Room temperature ionic liquids for the separation of actinides and fission products

by

Alok Rout

Enrolment No: CHEM02200704006
Indira Gandhi Centre for Atomic Research, Kalpakkam

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, Mumbai

April, 2012

Homi Bhaba National Institute

Recommendations of the Viva Voce Board

As members of the Viva Voce Board, we certify that we read the dissertation prepared by **Mr. Alok Rout** entitled **“Room Temperature Ionic Liquids for the Seprataion of Actinides and Fission Products”** and recommend that it may be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Chairperson – **Prof. U. Kamachi Mudali** U Kamachi Mudali Date: 8/8/12

Supervisor/Convenor – **Prof. T. G. Srinivasan** Date: 8.8.12

Member 1 – External examinor – **Prof. Ramesh L. Gardas** Gardas 8/8/12 Date:

Member 2 – **Prof. K. Nagarajan** K. Nagaraj 8/8/12 Date:

Member 3 – **Prof. N. Sivaraman** N. Sivaraman Date: 8/8/2012

Final approval and acceptance of this dissertation is contingent upon the candidate’s submission of the final copies of dissertation to HBNI.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it may be accepted as fulfilling the dissertation requirement.

Date: 8/8/2012

Place: Indira Gandhi Centre for Atomic Research, Kalpakkam

Statement by Author

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at Homi Bhaba National Institute (HBNI) and is deposited in the library to be made to borrowers under rules of the HBNI.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgement of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the Competent Authority of HBNI when in his or her judgement the proposed use of the material is in the interest of scholarship. In all other instances, permission must be obtained from the author.

A. Rout

(Alok Rout)

Kalpakkam

April 13, 2012

DECLARATION

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.

A. Rout

(Alok Rout)

Kalpakkam

April 13, 2012

Dedicated to…..

The Supreme Soul

Acknowledgement

In the first place, I would like to express my deep and sincere gratitude to my research supervisor Dr. T. G. Srnivasan, Raja Ramanna Fellow and former division head, FChD, Chemistry Group, IGCAR, for his constant encouragement and caring guidance. His acuteness, knowledge, and consistent thoughts have made my research life rewarding.

I will remain grateful forever to Dr. P. R. Vasudeva Rao, Director, Chemistry Group, IGCAR, who gave me an opportunity to work in the field of my interest. I was extremely fortunate to have his constructive comments and valuable suggestions in my paper works which has certainly improved the excellence of my dissertation.

I express my sincere thanks to Shri S. C. Chetal, Director, IGCAR, and Dr. Baldev Raj, former Director, IGCAR, for giving me chance to pursue my research at IGCAR.

I sincerely thank my Doctoral Committee members Dr. U. Kamachi Mudali, Dr. K. Nagarajan, Dr. N. Sivaraman and Dr. V. Ganesan, Dean, Chemical Science, IGCAR Campus for their time to time evaluation of the research work, and useful suggestions which unquestionably enhanced the quality of the dissertation.

I am extremely grateful to Mr. K. A. Venkatesan, for his heartfelt support, encouragement and loving guidance from the beginning of my research tenure. His constant inspiration, legacy towards learning, and ardent interest in the topic have undeniably improved my research knowledge.

I thank Dr. M. P. Antony for providing all the research facilities during my research work in H – 14 laboratory. My sincere thanks to Dr. M. Josheph, Dr. K. N. Sabarwal and SAIF, IITM for their kind support in characterizing all my ionic liquids. I am also obligated to Mr. C. R. Venkatsubramani for allowing me to use all the detector facilities for sample analysis.

I express my hearty thanks to all my laboratory buddies Shri Robert Selvan, Shri V.Sukumaran, Shri A. S. Suneesh, Shri Prasanta Kumar Nayak, Mrs K. V. Shyamala, Miss Deepika, Mrs Jayalakshmi, Shri Jammu Ravi, Mrs T. Prathibha and Dr. Kumaresan for their help and support. I owe my sincere thanks to all members of Chemistry Group, IGCAR for making my research environment enjoyable.

I record my special gratitude to my cherished friends Shri Swayam Malik, Shri Tarun kumar Sahoo, Shri Girish Padhy, Mrs Sulata Kumari Sahoo, Shri Bishnu Prasad Kar, Shri Prasanna Kumar Sahoo, Shri Pradeep Kumar Samantaray, Kamala Kanta Satpathy, Shri.Jayakumar, and Shri. Ch. Jagadeeswara Rao, who have given me continuous encouragement and moral support till the day. My precious moments with my all research scholar friends deserves a unique notice. Essentially, they are the regular source of inspiration during my doctoral work.

My warm gratitude goes to my parents, brother and sister for their unflagging love and support throughout my life. This achievement is simply impossible without them. I thank the supreme soul for helping me to reach this level.

At last but not the least, I would like to owe my sincere thanks to everybody who helped me to make this doctoral degree successful and at the same time, I convey my apology for not mentioning the names of all the helping hands by individual.

A Rout

Alok Rout

CONTENTS

Title **Page No.**

Synopsis

1. Introduction

The demand for energy is steadily increasing with ever increasing population and rapid industrialization all over the world. Huge consumption of natural energy resources, such as oil and gas, and the uncertainty in the development of renewable resources, makes nuclear option inevitable for the future energy demand. Nuclear reactors employ natural or enriched uranium as the fuel [1]. The spent nuclear fuel discharged from the nuclear reactor contains fissile elements such as plutonium and depleted uranium and several other elements formed by fission reaction, known as fission products. The spent nuclear fuel is therefore reprocessed to recover these fissile elements for the fabrication and further use to fuel reactors.

There are two different technologically viable methods available for reprocessing of spent nuclear fuel discharged from nuclear reactor. They are (i) Aqueous reprocessing, ii) Non aqueous reprocessing [2,3]. The first one is industrially well-established, PUREX (Plutonium Uranium Recovery by Extraction) process [2]. This process involves the following major steps: a) Fuel decladding, b) extraction of uranium and plutonium from aqueous phase, c) partitioning of plutonium from uranium and d) stripping of uranium. Dissolution is carried out by chop-leach method in which the spent nuclear fuel is cut into small pieces followed by treatment with nitric acid at 373 K in presence of air. The extraction of Pu(IV) and U(VI) from 3.0 M to 4.0 M nitric acid medium is then carried out by a solution of 1.1 M tri-n-butylphosphate (TBP) in *n*-dodecane (DD). During partitioning, the loaded organic is contacted with an aqueous solution containing uranous nitrate, to reduce Pu(IV) to inextractable Pu(III). U(VI) present in organic phase is later stripped with dilute nitric acid. The uranium and plutonium present in the strip are converted, after several complex processes, into respective oxides for feeding back into the reactor. The raffinate rejected after the extraction is known as “High-Level Liquid Waste” (HLLW), which contains all the radiotoxic fission products, trivalent actinides etc. in 3 – 4 M nitric acid medium.

There are two options available for the safe management of HLLW. The first one is the immobilization of HLLW in to glass or ceramic form followed by disposing them in deep geological repositories. The second options is partitioning of minor actinides and long lived fission products from HLLW and transmuting them in to short lived or stable nuclides. The first option is quite expensive and the presence of long lived radiotoxic elements necessitates the need for long-term surveillance for thousands of years. In contrast to this, the second option is economical, less time consuming and viable for the safe management of HLLW. In this method, the Ln(III) and An(III) are coextracted from HLLW followed by the mutual separation of lanthanides from actinides or vice versa. Several processes such as TRUEX, TRPO, DIDPA and DIAMEX have been studied for the co-extraction of trivalents from HLLW [4]. Similarly, TALSPEAK, SETFIC etc.[5] have been reported for the separation of lanthanides from actinides and vice versa. However, the undesirable limitation of the above processes are i) the chemical and radiolytic degradation of the solvent system and the generation of secondary aqueous wastes, ii) flash point of hydrocarbon diluents (e.g., the flash point of n dodecane is ~ 343 K), iii) difficulties in the Ln – An separation, iv) third phase formation etc.[6].

In the recent past, the room temperature ionic liquids have been receiving increased attention for possible applications in the area of nuclear fuel reprocessing and waste management [7-10]. Room temperature ionic liquids (RTIL) are compounds composed fully of dissociated ions and melt at temperatures lower than 373 K [11]. The RTILs have many attractive properties such as insignificant vapour pressure, ability to dissolve a wide range of organic and inorganic compounds, wide electrochemical window and tunability of properties by suitable combination of cation and anion etc. Consequently, there has been a significant increase in the studies related to the use of RTILs in aqueous reprocessing applications. Some of the striking features of RTILs that make them promising candidate for nuclear fuel cycle application are i) the selectivity of target metal ion can be easily manipulated by the change of cation-anion combinations of RTIL diluent, rather than redesigning the structure of extractant ii) presence of ionic liquid diluent in organic phase facilitates a new mode of recovery of metals by direct electrodeposition from the extracted phase iii) ionic liquids can be functionalized with organic moieties for task specific applications iv) RTILs can be designed to be completely incinerable, which would simplify the management of spent organic waste v) due to negligible vapour pressure of RTILs, the fire hazard is almost insignificant. In addition, unusual extraction of metal ions has been observed when traditional extractants are used in conjunction with RTIL diluents. Thus, RTILs provide excellent challenges and opportunities to researchers and also exhibit potential for technological applications through manipulation of their versatile properties.

The cationic or anionic part of the room temperature ionic liquid tethered covalently with organic functionalities, which can perform specific applications are known task specific ionic liquids (TSILs) [12]. Due to the presence of functional group, the resultant FIL is expected to show the properties of both ionic liquid and organic functionality. The earliest work on the synthesis of FILs was reported by Visser et al [13] which describes the extraction behavior of metal ions using several functionalized ionic liquids. Several authors have reported the application of TSILs (or FILs) for the recovery of metal ions of nuclear interest [14 - 17]. In the recent past, another class of IL extractants called ionic liquids with strongly coordinating anions [18,19] are becoming popular in addition to the functionalized ionic liquids. Usually, the conjugate base of the acids such as phosphate, diketonate etc, act as anions. The advantages [18] of such ionic liquids over functionalized ionic liquids are simple method of preparation, higher loading of metals, miscibility with molecular diluents such as toluene, xylene etc. These properties are very useful for some type of applications.

2. Organization of the thesis

The thesis is divided into seven chapters. The first chapter deals with a brief introduction to reprocessing of spent nuclear fuel, an introduction to room temperature ionic liquids, literature survey on RTILs, TSILs and ILs with strongly coordinating anions. The scope of the present study namely the recovery of actinides and fission products using ionic liquid as solvent medium is described in this chapter. Chapter 2 describes the materials, synthesis and characterization of ionic liquids, the details of instrumentation, analytical procedure and the experimental part of each study. Chapter 3 deals with the use of room temperature ionic liquids as diluents for the extraction of actinides (Pu(IV), U(VI) and Am(III)). Chapter 4 deals with the extraction – third phase formation behavior of Eu(III) in ionic liquid medium. This chapter also details the mutual separation of Eu(III) from Am(III) in ionic liquid medium. Chapter 5 describes the unusual separation of Pu(IV) from other actinides and fission products using couple of task specific ionic liquids. Chapter 6 deals with the application of some ionic liquids with strongly coordinating anions for the extraction of Pu(IV) from other metal ions. Chapter 7 provides the conclusions of the study.

Chapter 1 begins with a brief introduction to reprocessing of the spent nuclear fuel by PUREX process. The inherent advantages and the limitations were discussed. The introduction to the room temperature ionic liquids and their application for the separation of actinides, fission products are reported. A brief discussion on the task specific ionic liquids and ionic liquids with strongly coordinating anions are presented. The scope for the present study that deals with the application of RTILs for the separation and recovery of actinides and fission products from the nitric acid medium by solvent extraction procedure has been described.

Chapter 2 deals with the various chemicals and reagents used, synthesis and characterization of room temperature ionic liquids, task specific ionic liquids and ionic liquids containing strongly coordinating anions. Brief description of various experimental tools used for characterization of ionic liquid such as UV-visible, FT-IR, NMR, Mass Spectra is presented. The description of methods used for the measurement of radioactivity such as α-scintillation counting, NaI(Tl) detector, HpGe detector is presented. In addition, the other instrumental techniques used in the present study are also reported in this chapter. General experimental procedures adopted for the measurement of viscosity, density, water content, temperature effect and preparation of various solutions used in the study are described in detail. The experimental systematic adopted for the measurement of distribution ratio is reported.

Chapter 3 deals with a systematic study on the extraction of americium (III) from nitric acid medium by a solution of tri-n-butylphosphate (TBP) and n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4mimNTf_2$). The results were compared with that obtained with CMPO-TBP in *n*-dodecane (*n*-DD). The distribution ratio of ^{241}Am(III) in TBP-CMPO/$C_4mimNTf_2$ was measured as a function of various parameters such as concentrations of nitric acid, CMPO, C_4mimNO_3, $NaNO_3$ and TBP and temperature. Remarkably large distribution ratios were observed for the extraction of americium(III) when $C_4mimNTf_2$ acted as diluent and the extraction was insignificant in the absence of CMPO. Extraordinary extraction of americium was facilitated by the presence of RTIL. The solvent phase required only 0.05 M CMPO in RTIL medium instead of 0.2 M CMPO employed in TRUEX solution to obtain comparable extraction behavior. The stoichiometry of metal-solvate in organic phase was determined by the slope analysis of extraction data and it indicated the formation of 1:3 (Am : CMPO) complex in organic phase. However, the study showed that ion exchange mechanism for the extraction of americium (III) could not be excluded. The extraction of americium (III) by RTIL solution was accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration. The stripping of Am(III) from the ionic liquid phase was carried out using various complexing agents such as diethylenetriaminepentaacetic acid (DTPA), citric acid, acetohydroxamic acid (AHA) etc. Maximum stripping was observed using 0.03 M DTPA.

This chapter also describes the extraction behavior of U(VI), Pu(IV) and Am(III) from nitric acid medium by a solution of N,N-dimethyl-N,N-dioctyl-2,(2-hexyloxyethyl)malonamide (DMDOHEMA) in the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4mimNTf_2$). The distribution ratio of actinides in DMDOHEMA/$C_4mimNTf_2$ was measured as a function of various parameters such as the concentration of nitric acid, DMDOHEMA, C_4mimNO_3, $NaNO_3$, NTf_2^-, alkyl chain length of ionic liquid and temperature. The extraction of actinides in the absence of DMDOHEMA was insignificant and the distribution ratio achieved in conjunction with $C_4mimNTf_2$, was remarkable. The extractant DMDOHEMA showed excellent selectivity for U(VI) and Pu(IV) in ionic liquid diluent, whereas in *n*-DD, Am(III) was also co-extracted. Above 4 M nitric acid, the primary mode of Pu(IV) transfer in ionic liquid phase was found to be anion exchange and below 4 M nitric acid the investigations indicate that the most plausible mechanism of actinides transfer in ionic liquid phase was cation exchange of metal – solvate complex with C_4mim^+ cation exchange of ionic liquid. The distribution ratio of actinides decreased with increase of alkyl chain length of $C_nmimNTf_2$. The enthalpy change accompanied by the extraction of uranium(VI) and viscosity of the solvents were also measured. In both the above cases , the extraction stoichiometry was obtained from the slope analysis.

Chapter 4 deals with the extraction and third phase formation behavior of Eu(III) in CMPO - TBP extractants present in room temperature ionic liquid, $C_4mimNTf_2$ at 303 K. The distribution ratio (D_{Eu}) of Eu(III) in CMPO –TBP/$C_nmimNTf_2$ (n = 4, 6 and 8) was measured as a function of various parameters such as the concentrations of nitric acid, europium, CMPO, TBP, $NaNO_3$ and temperature. The distribution ratio of europium increased with the increase in the concentration of nitric acid reached a maximum value around 1 M followed by decrease. Loading of europium in CMPO-TBP/$C_4mimNTf_2$ increased with the increase in Eu(III) concentration without leading to the formation of third phase. The third phase formation is usually observed in conventional diluents at the limiting organic concentration of 9 mg/mL. However, nearly ~ 40 mg/mL could be loaded in 0.2 M CMPO-1.2 M TBP/$C_4mimNTf_2$ phase. In the absence of TBP i.e., 0.2M CMPO/$C_4mimNTf_2$) the extraction of Eu(III) resulted in a “crud-type precipitate” at the interphase. However the crud disappeared upon adding of TBP to the extent of 0.2 M. The stoichiometry of metal-solvate in organic phase was found to vary from 1: 3 (Eu: CMPO) at trace levels to 1:1 at higher europium loadings. The extraction of europium(III) by RTIL solution was accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration.

This chapter also describes the mutual separation of Eu(III) from Am(III) using the solution of bis(2-ethylhexyl)phosphoric acid (D2EHPA) or bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) in the room temperature ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide ($C_8mimNTf_2$). The effect of various parameters such as the concentrations of nitric acid, D2EHPA, HDEHDGA and diethylenetriaminepentaacetic acid (DTPA) on the extraction behavior of Am(III) and Eu(III) was also described. The differential complexing ability of the extractant in ionic liquid phase and DTPA in aqueous phase was exploited to optimize the conditions needed for effective separation of trivalent lanthanides from actinides. Among the extractants studied HDEHDGA was found to be superior to D2EHPA for such applications. At pH 3 and using 0.005 M DTPA, D2EHPA gave in a SF of ~35, however, HDEHDGA required only 10^{-4} M DTPA for achieving a SF of ~150. Excellent separation factors achieved with the use of the ionic liquid diluent indicates the feasibility of separating lanthanides from actinides present in high-level liquid waste (HLLW).

Chapter 5 describes the extraction behavior of plutonium (IV) from U(VI), Am(III) and other fission products using novel task specific ionic liquids (TSIL) such as diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide ($ImPNTf_2$) and N,N–dioctyl-2-(3-methyl imidazolium) bis(trifluoromethane sulfonyl)imide ($DOAImNTf_2$). The effect of aqueous phase acidity, TSIL concentrations, temperature and different additives (C_4mim^+, NO_3^- and NTf_2^-) on the separation of plutonium from other metal ions was studied. $D_{U(VI)}$ and $D_{Am(III)}$ were insignificant and were of the order of 10^{-2} -10^{-4} in 0.4M $ImPNTf_2/C_4mimNTf_2$ (or in 0.3 M $DOAImNTf_2/C_4mimNTf_2$). In contrast to this, $D_{Pu(IV)}$ was quite high and it decreased with increase in the concentration of aqueous nitric acid, reached a minimum at 4 -5M followed by the increase. The separation factor achieved for Pu(IV) over U(VI) using these TSILs were much higher than the values obtained for traditional neutral extractants. Similarly, the separation factors of Pu(IV) from U(VI) are 1 -2. SF of Pu(IV) over Am(III) is of the order of 10^3 -10^5 depending upon the concentration of nitric acid. The slope of 3 was obtained for Pu(IV) extraction in 0.4M $ImPNTf_2$ (or 0.3M $DOAImNTf_2$)/$C_4mimNTf_2$ from nitric acid suggesting three molecules of TSILs involved in the extraction process. The extraction of Pu(IV) was found to be exothermic in nature. The stripping of Pu(IV) from TSIL phase was achieved using complexing agents such as DTPA, AHA and citric acid.

Chapter 6 deals with the extraction behavior of Pu(IV) using some ionic liquids containing strongly coordinating anions (β-diketonate ions) such as alkylquaternaryammonium thenoyltrifluoroacetonate (R_4NTTA), and 1-alkyl-3-methylimidazolium thenoyltrifluoroacetonate ($C_n$mimTTA), with methyl, butyl, hexyl, heptyl and octyl moieties. The unique property of β-diketonate ionic liquids, namely, the miscibility in molecular diluents, was exploited to elucidate the mechanism of Pu(IV) extraction in these ionic liquids. The distribution ratio of plutonium (IV) in a solution of tri-n-octylmethylammonium thenoyltrifluoroacetonate (TOMATTA) present in tri-n-octylmethylammonium bis(trifluoromethylsulfonyl)imide (TOMANTf_2) (or xylene) and $C_n$mimTTA present in $C_n$mimNTf_2 was studied as a function of various parameters. The mechanism of Pu (IV) extraction in ammonium based and imidazolium based β-diketonate ionic liquids was elucidated. The study revealed that extraction was essentially controlled by the constituents of TOMATTA namely TOMAN, and HTTA, which could form upon nitric acid extraction. In addition, unlike alkylquaternary ammonium –TTA ionic liquids, the extraction of Pu(IV) in $C_n$mimTTA ionic liquid was essentially governed by the component HTTA at lower nitric acid concentrations (<2 M), and by the anion exchange of $C_n$mimNTf_2 at higher nitric acid concentrations. The excellent separation factors of Pu(IV) over other actinides (U(VI) and Am(III)) using these ionic liquids were reported in this chapter.

Similarly, this chapter also describes the miscibility of aliquot-336 based ionic liquid with phosphate, $[A336]^+[P204]^-$and diglycolamate, $[A336]^+[DGA]^-$ in the paraffinic diluents such as *n*-DD and its higher homologue. The extraction behavior of europium (III) in a solution of these ionic liquids present in different molecular diluents was studied as a function of various parameters such as pH, nature of diluent, concentration of ionic liquid. The data obtained were compared with those obtained in a solution composed of the precursors of ionic liquid. The extraction of europium (III) in $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ ionic liquids showed a strong dependence on the nature of molecular diluent used. The distribution ratio of Eu(III) increased with increase of pH; at pH > 2, the distribution ratios obtained in ionic liquids were much higher than their precursors. Eventhough the ionic liquid extracted Eu(III) and Am(III) to the same extent from the aqueous phase, it was possible to separate Eu(III) from Am(III) by adding DTPA to the aqueous phase. The distribution ratio and the SF achieved with the use of $[DGA]^-$ based ionic liquid were higher than $[P204]^-$ ionic liquid under similar conditions. Superior extraction of the target metals and excellent separation factors achieved with the use of these ionic liquids in conventional diluents indicates the feasibility of separating lanthanides from actinides. These ionic liquids seems to extract the trivalents as neutral metal (III) nitrate complex. Since the ionic liquid was converted to its precursor during equilibration with HNO_3, the study recommends the reconversion by the washing the ionic liquid phase with dilute acid before recycling.

The summary and conclusions of the present investigation were given in Chapter 7. Several ionic liquids containing organic moieties and strongly coordinating anions were synthesized and characterized by various analytical methods. The extraction behavior of some actinides and fission products in ionic liquid medium was studied as a function of various parameters. The ionic liquids in these studies acted either as diluent or as extractant. The results revealed that the extraction of metal ion was remarkable when ionic liquids were used in conjunction either with customary extractant or the diluent. Unusual extraction and selectivity of the target metal was generally observed when ionic liquid was used as solvent medium. In most cases, the stoichiometry of the metal-solvate was similar to the conventional system. However, the mechanism of extraction generally differed from those observed in molecular diluents, which requires deeper understanding. Use of RTIL diluent in place of *n*-DD in TRUEX solvent prevented the undesirable third phase formation during the extraction of trivalent actinides. It was possible to achieve high separation factor for the mutual separation of lanthanides from actinides using ionic liquid as the medium. The amide and phophonate functionalized ionic liquids offered huge scope of separating plutonium(IV) from other actinides and fission products. The ionic liquids containing strongly coordinating anions such as 1,3-diketonate, alkyl phosphate and diglycolamate were miscible in non-polar molecular diluents. The solubility in molecular diluents was exploited to determine the mechanism of metal ion extraction in ionic liquid phase.

3. Importance of the present work

The present study was aimed at exploring the feasibility of using room temperature ionic liquids, as diluents and extractants, for the separation of actinides and fission products from nitric acid medium. These studies were carried out for the first time. Several ionic liquids ranging from imidazolium to quaternary ammonium salts, amide and phosphonate functionalized ionic liquids and ionic liquids containing 1,3-diketonate, alkylphophate and diglycolamate anions have been synthesized and studied for the extraction. The studies indicate that extraordinary extraction of metal ions can be achieved, and the undesirable third phase formation can be avoided using ionic liquids as medium during solvent extraction procedure. Excellent separation of Eu(III) from Am(III) opens avenues for studying the Ln-An separation from high level liquid waste using ionic liquids. The task specific ionic liquids offer a new prospect of separating Pu(IV) from other actinides and fission products. The miscibility of ionic liquids containing coordinating anions in molecular diluents opens a new means of studying the mechanistic aspects of metal ion extraction in ionic liquid medium.

4. Future work

The results obtained in the present study on the separation of actinides and fission products using room temperature ionic liquid as a medium are encouraging. While, these new results show great promise, the physical and chemical properties of the ionic liquid need to be tuned to suit the ionic liquid for robust applications in reprocessing and waste management. This could be realized through further investigations on the physicochemical properties of room temperature ionic liquids. The fundamental properties of ionic liquids that govern solubility in aqueous phase, hydrophobicity, viscosity etc. need more understanding to enable the design of RTIL/FILs having the required properties for hydrometallurgical applications. Since the customary extractants in ionic liquid offer extraordinary selectivity of the target metal, the extraction behavior of the target can be studied using the existing extractants in a suitable ionic liquid. In addition, several ionic liquids can be functionalized with organic moieties and studied for the task specific applications.

5. References

[1] D. Olander, "Nuclear fuels – Present and future", J. Nucl. Mat. 389 **(2009)** 1-22.

[2] J. L. Swanson, "PUREX Process Flowsheets", In: Science and Technology of Tributyl phosphate, Eds. W.W. Schulz, L.L. Burger, J.D. Navratil, K.P. Bender, CRC Press Inc. Boca Raton, p 55, **1984**.

[3] Implications of Partitioning and Transmutation in Radioactive Waste Management. IAEA Technical Reports Series, STI/DOC/010/435, **2004**.

[4] Aspinall, H. C. Chemistry of f-Block Elements In : Advanced Chemistry Texts, Gordon and Breach Science Publishers, **2001**.

[5] B. A. Moyer, Ion Exchange and Solvent Extraction. A series of Advances, Volume 19, CRC Press, Taylor and Francies Group, 2010.

[6] Horwitz, E.P.; Kalina, M.A.; Kaplan, L. The extraction of selected transplutonium (III) and lanthanide (III) ions by dihexyl-N,N-diethylcarbamoylmethylphosphonate from aqueous nitrate media. Sep. Sci. Technol. 16 **(1981)** 417–437.

[7] I. Billard, A. Ouadi, C. Gaillard, Liquid–liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding. Anal Bioanal Chem. 400(6)**(2011)**1555-1566.

[8] Sung Ho Ha, R. N. Menchavez, Y. M. Koo, Reprocessing of spent nuclear waste using ionic liquids. Korean J. Chem. Eng. 27(5)**(2010)**1360-1365.

[9] P.R. Vasudeva Rao, K.A. Venkatesan, T.G. Srinivasan, Studies on applications of room temperature ionic liquids. Prog. Nuclear Energy 50**(2008)** 449-455.

[10] S. Dai, Y. H. Ju, C.E. Barnes, Solvent extraction of strontium nitrate by crown ether using room – temperature ionic liquids, J. Chem. Soc., Dalton Trans. **(1999)**1201 – 1202.

[11] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem. Rev. 99 **(1999)**2071- 2084.

[12] J.H. Davis Jr., Task-Specific Ionic Liquids. Chemistry Letters 33 **(2004)**1072 – 1077.

[13] A. E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. A. Sheff, Wierzbicki, J.H. Davis Jr., R.D. Rogers, Task specific ionic liquids for the extraction of metal ions from aqueous solutions. Chem. Commun. **(2001)** 135-136.

[14] A. Ouadi, B. Gadenne, P. Hesemann, J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, Task-Specific Ionic Liquids Bearing 2-Hydroxybenzylamine Units: Synthesis and Americium-Extraction Studies, Chem. Eur. J. 12 **(2006)** 3074 – 3081.

[15] A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, Solvent extraction of U(VI) by task specific ionic liquids bearing phosphoryl groups. Green Chem. 9 **(2007)**1160–1162.

[16] H. Luo, S. Dai, P. V. Bonnesen, A.C. Buchanan, Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an aza-crown ether fragment. J. Alloys and Compds. 418 **(2006)**195–199.

[17] I. L. Odinets, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. Nelyubina, Galina V. Myasoedova, N. P. Molochnikova, E. A. Zakharchenro, Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery. Dalton Trans. 39 **(2010)** 4170-4178.

[18] H. Mehdi, K. Binnemans, V. Hecke, L.V. Meervelt, P. Nockemann, Hydrophobic ionic liquids with strongly corodinating anions. Chem. Commun. **(2010)** 234-236.

[19] X. Sun, Y. Ji, F. Hu, Bo. He, Ji. Chen, D. Li, The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. Talanta 81**(2010)**1877–1883.

List of Schemes

List of Figures

List of tables

Chapter - 1

CHAPTER - 1

1.1 Nuclear energy

The economic growth of the world is directly proportional to the availability and consumption of electricity. Presently, the electric power is being produced from the natural energy resources such as coal, oil and gas etc. However, these resources are rapidly depleting. The impact of greenhouse gas emissions into the atmosphere, and the uncertainty in the development of renewable resources, nuclear option seems to be inevitable for meeting the future energy demand. Nuclear energy contributes about 6 % of the world’s energy and about 14% of the world’s total electricity. As of 2012, about 432 commercial nuclear reactors are producing about 366 GWe (gigawatts of electrical energy) all over the world [1] in operation in 30 countries and 65 plants with an installed capacity of 65 GW in 16 countries are under construction [2]. The estimated total energy demand of India by 2052 is around 1344 GWe and the current installed capacity of electricity generation is ~ 160 GWe [3]. By 2050, it is targeted to increase the electricity contributed from the nuclear energy from 3% to nearly 25% to satisfy our country’s energy requirement.

1.1.1 Nuclear power programme in India

A three-stage programme based on a closed nuclear fuel cycle has been envisaged and implemented in India by Dr. Homi J. Bhaba in early 50s for the effective utilization of these natural resources for the production of energy [4]. This was based on the limited uranium reserves (around 78,000 tonnes which is about 0.8% of that of the world) and availability of vast thorium resources (estimated to be around 3,60,000 tonnes which is about 32% of the world's reserves). The first stage deals with the production of power through natural uranium fuelled pressurised heavy water reactors (PHWR). Presently, there are two boiling water reactors (BWR) and fifteen PHWRs built at various locations of India are in operation and producing a total of around 4120 MWe [5].

The second stage involves the use of the depleted uranium and plutonium recovered from the spent fuels of PHWR as fuels for fast breeder reactors (FBR) to generate electricity as well as to breed ^{233}U from thorium which is used as blanket.

40 MWth Fast Breader Test Reactor (FBTR) is being operated successfully in Kalppakm for more than two decades [6]. 500 MWe Prototype Fast Breeder Reactor (PFBR) is in an advanced stage of construction at Kalpakkam. FBRs are capable of breeding of fuel than what they consume. Third stage is proposed to use ^{232}Th – ^{233}U as fuel as there are plenty of thorium resources in India. A 300 MWe Advanced Heavy Water Reactor (AHWR) [7] planned to be constructed soon, will use thorium-uranium and thorium- plutonium mixed oxides.

Nuclear fuel cycle encompasses uranium mining, uranium enrichment (if required), fuel fabrication, reactor operation, spent fuel reprocessing, vitrification, and waste disposal. Two types of nuclear fuel cycles have been proposed, namely (i) open fuel cycle, and (ii) closed fuel cycle. In open fuel cycle, the spent nuclear fuel after power generation is not reprocessed, but cooled and stored in a repository. This scheme is not suitable for India [8]. In closed fuel cycle, the spent fuel is reprocessed to recover unused uranium and plutonium, for utilization in fast breeder reactors.

1.1.2 Spent Fuel Reprocessing

A nuclear fuel cycle enabling the extraction of maximum energy in a safe manner and reducing the amounts of nuclear waste would always be preferable [9]. In this context, only closed nuclear fuel cycle can serve these requirements and lead to the sustainable energy production [10,11]. Hence, the reprocessing and recycling of spent nuclear fuel becomes an inevitable option in the back end of the nuclear fuel cycle. Two different technologically viable methods are available for the reprocessing of spent nuclear fuel coming out of the reactor. i) Aqueous reprocessing, ii) non aqueous reprocessing [12, 13]. The first one is the industrially well-established, PUREX process [12]. **P**lutonium **U**ranium **R**ecovery by **Ex**traction is known as PUREX process that involves the following major steps: a) Head end step, which includes fuel decladding, dissolution and feed preparation, b) extraction of uranium and plutonium from aqueous phase and c) partitioning of plutonium from uranium and stripping of uranium. Head end step is carried out by chop-leach method in which the spent nuclear fuel is cut into small pieces followed by dissolution of the fuel in nitric acid at 373 K in the presence of air. Extraction of Pu(IV) and U(VI) from 3.0 M to 4.0 M nitric acid medium is carried out by a solution of 1.1 M tri-n-butylphosphate (TBP) in *n*-dodecane (*n*-DD). The loaded organic is then contacted with an aqueous solution containing uranous nitrate, which selectively reduces Pu(IV) to Pu(III) and gets stripped to aqueous phase. U(VI) present in the organic phase is later stripped with 0.05 M nitric acid. The uranium and plutonium present in the strip are converted, after several complex processes, into respective oxides for feeding back into the reactor. The raffinate rejected after the extraction is known as “High-Level Liquid Waste” (HLLW), which contains all the radiotoxic fission products, actinides etc. in 3 – 4 M nitric acid medium. Since the radioactivity level of this waste solution is high, it is called HLLW.

PUREX PROCESS

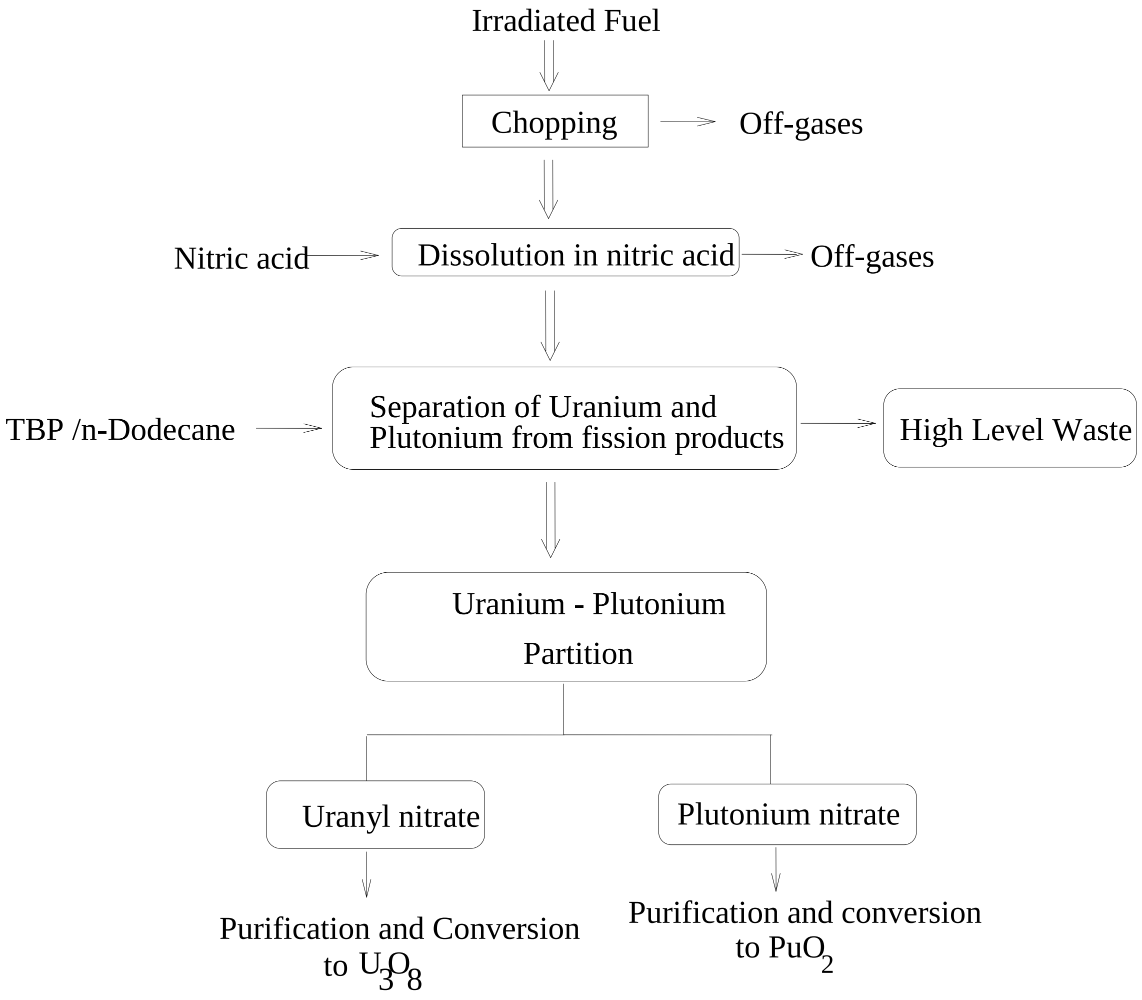


Figure 1.1. Schematic diagram of PUREX process

1.1.3 High Level Liquid Waste (HLLW)

The high level liquid waste obtained after the uranium and plutonium removal by PUREX process consists of minor actinides (^{241}Am(III), ^{243}Am(III) and ^{242,244,245}Cm), radiotoxic long lived fission products, activation products etc. Minor actinides, even though they are present in very small amount (0.1%), they are long lived α - emitter and strong contributors to the hazards encountered in HLLW. There are two options to handle

HLLW and to reduce the radioactivity and to have safe waste management, i) vitrification of HLLW in to the glass matrix followed by deposition in deep geological repositories and ii) removal of minor actinides from fission products followed by their transmutation in to short lived isotopes by neutron bombardment in accelerators or fast reactors. The first option is quite expensive as the long half lives and radiotoxicity coupled with aqueous mobility of these minor actinides necessitate the need for continuous long term surveillance of these repositories for several thousands of years. In contrast to this, the second option is acceptable as it is less time consuming and it decreases the waste management cost by reducing greatly the radiotoxicity. The radiotoxic inventory of the spent fuel is given in the figure 1.2 [14]. It is observed that it will take ~ 300,000 years to for the radiotoxic inventory of the spent fuel to reach the natural uranium level if disposed in to the repositories without reprocessing. Reprocessing of plutonium from the spent fuel decreases this value to 10,000 years. Along with plutonium and uranium the reprocessing of minor actinides would decrease this time period to only some few hundred years. The separation of minor actinides (trivalent actinides (An(III))) from the HLLW is a major issue in the back end of the nuclear fuel cycle. This is because of the presence of large amount of trivalent lanthanides (Ln(III)) fission products in HLLW, which constitute about a third of the total fission product inventory having chemistry quite similar to that of trivalent actinides. Due to high neutron absorption cross-section of Ln(III), the transmutation of An(III) is not possible. Thus Ln – An separation is the only option in order to have safe waste management.

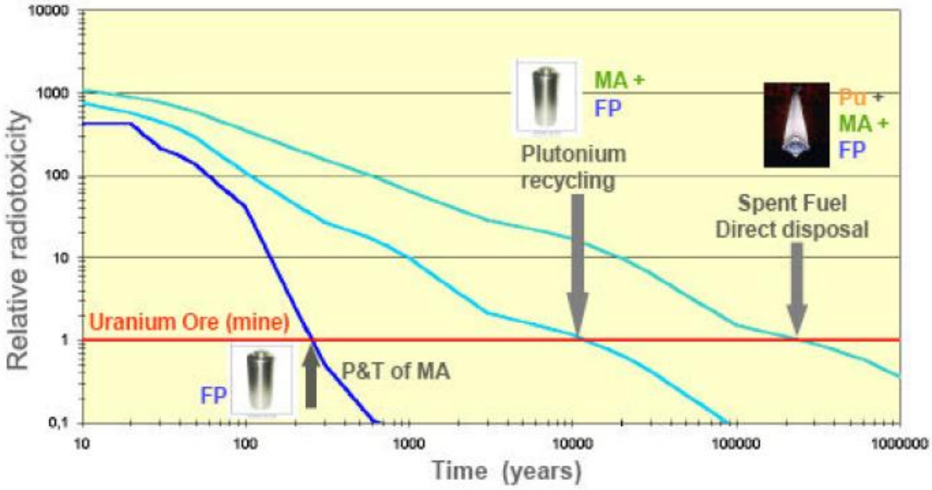


Figure 1.2. Radiotoxicity inventory of the spent fuel [14]

The separation of trivalent actinides and lanthanides from HLLW involves two steps. The first step is the co-extraction of An(III) and Ln(III) leading to eliminate 2/3 of the fission products. Several processes such as TRUEX, TRPO, DIDPA and DIAMEX process have been studied for the An(III)- Ln(III) co-extraction [15 - 17]. The extractants used in these processes are octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphinoxide (CMPO) and tri-n-butyl phosphate (TBP) for TRUEX, trialkylphosphinoxides for TRPO, diisodecylphosphric acid for DIDPA and *N*,*N*'-dimethyl-*N*,*N*'-dioctyl-2-hexylethoxy-malonamide (DMDOHEMA). After co-extraction of An(III) and Ln(III) from 3 - 4 M nitric acid (HLLW acidity), the metal ions are stripped back using dilute nitric acid (0.01 M) or using some complexing agents such as citric acid, lactic acid etc. The second step involves the mutual separation of Ln(III) from An(III) from the stripped solution adopting processes such as TALSPEAK, SETFICS, REVEARSE TALSPEAK etc. [15 -17].

1.2 Room Temperature ionic liquids

Volatile organic solvents (VOC) such as chloroform, dichloromethane, carbontetrachloride, acetone, chlrofluorocarbon(CFC) etc. are used as the reaction media for the synthesis of fine chemicals, pharmaceuticals, and petrochemicals. The major concern associated with the chemical industry is the generation of large volumes of hazardous wastes because of the demerits of VOCs such as high volatility, evolution of harmful gases and low theremal stability. These wastes are dumped into environment causing pollution of air and earth water posing danger to the human life and ecosystem. In this context, a new approach has received attention and is being called as Green Chemistry, Clean Chemistry etc. Green chemistry is an approach to the synthesis, manufacturing, and use of chemicals that reduce risks to ecology [18]. Furthermore, Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The term hazardous is used in a wide context including physical (e.g. flammability, explosion), toxicological (carcinogenic and mutagenic), and environmental (ozone depletion, climate change, and global warming) [19]. There is a demand all over the world to develop environmentally friendly chemical processes and products that require the development of novel and cost-effective approaches to prevent pollution [20]. The ideal solvent to be used in chemical industries should have a low volatility, should be chemically and physically stable, reusable and recyclable, and easy to handle. Clean technologies concern the reduction of waste from an industrial chemical process to a minimum, which requires the refinement and redesign of many current chemical processes [21].

The four possible alternate technologies are (guidelines of the Montreal protocol): 1) use of water as a solvent for synthesis 2) solvent free synthesis 3) use of supercritical fluids and 4) use of room temperature ionic liquids (RTILs) as solvents. During the last twenty years, water has emerged as a useful reaction medium. However its application is limited due to low solubility of organic reagents in water. Water is a protic solvent and has poisoning effects such as hydrolysis of the metal carbon bond. It can react with the metal by coordination, and hence cannot be used as a solvent for catalysts. Supercritical fluids (e.g. $ScCO_2$) are also described as new solvents for organic and catalytic reactions [22]. They are physically and chemically stable and can be classified as green solvents. However they need critical conditions (e.g. T_C, P_C) for their use, which is a serious limitation. Thus, the only option left is the use of room temperature ionic liquids as the solvent media.

The melting point of ionic liquid salts are directly proportional to the strong electrstatic interaction between the oppositely charged ions, which is related to the lattice energy of the salt as given below.

$$E = k \frac{Q_1 Q_2}{d} \tag{1.1}$$

Where Q_1 and Q_2 are the charges on cation and anion respectively, d is the distance between the ions and k is the madelung constant. With increase in the internuclear distance (d), the lattice energy (E) decreases. As a result, the melting point of the ionic salt decreases. For example, the melting point of NaCl is 803^0C which is due to the strong electrostatic interaction between Na^+ and Cl^- ions. This strong interaction between two ions are due to the symmetrical nature of both ions and equal size of both the ions. If Na^+ ion is replaced by a asymmetric, bulky organic cation such as imidazolium cation, the melting point of the resulting crystal decreases drastically nearly 10 – 12 times that of NaCl, due to the increase in the interionic distance between the oppositely charged ions. In other words, these bulky and unsymmetrical ions will have low lattice energies due to the steric hindrance offered by oppositely charged ions which prevents the close approach of oppositely charged ions and hence the compound exists in liquid state at room temperature.

