Design and synthesis of novel organic molecules for the selective extraction of metal ions from complex chemical matrices

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BHABHA ATOMIC RESEARCH CENTRE, MUMBAI

A thesis submitted to the Board of Studies in Chemical Sciences

In partial fulfillment of requirements for the Degree of

DOCTOR OF PHILOSOPHY

of

HOMI BHABHA NATIONAL INSTITUTE



December, 2018

Homi Bhabha National Institute

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DECLARATION

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I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

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List of Publications arising from the thesis

Journals

- "Evaluation of several novel diamide based ligands for selective extraction of tetravalent plutonium", Mallampalli Sivaramakrishna, Dhaval R. Raut, Sandip K. Nayak, Shashikant K. Nayak and Prasanta K. Mohapatra, *Radiochim. Acta*, 2017, 105(4), 303-310.
- "Unusual selective extraction of Pu⁴⁺ by some novel diamide ligands in a room temperature ionic liquid", Mallampalli Sivaramakrishna, Dhaval R. Raut, Shashikant Nayak, Sandip K. Nayak, Prasanta K. Mohapatra, Separation and Purification Technology, 2017, 181, 69-75.
- "Selective pertraction of plutonium(IV) from acidic feeds across PTFE flat sheets containing diamides with a tri-aryl-pyridine (TAP) Centre ", M. Sivaramkrishna, D.R. Raut, S.K. Nayak, S.K. Nayak, P.K. Mohapatra, *Journal of Environmental Chemical Engineering*, 2019, 7 (2), (Article number 102929).
- "Extraction of plutonium(IV) from acidic feeds using several diamides with a tri-phenyl pyridine centre", ", M. Sivaramkrishna, D.R. Raut, S.K. Nayak, S.K. Nayak, P.K. Mohapatra, *Journal of Radioanalytical and Nuclear Chemistry*, 2019, *320 (1)*, 245-253.

Conferences

 "Synthesis of New Metal Extractants with Preorganized Coordinating Sites".
Sivaramakrishna Mallampalli, S. K. Nayak, S. K. Nayak, P. R. Mohanty, Separation Science and Technology (SESTEC), 2014. 2. "DESIGN AND SYNTHESIS OF A NEW CLASS OF DIAMIDES FORSELECTIVE EXTRACTION OF PLUTONIUM", Sivaramakrishna Mallampalli, Sandip K. Nayak, Amar Kumar, D. Raut, P. K. Mohapatra, S. K. Nayak, Separation *Science and Technology (SESTEC)*, 2016.

 "Selective Extraction of Pu(IV) by Several Substituted Diamide Ligands
Dissolved in a Room Temperature Ionic Liquid", Sivaramakrishna M., D. R. Raut, S.
K. Nayak, S. K. Nayak, P. K. Mohapatra, Nuclear Chemistry and Allied Research (NUCAR), 2017.

4. "Selective Separation of Plutonium Using Flat Sheet Supported Liquid Membrane Employing Novel Diamide Ligand", **Sivaramakrishna Mallampalli**, S. K. Nayak, D. R. Raut, *Separation Science and Technology (SESTEC)*, **2018**.

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Dedicated to.....

Jagannath Swamy, Puri through my beloved parents Shri Ecoramasidhudu Ayyavaru Mallampalli and Smt. Surya Bhaskaram Mallampalli

ACKNOWLEDGEMENTS

I am very much grateful to my research guide Dr. S. K. Nayak for support and encouragement in completing this work and for giving me an opportunity to pursue various organic synthesis works. I cherish the moments during our discussions on the subject. I could have a flavor of organic synthesis because of him. I am very much thankful to Dr. P. K. Mohapatra who taught me the solvent extraction part for this work and given me the research experience of this wide spread field. I thank Shri S. K. Nayak for the immense support and encouragement. I thank him for the interest taken during pursuing this work. I am thankful to Dr. Sharmila Banerjee for the kind support. I thank Dr. S. K. Ghosh for the valuable suggestions and encouragement. I thank Dr S. Chattopadhyay and Dr. P. K. Pujari for encouragement and support. I thank Dr. Dhaval Raut for being with me and helping me during my works moreover for the good company with cherishing moments. I thank Dr. K. Sudarshan and Dr. Anupam Mathur for helping in my works. I thank Dr. A. K. Tyagi and Dr. Amar Kumar who supported me and given uplift to my hopes. I thank Dr. Smita Manohar and Shri Prabhakar for encouraging me. I express my sincere gratitude to Shri S. P. Pattanaik, Shri P. R. Mohanty, Shri A. L. N. Rao, Shri Rajnish Prakash, Shri M. Bhaskaran and Dr. Kamachi Mudali of Heavy Water Board for allowing me to continue my research work.

I am grateful to my teachers particularly Shri N. Govindarajan for the love and affection. I thank Shri G. V. Rao, Shri P. Surynarayana, Shri S. Venkateswarulu, Shri Kumar, Shri Nagesh and many all who inspired me starting from my school.

I thank my beloved friends Arunashish, Nitika, Soumyaditya, Dibakar, Kshama, Sucheta, Mrunesh, Manoj, Bhaskar, Trilochan, Shankar, Shitaljit, Seraj, Avinash, Amol and Rajesh. I specially thank Smrutilipi Mohanty, the inspiration for me at all times.

I thank Sudip Gorai, B. Deepak, R. Krishna Mohan and K. Tarakaram for being with me at all times during the completion of this work. I thank all the members of BOD, BARC each one by name for their support. I am thankful to Premjit Singh, C. P. Sahu, Veerendranath, Pradip, Jagannath, Kunal, Sandeep, Venkateswarulu, Anitha, Ramachadra Rao, Srilata, Hemanth, Raghuram, Srikant, Koteswara Rao, Bhagylaxmi, V. Sudhakar, Visweswara Rao, Dwivedi, Parimal, Ganesh, Alpesh, Sasmita, Tapas, Pragyanditi, Sharmaji and Ananya for their moral support. I thank J. A. Modal, Mr. & Mrs. K. V. Pinakapani, and S. Subrahmanyam. I express my gratitude to my beloved brother, Shri M. Mrithyunjayudu and his family, my sister, Smt. T. Uma and her family for their love support.

I sincerely share that this work got to completion with the immense support from various people and here sincerely expressing my gratitude to all of them.

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SYNOPSIS

The doctoral work comprises the synthesis of a new class of diamide ligands and evaluation of their potential in selective extraction of plutonium(IV) from aqueous nitric acid solutions. The work is divided into six chapters.

CHAPTER-1: GENERAL INTRODUCTION

The ever-increasing demand for power with increase in Indian population and modern lifestyle foresee the nuclear energy as the clean and alternative source of energy. The limitations with naturally occurring fuel resources are the large environmental hazard with huge amounts of subsequent waste and the difficulty in scale up to meet large power demands. Nuclear energy is an environment benign process with proper fuel recycling/waste management methodologies as the quantities of waste generated are quite small. The problems in Nuclear fuel sustenance due to limited resources of nuclear fuel and the options to address it like fuel reprocessing and utilization of thorium are envisaged in the vision of Shri Homi J. Bhabha as Three Stage Nuclear Power Program in India. Globally, PUREX process is used for extraction of unused uranium and plutonium from spent fuel using TBP as solvent. The raffinate left over is the High Level Waste (HLW). To reduce the volume and long-term radiotoxicity of HLW employing partitioning and transmutation of minor actinides while the cost of energy production remains economically viable is of current interest. As the present work comprises selective separation of plutonium, it is of relevance to consider its chemical aspects and uses.

The element plutonium (Pu) first produced in experiments by Glenn Seaborg (1940) occupies a unique place in the history of Science and Technology. Plutonium has been separated in ton quantities at industrial scale facilities. The chemistry of plutonium (Pu) occupies a great role in nuclear fuel production for power reactors, spent nuclear fuel

processing, strategic and non-proliferation purposes, nuclear waste disposal, and environmental monitoring. Radioisotope Thermoelectric Generators (RTG) use ²³⁸Pu as an isotope heat source and an energy conversion system to transform the heat produced in the decay of afore said isotope into electricity. Different extractants like organophosphorous reagents, monoamides, diamides, carbomoymethylphosphine oxides (CMPO), glycolamides, organophosphorous compounds with thio groups, polyaromatic compounds with nitrogen donor atoms like terpyridine, triazene etc. and their mixtures with decanoic acid or other neutral extractants, bipyridines and phenanthroline units with the tethered amide groups are being explored for their use in nuclear fuel reprocessing. Among these interesting and promising classes of ligands are polyaromatic nitrogen donor structures anchored with metal binding amide ligating groups. This class of compounds and their selectivity towards metal ion extraction are being explored in detail. The current work is about the synthesis of a new class of diamides by anchoring amide functional groups to polyaromatic pyridine containing structures and exploring their metal ion separation characteristics in different diluents of varying nature for nuclear applications, the results are as presented in the following chapters.

CHAPTER-2: EXPERIMENT TECHNIQUES

This chapter deals with the different techniques adopted during the study on selective extraction of metal ions including (i) properties of radio tracers used (¹³⁷Cs, ^{85,89}Sr, ^{152,154}Eu, ²³³U, ²³⁹Pu-dominantly ²³⁹Pu, ²⁴¹Am) as well as assaying their purity, (ii) plutonium valence adjustment and purification by HTTA extraction, (iii) method of metal ion equilibration by contacting two phases for its distribution studies, (iv) assay of gamma emitting radio tracers by both gross counting and spectroscopic analysis using NaI(Tl) and HPGe detectors respectively, (v) estimation of alpha and beta emitting radio tracers by liquid scintillation counter, (vi) collection of alpha spectra for radio tracers

present in different liquid phases, (vii) basic working principles of the detectors used in radio tracer assay, and (viii) estimation of the Th, Zr metal ion concentrations by ICP-OES and a brief description of the instrument working principle.

CHAPTER-3: SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF DIAMIDE LIGANDS

Developing ligands with enhanced size/stereo selective metal ion complexation and with optimum combination of hard and soft donor groups is the key factor required for more efficient metal ion separations. The design of the ligands is based on the perspectives from previously reported ligands having different molecular architectures. Extraction selectivity is being achieved with ligand structures having metal ion binding groups tether at specific locations on molecular scaffoldings. Importantly, different molecular scaffolds such as calixarenes, terpyridines, bipyridines, phenanthrolines, catechol, 7-oxabicyclo[2.2.1]heptane, triarylpyridines etc. are used as the central building blocks to impose specific steric constraints resulting in highly metal ion selective extractants. Terpyridines are well known for their selective metal ion binding nature and also for the specific steric orientations they provide to the metal ion binding amide functional groups attached.¹ Functionalised terpyridines are explored due to their selective metal ion binding as electroactive ligands in wavelength selective separations.² Pyridine as a spacer unit with metal binding groups at 2 and 6 positions is reported for selective metal ion complexation. 2,6-Diarylpyridine (DAP) moieties as the scaffoldings are useful in making molecules for metal ion chemo-sensors.^{3,4} In diamides, the alkyl groups on amide nitrogen and are generally asymmetric with one of longer alkyl group and the other of shorter methyl group to reduce the steric hindrance during metal ion binding. Also, the basic character of amide nitrogen influenced by the alkyl/aryl groups plays a big role in selective binding. Furthermore, distances between the coordinating sites, their numbers and nature (soft/hard) also play important roles. It has been observed that steric constraints on metal ion binding sites lend more selectivity to the ligands. Moreover, higher steric constraints may lead to loss in metal ion binding efficiency/characteristics. Keeping these facts into consideration, five different diamide ligands with 2,4,6-triarylpyridiene (L_I-L_{IV}) and 4-*n*-pentyl-2,6-diarylpyridine (L_V) as the central units respectively are perceived, synthesized and properly characterised. The amides synthesized are with long/short and linear/branched combinations of alkyl groups on amide nitrogen to study their effect on selectivity/extraction efficiency towards the metal ions. These classes of ligands are of green nature due to presence of C, H, N and O as the only constituents.

General methods of TAP/DAP moieties synthesis and the reaction mechanisms involved are cited in the literature.^{5,6} With careful modification of the existing protocols, synthesis of basic dihydroxy TAP/DAP scaffolds are accomplished in reasonably good yields. TAP/DAP-diols are synthesized under both by conventional heating and Microwave irradiation using variety of catalysts. Ultimately, the protocol using acetic acid catalyst in DMF solvent at 130^oC is found to be optimal to achieve the products in best yield.

The α -chloroacetamides (**8a-d**) needed for the etherification of phenols are accomplished by the reaction of α -chloroacetylchloride with a variety of symmetric secondary amines such as *iso*-butyl/butyl/octyl/2-ethylhexylamines. Coupling of α -chloroacetamides with TAP/DAP-diol are carried out in presence of K₂CO₃ and potassium iodide (as additive) in acetonitrile affording the desired diamides (L₁-L_v) in good yields (Figure 3.1). The compounds, L₁-L_v are fully characterized by spectroscopic data (IR, NMR, and MS).



Figure 3.1: Synthesis of novel diamide extractants.

The extractants are evaluated for their selective metal ion separation properties both in non-polar and polar diluents (including ionic liquid) having different dielectric and solvating/ complexing properties. The results of extraction are analyzed by the metal ion-ligand complex stoichiometries and their compatibility to diluents natures. Most of reports so far rely on amides with methyl group as one of the substituents on nitrogen to reduce the steric hindrance during metal ion complexation. However, in the present case diamides are synthesized with both long chain alkyl groups on nitrogen to impart higher steric hindrance/better selectivity. The results obtained and the corresponding analyses will be discussed in the following chapters.

CHAPTER-4: EVALUATION OF DIAMIDE LIGANDS FOR SELECTIVE EXTRACTION OF PLUTONIUM(IV) IN MOLECULAR DILUENTS

This chapter describes the Pu(IV) extraction characteristics of the ligands (L_I , L_{II} , L_{III} , L_{IV} and L_V) using (i) nitrobenzene and (ii) *iso*-decanol (ID)-*n*-dodecane (DD) mixture (5 % ID/DD; v/v) as diluents. Selection of proper diluent is an important part in the solvent extraction as extraction characteristics depend largely on its properties. Various types of diluents are used in solvent extraction such as (i) alkanes (*n*-hexane, dodecane etc.), (ii) aromatics (benzene, toluene, nitrobenzene etc.), (iii) ketones (cyclohexanone) and (iv) alcohols (octanol, *iso*-decanol etc.). Extent of radiolysis of

extractants depends on the type of diluents. As an example, nitrobenzene inhibits radiolysis of BTP molecules⁷ and DMSO is an efficient scavenger of hydrated electron generated during radiolysis.⁸

4.1 EVALUATION OF LIGANDS ($L_{I}-L_{IV}$) USING NITROBENZENE AS AN AROMATIC DILUENT.

Previously, diamides with terpyridine central unit are evaluated for their actinide ion extraction properties in diluents like nitrobenzene and octanol.¹ In the present case, we have designed a new class of TAP based diamides (L_I-L_{IV}) having triarylpyridine central unit with inclusion of additional oxygen between TAP and acetamide groups. Although, ligands L_I to L_{IV} are freely soluble in toluene, nitrobenzene, benzene and chloroform their solubility in *n*-dodecane is poor.

The extraction of Pu(IV) in the aromatic diluents is significant and the overall extraction trend for L_I and L_{II} with different diluents is in the order: nitrobenzene >> benzene >> chloroform while the order is marginally changed to nitrobenzene >> toluene >> benzene >> chloroform for L_{III} and L_{IV} . Solutions of ligands L_I-L_{IV} in nitrobenzene diluent (0.1 M) are used in all metal ion extraction studies. The extraction of Pu(IV) from 3 M nitric acid is faster with L_I and L_{IV} (branched chain, ≈ 5 min) and slower with L_{II} and L_{III} (linear chain, ≈ 30 min). The $D_{Pu(IV)}$ values obtained with 3 M HNO₃ feed solution followed the order, $L_{II} > L_I > L_{III} > L_{IV}$ indicating higher extraction efficiency with shorter amide alkyl chain ligands than the longer ones. In both the cases, diamides with linear alkyl chain dominated over the branched ones. For all the four ligands, L_I-L_{IV} , variation patterns of $D_{Pu(IV)}$ and $D_{U(VI)}$ with change in nitric acid concentration (0.5 to 6 N) in aqueous phase are similar. A sharp increase in $D_{Pu(IV)}$ values is observed by changing HNO₃ concentration from 0.5 to 2-3 M beyond which a marginal decrease is noted. Importantly, L_{II} has shown comparatively high $D_{Pu(V)}$ values at all feed

nitric acid concentrations. Gradual increase and attaining saturation at higher acidities is observed for $D_{U(VI)}$ which remains same for all the four ligands. From the separation factors obtained (Table 4.1.1) it is obviated that these ligands are highly selective towards Pu(IV) over Cs(I), Sr(II), U(VI), Am(III), Eu(III) and is higher at 2 to 3 M of HNO₃ concentration. The ligands have shown higher extraction and selectivity for plutonium over Th(IV) and very less extraction for Zr(IV). For both L_I (having *iso*-butyl group) and L_{II} (having *n*-butyl group), the stoichiometry of Pu(IV)-L complex is close to 1:2 by slope analysis method. This indicates higher lipophilicity of the extracted complex thereby higher D_{Pu(IV)}. On the other hand, predominantly 1:1 metal ligand stoichiometry is observed for both L_{III} and L_{IV} resulting in lower values of D_{Pu(IV)}. For stripping of plutonium, 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ solution is used when quantitative stripping (>99.9 %) from the loaded organic extract is achieved in a single contact. The kinetics of stripping is fast for L_{II} and L_{IV} (≈ 10 min) while it is relatively slow for L_I and L_{III} (≈ 30 min) for quantitative stripping. The radiolytic stabilities of L_I-L_{IV} are found to be reasonably good up to an absorbed dose 630 kGy.

Table 4.1.1: Separation factors for Pu(IV) over U(VI), Am(III), Eu(III), Cs(I), Sr(II) with0.1 M L_I - L_{IV} in nitrobenzene solvents from 3 M HNO3 aqueous phase.

Ligand	S.F. _{Pu/U} S.F. _{Pu/M}		S.F. _{U/M}
L _I	89	$>6.23 x 10^4$	>700
$\mathbf{L}_{\mathbf{II}}$	153	>1.07x10 ⁵	>700
$\mathbf{L}_{\mathbf{III}}$	49.4	$>2.47 \mathrm{x10}^4$	>500
L_{IV}	16.5	$>9.9 \times 10^{3}$	>600

Note: M = Am(III) or Eu(III) or Sr(II) or Cs(I)

4.2 EVALUATION OF LIGANDS (L_{III} - L_V) USING A MIXTURE OF iso-DECANOL AND n-DODECANE AS AN ALIPHATIC DILUENT

Long chain aliphatic compounds and their mixtures with long chain primary alcohols as phase modifiers are often the choice as diluents due to their high boiling points, green nature (made of C, H and O only), high flash points, low volatility, nominal cost, less health hazard, ease of availability etc.

Ligands L_I and L_{II} with shorter alkyl chains on amide nitrogen are not compatible with this type of diluents for use in metal ion extractions due to third phase formation on contact with nitric acid. To obviate the problem of low solubility of the TAP based ligands L_I-L_{IV} in aliphatic diluents, a new lipophilic ligand L_V is designed and synthesized using C-4 *n*-pentyl substituted DAP as backbone.

Although benzylic hydrogens in L_V are prone to radiolysis, it is of interest to explore its extraction properties due to more solubility in aliphatic diluents and presence of more basic pyridine nitrogen. Third phase formation not observed on contacting 0.1 M of L_V in *n*-dodecane even with high nitric acid concentrations (8 N) whereas L_I-L_{IV} form third phase at low nitric acid concentrations. Keeping in view of high metal loading conditions in practical applications, studies on L_V also pursued in presence of *iso*-decanol (as a phase modifier).

Consequently, solutions of the ligands $L_{III}-L_V$ in a diluent mixture of 5 % (v/v) iso-decanol in *n*-dodecane (5 % ID/DD) are taken for studying metal ion extraction properties form aqueous nitric acid solutions. The $D_{Pu(IV)}$ values decreased with increasing concentrations of *iso*-decanol due to possible solvation of amide oxygens by the modifier or the increased extraction of nitric acid competing with metal ion. The uptake of Pu(IV) is high for all the three ligands $L_{III}-L_V$. Time to reach equilibrium during Pu(IV) extraction is in the order L_{IV} (\approx 30 min) > L_{III} (\approx 15 min) > L_V (\approx 5 min). The $D_{Pu(IV)}$ values obtained with 3 M HNO₃ followed the trend: $L_{III} > L_V > L_{IV}$. For, L_{III} and L_V , variation patterns of $D_{Pu(IV)}$ with change in nitric acid concentration (0.5 to 6 N) in aqueous phase are similar whereas for L_{IV} a decrease at higher acidities is observed. The replacement of phenyl group of L_{III} with *n*-pentyl group to afford L_V resulted in fall of $D_{Pu(IV)}$ values and an increase in $D_{U(VI)}$.

For L_{III} - L_V , stoichiometry of Pu(IV)-L complex is found close to 1:2 by slope analysis method indicating presence of more than one species with 1:2 as a predominant entity along with minor amount of 1:1 complex. As expected, facile extraction of more lipophilic complexes $Pu(NO_3)_4(L)_2$ with $L_{III}-L_{IV}$ ligands to aliphatic diluent in comparison to nitrobenzene observed. Among the different combinations of reagents used of plutonium from the loaded organic for stripping phase, such as (i) 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃, (ii) 0.5 M Hydrazine + 0.5 M HNO₃, (iii) 0.5 M sulphamic acid + 0.5 M HNO₃ and (iv) 0.5 M oxalic acid, the first one is found to be most efficient. With the reagent (i), kinetics of plutonium stripping from its complexes with L_{IV} and L_{V} is relatively faster as compared tothat of L_{III} . Also, high separation factors for Pu(IV) over Cs(I), Sr(II), Eu(III), U(VI), Am(III), Zr(IV) and Th(IV) are obtained. The selectivity towards Pu(IV) over U(VI) and Am(III) is confirmed by alpha spectroscopy. The other elements ^{85,89}Sr(II), ¹³⁷Cs(I), ^{152,154}Eu(III) are monitored using gamma ray spectroscopy. Ligands shown high selectivity for trace amount of Pu(IV) over Nd(III) and U(VI) at g/L concentrations from aqueous nitric acid feed solutions (Table 4.2.1). After three cycles of operations, the efficiency of the solvents did not change during extraction (3 M HNO₃) and stripping (0.5 M NH₂OH + 1 M HNO₃).

Table 4.2.1: Solvent selectivity studies of L_{III} - L_V at 0.1 M concentration in 5 % ID/DD diluent from aqueous 3 M HNO₃ solutions containing plutonium at trace level and Uranium/Neodymium at relatively higher concentrations.

Ligand	DPu(IV) at 3 M HNO3DPu(IV) atFeed Nd concentration g/LFeed U concentration g/L		(IV) at 3 M H J concentrati	at 3 M HNO ₃ ncentration g/L		
	0.1	1	5	0.1	1	10
L _{III}	15.7 ± 0.7	17.5 ± 0.4	19.1 ± 1.89	14.9 ± 0.00	14.8 ± 1.20	19.2 ± 0.17
L_{IV}	10.3 ± 0.00	11.8 ± 1.00	12.8 ± 0.70	10.8 ± 0.16	11.2 ± 0.19	10.3 ± 0.06
L_{V}	11.7 ± 0.00	9.81 ± 0.64	14.7 ± 0.90	13.5 ± 1.88	12.2 ± 1.26	8.23 ± 0.45

CHAPTER-5: EVALUATION OF DIAMIDE LIGANDS (L_1-L_{IV}) IN RTIL $([C_8mim][Tf_2N])$ AS DILUENT FOR SELECTIVE EXTRACTION OF PLUTONIUM(IV)

Use of large volume of volatile organic compounds is of environment concern due to their detrimental effects on global atmosphere. To this end, effort has been made to develop green solvents in reducing the ecological risks.⁹ The possible ways of implementing the methodologies as green technology are (i) water as a solvent for synthesis, (ii) solvent free methods, (ii) use of supercritical fluids, and (iv) use of Room Temperature Ionic Liquids (RTIL) as solvents. The commonly used ILs are composed of alkyl imidazolium, pyridinium, quaternary ammonium etc. as cations and $[Tf_2N]^-$ (bis-trifluormethanesulfonimides), BF₄⁻ etc as anions. For the applications in solvent extraction an important requirement for RTILs is their water insolubility. Though the discovery of RTIL's dates back to 1914 their application to areas such as metal ion extraction is as late as 1990s. Visser et al.¹⁰, reported the extraction of actinide ions with a solution of CMPO in C₄mimPF₆, an RTIL with relatively high viscosity. In the present study of metal ion extraction, the ionic liquid N(n-octyl),N'(methyl)imidazolium trifluoromethanesulphonimide abbreviated as [C₈mim][Tf₂N] is used.

As observed in previous chapter, the ligand L_V obtained by the replacement of phenyl group of L_{III} with a pentyl group did not work as per our expectation, and accordingly no further study was carried out with L_V . For solvent extraction studies, 0.05 M solutions of each of the ligands L_I-L_{IV} in [C₈mim][Tf₂N] are used for extraction of Pu(IV) from 3 M nitric acid feed solutions. The extraction kinetics is fast. The extraction efficiency of the ligands for Pu(IV) is in the order: $L_{III} > L_{II} > L_I >> L_{IV}$. Ligands with linear and longer alkyl chain substitution on amide nitrogen have shown higher $D_{Pu(IV)}$ whereas in nitrobenzene diluent it is ligands with shorter and linear alkyl chain ($L_{II} > L_I > L_{III} > L_{IV}$). This is attributed to difference in stoichiometry of Pu(IV)-L complexes and their interactions with diluents. The solubility of more ligand solvated metal ion complexes is limited in RTIL in comparison to either nitrobenzene or 5 % ID/DD diluents due to its more polar nature/dielectric constant.

For all ligands $L_{I}-L_{IV}$, $D_{Pu(IV)}$ and $D_{U(VI)}$ values increase with increase in concentration of nitric acid in the aqueous phase with $D_{Pu(IV)} >>> D_{U(VI)}$. In contrast to the results with nitrobenzene/5 % ID/DD, the $D_{Pu(IV)}$ values did not fall/stabilize even at higher acidity using ionic liquid as diluents. [C_8 mim][Tf₂N] without dissolved ligand also has displayed considerable pick of Pu(IV) at 6 M HNO₃ by anion exchange mechanism. From the slope analysis experiments, the stoichiometry of extracted Pu(IV)-L complex is found to be 1:1.

For the ligands, L_{III} and L_{IV} the extraction mechanism is same both in nitrobenzene and RTIL with 1:1 stoichiometry which changed to 1:2 using 5 % ID/DD as

diluent. For the other ligands L_I and L_{II} , stoichiometries of plutonium complexes in nitrobenzene and RTIL diluents are found to be 1:2 and 1:1 respectively. 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ aqueous solution is used for stripping of Plutonium. The extraction selectivity towards Pu(IV) over other ions can be felt from the metal ion distribution ratio values mentioned in Table 5.1.

Table 5.1: Extraction of actinides and fission product metal ions employing L_I-L_{IV} at 0.05 M concentration in [C₈mim][NTf₂]. Aqueous phase: 3 M HNO₃.

Ligand	Distribution ratio for the metal ion					
	Pu(IV)	U(VI)	Am(III)	Eu(III)	Cs(I)	Sr(II)
L	12.9 ± 0.1	0.031 ± 0.001	< 1 x 10 ⁻⁴	$< 6.5 \text{ x } 10^{-4}$	0.014 ± 0.001	< 1 x 10 ⁻⁴
$\mathbf{L}_{\mathbf{II}}$	15.2 ± 0.1	0.035 ± 0.001	< 1 x 10 ⁻⁴	< 8.3 x 10 ⁻⁴	0.010 ± 0.000	< 1 x 10 ⁻⁴
$\mathbf{L}_{\mathbf{III}}$	17.9 ± 0.0	0.036 ± 0.000	< 1 x 10 ⁻⁴	< 1.4 x 10 ⁻³	0.011 ± 0.001	< 1 x 10 ⁻⁴
L _{IV}	4.27 ± 0.0	0.046 ± 0.001	< 1 x 10 ⁻⁴	$< 2.0 \text{ x } 10^{-4}$	0.11 ± 0.01	< 1 x 10 ⁻⁴

CHAPTER-6: EVALUATION OF DIAMIDE LIGANDS (L_{III} AND L_V) FOR SELECTIVE SEPARATION OF PLUTONIUM(IV) USING FLAT SHEET SUPPORTED LIQUID MEMBRANE

The low initial design and capital costs, low energy consumption for operation and the high separation factors achievable with membrane technology makes it highly attractive methodology for large scale operations. Requirement of small quantities of solvent make Supported Liquid Membrane (SLM) technique a very attractive one and acted as a better alternative to classical solvent extraction.¹¹ As both extraction and stripping proceed simultaneously the solvent won't get to saturation conditions and the

requirement of solvent becomes very less. This low solvent inventory makes the process highly economically viable at the same time generating very low quantities of secondary solvent waste after the usable life cycles of the Liquid Membrane (LM). Liquid membrane technology can be broadly classified as (i) Bulk Liquid Membranes (BLM), (ii) Emulsion Liquid Membranes (ELM) and (iii) Supported Liquid Membranes (SLM). For FSSLM studies, 0.1 M solutions of each of the ligands L_{III} and L_V in 5 % ID/DD are used as liquid membranes over PTFE flat sheet supports (pore size = $0.45 \mu m$; porosity = 72 %; nominal thickness = 85 μ m). Among the different combinations of reagents used for stripping of plutonium from the loaded organic phase, such as (i) $0.5 \text{ M} \text{ NH}_2\text{OH}.\text{HNO}_3 + 0.5\text{M} \text{ HNO}_3$, (ii) $0.5\text{M} \text{ Hydrazine} + 0.5\text{M} \text{ HNO}_3$, (iii) 0.5 M oxalic acid, the first one is found to be most efficient. There is a steady decrease in plutonium transport rate with the decreasing concentration of ligand in SLM. For FSSLM, the permeability coefficients increased almost linearly with the increase in ligand concentration indicating transport of plutonium through membrane mainly by diffusion process. From a 3 M HNO₃ feed solution of ²³⁹Pu (major isotope), ²³³U, ²⁴¹Am, ^{152,154}Eu, ¹³⁷Cs, ^{85,89}Sr (all in trace level), a selective transport of Plutonium through LM (0.1 M L_{III} in 5 % ID/DD) supported on PTFE flat sheet to the receiver solution (0.5 M NH₂OH + 1 M HNO₃) took place (Figure 6.1). However, a decrease in FSSLM stability is observed during the recycles which may be due to loss of LM form the support.



Figure 6.1: Alpha spectrum for Feed (at t = 0) and Receiver solution (t = 330 min). γ -Spectrum of (a) feed phase stock (b) feed phase at 180 min (c) receiver phase at 180 min and (d) feed phase at 330 min (e) receiver phase at 330 min.

CHAPTER-7: SUMMARY, CONCLUSIONS AND FUTURE PERSPECTIVES.

A new class of diamide ligands (L_I-L_V) with TAP/DAP backbone are designed and synthesized which have displayed high selectivity in extraction for Pu(IV). The efficiency of the synthesized diamides towards selective separation of plutonium has been screened using molecular diluents, ionic liquids and supported liquid membranes. From the observed data it is concluded that straight chain amide ligands are more efficient than branched ones. The ligand L_{II} in nitrobenzene and L_{III} in 5 % ID/D and $[C_8 mim][Tf_2N]$ diluents shown very high selective and efficient extraction of plutonium. L_{III} is a promising ligand for selective separation of plutonium form a mixture of U(VI), Am(III), Eu(III), Sr(II) and Cs(I) in nitric acid solutions using FSLM. Even among the tetravalent ions Pu(IV), Zr(IV) and Th(IV) the ligand L_{III} (0.1 M in 5 % ID/DD) has shown very good extraction selectivity towards Pu(IV) over the others from 3 M HNO₃ $(D_{Pu}: 15.7 \pm 0.7, D_{Th}: 0.28 \pm 0.02 \text{ and } D_{Zr}: 0.028 \pm 0.025)$. The ligands L_I-L_{IV} have shown good stability towards radiolysis in nitrobenzene diluent. Stripping characteristics for plutonium from the loaded solvents are highly satisfactory with low HNO₃ concentration (0.5 M) in the presence of NH₂OH.HNO₃ as areducing agent. As the diamide ligands with TAP/DAP backbone shown a great promise, there is further scope to
use these exotic backbones in designing other ligands. For example, the two hydroxyl groups in TAP and DAP can be used for making crown ethers for selective extraction of alkali/alkaline earth metal ions.

References:

- C. Marie, M. Miguirditchian, D. Guillaneux, J. Bisson, M. Pipelier and D. Dubreuil, *Solvent Extr. Ion Exch.*, 2011, 29, 292.
- S. R. Salpage, R. C. Lanzetta, Y. Zhou, J. C. Wang, T. E. Albrecht-Schmitt and K. Hanson, *Chem. Commun.*2018, *54*, 7507.
- 3. J. V. Mello and N. S. Finney, Org. Lett. 2001, 3, 4263.
- 4. A. G. Fang, J. V. Mello, and N. S. Finney, Org. Lett. 2003, 5, 967.
- 5. H. Xu, F-J Wang, M. Xin and Z. Zhang, Eur. J. Org. Chem., 2016, 925.
- 6. A. R. Khosropour, I. M. Baltork and F. Kiani, C. R. Chimie, 2011, 14, 441.
- M. Nilsson, S. Andersson, C. Ekberg, M. R. S. Foreman, M. J. Hudson, G. Skarnemark, *Radiochim. Acta*, 2006, 94, 103.
- 8. K. D Asmus and J. H. Fendler, J. Phys. Chem. 1968, 72, 4285.
- 9. P. T. Anastas, Critical Reviews in Analytical Chemistry, 1999, 29, 167.
- 10. A. E. Visser and R.D. Rogers, J. Solid State Chem. 2003, 171, 109.
- 11. R. Marr and A. Kopp, Int. Chem. Eng. 1982, 22, 44.

