Chapter III

Development of Synthesis Route for Malonamide Extractants and Actinide Partitioning Studies
Development of Synthesis Route for Malonamide Extractants and Actinide Partitioning Studies

3.1. Introduction

Steady growth of global nuclear fuel reprocessing activities implies a vital role of separation and radiochemists not only in developing efficient procedures for the separation and purification of actinides, but also for devising safe procedure for the management of high level waste (HLW) emanating in the PUREX process [1-3]. Possibility of the isolation of some pure radionuclides as valuable byproducts makes actinide partitioning further attractive strategy for HLW treatment. Use of universal fuel reprocessing extractant such as tri-n-butyl phosphate (TBP) for actinide partitioning is not possible without producing waste streams with high salt content. Thus, there is a need to develop versatile reagents capable of partitioning of actinides under the prevailing conditions of HLW.

In recent years, completely incinerable substituted diamides have been the focus of numerous studies in the back end of nuclear fuel cycle [4,5]. These extractants offer several advantages over organophosphorus compounds, especially with respect to (i) the innocuous nature of their degradation products, viz. carboxylic acids/amines; and (ii) the possibility of complete incineration of the spent solvent leading to reduced volume of the secondary waste [6-8]. In addition, the physico-chemical properties of this class of ligands can be tuned by the judicious choice of alkyl groups. In the last decade, several investigations have been conducted on the modification of diamide structure in order to further improve its extracting properties [3-5]. It has been observed that the introduction of etheric oxygen between the two amide groups (diglycolamide) or in attached side chain of malonamide (pentaalkyl diamides) causes significant enhancement in the extraction of trivalent actinides/lanthanides [9]. The malonamide based extraction process (DIAMEX) was proposed for actinide partitioning by French Commissariat a` l’Energie Atomique (CEA) [10]. The DIAMEX processes were mainly based on the use of two malonamides viz. \(N,N'\)-dimethyl-\(N,N'\)-dibutyl-2-tetradecylmalonamide (DMDBTDMA) and \(N,N'\)-dimethyl-\(N,N'\)-dioctyl-2-(2-(hexyloxy)ethyl)-malonamide (DMDOHEMA) (Figure 1.4). Unlike other proposed extractants for actinide partitioning, viz. octyl-(phenyl)-\(N,N\)-diisobutyl carbamoyl methyl phosphine oxide, (CMPO), \(N,N,N',N'\)-tetraoctyl diglycolamide (TODGA), \(N,N,N',N'\)-tetra-2-ethylhexyl diglycolamide (TEHDGA) and trialkyl phosphine oxide (TRPO), these diamides do not display any third-phase formation problem and the addition of phase modifier is avoided [11-17]. The malonamide extractants interact with HNO\(_3\) molecules and form
adducts with different stoichiometries (viz. disolvate, monosolvate, and hemisolvate) depending on the acidity of the aqueous medium [18]. Several studies related to the extraction of acids, metal ions under varying experimental conditions have been performed to understand the mechanism of extraction [19-24]. Based on this understanding, elaborate counter-current runs were performed for the evaluation of DIAMEX solvents [25-28]. Even though, initial experiments for proposed DIAMEX process were carried out using DMDBTDMA as an extractant, DMDOHEMA was identified at later stage as a better candidate in view of its superior solvating ability and higher affinity for An(III) [29,30]. Diamide extractants such as TODGA and DMDBTDMA dissolved in nonpolar diluent display aggregation tendency after equilibrating with aqueous solutions. This phenomenon has been studied by NMR spectroscopy, self-diffusion coefficient measurements and by vapor pressure osmometry (VPO) [18,31,32]. However, no systematic attempt has been made to compare the extraction behavior of Am(III) from different acid media (such as HCl, HNO₃, and HClO₄) employing DMDOHEMA and DMDBTDMA dissolved in n-dodecane as solvents.

Utilization of malonamides like DMDOHEMA for the partitioning of actinides in the back end of nuclear fuel cycle would heavily rely on the solvent extraction technique. It is imperative to carry out a systematic solvent extraction study to understand the extraction behavior of actinides and long-lived fission products employing DMDOHEMA as the extractant which is also going on in Europe [10]. This chapter is divided into two parts viz. Part A deals with the synthesis of malonamide extractants. DMDOHEMA has been synthesized by a relatively simpler route with a better yield than the earlier reported procedures. Part B describes, (i) actinide extraction studies under tracer as well as Pressurized Heavy Water Reactor - Simulated High Level Waste (PHWR-SHLW) conditions, (ii) effects of anions such as NO₃⁻, ClO₄⁻ and Cl⁻, and (iii) aggregation behavior of diamides by dynamic light scattering (DLS) measurements. The acid uptake constant of DMDOHEMA and the effect of feed acidity on the extraction of metal ions were also studied.
PART A: Synthesis of Malonamides by Modified Synthesis Route

