(III)</td>
<td>0.11±0.01</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>28.5±3.5</td>
<td>4.9±0.2</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>2.22±0.01</td>
<td>1.5±0.1</td>
</tr>
</tbody>
</table>

*Dₘ at 0.1M HNO₃

In view of low diamides concentration and low acidity of the aqueous phase (0.01M), there is no problem of acid loading and no deficiency of the free ligand available for extraction. Further, the extraction of Am(III) was significantly higher than the other actinide ions which was rather surprising. This is opposite to complexation mechanism of solvent extraction and evident for the ion exchange mechanism in RTILs [10,25-28,32].
Part B: Fluorescence Studies

This part deals with the Time Resolved Laser Induced Fluorescence Spectroscopy studies (TRLFS). TRLFS study has been performed to investigate the interaction of both the malonamides with Eu(III) in RTIL medium.

5.3. TRLFS Studies on Eu (III) Extraction by Malonamides

In the case of europium, the intensity ratio of the $^5D_0 \rightarrow ^7F_1$ ($\sim$588 nm) and $^5D_0 \rightarrow ^7F_2$ ($\sim$612 nm) transitions are very sensitive to the coordination environment reflecting the hypersensitive character of the $^5D_0 \rightarrow ^7F_2$ electronic transition [31]. With variation of the strength of the ligand field, the intensity of the emission at 612 nm changes. In contrast, the intensity of the peak at 588 nm is hardly affected by the strength of the ligand field. The relative intensities of the two transitions thus serve as a good indicator for examining a change of the symmetry and strength of the ligand field [31]. Besides luminescence emission, the excited state lifetime ($\tau_{\text{obs}}, \text{ms}$) reveals information about different lanthanide and actinide species. A vibronic coupling of Eu(III) excited state with O–H oscillators of coordinated water molecules provides a facile path for radiation less relaxation of the two f-elements. Ligands with N–H or C–H oscillators having vibronic frequencies similar to the O–H ones, are less effective as nonradiative deactivators of the Eu(III) excited states. If there is no contribution from other quenching ligands than water for the relaxation of the excited state, the hydration number of Eu(III) in different complexes can be related to the decay rate $k_{\text{obs}}$ ($k_{\text{obs}} = 1/\tau_{\text{obs}}$) by the following empirical correlations in equation (5.3) [37]:

$$nH_2O = 1.07k_{\text{obs}}(Eu) - 0.62$$ (5.3)

Spectroscopic investigations of actinides and lanthanides in ionic liquids were reported by various research groups (Billard et. al.[31] Mudring et. al.[38] and Dai et. al.[39]) TRLFS studies were performed on the Eu(III) extracted in RTIL [C$_4$ mim][NTf$_2$] (from 0.01M HNO$_3$) and in n-dodecane (from 3 M HNO$_3$) employing 0.02 M and 1 M malonamide extractants, respectively (Figure 5.12). The decrease in fluorescence intensity in the case of 1 M DMDOHEMA/n-dodecane system was attributed to (a) reduced lifetimes due to the presence of –OH vibrators, and (b) the absorption due to ligand molecule at 395 nm which is not available to Eu$^{3+}$ ions (Figure 5.13). On the other hand, no such problem was encountered in RTIL medium for both the extractants as the malonamide concentration was very less.
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**Figure 5.12:** Eu(III) extraction by malonamides in different organic media  
Aqueous phase: $10^{-4}$M Eu(III) in 3M and 0.01M HNO$_3$; Diluent(s): $n$-dodecane or IL

![Graph showing Eu(III) extraction by malonamides](image)

**Figure 5.13:** UV visible absorption for malonamides in $n$-dodecane  
Aqueous phase: 0.1M Eu(III) in 3M HNO$_3$ for sat. solution

![Graph showing UV absorption](image)

There was significant enhancement in the lifetime of the excited state for Eu(III) extracted in both the extractants [0.02M DMDBTDMA: 1285 $\mu$s; 0.02M DMDOHEMA: 1190 $\mu$s] as compared to Eu(III) extracted in $n$-dodecane media, indicating the absence of water molecules in the extracted species. However, the lifetime measurements in $n$-dodecane
medium suggested the presence of water molecules in the extracted species of Eu(III) [1M DMDBTDMA: 624 µs (one water molecule from equation 5.3); 1M DMDOHEMA: 490 µs (two water molecules from equation 5.3)].