Room temperature ionic liquids (or ionic liquids) are organic melts that exist as liquid at ambient temperature or they can be defined as the organic salts which exist as liquid below 100^0C [23 - 27]. They comprise bulky, assymmetric, organic cations and inorganic or organic anions [24]. Some examples of cation and anion combinations of ionic liquids are shown in Fig.1.3 [24]. The possible cations are alkyl ammonium, dialkylimidazolium, alkylpyridinium, alkylpyrazolium; alkylthiozolium, alkylsulphonium and alkylphosphonium ions and the anions are halides, nitrate, tetrafluoroborate, haloaluminates, hexafluorophosphate, alkylsulphonates, bis(trifluoromethanesulphonimide), trifluoromethanesulfonate etc. They have several fascinating properties such as near zero vapour pressure, high thermal and radiation stability, properties tunable depending on the nature of cations and anions, environmental friendly compared to VOCs, high selectivity etc. Out of these, most important properties is tunablity, i.e, by changing the cation anion combination, nearly 10^{18} of RTILs can be designed for specific applications [26, 27]. That is the reason RTILs are known as designer solvents.

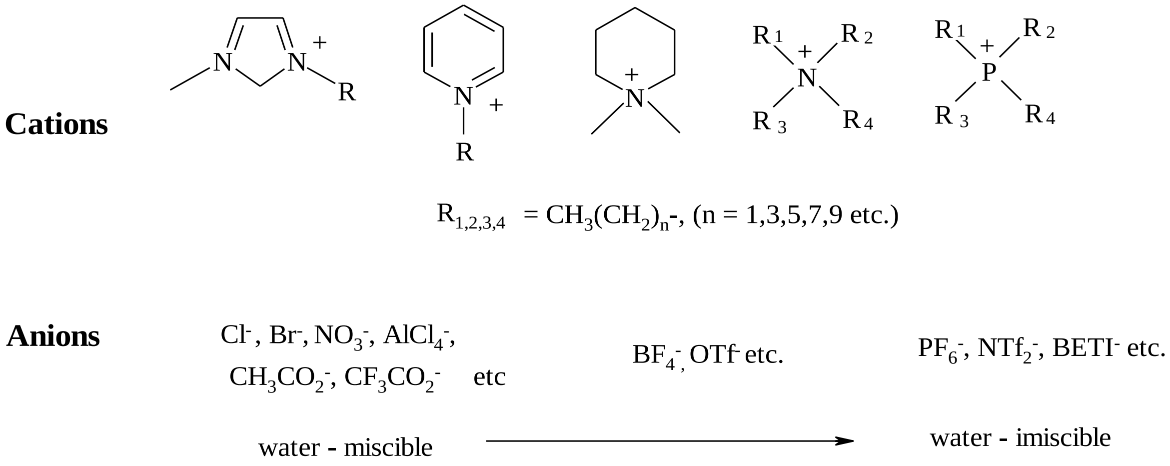


Figure 1.3. Some commonly used cations and anions for making RTILs

1.2.1 Early history of room temperature ionic liquids – in brief

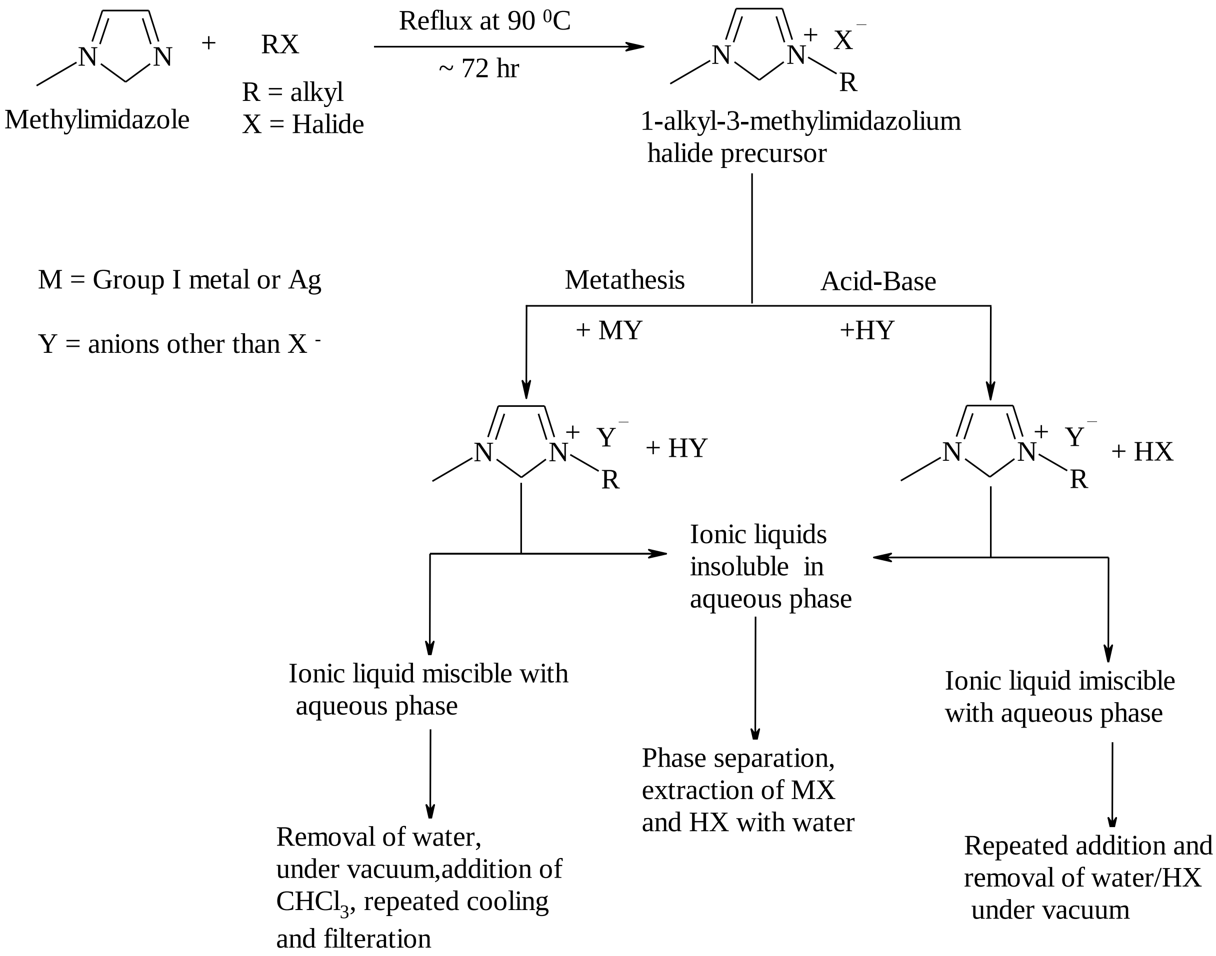
Room temperature ionic liquids are not new compounds and they are known since 1911. The first ionic liquids were prepared by P.C. Ray and J. N. Rakshit in 1911 [28]. They were nitrite salts of alkylammonium bases (for e.g., ethylammonium nitrite, which spontaneously decomposed upon standing). The first stable and useful ionic liquid, ethylammonium nitrate (m.p. 12.5^0C), was synthesized by Paul Walden in 1914 [29]. Later, these compounds failed to appear in literature for nearly three decades. Also there was little attention on these substances as they were not used widely [30]. Subsequently, the use of ionic liquids in various fields expanded that led to the synthesis of a variety of ionic liquids with desired physical and chemical properties. A complete history of ionic liquids is reported by Wilkes and Seddon in their review articles [27,24]. RTILs, based on their physicochemical properties can be classified in to three main generations. First generation ionic liquids which are mainly based on chloroaluminate anion ($AlCl_4^-$) in conjuction with di-alkylimidazolium and alkylpyridinium ions [31]. The first generation ionic liquids came in to existence after the invention of imidazolium choloroaluminate ionic liquids by Wilkes [31]. Again, these first generation ionic liquids are devided in to three types depending on anionic part; i) acidic chloroaluminate ionic liquids with > 50 mol% of $AlCl_3$, ii) basic chloaluminate with < 50 mol% of $AlCl_3$ and iii) neutral ionic liquids with equal mole ratio of both $AlCl_3$ and organic cation. These ionic liquids have some important properties such as tunable melting point, variable acidity range of the melt and tunable viscosity etc. Neverthless, due to their high hygroscopic nature, handling these types of ionic liquids required inert atmosphere which is major drawback of these generation ionic liquds. To avoid such demerits, Wilkes [32], disocovered a seris of new ionic liquids with tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) anions and imidazolium and pydinium ions as cations. These are known as second generation of ionic liquids. Ionic liquids with bis(trifluoromethanesulfonyl)imide (NTf_2^-), perfluoroalkylphosphate (FAP^-) anions are moisture stable and can easily handlled without inert atmosphere due to the hydrophobic nature of anions. These ionic liquids are regarded as the link between second and third generation ionicliquids.

The third generation ionic liquids are recent class of ionic liquids which mainly deal with task specific ionic liquids (TSILs) [33]. TSILs are the new subclass of ionic liquids wherein a functional moiety is tethered covalently either to the cationic or anionic moiety of the conventional ionic liquid. These TSILs have specific properties of selecting the species of interest from the mixture. Thus the ionic liquids that are thethered with functional moiety either in cation or anion part for a target specific application are known as task specific ionicliquids (TSILs) or funtionalized ionic liquids (FILs) [33 – 44]. Due to the presence of functional moiety TSILs act in variable role such as catalyst in organic synthesis, reaction media for gas absorption etc. [33-36], extractant in separation technology etc. [37-44]. A sub class of functionalised ionic liquids known as ionic liquids with strongly coordinating anion wherein the anion of the ionic liquid itself is a functional moiety [45-50]. The merits of these ionic liquids over grafted ionic liquids are i) easy method of synthesis ii) high metal loading ability iii) high miscibility in molecular diluents etc. However, the research in this class of ionic liquids are very preliminary and requires further study to establish their various applications in desired fields.

1.2.2 Synthesis of Ionic liquids

1.2.2.1 Conventional Ionic liquids

The general synthetic pathway of imidazolium based ionic liquids is reported elsewhere [51] and a similar procedure is given in scheme1.1. Huddulson *et al.* [52] also has reported the complete synthetic scheme of the preparation of imidazolium based ionic liquids. The ionic liquid, 1-alkyl-3-methylimidazolium halide is prepared by the refluxing distilled 1-methylimidazole with haloalkane (in most of the case chloroalkane) at 90^0C for ~ 72 hours

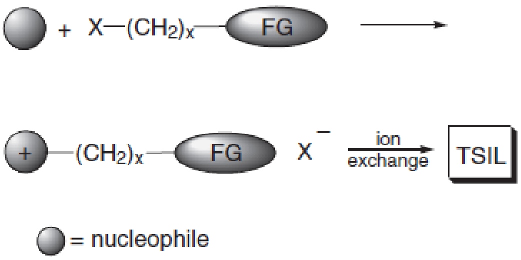


Scheme 1.1. Common routes for the preparation of ionic liquids [51]

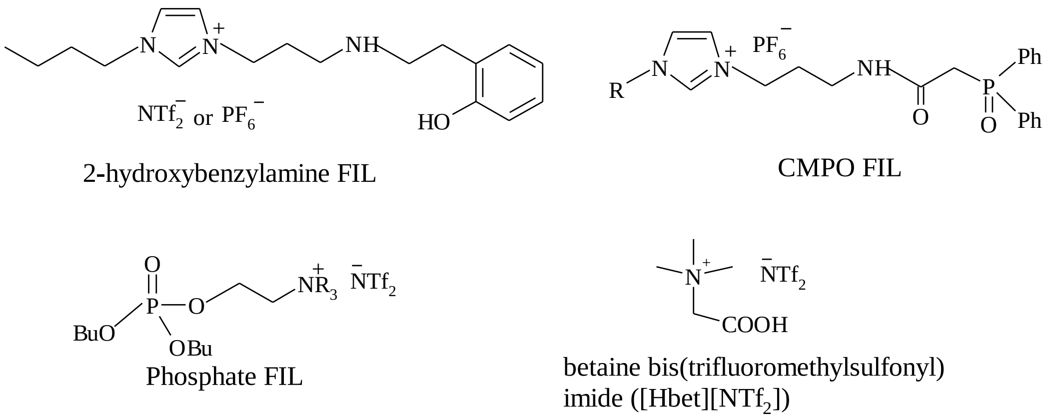
Only exception is chloroethane which is gaseous at room temperature and in this case, the alkylation is usually carried out in an autoclave, at autogenous pressures. The preparation of the 1-alkylpyridinium or 1-alkyl-2,3-dimethylimidazolium derivatives follows the same strategy, starting from pyridine or 1,2-dimethylimidazole and haloalkane respectively. The intermediate halo (or chloro) based ionic liquid is then converted to the more hydrophobic ionic liquid by exchanging the anion of a Group 1 metal or silver(I) salt, MY by metathesis reaction or by acid –base reaction with an acid HY. These reactions are stoichiometric and hence equimolar amount of waste MX or HX are produced. These steps are generally carried out in water medium and in some cases also organic solvents such as acetone [53]. Depending on the anion (and to a lesser extent, the cation) chosen, the resulting ionic liquid forms either a biphasic system with water, or a homogeneous solution. In the former case (e.g., in case of ILs with PF_6^- or NTf_2^- as anion), the final ionic liquid is washed thoroughly several times with double distilled water in order to avoid chloride impurity. In contrast to this, in case of water-miscible ionic liquids, the water is removed under reduced pressure followed by the addition of chloroform and repeated cooling to 330 K to precipitate MX followed by several filtration steps. The work-up of the water-miscible ionic liquids prepared by treatment with acid, includes repetitive addition of water and removal of water/HX under reduced pressure and elevated temperature. In both cases, the removal of chloride is incomplete. Halide-free ionic liquids can be obtained in the metathesis reaction, if a silver(I) salt is used instead of a Group 1 metal salt and residual silver ions can be removed quantitatively by electrolysis. However, this method is expensive and involves yet another clean-up stage and silver salts are produced as by-products. The synthesis of hydrophobic ionic liquids are therefore most often carried out by the metathesis reaction that deal with group I metal (Li, K etc.) salt with organophilic part as anion.

1.2.2.2 Task specific ionic liquids

The synthesis of TSILs (FILs) follows the analogous procedures as it is required for a convetional ionic liquid provided that the organic halide which is targeted to react with nucleophile such as imidazole moiety, must have a functional group of interest. Scheme 1.2 displays the general schematic of the synthesis of a TSIL reported by Davis [33]. The reaction condition for a synthesis of a TSIL depends on the type of functional group under investigation. Once the initial product is formed, the ion exchange is typically performed in order to bring the grafted cation in conjuction with the new anion of interest to make the final TSIL. Nucleophiles , normally used are methyl imidazolium, pyridinium, ammonium ions etc. Figure 1.4 shows some examples of task specific ionic liquids.



Scheme 1.2. Synthetic scheme of task specific (or functionalised ionic liquids) [33]



2-hydroxybenzylamine FIL

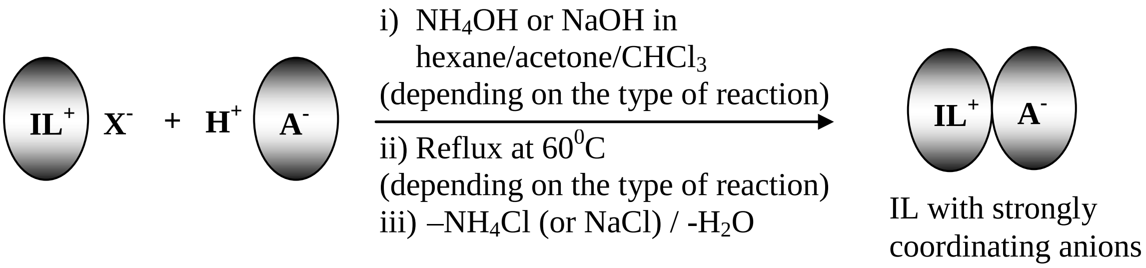
CMPO FIL

Phosphate FIL

betaine bis(trifluoromethylsulfonyl) imide ([Hbet][NTf_2])

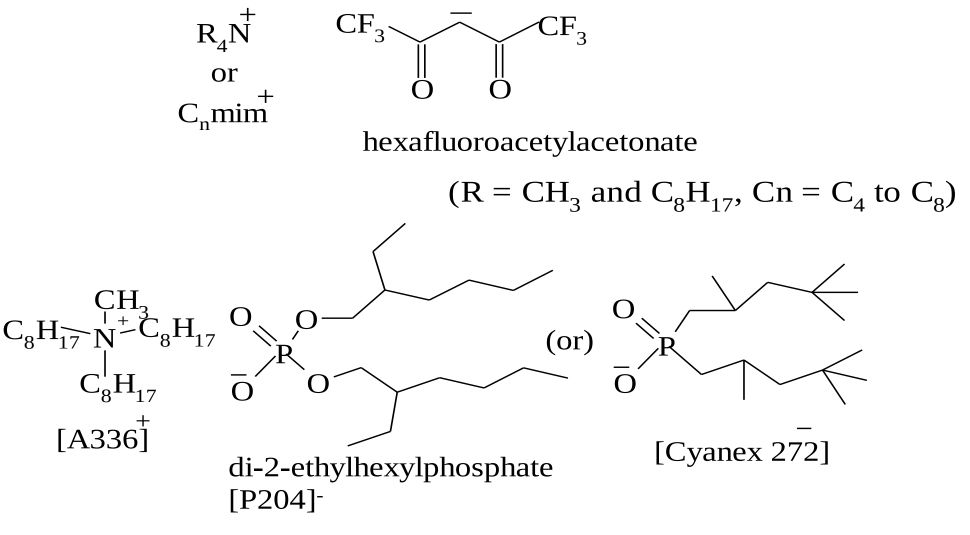
Figure 1.4. Examples of some task specific (or functionalized) ionic liquids

The synthetic procedure of ionic liquids with strongly coordinating anions is quite simple and less time consuming. The reaction involves the addition of the solution of IL cation precursor in acetone/methanol to the solution of IL anion precursor in acetone/methaol medium. Scheme 1.3 shown below gives the general synthetic procedure of these types of ionic liquids. Figure 1.5 shows some examples of ionic liquid cations and anions of these type of ionic liquids.



IL^+ = Imidazole or ammonium based, A^- = Anions of the acidic extractants

Scheme 1.3. Synthetic scheme of ionic liquids with strongly coordinating anions [46, 47]



hexafluoroacetylacetonate

(R = CH_3 and C_8H_{17}, Cn = C_4 to C_8)

[A336]$^+$

di-2-ethylhexylphosphate [P204]$^-$

[Cyanex 272]$^-$

Figure 1.5. Examples of some ILs with coordinating anions [46,47]

1.2.3 Fascinating properties of ionic liquids

Ionic Liquids have several fascinating properties out of which some of them relevant to the present thesis are i) negligible or near zero vapor pressure, ii) High radiation and thermal stability, iii) tunable properties i.e, the properties of a particular ionic liquids can be changed by changing cation – anion combination, iv) Polar and coordinating nature, v) Enviromentally benign. Below, are the brief description of some of the properties of RTILs.

1.2.3.1 Viscosity of room temperature ionic liquids

In general, the viscosities of RTILs are higher than that of aqueous solutions and traditional solvents [52]. It is obvious that the viscosity increases with increasing alkyl chain length, due to the increased possibility of Vander Waals interactions between the cations[54]. Along with the cations, RTIL anions also influence the viscosity. It depends upon the symmetry and tendency of the anion to form hydrogen bond. Table 1.2 [52] shows the variation of viscosity of some RTILs with cations and anions. RTIL impurities have a significant effect on viscosity as well as other properties. A report given by Seddon *et al.*[55] shows the variation of viscosity in presence of of water, sodium chloride, and organic solvents on IL physical properties. For example, C_4mimBF_4 with 0.01 molal Cl^- ion has a viscosity of 154 (mPa s^{-1}) and an increase to 0.5 molal Cl^- ion increases the viscosity to 201 (mPa s^{-1}). However, the viscosity of ammonium based ionic liquids are much higher than that of imidazolium based ionic liquids [56]. Table 1.1 shows the viscosity of some RTILs with respect to their cation-anion combination.

Table 1.1. Viscosity of some ionic liquids [52]

ILs with different anions	Viscosity (mPa.s)[25^0C]
C_4mimI	1110
C_4mimPF_6	450
$C_4mimNTf_2$	52
ILs with different cations	**Viscosity (mPa.s) [25^0C]**
C_4mimPF_6	450
C_6mimPF_6	585
C_8mimPF_6	682

1.2.3.2 Density

The density of the ionic liquids plays a vital role in the application of RTILs especially in separation processes. The simple halide based ionic liquids have significantly lower densities (density of C_8mimCl is similar to water, C_6mimCl is similar to dioxane [57] and the density increases with increase in the hydrophobicity of the anions such as PF_6^- or NTf_2^- ion. However, with increase in the alkyl chain length of the cation moiety, the density decreases gradually since the addition of CH_2- groups affects the effective packing. On the other hand, the density of quarternayry ammonium based ionic liquids with long alkyl chain (e.g., aliquat336) is lower than that of water [56]. Table 1.2. shows the density of some RTILs with respect to their cation-anion combination.

Table 1.2. Density of some ionic liquids with respect to the cation-anion variation [52,56]

ILs with different anions	*Density (g/cc)*
C_4mimCl	1.08
C_4mimBF_4	1.12
C_4mimPF_6	1.37
C_4mimNTf_2	1.43
ILs with different cations	***Density (g/cc)***
C_4mimCl	1.08
C_6mimCl	1.03
C_8mimCl	1.00
Aliquat336	0.88

1.2.3.3 Vapour pressure of ionic liquids

Due to the ionic nature, ionic liquids possess negligibly small vapor pressure, even at high temperatures. Therefore the volatile products, and even products with low vapor pressures, can be isolated from ionic liquids by distillation. However, some ionic liquids can be distilled at low pressure without decomposition [58] and even can be separated thermally [59]. Seddon and co-workers have demonstrated that some ionic liquids can be distilled at 473-573 K under reduced pressure. Rebelo *et al*. [60] have performed distillation of 1-decyl- 3-methylimidazolium and 1 dodecyl-3-methylimidazolium bis triflamide ionic liquids under reduced pressure, and predicted normal boiling points based on the data obtained from surface tension and density measurements. The predicted values of boiling temperatures were in the order of $[BF_4]^-$ > $[PF_6]^-$ > $[(CF_3SO_2)_2N]^-$ for a given cation (e.g. 1-alkyl-3-methylimidazolium cation). The vapour pressure of a series of 1-alkyl-3-methylimidazolium triflimide based ionic liquid (alkyl = ethyl, butyl, hexyl and octyl) is reported by Zaitsau *et al.*[61].

1.2.3.4 Radiation and thermal stability of ionic liquids

Ionic liquids, generally have high radiation and thermal stability. Allen *et al.* [62] investigated the radiation stability of 1, 3 - dialkylimidazolium nitrate/chloride ionic liquids under α-,β- and γ- radiation fields. The results indicate that their stabilities were comparable with that of benzene, and more than the mixture of tributylphosphate and odourless kerosene under similar irradiation conditions. These ionic liquids were stable up to 400 kGy. The enhanced stability was attributed to the combination of properties of ionic salt and aromaticity. Berthon *et al.* [63] studied the gamma radiolysis of C_4mimPF_6 and $C_4mimNTf_2$. It was reported that the properties such as density, surface tension and refractive index were unchanged upon irradiation up to 600 kGy. The overall concentrations of radiolysis products did not exceed 1 mol% when irradiated up to 1200 kGy. The radiochemical stability of C_4mimX (X= NTf_2^-, OTf^-, PF_6^- and BF_4^-) was investigated up to an absorbed dose of 2 MGy by Rouzo *et al* [64]. The degradation of ionic liquid increased in the order $NTf_2^- < OTf^- < PF_6^- < BF_4^-$. Berthon *et al* [65] investigated the radiolysis of ionic liquid containing quarternary ammonium cation. $MeBu_3NTf_2$ was reported to be stable at high radiation doses. The primary radiolytic products of the anion ($F^\bullet$ and $CF_3^\bullet$) combine with the radiolytic products of cation ($Bu^\bullet$, $Me^\bullet$ and $H^\bullet$) to form degradation products in small concentrations.

In general, most ILs have a high thermal stability because of their near zero vapour pressure. The thermal stability of different ionic liquids is nearly independent of cations but it decreases with increase in the anion hydrophilicty [66]. Halide anions dramatically reduce the thermal stability with the onset of decomposition occurring atleast 100 °C below the corresponding ILs with non-halide anions [67]. Relative anion stabilities have been suggested as $PF_6^- > NTf_2^- \sim BF_4^- >$ halides. Bonhote *et al.*[68] found that $C_2mimNTf_2$ was stable up to 400 °C and decomposed rapidly between 440 and 480^0C whereas C_2mimTA (TA = trifluoroacetate) was only stable to 150 °C and then decomposed rather slowly to 250 °C.

1.2.3.5 Polarity of ionic liquids

Polarity is related to the physical properties such as melting and boiling points, solubility, and intermolecular interactions [69]. Ionic liquids have been considered as polar solvents, such as those suitable for charged compounds, possibly because of their ionic nature. The first polarity investigation of ionic liquids using the solvatochromic dye method postulated that imidazolium-based ILs possess a polarity similar to lower alcohols [70]. Various methods were subsequently developed to determine the polarity of ILs [71-76]. Bonhote *et al.*[68] reported that the polarity of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulphonyl) imide similar to that of ethanol, and the apparent low dielectric constant was attributed to ion-pairing in the pure state. Seddon and co-workers reported the polarity of 1, 3-dialkylimidazolium based ionic liquids using absorption spectrum of solvatochromic dye Nile Red, and observed that the spectral features of tested ionic liquids were similar to that of short chain alcohols [76]. Dzyuba *et al.* [77] studied the polarity of ionic liquids, by incorporating functional groups such as hydroxy and alkoxy groups at C_1 position of 1,3-dialkylimidazolium cation, and observed an increase in the polarity.

1.2.3.6 Coordinating ability

The coordinating ability is a tendency to donate electrons to form a chemical bond [78]. A decade ago, ILs were generally perceived as non-coordinating, which implied that their anions were noncoordinating as well [79-83]. However, the recent reports confirm that ionic liquids are indeed coordinating in nature [84 - 86]. In traditional imidazolium IL systems, the coordinating abilities are determined by the anionic part rather than the cations [87]. The chloride or bromide displays strong coordinating abilities, and this has been proven by several characterization techniques like crystallographic as well as NMR and IR studies [88, 89]. The ionic liquid bearing the anions such as NTf_2^- and $[SO_3CF_3]^-$ are assumed to be non-coordinating because the negative charge is highly delocalized over electronegative fluorine atoms. However, recent studies suggest that NTf_2^- is a versatile coordinating anion that can interact with transition metals in various modes. For example, N-methyl-N-propylpyrrolidinium bis (triflouromethanesufonyl) imide [84] reacts with YbI_2, forming a complex in which the NTf_2^- anions coordinate with the Yb center in a chelating mode using the two oxygen atoms as donors. Ionic liquids can be designed to coordinate deliberately by incorporating coordination groups (task specific ionic liquids).

1.2.3.8 Environementally benign (Green Solvent)

As described in the *section 1.2.* ionic liquids are the potential solvents for clean and green approach to solve the problems encountered due to the green house effect and global warming issues. Ionic liquids are the most viable candidates for a new, clean and green technology; where waste streams are minimal and atom-efficiency is increased and as a result, environmental and cost benefits could be achieved. This is possible because of ionic liquids' "immeasurably" low vapor pressure under normal conditions. Some issues have recently been raised against the greenness of the ionic liquids [90, 91]. However, due to infinite designing possibilities, ILs can be made non-toxic, readily degradable, and even edible by a proper cation-anion combination [92, 93]. Recently, an article on greenness of ionic liquids is reported by Welton [94].

1.2.4 Applications of ionic liquids

The discovery of moisture stable room temperature ionic liquids [32] in late 1990's opened new avenues for studying their applications in various branches of science. Moisture stable ionic liquids, initially introduced for the replacement of VOCs in organic synthesis, emerged as a potential substitutes to molecular diluents in separation processes. Ionic liquids are finding several applications due to their various fascinating properties in vast area of science and technology. The application of ionic liquids in chemical industry is reported in detail by Plachkova and Seddon [24]. In electrochemical research, ionic liquids (as electrolytes) offer their potentiality by solving many issues dealing with electrodeposition of metal ions, metal plating, fuel cells, solar panels etc. [95-97] due to their high electrical conductivity and large electrochemical window. Ionic liquids are used as matrices in mass spectrometry, stationary phase for HPLC and gas chromatography columns. Also, these compounds were extensively used in catalytic processes for organic and organometallic reactions [98,99]. RTILs find special applications as solar heat transfer fluids in electric power plants using parabolic trough solar collector technology which is known as solar electric generating system (SEGS) [100]. Ionic liquids are used an alternative to VOCs in separation processes such as solvent extraction processes for the separation of organic solutes from aqueous medium [101], separation of metal ions [102-106], oil shale treatment [107]. A review on the applications of ionic liquids in chemical analysis, i.e., in extraction chromatography, electrochemistry, spectroscopy etc. is reported by Koel *et al.* [108]. Ionic liquids are also being used with high nitrogen content explosives for civil and military purposes in order to improve the safty in the handelling these materials [109].

Along with the spatial scopes of conventional ionic liquids, the task specific ionic liquids (or functional ionic liquids) have also focused their applications in different fields of research on ionic liquids. An excellent review on the application of task specific ionic liquids by Ralf Giernoth [36] wherein the applications of task specific ionic liquids as catalyst, medium in organic reaction, medium for gas absorption, etc have been detailed. Another recent review on the application of task-specific ILs deals with the use of TSILs as Active Pharmaceutical Ingredients (API) in pharmaceutical industries. are currently also finding their way into pharmaceutical products [110]. The fundamental idea is to incorporate a known active pharmaceutical component into the anion or the cation of the IL, or even into both. Apart from these, TSILs are used as novel extractant for the liquid - liquid extraction [37-44]. Rogers and Davis reported, the use of urea and thiourea functionalized TSIL to remove Hg^{2+} and Cd^{2+} from a contacted aqueous phase [37,38]. The results indicated that partition ratios of up to 300 were achievable with these TSIL, versus < 20 when the conventional IL 1-butyl-3-methylimidazolium hexafluorophosphate was used. Later work by Rogers demonstrated that TSIL oligoethers with linked imidazolium headgroups effected the selective, pH dependent removal of Hg^{2+} from water in the presence of Cd^{2+}. The application of various TSILs in different areas is reported by Davis *et al*. in his review on task specific ionic liquids [33]. Similarly, the TSILs where anion itself is a functional moiety (ionic liquids with coordinating anions) have several applications [45-50].

1.2.4.1 Application of ionic liquids in nuclear industries

Room temeparture ionic liquids are used in nuclear industries both as solvent for extraction studies and as electrolyte for the non-aqueous reprocessing. Excellent reviews on the application of room temperature ionic liquids in the area of nuclear fuel reprocessing and waste management [111-117] are availbale in the literature. Consequently, there has been a significant increase in the studies related to the use of RTILs in aqueous and non-aqueous reprocessing applications. As this thesis is aimed at the aqueous reprocessing application of RTILs, details of literature report is given below.

Essentially, RTILs are investigated as possible substitute to the molecular diluent in solvent extraction procedures and as an alternative to high temperature molten salt in non-aqueous reprocessing applications [111-117]. However, some RTILs have also been employed as liquid ion exchangers in various solvent extraction procedures with conventional diluents [118]. Some of the striking features of RTILs that make them promising for nuclear fuel cycle application are i) the selectivity of target metal ion can be easily manipulated by the change of cation-anion combinations of RTIL diluent, rather than redesigning the structure of extractant, ii) Presence of ionic diluent in organic phase facilitates a new mode of recovery of metals by direct electrodeposition from the extracted phase, iii) Ionic liquids can be functionalized with organic moieties for selective separation of actinides from fission products, iv) RTILs can be designed to be completely incinerable, which would simplify the management of spent organic waste, v) Due to negligible vapour pressure of RTILs, the fire hazard is almost insignificant.

a) As diluent

RTILs are used as a suitable alternate to the trditional diluents such as aromatic and paraffinic diluents in the nuclear industries since more than a decade. In this context, the separation of long lived fisson products (Cs^+ and Sr^{2+}) and other group I and II metal ions from aqueous phase using ionic liquid diluents has been reported by several research groups [119-127]. For example, Dai *et al.*[119] and susequently Visser *et al.*[120] attempted to separate group I and II metal ions from aqueous medium using a solution of crown ether in imidazolium based ionic liquid. The distribution ratios of strontium [119] observed in a solution of DCH18C6/ionic liquid were nearly three to four orders of magnitude higher than those observed in toluene and chloroform. It was shown that the distribution ratio could be manipulated by varying the substituents in the imidazolium moiety and counter anions. Dietz *et al.*[121,122] studied the extraction of Sr^{2+} from nitric acid medium in a solution of DCH18C6/$C_n$mimNTf_2 (n = 2,4,5,6,8) and highlighted the mechanistic aspects of the extraction of Sr^{2+} in DCH18C6/$C_n$mimNTf_2 (n = 5 and 10). The results were compared with those obtained in n-octanol diluent. Same group also explored the synergism of extractants in ionic liquid medium for the extraction of Sr^{2+}.

A systematic study of the extraction of actinides (mostly U(VI), Pu(IV) and Am(III)) and lanthanides in ionic liquid medium has been reported elsewhere [128-142]. Giridhar *et al.*[128] studied the extraction of U(VI) from nitric acid medium by a solution of TBP in C_4mimPF_6 or C_4mimNTf_2. The distribution ratios are compared with those obtained using 1.1 M TBP/*n*-DD. It is observed that the distribution ratio of U(VI) in 1.1M TBP/C_4mimPF_6 gradually increases from 0.05 to 33.2 with increase in the concentration of nitric acid from 0.01 M to 8 M. At nitric acid concentrations lower than 4 M, the distribution ratios obtained in 1.1 M TBP/C_4mimPF_6 are comparable with the distribution ratios observed in 1.1 M TBP/*n*-DD. The mechanistic aspects of U(VI) extraction in TBP dissolved in ionic liquid ($C_n$mimNTf_2) was investigated in detail by Dietz [130] and later on by Billard *et al.*[131] wherein the occurrence of ion exchange mechanism during metal ion transfer in to the ionic liquid phase is highlighted. Ikeda *et al.*[133] studied the extraction of uranyl ion in the solution of TBP and quaternary ammonium based ionic liquid diluent. The extraction of Pu(IV) from nitric acid medium by a solution of CMPO in C_8mimPF_6 was reported by Lohithakshan *et al.*[134]. They also studied [135] the extraction of Pu(IV) in DC18C6/C_4mimPF_6 (or C_6mimPF_6) and reported the cation exchange mechanism involving $Pu(CE)(NO_3)_2^{2+}$ species. Visser *et al.*[136] reported a preliminary investigation on extraction of f-block elements using a solution of 0.1 M CMPO -1.0 M TBP in C_4mimPF_6. The distribution ratios of Am(III), Pu(IV), Th(IV) and U(VI) were found to be an order higher in ionic liquid system than those obtained in *n*-DD under similar conditions. Nakashima *et al.* [137,138] studied, in detail, the extraction of trivalent lanthanides in CMPO/C_4mimPF_6 and highlighted the diluent property of C_4mimPF_6 over *n*-DD. The extraction of rare earth metals, Y^{3+} and Eu^{3+}, from Zn^{2+} containing aqueous solution was studied in HDODGA/$C_nmimNTf_2$ (n = 4, 8,12) [139]. The extraction behavior of UO_2^{2+}, Am^{3+}, Nd^{3+}, Eu^{3+} in a solution of dialkylphosphoric or dialkylphosphinic acid (HA) present in $C_{10}mimNTf_2$ was reported by Cocalia *et al.* [140] proposing the analogous extraction behavior of metal ions both in ionic liquid as well as *n*-DD. The liquid–liquid extraction of lanthanides (Ln^{3+}) from aqueous medium by a solution of TODGA/$C_nmimNTf_2$ (n =2,4,6) was investigated by Shimojo *et al.*[141]. Jensen *et al.*[142] studied the extraction of Eu(III) in HTTA/$C_4mimNTf_2$ and proposed the existence of anion exchange mechanism during the extraction.

b) As extractant (task specific ionic liquids)

Nockemann *et al.* [43] prepared several TSILs made up of imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium bis(trifluoromethyl-sulfonyl) imide salts, functionalized with a carboxyl group for the dissolution of several rare earth and transition metal metal oxides and hydroxides. The synthesis of 2-hydroxybenzylamine (LH_2) FIL and the extraction of ^{241}Am(III) from aqueous medium was reported by Ouadi *et al.*[40]. The distribution ratio of ^{241}Am(III) increased with increase of pH, reaching a maximum distribution value at ~ pH 8 to pH 10. Ouadi *et al.*[41] also synthesized a few TSILs containing phosphoryl moiety attached to the quarternary ammonium ion. The extraction of U(VI) from 3 M nitric acid medium was reported using these TSILs. The preliminary extraction data indicate the potential use of these FILs for applications related to uranium separation. Luo *et al.*[42] reported the synthesis of imidazolium based ionic liquids functionalized with monoaza-crown ether and studied the efficacy of these ionic liquids for the extraction of Cs^+ and Sr^{2+} from aqueous solutions. A general approach for the synthesis of diphenylcarbamoylmethylphosphine oxide moiety functionalized on imidazolium ion was reported by Odinets *et al.* [39]. Using this TSIL, they have studied the extraction of actinides. Recently, Oliver *et al.* [44] reported a new β-diketonate functionalized ionic liquid and studied the extraction of lanthanides using silica support (solid – liquid extraction). Recently, the application of these type of ionic liquids for the extraction of lanthanides have been appeared in the literature [46, 47].

1.3 Aim of the present work

The present study aims at exploring the feasibility of using room temperature ionic liquids as diluents and extractants, for the separation of actinides and fission products from nitric acid medium. The present study includes the synthesis of several ionic liquids ranging from imidazolium to quaternary ammonium salts, amide and phosphonate functionalized ionic liquids and ionic liquids containing 1,3-diketonate, alkylphophates and diglycolamate anions and employ them for the extraction studies. This thesis reports the use of ionic liquids as diluent in conjunction with the molecular extractants for the extraction of actinides, third phase formation behavior of Eu(III), and Ln-An separation. In the extractant prospect, it details i) the use of ionic liquids such as, amide and phosphonate functionalized ionic liquids for the target specific separation Pu(IV) from other actinides and fission products, ii) the unusual miscibility of the ionic liquids with strongly coordinating anions such as 1,3-diketonate, phosphate and diglycolamate ions in molecular diluents and the extraction studies using these ionic liquids.

1.4 References

[1]. Worlde Nuclear Association. Another drop in nuclear generation. *World Nuclear News, 05 May 2010.*

[2]. *http://www.euronuclear.org/info/encyclopedia/n/nuclear-power-plant-world-wide.htm*

[3]. R. B. Grover, S. Chandra, A strategy ofor growth of electrical energy in India, Document No. 10, Department of Atomic Energy, Mumbai, India, August 2004.Anil Kakodkar, Evolving Indian nuclear power progreamme-Rationale and perspective, public lecture at Indian academy of science, Bangalore, July 4, 2008.

[4]. H. J. Bhabha, The role of atomic power in India and its immediate possibilities, In: Proc. of the International Conf. on the Peaceful uses of Atomic Energy, 1, Geneva, 1955, p-103.

[5]. Nuclear Power Corporation of India Limited, Home page, http://www.npcil.nic.in.

[6]. IGC news letter, volume 86,2010, page 3, IGCAR, Kalpakkam, India.

[7]. http://www.dae.gov.in/gc/ahwr-leu-broc.pdf, BARC, DAE, India.
http://www.barc.ernet.in/publications/eb/golden/reactor/toc/chapter1/1.pdf

[8]. R. Chidambaram, C. Ganguly, Plutonium and thorium in the Indian nuclear programme, Curr.Sci. 70(1) (1996)21.

[9]. J. Foos, An industrial reality in France, In Nuclear Fuel Cycle Technologies: Closing the fuel cycle, 14th Annual conference of Indian nuclear society and 1st BRNS conference on nuclear fuel cycle held at IGCAR, Kalpakkam, 2003, IT-4/1.

[10]. R. Chidambaram, R.K. Sinha, Importance of closing the nuclear fuel cycle, Nuclear energy (2006) 90.

[11]. A. A. Kakodkar, Nuclear power in India: An inevitable option for sustainable development of a sixth humanity, World Nuclear Association Annual Symposium, London, 2002.

[12]. J. L. Swanson, “PUREX Process Flowsheets”, In: Science and Technology of Tributyl phosphate, Eds. W.W. Schulz, L.L. Burger, J.D. Navratil, K.P. Bender, CRC Press Inc. Boca Raton, p 55, 1984.

[13]. A. V. Bychkov, O. V. Skiba, “Review of non-aqueous nuclear fuel reprocessing and separation methods”, In: Chemical separation technologies and related

methods of nuclear waste management, Eds. G. R. Choppin, M. Kh. Khankhasayev., Kluwer academic publishers, Netherlands. 1999, pp. 71-98.

[14]. http://www.jaif.or.jp/ja/wnu_si_intro/...2009/m_salvatores_advanced_nfc.pdf

[15]. J. N. Mathur, M. Murli, K. L. Nash, Actinide Partitioning – A Review. Slvent Extr. Ion Exch. 19 (3) (2001) 357-390.

[16]. P. Paiva, P. Malik, Recent Advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes. J. Radioanal. Nucl. Chem. 261 (2) (2001) 485-496.

[17]. B. A. Moyer, Ion Exchange and Solvent Extraction. A series of Advances, Volume 19. CRC Press, Taylor and Francis Group 2010.

[18]. P. T. Anastas, Green Chemistry and the Role of Analytical Methodology Development. Critical Reviews in Analytical Chemistry 29 (3) (1999) 167-175.

[19]. P. T. Anastas, M. M. Kirchoff, Origins, Current Status, and Future Challenges of Green Chemistry. Acc. Chem. Res. 35 (9) (2002) 686-694.

[20]. I.T. Horvárth, Guest Editorial; Green Chemistry. Acc.Chem.Res. 35 (9) (2002) 685.

[21]. J.D. Holbrey, K.R. Seddon, Ionic Liquids. Clean Products and Processes 1 (4) (1999) 223-236.

[22]. P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous Catalysis in Supercritical Fluids. Chem. Rev. 99 (2) (1999) 475 –494.

[23]. T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (8) (1999) 2071- 2084.

[24]. P. V. Natalia, K. R. Seddon, Applications of ionic liquids in the chemical industry. Chem. Soc. Rev. 37 (1) (2008) 123-150.

[25]. M. Freemantle, “An introduction to Ionic liquids”, RSC Publishing, 2010.

[26]. K. R. Seddon, “Ionic liquids: A taste of the future”, Nat. Mater. (2003) 363-365.

[27]. J. S. Wilkes, A short history of ionic liquids—from molten salts to neoteric solvents. Green Chem. 4 (2) (2002)73-80.

[28]. P. C. Ray, J. N. Rakshit, Nitrites of the Alkylammonium Bases: Ethylammonium Nitrite, Dimethylammonium Nitrite, and Trimethylammonium Nitrite. J. Chem. Soc. Trans. 99 (1911) 1470-1475.

[29]. P. Walden, Bull. Acad.Imper.Sci. (St. Petersberg), (1914)1800.

[30]. S. Sugden, H. Wilkins, The Parachor and Chemical Constitution. Part XII. Fused metals and Salts. J. Chem. Soc. (1929) 1291-1298.

[31]. J. S. Wilkes, J. A. Levisky, R. A. Wilkes, C. L. Hussey, Dialkylimidazolium chloroaluminate melts: a new class of room temperature ionic liquids for electrochemistry, spectroscopy andsynthesis. Inorganic Chemsitry 21 (3) (1982)1263-1264.

[32]. J. S. Wilkes, M. J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. J. Chem. Soc., Chem. Commun. (1992) 965 - 967.

[33]. J. H. Davis Jr, Task-Specific Ionic Liquids. Chemistry Letters 33 (9) (2004) 1072-1077.

[34]. C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Ionic Phosphine Ligands with Cobaltocenium Backbone: Novel Ligands for the Highly Selective, Biphasic, Rhodium-Catalyzed Hydroformylation of 1-Octene in Ionic Liquids. Organometallics 19 (19) (2000) 3818 - 3823.