Several reports are available on the synthesis and evaluation of diamide extractants [33-36]. These studies mainly focused on the variation of alkyl substituent and synthesized a series of ligand molecules for their comparison in solvent extraction studies. It is important to mention that the starting materials for the synthesis of desired diamide molecules were, in general, acid chlorides and secondary amines. Bromination step was used for the insertion of side chain (oxaalkyl/alkyl) which requires highly corrosive PBr3 or Br2. It may appear an easy exercise for the synthesis of diamides on a laboratory scale using these corrosive reagents; one would prefer to go for innocuous reagents for large scale synthesis of diamides. This is particularly relevant for DIAMEX process extractants where high ligand inventory is required to perform the actinide partitioning studies. This part deals with the synthesis of malonamide extractants. DMDOHEMA has been synthesized by a modified route. The proposed route can be extended to other alkyl derivatives of malonamides. N,N'-dimethyl-N,N'-dibutyl-2-tetradecylmalonamide (DMDBTDMA) has been synthesized by using reported procedure [36].

An attempt was made to synthesize DMDOHEMA using diester and p-toluene sulphonyl (tosyl) chloride instead of the corrosive reagents like malonyl dichloride and PBr3. The additional advantage of tosyl chloride is easy replacement of hydrogen from primary -OH group of the 3-oxanonanol side chain.

3.2. Synthesis of DMDOHEMA

DMDOHEMA was synthesized in the following three steps:
(i) Synthesis of N,N'-dimethyl-N,N'-dioctyl malonamide (DMDOMA)
(ii) Synthesis of 3-oxanonyl side chain and
(iii) Coupling of 3-oxanonyl side chain with diamide backbone

3.2.1. Experimental details for synthesis

N-methyl octylamine (synthesis grade) procured from Alfa Aesar was freshly distilled before use. Diethyl malonate (synthesis grade), ethylene glycol (AR grade), 1-bromohexane (Puriss Grade), dichloromethane (DCM) (AR grade), dimethyl formamide (DMF) (AR grade), sodium hydride (60% suspension in mineral oil) were supplied by Spectrochem Pvt. Ltd., Mumbai, India. Sodium methoxide used was freshly prepared by known procedure [37].
3.2.2. Synthesis of N, N’-dimethyl- N, N’-dioctyl malonamide (DMDOMA)

DMDOMA was synthesized as per reported procedure [35]. As shown in Scheme 3.1 mixture (1:2 equivalents) of diethyl malonate (0.13 moles) and N-methyl octylamine (0.26 moles) was refluxed for three hours to yield DMDOMA (1). The reaction mixture was cooled to room temperature followed by the addition of 200 mL of DCM to dissolve the reaction mixture. This mixture was washed with 5 % HCl to remove the unreacted N-methyl octyl amine and then dried over anhydrous Na$_2$SO$_4$. DCM was removed by distillation under reduced pressure to get DMDOMA (1) as a viscous liquid (~78 % yield). It should be noted that the yield of product reported elsewhere was less than 40% [33,34].

The product was characterized as:

$^1$H NMR (300 MHz, CDCl$_3$), δ: 0.9(t, 6H, $J$= 3Hz, CH$_3$), 1.24 (m, 24H, CH$_2$), 2.9, 3.1 (t, 6H, $J$= 3Hz, CH$_3$), 3.3 (t, 4H, $J$= 7Hz, CH$_2$) 3.45 (s, 2H, CH$_2$)

MS m/z, C$_{21}$H$_{42}$N$_2$O$_2$: 354.32 (calculated), 354 (found).

IR: 1641 cm$^{-1}$ (stretching frequency for carbonyl group of 1).

Scheme 3.1: Synthesis of diamide backbone
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$^1$H NMR: DMDOA

$$\begin{align*}
\text{H}_3\text{C} & \quad \text{N} - \text{C}_8\text{H}_{17} \\
\text{O} & \quad \text{O} \\
\text{N} - \text{C}_8\text{H}_{17} & \\
\text{H}_3\text{C}^- &
\end{align*}$$
3.2.3. **Synthesis of 3-oxanonyl side chain**

This synthesis was carried out in two steps. In the first step, 0.8 moles of ethylene glycol was added drop wise under inert N\(_2\) atmosphere into saturated sodium methoxide solution in dry methanol (65 mL) (Scheme 3.2). The excess of methanol was removed by distillation. To this reaction mixture, 0.19 moles of 1-bromohexane was added and was heated overnight at 100°C. After the completion of the reaction, the product 3-oxanonanol (2) was extracted in hexane. Sodium bromide and excess of ethylene glycol were removed by water wash. The product (2) was obtained with 68% yield after column purification. The silica column of 100-200 mesh size was used for purification. Ethyl acetate in hexane (5-8%) was used as the eluent for the purification.