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Chapter – 1

GENERAL INTRODUCTION

1. General introduction

1.1 Preamble

This chapter discussed (i) the need for inevitable dependence on nuclear power, (ii) need of reprocessing of spent fuel for efficient separation of useful components, (iii) development of waste management/fuel recycling methodologies, (iv) requirement of separation of lanthanides (Ln) and actinides (An), (v) importance of plutonium recovery and its properties, (vi) design/development of solvents for fuel reprocessing, (vii) scope for designing plutonium selective solvents using sterically constrained scaffolds, (viii) overall aim of the thesis leading to synthesis/evaluation of plutonium selective solvents based on triarylpyridine (TAP)/diarylpyridine (DAP) scaffolds.

1.2 Nuclear energy and its need

The ever-increasing energy demands foresee the Nuclear energy as the clean alternative. The naturally occurring fuel resources like coal, oil, natural gas etc. have a limitation of exhaustion with continual burning process for energy needs. Moreover, the large environmental hazard with huge amounts of subsequent waste leftover is alarming. Resources like solar, wind and tidal are attractive alternative but the limitations are (i) feasibility to scale up for large demands of continually increasing population, (ii) ever growing need for electric power and (iii) the need for catering electric power in phase with rate of consumption. It is inevitable to give immense importance for nuclear energy for coping up to the power needs with concurrent prevention of damages to earth's atmosphere. Nuclear energy is an environment benign process with proper fuel recycling/waste management methodologies as the quantities of waste generated are quite small in comparison to fossil fuels generated emissions left to global atmosphere. The current nuclear energy production is by nuclear fission reactions. The attractive part of

nuclear fuel is the large specific power generation through bombardment of fissile nuclei with neutrons of suitable energy.

1.3 Nuclear fuel and sustenance

The natural fissile material contents are small so the major challenges lie in sustaining the nuclear energy program with high efficiency, low cost and minimum risk to the environment. One option being the breeding of fissile nuclei from fertile nuclei the other is opting for a closed fuel cycle program which primarily depends on recycling the spent nuclear fuel to obtain the unspent fissile uranium content and also recovering plutonium, produced by neutron capture reactions, for its subsequent use in fast reactors. For breeding fissile nuclei, the most attractive of option is generation of ²³³U from ²³²Th because of the high abundance of ²³²Th as the single naturally occurring isotope. The issue to be addressed is with the high half life ²³³Pa (about a month) that leads to its further neutron capture reactions in reactors.

$${}^{232}_{90}\text{Th} + {}^{1}_{0}\text{n} \rightarrow {}^{233}_{90}\text{Th} \xrightarrow{\beta^-, 22 \text{ min}} {}^{233}_{91}\text{Pa} \xrightarrow{\beta^-, 27 \text{ d}} {}^{233}_{92}\text{U}$$

The thermal neutron induced fission of the ²³⁵U leads to asymmetric fragmentation, mostly to two fragments (only 0.2 % to 0.3 % to three fragments), the masses of the fragments peaking around 95 (Zr through Pd) and 138 (Xe through Nd). The isotopes produced in fission process are having a greater number of neutrons than the stable isotopes of their corresponding elements and they undergo beta/gamma decay in this respect. Elements from nearly all blocks of the periodic table are produced in the fission process. Apart from fission reaction, the neutron induced transmutation reactions taking place in the fuel lead to the formation of transuranium elements.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U$$

$${}^{239}_{92}U \xrightarrow{\beta^{-}, 23.5 \text{ min}} {}^{239}_{93}Np \xrightarrow{\beta^{-}, 2.36 \text{ d}} {}^{239}_{94}Pu \ (t_{1/2} = 24,110 \text{ y})$$

The isotopic composition of the Pu produced in the reactor depends on the time of exposure to neutron flux. Neutron absorption by ²³⁹Pu leads to higher isotopes of the plutonium (²⁴¹Pu, ²⁴³Pu etc.). These heavier isotopes of plutonium undergo beta decay resulting to the production of transuranium actinide elements Np, Am, Cm etc.. The isotope ²³⁷Pu is formed by the ways

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{236}_{92}U + {}^{1}_{0}n \rightarrow {}^{237}_{92}U \xrightarrow{\beta^{-}}{}^{237}_{93}Np \xrightarrow{(d,2n)}{}^{237}_{94}Pu$$

$${}^{238}_{92}U \xrightarrow{(n,2n)}{}^{237}_{92}U \xrightarrow{\beta^{-}}{}^{237}_{93}Np \xrightarrow{(d,2n)}{}^{237}_{94}Pu$$

$${}^{235}_{93}U \xrightarrow{(\alpha,2n)}{}^{237}_{94}Pu$$

The management of spent fuel is an important issue and many problems need to be addressed. After ten years of cooling period the activity in the spent fuel is dominated by ¹³⁷Cs and the ⁹⁰Sr for up to few hundred years. The other challenging problem is due to the sustaining long-term alpha activity of transuranium actinides ²³⁷Np, ²³⁹Pu, ^{241,243}Am, ²⁴²Cm etc., in spent fuel (Figure 1.1). The spent fuel management methods of either (i) glass vitrification and storing in deep geological repositories or (ii) the transmutation of actinides to isotopes of short half-lives or stable nature in rectors/accelerator facilities, both require initial separation of actinides from spent fuel to decrease the volume of the waste to handle and to tackle the problem with elements of high neutron absorption cross section (lanthanides).



Figure 1.1: Composition of the spent fuel.¹



1.4 Nuclear Power Programme in India



For the effective utilisation of fuel resources and sustainable nuclear power generation, Dr. Homi J. Bhabha envisaged a three-stage nuclear power programme with closed fuel cycle (Figure 1.2). The available resources of uranium at < 130 USD/Kg are zero in India.² This stresses the need for India in adopting closed fuel cycle. This also addresses the problems associated with long term radiotoxicity. The first stage is about natural uranium fuelled Pressurised Heavy Water Reactors (PHWR). The second stage is based on the utilisation of recovered depleted uranium and plutonium form first stage reactor spent fuel for fuelling the Fast Breeder Reactors, which includes simultaneous breeding of ²³³U from ²³²Th blanketing. The third stage reactors are of ²³³U fuelled with ²³²Th blanket for breeding more fuel.

1.5 Actinides (An) and Lanthanides (Ln)

These elements constitute the 'f' block of the modern periodic table. Among the vast diversified chemistry of lanthanides and actinides, the purview of current interest includes

- (i) The interaction with ligands is predominantly by steric and electrostatically controlled for both An and Ln ions as are considered to be the hard acids,³ former being little softer than later.
- (ii) Both the Ln(III) and An(III) ions have similar electronic configuration and size.
- (iii) The coordination numbers are similar
- (iv) The most common oxidation state for both Ln and An ions is +3.

The 5f orbital of the An are more spatially diffused than the 4f orbital of the Ln resulting in their relatively higher softness. This property is useful in selective separation of An from Ln ions with ligands containing both N and S donor atoms. The recent explanation for the selective binding of N and S donor ligands with An than Ln ions is based on the relative energies and symmetries of metal and ligand orbitals.

1.6 Separation methods

Separation methods for reprocessing spent fuel to recover useful components include

- (i) Precipitation
- (ii) Chromatography
- (iii) Solvent extraction or Liquid-liquid extraction (IUPAC)
- (iv) Membrane separations

as aqueous routes and

- (i) Electrorefining of the molten slats
- (ii) Distillation of the fluoride salts Pyrochemical methods.

as non-aqueous routes.^{4,5}

Separation through non-aqueous routes are quite promising for future applications particularly to molten salt reactors where fissile metal fluoride salts dissolved in LiF and BeF_2 mixtures are used as fuel. The present work is on separation methods like solvent extraction and supported liquid membranes that are based on solvent selectivity and efficiency in binding to metal ions. The membrane based separations are of particular interest due to their added advantages of minimum solvent inventory and thereby less secondary waste generation etc. These involve highly selective/efficient separations with minimal capital cost. The details of the various advantages in membrane based separations are discussed in chapter – 6.

1.6.1 Precipitation

Precipitation is the first technology used at plant scale in fuel reprocessing. In the An ions from III to VI valence states all the hydroxide, phosphate and oxalates are insoluble; the fluorides, carbonates are soluble only in VI valence; whereas all the acetates are soluble except that are in VI valence at 1 M of H⁺ ion concentration.⁶ These fore mentioned characteristics also depend on acid content, counter ions, concentration terms, ionic strength, temperature, rate of addition of the regents etc..

The co-precipitation technique was used to separate plutonium from fission products and uranium. These include carriers like LaF₃ and BiPO₄. The process involves multiple of precipitation-dissolution cycles. BiPO₄ process has the feasibility to precipitation at high nitric acid concentrations.

The most common precipitation methods include oxalate, fluoride, hydroxide and peroxide. The oxalate precipitation of Pu(IV) and Pu(III) give Pu(C_2O_4)₂.6H₂O and Pu₂(C_2O_4)₃ respectively. This method suffers poor decontamination from Na, K and none from Am in both the options. Precipitation of Pu(O_2)₂ from acid solutions involves formation of a relatively pure precipitates but it has limitation due to presence of Fe, Cu, Mn or Ni ions that cause catalytic decomposition of H₂O₂. And also, the filterability of the precipitate depends highly on the conditions of precipitation. Even though Am(III) is removed completely it is not good in presence of thorium, neptunium and uranium that

form similar type of peroxide precipitates. To avoid the solubility losses and to obtain filterable precipitate, plutonium is precipitated in its trivalent state rather than tetravalent state. It gives moderate decontamination from impurities like Fe but not from Al, Zr or U. The hydroxide precipitation suffers from the inherent gelatinous nature of the precipitate and is difficult to filter the polymerised compounds.

1.6.2 Chromatography

This technique is generally based on the preferential exchange of ionic species of the same type of charge between the oppositely charged sites on the solid stationary phase and the liquid mobile phase. This distribution is based on relative affinity of stationary phase for different ions leading to lowering of the overall free energy of the system. Both cation and anion exchangers are used. In chelating type of resins, the metal binding groups are anchored to the polymer surface. The other method involves supporting of the metal binding liquid stationary phase in resin beads through encapsulation.⁷ In context to solvents this last technique is of more relevance.

This is an ideal technique for the separation of radio nuclides from a wide range of sample types. In this the advantages of solvent extraction are combined with operational feasibility and simplicity of chromatography. The reagent amounts used are small, the technique is rapid, the risk of cross contamination is removed and the equipments are compact. The three main parts of the technique are the inert solid support, the immobilised extractant and the mobile phase. The column instability is a problem. Bleeding of immobilised extractants from the inert solid support as the mobile aqueous phase transits is an issue that needs attention. The inert supports are in general silica, polymer of styrene and divinylbenzene etc. with the desired characteristics of rigid three dimensional structure, high specific area to incorporate more amounts of solvent, high mechanical strength and low swelling during solvent impregnation. The stationary

phase is in general same as the solvent mix of the liquid-liquid extraction. The impregnation of the stationary phase in inert support is done by different methods; wet impregnation, dry impregnation, modifier addition and the dynamic column method. During impregnation process the extractant fills the pores and then also adsorbed on the surface of the inert support through weak forces of physical interaction between the alkyl chains/aromatic rings of the extractant and the inert surface. This resin is packed in to chromatographic column for taking to application. The mobile phase is the nitric acid/hydrochloric acid or oxalic acid or any other selective complexing agents. Figure 1.3 shows the elution profile of a typical chromatogram. V_m is the volume of mobile phase in the column and V_R is the retention volume. The net retention volume V'_R is given by

$$V_{\rm R}^{\prime} = V_{\rm R} - V_{\rm m}$$

The retention (capacity or relative retention) factor is defined as

$$K^{R} = \frac{V_{R} - V_{m}}{V_{m}} = D.\frac{V_{s}}{V_{m}} = \frac{D}{\beta} = \frac{m_{s}}{m_{m}}$$

It is the number of mobile phase volumes of the column required to reach the elution peak maximum. Whereas β is the volume phase ratio and m_s , m_m are the equilibrium masses of component in the stationary and mobile phases respectively.

If W_r weight of resin and V_a volume of aqueous solution with a known concentration C_0 (or activity A_0) of solute is equilibrated by shaking together and if C_a (or activity A_a) is the equilibrium concentration of the aqueous phase, then the distribution of the solute between the two phases D_w (weight distribution ratio) is defined as

$$D_{w} = \frac{m_{s}}{m_{a}} \cdot \frac{V_{a}}{W_{r}} = \frac{(C_{0} - C_{a})}{C_{a}} \cdot \frac{V_{a}}{W_{r}} = \frac{(A_{0} - A_{a})}{A_{a}} \cdot \frac{V_{a}}{W_{r}}$$



Figure 1.3: Typical chromatogram for column elution of a component.

The D value analogous to solvent extraction is given by

$$D = D_w \cdot \frac{W_r}{V_s}$$
 and $K^R = D \cdot \frac{V_s}{V_m} = D_w \cdot \frac{W_r}{V_m}$

The separation factor SF defined as D_2/D_1 and is given by

$$SF = \frac{D_2}{D_1} = \frac{K_2^R}{K_1^R} = \frac{V_{R2} - V_m}{V_{R1} - V_m}$$

The acid dependence of D_w can be used to select the suitable acidity of the mobile phase to attain better separations.

1.6.3 Solvent extraction

Solvent extraction is based on the distribution of a component between two immiscible liquid phases leading to lowering of overall free energy of the system. The distribution is decided by the equilibration parameters. To aid attaining of equilibrium faster, the two liquids are mixed intimately to increase the interfacial area and thereafter left for separation in to two phases by coalescence of the liquid drops. To increase distribution of the non-polar extractant-metal ion complex to the organic phase by removing any solvating water molecules present in it, salting out agents like Al(NO₃)₃ etc. are added that decrease the activity of water. The separated two liquid phases are isolated. The component of interest is separated from the loaded organic phase by contacting with an aqueous phase, called stripping agent, now the distribution equilibrium being more favourable towards the aqueous phase. The quantification of the

equilibrium is by a parameter called Distribution coefficient (D) which is a ratio of the concentration of component in lighter face to the concentration in heavier phase.

The two immiscible phases in general are an aqueous acid solution and the organic solvent.

$$D = \frac{[M]_{org}}{[M]_{aq}}$$

where $[M]_{org}$ and $[M]_{aq}$ are the concentrations of the metal ion of interest in organic and aqueous phase respectively, irrespective of the form in which it is present.

The partition or extraction coefficient is defined as

$$D_{EC} = \frac{M_{org}}{M_{aq}}$$

where M_{org} and M_{aq} are amounts of the metal ion of interest in organic and aqueous phases respectively, irrespective of the form in which it is present. The decontamination factor is defined as

$$DF = \frac{M_t}{M_{aq}} = \frac{[M]_{org}}{[M]_{aq}} \cdot \frac{V_{org}}{V_{aq}} + 1$$

 M_t is the total amount of metal ion in both (organic and aqueous) phases and V_{org} , V_{aq} are the volumes of the organic and aqueous phases respectively. Another important parameter is the selectivity, denoted by separation factor (SF)

$$SF = \frac{D_{Species of interest}}{D_{impurity}}$$

The acid solutions in general are of nitric acid in nuclear fuel reprocessing. The organic solvent phase contains generally three components namely Diluent, Extractant and Phase modifier. Among these only one (extractant) or combinations of two (extractant and diluent) or all the three may be present in the organic phase depending on the requirement of process conditions. Phase modifiers are used for the better solubility of

metal-extractant complex in diluent phase. The metal ion complexing may be by one or a combination of two extractants. Acidic extractants are used commonly in combination with neutral extractants that act as phase modifiers. The neutral extractant molecules replace water molecules in coordination sphere (primary or secondary) of the metal ion-ligand complex of acidic extractants lending them more solubility in the diluent phase. If the D value for the species of interest with the combined extractant system is higher than the sum of the individual D values with each extractant separately, under the identical experiment conditions, then is called synergism and the converse of it as antagonism.

$$D_{AB} > D_A + D_B$$
 (Synergism)
 $D_{AB} < D_A + D_B$ (Antagonism)

The metal extractants can be classified in to four basic categories

- (i) Solvating or neutral type (TBP etc.)
- (ii) Acidic or cation exchange type (D2EHPA etc.)
- (iii) Basic or anion exchange type (Alamine 336, Aliquat etc.)
- (iv) Chelating type (acetylacetone, TTA, LIX etc.)

The extraction mechanism may involve (i) the solvation of neutral metal salt species by the extractant molecules in diluent phase or formation of reverse micelles by the extractant molecules with the metal species at centre or (ii) an ion pair formation between the extractant and the ionic metal salt species or (iii) chelation of the metal ions by the multidentate ligands.

Diluents play a major role on both efficiency and selectivity in metal ion extractions. Molecular diluents used in different extraction procedures are both aromatic and aliphatic in nature. In case of aliphatic diluents, long chain hydrocarbons are preferred due to their less toxicity, volatility and high boiling point etc. Currently, ionic liquid based diluents have received much attention due to their various beneficial attributes over conventional molecular diluents such as low volatility, high boiling point, and tuneable nature of their properties etc. However, their use at large scale is limited by high cost and non-availability of data on industrial processes for scale-up applications. The details on these diluents are discussed in Chapter – 4.

The process types for contacting the solvent and aqueous phases in multiple stages to achieve optimum separation and purification of the species of interest are (i) cross current, (ii) co current and (iii) counter current. Among these the counter current conditions give better recovery and higher separations of the required species with optimum amount of solvent.

Solvent extraction is the basic technique of separation science that is studied at large in industrial scale facilities and is the versatile technique with various types of contacting equipments like (i) mixer settlers, (ii) centrifugal contactors, (iii) pulsed columns, (iv) rotating disc contactors and (v) asymmetric rotating disc contactors for ease in scale up. Till now the most widely used technique across the world for nuclear fuel reprocessing is liquid-liquid extraction.

1.7 Spent fuel management

By 2020 the total quantity of spent fuel generated will be approximately 445000 tHM (world wide).² The central goal of nuclear sustainable development is (i) to enhance the effectiveness of natural resource utilization, (ii) to reduce the volume and long term radiotoxicity of high level waste employing partitioning and transmutation of minor actinides, (iii) to remain the cost of energy production economically viable. The burning of minor actinides in specially designed reactors will lead to increased production of power per gram of uranium.



Figure 1.4: Typical radiotoxicity profiles of components in spent fuel.

The backend of the fuel cycle can adopt any of the following strategies

- (i) Direct disposal in once through cycle. Vitrifying in glass matrix and storage in deep geological repositories
- (ii) Storing in near surface repositories and wait for the further decision.
- (iii) Reprocessing and recycling in closed fuel cycle. Portioning of long-lived minor actinides and transmuting them in dedicated accelerators/reactors to short lived/stable isotopes or burning them in reactors.

The closed fuel cycle has distinct advantages of effective utilisation of natural resources, minimising the waste and thereby minimising the environmental effect and decreases the hazards of long-term radiotoxicity. The long-term decay heat release and radiotoxicity of the spent fuel are shown in Figure 1.4.

1.7.1 PUREX (Plutonium Uranium Redox Extraction) process

PUREX (Plutonium Uranium Redox Extraction) process uses 20-30 % (v/v) tributylphosphate (TBP) in aliphatic hydrocarbon diluent as the solvent that separates uranium and plutonium from the spent fuel fission products at around 3 N HNO₃ (Figure 1.5).^{8,9} Plutonium in loaded solvent is then separated from uranium by reducing it

from Pu(IV) Pu(III) using ferrous to non-extractable by а sulphamate/hydroxylamine/U(IV) etc.. Uranium is stripped from the solvent by using acidified water (dil. HNO₃). In this process using multiple stages, pure products of uranium and plutonium are recovered. The leftover raffinate from the extraction circuits is labelled as HLW (High Level Waste) and sent for waste management. This HLW then undergoes partitioning process as a part of recovering valuable isotopes like ⁹⁹Mo, ¹³⁷Cs etc. and for waste management schemes. Bulks of the fission products (FP) have very low D values exceptions to zirconium, ruthenium and technetium. The lanthanides (Ln) and the minor actinides (minor An: ²⁴¹Am, ²⁴⁴Cm, ²³⁷Np) along with other isotopes ⁹⁹Tc, ¹²⁹I, ⁷⁹Se, ⁹³Zr, ¹³⁵Cs that are of importance from radiotoxicity point of view are retained in the HLW and are subjected to further partitioning.





The Ln and the fission products in the HLW have high neutron absorption cross sections, so it is required to separate them from before going for An transmutation. No process till now exists that separates actinides directly from the spent fuel. The common strategies involve the separation of Ln and Anions together from the PUREX raffinate and there by separating the mixture into An and Ln portions. As the present workis primarily on plutonium, the element that has set a milestone in nuclear history, it is of relevance to consider its chemistry in brief.

1.7.1.1 Plutonium

The element plutonium (Pu) occupies a unique place in the history of science and technology. Plutonium is first produced in experiments by Glenn Seaborg (1940), McMillan, Kennedy, and Wahl by bombarding uranium with deuterons to produce ²³⁸Pu

$${}^{238}_{92}\text{U} + {}^{2}_{1}\text{D} \rightarrow {}^{238}_{93}\text{Np} + 2 {}^{1}_{0}\text{n}$$
$${}^{238}_{93}\text{Np} \xrightarrow{\beta^{-}, 2.1 \text{ d}} {}^{238}_{94}\text{Pu} (t_{1/2} = 87.7 \text{ y})$$

²³⁸Pu is also produced by the following reaction

$${}^{237}_{93}\text{Np} + {}^{1}_{0}\text{n} \rightarrow {}^{238}_{93}\text{Np} + \gamma \xrightarrow{\beta^{-}}{}^{238}_{94}\text{Pu}$$

The other reaction that gives ²³⁸Pu is

$$^{242}_{96}\text{Cm} \xrightarrow{\alpha} ^{238}_{94}\text{Pu}$$

The Pu produced in the above nuclear reactions is separated from Np and Cm respectively by ion exchange chromatography and other techniques.¹⁰

The plutonium available in natural sources is mainly from manmade origin, two other isotopes that are in nature are ²³⁹Pu and ²⁴⁴Pu, the former arising from the nuclear reactions taking place in the uranium geological deposits and the later existing from the primordial times. Hoffman did mass spectroscopic measurements of plutonium separated from Precambrian bastnasite that confirmed the presence of ²⁴⁴Pu in nature, though existence of ²⁴⁴Pu as an extinct radioactivity has been postulated to explain the xenon isotope ratios in observed in meteorites, this is the fist indication of its existence in nature.¹¹ Plutonium has been separated in ton quantities at industrial scale facilities. The immense interest in plutonium production resulted from its dual role in both domestic power production and strategic utilities. The chemistry of plutonium (Pu) occupies a great role in (i) nuclear fuel production for reactors, (ii) spentnuclear fuel processing, (iii) nuclear waste disposal and (iv) environmental monitoring. Radioisotope Thermoelectric

Generators (RTG) use ²³⁸Pu as an isotope heat source and an energy conversion system to transform the heat produced in the decay of afore said isotope into electricity. The same isotope was used as a source of power in cardiac nuclear pacemakers and not in use at present. Another important area of application for ²³⁸Pu is in the Space Nuclear Auxiliary Power (SNAP) units, Multi Hundred Watt Radioisotope Thermoelectric Generators (MHW-RTGs), General Purpose Heat Source Radioisotope Thermoelectric Generators (GPHS-RTGs) and Light Weight Radioisotope Heater Units (LWRHUs) to power satellites and other instruments that are far away in space. These systems were used as power sources for instrument packages on the five Apollo missions to the Moon, the Viking unmanned Mars Lander, and the Pioneer and Voyager probes to the outer planets (Jupiter, Saturn, Uranus, Neptune and beyond).¹²

Plutonium is in the mid of the actinide series that reflects the presence of 5f valence electrons. The unique behaviour of the valence states of this element poses challenges towards the understanding of the chemical bonding in heavy metals. Plutonium shows multiple valences as shown in Figure 1.6, with complexing abilities ordering as

$$Pu^{4+} > Pu^{3+} \cong PuO_2^{2+} > PuO_2^{+}$$

The relative complexing ability of VI and III valence states depends on the ligand.^{13,14,15}

Each of these valence states undergo hydrolysis in the order¹⁶

$$Pu(IV) \gg Pu(VI) > Pu(III) > Pu(V)$$

with the polymerisation as the pH raises leading to precipitation at pH > 2 depending on the other conditions like redox potential, counter ion present, and concentrations etc..

Plutonium speciation places a vital role in its separation chemistry. Lower valence states (III, IV) are stabilised in acidic medium and the higher states (VI, VII) in alkaline medium. In nitric acid medium Pu(IV) is the most stable form. In case of simple aqua

ions Pu(III) forms nine coordinated tricapped trigonal prismatic structure, Pu(IV) mostly eight coordinated square anti prism or cubic distortions.¹⁰ Pu(III) forms all from $Pu(NO_3)^{2+}$ to $Pu(NO_3)_3$, whereas Pu(IV) forms complexes starting from $Pu(NO_3)^{3+}$ to $Pu(NO_3)_6^{2-}$. The exact distribution of the type of nitrate complex for Pu(IV) with varying nitric acid concentration even though of controversy, the non availability of negative complex can be ascertained (Table 1.1).



Figure 1.6: Actinide valence states (Including solid state).⁷

Table 1.1: Influence of HNO ₃ concentration on Pu(IV) s	species	12,17
Tuble 1.1. Influence of Theory concentration of Tuble		species.	

Number of NO ₃ groups in	HNO ₃ concentration	[HNO ₃]	Abundance of	
the Predominant Complex.	Range of Stability (M).	(M)	$Pu(NO_3)_6^{2-}$ (%)	
1	< 1.5	5	4	
2	1.5 – 2.1	6	10	
3	2.1 - 3.8	7	29	
4	3.8 - 5.6	8	50	
5	5.6 - 7.1	9	75	
6	> 7.1	10	91	

The Pu(IV)/Pu(III) and Pu(VI)/Pu(V) redox couples are rapidly reversible and are independent of the hydrogen ion concentration. The Pu(V)/Pu(IV) is not rapidly reversible and is dependent on the hydrogen ion concentration as it involves breaking and making of bonds.⁹ The redox potentials connecting the various couples of the Pu valence states are of comparable magnitude and are of values close to 1 V. The interest is on the redox potentials of Pu couples in acidic media (Table 1.2) that play a vital role in the extraction and stripping stages of separation processes.

Table 1.2: Formal electrochemical potentials for the Pu redox couples in aqueous acidic

 solutions (against the standard hydrogen electrode).¹⁸

Counto	Redox Potential (Volts)		
Couple	in 1M HNO ₃		
Pu(IV)/Pu(III)	+ 0.914		
Pu(V)/Pu(IV)	+ 1.188		
Pu(VI)/Pu(V)	+ 0.920		

Pu(IV) disproportionates at lower acid concentrations but is stable at higher acid concentrations.

$$3 Pu^{4+} + 2 H_2 0 \cong 2 Pu^{3+} + PuO_2^{2+} + 4 H^+$$

1.8 Design of different ligands for fuel reprocessing: Influence of process conditions and structural parameters on efficiency and selectivity

1.8.1 Crown ethers

Crown ethers are the promising class of compounds for the separation of Cs(I) and Sr(II) from the HLW till present. These are the cyclic polyethers and are often anchored

to other molecular scaffolds to augment their efficiency. The binding of metal ions by crown ethers is governed by (i) the size of crown ether cavity, (ii) molecular scaffold to which the crown ether is attached and (iii) hydration properties of the metal ion. The metal ions are hold in the crown ether cavity by ion-dipole interactions. The selectivity of crown ether for metal ions is decided by the size of both the ion and the cavity in a unique fashion. The substituents on crown ether structure affect significantly the encapsulation of metal ions by assuming certain conformations (spatial orientations) rendering better selectivity. As an example, the ligand di-tert-butyl-21-crown-7 has shown better extraction characteristics for Cs(I) ion when compared to its un-substituted analogues. The aromatic rings in crown ether moiety influences the metal ion extraction properties via cation- π -cloud interactions which has been observed in selective extraction of Cs(I) by dibenzo-18-crown-6 (Figure 1.7) where the metal ion is sandwiched by two extractant molecules. The presence of multiple ethereal oxygen atoms in crown ether based extractants imparts higher polarity leading to poor solubility in non polar diluents. This has invited the requirement of either a phase modifier or a polar diluent.

Calix[4]arenes are known for their selective binding to alkali/alkaline earth metal ions.¹⁹ The efficiency of extraction of the alkali metal ions decreases with the increase in calixarene cavity size as well as possible increase in number of conformations. Subsequently, calix-crowns have shown very promising selectivity towards Cs(I) under HLW conditions. Calix[4]arene in its 1,3-alternate conformation coupled with two crown-6 rings has been found to be highly selective for Cs(I) ion.²⁰ Both the cavity size and the aromatic ring π -cloud played important roles in efficient and selective extraction of Cs(I) ion.²¹ The recovery of Cs(I) from waste solution even at a very low concentrations became possible with a high selectivity and decontamination factor values sodium (NaNO₃) and other metal ions using over

calix[4]arene-bis(2,3-naphtho)-crown- 6^{22} The ease of extraction and stripping has made this class of ligands highly suitable for process applications. Similar to Cs(I) ion recovery, different crown ether ligands are studied for Sr(II) extraction but diglycolamides are found to be more suitable for potential applications.



Figure 1.7: Crown ether extractants (dibenzo-18-crown-6 and calix[4]crown-6).

1.8.2 Organophosphorus extractants

Organophosphorus compounds are explored as metal ion extractants due to their (i) controllable radiolysis, (ii) thermal stability and (iii) incinerator ash compatibility to phosphate glass. Tributylphosphate (TBP),²³ triisoamylphosphate (TiAP),²⁴ diamylamylphosphonate,²⁵ trialkylphosphine oxides (TRPO, R = C₆-C₈), Cyanex 923 (mixture of R₃P=O, R₂R'P=O, RR'₂P=O and R'₃P=O with R = C₆ and R' = C₈ hydrocarbon chains), carbomoylmethylphosphine oxides (CMPO)^{26,27} and several bi-dentate neutral organophosphorous^{28,29} compounds fall under this classification.

In PUREX process, 20-30% (v/v) TBP in *n*-dodecane diluent is used as solvent.³⁰ Hexavalent and tetravalent actinide ions are extracted and stripped at high and low nitric acid concentrations respectively. Trivalent actinide and lanthanide ions are extracted at relatively lower nitric acid concentrations in presence high nitrate salt content while the back extraction is accomplished with diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA) in glycolic acid solutions at pH 3.

As an alternative to PUREX and TRUEX extractants, other ligands such as TOPO and TRPO are developed by Chinese group.³¹ These are used as selective extractants for tetravalent and hexavalent actinides. U, Np and Pu are extracted from concentrated nitric acid. Np and Pu are stripped with oxalic acid and U with Na₂CO₃. Alternatively, U, Np and Pu can be stripped together with (NH₄)₂CO₃. Trivalent *An* (Am and Cm) and *Ln* are extracted from low nitric acid concentrations (0.7 M HNO₃, TRPO process)³² and stripping is achieved with conc. HNO₃ (5 M). TiAP is a better extractant than TBP for its high loading capacity for plutonium that is useful in processing of fast reactor spent fuels. Cyanex 923 poses problem of third phase formation at high uranium concentrations.

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is a commercially available extractant which has been used extensively. It is the material of choice for large scale operations because (i) sparingly soluble in aqueous solutions (ii) freely miscible with organic diluents (iii) both metal and sodium (during stripping) complexes are soluble in the organic phase and the solubility of these complexes can be further enhanced by means of a phase modifier (like TBP) and (iv) relatively low cost. For the extraction of *Ln* and *An* ions together, D2EHPA (0.2 M) and TBP (0.3 M) mixture in *n*-dodecane diluent is used. The extraction is carried out at pH 1-2 whereas stripping takes place with higher concentrations of nitric acid. Decomposition products and the impurities like pyrophosphoric acid and diphosphoric acid often hamper the back-extraction process.³³ D2EHPA is used as extractant in TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) process, invented by Weaver and Kappelmann³⁴ as well as in Reversed TALSPEAK process. Another extractant diisodecylphosphoricacid (DIDPA) behaves similar to D2EHPA and is used in presence of TBP phase modifier in processes similar to TALSPEAK.
CMPO group of extractants, particularly n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (0.2 M) along with TBP (1.2 M) in normal paraffinic hydrocarbon diluent is used in TRUEX (Trans Uranium EXtraction) process (Figure 1.8). It has the capability to extract An(III, IV and VI) and Ln(III) ions from nitric acid solutions. Am(III) and Pu(IV) extraction can be reversed by swing in nitric acid concentration whereas stripping of U(VI) needs aqueous solution of reagents like oxalate/carbonate. Inspite of their high efficiency, the phosphorus containing ligands are not completely incinerable. This has led to the design of facile combustible ligands containing only carbon, hydrogen, nitrogen and oxygen (CHNO) as these elements get transformed to gaseous oxides leaving no solid material during incineration.





Among the variety of sulphur donor organophosphorus ligands, thiophosphinic and thiophosphoric acids are well studied. Selectivity for Am(III) over Eu(III) is achieved with bis(2-ethyhexyl)dithiophosphoric acid (D2EHDTPA) containing soft sulphur donor atoms.

Extractants such as bis(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301) are extensively studied in this direction and found that the separation factors for Am(III) over Eu(III) increased with the increasing number of sulphur donor atoms in the ligand (Figure 1.9).^{35,36} The purity of the commercially available CYANEX 301 (73-85 %) has shown major influence in the separation of Am(III). Furthermore, degradation of these ligands with the time is not in favour to real industrial applications. Using saponified solvent mixture of CYANEX 301-TBP in kerosene as diluent, Am(III) is successfully extracted.³⁷





To obtain the ligands working in acidic range, the alkyl groups are replaced by phenyl/substituted phenyl rings. Much better separation of An(III) ions from lanthanide ions is observed using a combination of bis(2-chlorophenyl)dithiophosphinic acid (BCPDTP) and tris(2-ethylhexyl)phosphate (T2EHP), known by ALINA process (Actinide Lanthanide INtergroup separation from Acidic solutions). Synergism agent is necessary to cause separations by creating steric hindrance. As phenyl substituted extractants are insoluble in aliphatic diluents, toluene is used as the diluent. Higher separation factors for obtained Am(III) over Eu(III) are with bis(o-trifluoromethylphenyl)dithiophosphinic acid Increasing extractants. the number/positional change of trifluoromethyl groups on phenyl rings significantly reduce the selectivity. The replacement of sulphur atom by oxygen results in reversal of selectivity among Am(III) and Eu(III).³⁸ Similarly alkylphosphinic acids shown better separation factors than phosphoric aids. The branched alkylchain substituted compounds give better selectivity than the linear in toluene diluent from 1 M NaNO₃ feed solutions.