[35]. P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K. Kottsieper, O. Selzer, Chem. Commun. (2001) 451 - 452.

[36]. R. Giernoth, Task-Specific Ionic Liquids. Angew. Chem. Int. Ed. 49 (16) (2010) 2834–2839.

[37]. A. E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. A. Sheff, Wierzbicki, J.H. Davis Jr, R. D. Rogers, Task specific ionic liquids incorporating novel cations for the coordination and extraction of Hg^{2+} and Cd^{2+} : Synthesis, characterization and extraction studies. Envir. Sci. Technol. 36 (11) (2002) 2523-2529.

[38]. A. E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. A. Sheff, Wierzbicki, J.H. Davis Jr, R. D. Rogers, Task specific ionic liquids for the extraction of metal ions from aqueous solutions. Chem. Commun. (2001)135-136.

[39]. I. L. Odinets, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. Nelyubina, V. Myasoedova, V. Galina, N. P. Molochnikova, E. A. Zakharchenro, Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery. Dalton Trans. 39 (17) (2010) 4170-4178.

[40]. A. Ouadi, B. Gadenne, P. Hesemann, J. E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, Task-Specific Ionic Liquids Bearing 2-Hydroxybenzylamine Units: Synthesis and Americium-Extraction Studies. Chem. Eur. J. 12 (11) (2006) 3074 – 3081.

[41]. A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, Solvent extraction of U(VI) by task specific ionic liquids bearing phosphoryl groups. Green Chem. 9 (11) (2007) 1160–1162.

[42]. H. Luo, S. Dai, P. V. Bonnesen, A.C. Buchanan, Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an aza-crown ether fragment. J alloys and Compds. 418 (1-2) (2006) 195–199.

[43]. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K.V. Hecke, L. Van Meervelt, B. Kirchner, K. Binemanns, Task specific ionic liquid for solubilizing metal oxides. J. Phys.Chem.B, 110 (42) (2006) 20978-20992.

[44]. J. H. Olivier, F. Camerel, R. Ziessel, Lanthanide Ion Extraction by Trifluoromethyl-1,3-diketonate-Functionalised Ionic Liquids Adsorbed on Silica. Chem. Eur. J. 17 (33) (2011) 9113 - 9122.

[45]. R. A. Katritsky, S. Singh, K. Kirichenko, M. Smiglak, D. J. Holbrey, M. W. Reichert, K. S. Spear, R. D. Rogers In search of ionic liquids incorporating azolate anions. Chem Eur J. 12 (17) (2006) 4630 - 4641.

[46]. H. Mehdi, K. Binnemans, V. Hecke, L.V. Meervelt, P. Nockemann, Hydrophobic ionic liquids with strongly corodinating anions. Chem. Commun. (2010) 234-236.

[47]. X. Sun, Y. Ji, F. Hu, Bo. He, Ji. Chen, D. Li, The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. Talanta 81 (4-5) (2010) 1877–1883.

[48]. Y. Hua-Ling, W. Wei, C. Hong-Min, C. Ji, Extraction Mechanism of Rare Earths with Bifuncional Ionic Liquids (Bif-ILs) [A336][CA-12]/[A336][CA-100] in Nitrate Medium. Chin J Anal Chem. 39 (10) (2011) 1561–1566.

[49]. X. Sun, Y. Ji, L. Zhang, J. Chen, D. Li, Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE). J. Hazard. Matter. 182 (1-3) (2010) 447-452.

[50]. V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, I. I. Torocheshnikova, S. V. Smirnova, I. V. Pletnev, Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. Talanta 80 (3) (2010) 1177-1182.

[51]. A. Stark, K.R. Seddon, Ionic liquids, In: Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 26, John Wiley, New York, 2007.

[52]. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. Green Chem. 3 (4) (2001)156–164.

[53]. Z. G. Mu, F. Zhou, S. X. Zhang, Y. M. Liang, W. M. Liu, Preparation and Characterization of New Phosphonyl-Substituted Imidazolium Ionic Liquids. Helvetica Chem. Acta 87 (10) (2004) 2549 – 2555.

[54]. R. Hagiwara, Y. Ito, Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. J. Fluor. Chem. 105 (10) (2000) 221-227.

[55]. K. R. Seddon, A. Stark and M. J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. Pure Appl. Chem. 72 (12) (2001) 2275-2287.

[56]. J. P. Mikkola, P. Virtanen, R. Sjöholm, Aliquat 336 - A versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids. Green Chem. 8 (3) (2006) 250-255.

[57]. K. R. Seddon, A. Stark, M. J. Torres, Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. ACS Symposium Series, Chapter 4, Vol. 819, pp-34-39.

[58]. M. J. Earle, J. M. S. S. Esperança, M. A. Gilea, J. N.C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, The Distillation and Volatility of Ionic Liquids. Nature 439 (7078) (2006) 831-834.

[59]. P. Wasserscheid, Chemistry: Volatile Times for Ionic Liquids. Nature 439 (7078) (2006) 797-797.

[60]. L. P. N. Rebelo, J. N. C. Lopes, J. M. S. S. Esperanca, E. Filipe, On the Critical Temperature, Normal Boiling Point, and Vapor Pressure of Ionic Liquids. J. Phys. Chem. B 109 (13) (2005) 6040-6043.

[61]. D. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, Experimental vapour pressures of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides and a correlation scheme for estimation of vapourisation enthalpies of ionic liquids. J. Phys. Chem. A 110(2006)7303-7306.

[62]. D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims, R. C. Thied, An investigation of the radiochemical stability of ionic liquids. Green Chem. 4 (2) (2002)152-158.

[63]. L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz, P. Moisy, Influence of gamma irradiation on hydrophobic room-temperature ionic liquids [C_4MeIm]PF_6 and [C_4MeIm]$(CF_3SO_2)_2N$. Dalton Trans. 21 (2006) 2526-2534.

[64]. G. Le Rouzo, C. Lamouroux, V. Dauvois, A. Dannoux, S. Legand, D. Durand, P. Moisy, G. Moutiers, Anion effect on radiochemical stability of room-temperature ionic liquids under gamma irradiation. Dalton Trans. 31(2009) 6175-6184.

[65]. E. Bosse, L. Berthon, N. Zorz, J. Monget, C. Berthon, I. Bisel, S. Legand, P. Moisy, Stability of [$MeBu_3N$][Tf_2N] under gamma irradiation. Dalton Trans. 7 (2008) 924-931.

[66]. J. D. Holbrey, K. R. Seddon, The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates: Ionic liquids and ionic liquid crystals. J. Chem. Soc. Dalton Trans. 13 (1999) 2133 - 2139.

[67]. H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, Thermal properties of imidazolium ionic liquids. Thermochim. Acta 357 (2000) 97 – 102.

[68]. P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. Inorganic Chemistry 35 (5) (1996) 1168-1178.

[69]. G. Turian, “Polarity: From Electromagnetic Origins to Biological Take-Over,” Hamburg Kovač, 1994.

[70]. A. J. Carmichael, K. R. Seddon, “Polarity Study of Some 1-alkyl-3-methylimidazolium Ambient-Temperature Ionic Liquids with the Solvatochromic Dye, Nile Red.” Journal of Physical Organic Chemistry 13 (10) (2000) 591 - 595.

[71]. S. N. V. K. Aki, J. F. Brennecke, A. Samanta, “How Polar are Room-Temperature Ionic Liquids?” Chem. Comm. (2001) 413-414.

[72]. A. Kawai, T. Hidemori, K. Shibuya, “Polarity of Room-Temperature Ionic Liquid as Examined by EPR Spectroscopy.” Chem. Letters 33 (11) (2004) 1464-1465.

[73]. G. Angelini, C. Chiappe, P. D. Maria, “Determination of the Polarities of Some Ionic Liquids Using 2-nitrocyclohexanone as the Probe,” Journal of Organic Chemistry 70 (20) (2005) 8193-8196.

[74]. C. Wakai, A. Oleinikova, M. Ott, “How Polar are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-Based Ionic Liquid by Microwave Dielectric Spectroscopy.” Journal of Physical Chemistry B 109 (36) (2005) 17028-17030.

[75]. G. H. Tao, M. Zou, X. H. Wang, “Comparison of Polarities of Room-Temperature Ionic Liquids Using FT-IR Spectroscopic Probes,” Australian Journal of Chemistry 58 (5) (2005) 327-331.

[76]. T. Köddermann, C. Wertz, A. Heintz, "The Association of Water in Ionic Liquids: A Reliable Measure of Polarity," Angew. Chem. Int. Ed. 45 (22) (2006) 3697-3702.

[77]. S.V. Dzyuba, R.A. Bartsch, Expanding the Polarity of Ionic Liquids. Tetrahedron Letters 43 (26) (2002) 4657-4659.

[78]. R. J. P. Williams, R. D. Gillard, "Coordination Chemistry and Analysis," Pergamon Press, Oxford, 1987.

[79]. K. R. Seddon, "Ionic Liquids for Clean Technology." J. Chem. Tech. Biotechnol. 68 (4) (1997) 351-356.

[80]. T. Welton, "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," Chemical Reviews 99 (8) (1999) 2071-2083.

[81]. R. Sheldon, "Catalytic Reactions in Ionic Liquids". Chem. Comm. (2001)2399-2407.

[82]. C. M. Gordon, "New Developments in Catalysis Using Ionic Liquids." Applied Catalysis A: General. 222 (1-2) (2001) 101-117.

[83]. M. J. Earle, K. R. Seddon, "Ionic Liquids. Green Solvents for the Future". Pure and Applied Chemistry 72 (7) (2000) 1391-1398.

[84]. A. V. Mudering, A. Babai, S. Arenz, "The "Noncoordinating" Anion Tf_2N^- Coordinates to Yb^{2+}: A Structurally Characterized Tf_2N^- Complex from the Ionic Liquid [MPPyr][Tf_2N]," Angewandte Chemie International Eds. 44(34)(2005)5485-5488.

[85]. D. B. Williams, M. E. Stoll, B. L. Scott, "Coordination Chemistry of the bis(trifluoromethylsulfonyl)imide Anion: Molecular Interactions in Room Temperature Ionic Liquids". Chem. Commun. (2005) 1438-1440.

[86]. A. Babai, A. V. Mudering, "Crystal Engineering in Ionic Liquids. The Crystal Structures of $[Mppyr]_3[NdI_6]$ and $[Bmpyr]_4[NdI_6][Tf_2N]$". Inorganic Chemistry 45 (13) (2006) 4874-4876.

[87]. P. Wasserscheid and E. T. Welton, "Ionic Liquids in Synthesis," Wiley-VCH verlag GmbH & Co. KGaA, 2002.

[88]. A. G. Avent, P. A. Chaloner, M. P. Day, *et al.*, "Evidence for Hydrogen Bonding in Solutions of 1-ethyl-3-methylimidazolium Halides, and its Implications for Room-Temperature Halogenoaluminate(III) Ionic Liquids," Journal of the Chemical Society Dalton Trans. 23 (1994) 3405-3413.

[89]. Elaiwi, P. B. Hitchcock, K. R. Seddon, “Hydrogen Bonding in Imidazolium Salts and its Implications for Ambient-Temperature Halogenoaluminate(III) Ionic Liquids”. J. Chemical Soc. Dalton Trans. 21 (1995) 3467-3472.

[90]. D. R. MacFarlane, K.R. Seddon, Ionic liquids - progress in fundamental issues. Aust. J. Chem. 60 (1) (2007) 3-5.

[91]. R.P. Swatloski, J. D. Holbrey, R. D. Rogers, Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. Green Chem. 5 (4) (2003) 361-363.

[92]. J. R. Harjani, R. D. Singer, M. T. Garcia, “Biodegradable Pyridinium Ionic Liquids: Design, Synthesis and Evaluation”. Green Chem. 11(1) (2009) 83-90.

[93]. Y. Fan, M. Chen, C. Shentu, *et al*., “Ionic liquids Extraction of Para Red and Sudan Dyes from Chilli Powder, Chilli Oil and Food Additive Combined with High Performance Liquid Chromatography,” Analytica Chim. Acta 650 (1) (2009) 65-69.

[94]. T. Welton, Ionic liquids in green chemistry. Green Chem. 13 (2011) 225.

[95]. M. Galiński, A. Lewandowski, I. Stępniak, Ionic Liquids as Electrolytes. Electrochim. Acta 51 (26) (2006) 5567-5580.

[96]. D. S. Silvester, R. G. Compton, Electrochemistry in Room Temperature Ionic Liquids: A Review and Some Possible Applications. Z. Phys. Chem. 220 (10-11) (2006)1247-1274.

[97]. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada, S. Yanagida, Quasi-Solid-State Dye-Sensitized Solar Cells Using Room Temperature Molten Salts and a Low Molecular Weight Gelator. Chem. Commun. 4 (2002) 374-375.

[98]. P. J. Dyson, Review: Synthesis of organometallics and catalytic hydrogenations in ionic liquids. 16 (9) (2002) 495 – 500.

[99]. S. Chowdhury, R. S. Mohan, J. L. Scott, Reactivity of Ionic Liquids. Tetrahedron, 63 (11) (2007) 2363-2389.

[100]. M. E. V. Valkenburg, R. L. Vaughn, M. Williams, J. S. Wilkes, Ionic liquid heat transfer fluids, Fifteenth Symposium on Thermophysical Properties. June 22-27, 2003, Boulder, Colorado, U.S.A.

[101]. A. G. Fadeev, M. M. Meagher, Opportunities for Ionic Liquids in Recovery of Biofuels. Chem. Commun. 3(2000)295-296.

[102]. A. E. Visser, R. P. Swatloski, R. D. Rogers, pH-Dependent Partitioning in Room Temperature Ionic Liquids Provides a Link to Traditional Solvent Extraction Behavior. Green Chem. 2 (1) (2000)1- 4.

[103]. J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction. Chem. Commun. (1998) 1765 - 1766.

[104]. A. E. Visser, R. P. Swatloski, S. T. Griffina, D. H. Hartman, R. D. Rogers, Liquid/Liquid extraction of metal ions in room temperature ionic liquids. Sep. Sci. Technol. 36 (5&6) (2001)785–804.

[105]. R. Lertlapwasin, N. Bhawawet, A. Imyim, S. Fuangswasdi, Ionic liquid extraction of heavy metal ions by 2-aminothiophenol in 1-butyl-3-methylimidazolium hexafluorophosphate and their association constants. Separation Purification. Technol. 72 (1) (2010) 70-76.

[106]. Z. W. Pan, C. Ma, Y. Wu Zhang, Y. X. Huang, X. L. Chen, X. P. Zhang, Extraction Behavior of Rare Earths in Ion Liquid Extraction System Using 1-Butyl-3-Methyl-Imidazolium Hexafluorophosphate and Benzoyl Acetone. Adv. Material Res. 335-336 (2011)1428-1432.

[107]. M. Koel, J. R. Hollis, T. Lombardo, B. Smith, Ionic Liquids for oil shale Treatment. In Green Industrial Applications of Ionic Liquids. Ed: R. D. Rogers, K. R. Seddon, S. Volkov, NATO Science Series. II. Mathematics, Physics and Chemistry – Vol.92, Kluwer Academic Publishers in Cooperation with NATO Scientific Affairs Division, 2002, pp. 193-208.

[108]. M. Koel, Ionic liquids in chemical analysis, Crit. Rev. Anal. Chem. 35 (3) (2005) 177-192.

[109]. M. Smiglak, A. Metlen, R. D. Rogers, The Second Evolution of Ionic Liquids: From Solvents and Separations to Advanced Materials—Energetic Examples from the Ionic Liquid Cookbook. Acc. Chem. Res. 40 (11) (2007) 1182 – 1192.

[110]. R. Ferraz, L. C. Branco, C. Prudencio, J. P. Noronha, Z. Petrovski, Ionic Liquids as Active Pharmaceutical Ingredients. Chem MedChem. 6 (6) (2011) 975-985.

[111]. I. Billard, A. Ouadi, C. Gaillard, Liquid–liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding. Anal Bioanal Chem. 400 (6) (2011) 1555-66.

[112]. H. S. Ho, R. N. Menchavez, Y. M. Koo, Reprocessing of spent nuclear waste using ionic liquids. Korean J. Chem. Eng. 27 (5) (2010) 1360-1365.

[113]. V. A. Cocalia, K. E. Gutowski, R. D. Rogers, The coordination chemistry of actinides in ionic liquids: A review of experiment and simulation. Coordination Chem. Rev. 250 (7-8) (2006) 755-764.

[114]. P.R. Vasudeva Rao, K.A. Venkatesan, T. G. Srinivasan, “Studies on applications of room temperature ionic liquids”, Progress in Nuclear Energy 50 (2-6) (2008) 449-455.

[115]. K.A. Venkatesan, T.G. Srinivasan, P. R. Vasudeva Rao, A Review on the Electrochemical Applications of Room Temperature Ionic Liquids in Nuclear Fuel Cycle. J. Nucl. Radiochem. Sci.. 10 (2009) R1-R6.

[116]. P.R. Vasudeva Rao, K.A. Venkatesan, Alok Rout, T. G. Srinivasan, Potential Applications of Room Temperature Ionic Liquids for Fission Products and Actinide Separation. Sep. Sci. Technol. 47 (2) (2012) 204 – 222.

[117]. A. V. Mudring, S. Tang, Ionic Liquids for Lanthanide and Actinide Chemistry. Chem. Eur. J. 25 (18) (2010) 69-2581.

[118]. G. Koch, Reprocessing by quarternary ammonium nitrates: laboratory studies, In: Solvent Extraction Chemistry of metals. H.A.C. McKay, T.V. Healy, I.L. Jenkins (Eds.), McMillan, 1966, pp. 247 – 266.

[119]. S. Dai, C. E. Barnes, Y. H. Ju, Solvent extraction of strontium nitrate by crown ether using room-temperature ionic liquids. J. Chem. Soc., Dalton Trans. 9 (1999)1201-1202.

[120]. A.E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers, Traditional extractants in non-traditional solvents: Group 1 and 2 extractions by crown ethers in room temperature ionic liquids. Ind. Eng. Chem. Res. 39 (10) (2000) 3596 - 3604.

[121]. S. Chun, S. V. Dzyuba, R. A. Bartsch, Influence of structural variation in room temperature ionic liquids on the selectity and efficiency of competitive alkali metal salt. Extraction by crown ether. Anal. Chem. 73 (15) (2001) 3737-3741.

[122]. M. L. Dietz, J. A. Dzielawa, Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the ‘greenness’ of ionic liquids as diluents in liquid–liquid extraction. Chem. Commun. (2001) 2124–2125.

[123]. M. L. Dietz, J. A. Dzielawa, B. A. Ivan Laszak, Young, M. P. Jensen, Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. Green Chem. 5 (6) (2003) 682–685.

[124]. H. Luo, S. Dai, P. V. Bonnesen, T. J. Haverlock, B. A. Moyer, A. C. Buchanan III, A Striking Effect of Ionic-Liquid Anions in the Extraction of Sr+2 and Cs+ by Dicyclohexano-18-Crown-6. Solvent Extr. Ion Exch. 24 (1) (2006)19–31.

[125]. D. C. Stepinski, M. P. Jensen, J. A. Dzielawa, M. L. Dietz, Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids. Green Chem. 7 (2005) 151 – 157.

[126]. C. Xu, L. Yuan, X. Shen, M. Zhai, Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism radiation effect. Dalton Trans. 39 (2010) 3897–3902.

[127]. N. Turanov, V. K. Karandashev, V. E. Baulinc, Extraction of Alkaline Earth Metal Ions with TODGA in the Presence of Ionic Liquids. Solvent Extr. Ion Exch. 28 (3) (2010) 367–387.

[128]. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, Extraction of uranium(VI) from nitric acid medium by 1.1M tri-n-butylphosphate in ionic liquid diluent. J. Radioanal. Nucl. Chem. 265 (1) (2005) 31 – 38.

[129]. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, Effect of alkyl group in 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids on the extraction of uranium by tri-n-butylphosphate diluted in various ionic liquids. J. Nucl. Radiochem. Sci. 5 (2) (2004) 21 – 26.

[130]. M.L. Dietz, D. C. Stepinski, Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. Talanta 75 (2) (2008) 598–603.

[131]. I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg, Understanding the extraction mechanism in ionic liquids: UO_2^{2+}/ HNO_3/ TBP/ $C_4mimNTf_2$ as a Case Study. Solvent Extr. Ion Exch. 29 (4) (2011) 577-601.

[132]. Y. Shen, X. Tan, L. Wang, W. Wu, Extraction of the uranyl ion from the aqueous phase into an ionic liquid by diglycolamide. Separation Purification Technol. 78 (3) (2011) 298–302.

[133]. T. J. Bell, Y. Ikeda, The application of novel hydrophobic ionic liquids to the extraction of uranium(VI) from nitric acid medium and a determination of the uranyl complexes formed. Dalton Trans. 40 (2011) 10125-10130.

[134]. K. V. Lohithakshan, S. K. Aggarwal, Solvent extraction studies of Pu(IV) with CMPO in 1-octyl 3-methyl imidazolium hexa fluorophosphate (C_8mimPF_6) room temperature ionic liquid (RTIL). Radiochim. Acta 96 (2) (2008) 93-97.

[135]. K. V. Lohithakshan, S. K. Aggarwal, Solvent extraction studies of plutonium(IV) by crown ether dicyclohexyl-18-crown-6 (DC18C6) in 1-butyl-3-methyl imidazolium hexafluorophosphate (C_4mimPF_6) and 1-hexyl-3-methyl imidazolium hexafluorophosphate (C_6mimPF_6) room temperature ionic liquids (RTIL). Radiochim. Acta 99 (4) (2011) 201-205.

[136]. A. E. Visser, R. D. Rogers, Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry. J. Solid State Chem. 171(1-2) (2003)109-113.

[137]. K. Nakasima, F. Kubota, T. Maruyama, M. Goto, Feasibility of ionic liquids as alternative separation media for industrial solvent extraction process. Ind. Eng. Chem. Res. 44 (12) (2005) 4368-4372.

[138]. K. Nakasima, F. Kubota, T. Maruyama, M. Goto, Ionic liquids as a novel solvents for lanthanides extraction. Anal Sci. 19 (8) (2003)1097-1098.

[139]. F. Kubota, T. Maruyama, M. Goto, Application of ionic liquid to the extraction separation of rare earth by an effective diglycolamic acid extractant. Chem. Eng. Res. Jap. 44 (5) (2011) 307-312.

[140]. V. A. Cocalia, M. P. Jensen, J. D. Holbrey, S. K. Spear, D. C. Stepinski, R. D. Rogers, Identical extraction behavior and coordination of trivalent or hexavalent f – element cations using ionic liquid and molecular solvents. Dalton trans. (2005) 1966 -1971.

[141]. K. Shimojo, K. Kurahashi, H. Naganawa, Extraction behavior of lanthanides using a diglycolamide derivative TODGA in ionic liquids. Dalton Trans. 37 (2008) 5083–5088.

[142]. P. M. Jensen, J. Neuefeind, V. J. Beitz, S. Skanthakumar, L. Soderholm, Mechanisms of metal ion transfer into room-temperature ionic liquids: the role of anion exchange. J Am Chem Soc.125 (50) (2003)15466 - 15473.

Chapter - 2

CHAPTER - 2

Experimental

This chapter describes in detail, the synthesis and characterization of various room temperature ionic liquids and task specific ionic liquids (imidazolium and aliquot based). Different characterization techniques such as FT–IR, NMR (^{1}H and ^{13}C), Mass Spectrometry and elemental analysis have been discussed here. Experimental procedures such as liquid – liquid extraction of the metal ions, different counting techniques for the assay of radio nuclides etc. along with instruments and materials used for the above studies also have been detailed in this chapter.

2.1 Chemicals and reagents

1-methylimidazole

AR grade 1-methylimidazole was procured from M/s. Fluka Chemie GmbH, Buche, Switzerland and used after purification by distillation from solid potassium hydroxide.

Chloroalkane (Alkyl = butyl, pentyl, hexyl and octyl)

All types of chloroalkanes (AR garde) were procured from M/s. Acros, and purified by distillation over solid potassium hydroxide prior to use.

Bis(trifluoromethanesulfonyl)imide lithium salt ($LiNTf_2$)

AR grade $LiNTf_2$ (purity $\geq$ 99%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as recieved.

Diethyl (2-bromoethyl)-phosphonate

Diethyl (2-bromoethyl)-phosphonate (purity = 97%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany for the synthesis of ionic liquids.

Tri-*n*-octyl methylammonium chloride (TOMAC) (or Aliquat 336)

TOMAC (or Aliquat 336), analytical grade was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Tetraheptylammonium chloride (THEPAC)

Tetraheptylammonium chloride (purity 95%), analytical grade was procured from ACROS organics, New Jersey, USA and used as such.

OϕCMPO

n-Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphinoxide (OϕCMPO) was obatained from National Chemical Laboratory, Pune, India. Purification was done by column chromatography using neutral alumina as stationary phase and n-hexane as mobile phase prior to use to remove the acidic impurities. The absence of acidic impurities in

CMPO was confirmed from the insignificant $D_{Am(III)}$ obtained by using 0.2M OϕCMPO - 1.2M TBP/*n*-dodecane from 0.01M nitric acid medium as the aqueous phase.

Tri-*n*-butyl phosphate (TBP)

Tri-*n*-butyl phosphate (TBP) was obtained from M/s. Fluka Chemie GmbH, Buche, Switzerland. It was washed with dilute sodium carbonate solution (~ 0.2M) followed by distilled water and then dried under vacuum.

***n*-Dodecane (*n*-DD)**

n-Dodecane (99%) was obtained from Spectrochem Private Limited, Mumbai, India and used as such.

n-Tetradecane and *n*-Hexadecane

n-Tetradecane and *n*-Hexadecane (99%) were obtained from Spectrochem Private Limited, Mumbai, India and used as such.

Dichloromethane

Dichloromethane (AR grade) was obtained from Fischer Inorganics and Aromatics Limited, Chennai, India and used as such.

Diglycolic anhydride

Diglycolic Anhydride (technical grade, 90%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

DTPA

Diethylene triaminepentaacetic acid (98%), was procured from Acros Organics, Geel, Germany. The solution of DTPA was prepared by first dissolving with NaOH (1:5) in Millipore water and the pH of the solution was adjusted by HNO_3 to desired value.

HTTA

1-(2-theonoyl)-3,3,3-trifluoroacetone (HTTA), GR grade (98%) was procured Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such. The HTTA was used for the purification of plutonium solution by dissolving suitable amount of HTTA in xylene. Also HTTA was used for the synthesis of ionic liquids.

Acid solutions

The acid solutions (HNO_3, HCl, GR grade, Merck Specialities Private Limited, Mumbai, India) were prepared by the dilution of concentrated acids, and were standardized by standard acid-base titration methods using standardized NaOH solution using phenolphthalein as indicator.

Sodium Hydroxide

Sodium hydroxide (AR grade) was obtained from Ranbaxy Fine Chemicals

Limited, New Delhi, India and used as such.

Phenolpthalein

Phenolpthalein (Merck Specialities Private Limited, Mumbai, India) solution was prepared by dissolving ~ 500 mg of solid in 100 mL of 1:1 mixture of distilled water and ethanol.

Sodium Nitrate

Sodium Nitrate (AR grade) was obtained from Loba Chemie Private Limited, Mumbai, India and used as such.

Sodium Nitrite

Sodium Nitrite (AR grade) was obtained from s.d. fine – CHEM Limited, Mumbai, India and used as such.

Ammonia Solution

AR grade Ammonia Solution (about 25% NH_3, specific gravity 0.91) was obtained from Qualigens Fine Chemicals, Mumbai, India and used such.

Citric acid

AR grade citric acid, anhydrous was obtained from Otto Chemie, Mumbai, India, and used as such.

Acetohydroxamic Acid

AR grade acetohydroxamic acid (99%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Oxalic Acid

AR grade oxalic acid (98%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

EDTA

AR grade EDTA [bis(ethylenediaminetetraacetic acid)] was obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Methyl Thymol Blue

AR grade methyl thymol blue was obtained from s.d. fine – CHEM Limited, Mumbai, India. The solution of methyl blue was prepared by dissolving ~20 – 25 mg of it in 10 mL of distilled water for using as indicator for the standardization of europium solution.

Methanol

AR grade methanol was obtained from Ranbaxy Fine Chemicals Limited, New Delhi, India and used as such.

Ethyl acetate

AR grade ethylacetate was obtained from Fischer Inorganics and Aromatics Limited, Chennai, India, and used as such.

***n*-Hexane**

n-Hexane (AR grade) was obtained from Ranbaxy Fine Chemicals Limited, New Delhi, India and used as such.

Benzene, Toluene and Xylene

Benzene, toluene or xylene (low in sulfur, GR grade) was procured from Merck Specialties Private Limited, Mumbai, India and used as such.

Naphthalene

Scintillation grade naphthalene was procured from Loba Chemie Pvt. Ltd., Mumbai, India and used as such.

1, 4-Dioxane

1,4-Dioxane (AR grade) was procured from Merck Specialities Private Limited, Mumbai, India and purified prior to use to remove the peroxide impurities that are normally present as quenching impurities. About 2 litres of 1, 4 - Dioxane was refluxed with ~ 80 g of NaOH pellets for four hours. The dioxane was then distilled and the fraction that distilled between 373 – 375 K was collected after discarding the initial 100 mL fraction. This purified 1, 4 - Dioxane was used for the preparation of cocktail for liquid scintillation counting.

2,5- Diphenyl Oxazole (PPO)

Scintillation grade 2,5-diphenyl oxazole (PPO) was obtained from Loba Chemie Pvt. Ltd., Mumbai, India and used as such.

1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP)

Scintillation grade 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP) was obtained from Koch-Light Laboratories Ltd. Colnbrook Buch, England and used as such.

Tri-*n*-octyl phophinoxide (TOPO)

AR grade of tri-*n*-octyl-*n*-octylphosphine oxide (TOPO) (99%) was obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Di-*n*-octyl amine

Di-*n*-octyl amine (99%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Di-(2-ethyl)hexyl amine

Di-(2-ethyl)hexyl amine (99%) was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany and used as such.

Bis (2-ethylhexyl)phosphoric acid

AR grade bis(2-ethylhexyl)phosphoric acid (HDEHP) (98%) was obtained from M/s. Fluka Chemie GmbH, Buche, Switzerland and used without further purification.

Europium oxide

AR grade europium oxide, Eu_2O_3 (purity: 99.9%) procured from s.d.fine – CHEM limited, Mumbai and used for the preparation of the solution of europium nitrate.

2.2 Radionuclides

2.2.1 Plutonium – 239

Plutonium was obtained from Bhaba Atomic Research Centre (BARC), Mumbai as PuO_2. This was dissolved in the concentrated nitric acid and purified by anion exchange method. The isotopic composition of plutonium was as follows (values in atom %) ^{238}Pu: 0.017; ^{239}Pu: 93.60; ^{240}Pu: 6.24; ^{241}Pu: 0.12; ^{242}Pu: 0.023. The specific activity of this plutonium tracer was found to be 1.665×10^5 dpm/μg. Purified plutonium is in different oxidation states. From this purified solution of plutonium, a stock solution of Pu(IV) was prepared using HTTA extraction procedure.

HTTA extraction [1]

A small quantity of plutonium was taken in 1M HNO_3 and about 0.2 – 0.6mL of 2.5 M $NaNO_2$ solution was added drop wise with constant shaking. The resulting Pu(IV) solution was extracted with 0.5M HTTA/xylene solution. The organic phase was scrubbed with 1 M HNO_3 several times to remove Pu(III), Pu(VI) etc. and other impurities. The loaded plutonium was stripped by 8 M HNO_3 and used as a stock solution.

2.2.2 Americium – 241

^{241}Am(III) was obtained from Oak Ridge National Laboratory (ORNL), U.S.A. as AmO_2. It was dissolved in nitric acid and used without further purification.

2.2.3 Uranium – 233

^{233}U separated from irradiated ThO_2 was obtained from Reprocessing Group, IGCAR, Kalpakkam, India. It was further purified by solvent extraction with 5 % TBP/*n*-DD from 4M HNO_3. The loaded organic phase was subjected to scrubbing with 4M HNO_3 in order to remove the coextracted impurities. Then U-233 was stripped from the organic phase by 0.01M HNO_3.

2.2.4 Radioisotopes

$^{(152+154)}Eu$(III), along with other metal tracers (^{85}Sr(II), ^{144}Ce(IV), ^{60}Co(II), ^{54}Mn(II), ^{106}Ru(III) etc.) were procured from “Board of Radiation and Isotope Technology

(BRIT), Mumbai.

2.2.5 Tracer solution

A tracer of all actinides (^{233}U(VI), ^{239}Pu(IV), ^{241}Am(III)) and fission products ($^{(152+154)}$Eu(III), ^{144}Ce(IV), ^{101}Ru(III), ^{60}Co(III) etc.) (~ 4.3 x10^{-4} M) were diluted with double distilled water and used for all extraction studies.

2.3 Instrumentation

2.3.1 Karl-Fischer Titrator

A Karl – Fischer Titrator (Spectralab-AT 36) was used for the determination of water content. Samples with known weight were taken for the determination of water content. Calibration was carried out using known quantity of water. The method is based on the reaction between iodine and sulfur dioxide in aqueous medium. Water and iodine are consumed quantitatively in a 1:1 mole ratio in the reaction. Once all the water present in the sample is consumed, excess iodine is detected voltametrically. Pyridine free Karl-Fischer reagent was used for the determination of water content in the samples.

2.3.2 Electronic Single Pan Balance

A calibrated electronic single pan balance with a sensitivity of 0.01 mg was used to weigh chemicals and solutions.

2.3.3 UV – VIS spectrophotometer

UV-visible absorption spectra were obtained using Shimadzu UV-VIS spectrometer model UV-2500 with quartz cuvettes of path length 10 mm.

2.3.4 FTIR spectrometer

A BOMEM MB-100 FTIR spectrometer with a range of 4000 - 650 cm^{-1} with a resolution of 4 cm^{-1} was used for the measurement of IR spectra. The samples to be scanned were sandwiched between two zinc selenide windows. The sample compartment was purged with nitrogen gas for a sufficient period prior to scan.

2.3.5 Mass Spectrometer [Time – Of – Flight mass spectra (TOF-MS)]

A home built reflectron time of flight mass spectrometer was used for the mass analysis. Nicotinic acid is used as matrix and fourth harmonic of Nd-YAG laser (266 nm) is used for the desorption/ionization.

2.3.6 NMR spectrometer

A Bruker Avance III 500 MHz (AV 500) multi nuclei solution NMR spectrometer was used for structure analysis of synthesized ionic liquids and other extractants. MeOD and CD_3COCD_3 were used as solvents.

2.3.7 CHNS Analyzer

The carbon, nitrogen, and hydrogen content of the synthesized ionic liquids were determined by Elemental Vario EL CHNS analyzer. High pure argon was used as purge gas and high purity oxygen was used as combustion gas.

2.3.8 pH meter

All pH measurements were made with Cyberscan 500 pH, Metrohm. The meter was calibrated at 298 K with standard buffers of pH 4, 7 and 10.

2.3.9 Viscometer

A Brookfield viscometer was used for viscosity measurements (model number: DV II+). The viscometer is equipped with a small sample holder and adapter. Spindle number 18 (S18) was used for measuring the viscosity.

2.3.10 Thermostatted rotary water bath shaker

A refrigerated water bath (Poly Science, Model-9100, USA) with a temperature controlling accuracy of $\underline{+}$ 0.01^0C was used for the solvent extraction experiments. A JULABO make (F33-HE) refrigerated and heating circulator with a temperature controlling accuracy of $\underline{+}0.1^0$C and a heating immersion circulator with a temperature controlling accuracy of $\underline{+}0.01^0$C were also used for the experiments.

2.3.11 Rotary Evaporator

A rotary evaporator with model R-3000 from M/s. Buchi Laboratories Technique AG, Switzerland, was used for distilling off volatile solvents and drying ionic liquids in order to remove water content.

2.3.12 Vaccum Oven

Vaccum oven (Model No. IRI-021) with digital temperature control was utilized for drying ionic liquids prior to use. The oven was connected to a vaccum pump with pressure gauge and pressure control.

2.3.13 Gamma Counter

The activity of ^{241}Am(III), $^{(152+154)}$Eu(III) and other gamma emitting radioisotopes was measured using a gamma counter with single channel analyzer and well type NaI(Tl) detector. The NaI(Tl)-PMT integral assembly was procured from M/S Harshaw, U.S.A. and other electronic modules were obtained from ECIL (Electronic Corporation of India Limited), Hyderabad, India.

2.3.14 Liquid scintillation counter

An in-house fabricated liquid scintillation counter was used for measuring α -activity. In liquid scintillation counting, the energy of alpha particles is absorbed by the cocktail (solvent containing organic scintillators) and converted into photons in the visible region which in turn are converted into photoelectrons by photomultiplier tube and subsequently measured as an electronic pulse. 1,4-dioxane was used as the primary solvent, naphthalene and 2,5-diphenyloxazole (PPO) were used as the primary scintillator. 1,4-di-2-(5phenyloxazolyl)benzene (POPOP) was used as a wavelength shifter and tri-*n*-octylphosphine oxide (TOPO) as the complexing agent.

The liquid scintillation counter consists of a machined Perspex vial holder, coupled to a single low noise photo multiplier tube. The discriminator was set with ^{241}Am source and the efficiency was verified with a plutonium source.

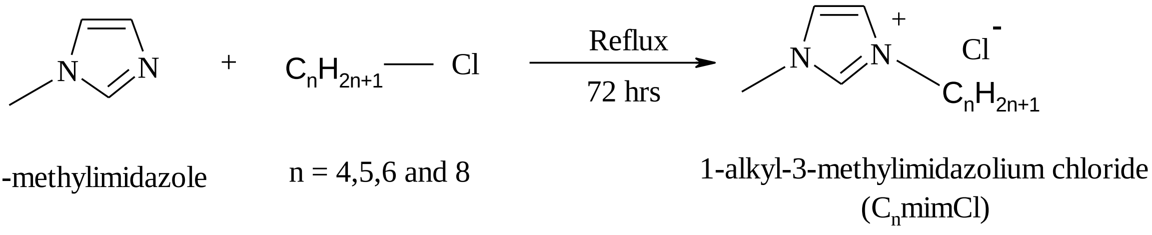
2.3.15 High Pure Gamma Spectrometer (HpGe Detector)

Gamma Spectrometry was used to identify fission products and their concentration. In this technique, a planar high pure germanium (HpGe) crystal semiconductor obtained from OXFORD Instruments, USA was used as the detector.

2.4 Synthesis and characterization of ionic liquid diluents and task specific ionic liquids (or functionalized ionic liquids)

2.4.1 Preparation of 1-alkyl-3-methylimidazolium chloride (C$_n$mimCl) [n = 4, 5, 6 and 8]

The preparation involves refluxing a mixture of 1-methylimidazole with 1-chloroalkane in the mole ratio of 1:1.2 at 343 K for 72 hours [2]. The resulting product was washed a few times with ethyl acetate and acetonitrile, and evaporated under vacuum at 343K. A white solid was obtained after cooling. A quantitative yield was obtained.



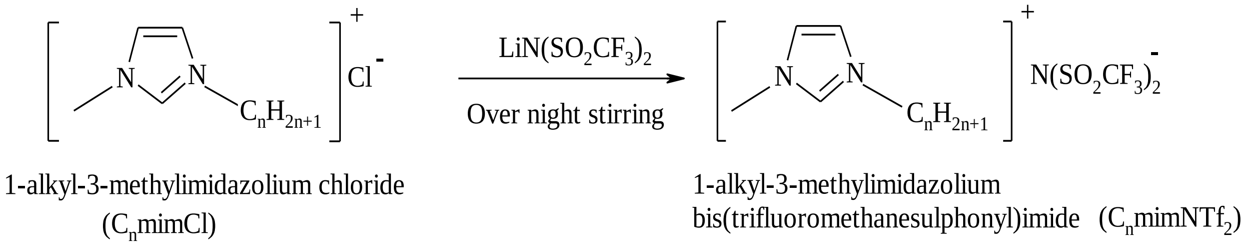
Scheme 2.1. Preparation of 1-alkyl-3-methyimidazolium chloride

Characterization of C$_n$mimCl

The carbon, nitrogen and hydrogen content of C$_n$mimCl were determined by CHNS analyzer. The measured values are listed along with theoretical values in parenthesis, C$_4$mmCl - C: 55 (54.9); H: 8.7 (8.6); N: 15.9 (16.0), C$_6$mimCl - C: 59.1 (59.2); H: 9.45 (9.37); N: 13.75 (13.81) and C$_8$mimCl – C: 62.2 (62.4); H: 9.9 (10); N: 12 (12.1).

2.4.2 Preparation of 1-alkyl-3-methylimidazolium bis(trifluoromethane-sulphonyl)imide, ($C_n$mimNTf$_2$)

Lithium salt of bis(trifluoromethanesulphonyl)imide (1.3 mol) was added to a solution of 1-butyl-3-methylimidazolium chloride (1 mol) in water kept at 273 K. The mixture was stirred overnight and the bottom layer of ionic liquid was separated and washed several times with water. The ionic liquid was evaporated to remove moisture at 343 K using a rotary evaporator under vacuum [3]. The yield of each ionic liquids was ~ 85%.



Scheme 2.2. Preparation of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

Characterization of $C_n$mimNTf$_2$

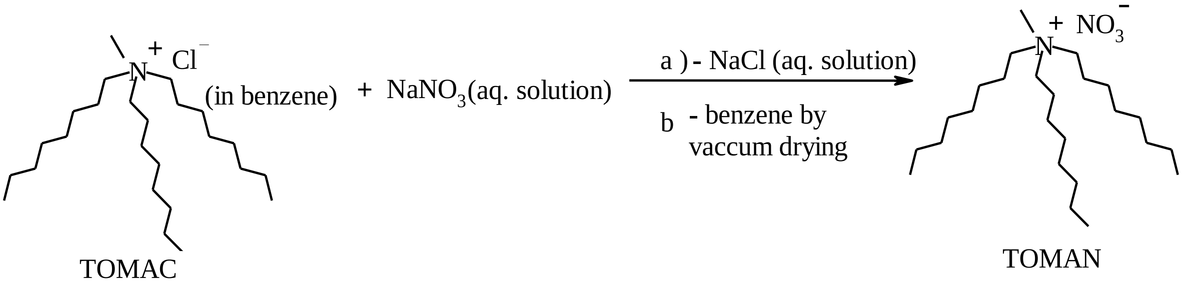
FT-IR (ZnSe, ν/cm^{-1}): 3170, 3121(CH stretch of imidazole ring), 2964, 2932, 2879 (aliphatic C-H stretch), 1565, 1465 (C-C symmetric stretch bands of imidazole ring), 1425, 1378 (C-H asymmetric stretch of CH_3), 1138 (SO_2 symmetric strech), 1192 (C-F asymmetric stretch), 1060 (S-N-S asymmetric stretch), 748 (imidazolium ring C-H bending).

δ_H of C_4mimNTf$_2$ (500 MHz; MeOD; Me_4Si): 8.76 (1H, s), 7.63 (1H, t), 7.58 (1H,t), 4.28 (2H,t), 3.98 (3H,s), 1.89 (2H,q), 1.36 (2H, sextet), 0.93 (3H,t). **δ_C of C_4mimNTf$_2$ (125 MHz; MeOD; Me_4Si)** : 136 (CH), 123.5 (CH), 122.2 (CH), 115 (CF_3 x 2), 49 (CH_2), 36 (CH_3), 31 (CH_2), 19 (CH_2), 13 (CH_3). **δ_H of C_5mimNTf$_2$(500 MHz; D_3CCOCD_3; Me_4Si)**: 8.77 (1H, s), 7.63 (1H, t), 7.58 (1H,t), 4.28 (2H,t), 4.01 (3H,s), 1.9 (2H,q), 1.33 (4H, m), 0.89 (3H,t). **δ_C of C_5mimNTf$_2$ (125 MHz; MeOD; Me_4Si)**: 136 (CH), 123.5 (CH), 122 (CH), 115 (CF_3 x 2), 49(CH_2), 46.8 (CH_2), 36 (CH_3), 31 (CH_2), 19 (CH_2), 13 (CH_3). **δ_H of C_6mimNTf$_2$(500 MHz; D_3CCOCD_3; Me_4Si)**: 8.9(1H, s), 7.63 (1H, t), 7.58 (1H,t), 4.33 (2H,t), 4.035 (3H,s), 1.94 (2H,q), 1.34 (6H, m), 0.89(3H,t). **δ_C of C_6mimNTf$_2$ (125 MHz; MeOD; Me_4Si)**: 136 (CH), 123.5 (CH), 122.2 (CH), 115 (CF_3 x 2), 49 (CH_2), 47 (CH_2), 36 (CH_3), 31 (CH_2), 22.2 (CH_2), 19 (CH_2), 14 (CH_3). **δ_H of C_8mimNTf$_2$ (500 MHz; MeOD; Me_4Si) :** 8.76 (1H, s), 7.63 (1H, t), 7.58 (1H,t), 4.21 (2H,t), 3.93 (3H,s), 1.89 (2H,q), 1.33 (10H, m), 0.91 (3H,t). **δ_C of C_8mimNTf$_2$ (125 MHz; MeOD; Me_4Si)** :

136 (CH), 123.5 (CH), 122.2 (CH), 115 (CF_3 x2), 53 (CH_2), 49.5 (CH_3), 47 (CH_2), 35,2 (CH_2), 31.4 (CH_2), 29.7 (CH_2), 25.77 (CH_2), 22.2 (CH_2), 14 (CH_3).