The compound was characterized as follows:

\(^1\text{H NMR}\) (300MHz, CDCl\(_3\)) \(\delta\): 0.9 (t, 3H, \(J=7\text{Hz}\), \(\text{CH}_3\)), 1.3 (m, 6H, \(\text{CH}_2\)), 1.6 (q, \(J=7\text{Hz}\), 2H, \(\text{CH}_2\)), 2.1 (br s, 1H, \(\text{OH}\)), 3.45 (t, 2H, \(J=7\text{Hz}\), \(\text{CH}_2\)), 3.55(t, 2H, \(J=2\text{Hz}\), \(\text{CH}_2\)), 3.74(t, 2H, \(J=4\text{Hz}\), \(\text{CH}_2\)).

**MS** \(m/z\), \(\text{C}_9\text{H}_{18}\text{O}_2\): 146.23 (calculated), 146 (found).

![Scheme 3.2: Synthesis of 3-oxa nonanol side chain (2)](image-url)
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\[ ^{1}H\text{NMR: 3-Oxanonal} \]

\[ \text{OH} \]

\[ \text{O} \]

\[ \text{H}_3\text{C} \]
As shown in Scheme 3.3, the second step involves the tosylation of 3-oxanonanol (2). It was achieved by dropwise addition of 0.14 moles of (2) in 60 mL triethyl amine (TEA) dissolved in dry DCM solvent, at 0°C under N₂ atmosphere. After five minutes of stirring, 0.2 moles of p-toluenesulphonyl (tosyl) chloride was added portion wise to the reaction mixture. The reaction progress was monitored by using the thin layer chromatography (TLC) by using 10 % ethyl acetate-hexane solvent system and was found to be complete in 2 h. The product tosyoxy 3-oxanonane (3) obtained was in 88% yield.

Purification of the product (3) was carried out by column chromatography using ethyl acetate in hexane 5-8 % as eluent.

The synthesized compound was characterized as:

**1H NMR** (300MHz, CDCl₃) δ: 0.9(t, 3H, J= 7Hz, CH₃), 1.5(m, 6H, CH₂), 1.6 (q, 2H, J= 7Hz, CH₂), 2.4(s, 3H, CH₃), 3.4 (t, 2H, J= 7Hz, CH₂), 3.6(t, 2H, J= 5Hz, CH₂), 4.18(t, 2H, J= 5Hz, CH₂), 7.33(d, 2H, J= 8Hz, CH), 7.80(d, 2H, J= 8Hz, CH).

**MS m/z**, C₁₅H₂₄O₄S: 300.41 (calculated), 300 (found).

![Scheme 3.3: Synthesis of tosylated 3-oxanonanol side chain (3)](image-url)
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$^1$H NMR: Tosyloxy-3-oxanohanol
3.2.4. Nucleophilic substitution of DMDOMA on tosylated 3-oxanonanol

Final step of the synthesis of DMDOHEMA (4) as depicted in Scheme 3.4, involves the coupling of the 3-oxanonyl group in 3 to the -CH2- of the malonyl carbon in 1. It was achieved by the generation of anion using NaH as a strong base. NaH (0.07 moles) was taken in a reaction flask and paraffin coating was removed by multiple hexane washings. The excess of hexane was removed from NaH prior to its dissolution in dry DMF and the resulting solution was cooled up to -10°C under inert nitrogen atmosphere. To this, 0.07 moles DMDOMA (1) dissolved in dry DMF was added dropwise with constant stirring. This was followed by slow addition of 0.07 moles of tosyloxy-3-oxanonanone (3) dissolved in dry DMF solution. The reaction mixture was allowed then to attain room temperature (25°C) and refluxed for 24 h under inert conditions. Product formation was monitored by TLC using the 50% ethyl acetate in hexane as the solvent system and aqueous KMnO4 as the staining agent. DMF was finally removed by vacuum distillation from reaction mixture and then extracted in ethyl acetate and washed with water. The product was purified by column chromatography using ethyl acetate in hexane (18-20 %, v/v) as eluent and the yield of the product was ~69 %.