**Table 5.3:** Fluorescence life time and number of water molecules associated with Eu(III) in aqueous and organic phases (RTIL and n-dodecane)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Life time, τ (µs)</th>
<th>Number of associated H₂O molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M DMDBTDMA/n-dodecane (org.)</td>
<td>624</td>
<td>1.07</td>
</tr>
<tr>
<td>1M DMDOHEMA/n-dodecane (org.)</td>
<td>490</td>
<td>1.54</td>
</tr>
<tr>
<td>0.02M DMDBTDMA/[C₄mim][NTf₂] (org.)</td>
<td>1285</td>
<td>0.18</td>
</tr>
<tr>
<td>0.02M DMDOHEMA/ [C₄mim][NTf₂] (org.)</td>
<td>1190</td>
<td>0.24</td>
</tr>
<tr>
<td>1M DMDBTDMA/n-dodecane (Aq.)</td>
<td>110</td>
<td>9.21</td>
</tr>
<tr>
<td>1M DMDOHEMA/n-dodecane (Aq.)</td>
<td>110</td>
<td>9.21</td>
</tr>
<tr>
<td>0.02M DMDBTDMA/[ C₄mim][NTf₂] (Aq.)</td>
<td>103</td>
<td>9.88</td>
</tr>
</tbody>
</table>

**Figure 5.14:** TRLFS of Eu(III) remaining in aqua. Phase; Aqueous phase: 10⁻⁴M Eu(III) in 3M and 0.01M HNO₃; Diluent(s): n-dodecane or IL

On the other hand, the life time measurements suggested that the extracted species in the RTIL medium were less hydrophilic as compared to n-dodecane medium which may be
responsible for relatively easy exchange with the imidazolium cation leading to better extraction.

The TRLFS spectra of aqueous phases obtained after Eu(III) extraction in RTIL phase showed negligible emission for both the malonamides. By contrast, significant concentrations of Eu(III) were found in the aqueous phases obtained after extraction using malonamide/n-dodecane as solvents as shown in Figure 5.14. Table 5.3 compares the nature of Eu(III) present in different organic and aqueous phases of RTIL and n-dodecane. In the nonpolar medium, Eu(III) is not extracted completely, while an opposite trend was seen in RTIL medium (Figure 5.14).

From TRLFS studies, we were able to conclude that the extracted species formed in RTIL was less hydrophilic due to less number of associated H₂O molecules.
Part C: Radiolytic Degradation Studies

This part deals with degradation behavior of malonamide/RTIL extraction system. The gamma radiolytic degradation of diamides/RTIL has been studied and the degradation products have been identified by various spectroscopic techniques.

5.4. Degradation Studies of Malonamides in RTIL Medium

During actinide partitioning work, the ligands are exposed to high energy ionizing radiations emitted by the radionuclides. Therefore, while optimizing any extractant or extraction system, it is important to evaluate its radiolytic stability of the solvents. Radiolytic stabilities of two malonamide extractants DMDOHEMA and DMDBTDMA dissolved in the RTIL ([C₄mim][NTf₂]) were investigated. Extractant solutions (0.02M) in RTIL were irradiated in a ⁶⁰Co gamma chamber (Dose rate: 4.2 kGy/h) for different durations equivalent to 281.4, 520.8, and 1041.6 kGy radiation dosage. These samples were analyzed by

a) Solvent extraction studies
b) IR spectral analysis
c) Gas chromatography – mass spectrometric (GC-MS) analysis