2.4.3 Preparation of tri-*n*-octylmethylammonium nitrate (TOMAN)

A solution of 250 mL of 0.5 M Aliquat-336 (tri-*n*-octylmethylammonium chloride, TOMAC) in benzene is equilibrated 3 to 4 times with 4 M sodium nitrate solution and the organic phase is separated. The aqueous phase and organic phase was checked for the absence of chloride ion and then washed extensively with water [4]. Benzene was removed by evaporation under reduced pressure in rotary evaporator at 343 K. A thick viscous liquid, which turned to semi solid upon cooling, was obtained. The synthetic pathway is given below in scheme 2.3.



Scheme 2.3. Preparation of trioctylmethylammonium nitrate (TOMAN)

2.4.4 Preparation of diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide ($ImPNTf_2$)

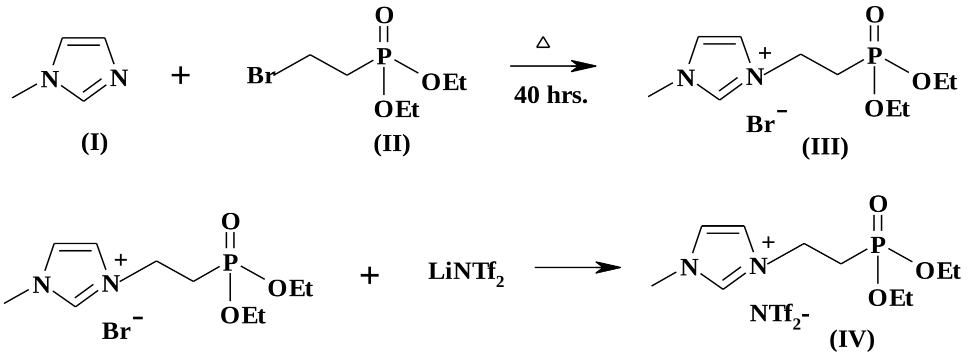
Synthesis of $ImPNTf_2$ involves the reaction of a mixture of 1-methylimidazole (0.1 mol) with diethyl-(2-bromoethyl)phosphonate (0.15 mol) at 373 K for about 40 hours [5]. The resulting product (ImPBr) was washed few times with hexane followed by acetonitrile and evaporated under vacuum. Near quantitative yield was obtained. The TSIL, $ImPNTf_2$ was prepared by adding a pre-cooled aqueous solution of $LiNTf_2$ (1.3 mole) to the aqueous solution of ImPBr (1 mol) at 298 K [5]. The entire mixture was stirred overnight and the bottom ionic liquid layer was separated, washed several times with water. The product was evaporated to remove moisture at 343 K using rotary evaporator. Yield obtained was 70%. Viscosity of $ImPNTf_2$ was 42 cP at 303 K. The synthetic pathways and the structure of $ImPNTf_2$ are given below in the scheme 2.4.

Characterization

FT-IR (ZnSe, ν/cm^{-1}) : 3175, 3122 (CH strech in imidazole ring), 2964,2932(CH strech of - CH_2), 1571 (C-C symmetric strech in imidazole ring), 1425,1378 (CH_3), 1138 (SO_2), 1058 (S-N-S asymmetric strech) 1210 (P = O strech), 750 (imidazole C-H bend);

^{1}H NMR (500 MHz, MeOD, Me_4Si, δ/ppm): 9.04 (1H, s), 7.69 (1H, t), 7.62 (1H t), 4.25 (2H. t), 3.97 (3H, s), 1.92 (2H, sext), 1.33 (11 H, m), 0.9 (3H, t).

MS(TOF-MS, m/z): $C_{10}H_{20}N_2PO_3^{+\cdot}$ (parent peak, m/z = 248), $C_6H_{10}N_2^{+\cdot}$ (*m/z* 111), $C_4H_6N_2^{+\cdot}$ (*m/z* 82), $C_5H_8N_2^{+\cdot}$ (*m/z* 96.7) (fragmented peaks)



Scheme 2.4. Synthesis of task specific ionic liquid, $ImPNTf_2$ (I) 1-Methylimidazole, (II) Diethyl-(2-bromoethyl)phosphonate (III) Diethyl-2-(3-methylimidazolium)ethylphosphonate bromide, ImPBr (IV) Diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethanesulfonyl)imide, $ImPNTf_2$

2.4.5 Preparation of *N, N*–dioctyl-2(3-methyl imidazolium) bis trifluoromethane sulfonamide ($DOAImNTf_2$) and its precursors

The reaction scheme for the synthesis of $DOAImNTf_2$ is shown in scheme 2.5. 2-chloro-(*N*, *N*-dioctyl)acetamide (III) was synthesized by stirring dioctylamine (I) (1eq) with chloroacetylchloride (II) (1eq) overnight under argon atmosphere (273 K) in the presence of triethylamine (TEA) and dichloromethane. The product was washed several times with distilled water to remove the quaternary ammonium salt, and dried in a rotary evaporator to remove water. The resulting 2-chloro-(*N*, *N*-dioctyl)acetamide (1 eq) was refluxed with 1–methylimidazole (IV) (1 eq) in acetonitrile medium at 80 – 90^{0}C for about 12 hrs [6] . The ionic liquid, *N,N*–dioctyl-2(3-methylimidazolium) chloride (V) (DOAImCl) was obtained after removing acetonitrile. The yield was near quantitative (~ 99%). The amide functionalized ionic liquid (VI), $DOAImNTf_2$, was prepared by adding a pre-cooled aqueous solution of $LiNTf_2$ (1.3 mole) to the aqueous solution of DOAImCl (1 mol) at 298 K. The entire mixture was stirred overnight. The ionic liquid layer settled at the bottom was separated, washed several times with distilled water to remove chloride ion (checked with acidified silver nitrate solution). The product was evaporated to remove moisture at 343 K using rotary evaporator. Yield obtained was 65%. Purity was > 98% and the water content (determined by Karl-Fischer titration) of the ionic liquid was determined to be less than 500 ppm.

Characterization

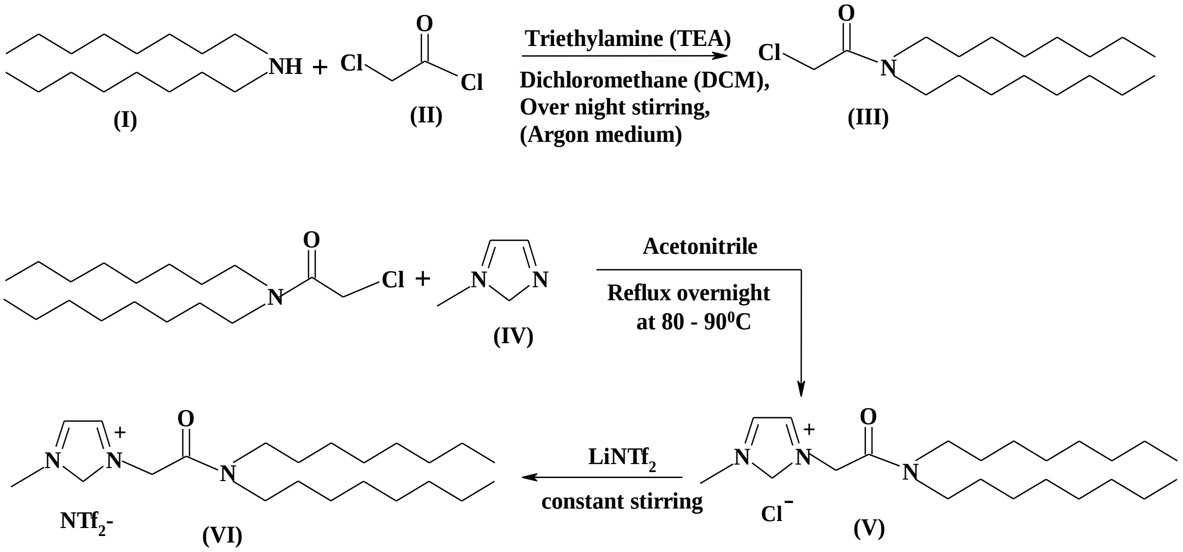
i) 2-chloro-(*N*,*N*-dioctyl)-acetamide

FT-IR (ZnSe, ν/cm^{-1}): 2932, 2868 (CH), 1425,1379 (CH$_3$), 1658 (CO**).** ^{1}**H NMR (500 MHz, CD$_3$COCD$_3$, Me$_4$Si, δ/ppm):**1.28 (12H, m),1.7(4H, m), 0.88(6H, m). ^{13}**C NMR(125 MHz; D$_3$CCOCD$_3$; Me$_4$Si):** 164.4(CO), 50.3(CH$_2$), 47(CH$_2$), 35(CH$_2$), 31(CH$_2$), 29(CH$_2$), 28(CH$_2$), 26(CH$_2$), 22.3(CH$_2$), 13.45(CH$_3$).

ii) DOAImNTf$_2$

FT-IR (ZnSe,ν/cm^{-1}): 3175 - 3122 (CH in imidazole ring), 2963, 2932, 2822 (CH), 1570 (C-C symmetric strech in imidazole ring), 1425,1378 (CH$_3$), 1138 (SO$_2$), 1658 (CO), 1058 (S-N-S asymmetric strech), ; ^{1}**H NMR (500 MHz, CD$_3$COCD$_3$, Me$_4$Si, δ/ppm) :** 8.97 (1H, s), 7.69 (t,1H, J = 1.5 Hz), 7.66 (t, 1H, J = 1.5 Hz), 5.4(2H. s), 3.97 (3H, s), 1.3 (12H, m), 1.77 (6H,m), 0.9 (3H, t). ^{13}**C NMR (125 MHz, CD$_3$COCD$_3$, Me$_4$Si, δ/ppm) :**163.8(CO), 138(CH), 123(CH), 122(CH),118(2xCF$_3$), 50.33(CH$_2$),48(CH$_2$), 35.8(CH$_2$), 31(CH$_2$), 29.3(CH$_2$), 28(CH$_2$), 26.6(CH$_2$), 22.3(CH$_2$), 13.4(CH$_3$).

MS (TOF, m/z): m/z = 364.5 (parent peak) which corresponds to the cation moiety of the ionic liquid.



Scheme 2.5. Synthesis of DOAImNTf$_2$ (I) N,N dioctylamine, (II) chloroacetylchloride, (III) 2-chloro-(N,N –dioctyl)acetamide, (IV) 1 –methylimidazole, (V) N,N-dioctyl-2-(3-methylimidazolium)acetamide chloride, DOAImCl, (V) N,N-dioctyl-2-(3-methylimidazolium)acetamide bis(trifluoromethanesulfonyl)imide, DOAImNTf$_2$

2.4.6 Synthesis of β- diketonate based ionic liquids

The synthesis of β- diketonate based ionic liquids and their precursors were carried out as per the procedure given elsewhere [7].

a) Synthesis of ammoniumtheonyltrifluoroacetylacetonate (NH_4TTA)

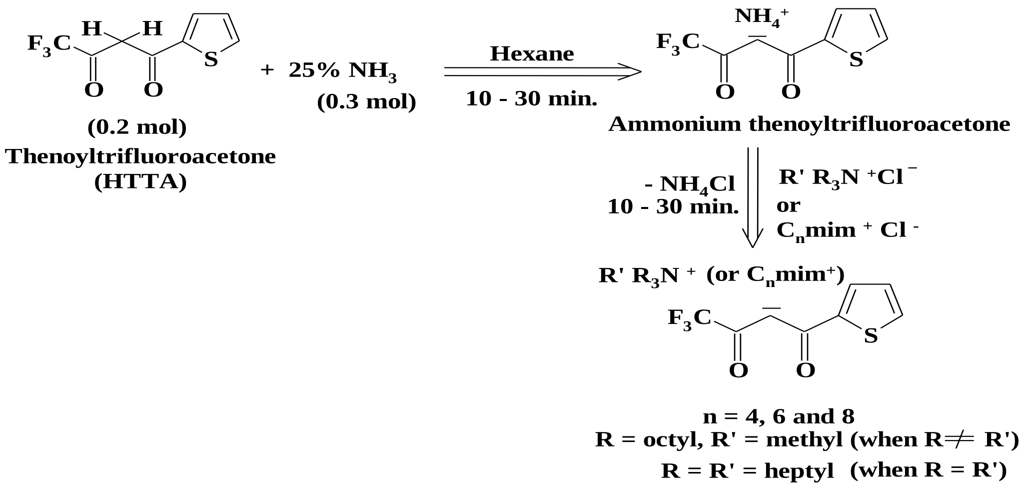
Ammonium thenoyltrifluoroacetonate was prepared by the drop wise addition of 25 % ammonia solution (0.3 mol) to the solution of theonyltrifluoroacetone (0.2 mol) in hexane. The mixture was stirred for about 15 minutes, and the white precipitate formed was filtered, washed with hexane, and dried at room temperature under reduced pressure, and stored in a vacuum desicator, after characterization by FT-IR and NMR (^{1}H and ^{13}C) spectroscopy as given below.

Characterization

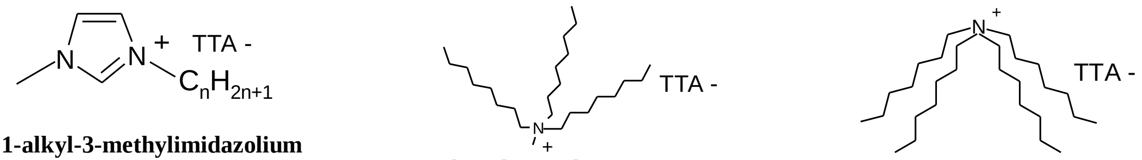
NH_4TTA: υ / cm^{-1}: 3080 (CH in aromatic ring), 2962, 2932, 2853 (CH stretch), 1580, 1640 (CO stretch), 1120, 1350 (CF stretch). **^{1}H NMR** (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm): 7.63 (1H,t), 7.58 (1H,t), 7.2 (4H,s ; broad), 7.1 (1H,t), 6.02 (1H,s). **^{13}C NMR** (125 MHz, CD_3COCD_3 , Me_4Si, δ/ppm): 178.1(CO), 169.02 (CO), 139.2, 134.6, 134, 127.7, 118.2 (CF_3), 87 (CH).

b) Synthesis of β-diketonate (or TTA -based) ionic liquids

The general synthetic procedure involved dropwise addition of ammonium thenoyltrifluoroactone (0.2 mol) in acetonitrile (10 mL) (or acetone) to the solution of TOMAC or $C_n$mimCl or THEPAC (0.2 mol, n = 4,6 and 8) in acetonitrile (10 mL) (or acetone). The mixture was stirred for about 20 minutes at room temperature. The precipitate formed was separated, and the filtrate was dried in a rotary evaporator at 333 K. A viscous liquid obtained, was washed several times with distilled water until the aqueous and organic phases were free from chloride ion (tested with acidified silver nitrate). The ionic liquid was then dried at 353 K for about 24 hrs in a rotary evaporator. The synthetic pathway is given below in the scheme 2.6. The structure of ionic liquids synthesized are given in the figure 2.1.



Scheme 2.6. Synthesis of different 1,3-diketonate based ionic liquids



1-alkyl-3-methylimidazolium thenoyltrifluoroacetonate ($C_n$mimTTA) ; n = 4, 6 and 8

Trioctyloctylmethylammonium thenoyltrifluoroacetonate (TOMATTA)

Tetraheptylammonium thenoyltrifluoroacetonate (THEPATTA)

Figure 2.1. Structure of 1,3 – diketonate based ionic liquids

Characterization

i) TOMATTA: υ / cm^{-1}: 3080 (CH in aromatic ring), 2962, 2932, 2853 (CH), 1580, 1640 (CO), 1120, 1350 (CF), 1380, 1470 (CH bending). **^{1}H NMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 0.9 (9H, m), 1.3 (30H, m),1.8 (6H,m), 3.25 (3H,s), 3.5 (6H,m), 7.7 (1H,t), 7.6 (1H,t),7.4 (1H,t), 5.85 (1H,s). **^{13}C NMR (125 MHz, CD_3COCD_3 , Me_4Si, δ/ppm):** 178.03 (CO),169.25 (CO), 139, 136.4, 134.4, 128.5, (aromatic), 118 (CF_3), 86.22 (CH), 61.27(CH_2N), 47.9 (CH_3N), 31.6, 29.3, 28.9, 28.2, 25.9 (various CH_2CH_2), 22 (CH_2CH_3), 13 (CH_3).

ii) THEPATTA: υ / cm^{-1}: 3080 (CH in aromatic ring), 2971, 2962, 2853 (CH), 1550, 1633 (CO), 1380, 1470(CH), 1124, 1169(CF). **^{1}H NMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 0.88 (12H, m), 1.34 (24H,m), 1.8 (8H,m), 3.45 (8H,m), 7.7 (1H,t), 7.58 (1H,t), 7.09 (1H,t), 5.92 (1H,s).**^{13}CNMR (125 MHz, CD_3COCD_3 , Me_4Si, δ/ppm):** 177.8 (CO), 169.03 (CO), 139.03, 134.3, 133.8, 127.88 (aromatic), 118(CF_3), 86.88 (CH), 58.53 (CH_2N), 31, 29, 28, 26 (various CH_2CH_2), 22.29 (CH_2CH_3), 13.4 (CH_3).

iii) C_4mimTTA : υ / cm^{-1}: 3175, 3122, 3080 (CH in aromatic ring), 2962, 2853 (CH), 1380, 1470 (CH_3), 1580, 1640 (CO), 1350, 1120 (CF). **^{1}H NMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 10.2 (1H,s), 7.74 (1H,t), 7.7 (1H,t), 7.57 (1H,t), 7.07 (1H,t), 7.34 (1H,t), 5.93 (1H,s), 4.4 (2H,t), 3.28 (3H,s), 4.08 (1H,s), 1.85 - 1.9 (2H,q), 1.37-1.33 (2H, sextet), 0.91 (1H,t).**^{13}C NMR (125 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 178.2 (CO), 168.9(CO), 138, 136, 134.7, 133.7, 128, 123.5, 122.16 (aromatics), 118 (CF_3), 86.4 (CH), 49 (CH_3), 35 (CH_2), 32 (CH_2), 19.13 (CH_2), 12.85 (CH_3).

iv) C_6mimTTA : υ / cm^{-1}: 3175, 3122, 3080 (CH in aromatic ring), 2962, 2853 (CH), 1380, 1466 (CH_3), 1575, 1634 (CO), 1120, 1350 (CF). **^{1}HNMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 10.4 (1H,s), 7.7 (1H,t), 7.68 (1H,t), 7.56 (1H,t), 7.3 (1H,t), 7.08 (1H,t), 0.84 (1H,t), 4.39 (2H,t), 4.08 (1H,s), 1.86 (2H,q), 1.36 (11H,m), 5.94 (1H,s), 1.3 (6H,m), 4.08 (1H,s), 4.37(3H,s). **^{13}C NMR (125 MHz, CD_3COCD_3 , Me_4Si, δ/ppm):** 178.2 (CO), 168.89 (CO), 139.8, 136.4, 134.5, 133.9, 128.6, 123.2, 122.1 (aromatics),118 (CF_3), 86.39 (CH), 49.2 (CH_2), 35.45 (CH_2), 30.3 (CH_2), 28.5 (CH_2), 25.6 (CH_2), 22.22 (CH_2), 13.36 (CH_3).

v) C_8mimTTA: υ / cm^{-1}: 3175, 3122, 3080 (CH in aromatic ring), 2962,2853 (CH), 1380, 1466 (CH_3), 1580, 1634 (CO), 1120, 1350 (CF). **^{1}HNMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 10.3 (1H,s), 7.7 (1H,t), 7.68 (1H,t), 7.56 (1H,t), 7.5 (1H,t), 7.12(1H,t), 0.86 (1H,t), 3.26 (3H,s), 4.39 (2H,t), 4.08 (1H,s), 1.89 (2H,q), 1.36 (11H,m), 5.93 (1H,s). **^{13}C NMR (125 MHz, CD_3COCD_3 , Me_4Si, δ/ppm):** 178.1 (CO), 169 (CO), 139.06, 136, 134.5, 133.9, 128.5, 123.5, 122.2 (aromatics), 118.5 (CF_3), 86.4 (CH), 49.2 (CH_3), 35 .5 (CH_2), 31.3 (CH_2), 29 (CH_2), 28.7 (CH_2), 25.9 (CH_2), 22.3(CH_2), 13.4 (CH_3).

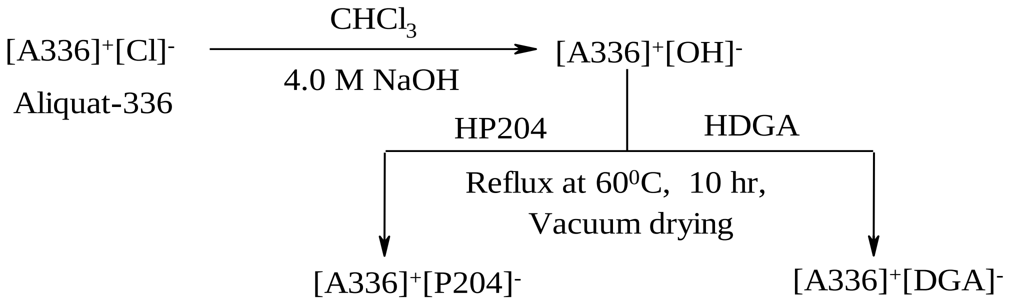
2.4.7 Synthesis of tri-*n*-octylmethylammonium (2-ethyl)hexylphophate,$[A336]^+[P204]^-$ and tri-*n*-octylmethylammonium bis(ethylhexyl)diglycolamate, $[A336]^+[DGA]^-$

The procedure for the synthesis of ionic liquids, $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ is shown in the scheme 2.7. Briefly, the first step involved the ion-exchange of chloride ion present in Aliquat-336 ($[A336]^+[Cl]^-$) by hydroxide ion by equilibrating 0.05 M Aliquat-336/$CHCl_3$ with 4 M NaOH for one hour. The aqueous phase was removed and the organic phase was equilibrated again with fresh sodium hydroxide. This procedure was repeated atleast 8 – 10 times until the Cl^- ion in aqueous and organic phase was negligible (checked with acidified $AgNO_3$ solution). The second step involved refluxing the $[A336]^+[OH]^-$ with HP204 (or HDGA) in 1 : 1 mole ratio at 60^0C for about 10 hr. The lower aqueous phase was separated and the ionic liquid phase (upper phase) was dried in a rotary evaporator at 70^0C for about 5 hrs. Near quantitative yield was obtained. The structure of the ionic liquids and their their precursors are shown in figure 2.2.

Characterisation

$[A336]^+[P204]^-$: ^{1}H NMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm): 0.89 (9H, m), 1.3 (30H,m),1.8 (6H,m), 3.25 (3H,s), 3.5 (6H,m), 1.29 (m, 6H), 1.33 (m, 12H), 1.42 (m, 4H), 1.45 (m, 4H), 1.45 (m, 1H), 1.51 (m, 1H). **^{13}C NMR (125 MHz, CD_3COCD_3, Me_4Si, δ/ppm) :** 61.24 (3 x CH_2N), 47.5 (CH_3N), 31.6, 29.3, 28.9, 28, 26 (various CH_2CH_2), 22.3 (CH_2CH_3), 13.4 (3 x CH_3), 26.1 (CH_2), 28.8 (CH_2), 31.2 (CH_2), 32.5 (CH_2), 36.5 (CH), 49.1 (CH_2), 11.5 (CH_3).

$[A336]^+[DGA]^-$: ^{1}H NMR (500 MHz, CD_3COCD_3, Me_4Si, δ/ppm): 0.89 (9H, m), 1.3 (30H,m),1.8 (6H,m), 3.25 (3H,s), 3.5 (6H,m), 4.3 (s, 2H, -OCH_2-), 4.08 (s, 2H, -CH_2O-), 3.2-3.35 (m, 4H, 2 x CH_2 - N), 2.97-3.02 (m, 2H, 2 x CH), 1.15-1.24 (m, 16H), 0.77-0.84 (m,12H). **^{13}C NMR (125MHz, CD_3COCD_3, Me_4Si, δ/ppm):** 61.24 (3 x CH_2N of $[A336]^+$), 47.5 (CH_3N), 31.6, 29.3, 28.9, 28, 26 (various CH_2CH_2), 22.3 (CH_2CH_3), 13.4 (3 x CH_3), 172.2 (CO), 172.1 (CO), 77.2(-OCH_2), 71.2 (-CH_2O -), 49.34 (2 x -CH_2-N of $[DGA]^-$), 37.16 (2 x CH), 30.35 (2 x -CH_2), 28.47(2 x CH_2), 23.6 (2 x CH_2), 22.85 (2 x CH_2), 13.93 (2 x CH_3), 10.4 (2 x CH_3).



HP204 = 2-(ethylhexyl)phosphoric acid
HDGA = bis-(ethylhexyl)diglycolamic acid

Scheme 2.7. Procedure adopted for the synthesis of the ionic liquids

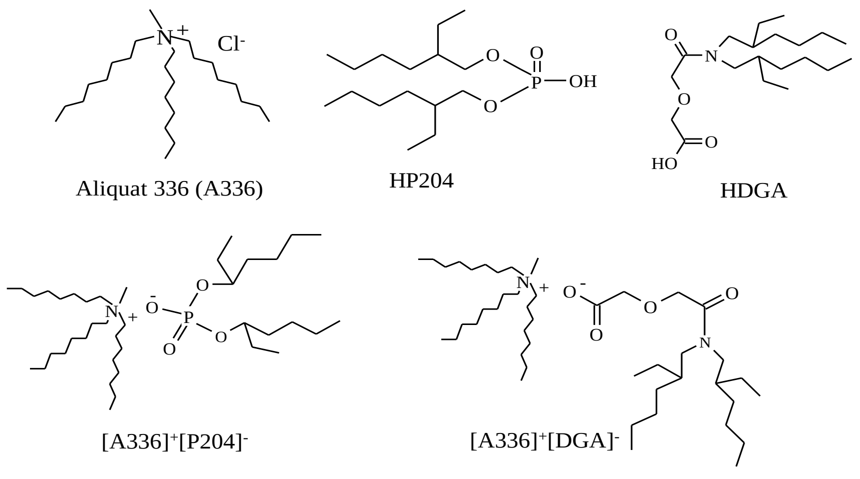
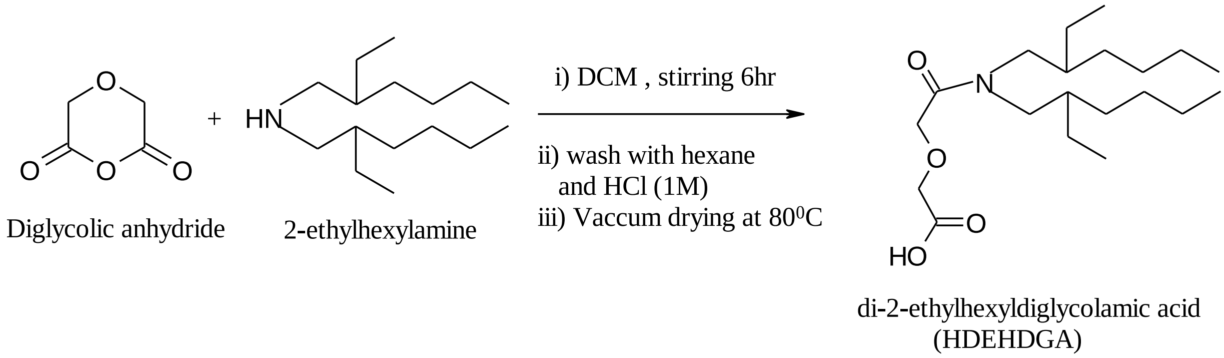


Figure 2.2. Structure of the ionic liquids and their precursors.

2.4.8 Synthesis of Di-2-ethylhexyldiglycolamic acid (HDEHDGA)

The synthetic details of di-2-ethylhexyldiglycolamic acid (HDEHDGA) was carried out as per the procedure given elsewhere [9]. Diglycolic anhydride (0.03 mol) was mixed with 30ml of dichloromethane and stirred in a round bottom flask equipped with a $CaCl_2$ guard tube for about 10minutes. Di-(2-ethyl)hexylamine (0.033 mol) was added drop-wise to the solution of diglycolicanhydride and the reaction mixture was then stirred at room temperature for about 6 hours. The crude reaction mixture was dried in a rotary evaporator at 353 K to remove the solvent, and then dissolved in hexane followed by washing with 1 M hydrochloric acid (20mL x 5). The organic phase was separated out and washed with distilled water (20mL x 5). The separated organic phase was dried in a rotary evaporator at 353 K. A pale yellow colored oil was obtained with > 90% yield. The synthetic pathway is given below in the scheme 2.8.



Scheme 2.8. Synthesis of Di-2-ethylhexyldiglycolamic acid

Characterization

υ/cm^{-1}: 3454 (COOH), 1739 (-CO in COOH), 1622(-CO in –CON), 1226. **^{1}H NMR ($CDCl_3$, δ/ppm relative to TMS):** 10.67 (s, 1H, COOH), 4.32 (s, 2H, $-OCH_2-$), 4.11 (s, 2H, $-CH_2O-$), 3.17-3.31 (m, 4H, 2 x CH_2 - N), 2.96-2.98 (m, 2H, 2 x CH), 1.15-1.24 (m, 16H, 8 x CH_2 of alkyl chain), 0.77-0.84(m, 12H, 4 x CH_3). **^{13}C NMR ($CDCl_3$, δ/ppm relative to TMS):** 172.22 (CO), 172.14 (CO), 77.21($-OCH_2$), 71.1($-CH_2O$ -), 49.34 (2 x $-CH_2-N$), 37.16 (2 x CH), 30.35 (2 x $-CH_2$), 28.47(2 x CH_2), 23.58 (2 x CH_2), 22.86 (2 x CH_2), 13.93 (2 x CH_3), 10.47 (2 x CH_3). **MS (EI+, m/z):** 356.5. All the above results confirm the purity and structure of HDEHDGA shown in scheme 2. 8.

Some typical spectra of the synthesized ionic liquids are shown in the section 2.7 (page 61 – 66) of this chapter for brevity. However, for simplicity and clarity, the characterizations of all the ionic liquids reported in the thesis are given in the form data as shown above.

2.5 Analytical Procedures

2.5.1 Preparation of Cocktail

Dioxane based scintillation cocktail was used for counting both aqueous and organic samples. 1,4-dioxane was used as solvent matrix (primary solvent), naphthalene and 2,5-diphenyl oxazole (PPO) were used as primary scntillator. 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP) was used as secondary scintillator (wave length shifter) and tri-*n*-

octyl phosphine oxide (TOPO) was used as the complexing agent. Above scintillation grade chemicals were used as the following compositions for the preparation of cocktail. Naphthalene: 10%; 2,5-diphenyl oxazole (PPO): 0.7%; 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP): 0.03% and tri-*n*-octyl phosphine oxide (TOPO): 4%. The prepared cocktail was stored in an amber coloured bottle [10] and 5 mL was used each time in scintillation vials for counting the samples. In order to avoid acid quenching encountered during the liquid scintillation counting, not more than 50 μL of the tracer containing samples were always taken for counting and samples with lower activity were counted for a longer time.

2.5.2 Standard uranyl nitrate solution

Nuclear pure uranium metal turnings were washed in carbon tetrachloride to remove the oil and dried over dry air. They were subsequently treated with 4 M nitric acid to remove the oxide layer to obtain a bright silvery surface. The turnings were then washed with water, acetone and finally dried under argon. A standard solution of around 30 mg/mL was made by dissolving 3 g of the dried metal in 10 mL of concentrated nitric acid, evaporating the solution to dryness and finally re-dissolving the uranyl nitrate and making up the solution to 100 mL with 0.01 M nitric acid. An aliquot of 250 μl of this solution was used for the standardization by 2,6-pyridinedicarboxylic acid (PDCA) solution.

2.5.3 PDCA solution

A solution of 0.01 M 2,6-pyridinedicarboxylic acid was prepared by dissolving 1 g of the salt and 0.5 g of sodium hydroxide in 500 mL of distilled water.

2.5.4 Standard europium nitrate solution

Europium nitrate solution was prepared by dissolving Eu_2O_3 in the concentrated nitric acid followed by drying under an IR lamp. The nitric acid was evaporated to dryness and the europium nitrate was redissolved in 0.01M HNO_3. The free acidity of $Eu(NO_3)_3$ solution was measured by acid-base titration along with potassium oxalate solution as a holding agent for Eu(III). The solution was then quantitatively transferred to a preweighed volumetric flask and filled up to the level by 0.01 M HNO_3. The solution of europium nitrate was standardized using a pre-standardized EDTA solution (0.05M) with methyl thymol blue as indicator. From this stock solution, different concentration of Eu(III) solution was prepared as per the requirement.

2.5.5 Potassium oxalate solution

This solution was prepared by dissolving potassium oxalate salt in double distilled water to saturation and adjusting pH to 7 by adding NaOH solution or dilute nitric acid. 5 mL of this solution was used to complex the metal ion under investigation during the titration with NaOH solution for the estimation of free acidity.

2.5.6 Standard EDTA solution

The solution of EDTA was prepared by dissolving required quantity of EDTA crystal by weight in distilled water to get the desired concentration solution. This solution was then standardized by using standard neodymium solution (5.135 mg/g), at pH 6 using methyl thymol blue.

2.5.7 Arsenazo III solution

Arsenazo III solution was prepared by dissolving 200 mg of sodium salt of Arsenazo (III) in 100 mL of 0.01 M sodium hydroxide solution.

2.5.8 pH buffer solutions

2.5.8.1 Buffer 1

A solution of 0.05 M potassium hydrogen phthalate dried at 110^0C was prepared in double distilled water. pH of this solution was 4.01 at 298K.

2.5.8.2 Buffer 2

A solution of 0.01M Borax ($Na_2B_4O_7.10H_2O$) was prepared in double distilled water. pH of this solution was 10 at 298K.

2.5.8.3 Buffer 3

Buffer solution of pH 7.0 was prepared by dissolving 14 gm of triethanolamine(TEA) in 80 mL of distilled water, neutralized by concentrated perchloric acid in order to adjust to pH 7.0 and allowed to stand overnight. The solution was then readjusted to pH 7.0 and diluted to 100 mL.

2.5.9 Nitric acid solutions

Nitric acid solutions were made by suitable dilution from pre-standardized nitric acid stock solution of 10 M concentration. The solutions thus obtained were analyzed by titration with standard sodium hydroxide using phenolphthalein as indicator.

2.5.10 Preparation of the solutions of aqueous complexing agents

Appropriate weight of various aqueous complexing agents such as citric acid, EDTA, DTPA, AHA and oxalic acid were dissolved in distilled water and made up to the required volume to get the solutions on molar basis. The acidity of the corresponding solutions was adjusted to required concentration by adding calculated amount of concentrated nitric acid (~10 M).

2.5.11 Solutions with various concentrations of NO_3^- ions

The total nitrate ion concentration was varied from 0.5 M to 2 M by taking appropriate amounts of sodium nitrate crystal and required quantity of nitric acid with higher concentration (~10 M) in distilled water (up to the required volume) in order to make the desired solution with fixed acidity.

2.5.12 Preparation of C_4mimNO_3 solution

Equivalent amount of the aqueous solution of C_4mimCl and that of $AgNO_3$ (1:1 molar ratio) were mixed for 10 – 15 minutes under constant stirring. The precipitate (AgCl) was filtered and the filtrate was made up to the required volume so as to give a desired concentration of C_4mimNO_3 and nitric acid (1.0 M or 3.0 M) in the resultant solution.

2.5.13 Preparation of solutions with various concentration of NTf_2^- ion

The concentration of NTf_2^- was varied from 0.1M to 0.5 M by taking appropriate amounts of $LiNTf_2$ salt and required quantity of concentrated nitric acid (8 M) in distilled water (up to the required volume) in order to make the desired solution with fixed acidity.

2.5.14 Preparation of solutions with various concentration of C_4mim^+ ion

The concentrations of C_4mim^+ ion in the required concentration of nitric acid (1M and 3M) were varied by taking appropriate amount (in mL) of C_4mimNO_3 solution in the 10 mL standard flask. The acidity of the prepared solution was adjusted to 1M or 3M by adding required quantity of 8M nitric acid to the standard flask followed by the addition of distilled water up to the level.

2.5.15 Liquid – liquid extraction studies

The distribution ratio of a species in a biphasic system is defined as the ratio of the concentration of the species in organic phase to that of in aqueous phase [11]. All the extraction studies were carried out at 298 K unless otherwise mentioned. The equilibration was carried out in a constant temperature water bath. Equal volumes of organic and aqueous phases were used for all extraction studies. A small equilibration tube, equipped with a stopper was used for extraction studies (length: 75 or 100 mm, diameter: 10 or14 mm) and immersed in water bath. The tubes were rotated in upside down manner for about one hour, and separated by centrifugation. Assay of metal tracers was done in both the phases by counting techniques such as liquid scintillation counting (for α, β - emitting radionuclides) and NaI(Tl) detector for γ - emitting radionuclides. The distribution ratio of metal ions (D_M) in both phases were determined as the ratio of the concentration of metal ions (expressed in terms of counts per unit time per unit volume) in organic phase to that in the aqueous phase. As given by the equation 2.1 given below. The separation factors between two metal ions were calculated from the equation 2.2.

$$D_{\mathrm{M}} = \frac{[\mathrm{M}]_{\mathrm{org}}}{[\mathrm{M}]_{\mathrm{aq}}} \tag{2.1}$$

M = Pu(IV) or U(VI) or Am(III) or Eu(III) or other fission products

$$\mathrm{SF} = \frac{D_{\mathrm{Pu(IV)}}}{D_{\mathrm{U(VI)}}} \text{ or } \frac{D_{\mathrm{Pu(IV)}}}{D_{\mathrm{Am(III)}}} \text{ or } \frac{D_{\mathrm{Am(III)}}}{D_{\mathrm{Eu(III)}}} \tag{2.2}$$

2.5.16 Enthalpy measurements

Temperature is an important parameter for the solvent extraction procedure in the reprocessing industries and the extraction trend drastically changes with the temperature [12]. The extraction may be exothermic or endothermic depending on the type of metal ion under investigation. In the present thesis, the effect of temperature on the extraction of some metal ions was studied to derive the enthalpy change accompanied during the extraction of the metal ions from the desired concentration of nitric acid phase by the van’t Hoff equation of the form shown in equation 2.3.

$$\frac{\partial \ln D}{\partial (1/\mathrm{T})} = \frac{-\Delta \mathrm{H}_{\mathrm{tot}}}{\mathrm{R}} \tag{2.3}$$

2.5.17 Viscosity measurements

In solvent extraction processes of spent fuels, viscosity of the extractants as well as diluents used plays a vital role. Viscosity of solvents should be moderate for a normal liquid – liquid extraction systems. The viscosity of all ionic liquids, task specific ionic liquids, their solutions and conventional extracting solvents were measured by the Brookfield viscometer (Model – II+) and have been reported in this thesis. The sample holder was connected to a water-circulated thermostat to maintain desired constant temperature. The activation energy (Ea) required for decreasing the viscosity can be determined from equation 2.4.

$$\eta = \eta_0 e^{E_a / RT} \tag{2.4}$$

2.6 Experimental procedures

2.6.1 Extraction Studies using CMPO – TBP/RTIL [$C_n$mimNTf$_2$ (n = 4, 6 and 8)]

2.6.1.1 Extraction of nitric acid

Extraction of nitric acid by organic phase [0.05M (or 0.2M) CMPO-1.2M TBP/C_4mimNTf$_2$ (or) *n*-DD] was obtained by equilibrating equal volumes of organic and nitric acid phases for one hour. The concentration of nitric acid in aqueous phase was varied from 1 M to 5 M. The amount of nitric acid present in organic and aqueous phase was determined by titrating a known volume of aliquot with pre-standardized sodium hydroxide using phenolphthalein as inidcator. In all titrations, the mass balance of nitric acid was ~99%. The amount of water present in organic phase was determined by Karl – Fischer titration.

2.6.1.2 Effect of HNO_3 concentration

Tri-n-butyl phosphate solution in C_4mimNTf$_2$ and TBP – CMPO in C_4mimNTf$_2$ (or *n* – DD) were prepared. The concentrations of TBP (0.1 – 2M) and CMPO (0.01-0.3 M) were varied in the solutions depending upon the nature of experiments. The organic phase was pre-equilibrated with desired concentration of nitric acid to fix the equilibrium acidity. The concentration of nitric acid in the test solution was varied from 0.01 M to 5 M depending on the nature of the experiments. Extraction of americium(III) and europium(III) as a function of nitric acid was studied by equilibrating organic and aqueous phase (1:1) spiked with corresponding tracers (^{241}Am(III) and $^{(152+154)}$Eu(III)). After one hour of equilibration, the radioactivity of ^{241}Am(III) and $^{(152+154)}$Eu(III) distributed between organic and aqueous phases was measured using a well-type NaI(Tl) scintillation detector. The distribution ratio (D_{Eu}) of europium was determined by using the equation 2.1. Similar experiment was also performed with TRUEX solvent. All the extraction studies for Eu(III) were carried out at 303 K (unless mentioned) and the studies were carried out for Am(III) at 298K (unless mentioned) in duplicate.

2.6.1.3 Effect of CMPO concentration

Owing to know the extraction stochiometry of Am(III) and Eu(III) in CMPO – TBP/RTIL system, the extraction study was carried out by equilibrating organic phase (CMPO-1.2 M TBP/C_4mimNTf$_2$) with varied concentration of CMPO (0.02 – 0.2M) with desired concentration of nitric acid solution (1M –5M) spiked with ^{241}Am (or $^{(152+154)}$Eu) tracer. The distribution ratio was measured by the equation 2.1.

2.6.1.4 Effect of C_4mim^+ concentration

This aqueous phase was equilibrated with organic phase (0.05 M CMPO-1.2 M TBP/$C_n$mimNTf$_2$) spiked with ^{241}Am and the distribution ratio was determined.

2.6.1.5 Effect of $[NO_3^-]_{aq.}$ and RTIL diluents

Effect of nitrate ion concentration on the extraction trend of Eu(III) and Am(III) in ionic liquid medium was carried out by varying the concentration of $NaNO_3$ in the aqueous phase (3M). The distribution ratio of Eu(III) was also measured as a function of alkyl chain length of ionic liquid diluents used.

2.6.1.6 Effect of temperature

Enthalpy change accompanied by the extraction of americium in 0.05 M (or 0.2M) CMPO-1.2 M TBP/C_4mimNTf$_2$ was determined by measuring the distribution ratio of americium (III) (or europium(III)) with desired concentration of nitric acid spiked with ^{241}Am (or $^{(152+154)}$Eu(III)) at various temperatures. The nitric acid concentration was varied from 1.0 to 5.0 M and the temperature was varied from 298 K to 333 K.

2.6.1.7 Effect of [Eu (III)] in aqueous phase

The effect of europium(III) concentration in aqueous phase was studied at 303K - 333K by equilibrating the organic phase with a solution of Eu(III) nitrate in nitric acid (1-5 M) spiked with $^{(152+154)}$Eu(III) tracer. The concentration of Eu(III) in aqueous phase was varied from 5 to 300 mg/mL (near saturation solubility).The loading of Eu in organic phase was determined by measuring the radioactivities of organic and aqueous phases. The radioactivity-balance (and thus mass balance) was ~100% in all the studies.

2.6.1.8 Density measurement

Equal volumes (1 mL) of organic (0.05M CMPO-1.2M TBP/C_4mimNTf$_2$) and aqueous phases (1 – 5M nitric acid) were shaken vigorously. After 10 minutes of vigorous shaking, the equilibration tube containing the phases was centrifuged. The organic and aqueous phase density were determined by transferring the respective phase into a 5 mL specific gravity bottle and measuring its weight using an electronic balance.