The synthesized product, DMDOHEMA, was characterized as:

$^1$H NMR (300MHz, CDCl$_3$), δ: 0.85(t, 9H, J= 7Hz, CH$_3$), 1.2-1.3(m, 26H, CH$_2$), 1.56 (m, 8H, CH$_2$), 2.9 (t, 6H, CH$_3$), 3.4 (m, 8H, CH$_2$), 3.9 (m, 1H, CH).

MS m/z, C$_{29}$H$_{58}$N$_2$O$_3$: 482.78 (calculated), 483 (found).

IR: 1651cm$^{-1}$ (>C=O, stretching frequency).

CHNS: C: 72.08% (71.94%), H: 12.01% (12.17%), N: 5.36% (5.79%) (Values in brackets refer to calculated contents)

Scheme 3.4: Nucleophilic substitution of malonamide with tosylated 3-oxanonanol
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$^1$H NMR: DMDHEMA

![NMR spectrum with chemical structures]
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3.3. Advantages of Modified Synthesis Route for DMDOHEMA

The proposed synthesis route of malonamide avoids the use of the corrosive malonyl dichloride and instead uses diethyl malonate. The staining of DMDOMA by aqueous KMnO₄ helped in monitoring the product purity by TLC in ethyl acetate and hexane (50 %, v/v) medium. The introduction of the oxaalkyl side chain was carried out by using ethylene glycol and hexyl bromide as the starting materials. The key step of protection of one of the hydroxyl groups of ethylene glycol was achieved by adding excess equivalents of the diol than n-bromohexane, which was facilitated by using freshly prepared sodium methoxide [36]. In earlier reports, side chain moiety was converted to its bromide derivative for the attachment to the malonyl skeleton. For this purpose, highly corrosive PBr₃ and Br₂ were used which were difficult to handle for a large scale synthesis [33,34]. Therefore, a simpler method of tosylation of 3-oxanonanol was followed, instead of bromination in relatively mild reaction conditions (yield: ~88 %). NaH was used as strong base in the final step involving coupling of diamide and tosylated 3-oxanonanol side chain, instead of conventionally used explosive and corrosive Li based reagents (n-butyl Li) [34]. It should be noted that the tosyloxy derivative is a better leaving group as compared to those of corresponding bromides due to its bulky size, and therefore provides better yield in the final C-alkylation step. The proposed route for diamide synthesis offers improved overall product yield (~60 %) as compared to the reported procedures (30-40 %) (Table 3.1) [33-35]. This route appears to be promising for the synthesis of other alkyl derivatives of the diamides and may be followed for their large scale synthesis.

Table 3.1: Comparison of developed method with conventional procedures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reported method [33-35]</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting material</td>
<td>Malonyl dichloride</td>
<td>Diethyl malonate</td>
</tr>
<tr>
<td></td>
<td>Hazardous, Unstable, Expensive</td>
<td></td>
</tr>
<tr>
<td>Side chain modification</td>
<td>Bromination by hazardous PBr₃</td>
<td>Tosylation; Easier in synthesis and cheaper</td>
</tr>
<tr>
<td>Coupling of Side chain</td>
<td>n-BuLi</td>
<td>NaH; cheaper and easily available</td>
</tr>
<tr>
<td></td>
<td>hazardous, inflammable, costly</td>
<td></td>
</tr>
<tr>
<td>Overall yield</td>
<td>30-40%</td>
<td>&gt; 55%</td>
</tr>
</tbody>
</table>
PART B: Partitioning Studies of Actinides under PHWR-SHLW Conditions Using DMDOHEMA as the Extractant

This part deals with actinide extraction studies under tracer as well as SHLW conditions. The synthesized product has been tested for the extraction behavior of $^{241}\text{Am}$, $^{237}\text{Np}$, $^{239}\text{Pu}$ tracers as well as that of these radionuclide under SHLW conditions. The performance of DMDOHEMA has been evaluated vis-à-vis other proposed extractants for actinide partitioning under PHWR-SHLW conditions. The stoichiometries of extracted species of Np(IV), Pu(IV) and Am(III) from 3M HNO$_3$ using different concentrations of DMDOHEMA in $n$-dodecane has been determined. The effect of the mineral acid (viz. HCl, HNO$_3$, and HClO$_4$) on the extraction of Am(III) has also been investigated employing DMDOHEMA and DMDBTDMA as extractants dissolved in $n$-dodecane. The experimental data has been explained in terms of the aggregation behavior of the diamides.