1.8.3 Malonamide extractants

Malonamides are the bi-dentate ligands with two amide oxygen binding sites. This class of ligands with variations in molecular structure are being explored for the past two decades in radioactive waste treatment. Unlike phosphorous ligands, these are completely incinerable leaving no solid radioactive waste. Moreover, diamides are weaker extractants than CMPO and therefore advantageous in back extraction processes. The other attractive features of diamides are (i) ease of their synthesis (ii) innocuous nature of degradation products and (iii) degradation products do not impede in stripping of Ln(III)/An(III) ions solvents at lower acidities The under this category include (i) dimethyldibutyltetradecylmalonamide (DMDBTDMA),

(ii) dimethyldioctylhexoxyethylmalonamide (DMDOHEMA) and

(iii) bicyclic malonamides etc. (Figure 1.10).

Studies involving malonamides with various structural modifications resulted in formulation of DIAMEX process (France).³⁹ The results so far infers the requirements of the diamides with typical structural feature: (i) one of the alkyl groups on amide nitrogen has to be small (methyl etc.) to allow complexation of carbonyl oxygen with the metal ions (ii) the choice of other substituent on amide nitrogen has to result in lower basic character (iii) longer alkyl chain (hydrophobic) substituent at the central carbon atom prevents third phase formation. Presence of alkoxy substituted alkyl chain on the central carbon, like hexoxyethyl,⁴⁰ resulted in (i) efficient inhibition of third phase formation, (ii) enhancement in extraction of transuranium elements, (iii) increase in radiation stability, and (iv) slowing down of hydrolytic degradation possibly by hydrogen bonding interactions. With diamides, the trivalent ions are extracted at > 3 M nitric acid

concentrations. The interference of Mo and Zr during the extraction of *Ln* and *An* ions can be minimized by adding oxalic acid/ketomalonic acid and hydrogen peroxide to the aqueous phase. The back extraction is by dilute HNO₃ (< 1M). The extraction affinity of *An* ions is in the order Pu(IV) > U(VI) > Am(III). Depending on nitric acid concentration, both solvation/ionpair mechanisms can operate.⁴¹ Incomplete stripping of co-extracted Pd and Ru is one of the drawbacks of DIAMEX process. The structural features imposed by the cyclic diamide significantly improved the extraction characteristics. The other diamides studied include succinamides and glutaramides.^{42,43,44}





1.8.4 Diglycolamide extractants

Sasaki and Choppin have demonstrated that the glycolamides have better extraction capabilities towards An(III) and An(IV) ions than malonamides.^{45,46} Reports shows that diglycolamides can act both as bidentate and tridentate ligands. The tridentate nature of diglycolamides (three oxygen atoms) results in enhanced extraction of An(III)and Ln(III) ions compared to bidentate malonamides. In contrast, the extraction of tetravalent and hexavalent ions increases marginally with diglycolamides. Because of their high extraction efficiency, diglycolamides can be used at lower concentrations than malonamides. Glycolamides with variable chain length of alkyl (lipophilc) groups on amide nitrogen are studied for their extraction properties. Diglycolamides with shorter alkyl chains are found to be soluble only in polar organic diluents. As expected, N,N,N',N'-tetraoctyldiglycolamide (TODGA) is soluble in *n*-dodecane, an amenable diluent for large scale applications (Figure 1.11). Speciation studies by slope analysis shown that three molecules of TODGA are involved in binding Th(IV), U(VI) and Pu(IV) whereas four in case of Am(III) and Cm(III) ions.⁴⁷ In contrast to malonamides the extractability for Ln(III) ions increases with increasing atomic number. The extraction of uranium decreases with the increase in alkyl chain length, propyl > butyl > hexyl.⁴⁸ The order of extractability for An ions is An(IV) > An(III) > An(VI) > An(V). Except for Zr(IV), Sr(II) and Ln(III) the fission products are very less extracted. Diglycolamide units anchored to different molecular structures have shown increased selectivity for Eu(III) over Am(III) compared to their extraction selectivity as such that are discussed in later sections.^{49,50,51} Back extraction of metal ions is with dilute HNO₃/water. TODGA has less radiation stability than malonamides (but is within the limits for plant operation) and is less affected by HNO₃.



Figure 1.11: Diglycolamides extractants.

1.8.5 Nitorgen donor extractants

Solvents with soft donor nitrogen ligands as compared to oxygen imparts high selectivity for soft acids such as An(III) over Ln(III) ions. Few important classes of nitrogenous ligands which have shown promise in selective metal ion extraction are terpyridines (terPy), triazenes and bistriazenes.

1.8.5.1 2,2':6',2"-Terpyridine and related extractants

2,2':6',2"-Terpyridine (terPy) itself has poor metal ion extractive properties, but showed synergism with 2-bromodecanoic acid. Initially, 2-bromodacnoic acid forms a neutral complex with metal ion followed by replacement of coordinated water molecules in complex by terPy thereby rendering more lipophilicity and increased solubility in diluents. However, it is a weaker extractant for both An(III) and Ln(III) ions. The selective separation of Am(III) in presence of Eu(III) from 0.1 M HNO₃ feed solutions (SF_{Am/Eu}: 7.2) is achieved with a mixture of terPy (0.1-0.5 M) and 2-bromodecanoic acid at 2:3 ratio in t-butylbenzene/TPH as diluent.⁵² The disadvantage of terPy based ligands is high water solubility of their conjugate acids. At low pH, all three nitrogens of terPy are likely to be protonated, which makes them unsuitable for large scale separation processes. Although terPy derivatives with long hydrophobic chain (i) 4'-octyl-2,2':6',2"-terpyridine (4'-octyl-terPy) and

(ii) 4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine (4,4',4"-tri(t-butyl)-terPy) also led to selective extraction of Am(III), water solubility of extractants could not be minimized (Figure 1.12).⁵³



Figure 1.12: TerPy and its derivative basedextractants.⁵⁴

This could be explained by the increase in basicity of the nitrogen with alkyl group substitution. At higher acid concentration, both covalent and ion pair mechanisms are operative during complexation: π back bonding interactions are observed in case of U(III) complexes.

1.8.5.2 2,4,6-Tri-2-pyridyl-1,3,5-triazine (TPTZ) and related extractants

In TPTZ ligands the central unit is 1,3,5 triazene ring. These ligands in combination with 2-bromodecanoic acid in TPH diluent shown better $D_{Am(III)}$ values than terPy ligands, under similar conditions.⁵⁵ 2,4,6-Tri-2-pyridyl-1,3,5-triazine is the first N donorligand to show $SF_{Am/Eu} > 10$. TPTZ derivatives with higher lipophilicity (Figure 1.13) were also synthesized and evaluated their extraction properties; in any case the ligands did not succeed for the extraction of metal ions from > 0.1 M HNO₃ solutions. TPTZ forms both 1:1 and 1:2 complexes with the trivalent lanthanides and actinides under different conditions.





2,4,6-Tri-2-pyridyl-1,3,5-triazine Tris(4-tert-butyl-2-pyridyl)-1,3,5-triazine

Figure 1.13: Few TPTZ based extractants.⁵⁵

TPTZ ligands are used in combination with lipophilic anionic reagents like 2-bromodecanoic acid, dinonylnapthalenesulphonic acid (DNNS) etc. Which form charge neutral complexes with An(III) ions. In case of decanoic acid and TPTZ combination, decanol is used as the diluent. t-Butylbenzene or CCl₄ is used as diluent in case of TPTZ combination with DNNS.



related ligands

Figure 1.14: BODO related extractants.

Pyridine ligands containing benzimidazole, benzoxazole, and benzothiazole substitutions⁵⁶ at 2 and 6 position are assessed for their properties in combination with 2-bromodecanoic acid for separation of *An* from *Ln* ions (Figure 1.14).⁵⁷ 2,6-Bis(benzoxazol-2-yl)-4-dodecyloxypyridine (BODO) and its branched ligands given $SF_{Am(III)/E(III)}$ in the range of 35 to 70 that increases with increasing acidity up to 0.1 M HNO₃, thereafter decreases at further higher acid concentrations.

1.8.5.4 Podant extractants

A number of polydentate podant N-donor ligands with varying structures have been reported for their ability to separate An(III) from Ln(III) ions.





Tris(2-pyridylmethyl)amine

N,N,N',N'-Tetrakis(2-pyridylmethyl)ethane -1,2-diamine (TPEN)

Figure 1.15: Podant TPEN.

The tetrapodal ligand such as N,N,N',N'-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (TPEN) has given promising results for selective extraction of Am(III) (Figure 1.15). In the absence of a synergism agent, solutions of TPEN (0.01 M) in nitrobenzene diluents selectively extracted Am(III) over Eu(III) from ammonium nitrate solutions (pH 4) as 1:1 complexes with high efficiency (D_{Am} and SF_{Am/Eu} ~ 100). Similar results are obtained in octan-1-ol as a diluent in the presence of decanoic acid as a co-extractant. This solvent did not work for more-acidic (pH < 4) aqueous solutions.

1.8.5.5 2,6-Bis(1,2,4-triazin-3-yl)pyridine (BTP) and related extractants

BTP class of ligands (Figure 1.16)^{58,59} are reported to have $SF_{Am(III)/Eu(III)} \leq 150$. 2-Bromodecanoic acid is required as a synergism agent for efficient extraction. In absence of lipophilic anionic source these ligands could extract $Am(NO_3)_3$ up to 1 M HNO₃ concentration ($D_{Am} \leq 61$). Tetrapropyl/tetraisopropyl substituted BTP derivatives are studied extensively and are shown to extract trisolvated complexes of Am(III) and Eu(III).⁶⁰



Figure 1.16: BTP related extractants.

Ligands with intermediate properties between terPy and BTP ligands called hemi-BTP ligands shown $SF_{Am(III)/Eu(III)} \leq 30$.⁶¹ These ligands could perform only in presence of 2-bromodecanoic acid. This class of ligands is susceptible to decomposition via hydrolysis of the triazine ring in a mixture of nitrous acid and nitric acid. Variety of ligands of this and related class are synthesized and tested for their *Ln/An* separation characteristics.

1.8.5.6 6,6'-Bis(1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) and related

$\begin{array}{c} (+) + (+)$

extractants



Tetra ethyl and tetra pentyl substituted BTBP ligands are observed for their high selectivity and distribution ratios towards Am(III) using hexanone as diluent. Stripping is carried out with glycolic acid solution. Like BTP ligands the D values for both Am and Eu trivalent ions increased with the increasing nitric acid concentration. These lignads are found to be more susceptible to radiolysis.⁶² Metal to ligand ratios are observed to be 1:1 and 1:2 in their metal ion complexes.

CyMe₄-BTBP (Figure 1.17) is the most promising candidate of this class of ligands with highest radiation stability. This ligand has shown great selectivity towards Am(III) and Cm(III) over the entire *Ln* series and yttrium. $D_{Am(III)}$ value around 4.5 and SF_{Am(III)/Eu(III)} of ~ 140 are obtained with ligand (0.02 M) in *n*-octanol from 0.5 M of HNO₃.⁶³ DMDOHEMA is added to the organic phase to improve the extraction kinetics from around 40 min to 5 min time to reach equilibrium. This ligand is stable towards hydrolysis upto 1 M nitric acid concentrations. The scrubbing of the *Ln* ions is carried out

with 0.5 M HNO₃, while 0.5 M glycolic acid solution is used for stripping of An ions. Successful counter current extraction studies for the separation of An and Ln ions from 2 M nitric acid solutions in centrifugal contactors is demonstrated at laboratory scale.⁶⁴ CyMe₄-BTBP is used in the development of GANEX (Group ActiNide EXtraction) process to extract An ions directly from PUREX raffinate obviating intermediate DIAMEX process. A mixture of CyMe₄-BTBP and TBP is used to selectively extract Am, Pu, Np and U from 4 M HNO₃ solutions at high metal loading.⁶⁵ Incidentally, each ligand behaved independently without any synergism during extraction of An ions with different oxidation states. Ligands with an additional pyridine ring, terpyridine with two triazine rings attached are reported and are not successful in their extraction behavior.⁶⁶ Phenanothroline derived CyMe₄-BTPhen were used in the separation of Am(III) and Cm(III) from the Ln ions with very high extraction efficiency and selectivity $(D_{Am} \ge 1000, SF_{Am/Eu} \approx 200-400$ for 1 to 4 M HNO₃). The extraction kinetics are faster compared to its 2,2'-bipyridine derived counterpart.⁶⁷ Benzylic position is more susceptible for radiolysis because of high stability associated with radicals formed. To avoid radiolytic degradation, ligands with no benzylic hydrogen atoms are synthesized.

1.8.6 Soft-Hard donor combination extractants

Development of useful ligands with hard/soft donors for selective extraction of metal ions remained a challenging task for future applications. The general approach is to tether the metal ion binding groups to proper molecular scaffoldings. They provide sterically constrained orientations to the tethered metal ion coordinating groups resulting in better selectivity. As an example, the selectivity for Eu(III) over Am(III) is significantly increased for TODGA extractants by attaching to triphenyl methane base unit. Similar increase in selectivity was observed by tethering dibutylglycolamide units to calixarene scaffolds. As discussed above, the mixtures of monoamides, diamides or

n-decanoic acid etc. with polydentate nitrogen donor extractants (CyMe₄-BTBP etc.) have shown beneficial metal ion extraction characteristics. This led to the design of ligands having amide groups tether to polyaromatic nitrogen donor molecular scaffolds. This improves the overall solubility of ligands in aliphatic diluents and also contributes to the improved extraction kinetics due to surface active nature of the attached amide functional groups. This also favors overall thermodynamic stability of the metal ion-ligand complex.

1.8.6.1 Triazine spacer extractants

Amide groups tether triazines (Figure 1.18) are synthesized and studied for their metal ion extraction behavior. However no beneficial effect was observed in their extraction properties compared to 2,4,6-tris(2-pyridyl)-1,3,5-triazineligands is reported. The hydrophobic nature is very much improved by alkyl chain on amide nitrogen, but the propensity to form inter-molecular hydrogen bonding through the same amide groups decreased the efficiency of extraction.⁶⁸



-trimethylhexanamide N(BPT)-cyclohexanecarboxamide N(BPT)-octanamide

Figure 1.18: Triazine based hard/soft donor combinations (a).

2,6-Bis(4,6-di-pivaloylamino-1,3,5-triazin-2-yl)-pyridine ligands (Figure 1.19) with four pendant amide groups are synthesized and studied for their extraction properties in octanol diluent from low nitric acid concentrations (up to 0.98 M). These ligands did not show any advantage than the BTP class of ligands. During complexation with the metal ions, amide groups became vulnerable to hydrolysis resulting in cleavage of amide bond.⁶⁹



2,6-Bis(4,6-di-pivaloylamino-1,3,5-triazin-2-yl)-pyridine

Figure 1.19: Triazines with hard/soft donor groups for metal complexation (b).

1.8.6.2 Pyridine spacer extractants

The other class of ligands that provoked interest is di-alkylarylamides of 2,6-pyridinedicarboxylic (dipicolinic) acid. *N*,*N*-Diethyl-*N*,*N*-di(p-tolyl)amide of dipicolinic acid (EtTDPA) is a promising ligand of this class (Figure 1.20).⁷⁰ Extraction of uranium, transplutonium and *Ln* ions is studied with this ligand from nitric acid media. Am(III) is preferentially extracted than Eu(III) with a separation factor of ~ 6 from 0.5-2 M concentrations of HNO₃.



Figure 1.20: Pyridine based ligands with hard/soft donors.

1.8.6.3 Podant skeleton spacer extractants



Figure 1.21: Podant based ligands with hard/soft donor combinations.

Anchoring of three amide groups on tris[(2-pyridyl)methyl]amine (tap) to form tris[6-((2-N,N-diethylcarbamoyl)pyridyl)methyl]amine (tpaam) makes another class of amide ligands (Figure 1.21). The *Ln* aqueous complexes of tap and tpaam have shown no marked difference with respect to the stability with a variation in entropy and enthalpy contributions to complexation.⁷¹

1.8.6.4 Phenanthroline spacer extractants

N,N'-Diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen) ligand with two amide functional groups tether to phenantroline a highly promising extractant for GANEX process, wherein excellent selectivity for An over Ln ions is reported (Figure 1.22). Here it has been argued that the soft nitrogen donors of phenanthroline ring induces the selectivity for minor An over Ln and the hard oxygen donors of amide groups favor the complexation with the lighter An i.e. Th, U, Np and Pu. Importantly, this is claimed to be the first efficient ligand for group separation of actinides from fission products in highly acidic solution and holds promising applications in the partitioning of nuclear waste.⁷²



Figure 1.22: Phenanthroline based ligands with hard/soft donor combinations.

1.8.6.5 Terpyridine spacer extractants

The other ligand class of interest is bitopic ligands with two amide groups tether to terpyridine moiety. N,N,N,N-tetraoctyl-6,6-(2,2:6,2-terpyridine)diamides (TOTPD) and N,N-diethyl-N,N-diphenyl-6,6-(2,2:6,2-terpyridine)diamide (DEDPTPD) ligands are synthesized and evaluated for their application in GANEX process (Figure 1.23). The terpyridine is expected to increase the selectivity for An over Ln ion and the attached amide groups are supposed to help in extraction from highly acidic media like 3 M HNO₃.⁷³ The better among reported are with long chain alkyl groups.



Tetraoctyl-terpyridine diamide (TOTPD)

Diethyldiphenyl-terpyridine diamide (DEDPTPD)

Figure 1.23: Terpyridine based ligands with hard/soft donor combinations.

The solvent extraction experiment results obtained with TOTPD ligand are shown in Table1.3.

Table 1.3: Extraction studies with terpyridine-amide combination ligands.⁷³

[ligand] (mol/L)	[HNO ₃] _{init.} (mol/L)	Distribution ratios $D_{\rm M}$				
		Metal	<i>n</i> -octanol	Nitrobenzen	e TPH	Tetrachloroethane
0.01	2.9	²³⁹ Pu(IV)	0.35	34	0.13	0.16
0.1	2.9	²³⁹ Pu(IV)	3.8	> 100	n.d.	n.d.
		$^{241}Am(III)$	0.015	0.119	n.d.	n.d.
0.1	2.9	²⁴⁴ Cm(III)	0.009	0.036	n.d.	n.d.
		¹⁵² Eu(III)	0.003	0.008	n.d.	n.d.
		¹³⁹ Ce(III)	0.002	0.019	n.d.	n.d.
0.1	2.6	U(VI)	0.31	14.1	n.d.	n.d.
0.1	3.0	$^{237}Np(V)^{*}$	0.78	5.8	n.d.	n.d.
0.1	3.0	²³⁷ Np(VI)	0.68	24.8	n.d.	n.d.

*The initial solution of Np(V) contains 6% of Np(VI), n.d: not determined

1.9 Overview of the present work

The present work is based on designing of ligands for selective extraction of plutonium. Design/synthesis of these new ligands is based on the judicious structural modification of reported ligands, and evaluation of their metal ion extraction properties. The structures of triarylpyridine and diarylpyridines are expected to provide sterically constrained orientations to the attached metal bending sites similar to terpyridine moieties (1.8.6.5). The diamides of interest were synthesized by tethering amide functional groups

to TAP-diol and DAP-diol scaffolds (Chapter – 2). The synthesis/characterization of ligands and the techniques/instruments for evaluation of their metal ion extraction properties along with mandatory safety precautionsare presented in Chapter – 2. The optimized procedure for the synthesis of the ligands has been provided in Chapter – 3. The evaluation of the ligands by solvent extraction methods for the selective extraction of plutonium both in molecular and ionic liquid diluents are discussed in Chapters 4 & 5. After arriving at the optimum composition of solvent mixture (ligand/diluents; $L_{III}/5$ % ID/DD) for efficient/selective extraction of plutonium, the same solvent composition is used for evaluation by membrane-based separations (FSSLM) and is discussed in Chapter – 6. At the end, out of five synthesized diamides with different structural features, the most potential diamide L_{III} for Pu extraction has been established on the basis of experimental data (Chapter – 7). The structural features of the ligands were correlated to their plutonium selective extraction properties.

Chapter – 2

EXPERIMENT TECHNIQUES

2 Experiment techniques

2.1 Preamble

This chapter deals with radiotracers, reagents and experiment techniques used for the synthesis and evaluation of new class of 2,4,6-triarylpyridine (TAP)/4-pentyl-2,6-diarylpyridine (DAP) bridged diamide ligands for plutonium ion extraction properties.

2.2 Chemical and Radiation Safety

2.2.1 Safety measures while chemical handling

Personal protective equipment (PPE) used while doing the experiments. All the reagent additions and reactions are carried out in fume hoods. Obtained special instructions if any before use from Safety Data Sheets (SDS) of a particular chemical. Do not breathe dust/fume/gas/mist/vapors/spray. Keep chemicals away from heat/sparks/open flames/hot surfaces. Aromatic compounds (nitrobenzene/toluene) are combustible liquids, toxic if swallowed, toxic in contact with skin, toxic if inhaled, may cause cancer, may damage fertility or the unborn child, causes damage to organs through prolonged or repeated exposure. Wear appropriate protective eye glasses or chemical safety goggles. Wear appropriate protective gloves and clothing to prevent skin exposure. Use air purifying respirators to avoid inhalation.

2.2.2 Safety measures while handling radioactive tracers

Radiotoxicity must be as low as possible for the isotopes of a particular element used for assay. Short-living isotopes are preferred to long-living ones and the amounts used must be kept to a minimum. The radioactive active sites are to be marked and separate from non-radioactive sites. Proper radiation symbols are to be used on containers and items that have come into contact with radioactive substances. The note sheets should be kept away from active zones. When handling radioactive materials, always appropriate protective clothing like lab coat has to be used. In case of risk for serious contamination, disposable clothing has to be used. Always wear gloves when handling radioactive substances and use proper removal/wearing procedures to avoid contamination from gloves to hands. Regularly check the radiation level of the hands. In case of any increase in activity over the background, the hands are to be washed thoroughly with soap water/sodium carbonate/oxalic acid/EDTA/KMnO4 depending on the extent of contamination. Shoe covers are to be worn in rooms where the floor may be contaminated. Appropriate radiation shields are to be used. The stock solution has to be stored safely after removing the amount of activity needed. To avoid internal contamination, strict hygiene is essential. Eating, smoking, drinking, and applying cosmetics are prohibited in radioactive labs. Pipetting devices are to be used in chemical labs. Hands are to be thoroughly washed while leaving the lab. Radiation level of the working area has to be under regular monitoring by Health Physics division. All radioactive waste has to be disposed in the appropriate marked containers. In case of an incident involving radioactive materials (e.g. spills), the Health Physics personnel has to be informed and proper decontamination procedures have to be followed.

2.3 Radiotracers and reagents

2.3.1 Radiotracers

In the present work ¹³⁷Cs, ^{85, 89}Sr, ^{152, 154}Eu, ²³³U, ²³⁹Pu (dominantly ²³⁹Pu) and ²⁴¹Am radio tracers are used to estimate the corresponding element concentrations in respective aqueous/organic phases for obtaining parameters like distribution coefficients etc. during metal ion extraction studies by different ligands. ¹³⁷Cs, ^{85, 89}Sr, ^{152, 154}Eu are

procured from Board of Radiation and Isotope Technology (BRIT), Mumbai and purities of them are evaluated by gamma spectrometry. ^{238, 239, 241}Pu are purified by the reported procedures.^{74,75} The purity of the tracers is ascertained by gamma spectrometry. ²³³U is produced by neutron irradiation of ²³²Th and is purified by chromatographic methods.^{76,77} Natural uranium is taken from UED, BARC. Neodymium nitrate is form Indian Rare Earths Limited, Mumbai.

The characteristics of the radio-nuclides used in the present work are delineated below. The data in the parenthesis indicate the half-life, decay mode and the gamma energy of the associated decay.

- 1. $^{137}Cs \ (t_{1/2} \ 30.2 \text{ y}, 100\% \ \beta^-, \gamma \ 661.7 \text{ KeV})$
- 2. $^{85,89}Sr$ ($t_{1/2}$ 64.8 y, 100% Electron Capture, γ 514, 909 KeV)
- 3. ${}^{152,154}Eu$ ($t_{1/2}$ 13.5 y, 28.58% β^+ and Electron Capture, γ 121.78 KeV)
- 4. $^{233}U (t_{1/2} 1.6 \times 10^5 \text{ y}, 100\% \alpha , \gamma 4.91 \text{ MeV})$
- 5. ^{239}Pu ($t_{1/2}$ 24110 y, 100% α , γ 5.24 MeV)
- 6. ²⁴¹Am ($t_{1/2}$ 432.2 y, 85.2% α 5.48 MeV and 35.9% γ 59.54 KeV)

The concentrations of the radiotracers in the solvent extraction experiments are approximately kept as 10^{-7} M for ²⁴¹Am; 10^{-6} M for ²³⁹Pu; 10^{-5} M for ²³³U, ^{152, 154}Eu, and ¹³⁷Cs; and 10^{-4} M for ^{85, 89}Sr.

2.3.2 Reagents for synthesis of ligands

3'-Hydroxyacetophenone and benzaldehyde are procured from SDFCL, Mumbai, α -chloroacetyl chloride (98 %) is procured from Fisher Scientific. All the amines used in synthesis are procured from Aldrich.

2.3.3 Reagents for evaluation of ligands

All reagents used are AR grade. Nitrobenzene and phenolpthalein are procured from Fluka Chemie A.G., Switzerland. Toluene is procured from B.D.H., Mumbai. Chloroform and benzene are procured from S. D. Fine chemicals, Mumbai. Suprapur nitric acid is procured from Merck, Germany. MilliQ water (18 MQ/cm) is obtained using Millipore, USA to make the solutions. NaOH is procured from BDH, Mumbai

2.4 Instruments and methods

2.4.1 Instruments for characterization of ligands

Microwave-assisted reactions are carried out in an Anton Paar microwave reactor (model SYNTHOS 3000). Melting points determined using Fisher-Johns melting point apparatus. IR spectra are scanned with a Jasco FT IR 4100 spectrophotometer. The ¹H and ¹³C-NMR spectra are recorded on Varian 500 MHz/Bruker AC 200/300 MHz spectrometer. Spectra are referenced to residual chloroform (δ 7.25 ppm, ¹H; 77.0 ppm, ¹³C). Low resolution mass spectra are recorded with a Variant 500 mass spectrometer (ESI) and HRMS on Bruker mass spectrometer (ESI).

Spectral data of known compounds is in accordance with those reported in the literature while the unknown compounds are characterized by spectral (IR, ¹H NMR, ¹³C NMR, MS) and HRMS data etc..

2.4.2 Instruments used to study extraction characteristics of ligands

2.4.2.1 Gamma counting



Figure 2.1: Gamma ray spectrometry using NaI (Tl) detector.

Two types of gamma counting/analysis methods followed. For samples containing single element gamma emitting nuclide, gross gamma counting technique is used. Gross gamma counting involves evaluating peak area under the selected region of interest at a particular energy of analyte spectrum. NaI(TI) scintillation counter (Figure 2.1) with $3'' \times 3''$ of well type detector that is connected to a multichannel analyzer having 7 % resolution at 662 KeV and efficiency greater than 95 % for moderate energy photons is used. The samples are taken in glass tubes of suitable size to place in the detector for measurement and counting is made to a suitable time to have greater than ten thousand counts to limit the counting statistical error within ± 1 .

Analysis by Gamma spectrometer is followed for samples containing more than one element gamma emitting nuclides. Gamma spectrometer with n-type HPGE detector (operated at liquid nitrogen temperature) with an energy resolution of 1.9 KeV at 1332 KeV is used for estimating the radiochemical purity and amount of the nuclides (Figure 2.2). The samples are taken in glass vials of suitable size to place in the sample holder and measurements are carried out for sufficient times depending on the samples associated activity to have greater than ten thousand counts to limit the counting statistical error within ± 1 .



Figure 2.2: Gamma ray spectrometry using HPGE detector.

2.4.2.2 Alpha counting

Two types of alpha counting/analysis methods are followed. For samples containing single element alpha emitting nuclide, liquid scintillation counter with PMT detector used. scintillating solution comprising 0.7 % is А (w/v)of 2,5-diphenyloxazole (PPO) scintillator and 0.03 % (w/v)of as 1,4-bis-[2-(5-phenyloxazolyl)]-benzene (POPOP) as wavelength shifter in dioxane solvent is used. 1 % (w/v) of trioctylphosphineoxide (TOPO) is added to the scintillating solution for keeping the metal ions in the form of soluble complexes. Sample aliquots of suitable size (10 to 50 µl) are used for measurement, taking in to consideration the quenching effects of nitric acid and nitrobenzene. The radio tracer amount and the counting time are considered such a way that the number of counts exceeds ten thousand to limit the counting statistical error within ± 1 .

Alpha spectrometer (Canberra make) is used for the analysis of the samples containing mixture of alpha emitting nuclides. The nuclides are electrodeposited on stainless steel circular planchettes for collecting the alpha spectra by the following procedure. Sample solutions of suitable activity in 0.5 M nitric acid ($\approx 40 \ \mu$ L) are taken into Teflon cylindrical electroplating cell ($\approx 50 \ m$) with stainless steel circular planchette (2 cm diameter) fixed at the bottom surface as cathode. Suitable quantity of *iso*-propanol is taken as electrolyte solution in to the cell. Pt wire anode is dipped in to the solution at the center of the cell. Current is passed at a suitable voltage for the required time period to complete electrodeposition of elements. The planchettes are taken out from the cell after electroplating, gently washed with ethanol and heated to red hot condition on burner flame to fix the electroplated elements on surface. After cooling to ambient temperature, planchettes are taken for analysis on Alpha spectrometer. Organic samples are directly taken on to stainless steel planchettes, dried under IR lamp for sufficient time and later heated to red hot condition on a burner flame to fix the material on to the surface. After cooling to ambient temperature, the planchettes are taken for analysis on alpha spectrometer.

2.4.2.3 ICP-OES

For measuring the concentrations of the inactive metal ions in sample solutions, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, HORIBA JOBIN YVON make) technique is used. The emission light intensities from the excited metal atom/ions are measured which are proportional to their respective concentrations in the sample solutions. For exciting the metal atom/ions the plasma generated from argon gas is used where the temperatures range from 7000 to 10000 ^oC along the axis of plasma.

The instrument used is of radial viewing type (Figure 2.3). The resolution is 5 pm below 410 nm and 10 pm above to it. The sample solutions are converted to aerosol through a nebulizer. Thereafter the aerosol passes through a cyclonic chamber to get rid of bigger liquid droplets that are drained out. Then the aerosol gets injected in to the argon generated plasma.



Figure 2.3: ICP-OES.

The argon gas being inert and having high ionization energy is used to generate plasma for attaining required high temperatures. Argon gas is less reactive towards analyte species and generates less interfering background for many analyte atoms/ions lines that makes it an attractive gas for plasma generation. The plasma sustenance is by coupling it to a Radio Frequency (RF) generator through copper coils that are cooled by water circulation (25-30 °C), maintained by a water chiller and circulation unit. The cooling gas, sheath gas and the nebulizer gas are all of argon gas only. The excited atoms/ions in the plasma emit light at characteristic wavelengths that are measured for intensities by photomultiplier tube detector arrangements. The instrument used is of sequential type analyzing one element concentration after the other instead of simultaneously for all. The intensities of the emitted light at characteristic wavelengths of elements are proportional to their respective concentrations and are used for obtaining calibration curve. The unknown concentrations are obtained by measuring the emitted intensities and the prior generated calibration curve.

2.5 Experiments on metal ion extraction characteristics of ligands



2.5.1 Solvent extraction – Extraction studies

Figure 2.4: Equilibration setup with a constant temperature water bath.

Metal ion extractions from aqueous phase (spiked with the radiotracers of elements of interest) to organic phase are carried out by equilibrating equal volumes (usually 1 mL) of both phases in leak tight Pyrex glass tubes that are placed in a thermostatic water bath (at 25 ± 0.1 °C) at a mixing rate of 45 rotations per minute (Figure 2.4). Subsequently, these tubes are rested and centrifuged for clear phase separation. Suitable aliquots (10 to 100 µL) of the samples both from organic and aqueous phases are taken for radiometric assay to obtain the metal ion radio nuclide concentrations in the corresponding phases. The distribution ratio (D) is calculated as the ratio of metal ion concentration in the organic phase to that in aqueous phase. All experiments are performed in duplicate and the data reported is the average of these two duplicate measurements. The material balance is within the error limit of ± 5 %.

2.5.2 Solvent extraction – Stripping studies

The metal ion (active isotope of element) loaded organic phase and the corresponding aqueous phase for stripping are equilibrated in a manner similar to that in extraction studies (2.5.1). In the present work, plutonium stripping from loaded organic is by contacting with an aqueous phase at low nitric acid concentration (≈ 0.5 N) containing a reducing/complexing agent. The percentage stripping value is obtained from the initial amount in the solvent phase and the amount that got stripped in to aqueous phase.

2.5.3 Purification of plutonium tracer

To adjust the plutonium valency to four, a pinch of sodium nitrite is added to its solutions in 1 M nitric acid.⁷⁸ From the nitric acid solution, Pu(IV) is extracted to 0.5 M solution of 2-thenyltrifluoroacetone (HTTA) in xylene diluent. Thereafter, the extracted Pu(IV) is stripped from the organic phase by equilibrating with 8 M nitric acid solution. The absence of ²⁴¹Am is confirmed by gamma spectroscopy. To prepare Pu(IV) solutions at different nitric acid concentrations the plutonium stripped solution (stock) at 8 M HNO₃ is diluted with 0.5 M HNO₃ solution in required ratios.

2.5.4 Purification of uranium tracer

²³³U tracer is produced by irradiation of ²³²Th in reactor. Subsequently ²³³U is purified from its daughter/decay products of ²³²U by anion exchange column chromatography.^{76,77} Anionic complex of uranium in 6 M HCl is retained in the column, whereas ²²⁸Th and its daughter products get eluted. The adsorbed impurities, if any, are removed from column by washing with 6 N HCl. Uranium is eluted from the column using 0.01 M HNO₃ and is preserved in 0.5 M nitric acid as a stock solution. The purity of ²³³U tracer is ensured by alpha spectrometry.

The other method for purification of ²³³U is by solvent extraction. Solvent with a composition of 5 % TBP in *n*-dodecane diluent is used to extract uranium from an aqueous solution of 4 M nitric acid. The loaded organic phase is then scrubbed with 4 M HNO₃ to remove the co-extracted impurities. ²³³U is stripped from the loaded organicphase with 0.01 M HNO₃ solution.