2.6.1.9 Strpping of americium(III)

Stripping of Am(III) from the ionic liquid phase was carried out using various complexing agents such as 1M citric acid, 0.5M AHA and 0.03M DTPA. The aqueous phase acidity was 0.1M.

The details of the results and discussions of Am(III) extraction have been discussed in the chapter 3(A) and that of Eu(III) have been discussed in the chapter 4(A) respectively.

2.6.2 Extraction studies using DMDOHEMA / RTIL [$C_n$mimNTf$_2$ (n = 4, 5 and 6)]

2.6.2.1 Extraction procedure

All the extraction studies were carried out at 298 K. Various solutions of DMDOHEMA (0.1 to 0.5 M) in $C_n$mimNTf$_2$ (n = 4, 5 and 6) were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. The equilibration procedure involved mixing of equal volumes of aqueous and organic phases (1ml each). The extraction of actinides as a function of nitric acid was studied by equilibrating the organic and aqueous phase consisting of desired concentration of nitric acid spiked with ^{233}U(VI) tracer (or ^{239}Pu(IV) or ^{241}Am(III) or other fission products). The concentration of nitric acid in the test solution was varied from 0.01 M to 8 M. After one hour of equilibration, the radioactivity of ^{233}U(VI) (or ^{239}Pu(IV)) in both the phases was measured by liquid scintillation counting and the radioactivity of ^{241}Am(III) was measured by a well-type NaI(Tl) scintillation detector.

2.6.2.2 Effect of C_4mim$^+$ and NTf$_2^-$ concentration

The effect of C_4mim$^+$ and NTf$_2^-$ concentration on the distribution ratio of actinides was studied by equilibrating desired concentration of nitric acid and C_4mim$^+$ (0.2 – 1M) or NTf$_2^-$ (0.1 – 0.5 M) ions spiked with ^{233}U(VI) (or ^{239}Pu(IV) or ^{241}Am(III)) tracer. The concentration of additives C_4mim$^+$ or NTf$_2^-$ was varied by adding the required quantity of C_4mimNO$_3$ or LiNTf$_2$ in aqueous phase.

2.6.2.3 Effect of DMDOHEMA concentration

The extraction of U(VI), Pu(IV) and Am(III) as a function of DMDOHEMA concentration in ionic liquid phase was studied by equilibrating the organic phase with aqueous phase containing desired concentration of nitric acid solution spiked with actinide tracers. DMDOHEMA concentration in ionic liquid phase was varied from 0.1 M to 0.5 M.

The details of the results and discussions of this study have been discussed in the chapter 3(B).

2.6.3 Mutual separation of Eu(III) from Am(III) studies in room temperature ionic liquid medium

All the extraction studies were carried out at 298 K unless otherwise mentioned. The organic phase (1 mL) was equilibrated with aqueous phase (1 mL) for one hour. The desired concentrations of HDEHDGA (or D2EHPA) varying from 0.02 M to 0.2 M in C_8mimNTf$_2$ were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. Extraction of americium(III) and europium(III) as a function of nitric was studied by equilibrating the organic phase with aqueous phase containing desired concentrations of DTPA and nitric acid spiked with ^{241}Am(III) (or $^{(152+154)}$Eu(III)) tracer. The pH of the aqueous solution was varied from 1 to 3.5. After one hour of equilibration, the radioactivity of ^{241}Am(III) and $^{(152+154)}$Eu(III) distributed between organic and aqueous phases were measured using a well-type NaI(Tl) scintillation detector. The pH of the aqueous phase at equilibrium was measured. The distribution ratio (D_M) of metal ion was determined using equation 2.1. The separation factors were computed using equation 2.2. The effect of concentrations of citric acid (CA), ethylenediamine tetraacetic acid (EDTA), acetohydroxamic acid (AHA), and DTPA in aqueous phase on the distribution ratio (D_M) was studied by varying their concentrations from 10^{-5} M to 0.05 M. Similarly the effect of [D2EHPA] and [HDEHDGA] in organic phase was studied by varying their concentrations from 0.02 M to 0.2 M.

The details of the results and discussions have been discussed in the chapter 4(B).

2.6.4 Extraction studies using task specific ionic liquids ($ImPNTf_2$ and $DOAImNTf_2$)

2.6.4.1 Effect of HNO_3 concentration

The extraction studies were carried out in the temperature range 298 K –343 K using a constant temperature water bath. The solutions of diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide,$ImPNTf_2$ (0.2–0.5 M) in $C_nmimNTf_2$ (n = 4,6 and 8) were prepared. Similarly, various solutions of N, N–dioctyl-2(3-methyl imidazolium) bis trifluoromethane sulfonamide, $DOAImNTf_2$ (0.1–0.4M) in $C_4mimNTf_2$ (or $C_6mimNTf_2$) were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. All extraction studies were carried out with organic to aqueous phase volume ratio of unity. The concentration of nitric acid in the test solution was varied from 0.35 M to 5 M depending on the nature of organic phase. After one hour of equilibration, the radioactivity of ^{239}Pu (or ^{233}U) distributed between the organic and aqueous phases were measured by liquid scintillation counting. The radioactivity of ^{241}Am was measured using a well-type NaI(Tl) scintillation detector. To know the extraction trend of other metal ions, the solution of $ImPNTf_2$ in $C_4mimNTf_2$ was equilibrated with 3 M HNO_3 spiked with high level liquid waste, HLLW (155 Gwd/Te). The radioactivity of fission products in both the phases was obtained from the gamma spectrometer using HpGe detector.

2.6.4.2 Effect of TSIL concentration

Extraction of plutonium (IV) as a function of the concentration of $ImPNTf_2$ (or $DOAImNTf_2$) concentration in $C_4mimNTf_2$ was studied by equilibrating the organic phase and desired concentration of nitric acid solution (1 – 5M for $ImPNTf_2$ and 0.5 – 5M for $DOAImNTf_2$) spiked with ^{239}Pu tracer. The concentration of $ImPNTf_2$ in ionic liquid was varied from 0.2 M to 0.5M. Similarly, the concentration of $DOAImNTf_2$ in ionic liquid was varied from 0.1 M to 0.4 M. The radioactivity of plutonium before and after equilibration was measured and the distribution ratios were determined. The extraction of nitric acid by organic phase [0.4 M $ImPNTf_2$ (or 0.3M $DOAImNTf_2$)/$C_4mimNTf_2$] was obtained by equilibrating equal volumes of organic and nitric acid phases for one hour. The concentration of nitric acid in aqueous phase was varied from 1 – 5 M in case of $ImPNTf_2$ and 0.5 M to 5 M in case of $DOAImNTf_2$. The amount of nitric acid present in organic and aqueous phase was determined by titrating the known volume of aliquot with sodium hydroxide to phenolpthalein end point.

2.6.4.3 Effect of NTf_2^- concentration

Extraction of plutonium (IV) at various concentrations of NTf_2^- in aqueous phase was studied by equilibrating $C_4mimNTf_2$ and 0.4 M $ImPNTf_2$ (or 0.3 M $DOAImNTf_2$) with 1, 3 and 5M nitric acid containing $LiNTf_2$ (0.1 – 0.5M) spiked with ^{239}Pu (IV) tracer and the distribution ratio of plutonium(IV) was determined. The aqueous phase (1 or 5M nitric acid) with varied concentration of NTf_2^- ion spiked with ^{239}Pu (IV) tracer was equilibrated with the solution of 0.3 M $DOAImNTf_2$ in $C_nmimNTf_2$ (n = 4 and 6) to know the effect of NTf_2^- on Pu (IV) extraction.

2.6.4.4 Effect of C_4mim^+ concentration

The concentration of C_4mim^+ in the aqueous phase was varied by adding aqueous soluble, C_4mimNO_3 (0.2 – 1 M) to the nitric acid (1 or 3 M). The aqueous phase was then equilibrated with 0.3M $DOAImNTf_2$/$C_4mimNTf_2$ spiked with ^{239}Pu (IV) tracer.

2.6.4.5 Effect of temperature

Enthalpy change accompanied by the extraction of plutonium(IV) by 0.4 M $ImPNTf_2$/$C_4mimNTf_2$ or by 0.3 M $DOAImNTf_2$/$C_4mimNTf_2$ was determined by measuring the distribution ratio at various temperatures. The nitric acid concentration in aqueous phase was varied from 1.0 to 5.0 M and the temperature of water bath was varied from 303 K to 333 K.

2.6.4.6 Stripping Studies

Stripping of Pu(IV) was carried out from the ionic liquid phase, 0.4 M $ImPNTf_2$ (or 0.3 M $DOAImNTf_2$)/$C_4mimNTf_2$ after the extraction from 3M nitric acid by employing the complexing agents in the aqueous phase. The complexing agents are 0.5M

AHA and 0.5 M -1 M citric acid (or 0.5 M for $DOAImNTf_2$ and 1 M for $ImPNTf_2$) as the complexing agents in the aqueous phase (0.5 M HNO_3).

The details of the results and discussions of the above study have been discussed in the chapter 5.

2.6.5 Extraction behavior of plutonium(IV) in β – diketonate based ILs

The solutions of TOMATTA (0.2 M) in $TOMANTf_2$ (or xylene), TOMAN (0.2 M) in xylene, HTTA (0.2M) in xylene and the mixture of 0.2M TOMAN and 0.2M HTTA in xylene [or $C_n$mimNTf_2 (n = 4, 6 and 8)] were prepared. Similarly, the solution of THEPATTA (0.2M) in benzene, THEPAN (0.2 M) in benzene and the mixture of 0.2M THEPAN and 0.2 M HTTA in xylene were prepared. For comparing the extraction behavior of these ammonium based ionic liquids with that of imidazolium based ionic liquids, the solutions of $C_n$mimTTA (0.2 M) in $C_n$mimNTf_2 were also prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid to fix the equilibrium acidity. All extraction studies were carried out with organic to aqueous phase ratio of unity. Extraction of plutonium(IV) (or U(VI) or Am(III)) as a function of nitric acid was studied by equilibrating 1 mL of organic with 1 mL of nitric acid solution containing ^{239}Pu(IV) or ^{233}U(VI) or ^{241}Am(III). The concentration of nitric acid in the test solution was varied from 0.5 M to 5 M. After an hour, the equilibration was stopped, and the radioactivity of ^{239}Pu (or ^{233}U) distributed between organic, and aqueous phases was measured by liquid scintillation counting. The radioactivity of ^{241}Am was measured using a well-type NaI(Tl) scintillation detector. The distribution ratio (D_{An}) of actinides, An (An = Pu(IV), U(VI), and Am(III)), in organic phase, was determined from the ratio of the ratioactivities of actinides in organic phase, and aqueous phase. The radioactivity balance was > 99% in all cases. Amount of nitric acid present in organic, and aqueous phase after equilibration of the test solution with 0.2 M TOMATTA in $TOMANTf_2$ (or xylene) and 0.2M $C_n$mimTTA in $C_n$mimNTf_2 was determined by titrating a known volume of aliquot (organic, and aqueous phases) with pre-standardized sodium hydroxide using phenolphthalein as indicator.

The details of the results and discussions of the above study have been discussed in the chapter 6(A).

2.6.6 Extraction behavior of europium(III) in Aliquat – based ionic liquids

All the extraction studies were carried out at 298 K. Various solutions at $[A336]^+[P204]^-$ or $[A336]^+[DGA]^-$ in a suitable diluent were prepared. The organic phase was pre-equilibrated with desired concentration of nitric acid. Extraction of europium(III) and americium(III) as a function of nitric was studied by equilibrating the organic phase (1 mL) with aqueous phase (1 mL) containing desired pH spiked with $^{(152+154)}$Eu(III) or ^{241}Am(III) tracer (20 mg/L in all experiments). The initial pH of the aqueous solution was varied from pH 1 to 4 using nitric acid. After one hour of equilibration, the radioactivity of ^{241}Am(III) and $^{(152+154)}$Eu(III) distributed between organic and aqueous phases were measured using a well-type NaI(Tl) scintillation detector. The pH of the aqueous phase at equilibrium was measured. The distribution ratio (D_M) of the metal ion and their separation factor (SF) were computed using equation 2.1 and 2.2 respectively. The effect of DTPA concentration in aqueous phase on the distribution ratio (D_M) was studied by varying the concentration of DTPA from 10^{-5} M to 10^{-3} M. Similarly the effect of $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ in organic phase was studied by varying the concentration of ionic liquid from 0.004 M to 0.05 M.

The details of the results and discussions of the above study have been discussed in the chapter 6(B).

2.7 Some typical spectra of synthesized ionic liquids and HDEHDGA

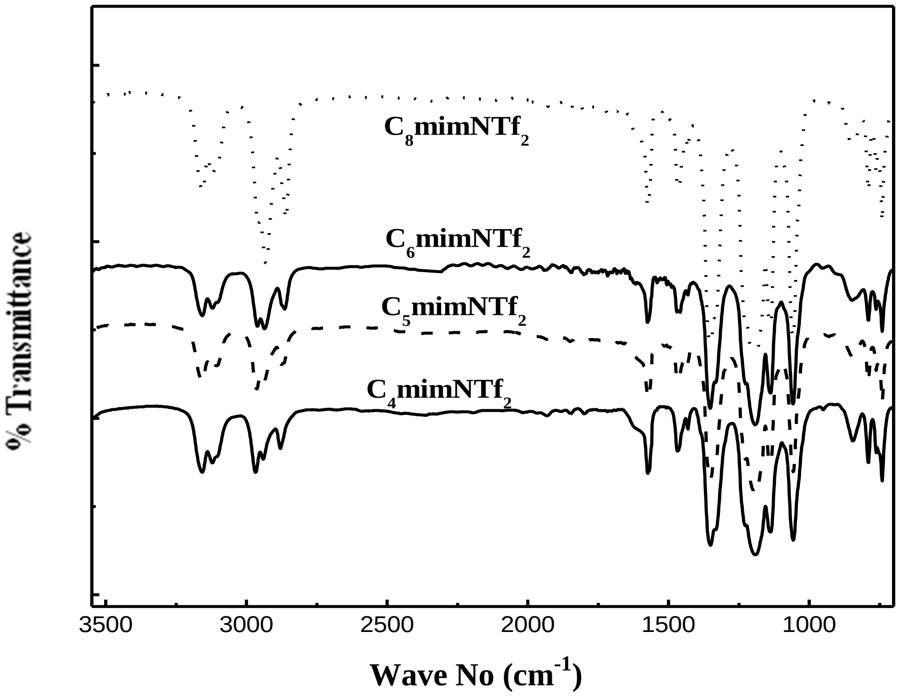


Figure 2.3. FTIR spectra of $C_n$mimNTf$_2$ (n = 4, 5, 6 and 8)

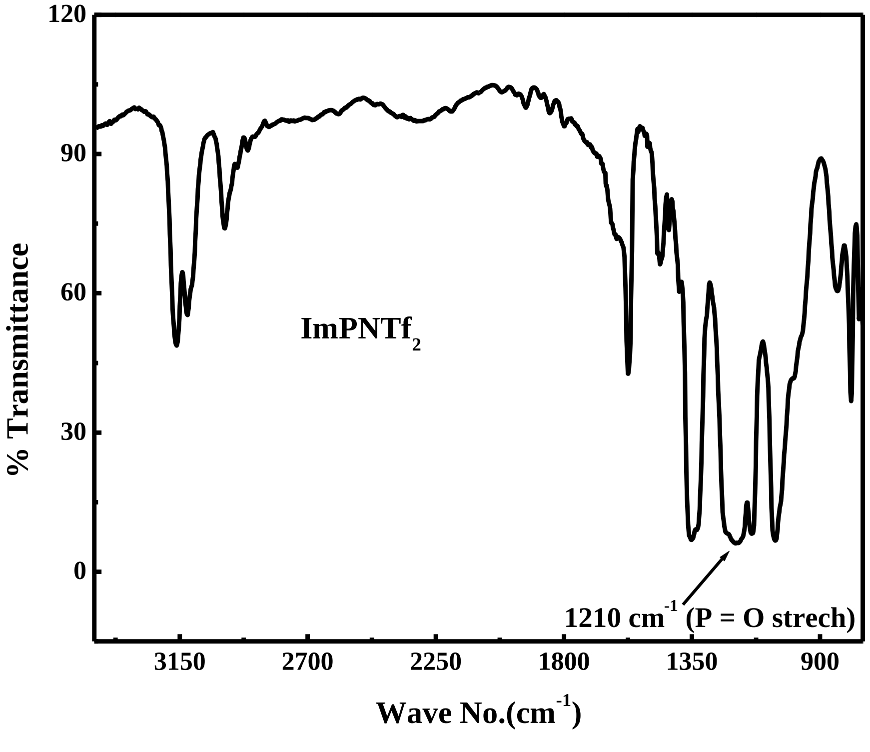


Figure 2.4. FTIR spectra of phosphonate based ionic liquid (ImPNTf$_2$)

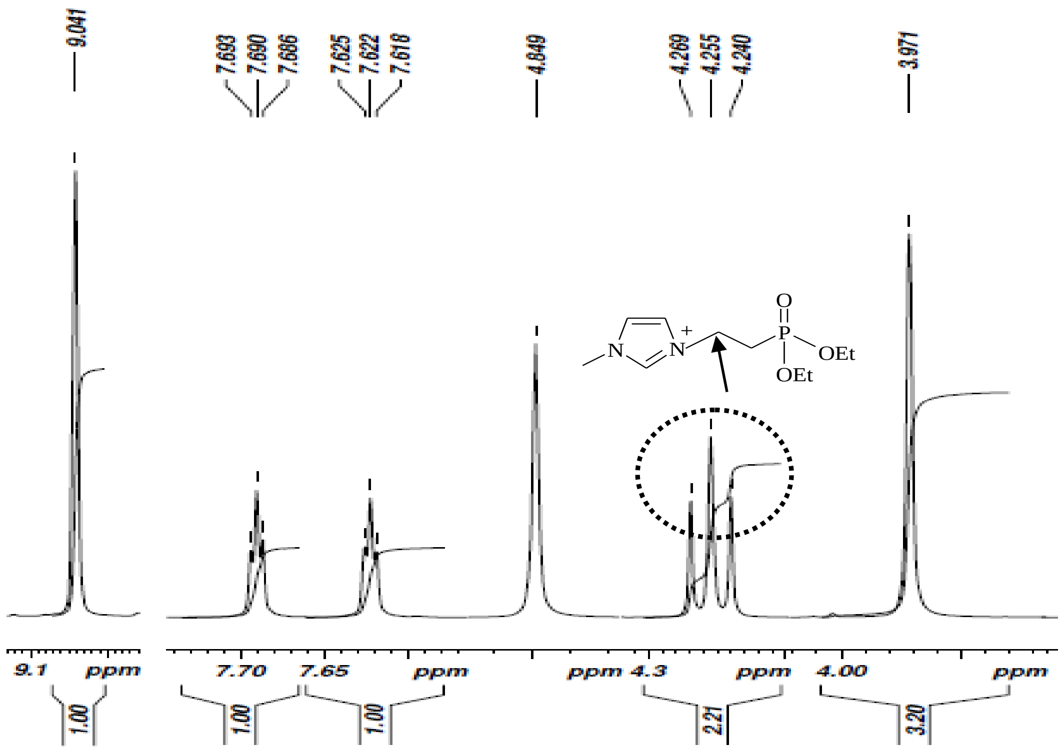


Figure 2.5. ^{1}H NMR spectrum of phosphonate based ionic liquid (ImPNTf$_2$)

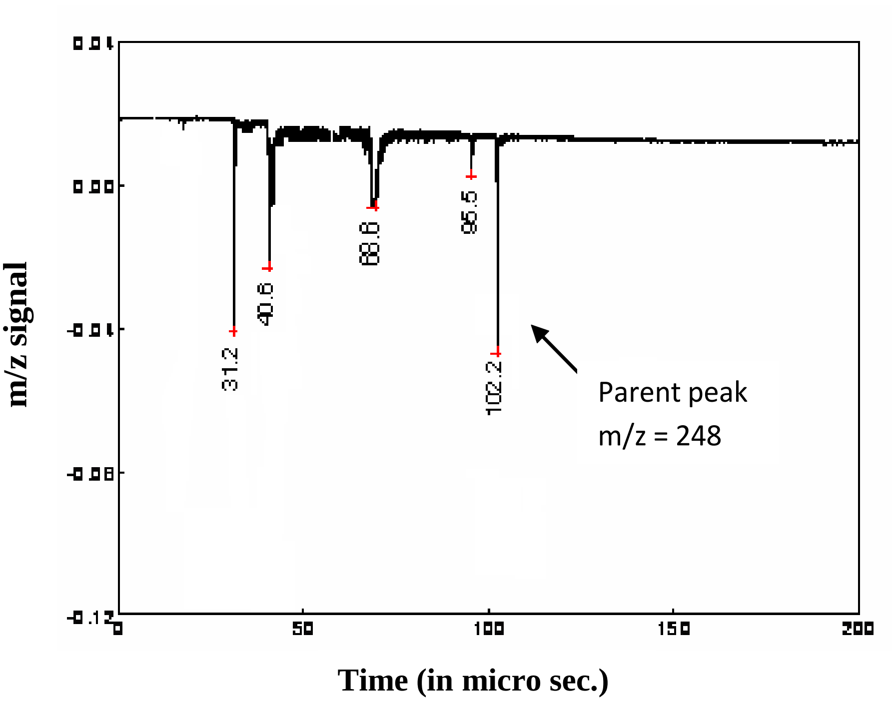


Figure 2.6. TOF – MS of phosphonate based ionic liquid (ImPNTf$_2$)

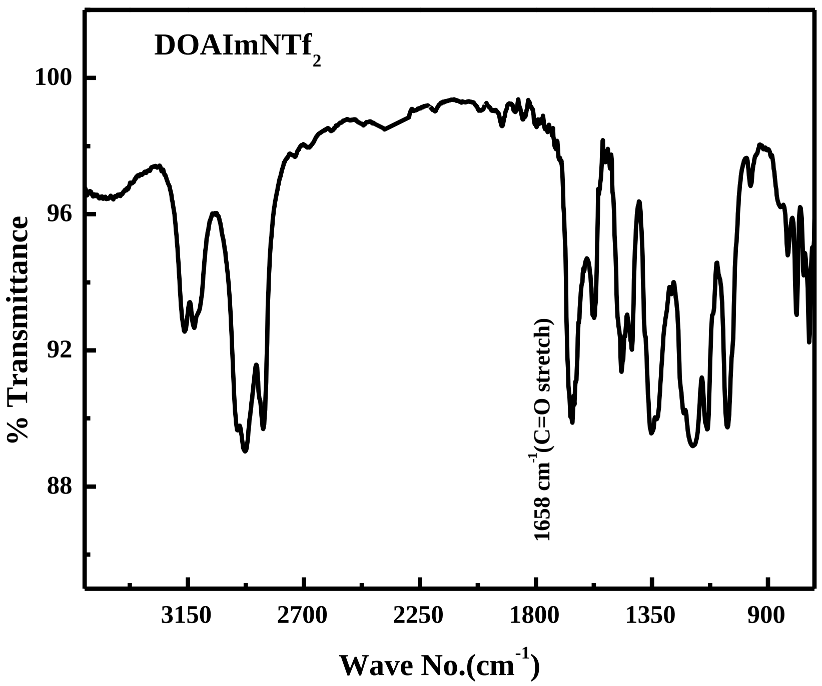


Figure 2.7. FTIR spectra of amide based ionic liquid (DOAImNTf$_2$)

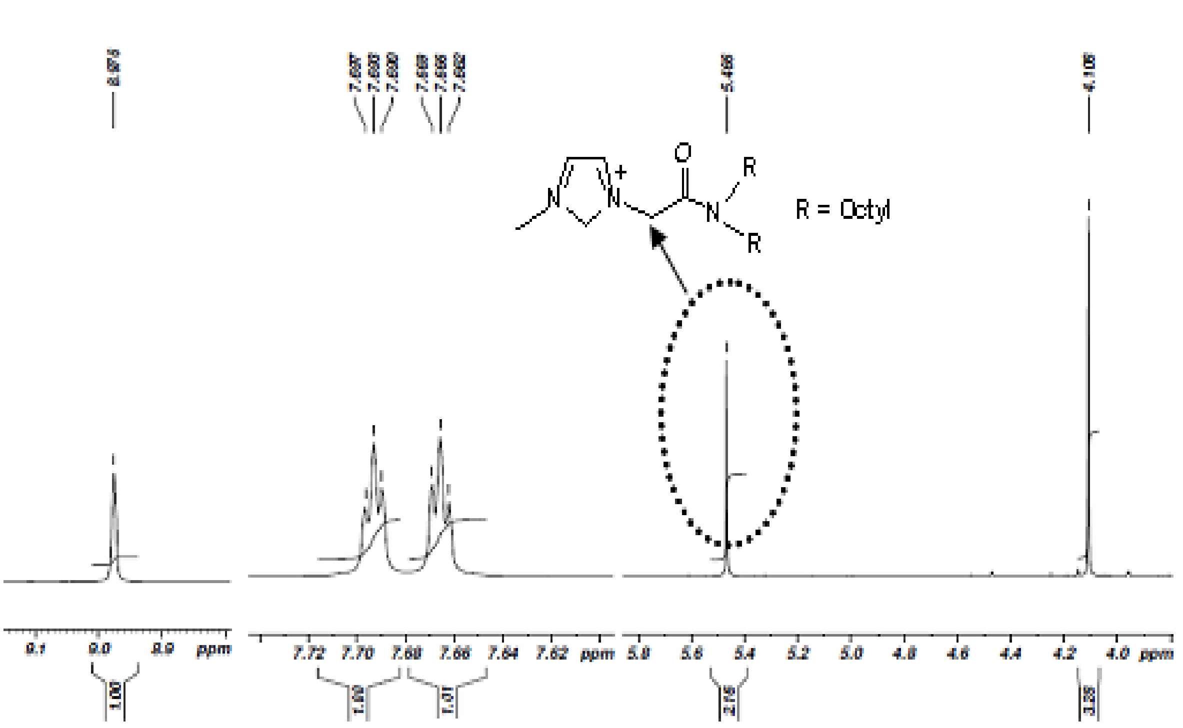


Figure 2.8. ^{1}H NMR spectrum of amide based ionic liquid (DOAImNTf$_2$)

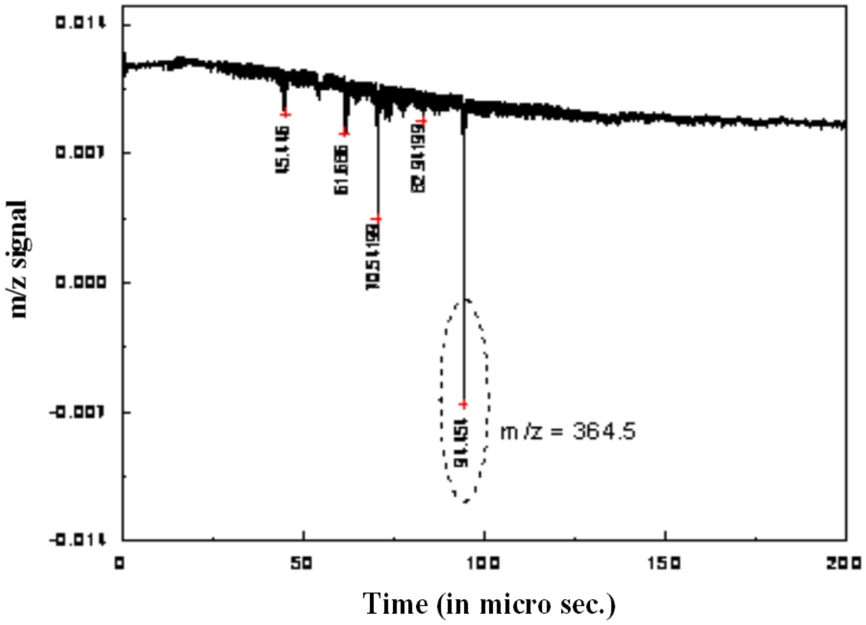


Figure 2.9. TOF – MS of amide based ionic liquid (DOAImNTf$_2$)

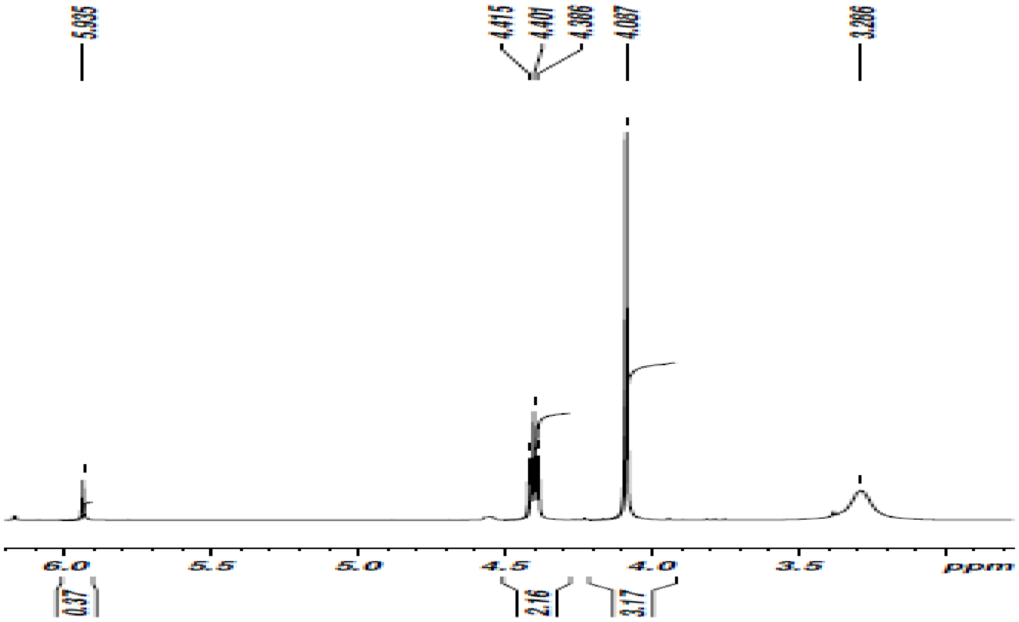


Figure 2.10 A. 1H NMR spectra of 1-butyl-3-methylimidazolium bis(trifluormethanesulfonyl)imide, C$_4$mimTTA

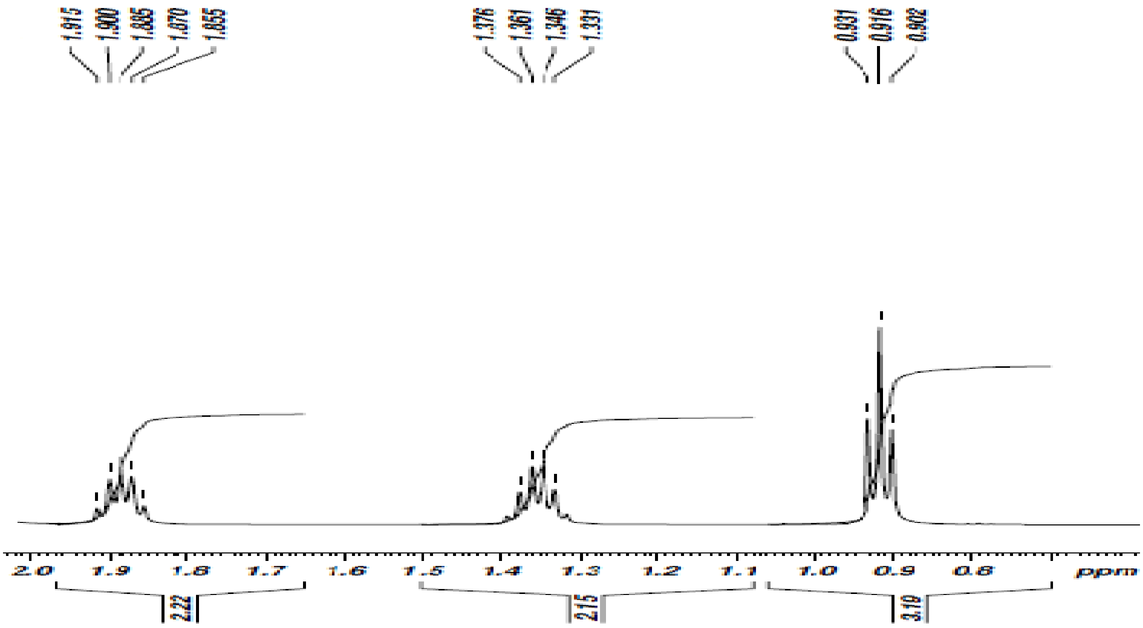


Figure 2.10 B. 1H NMR spectra of 1-butyl-3-methylimidazolium bis(trifluormethanesulfonyl)imide, C$_4$mimTTA

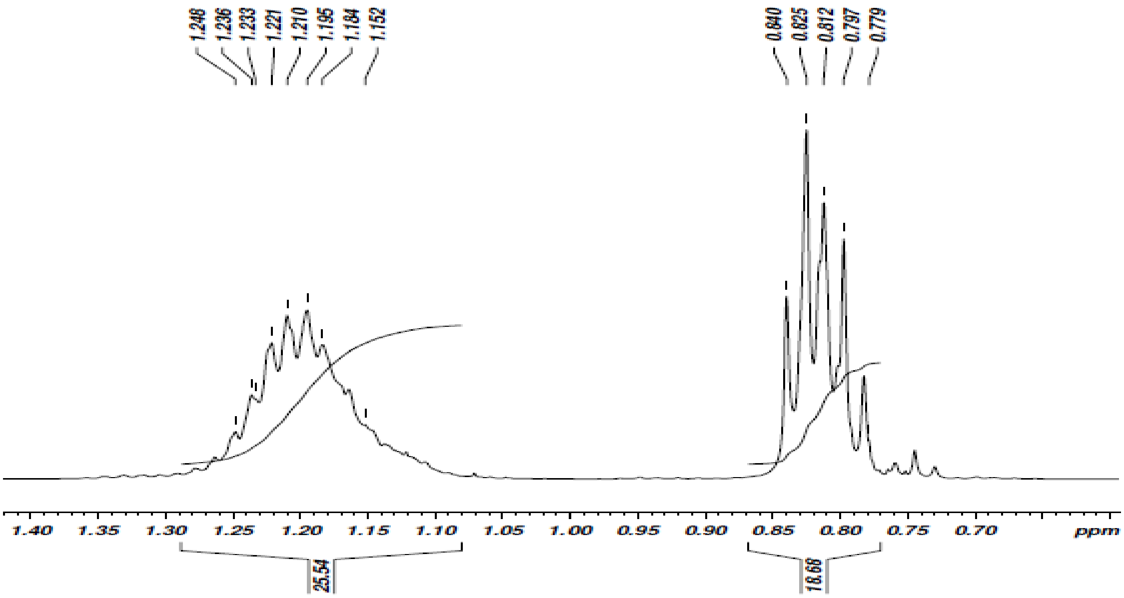


Figure 2.11 A. ^{1}H NMR spectra of Diglycolamic acid, HDEHDGA

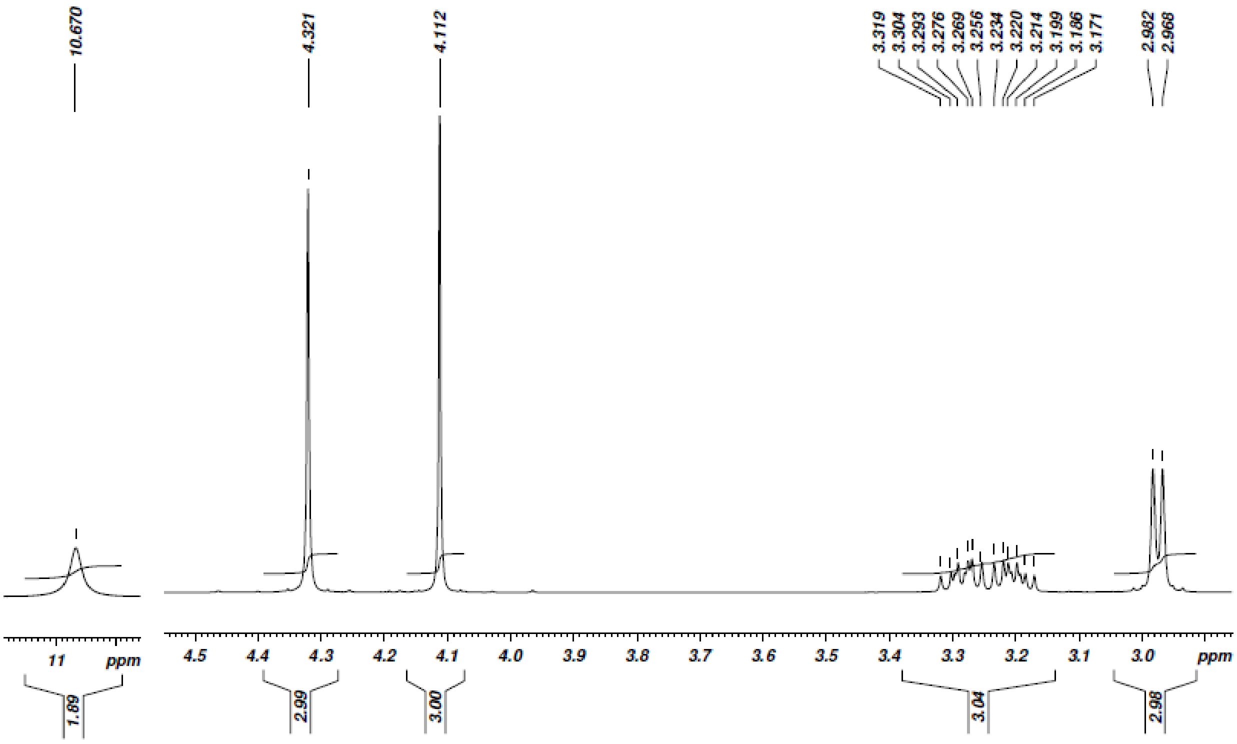


Figure 2.11 B. ^{1}H NMR spectra of Diglycolamic acid, HDEHDGA

2.8 References

1. P. R. Vasudeva Rao: PhD Thesis, Bombay university, 1978, pp 62.
2. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. Green Chem. 3 (4) (2001)156–164.
3. P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts, Inorganic Chemistry, 35 (5) (1996) 1168-1178.
4. G. Koch, Reprocessing by Quaternary Ammonium Nitrates: Laboratory Studies. In: Solvent Extraction Chemistry of Metals, Ed: Mckay, H. A. C., Healy, T. V., Jenkins, I. L. MacMillan, 1966, pp.247-266, England.
5. J. H. Davis Jr, Task-Specific Ionic Liquids. Chemistry Letters, 33(2004) 1072 - 1077.
6. K. M Lee, Y. T Lee, I. J. B. Lin, Supramolecular liquid crystals of amide functionalized imidazolium salts. J. Mater. Chem., 13 (5) (2003) 1079–1084.
7. H. Mehdi, , K. Binnemans, V. Hecke, L.V. Meervelt, P. Nockemann, Hydrophobic ionic liquids with strongly corodinating anions. Chem. Commun. (2010) 234-236.
8. X. Sun, Y. Ji, F. Hu, Bo. He, Ji. Chen, D. Li, The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. Talanta 81 (4-5) (2010) 1877–1883.
9. Y. Sasaki, G.R. Choppin, Solvent extraction of Eu, Th, U, Np and Am with N, N' –dimethyl-*N,N*' di-hexyl-3-oxapentanediamide and its analogous compounds, Anal. Sci. 12 (2) (1996) 225-230.
10. J. C. Warf, Extraction of Ce(IV) nitrate by Tributylphosphate, J. Am. Chem. Soc. 71 (9) (1949) 3257-3258.
11. B. A. Moyer, Ion Exchange and Solvent Extraction. A series of Advances, Volume 19, CRC Press, Taylor and Francis Group 2010.
12. L. L. Burger, The neutral organophosphorous compounds as extractants. Nucl. Sci. Eng. 16 (1963) 428 - 439.

Chapter - 3

CHAPTER – 3

Extraction behavior of some actinides using room temperature ionic liquids as diluent

This chapter deals with the application of room temperature ionic liquid as a diluent for the extraction of some actinides. The RTIL used in study is 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $C_n$mimNTf$_2$ (n = 4, 5 and 6). The results on extraction behavior of americium (III) in the solution of *n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyphosphine oxide (CMPO) and tri-n-butyl phosphate (TBP) in C_4mimNTf$_2$ are reported. Similarly, the extraction behavior of actinides (Pu(IV), U(VI) and Am(III)) in the solution of *N,N'*-DiMethyl-*N,N'*- Di-Octyl-2-(2-(hexyloxy)ethyl)malonamide (DMDOHEMA) in $C_n$mimNTf$_2$ (n = 4, 5 and 6) is discussed in detail.

3.1 Introduction

Room temperature ionic liquids [1] are receiving increased attention for possible applications in the area of nuclear fuel cycle [2-13]. Essentially they are explored as an alternative to the molecular diluent, *n*-DD in solvent extraction. The properties such as insignificant vapour pressure, amazing ability to dissolve organic and inorganic compounds, tunability to task-specific forms etc. make RTILs popular for aqueous reprocessing applications, and the wide electrochemical window of RTILs offers huge scope for non-aqueous reprocessing applications [6-10].

Dai *et al.* [2] and Visser *et al.* [4] studied the extraction of group I and II metal ions by crown ethers present in ionic liquid. Chun *et al.* [14] studied the influence of structural variation in RTILs on the selectivity and efficiency of competitive alkali metal ion extraction by crown ether. The results obtained from those studies indicated that the extractants in conjunction with RTIL diluents have provided an unprecedented extraction of target metals from aqueous solution under the condition that gives negligible or meager extraction with customary diluents. This was attributed to the extraordinary solvating ability of RTILs in extracted phase. Dietz and co-workers [15- 18] studied the extraction behavior of several metal ions of nuclear interest using neutral extractants like crown ether and tri-*n*-butyl phosphate (TBP) present in RTIL medium. The mechanism of extraction in RTIL phase was reported to differ significantly in RTIL medium depending upon the aqueous phase conditions. Ion exchange between target metal ion and RTIL was reported as one of the primary mode of metal transfer in RTIL phase. Dietz *et al.*[15 –18] proposed that unlike the customary diluents, RTIL diluents are not "inert" and may pose several implications on the "greenness" of the solvent in solvent extraction processes.

Americium–241 is one of the long-lived alpha-emitting radionuclide formed in significant quantities in a nuclear reactor. They are rejected in to high-level liquid waste (HLLW) after separating uranium and plutonium from the dissolver solution by PUREX process. The trivalent actinides are separated from HLLW by the TRUEX solvent composed of a mixture of 1.2 M tri-*n*-butyl phosphate - 0.2 M *N*-octyl(phenyl)-*N,N*-diisobutyl-carbamoylmethyphosphine oxide (CMPO) in *n*-dodecane [19]. Visser *et al.*[20] reported the distribution ratio of Am(III), Pu(IV), U(VI) and Th(IV) in 0.1 M CMPO/C_4mimPF_6 at various nitric acid concentrations. The distribution ratio of Am(III) was reported to decrease with increase in the concentration of nitric acid. However, detailed extraction behavior of Am (III) in RTIL solution was not reported. The extraction behavior of Pu(IV) in a solution of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in ionic liquid was reported by Lohithakshan *et al.*[11,12].

In addition to CMPO, amide based extractants are regarded as promising candidates for the separation of trivalent acinides from HLLW. They have gained prominence over phosphorous based extractants due to complete incenerablity and formation of aqueous soluble radiolytic degradation products [21-26]. Among the diamides, *N,N'*-DiMethyl-DiButyl-TetraDecylMalonamide (DMDBTDMA) and *N,N'*-DiMethyl-*N,N'*- Di-Octyl-2-(2-(hexyloxy)ethyl)Malonamide (DMDOHEMA) are regarded as promising extractants for the separation of minor actinides [23 - 26]. The latter compound, DMDOHEMA has some advantages such as enhanced organophilicity and limited third-phase formation over DMDBTDMA. Shimojo *et al.*[27] studied the extraction of lanthanides in a diglycolamide derivative tetraoctyldiglycolamide (TODGA) present in $C_n$mimNTf_2. The authors reported exceptional extraction in ionic liquid media as compared to the isooctane system. Shen *et al.*[13] reported the extraction of U(VI) in tetrabutyldiglycolamide (TBDA) and tetramethyldiglycolamide (MBDA) present in ionic liquid medium. Efficient extraction of U(VI) at low acidities was reported in this case also. The mode of uranyl ion partitioning in ionic liquid phase was shown to change from ion exchange to the traditional M-solvate complex with the increase of hydrophobicity of ionic liquid.