3.4. Solvent Extraction Studies

3.4.1. Stoichiometry of the extracted species of acid and actinide ions

An attempt was made to find the number of DMDOHEMA molecules attached to nitric acid as well as with different actinide ions such as Np(IV), Pu(IV), and Am(III) extracted into the organic phase. Depending on their relative concentrations, malonamides (A) can interact with HNO$_3$ to form a variety of species of the type A$_2$·HNO$_3$, A·HNO$_3$, A·(HNO$_3$)$_2$ etc. Equilibria governing the formation of these adduct influence the availability of the free ligand concentration as well as third-phase formation behavior of the extractant. Typical acid uptake equilibrium can be shown as follows:

$$
\text{H}^+ + \text{NO}_3^- + n\text{A}_{\text{org}} \leftrightarrow \text{HNO}_3 \cdot n\text{A}_{\text{org}}
$$

(3.1)

$$
K_H = \frac{[\text{HNO}_3 \cdot n\text{A}]}{[\text{H}^+] [\text{NO}_3^-] [\text{A}^n_{\text{free,org}}]}
$$

(3.2)

Taking logarithm on both sides of equation (3.2) and rearranging:

$$
\log[H^+]_{\text{org}} - 2\log[H^+]_{\text{aq}} = n\log[A]_{\text{free}} + \log K_H
$$

(3.3)

where, $[H^+]_{\text{org}} = [\text{HNO}_3 \cdot n\text{A}]_{\text{org}}$ and $[H^+]_{\text{aq}} = [\text{NO}_3^-]_{\text{aq}}$

$[H^+]_{\text{aq}}$ was calculated from the titre value ($T$) and dissociation constant of HNO$_3$ ($K_a$).

$$
K_a = \frac{[H^+][\text{NO}_3^-]}{[\text{HNO}_3]_{\text{aq}}} = \frac{[H^+]_{\text{aq}}^2}{T\cdot[H^+]_{\text{aq}}}
$$

(3.4)
where, \( T = ([H^+]_{aq} + [HNO_3]_{aq}) \) in aqueous phase.

Therefore, \( [H^+]_{aq}^2 + K_a \cdot [H^+]_{aq} \cdot T = 0 \) \( (K_a = 23.5, \text{ literature value}) \) (3.5)

\([H^+]_{aq}\) was obtained by solving the above quadratic equation.

\([A]_{free} = [A]_{initial} - [H^+]_{org} \) (assuming one HNO\(_3\) was bound to each malonamide extracted)

**Figure 3.1:** Variation of \( \log[H^+]_{org} - 2 \log[H^+]_{aq} \) vs \( \log[A]_{free} \)

A: DMDOHEMA; Diluent: \( n\)-dodecane; T: 298 K

From equation (3.3), it can be seen that a plot of \( \{\log[H^+]_{org} - 2\log[H^+]_{aq}\} \) against \( \log[A]_{free} \) should give a straight line with slope \( n \) i.e. the number of malonamide molecules bound to each HNO\(_3\) in the adduct formed. **Figure 3.1** shows a typical plot for DMDOHEMA where the slope of 1.28±0.07 suggests that 1:1 species is formed predominantly under the experimental conditions chosen in the present work. This observation is consistent with earlier reported work on acid uptake employing DMDBT DMA as the extractant [36].

Similarly, the distribution ratios of Am(III), Np(IV), Pu(IV) and from 3 M HNO\(_3\) were determined as a function of DMDOHEMA concentration [0.1-1.0 M for Am(III); 0.01-0.1 M for Np(IV) and Pu(IV)] dissolved in \( n\)-dodecane to know the stoichiometry of their extracted species in the organic phase. The log-log plots of \( D_M \) [M: Am(III), Np(IV) and Pu(IV)] vs. [DMDOHEMA] gave straight lines having slopes ~ 2 for Am(III) and ~3 for Np(IV) and Pu(IV) respectively (**Figures 3.2 & 3.3**). Therefore, the predominant extracted
species of Am(III), Np(IV) and Pu(IV) were Am(NO$_3$)$_3$·2A, Np(NO$_3$)$_4$·3A and Pu(NO$_3$)$_4$·3A, respectively.