2.5.5 Solvent radiation stability studies

Solvents are subjected to a specific amount of radiation dose by irradiating in gamma chamber equipped with ⁶⁰Co source (at 2 kGy/h dose rate). Aliquots are withdrawn periodically at different time intervals during irradiation and plutonium distribution values are determined under identical conditions to know the extent of degradation.

The gamma chamber used for irradiation studies consists of a lead flask with a ⁶⁰Co source pencil in a cylindrical array cage at its centre. At the centre of the source cage a vertically movable concentric cylindrical lead drawer was kept with a space for placing samples at its centre (sample chamber). The vertical movement of the drawer is by a rope and pulley arrangement connected to geared motor controlled by an electrical circuit panel. For irradiation, the drawer is lowered until the sample chamber is at the centre of the source cage.

The dose rate is standardized by measuring of ferric ions produced by oxidation in an irradiate sample of ferrous sulphate (Fricke dosimetry). The dose rate of the 60 Co irradiator is measured to be 2 kGy/h.

2.5.6 Metal ion – Ligand complex stoichiometry studies

The extraction of metal ions by neutral ligands from nitric acid solutions takes place by complexation to metal nitrate salts forming neutral organic phase soluble species.

$$\mathbf{M}_{(aq.)}^{m+} + \mathrm{m}\,\mathrm{NO}_{3\,(aq.)}^{-} + \mathrm{n}\,\mathbf{L}_{(\mathrm{org.})} \leftrightarrows \mathrm{M}(\mathrm{NO}_{3})_{\mathrm{m}}\mathbf{L}_{\mathrm{n\,(org.)}}$$

The equilibrium constant for the above reaction is expressed by

$$K_{ex.} = \frac{[M(NO_3)_m L_n]_{(org.)}}{[M^{m+}]_{(aq.)} [NO_3^-]_{(aq.)}^m [L]^n}$$

The terms in square brackets indicate the concentration of respective species under equilibrium conditions. The subscript indicates the phase in which the corresponding entity is present. The distribution ratio for the present system is given by

$$D_{M(m)} = \frac{[M(NO_3)_m L_n]_{(org.)}}{[M^{m+}]_{(aq.)}}$$

$$\Rightarrow K_{ex.} = \frac{D_{M(m)}}{[NO_3^-]_{(aq.)}^m [L]_{(org.)}^n}$$

$$\Rightarrow D_{M(m)} = K_{ex.}[NO_3^-]_{(aq.)}^m [L]_{(org.)}^n$$

Taking logarithm on both sides of the above expression gives

$$\log D_{M(m)} = \log K_{ex.} + m \log[NO_3^-]_{(aq.)} + n \log[L]_{(org.)}$$

Solvents with varying ligand concentration in diluent are subjected to metal ion (M^{m+}) extraction from nitric acid feed solutions to estimate $D_{M(m)}$ values. When the concentration of M^{m+} (tracer) used for the estimation of $D_{M(m)}$ and the pickup of nitric acid by the ligands are both very low when compared to feed values, it can be assumed that $[NO_3^-]_{(aq.)}$ is constant during extraction. $K_{ex.}$ is a constant at constant temperature. This makes possible to express the above equation as

$$\log D_{M(m)} = C + n \log[L]_{(org.)}$$

where

$$C = \log K_{ex.} + m \log[NO_3^-]_{(aq.)}.$$

Under fore mentioned conditions, C is a constant at constant temperature.

The plot of log $D_{M(m)}$ versus log[L]_(org.) gives a straight line with a slope (n) that is equal in magnitude to number of ligand molecules in the $[M(NO_3)_m L_n]_{(org.)}$ complex.⁷⁹

2.5.7 Acid uptake by solvent

Acid uptake from feed nitric acid solutions to the solvent phase is an indication of the basicity of ligands under study. The relative affinity of the ligands to nitric acid over metal ions is an important parameter as it may lead to suppression in metal ion D values at higher HNO₃ concentrations. The amount of acid pick by the solvent depends on the concentration of the ligand, diluent used and feed nitric acid concentration etc..

Sample volumes of the solvent are equilibrated with aqueous HNO₃ solutions of varying concentration (0.5 to 6 M) for 10 h duration. After allowing for settling and centrifugation, aliquot samples from the separated aqueous and organic layers are titrated with standard NaOH (0.01 N) solution to phenolphthalein indicator pink coloration for end point. The organic phases are titrated in aqueous ethanol medium, which is titrated earlier in the same method to find the alkali consumption for blank value.

2.5.8 Flat Sheet Supported Liquid Membrane (FSSLM) studies

Membranes (pore size = $0.45 \ \mu\text{m}$; porosity = $72 \ \%$; nominal thickness = $85 \ \mu\text{m}$) of polytetrafluoroethylene (PTFE) are procured from Sartorius, Germany. The double

compartment cell used with the provision for assembling the membrane in between is of in house make (Figure 2.5).



Figure 2.5: Experiment setup for FSSLM studies.

The FSSLM sheets are made with PTFE micro porous flat sheet membranes as a solid support. The membranes are soaked in the solvent of interest for about an hour after which are gently wiped with a tissue paper to remove excess of solvent on surface. The membrane is fitted to the cell with proper sealing. The feed and strippant solutions (20 ml each) are filled in to the respective chambers gently. The phases on either side of the membrane are kept under stirring at 200 rpm with the help of magnetic bars without disturbing the FSSLM. The samples are collected from the respective solution filling ports on the feed and receiver chambers for analysis. All the experiments are carried out under ambient conditions.

The cumulative transport (% $T_{tc})$ at a particular instance of time (t) for plutonium is obtained by

$$\% T_{tc} = 100 \times (C_{0f} - C_{tf})/C_{0f}$$

Where, C_{0f} ; Concentration of metal ion in the aqueous feed at time t = 0 and C_{tf} ; Concentration of metal ion in the aqueous feed at time t.

The percentage of metal ion that got transferred to receiver side in time t is given

$$\% T_{ts} = 100 \times C_{ts}/C_{0f}$$

Cts; Concentration of plutonium in the receiver phase at time t.

by

The percentage of plutonium retained in the membrane phase at time t is given by

$$\% T_{tm} = \% T_{tc} - \% T_{ts}$$

The samples from both feed and receiver chambers are analysed at different time intervals to obtain % T_{tc} , % T_{ts} and % T_{tm} .

Under the steady state conditions, the flux of plutonium through the feed phase becomes equal to the flux through the membrane (J). The change in plutonium concentration at the bulk feed phase can be described by the following first order differential equation

$$\frac{\mathrm{dC}_{\mathrm{tf}}}{\mathrm{dt}} + \mathrm{P}\left(\frac{\mathrm{Q}}{\mathrm{V}}\right)\mathrm{C}_{\mathrm{tf}} = 0$$

Q is the effective membrane area; V is the volume of bulk feed phase.

$$Q = A\epsilon$$

A is the exposed membrane area and ϵ is the porosity

P is the permeability coefficient of membrane which depends on membrane characteristics i.e. the nature of ligand, nature of diluents, composition of the solvent used for making membrane, wettability of supporting polymer sheet, thickness of membrane etc..

$$P = \frac{J}{[C_{tf}]}$$

J is the steady state flux of plutonium.

The solution to this equation can be written as

$$[C_{tf}] = [C_{0f}] \times e^{-P\left(\frac{Q}{V}\right)t}$$

In logarithmic form the above equation turns to

$$\ln \frac{[C_{tf}]}{[C_{0f}]} = -P\left(\frac{Q}{V}\right)t$$

From the above equation, the plot of $\ln \frac{[C_{tf}]}{[C_{of}]}$ versus time t gives a straight line with a slope of $-P\left(\frac{Q}{V}\right)$. From the known values of Q and V, the values of P are obtained.

Chapter – 3

SYNTHESIS AND CHARACTERIZATION OF

A NEW CLASS OF DIAMIDE LIGANDS

3 Synthesis and characterization of a new class of diamide ligands

3.1 Preamble

This chapter presents the design, synthesis and characterization of a new class of diamide extractants. Syntheses and structural characterization of the intermediates such as 2,4,6-triarylpyridine (TAP), 4-*n*-pentyl-2,6-diarylpyridine (DAP), α -chloroacetamides. Finally, the optimized protocol for diamide synthesis has been described.

3.2 Introduction

Metal ion selective extractants have important applications in a wide variety of fields including metallurgy, medicine and environmental control.^{80,81} The various applications of these ligands include (i) treatment of metal intoxication,⁸² (ii) complexation with radionuclides for scintigraphic imaging, (iii) cancer radiotherapy, (iv) metal complexing antibiotics and, (v) selective metal ion separations involving purification etc.. The major considerations in the design of metal ion-specific ligands are (i) steric effects involved during metal ion-ligand complexation, (ii) the nature/number of the donor atoms present in ligand, and (iii) the nature of the metal ion. In solvent extraction applications the design of ligands must also take into account the "process operating requirements" such as (i) low aqueous solubility, (ii) high loading capacity, (iii) rapid extraction/stripping kinetics and (iv) acceptable cost.⁸³

3.3 Design of the ligands

3.3.1 Types of donor and acceptor entities

After Sidgwick and Ahrland contributions to understand the nature of bonding in metal ion-ligand complexes, Pearson⁸⁴ has given a more general view on the classification of the donor and acceptors species and is based on the stability of the

adducts (acid-base) formed rather than the kinetics of their formation. Hard acids bind strongly to bases which strongly bind proton. Soft acids bind strongly to highly polarizable or unsaturated bases which often have lesser proton basicity. Bases are similarly divided into two categories, *viz.*, those that are polarizable or soft and those that are non-polarizable or hard, hardness being associated with good proton binding. This is well known as HSAB (Hard and Soft Acid Base Principle) classification. This gives no indication of the relative affinities of hard/soft acids for hard/soft bases but in conjunction with more sophisticated criteria such as the relative strength and softness ofacids and bases, is a useful guide for selecting the proper donor atoms in designing of ligand structure.

In case of metal ions the important properties are size, charge, electronic structure and the influence of attached counter ion groups (nitrate etc.). To estimate the stability of the metal ion-ligand complexes it is important to consider the corresponding acid and base strengths of metal ion and ligating groups along with their softness parameters (σ). The estimation of metal ion-ligand complex stabilities for different metal ions with a particular ligand is useful in predicting the separation factors (SF) during solvent extraction process. The other parameters like diluent, acid strength of aqueous phase, and presence of others ions also influence separation factors.

These attributes are highly important for designing efficient solvents in metal ion separations,^{85,86} as an example for the separation of Ga(II) and In(II)

$$SF = (S_{In} - S_{Ga})S_B + (\sigma_{In} - \sigma_{Ga})\sigma_B$$

 $S_{A (A=In,Ga)}$ and $\sigma_{A (A=In,Ga)}$ are the acid strengths and the softness parameters for the metal ions requiring separation respectively. Similarly, S_B and σ_B are the base strength and softness parameters of the ligand respectively.
3.3.2 Influence of neutral oxygen donors present in ligand structure

In general, addition of groups containing neutral oxygen donors to an existing ligand leads to an increase in selectivity for large metal ions over small ones,⁸⁷ permitting a prediction of size selectivity which, remarkably, does not appear to be sensitive to the nature of the metal ion.

3.3.3 Chelate effect

Ligands which can coordinate metal ion at two or more positions (chelating ligands) form more stable complexes than similar ligands which can only coordinate at a single position. This is especially true if five- or six-member chelate rings are formed. The greater stability of the chelated complex compared with an analogous non-chelated complex is termed the *"chelate effect* ", the effect appears to be mainly a result of entropy contributions. Increasing the size of the chelate ring from a five-member to a six-member ring (and further increases in chelate ring size) usually leads to a drop in complex stability due to less favorable enthalpy contributions as a result of steric strain.

3.3.4 Effect spacer unit on selectivity of ligands

Higher extraction selectivity is reported for ligands having metal ion binding groups (ethers, amides, amines, phosphates etc.) tether to molecular scaffolds. Calixarenes, terpyridines, bipyridines, phenanthrolines, catechol, 7-oxabicyclo[2.2.1]heptane, triarylpyridines etc. are used as the scaffolds that provide specific steric orientations to the tethered metal binding groups resulting in high metal ion selectivity. TODGA units anchored to triphenylmethane (trityl)^{49,50}, C-pivot glycolamides and diglycolamides have shown better selectivity for Eu(III) over Am(III).⁵¹ Calixarenes

with pendant glycolamide units (calixareneDGA) are reported for their better selectivity during trivalent Ln and An ion separations by Huang et.al..⁸⁸

Similarly, enhanced selectivity towards plutonium is reported for catechol spacer diamides compared to simple diamides (BenzoDODA).⁸⁹ The distribution coefficient reported with this ligand (0.1 M) in *n*-docane diluent is ~ 6 from 3 M nitric acid feed solutions. Plutonium selective oxa-diamide ligands (ODA) with a different spacer unit are reported.⁹⁰ These ligands have poor solubility in *n*-dodecane and require 30 % (v/v) *iso*-decanol in *n*-dodecane (30 % ID/DD) as the diluent. The distribution coefficients reported for this oxa-diamide ligand (0.1 M) in 30 % ID/DD diluent is 15.49 from 4 M nitric acid, which is ~ 5-6 for extractions from 3 M nitric acid solutions. Both the classes of ligands are reported with 2-ethylhexyl substituents on amide nitrogen (Figure 3.1).



Figure 3.1: Effect of spacer on selectivity of diamide ligands

3.4 Present work

3.4.1 Design of triarylpyridine based diamide ligands

Terpyridines are known for their selective complexation to softer metal ions. Furthermore, functionalized terpyridines are reported as electroactive ligands in wavelength selective separations of metal ions.⁹¹ Apart from functioning as polynitrogen donor, terpyridine can provide controlled spatial orientations to the metal ion coordinating groups tethered to it. The nature of metal ion coordinating groups attached to terpyridine spacer decides the lipophilic or hydrophilic nature of the ligand. Molecules with terpyridine spacer having tethered diamine tetra carboxylic acid (like EDTA) groups are reported for complexation with Eu(III) ion in aqueous medium (Figure 3.2).⁸⁷ Similarly lipophilic terpyridine spacer diamide ligands are reported for selective extraction of actinides.⁷³



Figure 3.2: (a) Actinide ion binding lipophilic ligand (b) Eu(III) binding hydrophilic ligand.

The presence of more number of nitrogen donors in the ligand structurers leads to (i) decreased compatibility with non polar diluents, (ii) increased solubility in aqueous acidic feed solutions. Decreasing the number of nitrogen and increasing the oxygen donor sites in this type of ligand structure may result in increased selectivity towards harder metal ions of the same group, provided the steric requirements are not much changed. Also, increase in number of oxygen donor sites in the ligand structure shifts the extraction selectivity towards larger metal ions.

The steric factors in ligand-metal ion complex are governed by the spacer unit and the locations at which the coordinating groups are tethered to it. Steric factors of ligands remain similar in changing from terpyridine to triarylpyridine/diarylpyrdine (Figure 3.3) spacers. The number of oxygen sites in the molecular structure can be increased by tethering amide groups to TAP/DAP units through phenolic ethereal oxygen bridges.



Figure 3.3: (a) Terpyridine and (b) 2,6-diarylpyridine spacer units.

Triarylpyridine and diarylpyridine spacer derived ligands are finding interest as fluorophores for making chemo sensors.^{92,93} The interaction of 2,6-dimesitylpyridine with Tl(I) and In(I) cations is studied for developing tractable molecular M(I) compounds which are soluble in organic media (Figure 3.4).⁹⁴



Figure 3.4: Diarylpyridine spacer derived fluorophores.

2,4,6-triarylpyridine (TAP) has the interesting properties as a fluorescent spacer in these applications. The present work is on TAP and DAP as spacer units in the synthesis of new class of metal ion coordinating ligands. TAP and DAP molecular structures with phenolic hydroxyl groups at required locations are synthesized and are tethered with different amide groups to have a new class of diamide ligands. TAP and DAP molecular

scaffolds have the complete incinerable and innocuous nature as are made of only C, H, N and O. The general ligand design is to have one of the alkyl groups on amide nitrogen as methyl to reduce the steric strain during metal ion complexation. Heavier alkyl groups on amide nitrogen lead to weaker ligand strength but with a simultaneous increase in metal ion selectivity. As the present interest is on highly metal ion selective binding ligands, both alkyl groups on amide nitrogen are chosen to be bulky that also increases the overall lipophilicity of the ligand.

3.4.2 Synthesis of new class of diamide ligands

Due to their different applications, large number of methods have been developed for the synthesis of triarylpyridines (TAP). Most commonly triarylpyridines are synthesized by Krohnke method using α -pyridylmethylketone with chalcone under acid/base catalysis (Figure 3.5). The triaryl pyridines are also synthesized in a three component one pot reaction of aldehyde, ketone and a source of ammonia (nitrogen) in presence of Lewis/Bronsted acid catalysts. Similarly, they are synthesized using (i) benzyl alcohol⁹⁵ in place of benzaldehyde,⁹⁶ (ii) benzyl amine as a substitute of aldehyde and nitrogen. The different catalysts used in the synthesis of TAP/DAP moieties include (i) ammonium carbonate both as a source of nitrogen as well as catalyst,⁹⁷ (iv) hetero-polyacid of phosphorous and tungsten, (v) Lewis acids like bismuth triflate,⁹⁸ acetate.99 like pentaflurophenylammonium solid (vi) hetero compounds (vii) bismuth nitrate on alumina, with urea as a source of nitrogen¹⁰⁰ and (viii) montmorillonite clay as a cost effective catalyst.¹⁰¹

For the formation of trtiarylpyridines two types of mechanisms are commonly proposed both through the prior formation of chalcone intermediate. Further condensation of chalcone with another ketone molecule forms 1,5-dione that is oxidized to 2,3-ene-1,5-dione with simultaneous reduction of another chalcone molecule to dihydrochalcone.^{102,103} Then the cyclization takes place by reaction of ammonia with either 2,3-ene-1,5-dione or 1,5-dione. In case of 2,3-ene-1,5-dione, pyridine ring is formed directly whereas in case of 1,5-dione formation of pyridine ring involves air as an oxidizing agent (Figure 3.5).



Figure 3.5: Formation of triarylpyridine via 1,5-dione and 2,3-ene-1,5-dione intermediates.

The other proposed mechanism for the formation of substituted pyridine includes Diels-Alder type of reaction as an intermediate step that involves no formation of dihydrochalcone (Figure 3.6).¹⁰⁴



Figure 3.6: Triarylpyridine formation through Diels-Alder type reaction.

The other class of compounds of present interest are 4-alkyl-2,6-diarylpyridines. Replacing aryl group at 4th position of the central pyridine ring in TAP with an alkyl group (DAP) is expected to cause change in basicity of the pyridine nitrogen and also affects the solubility of the synthesized ligand molecules in aliphatic diluents. These compounds are synthesized by different methods similar to triarylpyridines. An iodine catalyzed reaction (Figure 3.7) of natural amino acids/ketones to give 2,4,6-trisubstituted, 2,6-disubstituted and 3,5-disubstituted pyridines is reported by J. C. Xiang etc..¹⁰⁵



Figure 3.7: Formation of triarylpyridines/4-alkyl-2,6-diarylpyridines from amino acids.

The reaction is believed to proceed by iodination at alpha carbon of the ketone and its substitution by pyridine resulting in the formation of pyridinium salt. The decomposition of alpha amino acid gives corresponding aldehyde and ammonia. Subsequent condensation of these formed species along with one more molecule of ketone gives the final desired product.

Xu Zhang et al. reported that the condensation of amine and the ketone takes place in presence of trifluromethanesulphonic acid catalyst to give corresponding 2,4,6-trisubstituted pyridine (Figure 3.8).¹⁰⁶ In absence of amine under the reaction conditions, formation of trisubstituted benzene is reported.



Figure 3.8: Formation of triarylpyridine from benzyl amine and ketone.

Here also the proposed reaction mechanism involved the formation of aldehyde and ammonia by the decomposition of amine. Chalcone formation takes place by the reaction of ketone and aldehyde as an intermediate step. Condensation of these formed species gives the desired substituted pyridine compound.

Hui Xu et al. have reported that the reaction of primary amines with ketone in presence of iodine catalyst in chlorobenzene solvent gives the tri-substituted pyridines in good yields²⁸ (Figure 3.9).

$$R$$
 NH_2 + Ph $Chlorobenzene, 140^{\circ}C$ Ph N Ph

Figure 3.9: Formation of triarylpyridine from primary amine and ketone.

The present work involves synthesis of TAP/DAP molecules and tethering amide groups to them to have new class of diamide ligands.

3.4.3 Synthesis of TAP-diamides

3-(6-(3-hydroxyphenyl)-4-phenylpyridin-2-yl)phenol (TAP-diol) (4) is synthesized by the reaction between 3'-hydroxyacetophenone (1), benzaldehyde (2) and ammonium acetate (3) in presence of different catalysts and under different reaction conditions (Table 3.1) to obtain the optimum one (Figure 3.10). The reactions cited in literature for the synthesis of TAP/DAP involved protected phenols. However, in the present work phenols are used as such. So far, the only two methods reported for the direct synthesis of TAP-diol (4) are (i) condensation of pyridiniummethylketone with appropriate chalcone in presence of ammonium acetate and acetic acid⁸⁵ and (ii) refluxing ketone, aldehyde and ammoniumaceate mixture in excess acetic acid.⁸⁶ Following the reported procedures, the yields of the desired dihydroxytriarylpyridine from 3'-hydroxyacetophenone was not satisfactory. Therefore, efforts were made to optimize the reactions conditions for getting highest possible yield.



3-(6-(3-hydroxyphenyl)-4-phenylpyridin-2-yl)phenol.

Table 3.1: Ev	valuation	of reaction	conditions	for the	formation	of TAP-	diol ((4).
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Molar ratio		ratio			0/ Viold		
Entry	of	react	tants	Catalyst (mole %)	Reaction Conditions	70 Y IEIQ	
	1	2	3			01 4	
1	2	1	1.5	Bi(OTf) ₃ (5)	CH ₃ CN, 90 ^o C, 15 h.	30	
2	3	2	1.5	Bi(OTf) ₃ (5)	CH ₃ CN, 90 ^o C, 15 h.	27	
3	2	1	1.5	SbCl ₃ (15)	CH ₃ CN, 90 ^o C, 15 h.	-	
4 2	•	1	1.5	SbCl ₃ (15)	CH ₃ CN,	29	
	2	I	1.5		MW 400 W, 30 mi.		
E	5 2 1	1	1.5		DMSO,	20	
3		1		$SDCI_{3}(15)$	MW 400 W, 30 min	39	
C	2	2 1 15 PiCL(15)	1	$\mathbf{D}(\mathbf{C})$ (15)	CH ₃ CN,	20	
6 2	Z	. 1	1.3	$BICI_3(15)$	MW 400 W, 30 min	29	
7	2	1	3	SbCl ₃ (15)	DMF, 130 ^o C, 15 h	53	
8	2	1	4	CH ₃ COOH (0.25)	DMF, 130 ⁰ C, 12 h.	52	

The three component one-pot reaction was carried out under inert atmosphere. Formation of dihydrochalcone along with the desired product is observed. The method developed is feasible for scale up due to available and cost-effective starting reagents and has the scope for further improvements. α -Chloroacetamides are synthesized by the reaction of α -chloroacetyl chloride with the corresponding secondary amine in dichloromethane/chloroform solvent using triethylamine as HCl scavenger (Figure 3.11).



Figure 3.11: Synthesis of α-chloroacetamides.

Four different α -chloroaceatmides with short/long and linear/branched alkyl group substituents on amide nitrogen are synthesized. The nature of the alkyl groups on amide nitrogen influence the metal ion binding properties of the ligand thereby synthesized. The yields of the four α -chloroacetamides are good (Table 3.2). The α -chloroacetamides are reacted with TAP-diol (Figure 3.12) to obtain the corresponding diamide ligands.

Table 3.2: Reaction yields of the α -chloroacetamides isolated after purification.

Entry	Product	% Yield
1	8 a	96
2	8b	74
3	8c	75
4	8d	79



Figure 3.12: Scheme for the synthesis of TAP-diamide ligands L_I-L_{IV}.

Ligands L_I and L_{II} are freely soluble in nitrobenzene but they have very poor solubility in aliphatic diluents such as (i) *n*-dodecane and (ii) *n*-dodecane + *iso*-decanol (5 % v/v) mixture. TAP-diamides with long chain alkyl substituents on amide nitrogen, L_{III} and L_{IV} are synthesized that are expected to be more soluble in aliphatic diluents. Although, both L_{III} and L_{IV} have better solubility than L_I and L_{II} in *n*-dodecane under sonication, they formed third phase on contact with nitric acid. 5 % (v/v) *iso*-decanol in *n*-dodecane combination is found to be the better diluent system for L_{III} and L_{IV} and no third phase formation observed after contacting with nitric acid solutions. The solubility of all four synthesized ligands will be discussed in later chapters in detail. All the synthesized diamide ligands are purified and fully characterized before extraction studies.

3.4.4 Synthesis of DAP-diamide

It was felt that increasing lipophilicity of diamide without much change in structure will improve the solubility of the ligand in *n*-dodecane alone thereby increase in extraction of metal ions (plutonium). As alkyl group is more hydrophobic than phenyl ring, attempt was made to prepare 4-pentyl-2,6-diarylpyridine diol (**10**). Thus, compound

10 is synthesized following the similar protocol as that of TAP-diol except using trifluoromethanesulfonic acid as catalyst under atmospheric air conditions (Figure 3.13).



Figure 3.13: Synthesis of 3-(6-(3-hydroxyphenyl)-4-pentylpyridin-2-yl)phenol (DAP-diol).

The DAP-diol (10) is reacted with α -chloroacetamide (8c) to yield the desired ligand L_V (Figure 3.14). The ligand L_V is purified by column chromatography and took for evaluation of metal ion extraction properties.



Figure 3.14: Scheme for synthesis of diamide ligand L_V .

3.5 Experiment procedures

3.5.1 Typical procedure for the synthesis of 3-(6-(3-hydroxyphenyl)-4-phenylpyridin-2-yl)phenol (3; TAP-diol)

A mixture of 3'-hydroxyacetophenone (1, 27.23 g, 200 mmol), freshly distilled benzaldehyde (2, 12.74 g, 120 mmol), ammoniumacetate (3, 31.0 g, 400 mmol) and acetic

acid (2.9 ml, 50 mmol) in DMF (200 ml) was heated at 130°C for 12 hours when TLC showed complete disappearance of compound 1. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with water (3 x 50 ml), brine and dried (Na_2SO_4). Solvent was removed under vacuo and the crude product was purified by triturating with toluene and petroleum ether to afford pure 4 as white solid.

Yield: 17.65 g, 52 %; **MP:** 252°C; **IR (ATR):** υ 1551, 1583, 1614, 3331 cm⁻¹; ¹**H NMR** (**500 MHz, CD₃COCD₃):** δ 6.96 (dd, *J* = 8.0 and 2.5 Hz, 2H), 7.35 (t, *J* = 7.75 Hz, 2H), 7.50 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 7.5Hz, 2H), 7.88 (s, 2H), 7.95 (d, *J* = 7.0 Hz, 2H), 8.07 (s, 2H), 8.49 (s, 2H); ¹³C **NMR (125 MHz, CD₃OD):** δ 114.57, 116.69, 117.27, 118.80, 127.83, 129.62, 129.67, 130.22, 139.28, 141.56, 150.67, 157.59, 158.43; **MS (ESI):** 340.3 (m/z).

3.5.2 General procedure for the synthesis of 2-chloro-*N*,*N*-dialkylacetamides (8)

To an ice-cooled solution of dialkylamine (7, 50 mmol) and triethylamine (75 mmol) in dichloromethane (100 ml) was added 2-chloroacetyl chloride (6, 9.34 g, 65 mmol) drop-wise over 1 h. After the addition the mixture was stirred at 0 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with cold water and neutralized with aq. HCl (1 N). Extracted with chloroform (3 x 50 ml), washed with water, brine and dried (Na₂SO₄). Solvent was removed under vacuo and the crude product was purified by silica gel (300-400 mesh) column chromatography by eluting with 3-5 % EtOAc in hexane to afford the pure amide (8).



Figure 3.15: 2-Chloro-N,N-diisobutylacetamide(8a).

Pale orange red viscous oil; **Yield:** 73 %; **IR (neat):** υ 1389, 1467, 1653, 2873, 2961 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.84 (d, *J* = 6.5 Hz, 6H), 0.89 (d, *J* = 6.5 Hz, 6H), 1.89 (m, 1H), 1.99 (m, 1H), 3.10 (d, *J* = 8.0 Hz, 2H), 3.16 (d, *J* = 7.5 Hz, 2H), 4.05 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 19.86, 26.15, 27.59, 41.19, 52.88, 55.53, 166.95; MS (ESI): 206.1 (m/z).

3.5.2.2 N,N-Dibutyl-2-chloroacetamide(8b)¹⁰⁷



Figure3.16: N,N-Dibutyl-2-chloroacetamide (8b).

Pale orange red coloured viscous oil; **Yield:** 95 %; **IR (CHCl₃):** υ 1430, 1460, 1590, 1654, 2874, 2933, 2960 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.82-0.88 (m, 6H), 1.20-1.28 (m, 4H), 1.42-1.50 (m, 4H), 3.17-3.25 (m, 4H), 3.98 (s, 2H),;¹³C NMR (125 MHz, CDCl₃): δ 13.47, 13.54, 19.77, 19.82, 29.18, 30.92, 41.05, 45.71, 47.79, 165.80; MS (ESI): 206.1 (m/z).

3.5.2.3 2-Chloro-N,N-dioctylacetamide(8c)¹⁰⁷



Figure 3.17: 2-Chloro-N,N-dioctylacetamide (8c).

Pale orange red coloured viscous oil; **Yield:** 79 %; **IR (neat):** υ 1428, 1464, 1654, 2856, 2925 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.86-0.89 (m, 6H), 1.28 (m, 22H), 1.53-1.58 (m, 4H), 3.26 (t, *J* = 7.5 Hz, 2H), 3.31 (t, *J* = 8.0 Hz, 2H), 4.04 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 14.02, 22.58, 22.60, 26.84, 26.89, 27.33, 29.12, 29.17, 29.23, 29.31, 31.71, 31.76, 41.27, 46.23, 48.32, 166.02; MS (ESI): 318.1 (m/z).

3.5.2.4 2-Chloro-N,N-bis(2-ethylhexyl)acetamide(8d)¹⁰⁸



Figure3.18: 2-Chloro-N,N-bis(2-ethylhexyl)acetamide (8d).

Pale brownish coloured viscous oil; **Yield:** 75 %; **IR (neat):** υ 1460, 1586, 1655, 2873, 2930, 2959 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.85-0.91 (m, 12H), 1.25-1.34 (m, 16H), 1.56-1.59 (m, 1H), 1.68-1.71 (m, 1H), 3.18 (d, *J* = 7.5 Hz, 2H), 3.25-3.29 (m, 2H), 4.07 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 10.49, 10.76, 13.90, 13.93, 22.89, 22.92, 23.66, 23.78, 28.55, 28.69, 30.31, 30.45, 36.71, 38.42, 41.43, 48.67, 51.61, 166.99; MS (ESI): 318.3 (m/z).

3.5.3 General procedure for the synthesis of TAP-diamides (L_I-L_{IV})

A mixture of TAP-diol (4, 50 mmol), *N*,*N*-dialkyl 2-chloroacetamde (8a-8d, 110 mmol), K_2CO_3 (150 mmol) and KI (25 mmol) in dry acetonitrile (200 ml) was refluxed for 30 h when the reaction got completed. Acetonitrile was removed; water was added and extracted the crude product with ethyl acetate (3 x 50 ml). The organic layer was washed with water, brine and dried (Na₂SO₄). Solvent was removed under vacuo and the crude product was purified by silica gel (100-200 mesh) column chromatography to afford the pure TAP-diamide (L_I-L_{IV}).

3.5.3.1 N,N-Di-isobutyl TAP-diamide (L_I)

Pale orange red coloured viscous oil; **Yield:** 81 %; **IR** (**CHCl₃**): v 1548, 1584, 1655, 2873, 2933, 2963, 3011, 3063 cm⁻¹; ¹H NMR (**500** MHz, **CDCl₃**): δ 0.83 (t, *J* = 7.0 Hz, 12H), 0.96 (t, *J* = 6.5 Hz, 12H), 1.98-2.03 (m, 4H), 3.22 (d, *J* = 8.0 Hz, 4H), 3.24 (d, *J* = 8.0 Hz, 4H), 4.84 (s, 4H), 7.04-7.06 (m, 2H), 7.42 (t, *J* = 8.3 Hz, 2H), 7.48 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.74-7.81 (m, 4H), 7.87 (s, 2H); ¹³C NMR (**125** MHz, **CDCl₃**): δ 20.08, 20.11, 26.17, 27.41, 52.70, 54.46, 67.49, 113.73, 115.33, 117.47, 120.40, 127.16, 129.02, 129.12, 129.73, 138.88, 141.07, 150.22, 157.07, 158.60, 168.19; HRMS (ESI): m/z Calcd for C₄₃H₅₆N₃O₄ (M + H)⁺: 678.4265; Found: 678.4264.



Figure 3.19: N,N-Di-isobutyl TAP-diamide (L₁).

3.5.3.2 N,N-Dibutyl TAP-diamide (L_{II})

Pale orange red coloured viscous oil; **Yield:** 83 %; **IR (CHCl₃):** υ 1547, 1583, 1645, 2872, 2957, 3033, 3062 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.88 (t, *J* = 7.5 Hz, 6H), 0.94 (t, *J* = 7.5 Hz, 6H), 1.25-1.40 (m, 8H), 1.51-1.64 (m, 8H), 3.33-3.38 (m, 8H), 4.80 (s, 4H), 7.03-7.05 (m, 2H), 7.41-7.55 (m, 5H), 7.75-7.86 (m, 6H), 7.88 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 13.84, 20.15, 20.19,29.58, 31.13, 45.74, 47.17, 67.59, 113.65, 115.19, 117.44, 120.37, 127.15, 129.02, 129.13, 129.78, 138.89, 141.13, 150.19,

157.04, 158.62, 167.32; **HRMS (ESI):** m/z Calcd for C₄₃H₅₆N₃O₄ (M + H)⁺: 678.4265; Found: 678.4257.



Figure 3.20: N,N-Dibutyl TAP-diamide (L_{II}).