5.4.1. Am(III) extraction studies using irradiated malonamides /RTIL samples

Solvent extraction studies of Am(III) at 0.01M HNO₃ showed a sharp decrease in $D_{Am}$ values for both the extractants with increased absorbed dose [0.02 M DMDBTDMA: 81.20±5.16 (fresh solvent) to 0.057±0.002 (1041.6 kGy); 0.02M DMDOHEMA: 19.5±0.53 (fresh solvent) to 0.0038±0.0005 (1041.6 kGy)] (Figure 5.15). This was attributed to the decreased ligand concentration [40,41]. However, it was interesting to note that the decrease in $D_{Am}$ values for ionic liquid system was observed to greater extent as compared to those observed in the case of nonpolar diluents, such as $n$-dodecane [40]. This requires additional insights to explain the accelerated degradation of diamides in RTILs.
5.4.2. IR studies on irradiated diamide/RTIL

The gamma irradiated samples at different doses were subjected to IR spectral analysis. The change in the intensity of the signature peak of malonamides at 1641 cm\(^{-1}\) [32] was taken as the reference for accounting the decrease in malonamide concentration due to radiation degradation. There was an increase in the transmittance (%T) for the diamide signature peak which implied the decrease in the diamide concentration in the solution. Figure 5.16 and 5.17 shows the comparative IR spectra of the DMDBTDMA and DMDOHEMA irradiated with different radiation dosages. The IR spectra clearly indicate the decrease in diamide concentration with increase in radiation dose from 281.4 kGy to 1041.6 kGy (Table 5.4). It was observed that the relative change in %T at 1641 cm\(^{-1}\) for DMDOHEMA is lesser than that of DMDBTDMA, which indicated higher stability of DMDOHEMA in the RTIL medium. This is in agreement with earlier observations in nonpolar n-dodecane medium [40].
The decrease in Am(III) extraction with increased absorbed dose by the solvent was explained in terms of depletion in the ligand concentration. It is worth mentioning that the extracted species of Am(III) is expected to involve three ligand molecules. Therefore, even a marginal decrease in ligand concentration will significantly suppress its extraction.
Table 5.4: Change in %transmittance of signature peak 1641 cm\(^{-1}\) of malonamides by radiolytic degradation in RTIL medium ([C\(_4\)mim][NTf\(_2\)])

<table>
<thead>
<tr>
<th>Absorbed dose, kGy</th>
<th>%Transmittance at 1641 cm(^{-1})</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02M DMDBTDMA</td>
<td>0.02M DMDOHEMA</td>
</tr>
<tr>
<td>0.0</td>
<td>63.85</td>
<td>61.07</td>
</tr>
<tr>
<td>281.4</td>
<td>68.91</td>
<td>65.23</td>
</tr>
<tr>
<td>520.8</td>
<td>70.69</td>
<td>66.95</td>
</tr>
<tr>
<td>1041.6</td>
<td>80.10</td>
<td>74.68</td>
</tr>
</tbody>
</table>

5.4.3. GC-MS studies on irradiated samples

These studies were performed to elucidate the plausible mechanism for the degradation of extractant molecules or diluent caused by the radiation exposure. Generally, the radiolytic degradation of malonamides in nonpolar (n-dodecane) media, leads to the formation of amide acid, amide lactone, and secondary amine. In addition, hexyl alcohol was identified during the degradation of DMDOHEMA side chain in n-dodecane medium [39]. Recent reports on the degradation behavior of amides in RTILs suggested the radical mechanism for the degradation of different formamides and \(N, N, N', N'\)-tetra alkyl-substituted diglycolamides like TODGA [41,42]. But for DIAMEX solvents such as DMDBTDMA and DMDOHEMA in RTIL medium, no such systematic study was done before. In this context, irradiated samples were subjected for GC analysis to identify the degradation products of malonamides and of RTIL. However, the GC analysis is not possible in view of their low vapor pressure. Therefore, direct MS analysis of high molecular weight products was carried out using Shimadzu MS spectrometer and the masses were compared with the library data.