The objective of the studies discussed in this chapter is to report in the extraction behavior of americium(III) by TRUEX solvent (CMPO-TBP) present in ionic liquid medium namely, 1-butyl-3-methylimidazolium bis(trifluoromethansulfonyl)imide (C_4mimNTf$_2$) and to compare the results with that of the conventional TRUEX solution (CMPO – TBP /*n*-DD) in part “A”. In part “B”, it details the extraction behavior of some actinides (U(VI), Pu(IV) and Am(III)) in DMDOHEMA in the ionic liquid, 1-alkyl-3-methylimidazolium bis(trifluorometahnesulfonyl)imides ($C_n$mimNTf$_2$; n = 4,5 and 6).

The synthesis of ionic liquids, $C_n$mimNTf$_2$ (n = 4 – 6) and the details of the experimental parts of the present study has been discussed in the section 2.4.2, 2.6.1 and 2.6.2 of the chapter 2 respectively.

A. Extraction behavior of americium(III) in CMPO-TBP extractant in room temperature ionic liquid

3.2 Results and Discussions

3.2.1 Effect of nitric acid

The distribution ratios of americium(III) in CMPO-1.2 M TBP/C_4mimNTf$_2$ at various concentrations of nitric acid are tabulated in table 3.1. The data are compared with the distribution ratio of americium in TRUEX solvent as well as with 1.2 M TBP/C_4mimNTf$_2$. Extraction of Am(III) in 1.2 M TBP/C_4mimNTf$_2$ is insignificant and $D_{Am(III)}$ is of the order of ~10^{-2}. However, a remarkable enhancement in the distribution ratio is observed in the presence CMPO. The $D_{Am(III)}$ in 0.2 M CMPO-1.2 M TBP/C_4mimNTf$_2$ decreases from > 3000 to 274 with increase in the concentration of nitric acid from 1.0 M to 5.0 M. In contrast, a maximum *D* value of 23 obtained for the extraction of americium in TRUEX solvent at 3 M nitric acid. It is interesting to note from table 3.1 that in 3 M nitric acid medium, a CMPO concentration of 0.05 M (in RTIL) only is required for obtaining a comparable distribution ratio with that of TRUEX solvent. This indicates that by using C_4mimNTf$_2$ as diluent, the amount of CMPO needed for the extraction of Am(III) from high-level liquid waste (3 –4 M in nitric acid) can be minimized by a factor of four. Moreover, by using 0.2 M CMPO-1.2 M TBP/C_4mimNTf$_2$, the trivalent actinides can be extracted in fewer number of extraction stages as compared to extraction by TRUEX solvent.

Table 3.1. Distribution ratio of Am (III) in a solution of CMPO-1.2 M TBP in C_4mimNTf$_2$ (or *n*-DD) as a function of nitric acid concentration. T = 298 K, A/O =1, Volume = 1 mL, [Am(III)] =20 mg/L

$[HNO_3]_{eq.}$ /M	Distribution ratio of Am(III)				
	Concentration of CMPO in CMPO-1.2 M TBP/C_4mimNTf$_2$				TRUEX solvent (0.2 M CMPO-1.2 M TBP/*n*-DD)
	0.0 M	0.02 M	0.05 M	0.2 M	
1	0.03	7.7	151	> 3000	16.1
2	0.03	3.3	41	1792	22.7
3	0.04	2.2	27	905	22.6
4	0.05	1.8	17	485	20.4
5	0.07	1.5	12	274	17.3

3.2.2 Effect of C_4mim^+ concentration

It is observed from the table 3.1 that the extraction trend of actinides in molecular diluent (TRUEX solvent) follows the initial increase followed by the decrease in the distribution ratio at higher acidities. Generally, the extraction of actinides from nitric acid medium by a neutral extractant present in molecular diluent exhibits this trend. However, the unusual trend of decrease in the distribution ratio of americium (III) with increase in nitric acid concentration in case of ionic liquid indicates that the mode of americium (III) transfer in RTIL solution is different from *n*-DD system. In this context, Giridhar *et al.*[28] studied the extraction behavior of uranium (VI) by a neutral extractant TBP present in RTIL medium (RTIL= $C_4mimNTf_2$ and C_4mimPF_6) and reported the unique extraction characteristics depending upon the nature of RTIL. The decrease of distribution ratio was reported for the extraction of uranium (VI) in TBP/$C_4mimNTf_2$ at low nitric acid concentrations (< 0.5 M) and continuous increase of distribution ratio at high acid concentrations (> 5.0 M). The extraction observed at high nitric acid concentration was attributed to the contribution of ion exchange reaction arising from RTIL. In 1.0 – 4.0 M range, uranium (VI) was extracted as neutral uranyl nitrate complex, $UO_2(NO_3)_2(TBP)_2$, by RTIL phase. Similarly, Dietz *et al.* [15] reported the involvement of cation exchange mechanism for the extraction of uranium by TBP/$C_4mimNTf_2$ at low nitric acid concentrations (<0.5 M) and a neutral uranyl nitrate extraction at higher nitric acid concentrations. Moreover, Dietz *et al.* [16, 17] also reported the cation exchange mechanism for the extraction of Sr(II) by dicyclohexano-18-crown-6 (DCH18C6) present in 1-alkyl-3-methylimidazolium (C_nmim) based ionic liquids. The mechanism was reported to change from cation exchange to the ion pair extraction as the hydrophobicity of ionic liquid cation was increased. Nakashima *et al.* [29] proposed a cation exchange mechanism for the extraction of trivalent lanthanides by CMPO/C_4mimPF_6 (or $C_4mimNTf_2$). The equation proposed by Nakashima *et al.*[29] for the extraction of lanthanides is represented in equation 3.1.

$$M^{3+}_{aq} + x\,CMPO_{org} + 3\,C_4mim^{+}_{org} \Leftrightarrow (M^{3+}(CMPO)_x)_{org} + 3\,C_4mim^{+}_{aq} \qquad (3.1)$$

To study the involvement of ion exchange mechanism for the extraction of americium(III) in the present case, the distribution ratio of americium was measured at various concentrations of C_4mimNO_3 (soluble in aqueous phase) present in aqueous phase. Since the added C_4mimNO_3 was dissolved in the ionic liquid to some extent, the aqueous phase concentration of C_4mim^+ ion at equilibrium was not known. Thus, figure 3.1 shows the variation in the distribution ratio of Am(III) as a function of initial concentration of C_4mim^+ ion rather than equilibrium concentration. If the mechanism shown in equation 3.1 holds good for the extraction of americium (III), then log *D* against log [C_4mim^+] should result in a straight line with a negative slope. The plot of log *D* –log [C_4mim^+] is shown in figure 3.1. A slope value of –0.2 obtained in the present study indicates that extraction of americium is not exclusively governed by ion exchange reaction shown in equation 3.1.

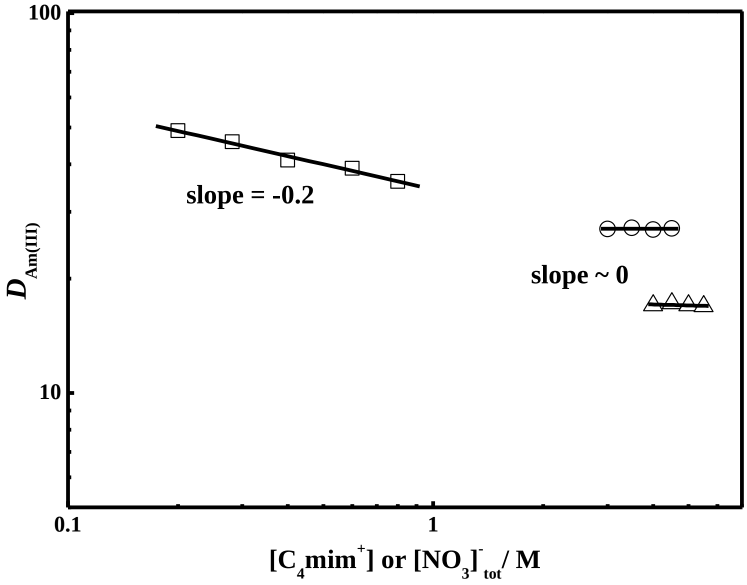


Figure 3.1. Variation of D with concentration of C_4mim^+ or $[NO_3]_{tot}$ for the extraction of Am(III) from nitric acid medium Solvent: 0.05 M CMPO-1.2 M TBP/$C_4mimNTf_2$; T = 298 K;

□ C_4mimNO_3 in 1 M nitric acid varied from 0.2 - 0.8 M.
○ $NaNO_3$ in 3 M nitric acid varied from 0.5 to 1.5 M.
△ $NaNO_3$ in 4 M nitric acid varied from 0.5 to 1.5 M.

Moreover, if ion exchange is the predominant mode for extraction, then a high distribution ratio could be expected for the extraction of Am(III) in RTIL alone. However, a negligible *D* value (~10^{-2}) obtained for americium extraction in the absence of CMPO (table 3.1). This indicates the necessity of CMPO in RTIL solution and excludes the predominance of ion exchange mechanism for americium (III) extraction. Nevertheless, the possibility of ion exchange process could not be ruled out since the distribution ratio of americium decreases with increase in the concentration of C_4mim^+ cation in aqueous phase. Figure 3.1 also shows the variation in distribution ratio for the extraction of americium (III) in 0.05 M CMPO-1.2 M TBP/$C_4mimNTf_2$ at different concentrations of nitrate ion in aqueous phase. It is observed that the changes in distribution ratio of americium are insignificant (slope $\simeq$ 0).

3.2.3 Effect of CMPO concentration

As reported by Horwitz *et al.* [30], the extraction stoichiometry of americium in TRUEX solution is determined by slope analysis. CMPO being a neutral ligand extracts americium (III) in the form of neutral americium (III) nitrate complex as shown in the equation 3.2. Thus at constant nitrate ion concentration, the variation of log D with log [CMPO] for the extraction of americium (III) can result in a slope (x) according to the equation 3.5.

$$\mathrm{Am^{3+}_{aq.}} + 3\mathrm{NO_{3\,aq.}^{-}} + \mathrm{x\,CMPO_{IL.}} \Leftrightarrow [\mathrm{Am(NO_3)_3.(CMPO)_x}]_{\mathrm{IL}} \tag{3.2}$$

$$\mathrm{K} = \frac{\mathrm{Am(NO_3)_3(CMPO)_x}\,]_{\mathrm{IL}}}{[\mathrm{Am^{3+}}]_{\mathrm{aq.}}[\mathrm{CMPO}]^{\mathrm{x}}[\mathrm{NO_3^-}]^{3}_{\mathrm{aq.}}} \tag{3.3}$$

$$\mathrm{K} = \frac{D}{[\mathrm{CMPO}]^{\mathrm{x}}[\mathrm{NO_3^-}]^{3}_{\mathrm{aq.}}} \tag{3.4}$$

$$\log D = \log \mathrm{K'} + \mathrm{x}\ \log\ [\mathrm{CMPO}]_{\mathrm{IL}} \tag{3.5}$$

Where $\mathrm{K}^{'}$ is constant at constant nitrate concentration. Figure 3.2 shows the plot of log D against log[CMPO]. It is seen that the D value increases with increase in the concentration of CMPO. A slope value of 3.0 (x = 3) is obtained for the extraction of americium(III) from 1.0 M nitric acid medium. Thus, the metal-solvate stoichiometry for the extraction of americium(III) in CMPO-TBP/$\mathrm{C_4mimNTf_2}$ resembles that of TRUEX system at 1.0 M nitric acid medium, wherein three molecules of CMPO are involved in co-ordination with americium in organic phase. A similar 1 : 3 complex ($\mathrm{Ln^{3+}}$:CMPO) was reported for the extraction of some trivalent lanthanides from neutral solution by CMPO/RTIL [29]. In 3.0 M nitric acid medium, the slope value decreases to 2.4. Mathur *et al.* [31] reported a similar value of 2.5 for the extraction of americium (III) from 3.0 M nitric acid medium by TRUEX solvent. Thus, the present study reveals that the stoichiometry of americium (III) transfer from 1.0 to 3.0 M nitric acid medium to CMPO-TBP/RTIL phase occurs with the stoichiometry observed for TRUEX solvent. However, in contrast to *n*-DD, the americium (III) transfer in the present case is facilitated by the unique solvating ability of RTIL that seems to be responsible for extraordinary extraction. In 5.0 M nitric acid medium, the slope value further reduces to 2.1. Under these conditions, the extraction of Am(III) by TRUEX solvent is not available in literature for comparison.

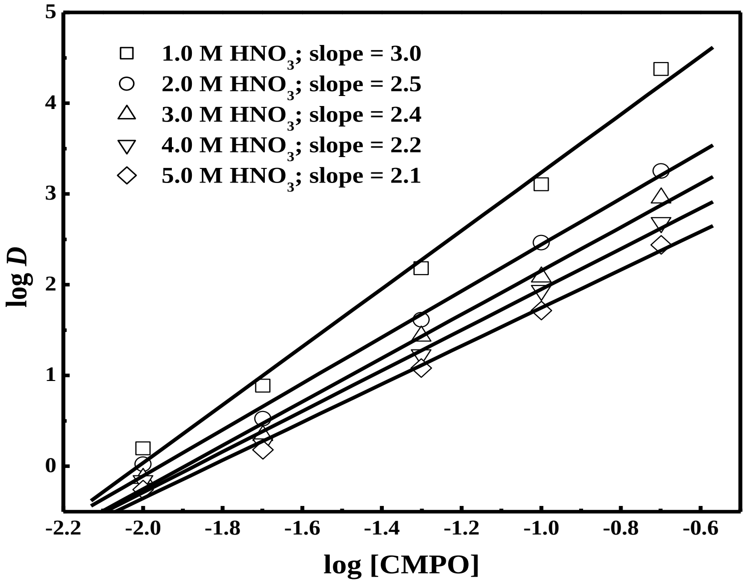


Figure 3.2. log *D* -log [CMPO] plot for the extraction of Am (III) from nitric acid medium at 298 K. O : A = 1 :1, Equilibration time = 1 hr

3.2.4 Effect of TBP concentration

The co-solvent, tri-*n*-butylphosphate in TRUEX solution acts as phase modifier. Mathur *et al.* [31] studied the variation of TBP concentration in TRUEX solution and reported the distribution ratio of several metal ions including americium (III). It was reported that TBP was not involved in extraction of americium (III) as the distribution ratio of americium decreased marginally with increase of TBP concentration. Similarly, the role of TBP in a solution of 0.05 M CMPO-TBP in $C_4mimNTf_2$ was studied by measuring the distribution ratios of americium at various concentrations of TBP. Table 3.2 shows the distribution ratios of americium (III) in 0.05 M CMPO-TBP/$C_4mimNTf_2$. It is observed that distribution values decrease gradually with increase in the concentration of TBP. The reason for such behavior is not clear at present, however, the decrease in *D* values indicate that TBP is not involved in the extraction of americium. In TRUEX solvent, TBP is added as modifier to avoid third phase formation. The results shown in table 3.2 may have several implications on third phase formation of trivalents, when RTILs are used as diluents in place of *n*-DD. The details on this study are reported in the chapter 4.

Table 3.2. Variation in the distribution ratio of americium (III) as a function of TBP concentration. Extractant: 0.05 M CMPO- TBP/C_4mimNTf$_2$, T = 298 K, A/O = 1 mL, [Am(III)] = 20 mg/L

[TBP]/M	$D_{Am(III)}$	
	3 M HNO_3	4 M HNO_3
0.0	643	161
0.1	228	128
0.25	102	76
0.5	66	42
0.8	38	23
1.2	27	17
2.0	16	13

3.2.5 Extraction nitric acid and water

Comparison in the extraction of nitric acid and water by TRUEX solvent and 0.05 M CMPO-1.2 M TBP/C_4mimNTf$_2$ is shown in figure 3.3. It is observed that the extraction of nitric acid by organic phase in both cases increases with increase in the concentration of nitric acid in aqueous phase. This could be due to the increase in protonation of TBP and CMPO in organic phase with increase of nitric acid concentration. The water extraction isotherms by organic phases are also shown in figure 3.3. The amount of water extracted by TRUEX solvent decreases with increase in the concentration of nitric acid. A similar behavior was also reported for the extraction of nitric acid by tri-*n*-butylphosphate/*n*-DD [32]. Increase in the concentration of nitric acid in aqueous phase reduces the water activity and lowers the extraction of water by organic phase. In contrast to this observation, extraction of water by RTIL phase increases with increase in the concentration of nitric acid. A similar behavior in case of extraction of water by TBP/C_4mimNTf$_2$ has been described elsewhere [28]. This could perhaps be due to the employment of ionic nature of the diluent (~1.5 M C_4mimNTf$_2$) that differs from molecular nature of *n*-DD. In addition nitric acid is also extracted by organic phase, which also requires water molecules for hydration. The combined effect of these water requirements seems to result in increase of water extraction with increase in the concentration of aqueous phase nitric acid. The equilibrium densities of organic phase contacted with various concentrations of nitric acid are shown in table 3.3. It is seen that the densities of organic and aqueous phase converge at ~1.2 g/mL when the 0.05 M CMPO-1.2 M TBP/C_4mimNTf$_2$ is equilibrated with 5.0 M nitric acid.

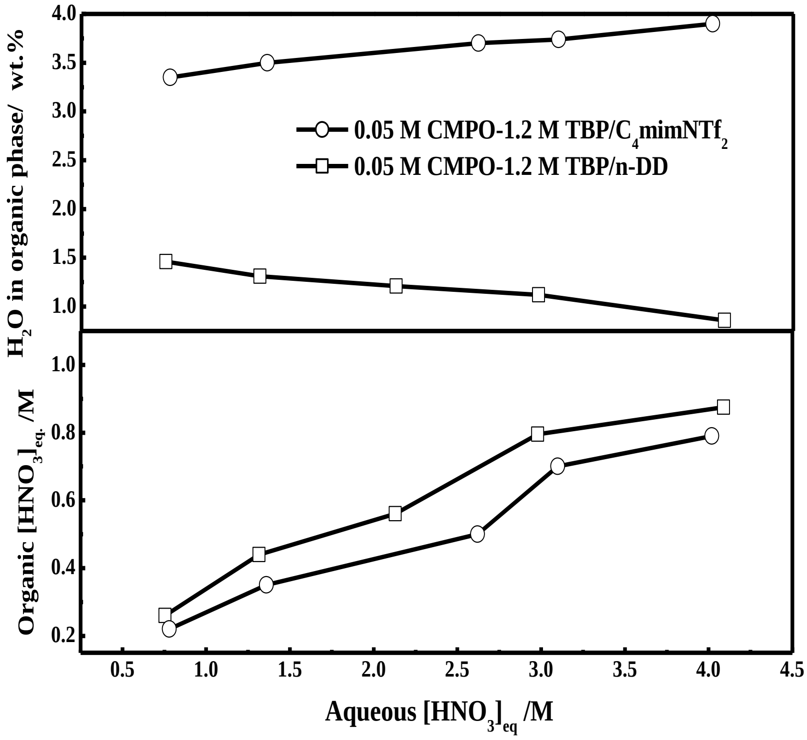


Figure 3.3. Comparison in the extraction of nitric acid and water in organic phase with concentration of nitric acid at 298 K. Solvent: 0.05 M CMPO-1.2 M TBP/C_4mimNTf$_2$ (or *n*-DD)

Table 3.3. Equilibrium densities of organic and aqueous phases at 298 K. Organic phase: 0.05 M CMPO-1.2 M TBP/C_4mimNTf$_2$ (or *n*-DD), Aqueous phase: Nitric acid (1 – 5 M), Equilibrium time: 1 hr, T = 298K, O/A = 1

$[HNO_3]_{ini}$ / M	Equilibrium densities (in g/mL)			
	Organic phase	**Aqueous phase**	**Organic phase**	**Aqueous phase**
1	1.25	1.01	0.82	1.02
2	1.25	1.04	0.83	1.04
3	1.24	1.07	0.84	1.08
4	1.26	1.10	0.85	1.1
5	1.24	1.20	0.85	1.13

3.2.6 Effect of Temperature

If the equilibrium concentrations of $[CMPO]_{org}$ and $[NO_3^-]$ given in equation 3.5 do not vary much with temperature range studied, then the enthalpy of extraction of americium(III) by 0.05 M CMPO –1.2 M TBP/C_4mimNTf$_2$ can be calculated by the van’t Hoff equation as given in the *section 2.5.16.* The plot of ln *D* against (1/T) for the extraction of americium (III) at various concentrations of nitric acid by CMPO-TBP solutions in C_4mimNTf$_2$ and *n*-DD are shown in figures 3.4 and 3.5 respectively. It is observed that the distribution ratio of americium (III) decreases with increase of temperature indicating that extraction reaction is exothermic in both the cases. The enthalpies of extraction, determined from the slope of straight lines, are given in table 3.4

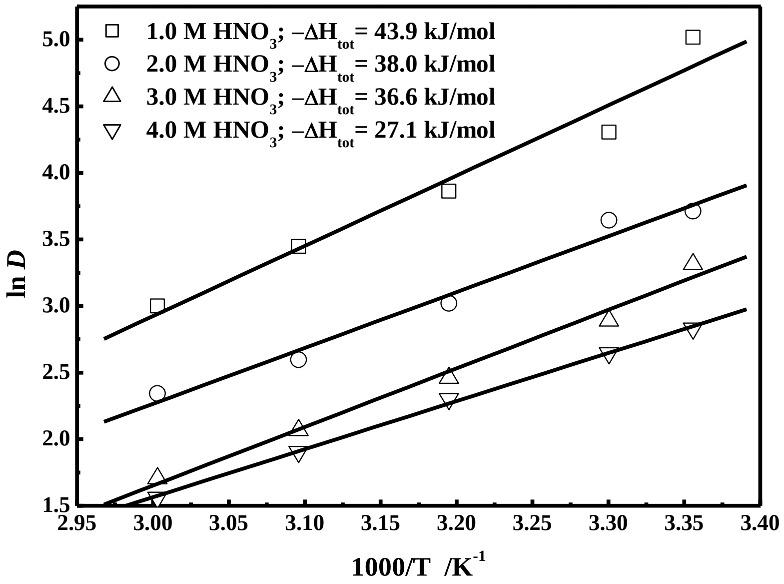


Figure 3.4. Variation of ln *D* with 1/T for the extraction of americium (III) from nitric acid medium using 0.05 M CMPO-1.2 M TBP/C$_4$mimNTf$_2$.

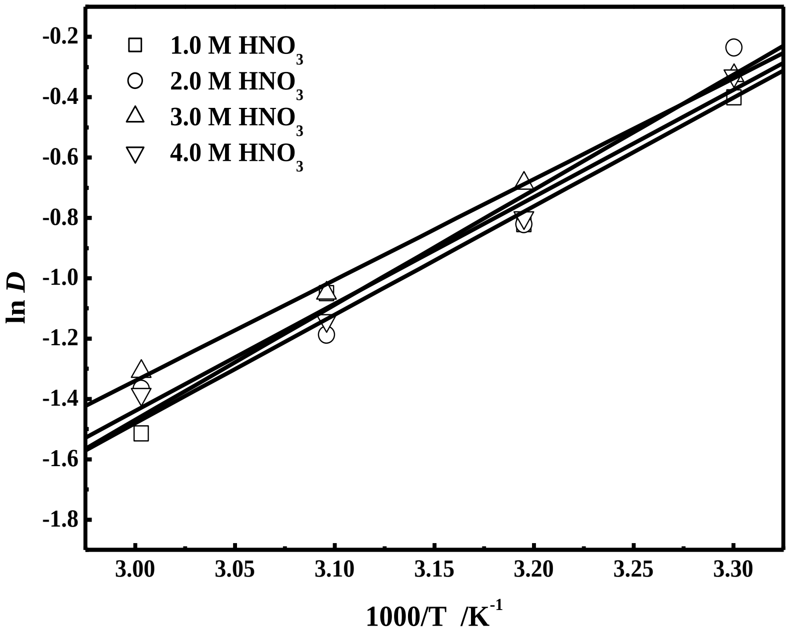


Figure 3.5. Variation of ln *D* with 1/T for the extraction of americium (III) from nitric acid medium by 0.05 M CMPO-1.2 M TBP/*n*-DD

Table 3.4. Comparison of enthalpy changes accompanied for the extraction of americium by 0.05 M CMPO-1.2 M TBP solutions in C_4mimNTf$_2$ and *n*-DD at various nitric acid concentrations

$[HNO_3]_{eq.}$ / M	$-\Delta H_{tot}$ / kJ mol^{-1}	
	C_4mimNTf$_2$ solution	*n*-DD solution
1	43.9	30.0
2	38.0	31.7
3	36.6	27.7
4	27.1	29.5

It can be seen that the exothermicity ($-\Delta H_{tot}$) decreases from 43.9 kJ/mol to 27.1 kJ/mol with increase in the concentration of nitric acid for the extraction of americium in RTIL solution. However, this trend is not observed for *n*-DD system, where the enthalpy change is about –30 kJ/mol irrespective of nitric acid concentrations. The decrease in the overall exothermicity with increase in the concentration of nitric acid could be due to several reactions [33] that can occur during the extraction of americium. The enthalpy change (ΔH_{tot}) during mass transfer consists of the enthalpy changes associated with (a) dehydration of metal ion (b) formation of neutral metal-nitrate species (c) transfer and dissolution of neutral species to organic phase (d) complexation of neutral species with ligand (e) deprotonaton of ligand if the neutral specie forms a complex with ligand existing as protonated complex (ligand—HNO_3) and (f) rearrangement of organic phase to attain stable configuration. Thus, the overall enthalpy change observed is the combination of various factors and the magnitude of enthalpy change is governed by one of the predominant factors indicated above occurring during extraction. The decrease in exothermicity observed in the present case with increase in the concentration of nitric acid could perhaps be attributed to the formation of CMPO–HNO_3 in organic phase at higher nitric acid concentrations. Since the extractant, CMPO, need to be deprotonated to form metal – solvate complex for extraction, the overall exothermic enthalpy change decreases with increase in the concentration of nitric acid.

3.2.7 Viscosity measurement

Figure 3.6 shows the effect of temperature on the viscosity (η, in cP) of 0.05 M CMPO-1.2 M TBP/C_4mimNTf$_2$. It can be seen that the viscosity decreases from 23 cP to 6 cP with increase of temperature from 303 K to 348 K; whereas the viscosity of 0.05 M CMPO-1.2 M TBP in *n*-DD remains almost constant at 3 – 4 cP at all temperatures investigated in the present study. The activation energy (E_a) required for decreasing the viscosity can be determined from arrhenius equation given in the *section 2.5.17* of the chapter-2 . Figure 3.6 shows the plot of η (in cP) against temperature. The energy of activation derived was 33.6 kJ/mol from the slope of straight line.

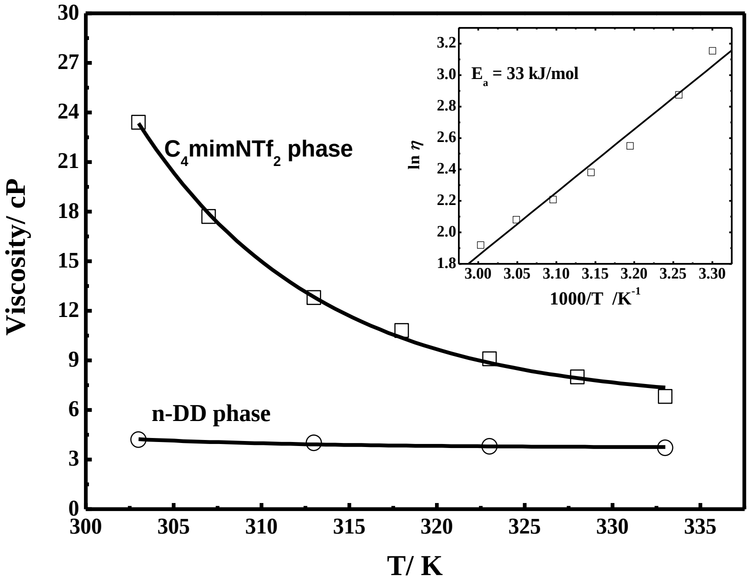


Figure 3.6. Variation of viscosity of 0.05 M CMPO- 1.2 M TBP solution in $C_4mimNTf_2$ or *n*-DD with temperature. Inset: Arrhenius plot

3.2.8 Stripping of americium(III)

Recovery of americium (III) from the loaded organic phase and recycling of ionic liquid phase is one of the important requirements for solvent extraction applications. It is observed from table 3.1 that distribution ratio of americium (III) decreases with increase in the concentration of nitric acid. This indicates that, unlike americium stripping from TRUEX solution, the stripping of americium (III) from ionic liquid phase could not be carried our using at low nitric acid concentration. Nakashima *et al.* [29] investigated the use of various reagents such as citric acid, acetohydroxamic acid, EDTA etc. for stripping some lanthanides from ionic liquid phase and suggested citric acid formulation for quantitative stripping. Figure 3.7 shows the stripping behavior of americium (III) from loaded RTIL phase by various stripping reagents. It is observed that maximum stripping could be observed using 0.03 M DTPA. However, more investigation is necessary in this regard to lower the number of stripping stages.

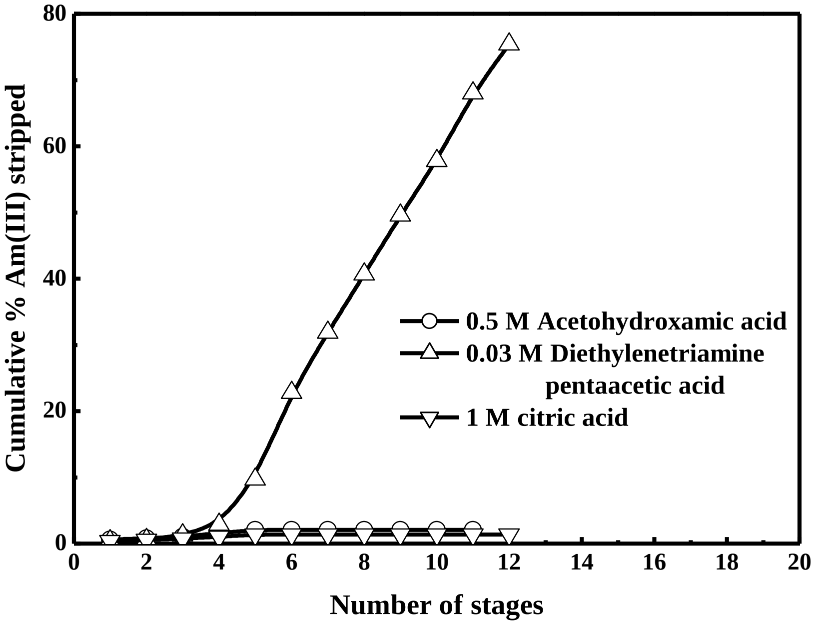


Figure 3.7. Stripping behavior of Am(III) from RTIL phase using various reagents at 298K.

3.3 Conclusions

The studies showed that the extraction of americium was facilitated by the presence of RTIL. About 0.05 M CMPO in RTIL medium only was needed instead of 0.2 M CMPO employed in TRUEX solution for comparable extraction behavior. For extraction from 1 M –5 M nitric acid, the stochiometry of americium extraction by CMPO-TBP/$C_4mimNTf_2$ resembled that of TRUEX solvent, wherein three molecules of CMPO were involved in co-ordination with americium in organic phase. The ion exchange mechanism for the extraction of americium (III) could not be excluded. The extraction of americium (III) in RTIL solution was accompanied by the release of energy and the exothermicity decreased with increase of nitric acid concentration.

B. Extraction behavior of some actinides (Pu(IV), U(VI) and Am(III) using malonamide – room temperature ionic liquid system

3.4 Results and Discussions

3.4.1 Extraction in $C_n$mimNTf$_2$

Figure 3.8 shows the the extraction of Pu(IV), U(VI) and Am(III) in C_4mimNTf$_2$. It is observed that $D_{Pu(IV)}$ is negligible ($D \leq 10^{-2}$) at nitric acid concentrations lower than 2 M. A gradual increase in the distribution ratio of Pu(IV) is observed above 3 M nitric acid. This behavior can be attributed to the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species present in aqueous phase with the NTf_2^- ion of ionic liquid phase. The details of the anion exchange mechanism for the extraction of Pu(IV) in $C_n$mimNTf$_2$ has been discussed in the *section- 5.2.1 and 5.2.2* of the chapter 5. In contrast to this observation, the distribution ratio of U(VI) and Am(III) in C_4mimNTf$_2$ is negligible at all acidities. Since these metal ions do not form anionic species with nitrate ion as compared to Pu(IV), they are not extracted by anion exchange [34].

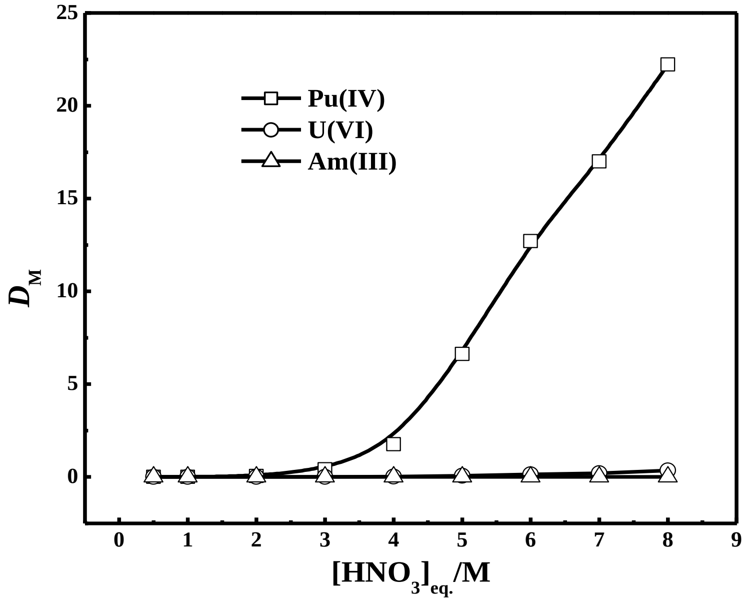


Figure 3.8. Distribution ratio of Pu(IV), U(VI) and Am(III) in C_4mimNTf$_2$. Aqueous phase: 0.5- 8.0 M HNO_3. Equilibrium time = 1hr, T= 298K

3.4.3 Extraction in DMDOHEMA/$C_n$mimNTf$_2$

Figure 3.9 shows the variation in the distribution ratio of Pu(IV) in 0.3 M DMDOHEMA/C_4mimNTf$_2$ as a function of nitric acid concentration. It is observed that the distribution ratio of Pu(IV) initially decreases with increase in the concentration of nitric acid. The distribution ratio reaches a minimum value at 3-4 M in nitric acid followed by increase in $D_{Pu(IV)}$ values. The trend observed in the presence of

DMDOHEMA shows that there could be a couple of modes through which plutonium (IV) is extracted in DMDOHEMA/C_4mimNTf$_2$ phase. The extraction trend observed above 4 M nitric acid in 0.3 M DMDOHEMA/C_4mimNTf$_2$ compares well the trend observed above 4 M in C_4mimNTf$_2$ (figure 3.8). This indicates that plutonium (IV) could be extracted by the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species with NTf_2^- of ionic liquid phase in 0.3 M DMDOHEMA/C_4mimNTf$_2$ also.

To confirm this, the variation in the distribution ratio of Pu(IV) in 0.3 M DMDOHEMA/$C_n$mimNTf$_2$ was studied as a function of $[NTf_2\ ]_{aq}^-$ at 5 M nitric acid. The results are shown in the figure 3.10. Since, the added LiNTf$_2$ was dissolved in the ionic liquid phase to some extent, the aqueous phase concentration of $[NTf_2]^-$ ion at equilibrium was not known. In view of this, figure 3.10 shows the variation in the distribution ratio of Pu(IV) as a function of initial concentration of NTf_2^- ion rather than equilibrium concentration. It is observed that the distribution ratio of plutonium (IV) decreases with increase in the concentration of NTf_2^- ion in aqueous phase as expected. The decreasing trend observed from such plot indicates the involvement of anion exchange of anionic Pu(IV) species with NTf_2^- of organic phase. Moreover, the slope observed is comparable with the slope reported for the extraction of Pu(IV) in C_4mimNTf$_2$ *(as discussed in the chapter 5: section- 5.2.2).* All these observations, indicate that the predominant mode of Pu(IV) extraction in 0.3 M DMDOHEMA/C_4mimNTf$_2$ above 4 M is through anion exchange. Since U(VI) and Am(III) do not form such anionic species in significant quantities, the anion exchange is not observed at high acid concentrations [34]. Otherwise the $D_{\mathrm{U(VI)}}$ and $D_{\mathrm{Am(III)}}$ would have increased with increase in the concentration of nitric acid like Pu(IV) extraction. In addition, the extraction of Am(III) in 0.3M DMDOHEMA/C_4mimNTf$_2$ above 2 M nitric acid is negligible.

Below 4 M nitric acid, the enhancement in distribution ratio of actinides in the presence of DMDOHEMA (figure 3.9) indicates the involvement of DMDOHEMA for extraction. In this range (0.5 – 4 M), the extraction of actinides could occur by ion exchange or by metal –solvate complex formation with DMDOHEMA/C_4mimNTf$_2$. The possibility of anion exchange is unlikely to occur in this region, since the abundance of anionic plutonium (IV) species (as well as U(VI) and Am(III) species) is negligible in the acid range 1 –3 M [34, 35]. It is well-known that plutonium (IV) is purified by anion exchange method only from 5 –6 M nitric acid. These characteristics indicate that the abundance of U(VI), Pu(IV) and Am(III) anionic species, below 4 M, is insignificant and it is unlikely that these actinides are extracted by anion exchange from 0.5 - 4 M nitric acid. However, the effect of $[NTf_2^-]_{ini.,aq.}$ on the extraction of these actinides in 0.3 M DMDOHEMA/C_4mimNTf$_2$ from 1 M nitric acid medium was studied and the results are shown in figure 3.11. It is observed that the distribution ratios of U(VI), Pu(IV) and Am(III) increase with increase in the concentration of $[NTf_2^-]_{ini.,aq.}$. This result is inconsistent with the anion exchange observed at 5 M HNO_3 (figure 3.10). The results confirm that anion exchange is not responsible for extraction of actinides from nitric acid concentration less than 4 M.

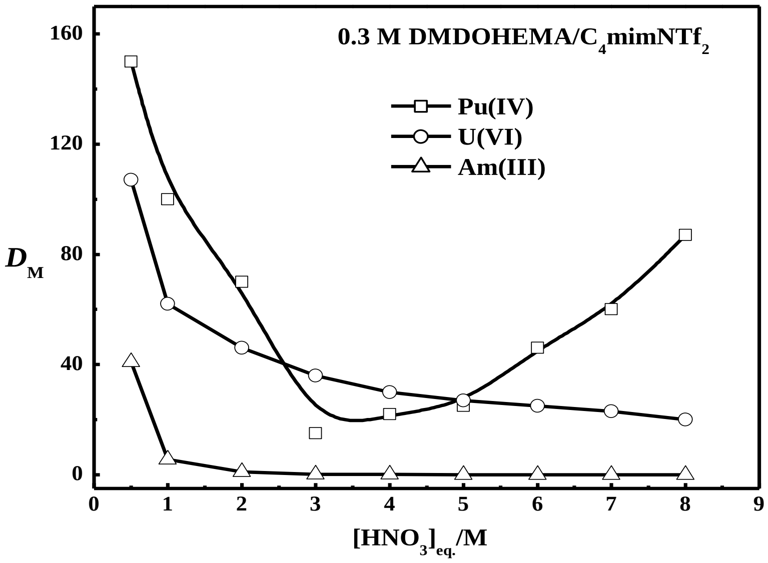


Figure 3.9 Distribution ratio of Pu(IV), U(VI) and Am(III) in 0.3 M DMDOHEMA/C_4mimNTf$_2$. Aqueous phase: 0.5- 8.0 M HNO_3, Equilibrium time = 1hr, T=298K.

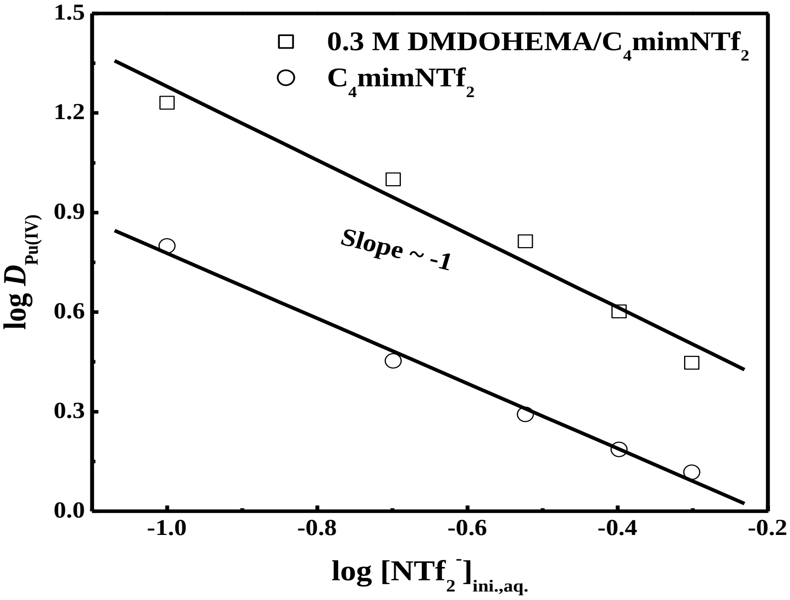


Figure 3.10. Variation of distribution ratio of Pu(IV) as a function of $[NTf_2]^-_{ini}$ in the aqueous phase. Organic phase: C_4mimNTf$_2$ (or 0.3 M DMDOHEMA/C_4mimNTf$_2$). Aqueous phase: 5 M HNO_3 + (0.1-0.5 M) $LiNTf_2$. Equilibrium time = 1 hr. T = 298 K.

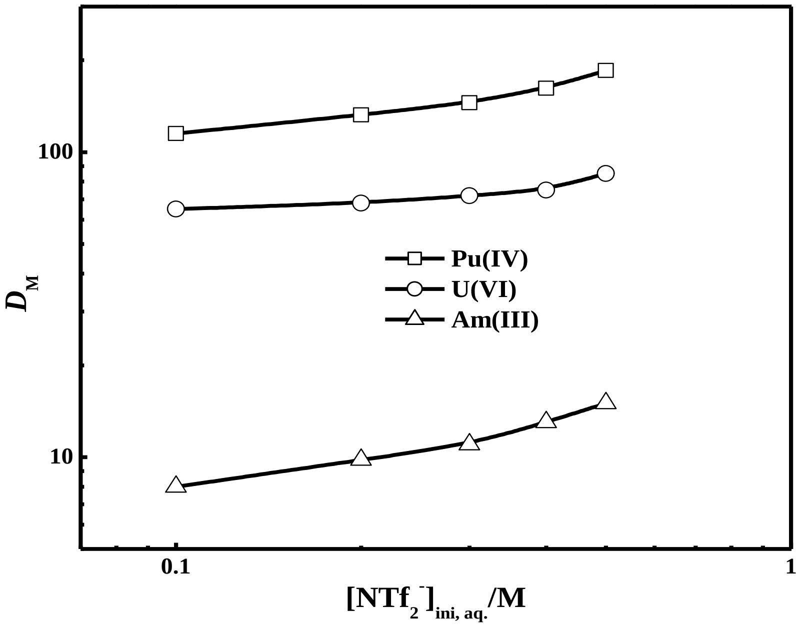


Figure 3.11. Variation in the distribution ratio of Pu(IV), U(VI) and Am(III) as a function of initial NTf_2^- concentration in the aqueous phase. Organic phase: 0.3 M DMDOHEMA/$C_4mimNTf_2$, Aqueous phase: 1 M HNO_3 + (0.1 - 0.5 M) $LiNTf_2$, T = 298 K, Equilibrium time = 1 hr, T - 298 K

3.4.4 Stoichiometry of extraction

Cation exchange is being reported as the primary mode of metal ion transfer in ionic liquid media [11-18, 27]. For instance, cation exchange is the predominant mode of metal ion transfer in systems such as Sr^{2+} in crown ether/ionic liquid [16], Pu(IV) in CMPO/ionic liquid [11], lanthanides in diglycolamide/ionic liquid [27] etc. In all those studies the authors reported the cation exchange of metal – solvate cation complex with C_4mim^+ ion of ionic liquid. Therefore the metal-solvate stoichiometry in the present case was investigated by the slope analysis of extraction data. The variation of D_M (M = U(VI), Pu(IV) and Am(III)) with [DMDOHEMA] is shown in the figure 3.12. Linear regression of the extraction data results in a slope of 2 for U(VI) and Pu(IV), indicating that two molecules of DMDOHEMA are involved in the extraction. This value is in good agreement with the value reported for molecular diluent [26]. In contrast to this observation as well as to those observed in molecular diluent (*n*-DD, slope 2) [23], a slope of 3 is obtained for the extraction of Am(III).