3.5.3.3 N,N-Dioctyl TAP-diamide (L_{III})



Figure 3.21: N,N-Dioctyl TAP-diamide (L_{III}).

Colourless viscous oil; **Yield:** 94 %; **IR (neat):** υ1548, 1584, 1650, 2855, 2925, 3033, 3062 cm⁻¹; ¹H **NMR (500 MHz, CDCl₃):** δ 0.83-0.87 (m, 12H), 1.23-1.29 (m, 40H), 1.54-1.67 (m, 8H), 3.33-3.37 (m, 8H), 4.80 (s, 4H), 7.03-7.05 (m, 2H), 7.41-7.55 (m, 5H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.81-7.84 (m, 4H), 7.88 (s, 2H); ¹³C **NMR (125 MHz, CDCl₃):**

δ 14.03, 14.06, 22.58, 22.61, 26.94, 27.00, 27.48, 29.05, 29.20, 29.32, 29.34, 31.72, 31.79, 45.99, 47.43, 67.70, 113.71, 115.13, 117.38, 120.37, 127.14, 129.00, 129.12, 129.76, 138.90, 141.12, 150.18, 157.00, 158.61, 167.34; **HRMS (ESI):** m/z Calcd for $C_{59}H_{88}N_{3}O_{4}$ (M + H)⁺: 902.6769; Found: 902.6807.

3.5.3.4 N,N-Bis(2-ethylhexyl)TAP-diamide (L_{IV})



Figure 3.22: N,N-Bis(2-ethylhexyl) TAP-diamide (L_{IV}).

Colorless viscous oil; **Yield:** 83 %; **IR (neat):** v 1548, 1585, 1650, 2872, 2927, 3033, 3063 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.78-0.85 (m, 12H), 0.87-0.93 (m, 12H), 1.17-1.37 (m, 28H), 1.64-1.66 (m, 8H), 3.28-3.31 (m, 8H), 4.83 (s, 4H), 7.02-7.04 (m, 2H), 7.40-7.54 (m, 5H), 7.75 (d, *J* = 7.0 Hz, 2H), 7.76-7.84 (m, 4H), 7.88 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 10.52, 10.93, 14.02, 14.04, 23.00, 23.72, 23.76, 23.94, 28.67, 28.86, 28.93, 30.48, 30.64, 36.59, 38.05, 48.37, 50.46, 67.67, 113.85, 115.08, 117.35, 120.39, 127.13, 128.79, 128.99, 129.12, 129.70, 138.91, 141.14, 150.13, 157.05, 158.56, 168.40; HRMS (ESI): m/z Calcd for C₅₉H₈₈N₃O₄ (M + H)⁺: 902.6769; Found: 902.6781.

3.5.4 Procedure for the synthesis of 3-(6-(3-hydroxyphenyl)-4-pentylpyridin-2-yl)phenol (10; DAP-diol)

A mixture of 3'-hydroxyacetophenone (1, 27.23 g, 200 mmol), freshly distilled hexanal (9, 12.02g, 120 mmol), ammoniumacetate (3, 31.0 g, 400 mmol) and trifluoromethane sulphonic acid (7.50 gm, 50 mmol) in DMF (200 ml) was heated at 130 °C for 12 hours when TLC showed complete disappearance of compound 1. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with water (3 x 50 ml), brine and dried (Na₂SO₄). Solvent was removed under vacuo and the crude product was purified by triturating with toluene and petroleum ether to afford pure **10** as brownish white thick waxy solid.



Figure 3.23: 3-(6-(3-hydroxyphenyl)-4-pentylpyridin-2-yl)phenol (10; DAP-diol).

Viscous oil; **Yield:** 20 g, 60 %; **MP:** low melting solid; **IR (ATR):** υ 1237, 1282, 1406, 1456, 1494, 1552, 1594, 1634, 2870, 2929, 2957, 3332 cm⁻¹; ¹H NMR (500 MHz, **CD₃COCD₃):** δ 0.93 (t, J = 7.5, 3H), 1.40 (t, J = 3.75, 4H), 1.88(m, 2Hz), 2.89 (t, J = 7.5 Hz, 2H), 6.93 (ddd, J = 8, 2.5 and 1Hz), 6.93 (ddd, J = 8.1, 2.4 and 1Hz, 1H), 7.29-7.30 (m, 2H), 7.31 (m, 1H), 7.33-7.35 (m, 1H), 7.42 (d, J = 1.5 Hz, 1H), 7.67 (dd, J = 8 and 1Hz, 1H), 7.74 (t, J = 2 Hz, 1H), 7.87 (d, J = 1.5 Hz, 1H). ¹³C NMR (125 MHz, **CD₃OCD₃):** δ 14.06, 22.97, 29.10, 114.57, 116.69, 117.27, 118.80, 127.83, 129.62, 129.67, 130.22, 139.28, 141.56, 150.67, 157.59, 158.43; MS (ESI): 340.3 (m/z).

3.5.5 Procedure for the synthesis of PDAP-diamide (L_V)

A mixture of PDAP-diol (4, 50 mmol), *N*,*N*-dioctyl 2-chloroacetamde (8c, 110 mmol), K_2CO_3 (150 mmol) and KI (25 mmol) in dry acetonitrile (200 ml) was refluxed for 30 h, when the reaction got completed acetonitrile was removed; water was added and extracted the crude product with ethyl acetate (3 x 50 ml). The organic layer was washed with water, brine and dried (Na₂SO₄). Solvent was removed under vacuo and the crude product was purified by silica gel (100-200 mesh) column chromatography to afford the pure PDAP-diamide (L_V).

Reddish oil; **Yield:** 98 %; **IR (neat):** v 1216, 1262, 1288, 1377, 1465, 1553, 1596, 1651, 2856, 2927, 2956, 3005 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.85-0.94 (m, 15H), 1.24-1.30 (m, 44H), 1.40-1.42 (m, 4H), 1.54 (m, 6H), 2.90 (t, 2H), 3.31-3.36 (m, 8H), 4.76 (d, J = 2 Hz, 4H), 7.01 (d, J = 8.5 Hz, 2H), 7.41-7.55 (m, 5H), 7.75 (d, J = 7.5 Hz, 2H), 7.81-7.84 (m, 4H), 7.88 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 14.03, 14.06, 22.58, 22.61, 26.94, 27.00, 27.48, 29.05, 29.20, 29.32, 29.34, 31.72, 31.79, 45.99, 47.43, 67.70, 113.71, 115.13, 117.38, 120.37, 127.14, 129.00, 129.12, 129.76, 138.90, 141.12, 150.18, 157.00, 158.61, 167.34; HRMS (ESI): m/z Calcd for C₅₉H₈₈N₃O₄ (M + H)⁺: 902.6769; Found: 902.6807.



Figure 3.24:PDAP-diamide (L_V).

Chapter – 4

EVALUATION OF DIAMIDE LIGANDS FOR SELECTIVE EXTRACTION OF PLUTONIUM(IV) IN MOLECULAR DILUENTS

4 Evaluation of diamide ligands for selective extraction of plutonium(IV) in molecular diluents

4.1 Preamble

In the present chapter, TAP spacer diamide ligands *viz.*; L_I (*iso*-butyl), L_{II} (*n*-octyl), L_{IV} (2-ethylhexyl) and one DAP spacer diamide ligand L_V (*n*-octyl) are evaluated in molecular diluents (i) nitrobenzene and (ii) 5 % (v/v) *iso*-decanol in *n*-dodecane (5 % ID/DD) for their selective metal ion extraction properties from nitric acid solutions. Gratifyingly, these ligands have shown high selectivity to Pu(IV) extraction.

4.2 Introduction

Beside the suitability of complexing ligand, screening for suitable diluents for better solubility of the metal ion-ligand complex formed is an important component during a solvent extraction study. An ideal diluent used in solvent extraction processes should satisfy the following attributes as

- (i) C, H, N, O should be the only constituents for complete incinerable nature.
- (ii) High flash point and preferably of high boiling point.
- (iii) Low freezing point, poor water solubility, compatibility under acidic/basic conditions, non-reactivity with the ligands and solute.
- (iv) Should not form third phases during solvent metal ion loading conditions.
- (v) Minimal decomposition under irradiation conditions.

According to Marcus¹⁰⁹ the diluents used in liquid-liquid extraction can be classified in five categories. Commonly used diluents in solvent extractions are (i) aliphatic molecules (hexane, dodecane etc.), (ii) aromatic ones (benzene, toluene,

nitrobenzene etc.), (iii) ketones (cyclohexanone etc.) and (iv) alcohols (octanol, iso-decanol etc.). In these aliphatic diluents come under class five while long chained primary alcohols are in class two according to the Marcus classification. Dielectric constants of aromatic diluents are usually higher due to the presence of polarizable π -electron clouds. Polar metal complexes gets dissolved in aromatic diluents through interactions of polarizable π electron cloud (cation- π interaction).¹¹⁰ This has been substantiated by the role that aromatic π -cloud interactions play during selective extraction of Cs(I) ion with calix[4]crown extractants.¹¹¹ The energy required by the extracted complex for cavity formation between the diluent molecules and its interaction energies with them decide the outcome of an extraction process. The energy for cavity formation by the extracted complex is low in non polar, less interacting aliphatic diluents, favoring extraction process whereas the interaction energy of the extracted complex with the diluent phase molecules is favorable in polar/polarizable diluents with high dielectric constant. Hildebrand¹¹² solubility parameter is based on the assumption that the same intermolecular attractive forces have to overcome to vaporize a liquid, as to dissolve a solute in it and is

$$\delta = \sqrt{\frac{\Delta H_{vap} - RT}{V_m}}$$

 ΔH_{vap} is the heat of vaporisation per mole, R is the gas constant, T is the temperature and V_m is the molar volume. Hansen parameter divides the Hildebrand parameter in to three parts, which corresponds to hydrogen interactions, dipole-induced dipole interactions and dispersion interactions.¹¹³

$$\delta^2 = \delta^2_{hydrogen} + \delta^2_{dipole} + \delta^2_{dispersion}$$

The interactions between a species and a surrounding diluent are commonly coupled to the Gibbs free energy of solvation. In order to summarize the cavity cost and the gaining in interaction energy between the solute/complex and surrounding molecules (aqueous as well as diluent molecules) Kamlet and Taft developed the solvatochromic parameters for a number of elements.¹¹⁴

$$\Delta_{\text{solv}} G_{\text{B}}^{\text{o}} = A_{\text{o}} + A_{\pi} \pi^* + A_{\alpha} \alpha + A_{\beta} \beta + A_{\delta} \delta^2$$

where α is the hydrogen bonding donation parameter for the diluent, β is the hydrogen bonding acceptance parameter for the diluent and π is the polarity or polarizability parameter for the diluent. 'A' is the characterized parameters for the solute. The first two terms show the dispersion interactions, while the second two are of hydrogen interaction and the last term correspond to the cavity cost. The common problem in using this calculation is the lack of information concerning the nature of the complex and therefore the lack of parameters concerning the complex.¹¹⁵

Terpyridine based diamides are evaluated for their selective actinide extraction properties in diluents like nitrobenzene and octanol etc..⁷³ The typical behavior of nitrobenzene in inhibiting the radiolysis of BTP molecules is studied by Nilsson et al.¹¹⁶ Similarly the scavenging of hydrated electron generated during radiolysis by DMSO is reported by Asmus et al..¹¹⁷

The new class of diamide ligands L_I-L_{IV} synthesized for the present study is freely soluble in toluene, nirobenzene, benzene and chloroform. Extraction studies $(O/A = 1, T_{mix} = 2 h)$ with these ligands L_I-L_{IV} (0.1 M) in toluene diluent from a mixture of rare earth element Ce, Dy, Er, Gd, Sm, Y and Yb (each at $\approx 200 \text{ mg/L}$) ions at both 0.5 and 2 N HNO₃ feed acids revealed no significant extraction, however little extraction of U(VI) and Th(IV) ions from 2 N HNO₃ solutions is observed. As toluene is supposed to undergo nitration under higher nitric acid concentration after prolonged periods of contact, this is not a diluent of choice. Ligands L_I-L_{IV} are freely soluble in nitrobenzene which is a commonly used diluent in solvent extraction studies of polyaromatic ligands. Ligands L_I-L_{IV} in nitrobenzene as an aromatic diluent are evaluated for their selective extraction of Pu(IV).

It is of interest to study the extraction properties of the ligands in aromatic diluents to understand the mechanism of metal ion extraction and the other related interactions. Still then, diluent is the major quantity in solvent mix and nitrobenzene even though of choice in case of polyaromatic ligands, due to its hazardous health effects, is not much preferable. From application point of view the long chain aliphatic diluents are of interest than the aromatic diluents because of their high flash point, low volatility and the less related health hazards etc.. Ligands $L_{I}-L_{II}$ are very less soluble in aliphatic diluents and form third phase on contact with nitric acid. The ligands $L_{III}-L_{IV}$ have better solubility in aliphatic diluents because of long chain alkyl substituents on amide nitrogens. Keeping this in consideration a new ligand L_V with increased aliphatic nature for better solubility in aliphatic diluents is synthesized. In this regard ligands $L_{III}-L_V$ (0.1 M) in 5 % ID/DD as an aliphatic diluent are studied for their selective extraction of Pu(IV) from nitric acid solutions.

4.3 Present work

4.3.1 Solubility of ligands L_I-L_{IV} in different molecular diluents

The solubility properties of the ligands $L_{I}-L_{IV}$ in different diluents are presented in Table 4.1. The ligands are appreciably soluble in aromatic diluents like benzene, toluene and nitrobenzene, freely soluble in chloroform whereas solubility in *n*-dodecane is very poor.

	Solubility in diluents						
Ligand	nitrobenzene	toluene	Benzene	Chloroform	<i>n</i> -dodecane		
L _I	Freely soluble	Soluble ^a	Soluble ^a	Freely soluble	Insoluble ^b		
L_{II}	Freely soluble	Soluble ^a	Soluble ^a	Freely soluble	Insoluble ^b		
L _{III}	Freely soluble	Soluble ^a	Soluble ^a	Freely soluble	Insoluble ^b		
L _{IV}	Freely soluble	Soluble ^a	Soluble ^a	Soluble	Insoluble ^b		

Table 4.1: Solubility of the diamide ligands L_I - L_{IV} in different organic diluents.

^aSoluble after 5 min of ultrasonification; ^bSoluble after prolonged ultrasonification but the organic phase splits on contact with nitric acid solutions.

Table 4.2: Extraction of Pu(IV) employing 0.1 M diamides $L_I - L_{IV}$ dissolved in differentorganicorganicorganicorganicorganicphase.

Ligand	D _{Pu(IV)} in diluents					
Liganu	Nitrobenzene	Toluene	Benzene	Chloroform		
L	62.3 ± 0.2	3.1 ± 0.2*	12.7 ± 0.6	0.10 ± 0.03		
L_{II}	107.2 ± 0.7	5.2 ± 0.4	9.2 ± 0.8	0.08 ± 0.01		
L _{III}	24.7 ± 0.4	8.0 ± 0.2	4.7 ± 0.1	0.07 ± 0.00		
L _{IV}	9.9 ± 0.1	2.9 ± 0.1	1.7 ± 0.1	0.01 0.00		

The extraction trend is a complex phenomenon dependent on various factors such as dielectric constant of the diluent, Schmidt's diluent parameter, Hildebrand solubility parameter, organophilicity of the extracted complex, etc. as discussed, which is not investigated here further. The results presented in Table 4.2 lead further studies to continue on extraction characteristics of L_I - L_{IV} in nitrobenzene diluents.

4.3.2 Kinetics of Pu(IV) extraction

Solutions of the ligands $L_{I}-L_{IV}$ (0.1 M) in nitrobenzene diluent are contacted with an equal volume of Pu(IV) aqueous solutions in 3 M nitric acid for different time intervals. After each step of contact, allowing for settling and centrifugation, the aliquot samples from aqueous and the corresponding organic phases are assayed for plutonium activity to obtain the contact time dependent variation of $D_{Pu(IV)}$ (Figure 4.1).



Figure 4.1: Contact time dependence of $D_{Pu(IV)}$ for L_I-L_{IV} (0.1 M) in nitrobenzene diluent from 3 M nitric acid solution.

The uptake of Pu(IV) is high for all the four ligands $L_{I}-L_{IV}$. The extraction of Pu(IV) from 3 M nitric acid is faster with L_{I} and L_{IV} (branched chain, \approx 5 min) and slower with L_{II} and L_{III} (linear chain, \approx 30 min). The $D_{Pu(IV)}$ values obtained with 3 M HNO₃ feed solution of Pu(IV) followed the order, $L_{II} > L_{I} > L_{IV}$ indicating

higher extraction efficiency with shorter alkyl chain amide ligands than the longer ones. In both the cases, diamides with linear alkyl chain dominated over the branched ones.

4.3.3 Effect of nitric acid concentration on $D_{Pu(IV)}$ and $D_{U(VI)}$

The dependence of $D_{Pu(IV)}$ on aqueous phase nitric acid concentration helps in establishing the extraction/stripping conditions and understanding of the mechanisms involved. This information is helpful at applications in fuel cycle with various streams of nitric acid having different concentrations of plutonium and composition depending on origin. The region of higher $D_{Pu(IV)}$ is suitable for extraction whereas the lower for stripping. Aqueous phase at different nitric acid concentrations (0.5-6 M) containing Pu(IV) is contacted with 0.1 M solutions of the ligand in nitrobenzene diluent for 2 h duration to ensure attainment of equilibrium. After allowing for settling and centrifugation, suitable aliquots from the separated aqueous and organic phases are analyzed for Pu(IV) activity. The corresponding $D_{Pu(IV)}$ values obtained against the aqueous phase nitric acid concentration for the four ligands L_I-L_{IV} are as shown in Figure 3.2.

The $D_{Pu(IV)}$ variation pattern is similar for the four ligands $L_{I}-L_{IV}$. Sharp increase in the $D_{Pu(IV)}$ values is observed from 0.5 to 2-3 M HNO₃ beyond which marginal decrease is noted. The initial sharp increase in $D_{Pu(IV)}$ value may be attributed to the positive dependence of Pu(IV) extraction on the nitrate ion concentration while the subsequent slow decrease in the $D_{Pu(IV)}$ values may be due to a growing competition between the metal ion and the hydrogen ion for the ligand molecules. At all acid concentrations the ligands $L_{I}-L_{IV}$ showed the systematic pattern with L_{II} dominating with respect to its $D_{Pu(IV)}$ value at all acidities.



Figure 4.2: Effect of aqueous phase nitric acid concentration on $D_{Pu(IV)}$ for L_I-L_{IV} (0.1 M) in nitrobenzene diluent.

Similar extraction studies are carried out with U(VI) solutions in nitric acid in exactly same way and under conditions mentioned above for Pu(IV) to understand the effect of aqueous phase nitric acid concentration on $D_{U(VI)}$ for all the four ligands $L_{I}-L_{IV}$. The results are as shown in Figure 4.3 and at all acidities much lower $D_{U(VI)}$ values than the $D_{Pu(IV)}$ are observed.

There is an initial increase and approaching saturation value at higher acidities observed for $D_{U(VI)}$ and the behavior is same for all four ligands L_I-L_{IV} . The difference in the metal ion extraction with the change in ligands is much lesser as compared to the case of Pu(IV). This can be attributed to steric factors imposed by the strained conformations of the ligands and also to the strain involved in coordination of the diamides in the equatorial plane of the uranyl ion. The SF ($D_{Pu(IV)}/D_{U(VI)}$) values get significantly affected with increasing aqueous phase HNO₃ concentration having lowest at 6 M HNO₃

(Table 4.4). Thus, all the four ligands L_I-L_{IV} are selective to Pu(IV) over U(VI) extraction and is higher in the 2-3 M of HNO₃ concentration range.



Figure 4.3: Effect of aqueous phase nitric acid concentration on $D_{U(VI)}$ for L_I-L_{IV} (0.1 M) in nitrobenzene diluent.

4.3.4 Estimation of acid uptake by the ligands

The details of the experiment procedure for estimation of acid uptake are in Chapter – II. Acid uptake is an indication of the basicity of the ligands under study and is useful in understanding the effect of aqueous phase acid concentration on metal ion distribution. The amount of acid pick depends on the diluent used, concentration of the ligand, feed nitric acid concentration etc.. Solutions of the ligands L_I-L_{IV} (0.1 M) in nitrobenzene diluent are contacted with aqueous HNO₃ solutions of varying concentration (0.5-6 M) for 10 h duration. After allowing for settling and centrifugation, the aliquots from the separated aqueous and organic layers are estimated for acid content. The acid picked by the ligands $L_{I}-L_{IV}$ increases systematically with the increasing aqueous phase acid concentration (Figure 4.4).



Figure 4.4: Effect of aqueous phase nitric acid concentration on acid pickup by $L_{I}-L_{IV}(0.1 \text{ M})$ nitrobenzene diluent.

4.3.5 Metal ion-Ligand complex stoichiometry studies

The extraction of Pu(IV) by the TAP/DAP-diamides (L) takes place by coordination to $Pu(NO_3)_4$ forming a charge neutral organic phase soluble complex, represented as

$$\operatorname{Pu}_{(\operatorname{aq.})}^{4+} + 4 \operatorname{NO}_{3}^{-}_{(\operatorname{aq.})} + n \mathbf{L}_{(\operatorname{org.})} \leftrightarrows \operatorname{Pu}(\operatorname{NO}_{3})_{4} \mathbf{L}_{n (\operatorname{org.})}$$

By the similar arguments made in Chapter – 2, based on the expressions for equilibrium constant and the distribution ratio, the relation between the $D_{Pu(IV)}$ and the [L] is expressed by

$$\log D_{Pu(IV)} = \log K_{ex.} + 4 \log[NO_3^-]_{(aq.)} + n \log[\mathbf{L}]_{(org.)}$$

The terms in square brackets indicate the concentration of respective species at equilibrium conditions. The subscript indicates the phase in which the corresponding entity is present.

Solvents with varying concentration of the ligand in nitrobenzene diluent are equilibrated with aqueous Pu(IV) solutions in 3 M HNO₃. After allowing for settling and centrifugation, the separated aqueous and organic layers are assayed for Pu(IV) activity to estimate $D_{Pu(IV)}$. As the amount of plutonium used for the estimation of $D_{Pu(IV)}$ is very small (tracer) as well as the nitric acid pick by the ligands is very small compared to 3 M HNO₃ concentration of the aqueous feed, it can be fairly assumed that $[NO_3^-]_{(aq,)}$ remains constant during extraction and also K_{ex} is a constant at constant temperature conditions. This makes it possible to express the above equation as

$$\log D_{M} = C + n \log[L]$$

where

$$C = \log K_{ex.} + 4 \log[NO_3^-]_{(aq.)}$$

C can be assumed to be a constant under fore mentioned conditions and at constant temperature. The plot of $\log D_{Pu(IV)}$ versus $\log [L]_{(org.)}$ gives a straight line with a slope that is equal in magnitude to number of ligand molecules in the $[Pu(NO_3)_4L_n]_{(org.)}$ complex.

By slope analysis (Figure 4.5), two different types of species exist during the extraction of Pu(IV) with ligands having short and long chain alkyl substitution on the amide nitrogen. Slope values close to 2 for L_I (*iso*-butyl) and L_{II} (*n*-butyl) indicate

extraction of mixed species. Pu(IV)-L complex with 1:2 stoichiometry is extracted to a larger extent along with minor amounts of 1:1. Conversely slope values close to 1 for both L_{III} (*n*-octyl) and L_{IV} (2-ethylhexyl) indicate Pu(IV)-L complex with 1:1 stoichiometry is predominantly extracted. Long chain alkyl substituents (*n*-octyl and 2-ethylhexyl) on amide nitrogen ($L_{III}-L_{IV}$) ensure higher lipophilicity of the Pu(IV)-L complex sufficing for extraction even with only one ligand. Also, the higher steric strain involved with $L_{III}-L_{IV}$ (bulky alkyl groups) during complexation limits the stoichiometry of Pu(IV)-L complex to 1:1. On the other hand, for the shorter alkyl chain ligands $L_{I}-L_{II}$ significantly higher lipophilicity of the Pu(IV)-L complex involving higher number of ligands results in higher $D_{Pu(IV)}$ compared to $L_{III}-L_{IV}$.



Figure 4.5: $D_{Pu(IV)}$ against L_I-L_{IV} concentration variation in nitrobenzene diluent for extraction from 3 M HNO₃ solutions.

 $D_{U(VI)}$ values are lower than one for all the ligands (L_I-L_{IV}). Similar to the case of $D_{Pu(IV)}$, the $D_{U(VI)}$ values are higher for L_I-L_{II} compared to $L_{III}-L_{IV}$. The plot of

 $\log D_{U(VI)}$ versus $\log [L]_{(org.)}$ for the case of L_I has given (Figure 4.6) the slope value near to unity indicating 1:1 complex formation between the uranyl nitrate and the ligand.



$$UO_2^{2+} + 2 NO_{3(aq.)}^{-} + \mathbf{L}_{(org.)} \Leftrightarrow UO_2(NO_3)_2 \mathbf{L}_{(org.)}$$

Figure 4.6: $D_{U(VI)}$ for extraction from feed at 3 M HNO₃ against varying L_I concentrationin in nitrobenzene diluent.

Species of the type $Pu(NO_3)_4(L)_2$ are extracted in case of TBMA (tetrabutylmalonamide) and TIBMA (tetra-isobutylmalonamide)¹¹⁸ similar to that observed with L_I-L_{II} in the present study. On the other hand, species of the type $Pu(NO_3)_4(L)_3$ is reported with DMDBTDMA.¹¹⁹ Species of the type, $Pu(NO_3)_4(L)$ is reported with OTDA¹¹⁹ in a diluent composition of 70 % *n*-dodecane + 30 % *iso*-decanol. Diluents have a significant role in deciding the nature of the extracted metal ion complex and observed that 1:1 species are extracted with OTDA when the diluent polarity is increased significantly by adding 30% *iso*-decanol.¹²⁰ It can be speculated that the Pu(IV) specificity observed in the present study could be attributed to the nature of the extracted species and also the rigid coordination environment with the present class of ligands.

4.3.6 Stripping studies

Recovery of extracted metal ions from the organic phase to a suitable aqueous phase is a pre-requisite to any process application. The extraction of plutonium from nitric acid solutions (3 M HNO₃) that contained significant amounts of Pu(III) (with characteristic blue coloration) given low D_{Pu} . It is clear that (Figure 4.2) low acidities are favorable for plutonium stripping. Keeping this in view a solution containing mixture of 0.5 M NH₂OH and 1 M HNO₃ that generates in effect 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ solution is used for stripping studies. In the present studies a combination of a reducing agent that transforms plutonium to less extractable trivalent state and a low acid concentration that supports low D_{Pu} is used for plutonium stripping. For practical applications, faster kinetics and quantitative stripping are required. Solutions of the four ligands $L_I - L_{IV}$ (0.1 M) in nitrobenzene diluents with a known preloaded plutonium activity are contacted with 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ aqueous solution at equal volume for different time intervals. After allowing for settling and centrifugation, the separated aqueous and organic layers are assayed for plutonium activity. The percentage stripping is estimated for different contact time intervals. The results obtained are shown in Figure 4.7. Quantitative stripping (> 99.9 %) of plutonium from the organic extract is achieved in a single contact. The stripping kinetics is fast for L_{II} and L_{IV} (\approx 10 min) while is relatively slow for L_I and L_{III} (\approx 30 min) for quantitative stripping.

In case of L_{IV} , both extraction and stripping kinetics are faster for plutonium. For the kinetics of plutonium, linear alkyl chain ligands L_{II} and L_{III} shown slower extraction and faster stripping whereas branched alkyl chain ligand L_{I} shown faster extraction and slower stripping.



Figure 4.7: Contact time dependence of plutonium stripping for L_I-L_{IV} (0.1 M) in nitrobenzene diluent.

4.3.7 Extraction selectivity of ligands for Pu(IV)

The purity of the metal ion recovered from a feed solution containing different other metal ions is decided by the selectivity of the solvent (ligand) during extraction. The extraction selectivity of a solvent to particular metal ion depends on (i) the type of extractant, (ii) diluent and modifier combinations, (iii) feed acid type and its concentration, (iv) the other metal ions present and their corresponding concentrations, (v) valence states of the metal ions present in feed, (vi) complexing agents that if any added to feed during extraction etc.. Ligands L_I-L_{IV} are evaluated to their selectivity for Pu(IV) over Cs(I), Sr(II), Eu(III), U(VI), Am(III), Th(IV) and Zr(IV) ions.

Solutions of the ligands L_I-L_{IV} (0.1 M) in nitrobenzene diluent are contacted separately with 3 M HNO₃ solutions of each individual Cs(I), Sr(II), Eu(III), U(VI), Am(III) tracer for 2 h time period. After allowing for settling and centrifugation, the
separated aqueous and organic layers are assayed for activity of the corresponding tracer element to estimate their D values. The D values obtained are presented in Table 4.3.

Table 4.3: Extraction of some actinides and fission product metal ions from 3 M HNO₃ with solutions of the ligands L_I-L_{IV} (0.1 M) in nitrobenzene diluent.

Ligand	Distribution ratio for the metal ion					
Liganu	Pu(IV)	U(VI)	Am(III)	Eu(III)	Cs(I)	Sr(II)
L _I	62.3 ± 0.2	0.7 ± 0.1	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$
L _{II}	107.2 ± 0.7	0.7 ± 0.0	$< 1 \text{ x } 10^{-3}$	< 1 x 10 ⁻³	< 1 x 10 ⁻³	< 1 x 10 ⁻³
$\mathbf{L}_{\mathbf{III}}$	24.7 ± 0.4	0.5 ± 0.0	$< 1 \text{ x } 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$
L _{IV}	9.9 ± 0.1	0.6 ± 0.0	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$

While U(VI) extraction is about 1 to 2 orders of magnitude lower as compared to the Pu(IV) extraction, Am(III) extraction is negligibly small (< 1.0×10^{-3}). The PUREX solvent extracts U(VI) to a much larger extent as compared to that of Pu(IV) whereas the results obtained with the present extractants are quite interesting. Malonamide ligands though extracted Pu(IV) to a much larger extent as compared to U(VI), there used to be quite significant extraction of Am(III).¹¹⁹ Negligible extraction of fission product ions such as Eu(III), Sr(II) and Cs(I) is observed for the presently used diamide extractants. The comparative extraction of Pu(IV) and U(VI) with their respective separation factors (SF) over metal ions like Cs(I), Sr(II), Eu(III), U(VI), Am(III) are presented in Table 4.4. The separation factor is achieved as the ratio of the distribution ratio for targeted metal ion over the distribution ratio for other metal ions. The SF values are most impressive for L_{II} while for L_{IV} are at least. The diamide ligands used in the present study shown some unusual specificity for Pu(IV) extraction.

Ligand	S.F. _{Pu/U}	S.F. _{Pu/M}	S.F. _{U/M}
L_{I}	89	$> 6.23 \mathrm{x10}^4$	> 700
L _{II}	153	> 1.07x10 ⁵	> 700
L _{III}	49.4	$> 2.47 \mathrm{x} 10^4$	> 500
L _{IV}	16.5	$> 9.9 \times 10^3$	> 600

Table 4.4: Separation factor values for Pu(IV) over U(VI), Am(III), Eu(III), Cs(I), Sr(II) with the ligands L_I - L_{IV} (0.1 M) in nitrobenzene diluents from 3 M HNO₃.

Note: M = Am(III) or Eu(III) or Sr(II) or Cs(I)

Ligands L_I-L_{IV} are evaluated for their selective extraction properties to plutonium over Th(IV) and Zr(IV). Solutions of the ligands L_I-L_{IV} (0.1 M) in nitrobenzene diluent are contacted separately with 3 M nitric acid solutions of Th(IV) (406 mg/L) and Zr(IV) (405mg/L) for 2 h duration. After contacting, the solutions are allowed for settling, centrifuged and the separated aqueous layer samples are analyzed on ICP-OES for the concentrations of corresponding metal ions. For Th: 269.242 nm and for Zr: 327.305 nm wavelength lines are selected for the estimation of emission intensities. The organic phase metal ion concentrations are estimated by the difference in concentration values from aqueous feed to raffinate samples. The D values are obtained from the ratio of organic to corresponding aqueous phase metal ion concentrations and the results are as present in Table 4.5. It is apparent from the results that zirconium extraction is very less whereas thorium got extracted tosome extent.

Table 4.5: Estimation of $D_{Th(IV)}$ and $D_{Zr(IV)}$ values for L_I-L_{IV} (0.1 M) in nitrobenzene diluent from 3 M HNO₃ aqueous solutions.

D value		Liga	ands	
D vulue	LI	L _{II}	L _{III}	L _{IV}
D_{Th}	1.30 ± 0.03	1.20 ± 0.04	1.08 ± 0.03	0.81 ± 0.03
D _{Zr}	< 10 ⁻³	0.001 ± 0.028	0.023 ± 0.027	0.26 ± 0.030

4.3.8 Radiation stability

The solvents used in nuclear industry should have high radiation stability for processing solutions containing highly radioactive metal ions. The type of radiation and the exposure time decide the amount of energy deposited. Ionizing radiations have more linear energy transfer (LET) rate than the electromagnetic radiations. The irradiation of the samples generates highly active free radical species that decompose the extractant molecules affecting the solvent extraction properties significantly. Because of low linear energy transfer in case of gamma rays the recombination of the generated free radicals is low. Organic extractants with aromatic groups are expected to be more resistant to radiolytic degradation as compared to those containing aliphatic groups.

The radiolytic stability of the ligand can be assessed by a variety of methods for example by monitoring the undegraded ligand or the degradation product. The radiolytic degradation can affect the metal ion extraction and hence, measuring the distribution ratio values of the metal ions is a good alternative practice. As this method can give a direct report on the metal ion extraction efficiency of the ligands, the same is followed here. Solutions of the ligands $L_{I}-L_{IV}$ (0.1 M) in nitro benzene diluent are subjected to irradiation in gamma chamber equipped with ⁶⁰Co source ($\approx 2 \text{ KGy/h}$) up to 630 kGy and

the $D_{Pu(IV)}$ values are monitored at various absorbed doses. The results (Figure 4.8) indicate reasonably good stability of all the four extractants. For L_{II} and L_{IV} , a linear decrease in the $D_{Pu(IV)}$ values is seen and about 40-45 % decrease in the distribution ratio values is attributed directly to the degradation of the ligands. On the other hand, the decrease in metal ion extraction with L_{I} is marginally lower and an increase in metal ion extraction observed for L_{III} has to be studied further.