![Graph showing the relationship between D$_{\text{Am}}$ and [DMDOHEMA]$_{\text{free}}$.](image)

**Figure 3.2:** $D_{\text{Am}}$ as a function of DMDOHEMA concentration; Aqueous phase: 3 M HNO$_3$; Diluent: $n$-dodecane; T: 298 K

The stoichiometry of the extracted species of Am(III) was conformed with the reported value [41]. However, a trisolvated species of Am(III) was reported using DMDBTDMA/$n$-dodecane at 3 M HNO$_3$ [36]. On the other hand, the formation of trisolvated species was reported for Pu(IV) using DMDBTDMA/$n$-dodecane as the solvent at 3 M HNO$_3$. To the best of our knowledge, no such study was reported on Np(IV) using DMDOHEMA as the extractant. Incidentally, the extracted species of Np(IV) and Pu(IV) seem to involve three DMDOHEMA molecules under the conditions of this study.
3.4.2. Effect of nature of acid on Am(III) extraction

The Am(III) extraction profile was obtained as a function of acidity using different acid solutions (viz. HCl, HNO₃, and HClO₄) employing 0.5 M DMDOHEMA and 0.5 M DMDBTDMA solutions in n-dodecane. **Figure 3.4** and **Figure 3.5** shows the variation of Am(III) distribution ratio (Dₐm) values with different HClO₄ (0.01-1 M), HNO₃ (0.1-3 M), and HCl (0.1-3 M) aqueous phase solutions, while 0.5 M DMDOHEMA and 0.5 M DMDBTDMA dissolved in n-dodecane as extractants. The Dₐm values followed the order: HClO₄ > HNO₃ > HCl for both the extractants. This observation was explained in terms of more favored aggregation of diamide molecules (viz. DMDOHEMA or DMDBTDMA) in the presence of HClO₄.
Figure 3.4: Variation of $D_{Am}$ with aqueous phase acidity; Extractant: 0.5 M DMDOHEMA/n-dodecane; T: 298 K

Figure 3.5: Variation of $D_{Am}$ with aqueous phase acidity; Extractant: 0.5 M DMDBTDMA/n-dodecane; T: 298 K
3.4.3. Dynamic Light Scattering Studies (DLS) on Aggregation behaviour of malonamides

As observed in the previous section, the nature of the mineral acid influences the metal ion extraction to a greater extent. In literature, similar behavior is observed in case of TODGA extractant. This behavior was explained using aggregation effect in malonamides [32]. To check the similar effect in case of the malonamides, the aggregation effect has been studied using DLS technique.

3.4.3.1. Theory of DLS measurements

The colloidal particles suspended in any liquid are under constant Brownian motion due to random collisions with liquid molecules surrounding the particle. As expected, the smaller particles move faster than the larger particles. When a monochromatic and coherent beam of light falls on such a suspension, the scattered light photons carry information about the size of the particles. DLS technique measures the fluctuations in the intensity of the scattered photons, which occur over short time intervals due to Brownian motion of the particles in the solution. The behavior of these fluctuations is described quantitatively by the intensity of the autocorrelation function, \( C(\tau) \) of the scattered intensity as given below [32],

\[
C(\tau) = A \left( 1 + \beta \int_{0}^{\infty} P(\Gamma) \exp(-\Gamma \tau) d\Gamma \right)
\]  \( (3.6) \)

where, \( A \) is baseline value, \( \beta \) is an instrumental constant and \( \Gamma \) is the characteristic line width of the distribution function \( P(\Gamma) \) and is related to the diffusion coefficient (D) of the species by the following expression:

\[
\Gamma = Dq^2
\]  \( (3.7) \)

where, \( q \) is the scattering vector and is constant for a given observation angle and wavelength of incident light. Assuming the scattering species to be hard sphere, the apparent hydrodynamic radius (\( r_h \)), of the particles or aggregate species can be calculated by Stokes-Einstein equation,

\[
r_h = \frac{k_B T}{6 \pi \eta D}
\]  \( (3.8) \)

Where, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature and \( \eta \) is the viscosity of the dispersion medium.
3.4.3.2. DLS measurements
The aggregate size measurement in the organic phase was performed using Zetasizer-3000 DLS spectrometer (Malvern Instrument Company, UK) with a 10 mW He-Ne laser beam at a wavelength of 488 nm. All the measurements were performed at a scattering angle of 90° in a cell of 4 mm path length at 25°C. The instrument was calibrated using standard colloidal suspension (polystyrene, Latex) before the size measurement of actual samples. The samples for DLS measurements were prepared by equilibrating the organic phases (0.5 M DMDOHEMA or 0.5 M DMDBTDMA dissolved in n-dodecane) with 1 M concentration of HCl/HNO\textsubscript{3}/HClO\textsubscript{4}. Each measurement was repeated at least five times to check the reproducibility of data. The error shown on the measured data are the standard deviation of multiple measurements.

3.4.3.3. Effect of nature of acid on aggregate size of malonamides
The higher extraction in the case of HClO\textsubscript{4} can be attributed to the perchlorate effect where perchlorate ions promote the phase transfer of metallic cations by disrupting H\textsubscript{2}O structure in the aqueous phase [42].