5.4.3.1. GC-MS Analysis

GC-MS spectra of irradiated samples have been recorded using Shimadzu gas chromatography - mass spectrum analyzer.
Spectra 1: DMDBTDMA: 281.4 kGy irradiated sample
Spectra 2: DMDBTDMA: 1041.6 kGy irradiated sample
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**Spectra 3:** DMDOHEMA: 281.4 kGy irradiated sample
Spectra 4: DMDOHEMA: 1041.6 kGy irradiated sample:
The desired fragment peaks were exposed to mass spectrometric data analysis. The comparison with available literature fragmentation data and possible fragmentation mechanism as shown in Figure 5.18 was used to characterize the fragments formed at different irradiated samples. The possible degradation products identified for DMDBTDMA and DMDOHEMA in RTIL medium are listed in Table 5.5.

Table 5.5: Possible degradation products for malonamides and their GCMS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>GC (min)</th>
<th>MS (m/z)</th>
<th>Fragment identified</th>
<th>% fragment formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMDBTDMA</td>
<td>22.63</td>
<td>44.05</td>
<td>N-methyl-N-decyl-butanamide</td>
<td>15.50</td>
</tr>
<tr>
<td>281.4 K Gy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>2.65</td>
<td>56.05</td>
<td>hexyl alcohol</td>
<td>5.97</td>
</tr>
<tr>
<td>281.4 K Gy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMDBTDMA</td>
<td>20.08</td>
<td>73.15</td>
<td>tetradecanal</td>
<td>3.56</td>
</tr>
<tr>
<td>1041.6 K Gy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>1.62</td>
<td>42.60</td>
<td>hexyl methyl ketone</td>
<td>71.95</td>
</tr>
<tr>
<td>1041.6 K Gy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.18: Schematic for radiolytic degradation of malonamides in RTIL medium has been found similar to that earlier reported radical degradation mechanism of diglycolamides (Figure 5.18) [41,42]. But the radiation stability is found to be relatively inferior than that in n-dodecane. This suggested that the aromatic cation imidazolium moiety was unable to protect the damage by alkyl chain radical formations. Similar observation has been reported earlier for diglycolamide extractants [40-42]. Such degradation behavior is contradictory to that in nonpolar medium.
where the aromatic hydrocarbons are added to the organic phase. These aromatic hydrocarbons act as the radical stabilizers or quenchers and eventually minimize the extractant degradations in nonpolar systems.

5.5. Conclusions

Am(III) extraction has been compared for RTIL medium using two malonamides DMDBTDMA and DMDOHEMA extractants. These studies showed that there is a possibility of significant reduction in the extractant inventory in the RTIL medium as compared to that in the n-dodecane medium. Based on these studies, [C₄mim][NTf₂] was identified as suitable RTIL as diluent. The extraction kinetics for Am(III) in [C₄mim][NTf₂] is fast enough to get complete extraction in less than 30 min. However, one needs to further improve the extraction kinetics to make use of RTILs in separation processes. During Am(III) extraction studies, both malonamides showed the formation of trisolvated species at lower ligand concentration (up to 0.02 M) and disolvated species at higher ligand concentration (>0.02 M) in [C₄mim][NTf₂] RTIL medium. Several metal ions such as U(VI), Np(IV), Np(VI), Pu(IV), Pu(VI), and Eu(III) were also extracted efficiently in RTIL medium than in nonpolar medium. DMDBTDMA shows better extractability than DMDOHEMA in RTIL medium. TRLFS study of Eu(III) indicated the absence of water molecule in the extracted species in RTIL medium suggesting more hydrophobic nature of the extracted species as compared to that in n-dodecane medium. The radiolytic stability studies showed a sharp decrease in extractability of Am(III) which was attributed to decrease in diamide concentration. IR studies indicate that DMDOHEMA is relatively more resistant to radiolytic degradation as compared to DMDBTDMA. The degradation products of diamides were identified as N-methyl-N-decyl-butanamide and tetradecanal (for DMDBTDMA) and n-hexyl alcohol and n-hexyl methyl ketone (for DMDOHEMA). These studies indicate that detailed investigations on the extraction behavior of different oxidation states of metal ion are required to get insights of their interesting extraction behavior in RTILs.

5.6. References


Chapter V

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