Figure 4.8: Extraction of Pu(IV) from 3 M HNO₃ solutions using L_I-L_{IV} (0.1 M) in nitrobenzene diluent that are exposed to varying amounts of gammaray dose.

4.4 Evaluation of L_I-L_{IV} in 5 % ID/DD for selective extraction of Pu(IV)

4.4.1 Optimization of solvent composition

Ligands $L_I - L_V$ are soluble in *n*-dodecane diluent to different extents (with prolonged sonication for L_I and L_{II}) but these solvent phases get split in to two layers on contact with nitric acid solutions, to overcome this *iso*-decanol is used as a phase modifier. Long chain aliphatic alcohols are better known for their phase modifier characteristics in inhibiting third phase formation for use in case of amide extractants.¹²⁰ Ligands L_I and L_{II} (0.1 M) in 5 % (v/v) *iso*-decanol + *n*-dodecane mixture (5 % ID/DD) forming third phase on contact with nitric acid solutions. But the solutions of $L_{III}-L_V$ (0.1 M) in 5 % ID/DD that are having long chain alkyl substitution on amide nitrogen did not show such organic phase splitting on contacting with nitric acid solutions.

To optimize the amount of phase modifier required, $D_{Pu(IV)}$ values for $L_{III}-L_V(0.1 \text{ M})$ in different diluent compositions that vary in volume percentage of *iso*-decanol in *n*-dodecane are estimated. The $D_{Pu(IV)}$ values for the ligands decreased with diluent compositions of increasing *iso*-decanol in *n*-dodecane (Table 4.6).

Table 4.6: $D_{Pu(IV)}$ values for L_{III} - L_V (0.1 M) in diluent mixtures that vary in volume percent of *iso*-decanol in *n*-dodecane, from 3 M HNO₃.

Ligand	<i>n</i> -dodecane	5 % (v/v) <i>iso</i> -decanol in <i>n</i> -dodecane	10 % (v/v) <i>iso</i> -decanol in <i>n</i> -dodecane	20 % (v/v) <i>iso</i> -decanol in <i>n</i> -dodecane
L _{III}	Nil*	15.50 ± 0.09	8.44 ± 0.04	4.06 ± 0.10
L _{IV}	Nil*	9.80 ± 0.02	9.30 ± 0.04	1.30 ± 0.09
L _V	Nil*	12.20 ± 0.02	5.01 ± 0.04	0.89 ± 0.08

*:-Organic phase splits into two phases on contact with the aq.nitric acid phase.

Similar type of decrease in $D_{Pu(IV)}$ values was observed for the malonamide extractants ((C₄H₉(CH₃)NCO)₂CHC₂H₄OC₆H₁₃) against diluent mixtures with increasing amounts of decanol in benzene.¹²² The decrease in $D_{Pu(IV)}$ may be due to the aggregation of alcohol molecules through hydrogen bonding around the carbonyl oxygen of the amide groups or the increased extraction of acid that competes with the metal ion complexation. 5 % ID/DD is chosen as the diluent phase. The ligand L_V (0.1 M) in 5 % ID/DD did not show any phase splitting even after contacting with 8 M HNO₃.

4.4.2 Kinetics of Pu(IV) extraction

Solutions of the ligands $L_{III}-L_V(0.1 \text{ M})$ in 5 % ID/DD diluent are contacted with equal volumes of Pu(IV) aqueous solutions in 3 M nitric acid for different time intervals. After settling and centrifugation the aliquots from separated aqueous and the corresponding organic phases are assayed for plutonium activity. The $D_{Pu(IV)}$ values obtained against contact time are presented in Figure 4.9.

The uptake of Pu(IV) is high for all the three ligands L_{III} - L_V . The extraction of Pu(IV) from 3 M nitric acid is faster with $L_V \approx 5 \text{ min}$ and slower with $L_{III} \approx 15-20 \text{ min}$ and L_{IV} (\approx 30 min). Ligands with linear alkyl chain substitution on amide nitrogen reached equilibrium faster than with branched chain and is in reverse to the case of aromatic nitrobenzene diluent (Figure 4.1). The replacement of phenyl group at fourth position of the pyridine ring with *n*-pentyl group to have L_V resulted in increased kinetics of extraction that may be associated with increased distribution of the ligand towards the aqueous phase (more basic pyridine nitrogen). The D_{Pu(IV)} values obtained with 3 M HNO₃ feed solution followed the order $L_{III} > L_V > L_{IV}$ indicating higher extraction efficiency with linear alkyl chain amide ligands than the branched ones. The new class of ligand L_V has shown lower $D_{Pu(IV)}$ (12.20 ± 0.02) compared to L_{III} (15.50 ± 0.09). The replacement of phenyl group with alkyl at 4th position of pyridine ring is expected to increase the basicity of nitrogen in pyridine ring affecting its donor characteristics but is not reflected in nitric acid pickup studies. Even though no evidence on the participation of pyridine nitrogen in metal binding is established, the reasons are to be studied for the decrease in $D_{Pu(IV)}$ observed from L_{III} to L_V .



Figure 4.9: Contact time dependence of $D_{Pu(IV)}$ for L_{III} - L_{IV} (0.1 M) in 5 % ID/DD diluent from 3 M nitric acid feed solutions.

4.4.3 Effect of nitric acid concentration on $D_{Pu(IV)}$ and $D_{U(VI)}$

Aqueous phases having Pu(IV) tracer at different nitric acid concentrations (0.5-6 M) are contacted with solutions of the ligands $L_{III}-L_V$ (0.1 M) in 5 % ID/DD diluent for 2 h, to ensure complete equilibration. After allowing for settling and centrifugation, the separated aqueous and organic layers are assayed for Pu(IV) activity. The $D_{Pu(IV)}$ values obtained for $L_{III}-L_V$ against the aqueous phase nitric acid concentration are presented in Figure 4.10.

The $D_{Pu(IV)}$ variation pattern in extraction is similar for the ligands L_{III} and L_V . For L_{IV} , fall in $D_{Pu(IV)}$ at higher nitric acid concentrations is observed. $D_{Pu(IV)}$ values increased sharply from 0.5 to 2-3 M feed nitric acid concentrations with only marginal increase beyond. The initial sharp increase in $D_{Pu(IV)}$ values may be attributed to the positive dependence of Pu(IV) extraction on the nitrate ion concentration while the subsequent slow increase in the $D_{Pu(IV)}$ values may be due to a growing competition between the metal ion and the hydrogen ion for the ligand molecules. In case of nitrobenzene diluent there is a marginal fall in $D_{Pu(IV)}$ beyond 3 M nitric acid concentrations. The higher dielectric constant of nitrobenzene may help for better bonding between nitric acid and the ligands and also to better solubility of the L-HNO₃ complex. There is significant fall in $D_{Pu(IV)}$ for L_{IV} at feed acidities higher than 2 M nitric acid and is similar in both nitrobenzene and the 5 % ID/DD diluent.



Figure 4.10: $D_{Pu(IV)}$ dependence on aqueous feed HNO₃ concentration for L_{III} - L_V (0.1 M) in 5 % ID/DD diluent.

From the observed D values uranium get extracted to much lower amounts in comparison to plutonium. The $D_{U(VI)}$ values against feed HNO₃ concentration are presented in Figure 4.3.

At all concentrations of feed nitric acid (0.5-6 M), L_V has shown the highest extraction of U(VI) in comparison to L_{III} and L_{IV} . After 4 N HNO₃feed concentration, the $D_{U(VI)}$ for L_V crossed unity. Compared to L_{III} in case of L_V , the $D_{Pu(IV)}$ got lowered whereas $D_{U(VI)}$ increased at all feed acid concentrations. The variation in the extraction behavior associated with replacement of phenyl group by *n*-pentyl group indicates that this class of ligands can be tuned for desired extraction properties by proper selection of substituent and its specific position on the pyridine ring.



Figure 4.11: $D_{U(VI)}$ values for L_{III} - L_V (0.1 M) in 5 % ID/DD diluent against feed nitric acid concentration.

4.4.4 Estimation of acid uptake by the ligands

Ligands L_{III} - L_V at different concentrations from 0.02 to 0.1 M in 5 % ID/DD are contacted with 3 M HNO₃ solutions for 5 h and the results on acid uptake are presented in Table 4.7.

	Acid uptake by organic phase, M					
[Ligand], M	from	from 3 M HNO ₃ as Aqueous Feed				
	L _{III}	L _{IV}	L _v			
0.02	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.00			
0.04	0.07 ± 0.00	0.06 ± 0.01	0.05 ± 0.02			
0.06	0.08 ± 0.00	0.08 ± 0.02	0.08 ± 0.01			
0.08	0.11 ± 0.01	0.10 ± 0.00	0.11 ± 0.00			
0.10	0.16 ± 0.01	0.14 ± 0.01	0.15 ± 0.00			

Table 4.7: Acid uptake by L_{III} - L_V (0.02 to 0.1 M in 5 % ID/DD) from 3 M HNO₃ feed.

There is no marked variation in the acid uptake by the ligands in concentration range studied. No significant increase in acid uptake by L_V compared to L_{III} even with expected increased basicity of the pyridine nitrogen.

4.4.5 Studies on Metal ion-Ligand complex stoichiometry

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The Pu(IV) extraction mechanism by the ligands is same as to that in nitrobenzene diluent (Figures 4.2 and 4.10).

$$\operatorname{Pu}_{(\operatorname{aq.})}^{4+} + 4 \operatorname{NO}_{3(\operatorname{aq.})}^{-} + n \operatorname{L}_{(\operatorname{org.})} \leftrightarrows \operatorname{Pu}(\operatorname{NO}_{3})_{4} \operatorname{L}_{n(\operatorname{org.})}$$

As is discussed in case of nitrobenzene, the plot of $\log D_{Pu(IV)}$ versus $\log [L]_{(org.)}$ gives a straight line with a slope that is equal in magnitude to number of ligand molecules in the $[Pu(NO_3)_4L_n]_{(org.)}$ complex.

Solvents with different concentrations of the ligands (L_{III} - L_V) in 5 % ID/DD diluent are subjected to equilibration with solutions of Pu(IV) tracer in 3 M nitric acid and the corresponding $D_{Pu(IV)}$ values obtained against the ligand concentrations are presented in Figure 4.12.



Figure 4.12: Variation in $D_{Pu(IV)}$ against L_{III} - L_V concentration in 5 % ID/DD diluent for extraction from 3 M HNO₃.

Slope values close to 2 for all the three ligands L_{III} - L_V indicate extraction of mixed species. Two different types of complexes are extracted with Pu(IV)-L ratios of 1:2 and 1:1. In case of L_{III} , complexes with Pu(IV)-L ratios of 1:2 are extracted to a large extent with very small amount of 1:1 whereas for L_{IV} and L_V a mixture of both 1:2 and 1:1 are extracted with the former dominating.

The Kex. values are obtained from the relation

$$K_{ex.} = \frac{D_{M.}}{[NO_3^-]^4_{(aq.)} [L]^n_{(org.)}}$$

The predicted extracted species for the ligands along with their corresponding K_{ex} values are as presented in Table 4.8.

The K_{ex} values indicate highly thermodynamical favored complexation of plutonium with ligands. The complexes with Pu-L ratio of 1:2 are more favorably extracted compared to 1:1 due to their higher lipophilicity. The ligands are of polyaromatic in nature that accounts for more favorable interactions of the metal ion-ligand complexes with aromatic diluents than aliphatic ones. This corroborates with the fact of higher $D_{Pu(IV)}$ values obtained in nitrobenzene diluent (L_{III} : $D_{Pu(IV)} = 24.7 \pm 0.4$) compared to 5 % ID/DD (L_{III} : $D_{Pu(IV)} = 15.50 \pm 0.09$).

Table 4.8: Estimation of K_{ex} values for the different plutonium metal ion-ligandcomplexes extracted.

Ligand	Extracted species	K _{ex}
L _{III}	$Pu(NO_3)_4.L_2$	18.77
т	Pu(NO ₃) ₄ .L	01.20
L _{IV}	$Pu(NO_3)_4.L_2$	11.96
т	Pu(NO ₃) ₄ .L	01.51
L_V	$Pu(NO_3)_4.L_2$	15.06

4.4.6 Stripping studies

Similarities in Pu(IV) extraction characteristics of the ligands in nitrobenzene and 5 % ID/DD diluents infers similar conditions for stripping. Stripping of Pu(IV) is favored

by low acid concentrations and reducing conditions. The Pu(IV) loaded solvents $L_{III}-L_V$ (0.1 M) in 5 % ID/DD are subjected to stripping with an aqueous solution of 0.5 M NH₂OH and 1 M HNO₃. The kinetics is faster with quantitative stripping (\approx 10 min) for L_{IV} and L_V (Figure 4.5). For L_{III} a stripping of > 99 % plutonium is attained with faster rates.



Figure 4.13: Percentage stripping of plutonium against the contact time for L_{III} -L_V (0.1 M) in 5 % ID/DDdiluent.

As is observed in the present studies, L_{III} is showing better selective extraction characteristics for Pu(IV). Stripping of plutonium is found to be inferior in case of L_{III} relative to L_{IV} and L_V (Figure 4.13) and provokes to search for better stripping agents. The stripping agents studied for L_{III} are (i) 0.5 M hydroxylamine + 0.5 M HNO₃, (ii) 0.5 M hydrazine + 0.5 M HNO₃, (iii) 0.5 M sulphamic acid + 0.5 M HNO₃ and (iv) 0.5 M oxalic acid among which the former two shown superior characteristics. The results of plutonium stripping characteristics with various reagents from L_{III} are presented in Table 4.9.

Results in Table 4.9 indicate that both solution mixtures (i) 0.5 M hydroxylamine + 1 M HNO₃ and (ii) 0.5 M hydrazine + 1M HNO₃ show similar plutonium stripping behavior with relatively faster kinetics for the former. From these observations, the aqueous solution of 0.5 M hydroxylamine + 1 M HNO₃ is the better stripping agent.

Table 4.9: Stripping of plutonium from loaded solvent L_{III} (0.1 M) in 5 % ID/DD using various reagents.

	% (C	umulative) Strippin	g of Pu(IV) from			
Equilibration	0.1 M of L _{III} in 5 % ID/DD					
time, min	0.5 M	0.5 M Hydrazine	0.5 M	0.5 M		
	Hydroxylamine	+ 1 M HNO ₃	sulphamic acid	oxalic acid		
	+ 1 M HNO ₃		+ 0.5 M HNO ₃			
05	99.2	95.0	79.9	98.9		
10	99.2	98.9	80.9	98.8		
20	99.2	99.4	80.4	98.6		
30	99.1	99.6	80.2	98.8		
60	99.1	99.7	80.9	98.6		
180	99.3	99.6	87.7	98.7		

4.4.7 Extraction selectivity of ligands for Pu(IV)

Ligands $L_{III}-L_V$ are evaluated for Pu(IV) selectivity over Cs(I), Sr(II), Eu(III), U(VI), Am(III), Zr(IV) and Th(IV). Solutions of the ligands (0.1 M) in 5 % ID/DD

diluent are contacted with 3 M nitric acid solutions containing tracers of the different metal ions of interest separately for 2 h duration, allowed for settling and centrifuged. Organic and aqueous layer samples are assayed for the corresponding element to obtain D values (Table 4.10).

Table 4.10: Extraction behavior of few actinides and fission product metal ions from 3 M HNO₃with $L_{III}-L_V(0.1 \text{ M})$ in 5 % ID/DD diluent.

Ligand		Distribution ratio for metal ion at 3 M HNO ₃						
Liganu -	Pu(IV)	U(VI)	Am(III)	Eu(III)	Cs(I)	Sr(II)		
L _{III}	15.9 ± 0.20	0.23 ± 0.01	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$		
L _{IV}	09.8 ± 0.02	0.24 ± 0.01	$< 1 \times 10^{-3}$	$< 1 \text{ x } 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$		
L_V	12.2 ± 01.19	0.44 ± 0.01	$< 1 \text{ x } 10^{-3}$	$< 1 \times 10^{-3}$	$< 1 \text{ x } 10^{-3}$	$< 1 \times 10^{-3}$		

The results in Table 4.10 indicate high separation factor for Pu(IV) over the other ions studied. It is of interest to evaluate extraction selectivity of the ligands for Pu(IV) from solutions containing a mixture of different metal ions.

The mixture of radio tracers of the ions Eu(III), U(VI), Am(III), Sr(II), Cs(I) and Pu(IV) in 3 M HNO₃solution is subjected to extraction by contacting with L_{III} and L_V (0.1 M) in 5 % ID/DD for 2 h. The organic and the aqueous layer samples are analyzed by Alpha and Gamma spectroscopy. The extraction selectivity of L_{III} and L_V to Pu(IV) over U(VI) and Am(III) is observed from the alpha spectra as shown in Figure 4.14 and Figure 4.15 respectively.



Figure 4.14: Alpha spectra of samples for the extraction with L_{III} (0.1 M) in 5 % ID/DD from 3 M HNO₃ containing ^{152, 154}Eu(III), ²³³U(VI), ²⁴¹Am(III), ^{85, 89}Sr(II), ¹³⁷Cs(I) and ^{239,238}Pu (dominantly ²³⁹Pu) tracers.



Figure 4.15: Alpha spectra of samples for the extraction with L_V (0.1 M) in 5 % ID/DD from 3 M HNO₃ containing ^{152, 154}Eu(III),²³³U(VI), ²⁴¹Am(III), ^{85, 89}Sr(II), ¹³⁷Cs(I) and ^{239, 238}Pu (dominantly ²³⁹Pu).

The organic samples after IR drying and fixing on stainless steel planchettes by heating to red hot over burner flame are taken for collecting the alpha spectra. Alpha spectrum of L_V organic phase shows slight pick of uranium during extraction. The extraction selectivity of L_{III} and L_V to Pu(IV) over Cs(I), Sr(II), Eu(III) and Am(III) ions is observed from the gamma spectra as shown in Figure 4.16 and Figure 4.17 respectively. The other elements ^{85, 89}Sr(II), ¹³⁷Cs(I), ^{152, 154}Eu(III) are monitored from their gamma spectra.



Figure 4.16: Gamma spectra of samples for the extraction with 0.1 M L_{III} in 5 % ID/DD from 3 M HNO₃ containing ^{152, 154}Eu(III),²³³U(VI), ²⁴¹Am(III), ^{85, 89}Sr(II), ¹³⁷Cs(I) and ^{239, 238}Pu (dominantly ²³⁹Pu) tracers.

In nuclear fuel reprocessing streams, plutonium will be at much lower concentrations than the U(VI) or lanthanides. Though selectivity of L_{III} and L_V for Pu(IV) over Eu(III) and U(VI) is established all at their trace level concentrations, it is of challenge to extract trace concentrations of Pu(IV) over g/L concentrations of Nd(III) and U(VI) in nitric acid feed solutions. The typical waste from PHWR contains Nd at

860 mg/L (as oxide), the highest concentration among the lanthanides present and U at 20 gm/L (as nitrate salt). Selectivity of the ligands $L_{III}-L_V$ for trace amount of Pu(IV) from a 3 M nitric acid solution of U(VI) (0.1, 1 and 10 gm/L) and Nd(III) (0.1, 1 and 5 gm/L) respectively are evaluated (Table 4.11(a) and Table 4.11(b)).



Figure 4.17: Gamma spectra of samples for the extraction with 0.1 M L_{III} in 5 % ID/DD from 3 M HNO₃ containing ^{152, 154}Eu(III), ²³³U(VI), ²⁴¹Am(III), ^{85, 89}Sr(II), ¹³⁷Cs(I) and ^{239, 238}Pu (dominantly ²³⁹Pu) tracers.

From the observations based on alpha and gamma spectra it is clear that both the ligands L_{III} and L_V are highly selective for Pu(IV) extraction with preference for L_{III} .

D _{Pu(IV)} at 3 M HNO ₃ Feed U concentration g/L				
0.1 1 10				
14.9 ± 0.00	14.8 ± 1.20	19.2 ± 0.17		
10.8 ± 0.16	11.2 ± 0.19	10.3 ± 0.06		
13.5 ± 1.88	12.2 ± 1.26	8.23 ± 0.45		
	D_{Pu} Feed 0 0.1 14.9 ± 0.00 10.8 ± 0.16 13.5 ± 1.88	DPu(IV) at 3 M HNFeed U concentration0.11 14.9 ± 0.00 14.8 ± 1.20 10.8 ± 0.16 11.2 ± 0.19 13.5 ± 1.88 12.2 ± 1.26		

Table 4.11 (a): Extraction selectivity of ligands L_{III} - L_V (0.1 M) in 5 % ID/DD for Pu(IV) at trace over uranium at gm/L concentrations from 3 M nitric acid solutions.

It is observed that for L_{III} and L_{IV} there is an increase in $D_{Pu(IV)}$ with increase in Nd(III) or U(VI) nitrate concentrations. For L_V there is a decrease in $D_{Pu(IV)}$ with increase in U(VI) nitrate concentration. This is in agreement with higher $D_{U(VI)}$ observed for L_V compared to L_{III} and L_{IV} as well as its continual increase with increasing feed nitrate (nitric acid) concentrations (Figure 4.11). The increasing concentrations of U(VI) and nitrate favored increase in $D_{U(VI)}$ for L_V with a resulting decrease in $D_{Pu(IV)}$. These results clearly indicate the superiority of L_{III} over L_{IV} - L_V in selective extraction of plutonium.

Table 4.11 (b): Extraction selectivity of ligands L_{III} - L_V (0.1 M) in 5 % ID/DD for Pu(IV) at trace over neodymium at gm/L concentrations from 3 M nitric acid solutions.

	D _{Pu(IV)} at 3 M HNO ₃				
Ligand	Feed Nd concentration g/L				
	0.1	1	5		
L _{III}	15.7 ± 0.7	17.5 ± 0.4	19.1 ± 1.89		
L _{IV}	10.3 ± 0.00	11.8 ± 1.00	12.8 ± 0.70		
L_V	11.7 ± 0.00	9.81 ± 0.64	14.7 ± 0.90		

Ligands L_{III} and L_{IV} are evaluated for their Th(IV) and Zr(IV) extraction. Solutions of the ligands in 5 % ID/DD are contacted with 3 M nitric acid solutions containing 406 mg/L of Th(IV) and 405 mg/L of Zr(IV) separately for 2 h duration. After allowing for settling and centrifugation the separated aqueous layer samples are analyzed on ICP-OES for Th (269.242 nm) and Zr (327.305 nm) concentrations. The organic phase metal ion concentrations are estimated by the difference in aqueous feed and raffinate concentrations. The degree of extraction follows the order: Pu >> Th >>> Zr (Table 4.12). The D_{Th(IV)} and D_{Zr(IV)} values are lower in 5 % ID/DD as compared to nitrobenzene as diluent. The separation factors with L_{III} for Pu(IV) over Th(IV) in nitrobenzene and 5 % ID/DD diluents are 56.8 and 51.6 respectively. Similarly, SF value for Pu(IV) over Zr(IV) are 567.9 and 4900 respectively under identical conditions.

Table 4.12: Estimation of $D_{Th(IV)}$ and $D_{Zr(IV)}$ values for L_{III} - L_{IV} (0.1 M) in 5 % ID/DD for extraction from 3 M HNO₃ solutions.

D value	Liga	ands
D value	LIII	L _{IV}
D_{Th}	0.28 ± 0.02	0.19 ± 0.02
D_{Zr}	0.028 ± 0.025	0.02 ± 0.034

4.4.8 Recycling of extractants

Reusability is an important aspect for the solvents at process applications. More the number of recycles a solvent can undergo without any significant changes in extraction properties under the process conditions higher is beneficial as it reduces inventory, secondary waste generation and its associated safe disposal expenditure.

	% Extraction	% Strinning	% Extraction	% Strinning	% Extraction
Ligand	(stage I)	(stage I)	(stage II)	(stage II)	(stage III)
LI	95.6	97.7	95.5	97.8	95.2
L _{II}	90.7	99.8	90.2	99.2	91.2
L_{III}	93.8	96.6	93.4	96.1	94.5

Table 4.13: Solvent recycling studies of L_{III} - L_V (0.1 M) in 5 % ID/DD. Feed: 3 M HNO₃ containing Pu(IV) tracer. Strippant: 0.5 M NH₂OH + 1 M HNO₃.

Ligands $L_{III}-L_V(0.1 \text{ M})$ in 5 % ID/DD are subjected to 3 stages of extraction from 3 M HNO₃ feed and 2 stages of stripping with 0.5 M NH₂OH + 1 M HNO₃ aqueous solution for plutonium, in recycle. The results (Table 4.13) indicate no decomposition of ligands during solvent recycle as are no significant changes in the plutonium extraction characteristics.

4.5 Conclusions

The new class of diamide ligands (3,3'-bis(2-oxydialkylacetamide)triarylpyridine) are evaluated for their Pu(IV) selective extraction characteristics both in aromatic (nitrobenzene) and aliphatic (5 % ID/DD) molecular diluents. The ligands having linear/branched alkyl groups with four/eight carbon chain length as substituents on amide nitrogens are evaluated for extraction of the actinides in nitrobenzene (L_I - L_{IV}) and in 5 % ID/DD (L_{III} - L_V) diluents. Promising results obtained for selective extraction of Pu(IV). The metal ion extraction mechanism primarily conformed to a solvation type in both aromatic (nitrobenzene) and aliphatic (5 % ID/DD) diluents with Pu to L ratios of

both 1:1 and 1:2. The extraction of Am(III), Eu(III), Cs(I) and Sr(II) is negligible $(< 1 \times 10^{-3})$ and U(VI) extraction is one to two orders of magnitude lower than that of Pu(IV). Although, both ligands L_{III} and L_{IV} displayed high selectivity for Pu(IV) over Zr(IV) and Th(IV), L_{III} was considered to the best candidate for selective extraction of Pu(IV).

The metal ion extraction data for TOTPDA (Figure 4.18), L_{II} and L_{III} (0.1 M) in nitrobenzene diluent from ≈ 3 M nitric acid solutions are presented in Table 4.14 indicating effect of variation in ligand structure on overall selectivity and efficiency for plutonium extraction.

Table 4.14: Comparison of L_{II}, L_{III} and TOTPDA ligands at 0.1 M concentrations in nitrobenzene diluent for their efficiency and selectivity to Pu(IV) extraction from ≈ 3 M HNO₃ solutions.⁷³

Ligand _	Distribution ratio for the metal ion					
	Pu(IV)	U(VI)	Am(III)	Eu(III)		
L _{II}	107.2 ± 0.7	0.7 ± 0.0	$< 1 \times 10^{-3}$	$< 1 \times 10^{-3}$		
$\mathbf{L}_{\mathbf{III}}$	24.7 ± 0.4	0.5 ± 0.0	$< 1 \ge 10^{-3}$	$< 1 \times 10^{-3}$		
*TOTPDA	> 100	14.1	0.119	0.008		

*D values are obtained from a feed solution having a mixture of metal ions. In case of L_{II} and L_{III} the D values are obtained with solutions of each metal ion separately.

Fast kinetics of plutonium extraction and stripping are observed for the new class of diamide ligands in molecular diluents. The radiolytic stability of ligands $L_{I}-L_{IV}$ is found to be reasonably good up to an absorbed dose 630 kGy.



Figure 4.18: Structures of L_{II}, L_{III} and to-terpyda ligands.

During extraction studies, it was observed that aliphatic diluents give better Pu(IV) selectivity even though D values are lower compared to aromatic diluents.

Among all the ligands, L_{III} displayed highest potential towards selective extraction of Pu(IV) in aliphatic diluents.

Chapter – 5

EVALUATION OF DIAMIDE LIGANDS (L_I-L_{IV}) IN

RTIL [C₈mim][Tf₂N] AS A DILUENT

FOR SELECTIVE EXTRACTION OF PLUTONIUM(IV)

5 Evaluation of diamide ligands (L_I-L_{IV}) in RTIL [C₈mim][Tf₂N] as a diluent for selective extraction of plutonium(IV).

5.1 Preamble

In this chapter 3,3'-bis(2-oxydialkylacetamide)triarylpyridine ligands *viz.*; L_I (*iso*-butyl), L_{II} (*n*-butyl), L_{III} (*n*-octyl), L_{IV} (2-ethylhexyl) in Room Temperature Ionic Liquids (RTIL) diluents are evaluated for Pu(IV) selective extraction characteristics from nitric acid solutions.

5.2 Introduction

Volatile Organic compounds are of major concern due to their hazardous effects on environmental issues influencing the global atmosphere. Green chemistry is of one of the approaches in reducing the ecological risks.¹²³ The possible ways of implementing the methodologies as green technology are (i) using water as a solvent for synthesis, (ii) completely solvent free synthesis, (iii) using supercritical fluids as alternatives and (iv) use of Room Temperature Ionic Liquids (RTIL) as solvents. As compared to super critical fluids (such as CO₂), RTIL have their own distinct advantages in many applications as there is no need of maintaining the conditions to attain super critical state.

Ionic liquids (IL) are the organic salts that exist in liquid state below 100° C whereas RTIL at ambient temperature.¹²⁴ The asymmetric nature of either anion or cation that do not favor to attain long range order for gaining crystal stabilization energy allows them to stay in liquid state at low temperatures in contrast to inorganic salts NaCl (M.P. 803 $^{\circ}$ C) etc..¹²⁵ The common ILs are composed of alkyl imidazolium, pyridinium, quaternary ammonium etc. as cations and BF₄⁻, AlCl₄⁻, PF₆⁻, NTf₂⁻ (bis-trifluormethanesulfonimides) etc. as anions. The important characteristic of ionic

liquids required for applications in solvent extraction is their water insolubility. Some of the water insoluble combinations of anions and cations that are of relevance are shown in Figure 5.1. The most attractive features of ionic liquids are (i) near zero vapor pressure, (ii) high thermal and radiation stability, (iii) high electrochemical window, (iv) tunable nature of the properties by different choices in choosing and designing anion and cationic parts of these designer solvents, (v) environmental friendly nature in comparison to volatile organic solvents.^{126,127,128} The other important class includes task specific ionic liquids where the functional groups for specific application are tethered to either anionic or cationic part of the ionic liquid.



PF₆ NTf₂ BETI

Figure 5.1: Common cation and anionic species of ionic liquids in applications.

Though the discovery of RTIL's dates back to 1914,¹²⁹ their application to areas such as metal ion extraction is as late as 1990's. Visser et al.,¹³⁰ reported the extraction of actinide ions with a solution of CMPO in C₄mimPF₆, an RTIL with a relatively high viscosity. The viscosity of the RTIL is reported to be of little consequence and an enormous increase in the metal ion extraction is reported. Analogous huge increase in the extraction of Sr²⁺ is reported when an RTIL based solvent system containing crown ether is used.¹³¹

The properties of imidazolium based IL are tuned by proper length of the alkyl chain on the cationic ring (Fugure 5.2). In the present study the ionic liquid used as diluent is N(n-octyl),N'(methyl)imidazolium trifluoromethanesulphonimide abbreviated as $[C_8mim][Tf_2N]$.



Figure 5.2: Imidazolium cation based ionic liquid [C₈mim][Tf₂N].

5.3 Present work

The ligands $L_{I}-L_{IV}$ are evaluated for the selective extraction of Pu(IV) in $[C_8mim][Tf_2N]$.

5.3.1 Kinetics of Pu(IV) extraction

Solutions of the ligands $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][Tf₂N] are contacted with aqueous solutions of Pu(IV) tracer in 3 M HNO₃ for different time intervals. After each contact time interval the tubes are rested, centrifuged and suitable aliquots from both organic and aqueous phase are assayed for Pu(IV) activity to obtain $D_{Pu(IV)}$ values (Figure 5.3).

The extraction of Pu(IV) from 3 M nitric acid is faster with L_I-L_{III} (\approx 10 min) relative to L_{IV} (\approx 20 min). Similar trend is observed with U(VI) extraction kinetics but distribution values are very low. Though analogous fast extraction kinetics has been reported in several extraction systems involving ionic liquids as the diluents,^{132,133,134} there are stray cases where somewhat slow extraction kinetics has been reported¹³⁵ and as high as 30 h are needed in some other cases to attain equilibrium D values.¹³⁶ The fast extraction kinetics indicates easier complexation and extraction that are related to steric control by the aromatic frame work between two amide groups.

The Pu(IV) extraction by the ligands is in the order of $L_{III} > L_{II} > L_{I} >> L_{IV}$ (Table 5.4). Higher $D_{Pu(IV)}$ values are by the ligands with linear and longer alkyl chain substitution on amide nitrogens whereas it is by the ligands with shorter and linear alkyl chain substitution on amide nitrogens in case of nitro benzene diluent, $L_{II} > L_{I} > L_{III} > L_{IV}.$



Figure 5.3: $D_{Pu(IV)}$ for $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][Tf₂N] diluent against contact time, from 3 M nitric acid solutions.

This can be explained based on Pu-L stoichiometries (Figure 4.5 and Figure 5.6) in metal ion-ligand complexes and their interactions with diluent molecules. Ligand L_{IV} has shown the least $D_{Pu(IV)}$ values in all diluents studied including 5 % ID/DD. The ligands with branched alkyl groups L_{II} (*iso*-butyl) and L_{IV} (2-ethylhexyl) have lower metal ion extraction due to steric factors. Ligand L_{IV} (2-ethylhexyl) imparting the highest steric constraints has the lowest metal ion extraction. Among the two straight chain alkyl group bearing ligands L_{II} (*n*-butyl) and L_{III} (*n*-octyl), the metal ion complexes of the later are extracted favourably to $[C_8mim][NTf_2]$ diluent, apparently from the fact 'like dissolves like'. The extraction of U(VI) is very less and comparable for all the four ligands while L_{IV} showing marginally higher extraction. The observed uranium extraction may be due to the favourable partitioning of the anionic species which are also seen in the absence of the ligand (Table 5.1).

5.3.2 Effect of nitric acid concentration on $D_{Pu(IV)}$ and $D_{U(VI)}$

Solutions of the ligands L_I-L_{IV} (0.05 M) in [C₈mim][Tf₂N] are contacted with aqueous nitric acid solutions of varying concentration (1-6 M) containing Pu(IV) tracer. The contacting is for 2 h duration to ensure equilibration. Similar extraction experiment with U(VI) tracer is also carried out. The corresponding $D_{Pu(IV)}$ and $D_{U(VI)}$ values obtained for the lignads L_I-L_{IV} against the aqueous phase nitric acid concentrations are shown in Figure 5.4. For all ligands L_I-L_{IV} , the $D_{Pu(IV)}$ are much higher than the $D_{U(VI)}$ ensuring high selectivity to the plutonium.