**Table 3.2:** Effect of nature of acid on the aggregation behavior of diamides; Diluent: n-dodecane; T: 25±2°C

<table>
<thead>
<tr>
<th>Aqueous phase</th>
<th>Aggregate size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5M DMDOHEMA</td>
</tr>
<tr>
<td>No acid</td>
<td>3.71±0.02</td>
</tr>
<tr>
<td>1M HCl</td>
<td>4.00±0.16</td>
</tr>
<tr>
<td>1M HNO\textsubscript{3}</td>
<td>4.79±0.41</td>
</tr>
<tr>
<td>1M HClO\textsubscript{4}</td>
<td>15.12±1.37</td>
</tr>
</tbody>
</table>

There was a direct correlation between the extraction of Am(III) and the aggregation behavior of diamide molecules in the presence of these acids (Table 3.2). The limiting organic concentration (LOC) of HClO\textsubscript{4} in 0.5 M DMDOHEMA or DMDBTDMA solutions in n-dodecane were ~0.2 M, which were derived from the equilibration of the organic phases with 2 M HClO\textsubscript{4}. It is important to mention that 0.5 M DMDBTDMA/n-dodecane formed a third-phase at 3.7 M HNO\textsubscript{3} while, 1M DMDBTDMA/n-dodecane showed third-phase above 6.2 M and for 1.5 M. A third-phase did not appear even at 9.5 M HNO\textsubscript{3}. It is obvious that the third-
phase formation tendency is more in the case of HClO\textsubscript{4} as compared to that of HNO\textsubscript{3}, which was attributed to enhanced interaction between diamide-HClO\textsubscript{4} aggregates.

### 3.4.4. Extraction studies under PHWR-SHLW conditions

#### 3.4.4.1. Preparation of PHWR-SHLW

SHLW used in the present work refers to the Pressurized Heavy Water Reactor (PHWR) where the fuel is natural uranium and burn up of spent fuel is \(~6500\text{MWD/THM}\) (Megawatt day per ton of heavy metals). Raffinate of the Plutonium Uranium Extraction (PUREX) process is concentrated about four times to arrive at HLW. The SHLW (Table 2.1) was prepared by dissolving desired weights of different salts (mainly nitrates/oxides) in nitric acid medium and final acidity was adjusted to 3 M.

#### 3.4.4.2. Extraction studies of actinides

Table 3.3 lists the distribution ratio values for different metal ions using 1 M DMDOHEMA/\textit{n}-dodecane as extractant at 3M HNO\textsubscript{3} as well as in the presence of SHLW solution. It is evident that \(D_{M}\) values of metal ions (M: Am(III), Np(IV), Np(VI), Pu(IV), U(VI)) are high enough for extraction under SHLW conditions. Interestingly, there was an increase in \(D_{Np}\) values (without valency adjustment) in the presence of PHWR-SHLW. This enhancement was attributed to partial oxidation of Np to Np(VI), which was independently confirmed by spectrophotometry.

**Table 3.3:** Distribution behavior of different metal ions; Extractant: 1 M DMDOHEMA/ \textit{n}-dodecane; T: 25±2 °C

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>(D_M) (3\text{M}) HNO\textsubscript{3}</th>
<th>(D_M) SHLW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am(III)</td>
<td>15.5±0.3</td>
<td>12.40±0.5</td>
</tr>
<tr>
<td>Np(^*)</td>
<td>5.4±0.1</td>
<td>19.7±1.6 (38.9±2.1)(^**)</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>33.0±1.1</td>
<td>22.5±1.2 (32.5±1.9)(^**)</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>25.0±0.9</td>
<td>21.2±0.9 (42.0±2.3)(^**)</td>
</tr>
<tr>
<td>Pu(^*)</td>
<td>34.5±1.7</td>
<td>27.1±0.8</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>38.5±1.3</td>
<td>23.4±1.3</td>
</tr>
<tr>
<td>U(VI)</td>
<td>24.0±1.9</td>
<td>22.4±0.7</td>
</tr>
</tbody>
</table>

\(^*\) No valency adjustment;\(^**\) Values in brackets refer to SHLW containing 0.1 M oxalic acid + 0.05 M HEDTA (N (2-hydroxyethyl) ethylenediamine triacetic acid)
The presence of 0.1 M oxalic acid + 0.05 M \(N\)-(2-hydroxyethyl) ethylenediamine triacetic acid (HEDTA) in the SHLW solution suppresses the extraction of metal ions like Zr(IV) and Pd(II) and makes available free ligand molecules for the extraction of desired actinide cations like Np(IV), and Np(VI) \[28\]. Therefore, extraction studies with DMDOHEMA were also performed in the presence of 0.1 M oxalic acid + 0.05 M HEDTA in the SHLW solution. In general, the addition of the complexing solutions in SHLW appears to enhance the extraction of different Np cations. This study suggested the co-recovery of Np along with Am(III) during actinide partitioning using DMDOHEMA as the extractant.