Figure 3.13 shows, the IR spectra of DMDOHEMA/$C_4mimNTf_2$ before and after the extraction of U(VI) in ionic liquid phase. It is observed that the transmittance band occurring at 1640 cm^{-1}, due to >C=O stretching, is broadened and shifted to 1602 cm^{-1} upon uranium(VI) extraction from 0.1 M nitric acid medium in 0.3 M

DMDOHEMA/C_4mimNTf$_2$. This indicates that the carbonyl moiety of DMDOHEMA is involved in coordination with U(VI) after extraction. The possibility of a cation exchange of the M-solvate complex with C_4mim^+ ion of the ionic liquid was investigated by measuring the absorbance of C_4mim^+ cation (~ 250 nm) in nitric acid medium obtained after extraction.

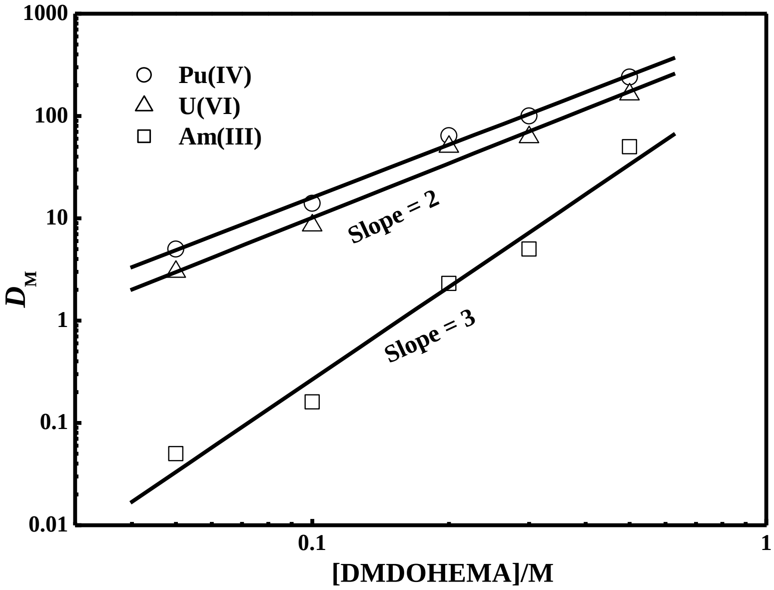


Figure 3.12. Variation in the distribution ratio of Pu(IV), U(VI) and Am(III) as a function of DMDOHEMA concentration in ionic liquid phase. Organic phase: 0.05 - 0.5 M DMDOHEMA/C_4mimNTf$_2$, Aqueous phase: 3 M HNO_3, Equilibrium time = 1 hr, T = 298 K, O/A = 1

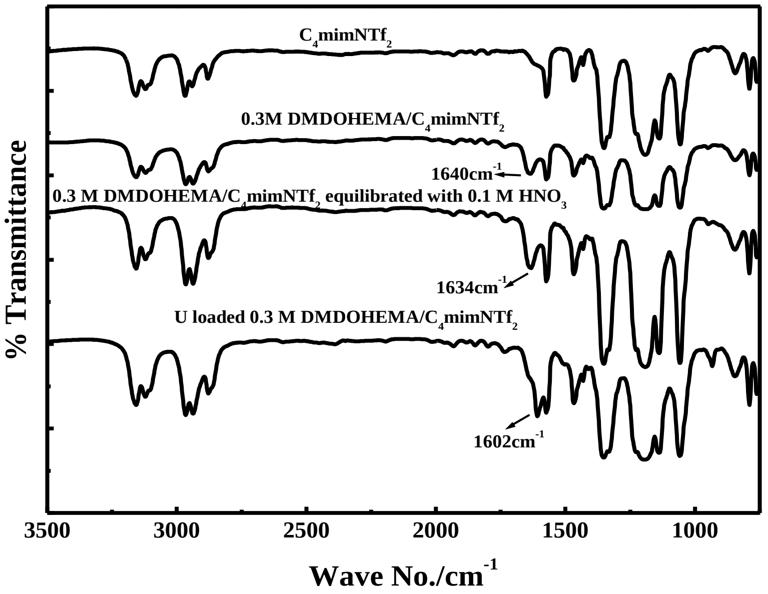


Figure 3.13. FTIR spectra of ionic liquid solutions

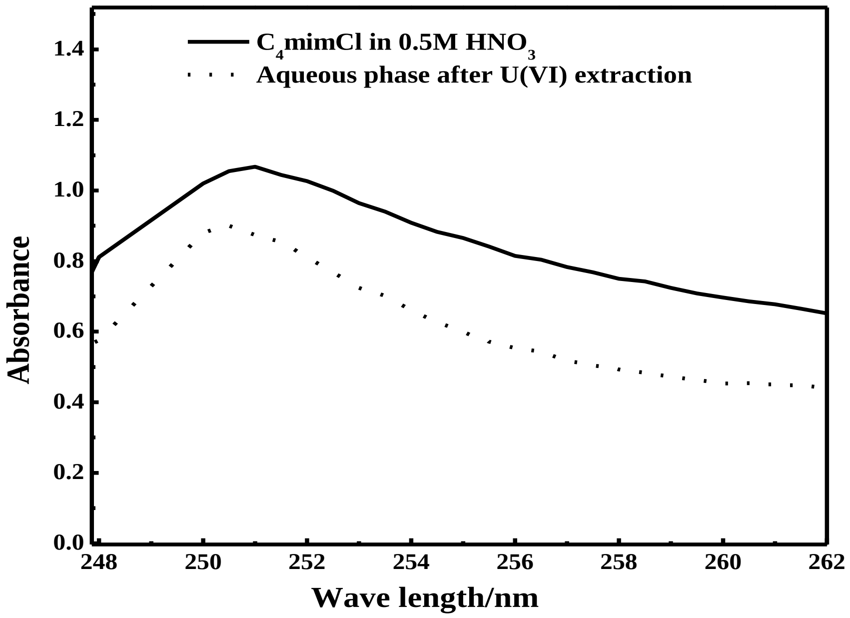


Figure 3.14. Comparison in the absorption spectra of C_4mimCl (10^{-2} M in 0.5 M nitric acid) and the aqueous phase obtained after U(VI) extraction. The aqueous phase used for extraction was U(VI) (10^{-3} M) in 0.5 M nitric acid and organic phase was (0.3 M DMDOHEMA/C_4mimNTf$_2$

Figure 3.14 given above, shows the UV-visible absorption spectrum of C_4mimCl in 0.5 M nitric acid. It is observed that the absorption maximum is observed at the λ_{max} of 250 nm. Figure 3.14 also shows the absorption spectrum of aqueous phase obtained after the extraction of uranium(VI) from 0.5 M nitric acid medium. Comparable absorption spectrum observed in this case confirms that U(VI) is likely to be extracted by cation exchange mechanism below 4 M nitric acid medium. A similar mechanism could be responsible for the extraction of Pu (IV) and Am (III) also in ionic liquid medium below 4 M nitric acid. Based on these observations the equation 3.6 can be proposed for the extraction of actinides from nitric acid medium below 4 M.

$$M^{n+}_{aq} + m\ \mathrm{DMDOHEMA}_{IL} + n\ C_4\mathrm{mim}^{+}_{IL} \Leftrightarrow \{M(\mathrm{DMDOHEMA})_m\}^{n+}_{IL} + n\ C_4\mathrm{mim}^{+}_{aq} \qquad (3.6)$$

3.4.5 Nature of diluent

Figure 3.15 shows the variation in the distribution ratio of actinides in 0.3 M DMDOHEMA/$C_n$mimNTf$_2$ (n = 4 - 6). It is observed that the distribution ratio of actinides decreases with increase in the chain length of alkyl group in $C_n$mimNTf$_2$. A similar behavior was also reported for the extraction of U(VI) and other metal ions in various systems [13,15]. This was attributed to the suppression in ion exchange mode of actinide transfer in ionic liquid phase, and switchover of extraction mechanism from ion exchange to the traditional solvation with the increase of hydrophobicity of ionic liquid (increasing chain length) [15].

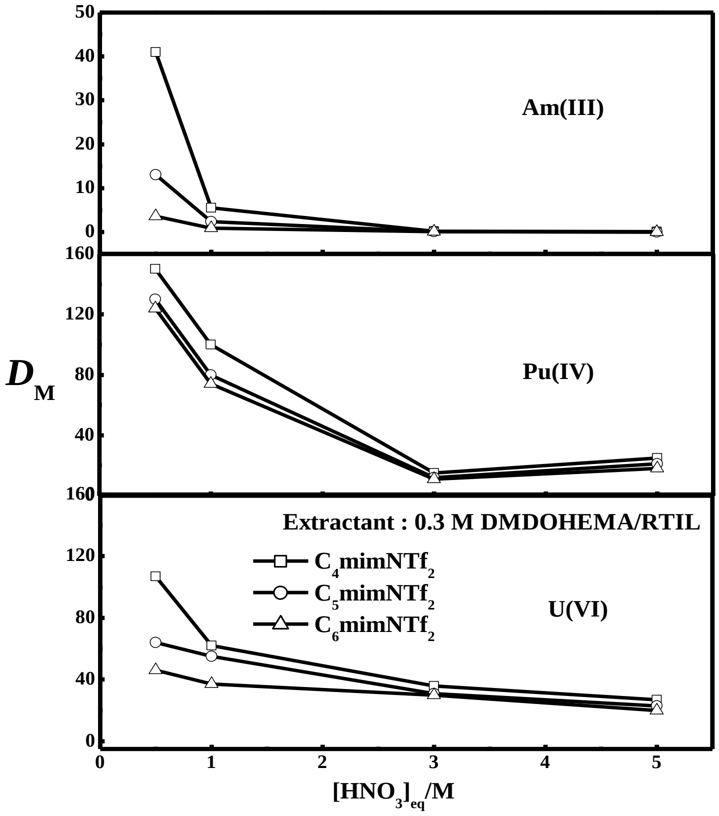


Figure 3.15. Variation in the distribution ratio of U(VI), Pu(IV) and Am(III) as a function of alkyl chain length of $C_n$mimNTf$_2$.
Organic phase: 0.3 M DMDOHEMA/$C_n$mimNTf$_2$, Aqueous phase: 0.1 - 5.0 M HNO_3, Equilibrium time = 1hr, T = 298K

3.4.6 Separation factor

Table 3.5 shows the separation factor (SF) of U(VI) and Pu(IV) achieved with the use of 0.3 M DMDOHEMA/C_4mimNTf$_2$ from other radionuclides. It is observed that a SF of > 1000 is achieved for U(VI) from radionuclides such as ^{85}Sr, ^{60}Co, ^{54}Mn and ^{106}Ru. Similarly, a SF of >1000 for Pu(IV) is achieved from ^{60}Co, ^{54}Mn and ^{106}Ru. It is interesting to compare the distribution values obtained in the present study with those obtained in conventional molecular diluent *n*-DD. It was reported [24] that the distribution ratio of U(VI) in 1 M DMDOHEMA/*n*-DD increases from the value of ~ 3 at 0.1 M HNO_3 to ~200 at 4 M HNO_3. Patil *et al.* [25] reported the distribution ratios of 34.1 and 15.5 for Pu(IV) and Am(III) extraction from 3 M HNO_3 using 1 M DMDOHEMA/*n*-DD. These studies [21, 23 - 26] indicates that DMDOHEMA extracts Pu(IV), U(VI) as well as Am(III) when the diluent used was *n*-DD. In contrast to that study, the extraction of

Am(III) is insignificant in the present case using ionic liquid diluent (< 10^{-2}) as compared to U(VI) and Pu(IV) (see figure 3.8). This indicates that ionic liquid diluents offers enhanced stability to the U(VI) and Pu(IV) complex in organic phase. Table 3.6 shows the comparison in the distribution ratio of actinides in various amide/ionic liquid systems. It is observed that DMDOHEMA in conjunction with the ionic liquid exhibits excellent extraction of actinides from nitric acid medium, over other amide/ionic liquid systems.

Table 3.5. Decontamination factors of U(VI) and Pu(IV) at 3 M HNO_3 . Organic phase : 0.3 M DMDOHEMA / $C_4mimNTf_2$, Aq. Phase : 3M HNO_3

Radioisotopes	**Separation factors of**	
	U(VI) [SF = $D_{U(VI)} / D_M{}^{n+}$]	**Pu(IV) [SF = $D_{Pu(IV)} / D_M{}^{n+}$]**
^{241}Am(III)	228	107
$^{(152+154)}$Eu(III)	200	94
^{85}Sr(II)	1000	400
^{139}Ce(IV)	400	166
^{60}Co(II)	3600	1500
^{54}Mn(II)	2570	1070
^{106}Ru(III)	2500	1000

Table 3.6. Distribution ratios of Pu(IV), U(VI) and Am(III) in various amide/ionic liquid systems. Organic phase: Extractants in ionic liquid diluent, Aqueous phase: 1 M HNO_3 spiked with the actinide tracers, Equilibrium time: 1 hr, Temperature = 298 K, O/A = 1

Solvent systems	Distribution ratio of		
	U (VI)	Am(III)	Pu (IV)
Present study (0.3 M MDOHEMA/$C_4mimNTf_2$)	62	41	100
0.01 M TBDA/C_4mimPF_6	2.75 [13]	---	---
0.01 M MBDA/ C_4mimPF_6	2.25 [13]	---	---
0.5 M DOBA/$C_4mimNTf_2$	0.15 [36]	0.007	0.05 [36]
1 M DHOA/$C_4mimNTf_2$	0.93	0.01	2

TBDA – Tetrabutyldiglycolamide, MBDA – Methylbutyldiglycolamide, DOBA – Di-n-octylbutyramide, DHOA – Di-n-hexyloctanamide, C_4mimPF_6 – 1-butyl-3-methylimidazoilum hexafluorophosphate.

3. 4. 7 Viscosity measurement

Figure 3.16 shows the effect of temperature on the viscosity (η, in cP) of 0.3M DMDOHEMA/C_4mimNTf_2 in comparision with the viscosity of C_4mimNTf_2 and neat DMDOHEMA. It is observed that the viscosity of 0.3 M DMDOHEMA/C_4mimNTf_2 decreases from 60 cP to 16 cP with increase of temperature from 298 K to 333 K.

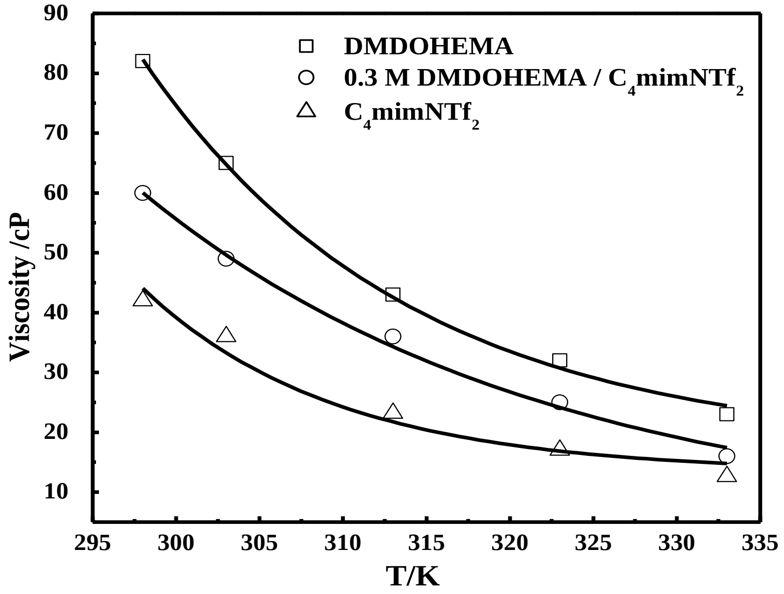


Figure 3.16. Viscosity of DMDOHEMA, C_4mimNTf_2 and 0.3 M DMDOHEMA/C_4mimNTf_2

3.5 Conclusions

The extraction behavior of Pu(IV), U(VI) and Am(III) in DMDOHEMA/ionic liquid solution was studied. The extractant DMDOHEMA showed excellent selectivity for U(VI) and Pu(IV) in ionic liquid diluent, whereas in *n*-DD, Am(III) was also co-extracted. Above 4 M nitric acid, the primary mode of Pu(IV) transfer in ionic liquid phase was found to be anion exchange. However, below 4 M nitric acid the investigations indicate that the most plausible mechanism of actinides transfer in ionic liquid phase was cation exchange of metal – solvate complex with C_4mim^+ cation of ionic liquid. The distribution ratio of actinides decreased with increase of alkyl chain length of $C_n$mimNTf_2 and SF of > 1000 was obtained for actinides from many fission products. Above studies confirmed that the malonamide, DMDOHEMA, in conjunction with the ionic liquid showed excellent extraction of U(VI) and Pu(IV) from nitric acid medium, indicating DMDOHEMA/ionic liquid, a promising candidate for reprocessing applications.

3.6 References

1. T. Welton, Room – Temperature Ionic Liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (8) (1999) 2071-2083.
2. S. Dai, Y. H. Ju, C.E. Barnes, Solvent extraction of strontium nitrate by crown ether using room – temperature ionic liquids, J. Chem. Soc., Dalton Trans. 9 (1999) 1201 – 1202.
3. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P.R. Vasudeva Rao, Effect of alkyl group in 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids on the extraction of uranium by tri-n-butylphosphate diluted with ionic liquids. J. Nucl. Radiochem. Sci. 5 (2) (2004) 21-26.
4. A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers,: Traditional extractants in non-traditional solvents: Group 1 and 2 extraction by crown ethers in room temperature ionic liquids. Ind. Eng. Chem. Res. 39 (10) (2000) 3596 – 3604.
5. I. Billard, A. Ouadi, C. Gaillard, Liquid–liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding. Anal Bioanal Chem. 400 (6) (2011)1555-1566.
6. H. S. Ho, R. N. Menchavez, Y. M. Koo, Reprocessing of spent nuclear waste using ionic liquids, Korean J. Chem. Eng. 27 (5) (2010) 1360-1365.
7. S. I. Nikitenko, C. Cannes, C. L. Naour, P. Moisy, D. Trubert, Spectroscopic and Electrochemical Studies of U(IV)-Hexachloro Complexes in Hydrophobic Room-Temperature Ionic Liquids [BuMeIm][Tf_2N] and [$MeBu_3N$][Tf_2N]. Inorg. Chem. 44 (25) (2005) 9497 – 9505.
8. A. I. Bhatt, I. May, V. A. Volkovich, D. Collison, M. Helliwell. I. B. Polovov, R. G. Lewin, Structural characterization of a Lanthanum Bistriflimide complex, $La(N(SO_2CF_3)_2)_3(H_2O)_3$, and an Investigation of La, Sm, and Eu electrochemistry in a Room-Temperature Ionic Liquid [Me_3NnBu][$N(SO_2CF_3)_2$]. Inorg. Chem. 44 (14) (2005) 4934-4940..
9. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P.R. Vasudeva Rao, Electrochemical behavior of uranium(VI) in 1-butyl-3-methylimidazolium chloride and thermal characterization of uranium oxide deposit. Electrochim. Acta 52 (9) (2007) 3006-3012.
10. K. A. Venkatesan, T. G. Srinivasan, P.R. Vasudeva Rao, Electrochemical behavior of uranium(VI) in 1-butyl-3-methylimidazolium chloride and thermal characterization of uranium oxide deposit. A Review on the Electrochemical Applications of Room

Temperature Ionic Liquids in Nuclear Fuel Cycle. J. Radiochem. Nucl. Sci. 10 (2009) R1-R6.

11. K. V. Lohithakshan, S. K. Aggarwal, Solvent extraction studies of Pu(IV) with CMPO in 1-octyl 3-methylimidazolium hexa fluorophosphate (C_8mimPF_6) room temperature ionic liquid (RTIL), Radiochim. Acta 96 (2) (2008) 93–97.
12. K. V. Lohithakshan, S. K. Aggarwal, Solvent extraction studies of plutonium(IV) by crown etherdicyclohexyl-18-crown-6 (DC18C6) in 1-butyl-3-methyl imidazolium hexafluorophosphate (C_4mimPF_6) and 1-hexyl-3-methyl imidazolium hexafluorophosphate (C_6mimPF_6) room temperature ionic liquids (RTIL), Radiochim. Acta 99 (4) (2011) 201–205.
13. Y. Shen, X. Tan, L. Wang, W. Wu, Extraction of the uranyl ion from the aqueous phase into an ionic liquid by diglycolamide, Separation purification Technol. (2011) 78 (3) 298–302.
14. S. Chun, S. V. Dzyuba, R. A. Bartsch, Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by crown ether. Anal. Chem. 73 (15) (2001) 3737 - 3741.
15. M.L. Dietz, D. C. Stepinski, Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. Talanta 75 (2) (2008) 598 - 603.
16. M. L. Dietz, J.A. Dzielawa, I. L. Blake, A. Young, M. P. Jensen, Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. Green Chem. 5 (6) (2003) 682 - 685.
17. M. L. Dietz, J. A. Dzielawa, Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the ‘greenness’ of ionic liquids as diluents in liquid–liquid extraction. Chem. Commun. (2001) 2124 – 2125.
18. D. C. Stepinski, M. P. Jensen, J. A. Dzielawa, M. L. Dietz, Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids. Green Chem. 7 (2005) 151 – 157.
19. W.W. Schulz, E. P. Horwltz, Recent progress in the extraction chemistry of actinide ions. J. Less-Common Metals. 122 (1986) 125 - 138.
20. A. E. Visser, R. D. Rogers, Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry. J. Solid State Chem. 171 (1-2) (2003)109 – 113.

21. E. A. Mowafy, H. F. Aly, Extraction behavior of trivalent lanthanides from nitrate medium by selected substituted malonamides, Solvent Extr. Ion Exch. 24 (5) (2006) 677-692.
22. G. Modolo, H. Vijgen, D. S. Purry, B. Christiansen, R. Malmbeck, C. Sorel, P. Baron, DIAMEX counter-current extraction process for recovery of trivalent actinides from simulated high active concentrate, Sep. Sci. Technol. 42 (3) (2007) 439 – 452.
23. B. Gannaz, R. Chiarizia, M. R. Antonio, C. Hill, G. Cote, Extraction of lanthanides(III)and actinides(III) by mixture of malonamide and dialkylphopshoric acid, Solvent Extr. Ion Exch. 25 (3) (2007) 313 - 337.
24. R. Deivanayaki, C. V. S. Brahmananda Rao, K. N. Sabharwal, T. G. Srinivasan, P. R. Vasudeva Rao, Studies on extraction of Uranium(VI) and Americium(III) by DMDOHEMA (DimethylDioctylHexylEthoxyEthoxyMalonamide). In: Proceedings of DAE-BRNS Symposium on Nuclear and Radiochemistry, NUCAR 2009, SVKM Mithibai College, January 7-10, 2009, Vile Parle, Mumbai, India, pp -293 - 294.
25. A. B. Patil, V. S. Shinde, P.N. Pathak, P. K. Mohapatra, V.K. Manchanda, New synthesis route for *N,N* -dimethyl-*N,N* -dioctyl -2,(2 -hexyloxyethyl) malonamide (DMDOHEMA) and its evaluation under simulated high-level waste conditions. In : Proceedings of DAE-BRNS Symposium on Nuclear and Radiochemistry (NUCAR 2011), 2011, pp. 194 – 195.
26. E. A. Mowafy, H. F. Aly, Extraction behaviours of Nd(III), Eu(III), La(III), Am(III) and U(VI) with some substituted malonamides from nitrate medium, Solvent Extr. Ion Exch. 20 (2) (2002) 177 – 194.
27. K. Shimojo, K. Kurahashi, H. Naganawa, Extraction behavior of lanthanides using a diglycolamide derivative TODGA in ionic liquids, J. Chem. Soc., Dalton Trans. (2008) 5083-5088.
28. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P.R. Vasudeva Rao, Extraction of uranium (VI) from nitric acid medium by 1.1 m tri-n-butylphosphate in ionic liquid diluent. J. Radioanal. Nucl. Chem. 265 (1) (2005) 31 - 38.
29. K. Nakashima, F. Kubota, T. Maruyama, M. Goto, Feasibility of ionic liquids as alternative separation media for industrial solvent extraction process. Ind. Eng. Chem. Res. 44 (12) (2005) 4368 - 4372.
30. E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, H. Diamond, Selected alkyl(phenyl)-*N,N*-dialkylcarbamoylmethylphosphine oxides as extractants for Am(III) from nitric acid media. Sep. Sci and Technol. 17 (10) (1982) 1261 – 1279.

31. J. N. Mathur, M. S. Murali, P. R. Natrajan, L.P. Badheka, A. Banerji, Extraction of actinides and fission products by octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide from nitric acid media. Talanta 39 (5) (1992) 493 – 496.
32. W. Davis Jr., Thermodynamics of extraction of nitric acid by tri-n-butylphosphate – hydrocarbon diluent solutions. Nucl. Sci. Eng. 14 (1962) 159 - 169.
33. L.L. Burger, The neutral organophosphorous compounds as extractants. Nucl. Sci. Eng. 16 (1963) 428 – 439.
34. J. J. Katz, G. T. Seaborg, L. R. Morss, Chemistry of actinide elements, second edition, Chapman and Hall, USA (1987).
35. J. L. Ryan, E. J. Wheelwright, Recovery and Purification of Plutonium by Anion Exchange, Ind. Eng. Chem. 51(1) (1959) 60 – 65.
36. Alok Rout, K.A.Venkatesan, T.G.Srinivasan, P.R.Vasudev Rao, Extraction behavior of actinides and fission products in amide functionalized ionic liquid. Separation purification Technol. DOI; 10.1016/j.seppur.2012-01.020.

Chapter - 4

CHAPTER - 4

Extraction – Third phase formation behavior of Eu(III) and its mutual separation from Am(III) using room temperature ionic liquid medium

This chapter discusses the extraction and third phase formation behavior of the Eu(III) in a TRUEX solvent present in ionic liquid medium. The distribution ratio of Eu(III) was studied at various equilibrium concentration of nitric acid, Eu(III) loading in the aqueous phase, temperature, concentration of TBP, CMPO etc. This chapter also dicsusses the mutual separation of europium(III) from americium(III) in RTIL medium. The extraction of Eu(III) and Am(III) was carried out in the solution of bis(2-ethylhexyl) phosphoric acid (D2EHPA) or bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) in the RTIL, 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $C_8mimNTf_2$. diethylenetriaminepentacetic acid (DTPA) was used as the complexing agent in the aqueous phase for separating Eu(III) from Am(III).

4.1 Introduction

In solvent extraction, the “third phase formation” refers to the splitting of organic phase in to two under high loading of acid/metal ion in to the organic phase [1-3]. The third phase is formed due to the incompatibility of polar metal-solvate (or acid-solvate) with non-polar hydrocarbon diluent. The lighter phase is rich in diluent and the heavier phase contains high concentration of extractant and metal-solvate. The heavy phase is known as “Third Phase”, with density intermediate between diluent rich organic and aqueous phases. Therefore it usually accumulates at the interface [4]. This phenomenon is well-known and has been investigated extensively in various systems [5 - 7]. Several parameters such as temperature, nature of diluent, equilibrium aqueous phase acidity, extractant structure, extractant concentration etc., can influence third phase formation. The maximum concentration of metal ion in the organic phase above which the organic phase would split into two phases is called limiting organic concentration (LOC) and the corresponding critical aqueous concentration of metal ion in the aqueous phase is called critical aqueous concentration (CAC) [5]. Thus, it is desirable to restrict the metal loading much below LOC, in systems that are prone to third phase formation, as it complicates the hydrodynamics of solvent extraction and may lead to criticality in case of extraction of fissile elements. TRUEX process [8] has been adopted, worldwide, for the recovery of trivalent lanthanides and actinides (Am(III)), from high-level liquid waste (HLLW). The solvent is composed of mixture of 0.2M *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyphosphine oxide (CMPO) – 1.2 M TBP in *n*-dodecane [9,10].

The LOC of Eu(III) in TRUEX solvent is ~ 9 mg/mL and CAC value is ~ 6 mg/mL at 303 K [11]. The use of ionic diluent in solvent extraction would be expected to change the physical and chemical properties of organic phase [12]. Therefore, it is interesting to study the behavior of third phase formation in TRUEX solventpresent in ionic liquid medium.

The most challenging task at the back end of the nuclear fuel cycle after the group sparation is the individual separation of lanthanides from actinides viceversa. This separation is difficult to accomplish due to the similarities in the chemical properties of the trivalent actinides and lanthanides present in the waste (HLLW) [13 - 16]. However there are some marginal differences with respect to the chemical reactivity of lanthanides and actinides towards certain reagents, and such differences have been exploited for the Ln/An separation. In this context, several authors have reported the separation of lanthanides from actinides or vice versa using liquid-liquid extraction procedures [17-20]. In the recent past TALSPEAK (Trivalent Actinides and Lanthanides Separation by Phosphorous based Extractants from Aqueous Komplexes) process is emerging as the promising technique [20-23] for such applications. This process essentially exploits the differential complexing abilities of lanthanides and actinides towards the extractant, bis(2-ethylhexyl) phosphoric acid (D2EHPA), and the aqueous soluble complexing agent diethylenetriamine-*N, N, N', N", N'"*-pentaaceticacid (DTPA) for efficient separation [21-23].

In addition, alkyldiglycolamides (DGA) are emerging as superior candidates for the separation of trivalents from high-level liquid waste [24-31]. Introduction of an etheric oxygen between the two amide groups, as in DGA's, increases the extraction of minor actinides due to the enhanced tridentate complex formation with trivalents. Since, the extractant, HDEHDGA being a derivative of glycolamic acid, it is also expected to be a superior candidate for the separation of lanthanides and actinides from aqueous medium. The structure of HDEHDGA, D2EHPA, $C_8mimNTf_2$ and DTPA are shown in figure 1. Shimojo *et al.* [29-31] studied the extraction behavior of lanthanides using *N,N*-dioctyldiglycolamic acid (DODGAA) and reported the mutual separation of lighter, middle and heavier lanthanides using DODGAA and tetrakis(2-pyridylmethyl)ethylenediamine (TPEN).

This chapter deals with the extraction and third phase formation behavior of Eu(III) in CMPO – TBP/IL system in part "A" and its mutual separation from Am(III) using two different class of acidic extracatants (bis(2-ethylhexyl)phosphoric acid, D2EHPA and bis(2-ethylhexyl)diglycolamic acid, HDEHDGA) in ionic liquid medium in part "B".

The synthesis of ionic liquids and the extractant (HDEHDGA) have been discussed in discussed in the section 2.4.2 and 2.4.8. The experimental parts of the present chapter have been detailed in the section 2.6.1 and 2.6.3 of the chapter 2 respectively.

A. Extraction – Third phase formation behavior of Eu(III) in room temperature ionic liquid medium

4.2 Results and discussions

4.2.1 Effect of nitric acid

Figure 4.1 shows the variation in the distribution ratio of Eu(III) in 0.2 M CMPO-1.2 M TBP/$C_4mimNTf_2$ with the equilibrium concentration of nitric acid (0.01 – 5 M) in aqueous phase at 303 K. The data are compared with the distribution ratio of Eu(III) in TRUEX solvent (0.2 M CMPO-1.2 M TBP/*n*-DD) at 303 K. Extraction of Eu(III) in 1.2 M TBP/$C_4mimNTf_2$ was determined to be insignificant and it was of the order of 10^{-2}. However, remarkable enhancement in the distribution ratio is observed in the presence of CMPO. It is interesting to compare the extraction behavior of Eu(III) by TRUEX extractants present in ionic liquid and *n*-DD medium. In ionic liquid medium, the D values increases from 435 at 0.01 M nitric acid reaches a maximum value of ~1200 at 0.5 M followed by decrease in *D* values. However, in dodecane system the distribution ratio increases from 10^{-3} at 0.01 M nitric acid reaches a maximum value of 13 at 3 M nitric acid followed by decrease. The reason for the differences in the distribution ratios observed in molecular and ionic liquid systems is not clear, however, the study indicates that use of ionic liquid enhances the distribution ratio of Eu(III).

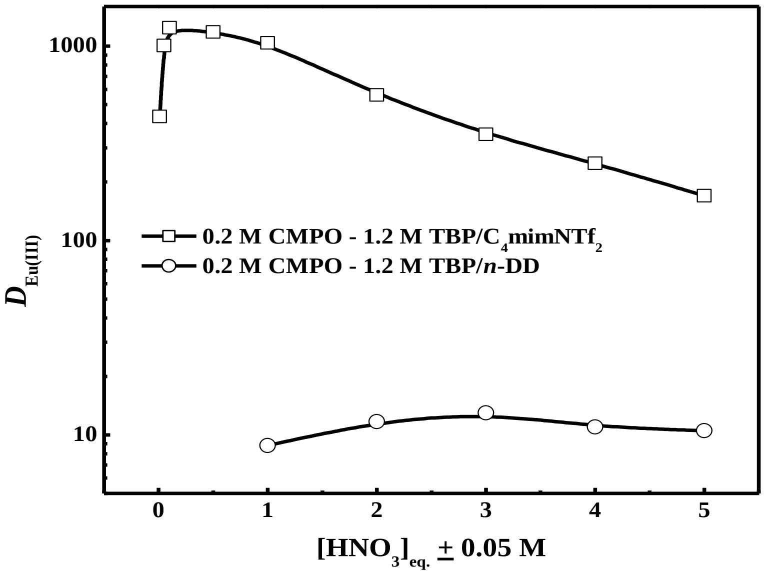


Figure 4.1. Variation in the distribution ratio of $^{(152+154)}$Eu(III) with concentration of nitric acid at 303K. Organic phase : 0.2 M CMPO -1.2 M TBP/$C_4mimNTf_2$ (or *n*-DD),Aqueous phae: 0.01 M HNO_3 spiked with $^{(152+154)}$Eu(III) tracer

4.2.2 Effect of IL diluents

The extraction of Eu(III) in CMPO – TBP in $C_n$mimNTf$_2$ (n = 4, 6 and 8) as a function of nitric acid concentration was studied and the results are shown in figure 4.2. It is observed that the distribution ratio of $^{(152+154)}$Eu(III) decreases with increase in the chain length of alkyl group attached to the cation part of the ionic liquid. This observation is not new to ionic liquid systems. This was attributed by the several authors [12, 32] to the decrease in the ability of ionic liquids to undergo ion exchange with increase of hydrophobicity.

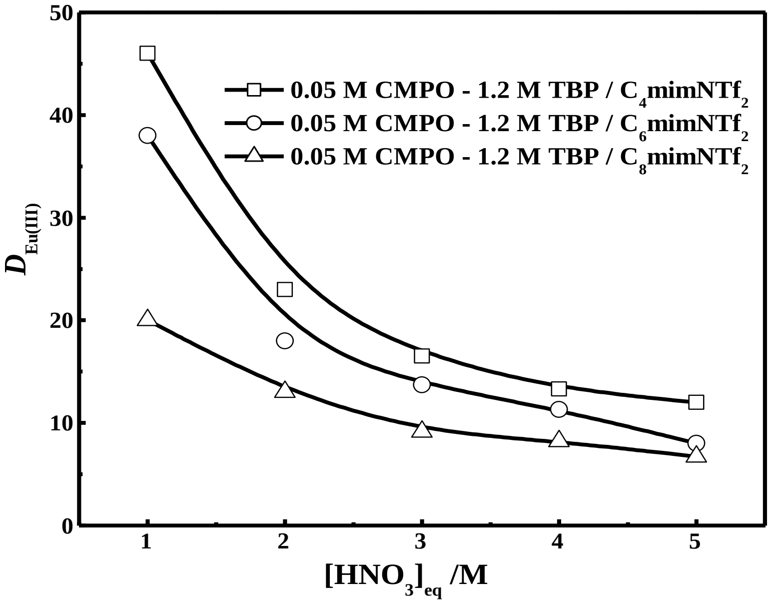


Figure 4.2. Distribution ratio of $^{(152+154)}$Eu(III) in 0.05 M CMPO - 1.2 M TBP/C_4mimNTf$_2$(or C_6mimNTf$_2$ or C_8mimNTf$_2$. O/A =1:1, T = 303 K, Equilibration time = 1 hr

4.2.3 Effect of Eu (III) loading

Table 4.1 shows the variation of europium loading in a solution of 0.2 M CMPO-1.2 M TBP in C_4mimNTf$_2$ as a function of its initial concentration in aqueous phase. The solubility limit of europium(III) nitrate in 1 - 5 M nitric acid is ~ 300 mg/mL. Therefore, the aqueous phase concentration of europium was varied from 20 to 300 mg/mL. It is observed that loading of europium in ionic liquid phase increases from ~12 to 40 mg/mL with increase in Eu(III) concentration in the aqueous phase. Interestingly in all cases, the anticipated third phase formation was not observed, whereas, in conventional *n*-DD system, the LOC was 9 mg/mL only. The correct reason for the absence of third phase in ionic liquid system is not clear at present, however, it can be attributed, perhaps, to the polar nature of ionic liquid, C_4mimNTf$_2$, and its ability to dissolve/stabilize the Eu(III)–

solvate complex. Increasing the concentration of nitric acid (1 – 5 M) marginally reduces the loading of europium in organic phase.

Table 4.1. Variation of europium(III) loading in 0.2 M CMPO – 1.2 M TBP/C$_4$mimNTf$_2$ at various initial concentrations

[Eu(III)]$_{ini}$, mg/mL	Organic loading(mg/mL) at different equilibrium acidities and temperatures					
	1M		3M		5M	
	303K	333K	303K	333K	303K	333K
20	12.1	11.2	12.2	11.2	12.4	10.9
50	16.0	15.0	16.1	14.9	15.7	15.1
100	22.7	18.7	24.2	20.5	21.0	20.0
150	26.2	24.7	25.4	23.3	24.2	23.7
200	32.1	28.8	30.1	29.8	30.5	27.6
250	36.3	35.2	36.3	33.1	34.1	32.6
300	43.2	42.2	38.5	37.7	36.4	34.1

4.2.4 Effect of CMPO concentration

The stoichiometry of trivalent lanthanides can be determined by the slope analysis of the extraction data. The plot of logD_{Eu} against log [CMPO]$_{org}$ gives the number of extractant molecules solvating Eu(III). CMPO being neutral extractant, extracts Eu(III) in neutral form by the reaction represented by equation (4.1).

$$Eu^{3+}_{aq.} + 3NO^-_{3\,aq.} + x\,CMPO_{IL.} \Leftrightarrow [Eu(NO_3)_3.(CMPO)_x]_{IL} \tag{4.1}$$

$$K = \frac{[Eu(NO_3)_3(CMPO)_x]_{IL}}{[Eu^{3+}]_{aq.}[CMPO]^x_{IL}[NO^-_3]^3_{aq.}} \tag{4.2}$$

$$K = \frac{D_{Eu}}{[CMPO]^x_{IL}[NO^-_3]^3_{aq.}} \tag{4.3}$$

At constant nitrate ion concentration the variation of log D_{Eu} with log [CMPO]$_{org}$ is shown in equation 4.4.

$$\log D_{Eu} = \log K' + x\log\left[CMPO\right]^-_{IL} \tag{4.4}$$

where K' is constant at constant nitrate concentration. The plot of log D_{Eu} against log [CMPO]$_{org}$ is shown in figure 4.3. It is seen that D_{Eu} value increases with increase in the concentration of CMPO. A slope value of 3.0 is obtained for the extraction of europium (III) from 1.0 M nitric acid medium. Thus, the metal-solvate stoichiometry for the extraction of europium(III) by CMPO-TBP/C_4mimNTf$_2$ resembles that of TRUEX system at 1.0 M nitric acid medium, wherein three molecules of CMPO are involved in co-ordination with europium in organic phase. A similar 1 : 3 complex (Ln^{3+} :CMPO) was reported for the extraction of some trivalent lanthanides from neutral solution by CMPO/RTIL [33]. In chapter 3, the stoichiometry of Am(III) in CMPO – TBP/C_4mimNTf$_2$ is reported as 3 in 1.0 M nitric acid. However, in 3.0 M nitric acid medium, the slope decreases to 2.8 (~3) and at 5.0 M nitric acid medium the value decreases to 2 as shown in figure 4.3. However, extending this slope analysis technique to determine the stoichiometry at higher metal loadings would involve large error as the equilibrium concentration of $[CMPO]_{IL}$ in equation 4.4 is not known.

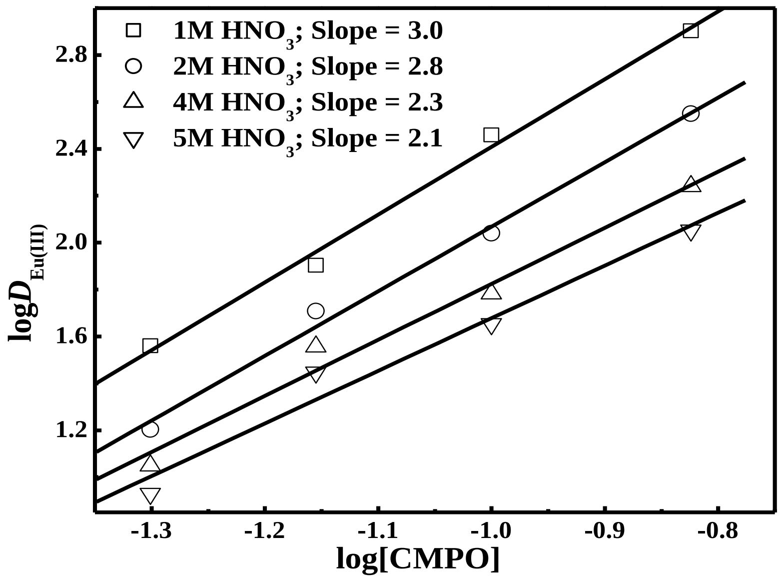


Figure 4.3. log D - log[CMPO] plot for the extraction of Eu(III) at 303 K. O:A = 1:1, Equilibration time = 1 hr

Table 4.2. Variation of europium(III) loading from 3 M nitric acid medium as a function of CMPO concentration in CMPO – 1.2 M TBP/C_4mimNTf$_2$. T=303 K, $[HNO_3]_{eq}$ = 3 M

$[Eu]_{ini}$, mg/mL	$[CMPO]_{ini}$ in CMPO - 1.2 M TBP/C_4mimNTf$_2$				
	0.1 M	0.15 M	0.2 M	0.25 M	0.3M
20	7.1	9.2	12.2	15.3	17.5
50	9.8	12.1	16.1	18.2	20.7
100	16.2	18.0	24.2	25.4	28.6
200	24.5	28.2	30.1	33.3	38.7

Nevertheless, the variation of europium loading as a function of $[CMPO]_{ini}$ and $[Eu]_{ini}$ was studied and the data are presented in table 4.2 shown above. It is observed that loading increases with increase in the concentration of $[CMPO]_{ini}$ and $[Eu]_{ini}$. From table 4.1, at the saturation solubility of europium(III) in nitric acid (~300 mg/mL), the loading of europium in 0.2 M CMPO-1.2 M TBP/C_4mimNTf$_2$ phase is ~40 mg/mL (Eu = 0.26 mmol/mL). This corresponds to the stoichiometry of Eu :CMPO as ~1 : 0.8. Several authors [9, 34-36] have determined the metal-solvate stoichiometry of lanthanides in CMPO phase by slope analysis as 1: 3 (Ln: CMPO) and also predicted theoretically that it can range from 1: 3 to 1: 1. The present study is the first kind of proof that the metal-solvate stoichiometry is near 1:1 in TRUEX solution which is otherwise indeterminable due to third phase formation in conventional *n*-DD system. The study thus indicates that the stoichiometry of Eu: CMPO varies depending upon loading of europium, from 1: 3 at trace levels, to 1 : 1 at higher loadings in ionic liquid medium.