In contrast to the case of nitrobenzene/5 % ID/DD diluents, the $D_{Pu(IV)}$ values did not fall/stabilize at higher nitric acid concentrations using ionic liquid diluent. The $D_{Pu(IV)}$ and $D_{U(VI)}$ values obtained for $[C_8mim][Tf_2N]$ diluent without any dissolved ligand (Table 5.1) indicate that there is a considerable pick of Pu(IV) at 6 M HNO₃ feed by anion exchange. The exchanging anions can be either $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ whose formation gradually increases above 3 M HNO₃ concentration. In case of U(VI)/Am(III), an acid concentration > 6-7 M is required for anion exchange to start considerably.¹³⁷

In case of molecular diluents, the extraction of a metal ion usually increases with increasing feed nitric acid concentration which is attributed to a solvation mechanism of the type

$$\mathsf{M}^{\mathsf{n}+}_{(\mathsf{aq}.)} + \mathsf{n}\,\mathsf{NO}^-_{3\,(\mathsf{aq}.)} + \mathsf{x}\,\mathbf{L}_{(\mathsf{org}.)} \, \leftrightarrows \, \mathsf{M}(\mathsf{NO}_3)_{\mathsf{n}}\mathbf{L}_{\mathsf{x}\,(\mathsf{org}.)}$$

where, the subscripts 'org.' and 'aq.' represent the species present in the organic and aqueous phases respectively.



Figure 5.4: $D_{Pu(IV)}$ and $D_{U(VI)}$ dependence on aqueous feed HNO₃ concentration for $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][Tf₂N] diluent.

This could be different in an ionic liquid medium. The metal ion extraction by cation exchange mechanism is often reported in ionic liquid based solvent systems, as shown below.

$$M_{(aq.)}^{n+} + n C_4 mim_{(IL)}^+ + x L_{IL} \leftrightarrows ML_{x(IL)}^{n+} + n C_4 mim_{(aq.)}^+$$

The subscript 'IL' represents the species present in ionic liquid phase. In extractions with neutral donor ligands in shorter alkyl chain bearing ionic liquid diluents

such as C_4 mimNTf₂, both solvation and ion-pair extraction mechanisms are reported.^{138,139}

The extraction of both Pu(IV) and U(VI) increased with the feed HNO_3 concentration over the entire range (1-6 M) except in the case of Pu(IV)- L_{IV} (Figure 5.4). The increase in metal ion extraction with increasing HNO_3 concentration may be considered analogous to the 'solvation' mechanism similar to that in molecular diluents.

$$Pu_{(aq.)}^{4+} + 4 NO_{3(aq.)}^{-} + n \mathbf{L}_{(IL)} \leq Pu(NO_{3})_{4} \mathbf{L}_{n(IL)}$$

Table 5.1: Extraction of U(VI) and Pu(IV) into $[C_8mim][NTf_2]$ in the absence of the diamide ligands from varying concentrations of HNO₃. The amounts of HNO₃ extracted into the ionic liquid phase (in %) are also indicated.

Feed	[C ₈ mim][Tf ₂ N] diluent				
[HNO ₃](M)	D _{Pu(IV)}	D _{U(VI)}	Acid Extracted (%)		
0.5	$< 1 \text{ x } 10^{-3}$	$< 1 \text{ x } 10^{-3}$	0.03 ± 0.01		
1	0.013 ± 0.00	$< 1 \text{ x } 10^{-3}$	0.07 ± 0.01		
2	0.38 ± 0.01	3 x 10 ⁻³	0.09 ± 0.00		
3	1.58 ± 0.01	9.1 x 10 ⁻³	0.13 ± 0.05		
4	2.12 ± 0.24	0.025 ± 0.000	0.21 ± 0.01		
6	26.2 ± 2.4	0.122 ± 0.001	0.50 ± 0.03		

The present trend in Pu(IV) extraction with HNO₃ concentration is entirely in contrast to that reported for malonamide (0.3 M) in $C_n \text{mimNTf}_2$ (where n = 4, 6, 8)¹⁴⁰ wherein anion exchange mechanism at < 1 M HNO₃ concentrations was ruled out and suggested cation-exchange or solvation. On the other hand, for solvent system containing TBP in C₄mim.PF₆, a solvation mechanism is reported by Giridhar et al.¹⁴¹ The metal ion extraction by [C₈mim][Tf₂N] diluent in absence of the extractants is quite significant

(Table 5.1) at higher HNO₃ concentrations. Therefore, it is pertinent to make corrections to the D values for the contribution from extraction of anionic complexes by the ionic liquid diluent alone. Though the corrections do not affect the $D_{U(VI)}$ values to any significant amount (in absolute numbers though highest decrease is seen at 6 M HNO₃), those involving Pu have significant contributions from the anionic species extraction.

Table 5.2: Extraction of U(VI) and Pu(IV) by $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][NTf₂] from varying concentrations of HNO₃. The corrected D values for anion exchange contribution are shown inside parentheses.

Feed, HNO3,	$D_{U(VI)}$ in the presence of the ligand (corrected $D_{U(VI)}$)			$D_{Pu(IV)}$ in the presence of the ligand (corrected $D_{Pu(IV)}$)				
Μ	L_I	LII	$\mathbf{L}_{\mathbf{III}}$	$\mathbf{L}_{\mathbf{IV}}$	$\mathbf{L}_{\mathbf{I}}$	$\mathbf{L}_{\mathbf{H}}$	L _{III}	L _{IV}
1	0.002	0.002	0.003	0.003	0.130	0.410	0.083	0.01
	(0.001)	(0.001)	(0.002)	(0.002)	(0.117)	(0.397)	(0.070)	(0.001)
3	0.031	0.035	0.036	0.046	12.9	15.2	17.9	4.27
	(0.030)	(0.034)	(0.035)	(0.045)	(11.3)	(13.6)	(16.3)	(2.69)
6	0.242	0.272	0.296	0.450	68.9	69.0	78.2	31.8
	(0.12)	(0.15)	(0.174)	(0.328)	(42.7)	(42.8)	(52.0)	(5.6)

The observed D values of the metal ions at 1 M, 3 M and 6 M HNO₃ concentrations along with the corrected D values obtained by subtracting contribution from anionic complex extraction are presented in Table 5.2. The results show that at 6 M HNO₃, there is a significant contribution to D values by the anionic complex extraction and is erroneous to consider that these observed values are due to extraction by

diamide ligands alone. As is seen in Figure 5.5, the sharp increase in the $D_{Pu(IV)}$ values at 6 M HNO₃ is drastically reduced by corrections for anionic species extraction, to such as an extent that for L_{IV} a very little increase with HNO₃ concentration is seen. Therefore, for the speciation studies, 6 M HNO₃ concentration is not considered.

Extraction studies with four diamides with varying feed nitric acid concentrations (1-6 M), revealed the highest extraction for Pu(IV) with L_{III} , whereas L_{IV} displayed higher affinity for U(VI).



Figure 5.5: Plots of Pu(IV) and U(VI) extractionby L_I-L_{IV} (0.05 M) in [C₈mim][NTf₂] at three different HNO₃ concentrations, without and with consideration of anionic species extraction.

5.3.3 Estimation of acid uptake by the ligands

Solutions of the ligands L_1-L_{IV} (0.05 M) in [C₈mim][Tf₂N] diluent are contacted with HNO₃ solutions of varying concentration (1-6 M). The aliquots from aqueous and organic layers are titrated with standard NaOH solution to phenolphthalein indicator end point. The organic phases are titrated in aqueous ethanol medium, which is titrated earlier in the same method to find out the alkali consumption i.e. blank value. Each distribution value is obtained in duplicate and the agreement between these values is within ±2%. The data obtained for organic phase acid pick at different aqueous phase nitric acid concentrations for $L_{I}-L_{IV}$ is shown in Table 5.3. There is a systematic increase in acid pick by the organic phase with the increasing acid concentration in aqueous phase. The acid pick is higher at higher aqueous acidities in case of ionic liquids due to extraction by ion exchange mechanism.

Table 5.3: Acid extraction by $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][NTf₂] from varying concentrations of feed nitric acid.

		Acid uptake by o	organic phase, M					
Feed, HNO ₃ , M	for 0.05 M ligand in [C ₈ mim][Tf ₂ N]							
	L _I	LII	L _{III}	L _{IV}				
0.5	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.00				
1	0.08 ± 0.00	0.06 ± 0.01	0.07 ± 0.01	0.07 ± 0.00				
2	0.10 ± 0.01	0.12 ± 0.00	0.09 ± 0.00	0.13 ± 0.01				
3	0.15 ± 0.00	0.16 ± 0.04	0.13 ± 0.05	0.12 ± 0.05				
4	0.25 ± 0.01	0.23 ± 0.00	0.21 ± 0.01	0.21 ± 0.00				
6	0.51 ± 0.02	0.52 ± 0.01	0.50 ± 0.03	0.50 0.00				

5.3.4 Metal ion-Ligandcomplex stoichiometry studies

The extraction mechanism is expected to be same as that in molecular diluents

$$\operatorname{Pu}_{(\operatorname{aq.})}^{4+} + 4 \operatorname{NO}_{3}^{-}_{(\operatorname{aq.})} + n \mathbf{L}_{(\operatorname{IL.})} \leftrightarrows \operatorname{Pu}(\operatorname{NO}_{3})_{4} \mathbf{L}_{n (\operatorname{IL.})}$$

The relation between the K_{ex} and $D_{Pu(IV)}$ can be expressed as

$$\log D_{Pu(IV)} = \log K_{ex.} + 4 \log NO_{3 (aq.)}^{-} + n \log [L]_{IL}$$

From similar arguments that are expected to be valid for nitrobenzene and 5 % ID/DD diluent systems and the information obtained from ligand acid pick studies, the above equation converges to

$$\log D_{M} = C + n \log [\mathbf{L}]_{IL}$$
$$C = \log K_{ex.} + 4 \log NO_{3(aq.)}^{-}$$

C can be fairly assumed to be a constant value.

The plot of log D_M versus log $[L]_{IL}$ gives a straight line with a slope that is equal in magnitude to number of ligand molecules in the Pu(NO₃)₄L_{n (IL)} complex.

From the slope of the straight lines in Figure 5.6, the complexes extracted are with Pu-L ratio of 1:1 in case of all the ligands $L_{I-L_{IV}}$. The extraction mechanism is same for the ligands $L_{III}-L_{IV}$ both in nitrobenzene and IL diluents. The complexes with Pu-L ratio of 1:2 are extracted in case of $L_{I}-L_{II}$ in nitrobenzene diluent. In 5 % ID/DD diluent, for L_{III} complexes with Pu-L ratio of 1:2 are extracted to a larger extent with very small amounts of 1:1 whereas for L_{IV} a mixture of both 1:2 (higher) and 1:1 is extracted.

The above observation is in sharp contrast to the 1:2 (Pu-L) species reported with the *N*,*N'*-dimethyl-*N*,*N'*-dioctyl-2-(2-hexyloxyethyl) malonamide (DMDOHEMA).¹³¹ The variation in the extracted species is dependent on many factors of which the present study considerations are the nature of the ligand and the increased HNO₃ concentration as compared to that reported in literature.^{140, 141} The Pu-L ratio of 1:1 in extracted complexes suggests a $D_{Pu(IV)}$ values ca. 26, 30, 36 and 8.5 for L_I-L_{IV} (0.1 M) respectively from 3 M HNO₃, which are almost half to that reported for nitrobenzene medium making the ionic liquid based solvent system significantly inferior to that of molecular diluent. Though the extraction of the metal ion is often higher in ionic liquid diluents (sometimes as high as 2-3 orders of magnitude¹²⁹) as compared with molecular diluents, this is one of the rare examples where the converse results observed. In such cases involving ionic liquids, a cation-exchange mechanism has been suggested to be operative.



Figure 5.6: Plots of $D_{Pu(IV)}$ against ligand (L_I-L_{IV}) concentrations in $[C_8mim][NTf_2]$ from 3 M nitric acid feed.

It may be concluded that in diluents of high dielectric constant, 1:1 Pu-L complexes are extracted to organic phase whilein low dielectric constant diluents more solvated species with 1:2 are extracted along with minor quantities of 1:1 complexes.
5.3.5 Stripping studies

One of the major challenges in ionic liquid based extraction systems is to find suitable stripping conditions. This is due to the fact that the metal ion extraction is many times higher in ionic liquids as compared to that observed in molecular diluents. But the present case it is otherwise. Secondly, in most cases, cation exchange mechanism is observed which makes the back extraction rather difficult while using a lower acid concentration of the feed as the strippant. It is not possible to back extract Pu(IV) ion from the ionic liquid extract using low concentration of HNO₃ (for example, 0.01 M), due to the possibility of hydrolysis.¹⁵ In present case of ligands no such cation exchange extraction is confirmed. Therefore, complexing agent/reducing agent at low nitric acid concentration are suitable for Pu(IV) back extraction from the ionic liquid extract. Because of the concerned similarities of the ligands in Pu(IV) extraction properties both for IL and molecular diluents, low acid and reducing conditions are expected to favor stripping. A solution containing of 0.5 M NH₂OH and 1 M HNO₃ that generates in situ a solution of around 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ is used for stripping studies. The other stripping agent studied is 0.5 M oxalic acid. For practical applications, the stripping kinetics has to be faster. The Pu(IV) loaded solvents of the lignads L_I-L_{IV} (0.05 M) in $[C_8 mim][Tf_2N]$ are subjected to stripping with the above mentioned reagents separately and the results are as shown in Figure 5.7. With both reagents, quantitative stripping of plutonium is seen though they differ in kinetics. The kinetics for quantitative stripping is faster (10 min) with 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃ whereas slower with oxalic acid (> 1 h). This is due to the fact that the reduction to the trivalent state is almost instantaneous and the D values for the analogous trivalent actinide ion is < 0.001(Table 5.4) even at 3 M nitric acid concentration.



Figure 5.7: Kinetics of plutonium stripping from loaded solvents of L_I-L_{IV} (0.05 M) in ionic liquid diluent using 0.5 M oxalic acid and a mixture of 0.5 M NH₂OH.HNO₃ + 0.5 M HNO₃.

The ligands with linear alkyl chain substitution on amide nitrogens (L_{II} and L_{III}) shown better extraction and stripping characteristics for Plutonium as compared with the branched ones.

5.3.6 Extraction selectivity ofligands for Pu(IV)

Ligands L_I-L_{IV} are evaluated for Pu(IV) selective extraction over Cs(I), Sr(II), Eu(III), U(VI) and Am(III). Solutions of the ligands L_I-L_{IV} (0.05 M) in [C₈mim][Tf₂N] diluent are contacted with 3 M HNO₃ solutions containing tracers of the different metal ions of interest separately for 2 h duration, allowed for settling and centrifuged. Samples from organic and aqueous layers are assayed to estimate the D values for the corresponding metal ions and the results are as presented in Table 5.4.

Table 5.4: Extraction of few actinides and fission product metal ions employing $L_{I}-L_{IV}$ (0.05 M) in [C₈mim][NTf₂] from 3 M HNO₃.

Ligand	Distribution ratio for the metal ion						
	Pu(IV)	U(VI)	Eu(III)	Cs(I)	Am(III)		
					or Sr(II)		
L	12.9 ± 0.1	0.031 ± 0.001	$< 6.5 \text{ x } 10^{-4}$	0.014 ± 0.001	$< 1 \text{ x } 10^{-4}$		
LII	15.2 ± 0.1	0.035 ± 0.001	$< 8.3 \text{ x } 10^{-4}$	0.010 ± 0.000	< 1 x 10 ⁻⁴		
L _{III}	17.9 ± 0.0	0.036 ± 0.000	$< 1.4 \text{ x } 10^{-3}$	0.011 ± 0.001	< 1 x 10 ⁻⁴		
L _{IV}	4.27 ± 0.00	0.046 ± 0.001	$< 2.0 \text{ x } 10^{-4}$	0.11 ± 0.01	< 1 x 10 ⁻⁴		

The order of metal ion extraction is $Pu(IV) \gg U(VI) \sim Cs(I) \geq Am(III) \sim Eu(III) \sim Sr(II).$ Though non-extractability of Am(III), Eu(III), and Sr(II) can be explained on the basis of data obtained in nitrobenzene diluent, extraction of Cs(I) is attributed to the partitioning of the metal ion (which is not hydrated to any significant extent) into the ionic liquid phase. This could be explained by the exchange of $C_{s}(I)$ ion with the $C_{8}mim^{+}$ ion (towards the aqueous phase) similar to the cation exchange mechanism. In the absence of the ligands, a D value of 0.021 ± 0.002 is obtained for Cs(I) from 3 M HNO₃ which suggested absence of ligand assisted extraction. The results (Table 5.4) also suggest that Pu(IV) ion can be selectively extracted from amixture of mono-, bi-, tri- and hexa-valent actinide and fission product ions with reasonably high separation factor. Higher SF value with respect to U (D_{Pu}/D_U) is obtained with L_{III} (497) whereas alow value of 92 is with L_{IV} . On the other hand, SF values ca.18,000 or higher are obtained for Am(III), Eu(III) and Sr(II) making the ionic liquid

based solvent system as one of the most efficient one for Pu(IV) extraction from a mixture of actinides and fission products.

5.4 Conclusions

The four diamide ligands (3,3'-bis(2-oxydialkylacetamide)triarylpyridine) L_I-L_{IV} with linear/branched alkyl groups having four/eight carbon chains are evaluated in IL ([C₈mim][NTf₂]) diluent for the extraction of the actinides, and promising results obtained for selective extraction of plutonium. The metal ion extraction primarily confirmed to a solvation type of mechanism showing an increase in D_{Pu(IV)} with corresponding increase in HNO₃ concentration. The metal to ligand ratio is observed to be 1:1 with a good ligand economy in extraction process.

All the four diamide ligands are highly selective for Pu(IV) extraction as that of Am(III), Eu(III), and Sr(II) is negligible (D < 1 x 10^{-3}) whereas U(VI), Cs(I) extraction is one to two orders of magnitude lower than that of Pu(IV). Though ligand assisted extraction is the main factor for Pu(IV) ion extraction, both U(VI) and Cs(I) ion extractions have very little role for the ligand. Even for Pu(IV) ion extraction, the role of ligand is significantly lower due to acompeting anion exchange extraction mechanism at 6 M nitric acid concentration. Both the extraction and stripping kinetics are fast. Though ionic liquid based solvent systems are reported to result in an enormous increase in metal ion extraction, the present case gives a rare example where the metal ion extractionis lower in the ionic liquid based solvent as compared to that observed in molecular diluent based solvent system. The separation factor SF_{Pu/U} is high for all the ligands L_I-L_{IV} in ionic liquid in comparison with either nitrobenzene or 5 % ID/DD diluents (Table 5.5).

Ligand	S.F. _{Pu/U}	S.F. _{Pu/U}	S.F. _{Pu/U}
	(Nitrobenzene)	(5 % ID/DD)	([C ₈ mim][Tf ₂ N])
L	89		416.1
L_{II}	153		434.3
L _{III}	49.4	69.5	497.2
L _{IV}	16.5	40.8	92.8

Table 5.5: Separation factors for plutonium over uranium in different diluents;nitrobenzene, 5 % ID/DD and $[C_8mim][Tf_2N]$.

Chapter – 6

EVALUATION OF DIAMIDE LIGANDS (L_{III} AND L_{IV}) FOR SELECTIVE SEPARATION OF PLUTONIUM(IV) USING FLAT SHEET SUPPORTED LIQUID MEMBRANE

6 Evaluation of diamide ligands (L_{III} and L_{IV}) for selective separation of plutonium(IV) using flat sheet supported liquid membrane.

6.1 Preamble

In this chapter the selective permeation of Pu(IV) through Flat Sheet Supported Liquid Membrane (FSSLM) is studied. Solutionsof L_{III} and L_V (0.1 M) in a mixture of 5 % (v/v) isodecanol in *n*-dodecane (5 % ID/DD) as diluent are used to make liquid membranes on PTFE microporous membrane support. The most promising ligand L_{III} observed earlier in solvent extraction studies is used with FSSLM for selective separation of plutonium.

6.2 Introduction

The low initial design and capital costs, low energy consumption for operation and the high separation factors achievable made the membrane techniques highly attractive for large scale operations.^{142,143} A membrane is a selective barrier between two phases (feed and receiver) that is permeable to certain components of the feed phase to receiver phase retaining others in the former. According to International Union of Pure and Applied Chemistry (IUPAC) there are three types of membranes depending on pore diameter (PD) which are (i) microporous (PD < 2 nm) (ii) mesoporous (PD between 2 to 50 nm) and (iii) macroporous (PD > 50 nm).¹⁴⁴ The membranes are of two types, active or passive. In case of passive membranes the transport of species is driven by pressure, concentration, chemical or electrical gradients. Based on driving force for separation, the various types of membranes are (i) reverse osmosis, (ii) nanofiltration, (iii) ultrafiltration, (iv) microfiltration, (v) electro-dialysis, (vi) diffusion-dialysis, (vii) bipolar electrolysis and (viii) liquid membranes.

The separation by liquid membranes involves simultaneous extraction and stripping through a thin liquid membrane which separates the feed and strippant (receiver) solutions. The very small quantities of solvent requirement makes FSSLM technique a very attractive alternative to solvent extraction.¹⁴⁵ As the extraction and stripping proceed simultaneously the solvent won't get to saturation conditions and the requirement of solvent becomes very less. Requirement of low initial solvent inventory and very low quantities of secondary solvent waste generation after the usable life cycles of the Supported Liquid Membrane (SLM), makes the process highly economically viable. Liquid membrane technology can be broadly classified as (i) Bulk Liquid Membranes (BLM) (ii) Emulsion Liquid Membranes (ELM) and (iii) Supported Liquid Membranes (SLM). SLM's are different from the former two in immobilization of solvent on a microporous membrane support. The membrane support can be of flat sheet type in which case it is 'Flat Sheet Supported Liquid Membrane' (FSSLM) or in case of hollow fiber it is 'Hollow Fiber Supported Liquid Membrane (HFSLM)'. The attractive part of membrane technology is the transport of metal ion across the membrane even against the concentration gradient also as the transport is governed by the difference in conditions from extraction to stripping on either side of the membrane. The transport of species across liquid membrane is controlled by (i) acidity and composition of the liquid phases on either side, (ii) concentration of the ligand, (iii) nature of ligand and diluent in solvent mix, (iv) viscosity of the solvent and (v) porosity and thickness of the membrane etc..146

HFSLM technique for the separation of plutonium from Cs, Ru, Eu and other metal ions in liquid wastes generated from nuclear chemical facilities is reported by Rasthore et al.. A solution of metal ions in 3 M HNO₃ is used as feed whereas receiving phase is hydroxylamine (reducing agent) solution. Liquid membrane is of solvent mix,

TBP in *n*-dodecane diluent.^{147,148} The transport of Pu(IV) nitrate across macro cyclic di-cyclohexano-18-crown[6] in toluene diluent as liquid membraneis reported for its separation from Cs, Ru and Sb ions. The fall in plutonium transport across liquid membrane with increasing crown ether concentration in toluene is ascribed to increase in viscosity of the membrane phase.¹⁴⁹ Selective separation of plutonium from different metal ions across the 2-ethylhexyl(2-ethylhexyl)phosphonic acid in *n*-dodecane liquid membrane to oxalic acid solution as receiving phase is reported¹⁵⁰ and similar to the fore said crown ether studies here also increase of extractant concentration above 20 % led to the saturation/fall in plutonium transport due to the increased viscosity of the SLM phase. Selective separation of uranium, transuranium elements and rare earth fission products across SLM of TRUEX solvent from the feed solutions containing other fission and corrosion products is reported by Danesi et al.¹⁵¹ A mixture of CMPO (0.25 M) and TBP (0.75 M) in decalin diluent is used to form liquid membrane on thin microporous polypropylene sheet support and permeability coefficients of U(VI), Np(V), Pu(IV) and Am(III) are evaluated. The transport of nitric acid (at slower rates) along with actinide ions across the liquid memebrane is reported. Transport of americium and plutonium through dihexyl-*N*,*N*-diethylcabomoylmethylphosphonate liquid membrane supported on polypropylene hollow fiber is studied by Muscatello et al.. Transport of appreciable amount of ions is observed for feeds at high nitrate and low nitric acid (0.1 M) concentrations with oxalic acid (0.25 M) receiving phase.¹⁵²

In the present study, FSSLM was used for metal ion separations. The typical FSSLM set up is shown in Figure 6.1. The feed and strip (receiver) phases are kept under stirred condition to remove the concentration gradients and are separated by a membrane, the pores of which are pre-occupied by the solvent of interest to form liquid membrane.

The two major types of transport across the membrane are (i) the coupled transport in which the transport against the concentration gradient is achieved by utilizing the existing concentration gradient of a second species present in the system (ii) the facilitated transport in which the organic solvent present in the micro pores of the membrane facilitates the transport of metal ions through its interaction.^{153,154}



Figure 6.1: Typical laboratory setup for FSLM studies

The mechanism of extraction in facilitated transport depends on the nature of the organic solvent immobilized in the micro pores. In case of cation exchangers the mechanism follows counter current process in which the [H⁺] plays the role for driving force.

$$M^+ + HX_{(membrane)} \Leftrightarrow MX_{(membrane)} + H^+$$

Whereas in case of neutral metal complexing agents the transport takes place by coupled co-current mechanism in which counter ions plays the role as driving force.

 $M^{n+} + n A^{-} + m L_{(membrane)} \Leftrightarrow MA_n L_{m(membrane)}$

As the present ligands under study are of neutral type and the mechanism of transport is supposed to be coupled co-current type.

6.3 Present work

The FSSLM experiments are carried out as presented in Chapter – III. The main emphasis is given to the ligand L_{III} which has shown best Pu(IV) selective separation characteristics among the ligands L_{I} - L_{V} during solvent extraction studies.

6.3.1 Selection of receiver phase for plutonium

After evaluating the ligands in aromatic, aliphatic and ionic liquid diluents by solvent extraction technique for selective separation of Pu(IV), the ligands L_{III} and L_V in their aliphatic diluent mixtureare chosen for FSSLM studies. The ligand of present interest is L_{III} as it has shown best Pu(IV) selective separation characteristics in solvent extraction studies. The FSSLM is prepared by soaking PTFE microporous membrane in the solvent mix L (0.1 M) in 5 % ID/DD for ~ 1 h period, after which it is gently wiped with the tissue paper to remove excess solvent on its surface. The FSSLM is fitted in mid of the two compartment cell and then filled the two compartments separated by membrane with the respective solutions of feed and receiver phase. Samples are collected at different time intervals from both the compartments for analysis.

Three different type of strippants (i) 0.5 M $NH_2OH + 1$ M HNO_3 , (ii) 0.5 M $NH_2NH_2 + 1$ M HNO_3 and (iii) 0.5 M (COOH)_2 (oxalic acid) as aqueous solutions are studied for the efficiency of plutonium stripping at receiving phase. L_{III} (0.1 M) in 5 % ID/DD is used to make FSSLM on PTFE sheet as is fore mentioned. In each case feed is 3 M HNO_3 containing Pu(IV) tracer. At different time intervals 't', the parameters such as (i) cumulative transport (% T_{tc}), (ii) percentage of metal transferred to receiver phase % T_{ts} and (iii) percentage of plutonium retained in the membrane phase % T_{tm} are estimated from the concentrations of plutonium in both feed and receiving chambers, and the results are summarized in Figure 6.2.

Among the three stripping agents used, $0.5 \text{ M NH}_2\text{OH} + 1 \text{ M HNO}_3$ solution gave the best results. In case of oxalic acid, after 5 h period ~ 81 % of plutonium got entrapped inside the FSSLM whereas only 15 % got transferred to receiver phase and 4 % retained in the feed phase. Although, oxalic acid performed efficiently in stripping process during solvent extraction studies but failed in case of FSSLM. Because of the concern of hydrazine toxicity, hydroxyl amine is of better choice.



Figure 6.2: Selection of strippant. FSSLM: L_{III} (0.1 M) in 5 % ID/DD diluent supported on PTFE microporous membrane. Feed: 3 M HNO₃, Receiver: variable.

The same stripping agent 0.5 M NH₂OH + 1 M HNO₃ is used in FSSLM studies of L_V also as the metal ion coordinating amide groups are same both in L_{III} and L_V ligands. L_V (0.1 M) in 5 % ID/DD is used for preparing the liquid membrane. Feed is 3 M HNO₃ with Pu(IV) tracer. The results are shown in Figure 6.3 and are similar to the case ofligand L_{III} .



Figure 6.3: FSSLM transport characteristics of Pu(IV) using L_V (0.1 M) in 5 % ID/DD supported on microporous PTFE sheet. Feed: 3 M HNO₃ containing Pu(IV) tracer, Receiver: 0.5 M NH₂OH + 1 M HNO₃.

6.3.2 FSSLM permeation studies for Pu(IV)

The facilitated transport model for SLMs is described by Danesi*et al*.^{155,156} This is based on the assumption that the chemical reactions at the aqueous-membrane interfaces *i.e.* the metal ion-ligand complex formation and its dissociation during stripping are instantaneous. This implies that the local equilibrium always exists at the aqueous-membrane interface and the metal ion transport rate will be determined by the diffusion rates through the aqueous (Nernst films) and the liquid membrane (membrane diffusion) phases. The flux of metal ions through liquid membrane can be described by Flicks diffusion law which is based on few assumptions: (i) there is no accumulation of metal ion-ligand complexes at the receiver side interface i.e. the stripping is complete and instantaneous (ii) the membrane polarity (dielectric constant) is low such a way that the concentration of charged species present in it are negligible (iii) diluent alone does not extract the metal ions (iv) the concentration gradients at the interfaces are linear and (v) the nitrate ion concentration remains constant at the feed phase. As describedin Chapter - IV, the increased extraction of Pu(IV) with increased concentrations of nitric acid together with high $D_{Pu(IV)}$ values obtained in presence of higher concentrations of U(VI)/Nd(III) nitrates indicate that the extraction takes place by solvation of neutral Pu(NO₃)₄ species. As is mentioned in Chapter – II, the plot of $\ln \frac{[C_{tf}]}{[C_{off}]}$ versus time 't' gives a straight line with a slope of $-P(\frac{Q}{V})$. From the known values of effective membrane area (Q) and the volume of the feed phase (V), the values of permeability coefficient 'P' is obtained.

Solutions with varying concentration of the ligand L_{III} (0.01-0.1 M) in 5 % ID/DD diluent are used to make the FSSLMs that are subjected to studies on Pu(IV) transport characteristics and the results are shown in Figure 6.4. The feed solutions are the 3 M nitric acid containing Pu(IV) tracer whereas receiver solutions are of 0.5 M NH₂OH + 1 M HNO₃ that are on either side of the FSSLMs. There is a steady decrease in plutonium transport rate with the decreasing concentration of L_{III} . The permeability coefficients for FSSLMs are increasing almost in a linear fashion with the increasing ligand concentration in 5 % ID/DD (Figure 6.5) indicating diffusion mechanism for the transport of plutonium across the membrane phase. In all cases there is no detectable transport of nitric acid across membranes as is observed by estimating acid content in the receiver phase.



Figure 6.4: FSSLM transport characteristics for Pu(IV): L_{III} in 5 % ID/DD diluents at varying concentration from 0.01 to 0.1 M. Feed: 3 M HNO₃ containing Pu(IV) tracer, Receiver: 0.5 M NH₂OH + 1 M HNO₃.



Figure 6.5: Permeability coefficients of FSSLMs versus L_{III} concentration in 5 % ID/DD. Feed: 3 M HNO₃ containing Pu(IV) tracer, Receiver: 0.5 M NH₂OH + 1 M HNO₃.

6.3.3 FSSLM selectivity towards Plutonium

FSSLM made of L_{III} (0.1 M) in 5 % ID/DD on PTFE membrane is studied for the selective transport of plutonium. A mixture of ²³⁹Pu (major isotope), ²³³U, ²⁴¹Am, ^{152, 154}Eu, ¹³⁷Cs, ^{85, 89}Sr tracers in 3 M HNO₃ is taken as feed phase and a solution of 0.5 M NH₂OH + 1 M HNO₃ as receiver phase. Alpha spectrometry is used to monitor ²³³U, ^{238, 239, 240}Pu and ²⁴¹Am. After a period of 5.5 h, the feed and receiver phase samples are electroplated on stainless steel planchettes and analyzed by alpha spectrometry. The results indicate that there is no detectable transport of uranium or americium with selective transport of plutonium across the membrane (Figure 6.6). To investigate the possible transport of Am, Eu, Sr and Cs, the samples at different time intervals from feed (t = 0, 180, 330 min) and receiver (t = 180, 330 min) phases are collected and analyzed by Gamma spectrometer with HPGe detector. The results (Figure 6.7) clearly indicate that there is no transport of these elements across the membrane.



Figure 6.6: Alpha spectrum for Feed (at t=0) and Receiver solution (t = 5.5 h). L_{III} (0.1 M) in 5 % ID/DD as LM on 0.45 μ PTFE flat sheet support.



Figure 6.7: Gamma-spectrum of (a) Feed phase stock at 0 min (b) Feed phase stock after 180 min (c) Receiver phase after 180 min and (d) Feed phase after 330 min (e) Receiver phase after 330 min.

6.3.4 Recycling of FSSLM

The stability of FSSLM is evaluated by recycling after different time intervals for the transport of plutonium each time with fresh feed and strip solutions, the results are presented in Table 6.1. There is a gradual decrease in the percentage transport of plutonium with the number of FSSLM recycling which may be due to loss of LM from the pores of the PTFE support.¹⁵⁷

It can be seen from Figure 5.8 that the transport of plutonium reaching to more than 65 % after a period of 25 h in all cases.

Day	Transportation	P x 10 ³ ,		
	Feed Phase	Receiver Phase	Membrane Phase	cm/sec
1	04.4	92.5 (93.9)	03.10	1.14 ± 0.04
2	14.1	76.4 (94.8)	02.87	0.66 ± 0.04
5	35.9	50.0 (80.5)	14.10	0.32 ± 0.02
10	62.6	18.8 (68.7)	16.11	0.15 ± 0.10

 Table 6.1: Permeation coefficients of membrane phase for Pu(IV) at different time periods.



Figure 6.8: Studies on stability of FSSLM; Solution of L_{III} (0.1 M) in 5 % ID/DD supported on microporous PTFE flat sheet. Feed: 3 M HNO₃ containing Pu(IV) tracer, Receiver: 0.5 M NH₂OH + 1 M HNO₃.