3.4.4.3. Extraction studies of fission/activation product(s)

The distribution behavior of various fission/activation products under SHLW conditions spiked with diluted aliquot of a High Active Waste (HAW) sample from the PUREX process stream of PREFRE plant, Tarapur, India, is depicted in Table 3.4.

As expected, the trivalent, and tetravalent actinide ions were extracted under SHLW conditions. There was significant extraction of fission products such as \(^{155}\)Eu, \(^{144}\)Ce; while the activation products such as \(^{137}\)Cs, \(^{125}\)Sb, \(^{106}\)Ru were poorly extracted.

Table 3.4: Fission/activation product(s) distribution data under SHLW conditions using 1 M DMDOHEMA/\(n\)-dodecane as solvent; T: 25±2 °C

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>(D_M) under SHLW conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{154})Eu</td>
<td>7.0 ± 0.2</td>
</tr>
<tr>
<td>(^{144})Ce</td>
<td>13.4 ± 0.8</td>
</tr>
<tr>
<td>(^{106})Ru</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>(^{137})Cs</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>(^{125})Sb</td>
<td>&lt; 10(^{-3})</td>
</tr>
</tbody>
</table>

3.4.4.4. Stripping studies of Am(III)

In actinide partitioning studies along with the higher \(D_M\) values, the stripping should be efficient to facilitate the recovery of extracted metal ions from the loaded organic phases. Sometimes the lower \(D_M\) values of the malonamide extractants may help for such applications. Stripping studies using 0.01 M HNO\(_3\) solution as strippant and maintaining organic-to-aqueous phase ratio (O/A) as 1 showed that two contacts were sufficient for quantitative stripping (>99.9%) of \(^{241}\)Am from the loaded 1M DMDOHEMA/\(n\)-dodecane under SHLW conditions.
3.4.4.5. **Comparison of DMDOHEMA with other extractants**

The extraction data of Am(III) was also compared with those of other proposed extractants at 3M HNO$_3$ (Table 3.5). DMDOHEMA/dodecane appeared better solvent for actinide partitioning as compared to literature $D_{\text{Am}}$ values $[28,31,36,41]$ of 30% TRPO, 1M DMDBTDMA. On the other hand, 0.1 M TODGA and 0.2 M TEHDGA are distinctly better extractants for actinide partitioning from high-level waste solutions.

**Table 3.5:** Comparison of Am(III) extraction by different extractants with DMDOHEMA, $T = 25 \pm 2 \, ^{\circ}C$

<table>
<thead>
<tr>
<th>Extractant</th>
<th>$D_{\text{Am}}$ at 3M HNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M DMDOHEMA in $n$-dodecane</td>
<td>15.5</td>
</tr>
<tr>
<td>30% TRPO in Kerosene</td>
<td>0.8</td>
</tr>
<tr>
<td>1M DMDBTDMA in $n$-dodecane</td>
<td>10</td>
</tr>
<tr>
<td>0.1M TODGA + 0.5M DHOA in $n$-dodecane</td>
<td>300</td>
</tr>
<tr>
<td>0.2M TEHDGA in + 30% (v/v) iso-decanol in $n$-dodecane</td>
<td>100</td>
</tr>
</tbody>
</table>

3.5. **Conclusion**

A modified synthesis route has been developed for DMDOHEMA with better yield compared to conventional methods. This method can be applied to synthesize several other diamide compounds with varying alkyl substituents. Ligand variation studies suggested that extracted Am(III), and Np(IV)/Pu(IV) cations form disolvated and trisolvated extracted species, respectively. DMDOHEMA was also evaluated for actinide partitioning under SHLW conditions. DMDOHEMA extraction values for An(III) and Ln(III) are high enough for their quantitative extraction under SHLW conditions. The nature of mineral acids (viz. HCl, HNO$_3$, and HClO$_4$) had a prominent effect on the extraction profiles of Am(III) using these diamides. The $D_{\text{Am}}$ values followed the order: HClO$_4$ > HNO$_3$ > HCl which was explained in terms of the aggregation of diamide molecules. Our findings suggested the possible application of the present solvent system for the partitioning of actinides from HLW solution.

3.6. **References**