6.4 Conclusions

Highly selective transport of Pu(IV) through FSSLM L_{III} (0.1 M) in 5 % ID/DD diluent on microporous PTFE sheet is observed from the 3 M HNO₃ feed in presence of Cs(I), Sr(II), Eu(III), U(VI) and Am(III) to the receiver phase containing 0.5 M NH₂OH + 1 M HNO₃. The observed permeability coefficient for Pu(IV) is 1.14 × 10⁻³ cm/sec. The mechanism of Pu(IV) transport across the FSSLM is explained by diffusion pathway. Among the different strippants explored [oxalic acid, hydrazine (N₂H₄) and hydroxyl amine (NH₂OH)], a solution of 0.5 M hydroxyl amine in 1 M HNO₃ has displayed the highest efficiency. However, the stability of FSSLM poses constraints in their recycling. Replacement of *iso*-decanol with a more hydrophobic phase modifier and increased salt content on the receiver side may improve the life time of FSSLM.¹⁵⁸ Different causes for membrane degradation and the preventive measures to increase the recycle number is discussed in detail by Kocherginsky etc al.,¹⁵⁹ which will be useful for future study on the improvement of membrane lifetime.

Chapter – 7

SUMMARY, CONCLUSIONS AND

FUTURE PERSPECTIVES

7. Summary, conclusions and future perspectives

7.1 Preamble

This chapter summarizes the results of present study starting from synthesis to evaluation of the ligands L_I-L_V for selective separation of plutonium with the conclusions arrived and the future perspectives of this work.

7.2 Design of and synthesis of a new class of diamide ligands

Ligands with metal coordinating groups tethered to terpyridine/2,6-diarylpyridine scaffolds are known for their selective metal ion binding. The selectivity in complexation of metal ions is differs by the nature of donor atoms and the steric constraints posed by the ligands. The ligands (L_I - L_V) are designed based on the previously reported terpyridine based ligands (Figure 7.1) which have shown promising results in selective extraction of group actinides. Designing of these extractants is based on the hard and soft nature of the ligating centers (O/N) beside the nature of alkyl groups on amide nitrogen.



Figure 7.1: Tepyridine based ligands with promising results for selective actinide extraction (Earlier reported by Marie et al.).

A new class of diamide ligands (L_I-L_V) with triaryl-/diarylpyridine (TAP/DAP) backbone are designed and synthesized.



Figure 7.2: 3',3"-bis(2-oxydialkylacetamide)-2,4,6-triarylpyridine (TAP-diol) and 3',3"-bis(2-oxydialkylacetamide)-4-pentyl-2,6-triarylpyridine (DAP-diol).

The molecular structures TAP/DAP are expected to provide the steric constraints on the metal coordinating amide groups attached to them. An optimized protocol for the synthesis of the basic molecular scaffolds (TAP-diol/DAP-diol) was developed wherein a mixture of 3'-hydroxyacetophenone, benzaldehyde (TAP-diol) or hexanal (DAP-diol), ammoniumacetate, catalytic amount of acetic acid (TAP-diol)/trifluoromethane sulfonic acid (DAP-diol) in dimethylformaimide (DMF) is heated at 130^oC for 12 h to afford TAP-diol or DAP-diol (Figure 7.2) respectively in synthetically acceptable yields. These are then condensed with the different α -chloroacetamides to obtain the corresponding diamide ligands L_I-L_V in good yields (Figure 7.3).



Figure 7.3: The structures of new class of diamides synthesized (L_I-L_V)

7.3 Evaluation of the synthesized ligands for selective separation of metal ions

The ligands synthesized are evaluated for selective extraction of metal ions by both (i) solvent extraction and (ii) FSSLM methods the details of which are as follows.

7.3.1 Evaluation of extraction efficiency/selectivity of synthesized ligands for metal ions by solvent extraction

7.3.1.1 Effect of diluents

Gratifyingly, all the designed ligands have displayed high selectivity for Pu(IV) separation both in molecular and ionic liquid diluents under 2-3 N HNO₃ feed acid conditions and the mechanism of extraction is observed to be of solvation type. However, the metal ion-ligand stoichiometry differs both on the nature of diamides as well as the diluents. For example, the Pu(IV) complexation using L_I and L_{II} in aromatic diluents (nitrobenzene) led to the formation of Pu(NO₃)₄ L_2 complex while Pu(NO₃)₄L complex was formed with L_{III} - L_{IV} . In case of aliphatic diluents, plutonium is extracted mostly in the form of Pu(NO₃)₄ L_2 complex by L_{III} whereas L_{IV} and L_V extract as a mixture of Pu(NO₃)₄ L_2 (major) complexes.

In case of ionic liquid diluent ($[C_8mim][Tf_2N]$) the major component extracted is $Pu(NO_3)_4L$ for all the ligands L_I-L_{IV} indicating good ligand economy. The extraction of metal ions is in general higher in ionic liquid diluents when compared to molecular diluents. However, with the present diamides there is a decrease in $D_{Pu(IV)}$ values in ionic liquid diluent compared to molecular liquid diluents. This addresses the commonly faced problem

of metal ion back extraction from ionic liquids. Very high selective separations of plutonium are achieved in ionic liquid diluents.

Among the diluents used in the present study, the order of $D_{Pu(IV)}$ values is aromatic > aliphatic > ionic liquid. Even then, the aliphatic diluents are more suitable for large scale applications due to their beneficial attributes as diluents as discussed in Chapter - 4. In molecular diluents higher separation factors for L_{III} were attained in aliphatic diluents compared to aromatic ones.

This infers that the higher efficiency of the ligands can be achieved with using aliphatic diluents than aromatic.

7.3.1.2 Effect of linear/branched substitution on amide nitrogens

As an outcome using different amides in various diluents, in terms of $D_{Pu(IV)}$, interestingly linear alkyl chain diamides L_{II} and L_{III} are found to be superior than the amides with branched alkyl group substitution, L_I and L_{IV} . This is in converse to the earlier reported plutonium selective ligands, ODA and BenzoDODA (Figure 3.1). The extraction of Pu(IV) is faster with branched alkyl chain diamides in comparison to linear chain diamides in nitrobenzene diluents, which is in contrast to aliphatic diluents where linear alkyl diamides have faster Pu(IV) extraction kinetics.

This further emphasizes the preference of liner chain alkyl substitution on amide nitrogens of this class of diamide ligands in aliphatic diluents.

7.3.1.3 Effect of lipophilicity and the substituent on central pyridine ring (lipophilicity)

In case of aliphatic diluent, the ligands L_I and L_{II} are not suitable for extraction studies. The long chain alkyl group containing diamide ligands $L_{III}-L_V$ are amenable for metal ion extraction in *n*-dodecane diluent in presence of isodecanolas phase modifier (5 % v/v).

In regard to solubility of the ligands, the ligand L_V with increased aliphatic nature compared to L_{III} though shown better solubility in aliphatic diluents as observed from ease of solubility etc., the overall selectivity for Pu(IV) over U(VI) is lowered.

This clearly indicates that the nature of group (and possibly the position of its substitution) on central pyridine ring affects the overall efficiency and selectivity of the diamide ligands. This prompted to design new ligands with different extraction properties.

7.3.1.4 Metal ion extraction selectivity of diamides

Among the ligands $L_{I}-L_{V}$, L_{III} is found to be most promising for selective separation of plutonium in the presence of U(VI), Am(III), Eu(III), Sr(II) and Cs(I) in nitric acid solutions. Even among the tetravalent ions Pu(IV), Zr(IV) and Th(IV), L_{III} (0.1 M in 5 % ID/DD) has shown high extraction selectivity towards Pu(IV) from 3 M HNO₃ (D_{Pu}: 15.7 ± 0.7, D_{Th}: 0.28 ± 0.02 and D_{Zr}: 0.028 ± 0.025). The ligands $L_{I}-L_{IV}$ have shown good stability towards radiolysis in nitrobenzene diluent. Stripping characteristics for plutonium from the loaded solvents are highly satisfactory with low HNO₃ concentration (0.5 M) in the presence of NH₂OH.HNO₃ as areducing agent.

7.4 Evaluation of diamide L_{III} by FSSLM for selective separation of plutonium

Separation of metal ions through FSSLM technique needs less ligand inventory. Thus, ligand L_{III} which was found to be best among L_I-L_V for its selective and efficient separation of plutonium by solvent extraction, is used for selective separation of plutonium via FSSLM technique in presence of U(VI), Am(III), Eu(III), Sr(II) and Cs(I)ions in 3 M nitric acid solution. The solution of L_{III} (0.1 M) in 5% ID/DD is used to make FSSLM on PTFE microporous sheet. A promising result for the selective and efficient separation plutonium obtained. The membrane stability is to be addressed.

The current study shows that diamide ligands with TAP scaffold having longer linear alkyl group substitutions on amide nitrogen in aliphatic diluents are highly efficient in plutonium selective separation in presence of other ions like U(VI), Am(III), Eu(III), Sr(II), Cs(I), Sr(II), Th(IV), and Zr(IV) from 2-3 M nitric feed solutions.

The results generated during the investigation on metal ion separation revealed that the present class of diamide ligands is highly promising in selective separation of plutonium from different sources: (i) dissolver solutions in fuel reprocessing (ii) laboratory waste chemicals solutions, (iii) separation from americium generated in plutonium storages, for safe handling (iv) pre-concentration in the analysis of environment samples.

7.5 Future perspectives

Better understanding of the nature of metal-ligand bonding and other mechanistic details may further help in designing of hydrophilic diamide ligands which can be deployed

in removing plutonium from biological systems in case of accidental ingestions. There is a scope to reduce the lipophilicity of ligands for better aqueous solubility by converting the amide groups to carboxylic acid groups (Figure 3.2). As the diamide ligands with TAP/DAP backbone shown a great promise, there is further scope to use these exotic backbones in designing other class of ligands. For example, the two hydroxyl groups in TAP and DAP can be exploited for making exotic class of crown ethers for selective extraction of different metal ions. The position of hydroxyl groups on aromatic rings in TAP/DAP can be judiciously varied to achieve more potent ligands.

REFERENCES

<u>Chapter –1</u>

- 1. S. S. Hecker, Los Alamos Science, 2000,26,10.
- 2. IAEA Report2015 (2009 updated).
- 3. R. G. Pearson, J. Am. Chem. Soc., 1963, 85, 3533.
- R. Malmbeck, C. Nourry, M. Ougier, P. Soucek, J. P. Glatz, T. Kato*, T. Koyama, *Energy Procedia*, 2011, 7, 93.
- 5. "Spent Fuel Reprocessing Options", IAEA-TECDOC-1587, IAEA 2008.
- D. L. Clark, S. S. Hecker, G. D. Jarvinen, and M. P. Neu; Chapter: *Plutonium*, L. R. Morss, N. Edelstein, J. Fuger and J. J. Katz, (Eds.)., The Chemistry of the Actinide and Transactinide Elements (*Volumes 1-6*), Springer, The Netherlands, 2010.
- 7. H. Eschrich, W. Ochsenfeld, Sep. Sci. Technol., 1980, 15(4), 697.
- (i) J. L. Swanson; Chapter: PUREX Process Flowsheets. W. W. Schulz, L. L. Burger, J. D. Navratil and K. P. Bender, (Eds.). Science and Technology of Tributyl Phosphate, CRC Press Inc., Boca Raton, 1984, 55.
- 9. B. Lanham and T. C. Runion, Purex Process for Plutonium and Uranium Recovery, ORNL-479, **1949**, 3.
- 10. G. Kessler, Nuc. Sci. and Eng., 2007, 155, 53.
- 11. D. C. Hoffman, F. O. Lawrence, J. L. Mewherter, F. M. Rourke, Nature, 1971, 234, 132.
- 12. L. V. Lipis, B. G. Pozharskiain and V. V. Fomin, J.Structt. Chem., 1960, 1(2), 125.
- 13. Patricia Paviet-Hartmann, Plutonium Chemistry, NAMP (DOE), 2012.
- 14. A. B. Garrett, Ohio J. of Sci., 1947, 47 (3), 1947.
- 15. J. M. Cleveland, Coordin. Chem. Rev., 1970, 5, 101.

- N. C. O'boyle, G. P. Nicholson, T. J. Piper, D. M. Taylorl, D. R. Williams and G. Williams, *Appl.Radiat.lsot.*, **1997**, *48 (2)*, 183.
- 17. J. L. Ryan, J. Phys. Chem., 1960, 64 (10), 1375.
- P. I. Artyukhin, A. D. Gel'manand V. I. Medvedovskii, *DokladyAkad. Nauk* S.S.S.R,1958,120,98.
- 19. A. Zinkeand E. Ziegler, Chem. Ber., 1944, 77, 26443.
- 20. P. Thuery, M. Nierlich, V. Lamare, J. F. Dozol, Z. Asfariand J. Vicens, J. Incl. Phenom. Macrocycl. Chem., 2000, 36, 375.
- 21. R. Ungaro, A. Casnati, F. Ugozzoli, A.Pochini, J. F. Dozol, C. Hill and H. Rouquette, *Angew. Chem. Int. Ed. Eng.*, **1994**, *33*, 1506.
- T. J. Haverlock, R. A. Sachleben, P. V. Bonnesenand B. A. Moyer, J. Incl.Phenom., 2000, 36, 21.
- 23. W. W. Schulz, K. P. Bender, L. L. Burger and J. D. Navratil, *Science and Technology of tributyl phosphate*". U.S..
- 24. S. H. Hasan, J. P. Shukla, J. Radioanal. Nucl. Chem., 2003, 258(3), 563.
- R. C. V. S. Brahmmananda, T. G. Srinivasan and P. R. Vasudeva Rao, *Solv. Extr. Ion Exch.*,
 2007, 25, 771.
- 26. W. Schulz and E. P. Horwitz, Sep. Sci. Technol., 1988, 23, 1191.
- 27. E. P. Horwitz and D. G. Kalina, Solvent Extr. Ion Exch., 1984, 2, 179.
- A. M. Rozen, V.I. Volk, A. Yu. Vakhrushin, B. S. Zakharkin, N. A. Kartasheva, B.V. Krupnov and Z. I. Nikolotova, *Radiochemistry*, 1999, 41, 215.
- 29. Y. Sasaki and S. Umetani, J. Nucl. Sci. Tech., 2006, 43, 794.
- 30. L. Cécille, D.Landat, and F. Mannone, Radiochem. Radioanal. Letters, 1977, 31,19.

- 31. Y. Zhu, C. Song and R. Jiao, Nuclear Technology, 1994, 108, 361.
- J. P. Glatz, C. Song, L. Koch, H. Bokelund and X. M He, Proceedings of the Int. Conf. on Evaluation of Emerging Nuclear Fuel Cycle Systems, Global'95, 1995, 548.
- K. L. Nash, R. E.Barrans, R. Chiarizia, M. L. Dietz, M. P. Jensen, P. G. Rickert, B. A. Moyer, P. V. Bonnesen, J. C. Bryan and R. A. Sachleben, *Solvent Extr. Ion Exch.*, 2000, 14,605.
- 34. B. Weaver and F. A. Kappelmann, J. Inorg. Nucl. Chem., 1968, 30, 263.
- 35. Y. J. Zhu, R. Z. Jiao, Radiochim. Acta, 1995, 69, 191.
- 36. Y. J. Zhu, J. Chen and R.Z. Jiao, Solv. Extr. Ion Exch., 1996, 14, 61.
- 37. X. Wang, Y. Zhu and R.Jiao, J.Radioanal. Nucl. Chem., 2002, 251, 487.
- J. R. Klaehn, D. R. Peterman, M. K. Harrup, R. D. Tillotson, T. A. Luther, J. D. Law and L. M. Daniels, *Inorg. Chim. Acta*, 2008, 361, 2522.
- C. Cuillerdier, C. Musikas, P.Hoel, L.Nigond, and X.Vitart, Sep. Sci. Technol., 1991, 26,1229.
- 40. L. Spjuth, J. O. Liljenzin, M. J. Hudson, M. G. B. Drew, P. B.Iveson and C.Madic, *Solvent Extr.Ion Exch.*, **2000**, *18*, 1.
- 41. C. Madic and M. Hudson, European Commission, EUR 18038, 1998.
- 42. X. F. Tan, Y. S. Wang, T. Z. Tan, G. F. Zhou and B. R. Bao, *J. Radioanal.Nucl.Chem*, 1999,242,123.
- 43. M. C. Charbonnel and C.Musikas, Solvent Extr . IonExch., 1988, 6, 461.
- 44. M. C. Charbonnel and C.Musikas, Solvent Extr. Ion Exch., 1989, 7, 1007.
- 45. Y. Sasaki and G. R. Choppin, Anal. Sci. 1996, 12, 225.
- 46. Y. Sasaki, G. R. Choppin, Radiochim. Acta., 1998, 80, 85.

- 47. Y. Sasaki, Y.Sugo, S. Suzuki and S.Tachimori, Solvent Extr. Ion Exch., 2001, 19, 91.
- 48. E. A. Mowafy, H. F. Aly, Solv. Extr. Ion Exch., 2007, 25, 205.
- K. Matloka, A. Gelis, M. Regalbuto, G. Vandegrift and M. J. Scott, *Dalton Trans.*, 2005, 23, 3719.
- K. Matloka, A. Gelis, M. Regalbuto, G. Vandegrift and M. J. Scott, Sep. Sci. Technol., 2006, 41, 2129.
- 51. D. Jańczewski, D. N. Reinhoudt, W. Verboom, C. Hill, C.Allignol and M. Duchesne, *New J. Chem.*, **2008**, *32*, 490.
- I. Hagström, L. Spjuth, A. Enarsson, J. O. Liljenzin, M. Skålberg, M. J. Hudson, P. B. Iveson, C. Madic, P. Y. Cordier, C. Hill and N. Francois, *Solvent Extr.Ion Exch.*, 1999, 17, 221.
- 53. P. Y. Cordier, C. Hill, P. Baron, C. Madic, M. J. Hudson and J. O. Liljenzin, *J.Alloys Compd.*, **1998**, 738, 271.
- 54. F. W. Lewis, M. J. Hudson and L. M. Harwood, Syn. Lett., 2011, 18, 2609.
- 55. (a) F. H. Case and E.Koft, *J.Am.Chem.Soc.*, 1959, *81*,905.(b) J. H. Forsberg, V. T. Spaziano,
 S. P. Klump and K. M. Sanders, *J.Heterocycl.Chem.*, 1988, 25, 767. (c) M. J. Hudson, G. Y.
 S. Chan, C. Madic and P. Baron, GB 2296917A, 1996. (d) M. G. B. Drew, M. J. Hudson, P.
 B. Iveson, M. L. Russell and C. Madic, *ActaCrystallogr., Sect. C*, 1998, *54*, 985.
- 56. A. W. Addison and P. J. J. Burke, Heterocycl. Chem., 1981, 18,803.
- M. G. B.Drew, C. Hill, M. J. Hudson, P. B.Iveson, C. Madic, L. Vaillant and T. G. A.Youngs, *New J. Chem.*, 2004, 28.
- 58. F. H. J. Case, Heterocycl. Chem., 1971, 8, 1043.
- 59. Z. Kolarik, U. Müllich and F.Gassner, Solvent Extr. Ion Exch., 1999, 17, 23.

- 60. Z. Kolarik, U. Müllich and F. Gassner, Solvent Extr. Ion Exch., 1999, 17, 1155.
- M. J. Hudson, M. G. B. Drew, M. R. St. J. Foreman, C. Hill, N.Huet, C. Madic and T. G. A. Youngs, *Dalton Trans.*, 2003, 1675.
- (a) M. R. St. J.Foreman, M. J. Hudson, A. Geist, C.Madicand M.Weigl, *Solvent Extr.Ion Exch.*, 2005, 23, 645.(b) M. Nilsson, S. Andersson, F. Drouet, C. Ekberg, M. Foreman, M. Hudson, J. O. Liljenzin, D. Magnusson and G. Skarnemark, *Solvent Extr. Ion Exch.*, 2006, 24, 299.
- 63. A. Geist, C. Hill, G. Modolo, M. R. St. J. Foreman, M. Weigl, K. Gompper, M. J. Hudson and C.Madic, *Solvent Extr. IonExch.*, 2006, 24, 463.
- 64. D. Magnusson, B. Christiansen, J. P. Glatz, R. Malmbeck, G.Modolo, D. Serrano-Purroy, and C. Sorel, *Radiochim.Acta*, **2009**, *97*, 155.
- 65. E. Aneheim, C. Ekberg, A. Fermvik, J. Foreman, T. Retegan and G. Skarnemark, *Solvent Extr.Ion Exch.*, **2010**,*28*, 437.
- F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, G.Modolo, M. Sypula, J. F. Desreux, N. Bouslimani and G. Vidick, *Dalton Trans.*, 2010, 39, 5172.
- F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T. H. Vu and J. P. Simonin, *J.Am.Chem.Soc.*, 2011, 133, 13093.
- Nathalie Boubals, Michael G. B. Drew, Clément Hill, Michael J. Hudson, Peter B. Iveson, Charles Madic, Mark L. Russella and Tristan G. A. Youngsa, *Dalton Trans.*, 2002, 55.
- Michael G. B. Drew, Clement Hill, Michael J. Hudson, Peter B. Iveson, Charles Madicband Tristan G. A. Youngs, *Dalton Trans.*, 2004, 244.

- 70. V. A. Babain, M. Yu. Alyapyshev and R. N. Kiseleva, Radiochim. Acta, 2007, 95, 217.
- 71. F. Bravard, C. Rosset and P.Delangle, *Dalton Trans.*, 2004, 2012.
- Cheng-Liang Xiao, Cong-Zhi Wang, Li-Yong Yuan, Bin Li, Hui He, Shuao Wang, Yu-Liang Zhao, Zhi-Fang Chai and Wei-Qun Shi, *Inorg. Chem.*, 2014, 53 (3), 1712.
- 73. C. Marie , M. Miguirditchian , D. Guillaneux , J. Bisson , M. Pipelierand D.Dubreuil, *Solvent Extr. Ion Exch.*, **2011**, *29*, 292.

<u>Chapter – 2</u>

- 74. D.E. Ryan and A.W. Wheelright, Ind. Eng. Chem., 1959, 51, 60.
- J.N. Mathur, M.S. Murali, P.R. Natarajan, L.P. Badheka and A. Banerji, *Talanta*, 1992,39, 493.
- N. Srinivasan, M.N. Nadkarni, G.R. Balasubramanian, R.T. Chitnis and H.R. Siddiqui, *Report-643, BARC, Mumba, India*, 1972.
- S. S. Rattan, A.V.R. Reddy, V.S. Mallapurkar, R.J. Singh and Satya Prakash, *J. Radioanal. Nucl. Chem.*, **1981**,67, 85.
- 78. M. S. Sajun, V. V. Ramakrishna and S. K. Patil, Thermochim. Acta, 1981, 47,277.
- 79. N. Codamines, C. Musikas, Solvent Extr. Ion Exch., 1992, 10, 69

<u>Chapter – 3</u>

- 80. M. Adib, H. Tahermansouri, S. A. Koloogani, B. Mohammadi and H. R.Bijanzadeh, *Tetrahedron Letters*, **2006**, *47*, 5957.
- 81. K. Dimroth, C. Reichardt and K. Vogel. OSC 1973, 5, 1135.
- 82. A. T. Balaban, *CR(C)* **1963**, *256*, 4239.
- 83. Naser Montazeriand SaberMahjoob. Chinese Chemical Letters, 2012, 23, 419.
- 84. J. Li, P. He and C. Yu. Tetrahedron, 2012, 68, 4138.

- R. Karkia, P. Thapaa, M. J. Kanga, T. C. Jeonga, J. M. Namb, H. L.Kimb, Y.Nac, W. J. Chod, Y.Kwonb and E. S. Lee. *Bioorganic & Medicinal Chemistry*, 2010, 18, 3066.
- 86. M. Kamali, A. Shockravi, R.Mohtasham, and S. P.Moghanlo. ARKIVOC, 2014, IV, 242.
- 87. H.L. Handl and R.J. Gillies, Life Sciences, 2005,77, 361.
- H. Huang, D. Songdong, L. Ning, W. Yuxuan, S. Dongping and H. Song, Separation and Purification Technology, 2014, 123, 235.
- R. Ruhela, S. Panja, B. S. Tomar, A. K. Singh, S.C. Tripathi, P. M. Gandhi and R. C. Hubli, Separation and Purification Technology, 2014, 124, 49.
- 90. S. Shikha, PSurajit, A. Bhattachariya, P. S. Dhami, P. M. Gandhi, S. K. Ghosh, *Dalton Transactions*, 2015, 44, 12771
- 91. S. R. Salpage, R. C. Lanzetta, Y. Zhou, J. C. Wang, T. E. Albrecht-Schmitt and K. Hanson, *Chem. Commun.***2018**, *54*, 7507.
- 92. J. V. Mello and N. S. Finney. Organic Letters, 2001, 3, 4263.
- 93. A. G. Fang, J. V. Mello, and N. S. Finney. Organic Letters, 2003, 5(7), 967.
- 94. H. B. Mansaray, C. Y. Tang, D.Vidovic, A. L. Thompson, and S. Aldridge. *Inoranic Chemistry*, **2012**, *51*, 13017.
- 95. A. R. Khosropour, I. M. Baltork and F.Kiani. C. R. Chimie, 2011, 14, 441.
- 96. M.Adib, H.Tahermansouri,S. A.Koloogani,B.Mohammadia and H. R.Bijanzadeh. *Tetrahedron Letters*, **2008**,*47*, 5957.
- 97. J. Li, P. He and C. Yu. Tetrahedron, 2012, 68, 4138.
- P. V. Shinde, V. B. Labade, J. B. Gujar, B. B. Shingate and M. S. Shingare. *Tetrahedron Letters*, 2012,53, 1523.
- 99. N.Montazeriand S.Mahjoob. Chinese Chemical Letters, 2012, 23, 419.

- 100. A. Kumar, S.Koul, T. K.Razdan and K. K. Kapoor. Tetrahedron Letters, 2006, 47, 837.
- 101. V. Kannan and K. Sreekumar. Modern Research in Catalysis, 2013, 2, 42.
- 102. K. Dimroth, C.Reichardt and K. Vogel. OSC, 1973, 5, 1135.
- 103. A. T. Balaban, *CR(C)*, **1963**, *256*, 4239.
- 104. M. Adib, H. Tahermansouri, S. A.Koloogani, B. Mohammadi and H. R.Bijanzadeh, *Tetrahedron Letters*, **2006**, *47*, 5957.
- 105. J. C. Xiang, M. Wang, Y. Cheng, and A. X. Wu, Org. Lett., 2016, 18, 24.
- 106. X. Zhang, Z. Wang, K. Xu, Y. Feng, W. Zhao, X. Xu, Y. Yana and W. Yi, *Green Chem.*, **2016**, *18*, 2313.
- 107. S. Kannan, K. V. Chetty, V. Venugopal, M. G. B. Drew, Dalton Trans. 2004, 3604.
- 108. T. Raphael, L.Antoine, A. Guilhem, B. Fabien, D. Sandrine, B. Gilles, M. Manuel and P. R. Stephane, *Solvent Extraction and Ion Exchange*, **2014**, *32*, 478.

<u>Chapter – 4</u>

- 109. Y. Marcus, J Rydberg, M Cox, Claude Musikas and R. Gregory Choppin, *Solvent extraction principles and practice*, chapter 2, Marcel Dekker, Inc, New York, **2004**.
- 110. T. Sekine and T. Ishii, Bulletin of the chemical society of Japan, 1970, 43,2422.
- 111. P. Thuery, M. Nierlich, Z. Asfari, J Vicens and J.F. Dozol, Polyhedron, 2000, 19, 1749.
- 112. J. H. Hildebrand, Prausnitz and R. L. Scott, *Regular and Related Solutions*, Appendix 5, Van Nostrand Reinhold Ltd, New York, **1970**.
- 113. C. M. Hansen, Journal of Paint Technology, 1967, 39, 104.
- 114. R.W. Taft, J. L. M. Abboud, M. J. Kamlet and M. H Abraham, *Journal of Organic chemistry*, **1983**, *48*, 2877.
- 115. E. Löfström-Engdahl, E. Aneheim, C. Ekberg, M. Foreman and G.Skarnemark, *Proceedings* of the First ACSEPT International Workshop, Lisbon, Portugal, 31 March 2 April **2010**.
- 116. M. Nilsson, S. Andersson, C. Ekberg, M. R. S. Foreman, M. J. Hudson and G. Skarnemark, *Radiochimica acta*,**2006**, 94, 103.
- 117. K. D.Asmus and J. H. Fendler, The journal of physical chemistry, 1968, 72, 4285.
- 118. G. M. Nair, D. R. Prabhu, G. R. Mahajan, J. P. Shukla, *Solvent Extr. Ion Exch.*, 11, 1993, 831.
- 119.G. R. Mahajana, D. R. Prabhua, V. K. Manchandaa, L. P. Badheka, *Waste Manage.*, 18, 1998, 125.
- 120. S. Sharma, S. Panja, A. Bhattachariya, P. S. Dhami, P. M. Gandhi, S. K. Ghosh, *Dalton Trans.*, **45**, 2016, 7737.
- 121. R.K. Jha, P.N. Pathak, K. K. Gupta, P. G. Kulkarni, P. B. Gurba, P. Janardan, R. D. Changarani, P. K. Dey and V. K. Manchanda, *Desalination and Water Treatment*, 2009, 1268.
- 122. C. Cuillerdier and C. Musikas, Sep. Sci. Technol., 1993, 28(1-3), 115.

<u>Chapter – 5</u>

- 123. P. T. Anastas, Critical Reviews in Analytical Chemistry, 1999,29(3), 167.
- 124. T. Welton, Chem. Rev., 1999, 99(8), 2071.
- 125. P. V. Natalia and K. R. Seddon, Chem. Soc. Rev., 2008, 37(1), 123.
- 126. J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem.Commun.*, **1998**, 1765.
- 127. K. Binnemans, Chem. Rev., 2007,107, 2592.
- 128. T. Welton, Chem. Rev., 1999, 99, 2071.

- 129. P. Walden, Bull. Russ. Acad. Sci., 1914, 8, 405.
- 130. A. E. Visser and R.D. Rogers, J. Solid State Chem., 2003, 171, 109.
- 131. S. Dai, Y.H. Ju, C.E. Barnes, J. Chem. Soc. Dalton Trans., 1999, 1201.
- 132. X. Huang, Q. Zhang, J. Liu, H. He, W. Zhu and X. Wang, J. Radioanal. Nucl. Chem., 2013,298, 41.
- 133. M. Sun, L.Y. Yuan, N. Tan, Y.L. Zhao, Z.F. Chai and W.Q. Shi, *Radiochim.Acta*, 2014, *102*, 87.
- 134. K. Shimojo, K. Kurahashi and H. Naganawa, Dalton Trans., 2008, 5083.
- 135. S.J. Yoon, J.G. Lee, H. Tajima, A. Yamasaki, F. Kiyono, T. Nakazato and H. Tao, *J. Ind. Eng. Chem.*, **2010**, *16*, 350.
- 136. D.R. Prabhu, D.R. Raut, M.S. Murali and P.K. Mohapatra, Radiochim. Acta, (in press).
- 137.J. J. Katz, G. T. Seaborg and L. R. Morss, *Chemistry of actinide elements*, second edition, Chapman and Hall, USA, 1987
- 138. I. Billard, Chapter: "Ionic liquids: New hopes for efficient lanthanide/actinide extraction andseparation", *Handbook on the Physics and Chemistry of Rare Earths*, J. C. G. Bunzli andV. Pecharsky. (Eds.), Elsevier Science Pub. B.V., Amsterdam, **2013**. pp. 213-373.
- 139. X. Sun, H. Luo, S. Dai, Chem. Rev., 2012,112, 2100.
- 140. A. Rout, K.A. Venkatesan, T. Srinivasan and P.R. Vasudeva Rao, J. Hazard. Mater., 2012, 62, 221.
- 141. A. B. Patil, P. Pathak, V.S. Shinde, S.V. Godbole and P.K. Mohapatra, *Dalton Trans.*, 2013, 42, 1519.

<u>Chapter – 6</u>

142. H.J, Fendler, J. Membr. Sci., 1987, 30, 323.

- 143. R.D. Noble, Sep. Sci. Technol., 1987, 22, 731.
- 144. Ritu D. Ambashtaand Mika E.T. Sillanpaa, J. of Env. Radioactivity, 2012,105, 76.
- 145. R. Marr and A. Kopp, Int. Chem. Eng., 1982, 22, 44.
- 146. M. Rovira and A.M. Sastre, J. Membr. Sci., 1998,149, 241.
- 147. N. S. Rathore, J.V. Sonawanea, Anil Kumara, A.K. Venugopalana, R.K. Singha, D.D. Bajpaia and J.P. Shuklab, *Journal of Membrane Science*, **2001**,*189*, 119.
- 148. N. S. Rathore, J. V. Sonawan, S. K. Gupta, Anil Kumar Pabby, A. K. Venugopalan, R. D. Changraniand P. K. Dey, Sep. Sci. and Tech., 2004,39(6), 1295.
- 149. J. P. Shukla, Anil Kumar and R. K. Singh, *Separation Science and Technology*, 1992, 27(4), 447.
- 150. C.S. Kedari, S.S. Pandit and A. Ramanujam, J. of Membr. Sci., 1999, 156, 187.
- 151. Ritu D. Ambashtaand Mika E.T. Sillanpaa, J. of Env. Radioactivity, 2012,105, 76.
- 152. Anthony C. Muscatello, James D. Navratil Milton E. Killion and Marlene Y. Price, *Sep. Sci. and Tech.*, **1987**,*22(2-3)*,843.
- 153. R. W. Baker, M. E. Tuttle, D. J. Kelly and H.K. Lonsdale, J. Membr. Sci., 1977, 2, 213.
- 154. W.C. Babcock, R.W. Baker, E.D. Lachapelle, K.L. Smith, J. Membr. Sci., 1980, 7, 89.
- 155. P.R. Danesi, Sep. Sci. Technol., 1985, 19, 857.
- 156. P.R. Danesi, E.P. Horwitz and P.G. Rickert, J. Phys. Chem., 1983,87, 4708.
- 157. P.R. Danesi, L. Reichley-Yinger and P. Rickert, J. Membr. Sci., 1987, 31, 117.
- 158. A. M. Neplenbroek, D. bargeman and C. A. Smolders, J. of Membr. Sci., 1992, 67, 121.
- 159. N. M. Kocherginsky, Qian Yang and Lalitha Seelam, Sep. Sci. and Purfici. Tech., 2007, 53, 171.