4.2.5 Role of TBP

Tri-n-butyl phosphate is added to TRUEX solution to modify the organic phase and to circumvent third phase formation. Nagasaki et al. [6] investigated the third phase formation in CMPO-TBP-DD-HNO_3 system. The boundary of third phase formation was determined as a function of concentrations of CMPO and TBP, and temperature. Mathur et al. [37] studied the variation of TBP concentration in TRUEX solution and reported the distribution ratios of several metal ions including americium (III). Chapter 3 describes the variation of extraction of Am(III) with the concentration of TBP in TRUEX extractant /C_4mimNTf$_2$. In both cases mentioned above it was reported that TBP was not involved in extraction of americium (III) as the distribution ratio of americium decreased marginally with increase of TBP concentration. Table 4.3 shows the distribution ratio of Eu(III) in 0.2 M CMPO-TBP-C_4mimNTf$_2$ as a function of concentrations of TBP and HNO_3. It is observed that D_{Eu} decreases with increase in the concentration of TBP. As expected in this ionic liquid system, third phase formation was not observed in all cases. Thus, it appears that TBP in CMPO-TBP/C_4mimNTf$_2$ has very little role in view of the absence of third phase formation and addition of TBP only reduces the distribution ratio of europium. This indicates that 0.2 M CMPO/C_4mimNTf$_2$ may be adequate for the extraction of trivalents from nitric acid medium. However, when the initial concentration of Eu(III) in the feed was increased above 10 mg/mL, a “crud –type” precipitate was observed at the interphase during the extraction in 0.2 M CMPO/C_4mimNTf$_2$ and the “crud” increases with increase in the concentration of Eu in the aqueous phase. In addition, the “crud” undergoes dissolution by the addition of TBP to the extent of ~0.2 M in organic phase. This shows that a modifier like TBP is required to the extent of 0.2 M in ionic liquid phase. Table 4.4 shows the “crud” formation behavior in 0.2 M CMPO- TBP/$C_4mimNTf_2$ as a function of TBP and nitric acid concentration.

Table 4.3. Distribution ratio of $^{(152+154)}$Eu(III) in 0.2 M CMPO – TBP/$C_4mimNTf_2$. T = 303K

$[HNO_3]_{eq}$ ± 0.05 M	[TBP] in 0.2MCMPO – TBP/$C_4mimNTf_2$				
	0 M	0.1 M	0.3 M	0.8 M	1.2 M
1	1750	1672	1425	1140	1040
3	1142	950	690	425	352
5	800	550	416	250	170

The initial aqueous phase concentration of $[Eu]_{ini}$ was fixed at 300 mg/mL. In the absence of TBP, “crud” was observed in all cases. However, with increase in TBP concentration the “crud – formation” is reduced. When 0.2 M CMPO-0.2 M TBP/$C_4mimNTf_2$ is used for extracting europium from in 1 –5 M nitric acid, “crud” – formation is not observed. This behavior is similar to the third phase formation of TRUEX solution with nitric acid medium reported by Liansheng *et al.* [38]. It was reported that when TBP was not present (i.e. in CMPO/n-DD), third phase formation was observed after equilibrating 0.5 M nitric acid and its ability to form third phase decreased with increase in the ratio of [TBP]/[CMPO]. At [TBP]/[CMPO] ratio above 3, third phase was not observed even at 6 M nitric acid. Comparing the Liansheng *et al.* [38] data with the present study, it seems that modifier, such as TBP, is necessary even in $C_4mimNTf_2$ system, perhaps to other RTILs systems also, to avoid “crud” formation. However, the present study on “crud” formation is very preliminary and more studies are needed in this regard to understand the mechanism and arrive at other parameters influencing this phenomenon.

Table 4.4. “Crud” formation behavior in 0.2 M CMPO-TBP/$C_4mimNTf_2$. $[Eu]_{ini}$ = 300 mg/mL, T = 303K

$[HNO_3]_{eq}$ ± 0.05 M	[TBP] in 0.2MCMPO – 1.2M TBP/C4mimNTf2			
	0 M	0.1 M	0.15 M	0.2 M
1	Yes	Yes	Partial	No
3	Yes	Yes	Not clear	No
5	Yes	Yes	Not clear	No

4.2.6 Effect of Temperature

The enthalpy change accompanied by the extraction of europium(III) from nitric acid medium by a solution of 0.2 M CMPO –1.2 M TBP in C_4mimNTf$_2$ was determined by van’t Hoff equation as shown in the *section – 2.5.16* of the chapter 2. The plot of lnD_{Eu} against (1/T) for the extraction of europium(III) at various concentrations of nitric acid is shown figure 4.4. It is observed that distribution ratio of europium(III) decreases with increase of temperature indicating the exothermic nature of the extraction. The exothermicity (- ΔH_{tot}), determined from the slope of the plot, shown in figure 4.4, decreases from 27.4 ± 0.068 kJ/mol to 21± 0.066 kJ/mol with increase of equilibrium nitric acid concentration from 1 to 5 M. The decrease in exothermicity observed in the present case could perhaps be attributed to the formation of CMPO–HNO_3 in organic phase at higher nitric acid concentrations. Extraction of nitric acid by 0.2 M CMPO – 1.2 M TBP/C_4mimNTf$_2$ increases from 0.2 to 0.8 M, when the initial concentration of nitric acid in aqueous phase increases from 1 to 4 M. Since the extractant, CMPO, needs to be deprotonated to form metal–solvate complex for extraction, the overall exothermic enthalpy change decreases with increase in the concentration of nitric acid.

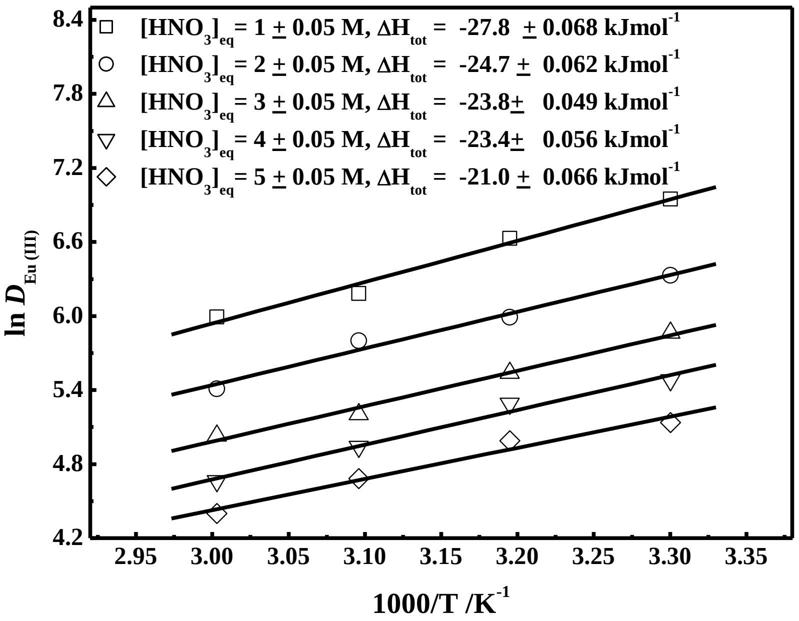


Figure 4.4. Variation of ln $D_{Eu(III)}$ with 1/T for the extraction of $^{(152+154)}$Eu(III) from nitric acid medium Organic phase = 0.2 M CMPO - 1.2 M TBP/C_4mimNTf$_2$, Aqueous phase = 1 - 5 M nitric acid spiked with $^{(152+154)}$Eu(III) tracer

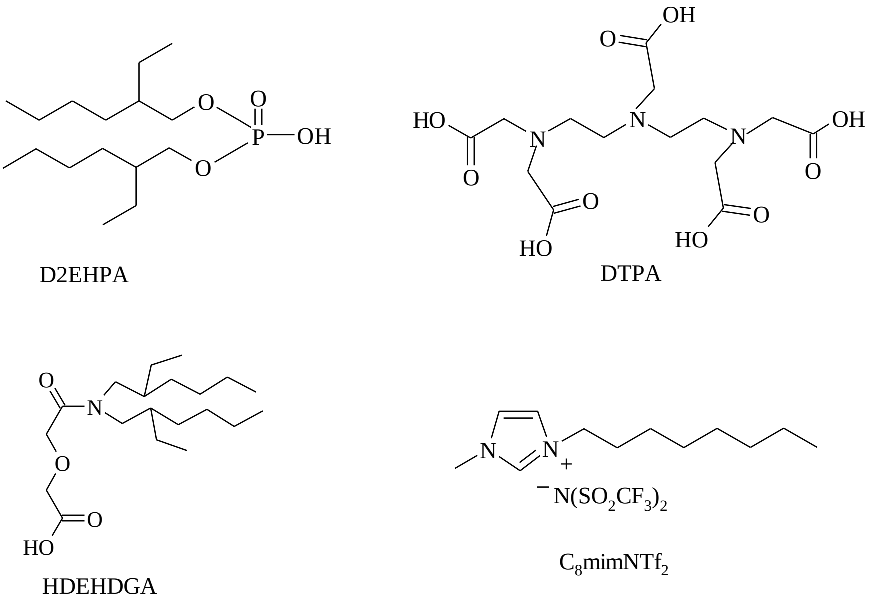
4.3 Conclusions

Use of RTIL diluent such as $C_4mimNTf_2$ in place of *n*-DD in 0.2 M CMPO – 1.2 M TBP system prevents undesirable third phase formation during the extraction of trivalent lanthanides and actinides. While the LOC of Eu(III) in *n*-DD was ~9 mg/mL, nearly ~ 40 mg/mL loading could be achieved with the use of 0.2 M CMPO-1.2 M TBP/$C_4mimNTf_2$ phase without any third phase formation. The stoichiometry of Eu : CMPO in RTIL phase varies, depending upon loading, from 1:3 at tracer levels to ~1:1 at higher metal loadings. Even at $[Eu]_{ini}$ = 20 mg/mL, the stoichiometry of Eu : CMPO in $C_4mimNTf_2$ was 1:3. In the absence of TBP, i.e, 0.2 M CMPO/$C_4mimNTf_2$, the extraction of Eu(III) results in a “crud type-precipitate” at the interphase and it disappeared with the addition of TBP to the extent of 0.2 M. The study indicates, that presence of TBP in $C_4mimNTf_2$ is required to modify the RTILs phase for preventing the observed phenomenon. The extraction of europium(III) by RTIL solution was accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration.

B. Mutual separation of Eu(III) from Am(III) in room temperature ionic liquid medium

4.4 Results and Discussions

The structure of the ionic liquid, C_8mimNTf$_2$ (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide), extractant [D2EHPA (bis(2-ethylhexyl)phosphoric acid) and HDEHDGA (bis(2-ethylhexyl)diglycolamic acid)] and DTPA (diethylenetriaminepentaacetic acid) are shown in the figure 4.5.



D2EHPA DTPA

HDEHDGA C_8mimNTf$_2$

Figure 4.5 Structure of D2EHPA, HDEHDGA , C_8mimNTf$_2$ and DTPA.

4.4.1 Effect of nitric acid

The distribution ratio of Eu(III) and Am(III) in a solution of 0.05 M D2EHPA in C_8mimNTf$_2$ as a function of aqueous phase pH is shown in the figure 4.6. It also shows the distribution ratio of Eu(III) and Am(III) obtained in a solution of 0.05 M HDEHDGA in C_8mimNTf$_2$. It is observed that the distribution ratio of Eu(III) and Am(III) increases with increase of pH in both cases. This could be due to the enhanced dissociation of D2EHPA and HDEHDGA with increase of pH. Higher distribution ratios obtained with the use of C_8mimNTf$_2$ in the present study (figure 4.6), confirms that the extractant in conjunction with the ionic liquid diluent provides enhanced stability of extracted complexes. However, the separation factor (= $D_{\mathrm{Eu(III)}}/D_{\mathrm{Am(III)}}$) remains at 1-2 in all cases, indicating the requirement of organic or aqueous phase modifiers for mutual separation.

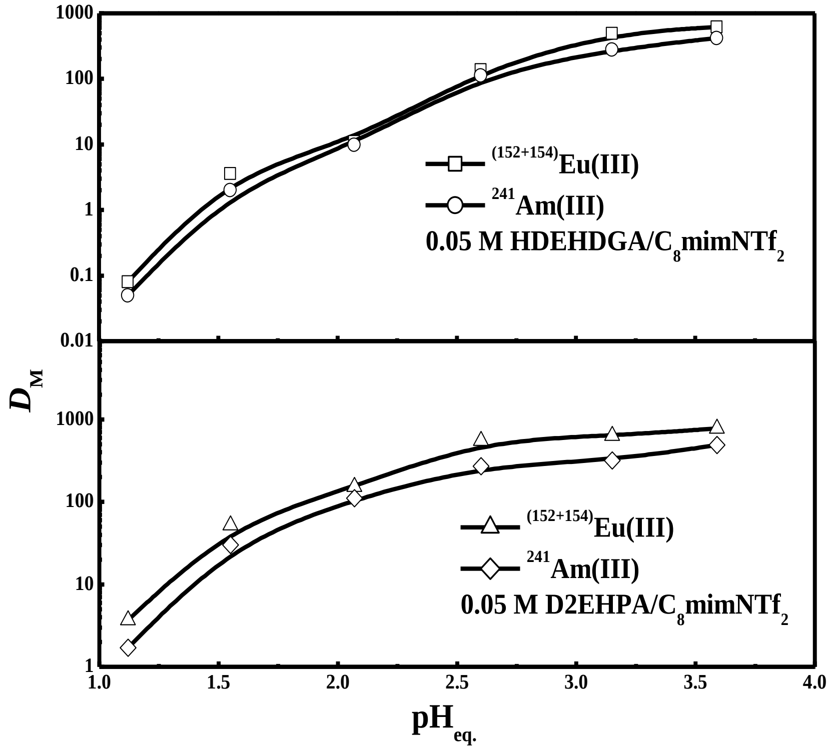


Figure 4.6. Distribution ratio of Eu(III) and Am(III) in a solution of 0.05 M D2EHPA (or HDEHDGA) in $C_8mimNTf_2$ as a function of pH, T = 298 K, A/O = 1, [M(III)] =20 mg/L

4.4.2 Effect of aqueous phase complexing agents

The processes developed for the mutual separation of lanthanides from actinides or vice versa, usually exploited the differential complexing abilities of the extractant present in organic phase and the complexing agent present in aqueous phase towards lanthanides and actinides [20-23]. In this context, the extraction of Eu(III) and Am(III) was studied in the presence of various aqueous soluble complexing agents. The dependence of the separation factor on the nature of complexing agent is shown in table 4.5. It is observed that among the various complexing agents studied, diethylenetriamine-*N,N,N',N'',N'''*-pentaaceticacid (DTPA) seems to be a potential reagent for the separation of Eu(III) from Am(III). The applications of DTPA is well-known for Ln-An separation in molecular diluent systems are reported elsewhere [20–23]. Figure 4.7 shows the variation in the distribution ratio of $^{(152+154)}$Eu(III) and ^{241}Am(III) in 0.05 M D2EHPA/$C_8mimNTf_2$ as a function of pH at a fixed concentration of 0.005 M DTPA in aqueous phase. It is observed that the presence of DTPA in aqueous phase decreases the distribution ratio of both the metal ions (compare with figure 4.6).

Table 4.5. Effect of the nature of complexing agents in aqueous phase on the distribution ratios of Eu(III) and Am(III) and their separation factors. Organic phase: 0.05 M D2EHPA (or 0.05 M HDEHDGA) in $C_8mimNTf_2$, Aqueous phase: pH ~3 + complexing agents, T = 298 K, A/O =1, [M(III)] =20 mg/L, SF = $D_{Eu(III)}$ / $D_{Am(III)}$

Complexing agents	Concentration /M	D2EHPA/ $C_8mimNTf_2$		SF	HDEHDGA/ $C_8mimNTf_2$		SF
		$D_{Eu(III)}$	$D_{Am(III)}$		$D_{Eu(III)}$	$D_{Am(III)}$	
AHA	0.005	523	277	1. 8	475	94	5.1
CA		187	86	2.17	106	197	0.5
EDTA		16.2	1.25	13	0.28	0.05	5.6
DTPA		4.2	0.12	35	0.04	0.002	20
AHA	10^{-4}	555	285	1.9	480	142	3.3
CA		202	105	1.9	250	270	0.9
EDTA		66	44	1.5	10	0.17	59
DTPA		133	7.25	18	6	0.04	150

AHA is acetohydroxamic acid, EDTA is ethylenediaminetetraacetic acid, CA is citric acid and DTPA is diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid

Since these metal ions are existing in trivalent oxidation state (Eu(III) and Am(III)), it is likely that they exhibit a preferential complexation with H_2A^{3-} species of DTPA (speciation discussed below) in aqueous phase and lowers the distribution ratio. It is also observed from figure 4.7 that the distribution ratio initially increases with increase of pH reaches a maximum value at pH 2 followed by decrease in distribution values. This could be attributed to the differences in the dissociation of D2EHPA and DTPA at a given pH. The pK_a value of the monobasic acid, D2EHPA, is 1.47 [39,40] and the pK_a values [41] of DTPA (pentabasic acid) are pK_{a1} is 1.9, pK_{a2} is 2.7, pK_{a3} is 4.42, pK_{a4} is 10.62 and pK_{a5} is 12.59. From the pK_a values of both D2EHPA and DTPA, the fraction of A^- (arises from the H^+ dissociation of D2EHPA) was determined and it was found to increase above pH 1 and the fraction of H_2A^{3-} form arising from DTPA was insignificant below pH 2. Under these conditions, the extraction of both Am(III) and Eu(III), seems to be controlled by dissociated form of D2EHPA and therefore the *D* values of Eu(III) and Am(III) increases with increase of pH. Above pH 2, the fraction of H_2A^{3-} arising from DTPA, that seems to be responsible for efficient complexation with the metal ions in aqueous phase, was found to increase and therefore the distribution ratio of Eu(III) and Am(III) decreases with increase of pH subsequently as shown in figure 4.7. A similar explanation could be attributed to the observed behavior in case of HDEHDGA, which is also a monobasic acid. Comparison of figure 4.7 and figure 4.6 indicates that the presence of DTPA in aqueous phase decreases the distribution ratio of both Eu(III) and Am(III). However, since the DTPA forms a stable complex with Am(III) than Eu(III) [17-20], the separation of Eu(III) from Am(III) could be achieved with the use of DTPA. From figure 4.7, the SF(= $D_{\mathrm{Eu(III)}}$ / $D_{\mathrm{Am(III)}}$) can be determined and it increases from 2.3 to 44 in case of D2EHPA, and 5.8 to 428 in case of HDEHDGA, with the increase of pH from 1 to 3.5.

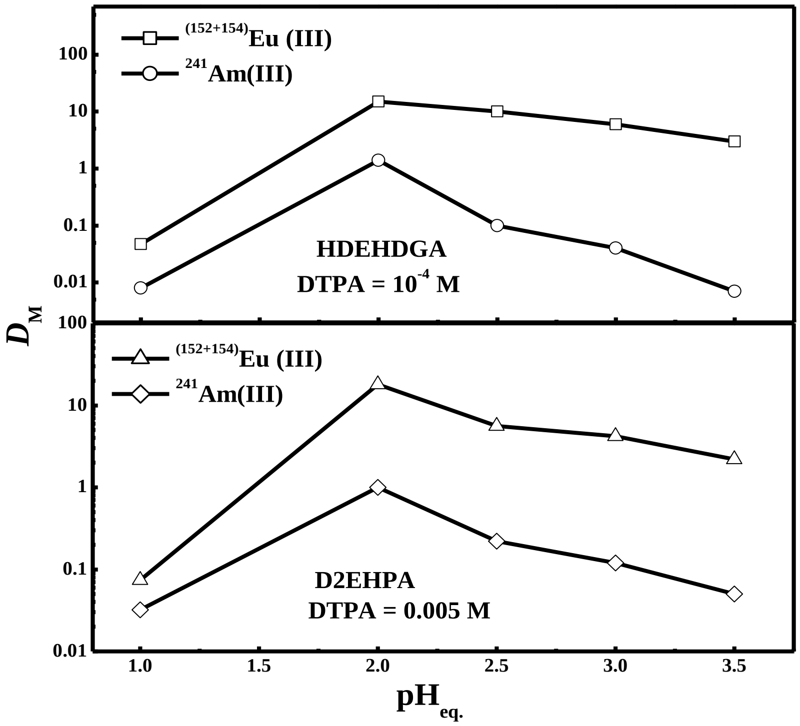


Figure 4.7. Variation in the distribution ratio of Eu(III) and Am(III)) as a function of pH. Organic phase : 0.05 M D2EHPA (or HDEHDGA)/C_8mimNTf$_2$, Aqueous phase: 0.005 M (or 10^{-4} M) DTPA + varied pH, T = 298 K, O/A = 1, [M(III)] = 20 mg/L

4.4.3 Effect of [DTPA] on SFs

Table 4.6 shows the variation in the distribution ratio of Eu(III) and Am(III) as a function of concentration of DTPA at a fixed pH ~ 3 in aqueous phase. It is observed that the distribution ratios decrease in both the cases with increase in the concentration of DTPA. This could be attributed due to the increased formation of M-DTPA complex in aqueous phase that lowers the distribution values. However it is interesting to observe that the SF of Eu(III) over Am(III) increases with increase of [DTPA], and reaches a maximum in both cases at a particular DTPA concentration, followed by decrease. This could, perhaps, be attributed to the differential complexing abilities of DTPA and D2EHPA under the given conditions. Moreover, at higher DTPA concentrations the distribution ratio of Eu(III) is reduced to a larger extent. Unlike D2EHPA, the SF achieved with the use of HDEHDGA is much higher and requires only 10^{-4}-10^{-5} M DTPA for efficient separation. A maximum SF of ~ 150 is achieved with the use of 10^{-4} M DTPA and 0.05 M HDEHDGA/C_8mimNTf$_2$.

Table 4.6. Effect of DTPA on the distribution ratios of Eu(III) and Am(III) and their separation factors. Organic phase: 0.05M D2EHPA (or 0.05M HDEHDGA) in C_8mimNTf$_2$, Aqueous phase: pH ~3 + varied [DTPA], T = 298 K, A/O =1, [M(III)] =20 mg/L, SF = $D_{Eu(III)}$ / $D_{Am(III)}$

[DTPA]$_{aq.}$ /M	**D2EHPA/C_8mimNTf$_2$**		**SF**	**HDEHDGA/C_8mimNTf$_2$**		**SF**
	$D_{Eu(III)}$	**$D_{Am(III)}$**		**$D_{Eu(III)}$**	**$D_{Am(III)}$**	
0	637	318	2	496	278	1.8
10^{-5}	--	--	--	115	0.9	127
10^{-4}	133	7.25	18	6	0.04	150
0.001	54	2.3	23.5	0.35	0.01	35
0.005	4.2	0.12	35	0.04	0.002	20
0.01	0.8	0.024	33	0.01	0.001	10
0.05	0.011	0.001	11	0.007	0.001	7

Table 4.7 compares the distribution ratio for the extraction of Eu(III) and Am(III) in HDEHDGA present in either ionic liquid or conventional molecular diluent (*n*-DD) at a constant pH of 3. It is observed that the separation factors are higher in ionic liquid diluent when the concentration of DTPA is $\leq 10^{-4}$ M. Higher SF are indeed necessary for the quantitative separation of Eu(III) with lesser number of stages during counter current operation. However, at higher DTPA concentrations, the distribution ratio decreases to very low value in both cases (*n*-DD and C_8mimNTf$_2$) and the metal ions are inextractable by the organic phase. This condition, even though the computed separation factors (e.g. at DTPA 0.005 M) are “good”, they are not useful for practical separations. In the case of D2EHPA system, a similar data could not be generated for D2EHPA in molecular diluent (*n*-DD) due to phase disengagement problem while equilibrating with nitric acid [23].

Table 4.7. Distribution ratios of Eu(III) and Am(III) and their separation factors. Organic phase: 0.05M HDEHDGA in C_8mimNTf$_2$ or *n*-DD, Aqueous phase: pH ~3 + varied [DTPA], T = 298 K, A/O =1, [M(III)] =20 mg/L, SF = $D_{Eu(III)}$ / $D_{Am(III)}$

$[DTPA]_{aq.}$ /M	**HDEHDGA/*n*-DD**		**SF**	**HDEHDGA/C_8mimNTf$_2$**		**SF**
	$D_{Eu(III)}$	**$D_{Am(III)}$**		**$D_{Eu(III)}$**	**$D_{Am(III)}$**	
0	122	94	1.3	496	278	1.8
10^{-5}	90	7	12.8	115	0.9	127
10^{-4}	40	0.6	66	6	0.04	150
0.001	4	0.06	66	0.35	0.01	35
0.005	0.5	0.05	10	0.04	0.002	20

4.4.4 Effect of [D2EHPA] and [HDEHDGA]

Figure 4.8 shows the variation in the distribution ratio of $^{(152+154)}$Eu(III) and ^{241}Am(III) as a function of concentration of the extractant in organic phase at a desired concentration of DTPA and pH ~ 3 in aqueous phase. It is observed that the distribution ratio increases with increase in the concentration of extractant. The extraction trend observed in figure 4.8 as well as in figure 4.6 indicates the involvement of cation exchange mechanism for the extraction of trivalents (M^{3+}) as indicated in equation 4.5.

$$3\ D2EHPA_{IL} + M_{aq}^{3+} \Leftrightarrow \{M(D2EHP)_3\}_{IL} + 3H_{aq}^{+} \tag{4.5}$$

D2EHP is the dissociated form of D2EHPA. The equilibrium constant for the above reaction is given by

$$K = \frac{[M(D2EHP)_3]_{IL}\ [H^+]_{aq}^3}{[M^{3+}]_{aq}\ [D2EHPA]_{IL}^3} \tag{4.6}$$

$$K = \frac{D_M\ \ [H^+]_{aq}^3}{[D2EHPA]_{IL}^3} \tag{4.7}$$

where D_M is defined in equation 1. At a constant pH, the variation of D_M with D2EHPA is given by equation 6.

$$\log D_M = \log K^1 + 3 \log [D2EHPA]_{IL} \tag{4.8}$$

where $K^1 = K / [H^+]^3_{aq}$.

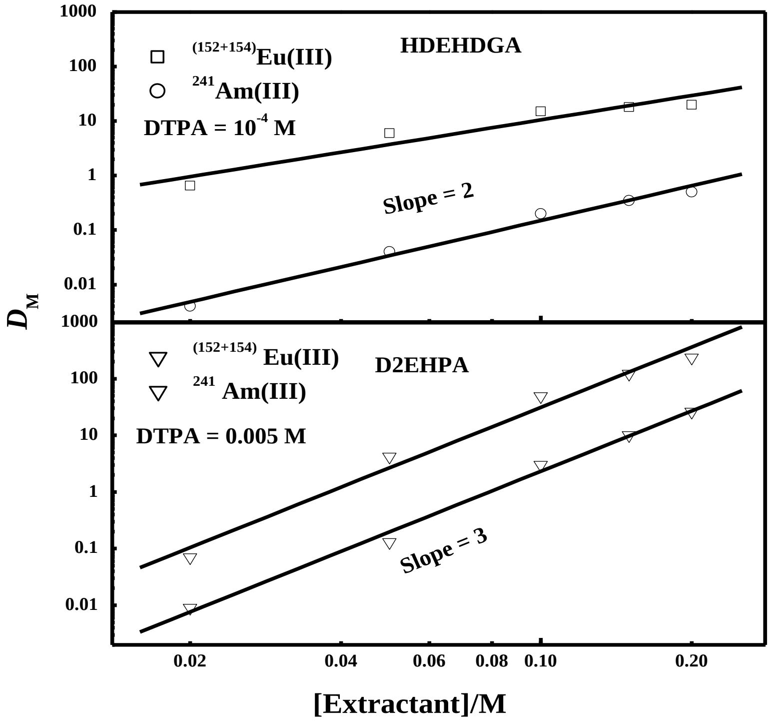


Figure 4.8. Variation in the distribution ratio of Eu(III) and Am(III) as a function of the extractant concentration. Organic phase : 0.05 M D2EHPA (or HDEHDGA)/C$_8$mimNTf$_2$, Aqueous phase : 0.005 M (or 10^{-4}M) DTPA + varied pH, T = 298 K,O/A = 1, [M(III)] = 20 mg/L

Thus the plot of log D_M against log [D2EHPA]$_{org}$ should result in a slope of 3. At pH 3, the variation of log D_M against log [D2EHPA]$_{org}$ is shown in figure 4.8. Linear regression of distribution data results in the slope of 3 for D2EHPA indicating 3 molecules of D2EHPA are involved in the extraction step. However, a slope of ~2 is obtained when HDEHDGA acted as extractant. Such deviations have been reported when ionic liquids are used as diluents [12] as well as in the *section 4.2.4* of the part “A”. The separation factor decreases significantly from 72 to 9 and from 162 to 40 with the increase in the concentration of D2EHPA and HDEHDGA respectively, from 0.02 to 0.2 M. This could be due to the extraction of both $^{(152+154)}$Eu(III) and ^{241}Am(III) with increase in the concentration of the extractants. To understand the observed difference in the stoichiometry of extraction between these two extractants, the variation in the distribution ratio of europium (III) and americium (III) as a function of extractant concentration in the absence of DTPA was studied. The plot of log D_M against log [Extractant] is shown in figure 4.9. Linear regression analysis of the distribution data results in the slopes of 2.92 and 2.78, respectively, for D2EHPA and HDEHDGA extractants. This indicates that about 3 molecules of D2EHPA and HDEHDGA are involved in the extraction step.

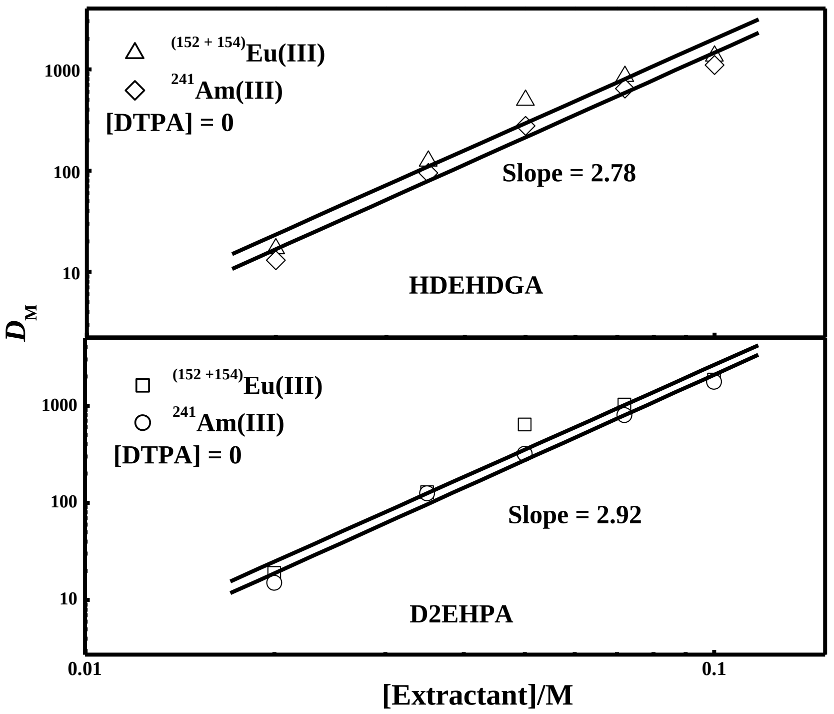


Figure 4.9. Variation in the distribution ratio of Eu(III) and Am(III) as a function of the extractant concentration. Organic phase : 0.05 M D2EHPA (or HDEHDGA)/C_8mimNTf$_2$, Aqueous phase : Varied pH, T = 298 K,O/A = 1, [M(III)] = 20 mg/L

The slope obtained in the present study agree well with the stoichiometry and slope reported by Kubota *et al.* [31] for the extraction of various lanthanides in diglycolamic acid. Moreover, they also reported the involvement of ion exchange mechanism as shown in equation 4.5. Comparing these results with those obtained in the presence of DTPA (figure 4.8) indicates that the M-extractant stoichiometry of Eu(III) and Am(III) extraction in D2EHPA seems to be similar. However, in HDEHDGA system, DTPA seems to be playing some role in the extraction of Eu(III) and Am(III). The correct reason for this discrepancy is not evident from the present data and more studies may be needed to understand the intricacy of extraction.

4.5 Conclusions

The room temperature ionic liquid, $C_8mimNTf_2$ was explored as a diluent for the separation of trivalent lanthanides from actinides. The extraction behavior of ^{241}Am(III) and $^{(152+154)}$Eu(III) in a solution of D2EHPA or HDEHDGA in $C_8mimNTf_2$, was studied. The results confirmed that these extractants in conjunction with the present ionic liquid provides extraordinary extraction of Am(III) and Eu(III) from aqueous solutions of widely differing compositions. Among all the complexing agents used, DTPA was found to be more potential candidate in conjuction with ionic liquid for the separation of Eu(III) from Am(III). The differential complexing ability of the extractant in ionic liquid phase and DTPA in aqueous phase was exploited to optimize the conditions needed for effective separation of trivalent lanthanides from actinides. The stoichiometry of metal – solvate was found to be 3. Among the extractants studied HDEHDGA was found to be superior to D2EHPA for such applications. At pH 3 and using 0.005 M DTPA, D2EHPA gave in a SF of ~35, however, HDEHDGA required only 10^{-4} M DTPA for achieving a SF of ~150.

4.6 References

[1] Z. Kolarik, The formation of a third phase in the extraction of Pu(IV), U(IV) and Th(IV) nitrates with tributyl phosphate in alkane diluents. ISEC'77, Can. Inst. Mining Metallurgy, CIM Spec. Toronto, Canada, (1979) (21)178.

[2] T. V. Healy, H. A. C. Mckay, The extraction of nitrates by tri-n-butyl phosphate(TBP). Part 2-The nature of the TBP phase. Trans. Faraday Soc. 52 (1956)633.

[3] P. R. Vasudeva Rao, R. Dhamodaran, T. G. Srinivasan, C. K. Mathews. The effect of diluents on third phase formation in thorium nitrate – TBP system: Some novel empirical correlations. Solvent Extr.Ion Exch. 11 (4) (1993) 645-662.

[4] K. Gonda, K. Oka, Accumulation process of plutonium third phase in mixture settlers. Nuclear Technology 64 (1984) 14 -18.

[5] P.R.Vasudev Rao, Z. Kolarik, A Review of third phase formation in extraction of actinides by neutral organophosphorus extractants. Solvent Extr. Ion Exch. 14 (6) (1996) 955-993.

[6] S. Nagasaki, D. S. Wisnubroto, Y. Enokida, A. Suzuki, Third phase formation in nitric acid extraction by octyl(phenyl)-*N*,*N*-diisobutyl carbamoyl methylphosphinoxide. Solvent Extr. Ion Exch. 12 (2) (1994) 459 - 473.

[7] T.G. Srinivasan, R. Dhamodaran,; Vijayasaradhi, S.; Suresh, A.; Vasudeva Rao, P.R.: Third phase formation in extraction of thorium nitrate by mixtures of trialkyl phosphates. Solvent Extr.Ion Exch. 16 (4) (1998) 1001-1011.

[8] B. A. Moyer, Ion Exchange and Solvent Extraction. A series of Advances, Volume 19. CRC Press, Taylor and Francis Group 2010.

[9] E.P. Horwitz, M.A. Kalina, L. Kaplan, The extraction of selected transplutonium (III) and lanthanide (III) ions by dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate from aqueous nitrate media. Sep. Sci. Technol. 16 (4) (1981) 417–437.

[10] E.P. Horwitz, D.G. Kalina, L. Kalpan, G.W. Mason, H.D. Diamond, Selected alkyl(phenyl)-*N*,*N*-dialkylcarbamoylmethylphosphine oxides as extractants for Am(III) from nitric acid media. Sep. Sci. Technol. 17 (10) (1982) 1261 – 1279.

[11] A. Suresh, C.V.S.Brahmananda Rao, K. N. Sabharwal, T. G. Srinivasan, P.R.Vasudeva Rao, Third phase formation in the extraction of Nd(III) by octyl(phenyl)-*N*,*N*-diisobutyl carbamoyl methylphosphinoxide (OϕCMPO), Solvent

Extr. Ion Exch. 17(1) (1999) 73-78.T. Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. Chem. Rev. 99 (8) (1999) 2071- 2084.

[12] M.L. Dietz, D. C. Stepinski , Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. Talanta 75 (2) (2008) 598–603.

[13] G. R. Choppin, Comparative solution chemistry of the 4f and 5f elements. J. Alloys Compds. 223 (2) (1995) 174–179.

[14] N. B. Mikheev, V. I. Spytsin, R. A. Dyachkova, L. N. Auerman, Energetics of 5f- and 4f-orbitals and 5f- and 4f-elements similarity. J. Phys. Colloques 40 (C4) (1979) 230–232.

[15] H. C. Aspinall, Chemistry of f-block elements, advanced chemistry texts. Gordon and Breach Science Publishers, New York (2001).

[16] N. N. Greenwood, A. Earnshaw, Chemistry of elements. Elsevier Publishers, Amsterdam (2010).

[17] T. Matsumura, Y. Inaba, A. Mori, K. Takeshita, Am/Eu Separation with a new ligand, *N,N,N',N'*- tetrakis ((4-butoxypyridin-2-yl)methyl) ethylenediamine (TBPEN), a hydrophobic derivatives of TPEN. J. Nucl. Sci. Technol. 47 (2) (2010) 123-126.

[18] Y. Sasaki, Y. Morita, Y. Kitatsuji, T. Kimura, Mutual separation of actinides from middle lanthanides by the combination of two neutral donors, *N,N,N',N'*-Tetraoctyl-3,6-dioxaoctanediamide and *N,N,N',N'*-Tetraethyldiglycolamide. Chem. Lett. 39 (8) (2010) 898 - .

[19] T. Suzuki, K. Otake, M. Sato, A. Ikeda, M. Aida, Y. Fujii, M. Hara, T. Mitsugashira, M. Ozawa, Separation of americium and curium by use of tertiary pyridine resin in nitric acid/methanol mixed solvent system. J. Radioanal. Nucl. Chem. 272 (2) (2007) 257- 262.

[20] M. Nilsson, K. L. Nash, A Review of the development and Operational Characteristics of the TALSPEAK Process. Solvent Extr. Ion Exch. 25 (6) (2007) 665–701.

[21] G.W. Weaver, F. A. Kappelmann, A new method for separating americium from curium from the lanthanides by extraction from an aqueous solution of aminopolyacetic acid complexed with a monoacidic organophosphate of Phosphonate ORNL/3559 (1964) TID-4500.

[22] C. J. Leggett, G. Liu, M. P. Jensen, Do Aqueous Ternary Complexes Influence the TALSPEAK Process ? Solvent Extr. Ion Exch. 28 (3) (2010) 313-334.

[23] A.S. Suneesh, J. Ravi, K.A. Venkatesan, M.P. Antony, T.G. Srinivasan and P.R. Vasudeva Rao, Lanthanide–actinide separation by bis-2-ethylhexylphosphoric acid from citric acid–nitric acid medium. J. Radioanal. Nucl. Chem., 285 (3) (2010) 653–658.

[24] Y. Sasaki, G.R. Choppin, Solvent extraction of Eu, Th, U, Np and Am with N, N' – dimethyl-*N,N*' di-hexyl-3-oxapentanediamide and its analogous compounds. Anal. Sci. 12 (2) (1996) 225-230.

[25] S. A. Ansari, P.N. PathakV.K. , Manchanda, M. Hussain, A.K. Prasad, V.S. Parmar, *N,N,N'N'*-Tetraoctyl diglycolamide (TODGA): a promising extractant for actinide-partitioning from high level waste (HLW). Solvent Extr. Ion Exch. 23 (4) (2005) 463-479.

[26] G. Modolo, H. Asp, H. Vijgen, R. Malmbeck, D. Magnusson, C. Sorel, Demonstration of TODGA based continuous current extraction process for the partitioning of actinides from a simulated PUREX raffinate, Part II: Centrifugal contactor runs. Solvent Extr. Ion Exch. 19 (1) (2008) 62-76.

[27] D. Magnusson, B. Christiansen, J.P. Glatz, R. Malmeck, G. Modolo, D. S. Purroy, C. Sorel, Demonstration of a TODGA based extraction process for the partitioning of minor actinides from a PUREX raffinate. Solvent Extr. Ion Exch. 27 (1) (2009) 26-35.

[28] E.A. Mowafy, H.F.Aly, Synthesis of some N, N, N'N'-tetraalkyl-3-oxa-pentane-1, 5-diamide and their applications in solvent extraction. Solvent Extr. Ion Exch. 25 (2) (2007) 205-224.

[29] H. Naganawa, K. Shimojo, H. Mitamura, Y. Sugo, J. Noro, M. Goto, A new "green" extractant of the diglycolamic acid type for lanthanides. Solvent Extr. Res. Dev., Jpn. 14 (2007) 151-159.

[30] K. Shimojo, H. Naganawa, J. Noro, F. Kubota, M. Goto, Extraction behavior and separation of lanthanides with a diglycolamic acid derivative and a nitrogen-donor ligand. Anal. Sci. 23 (2007) 1427-1430.

[31] F. Kubota, Y. Shimobori, Y. Koyanagi, K. Shimojo, N. Kamiya, M. Goto, Uphill transport of rare-earth metals through a highly stable supported liquid membrane based on an ionic liquid. Anal. Sci. 26 (3) (2010) 289-290.

[32] Y. Shen, X. Tan, L. Wang, W. Wu, Extraction of the uranyl ion from the aqueous phase into an ionic liquid by diglycolamide. Separation purification Technol. 78 (3) (2011) 298–302.

[33] K. Nakashima, F. Kubota, T. Maruyama, M. Goto, Feasibility of ionic liquids as alternative separation media for industrial solvent extraction process. Ind. Eng. Chem. Res. 44 (12) (2005) 4368 – 4372.

[34] S. Belair, A. Labet, C. Mariet, P.Dannus, Modeling of the extraction of nitric acid and neodymium nitrate from aqueous solutions over a wide range of activities by CMPO. Solvent Extr. Ion Exch. 23 (4) (2005) 481-499.

[35] M.L.P. Reddy, A. Damodaran, J.N. Mathur, M.S. Murali, M.V. Balarama Krishna, R. H. Iyer.The itinerant extraction behavior of f-elements and yttrium with octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide. Solvent Extr. Ion Exch. 14 (5) (1996) 793–816.

[36] M.Y. Koma, S. Watanabe, Y. Namoto, Trivalent f-element intra-group separation by solvent extraction with CMPO-complexant system. J.Nucl. Sci. Technol. 35 (2) (1998) 130–136.

[37] J.N. Mathur, M.S. Murali, P.R. Natrajan, L.P. Badheka, A. Banerji, Extraction of actinides and fission products by octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl-phosphine oxide from nitric acid media. Talanta 39 (5) (1992) 493–496.

[38] W. Liansheng , M. Casarci, G.M. Gasparini, The extraction of Eu(III) from acidic media by octyl(phenyl)-*N,N*-diisobutyl carbamoyl methylphosphinoxide. Solvent extr. Ion Exch. 8(1) (1990) 49 - 64.

[39] S.H. Hilal, A. Carreira, S.W. Karikhoff, Estimation of chemical reactivity and parameters and physical properties of organic molecules using SPARC. In: Quantitative Treatments of Solute/Solvent Interactions: Theoretical and Computational Chemistry Vol. 1 NY, NY: Elsevier (1994) p 291 – 353.

[40] I. Szymanowski, G. Cote, I. Blondet, C. Bouvier, D. Bauer, J. L. Sabot, Interfacial activity of bis(2-ethylhexyl)phosphoric acid in model liquid-liquid extraction systems. Hydrometallurgy, 44 (1-2) (1997) 163 – 178.

[41] E. J. Durham, D. P. Ryskiewich, The acid dissociation constants of diethylenetriaminepentaacetic acid and the stability constants of some of its metal chelates. J. Am. Chem. Soc. 80 (18) (1958) 4812-4817.

Chapter - 5

CHAPTER - 5

Unusal separation of plutonium(IV) from other actinides and fission products using novel functionalized ionic liquids (FILs)

This chapter deals with the extraction behavior of actinides and fission products by using a couple of functionalized ionic liquids (FILs) (or task specific ionic liquids, TSILs) such as diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide ($ImPNTf_2$) and amide based TSIL, *N,N*–dioctyl-2(3-methyl imidazolium) bis trifluoromethane sulfonamide ($DOAImNTf_2$). The effect of aqueous phase acidity, TSIL concentrations, temperature, different additives etc. on the separation of plutonium from other metal ions have been discussed.

5.1 Introduction

Ionic liquids with cationic or anionic part tethered covalently with organic functionalities, which can perform target specific applications are known as task specific ionic liquids (TSILs) [1]. The presence of functional group in TSIL exhibits unique and synergistic properties of both ionic liquid and organic functionality. Visser *et al.*[2,3] prepared several task specific functionalities attached to imidazolium moiety and reported an enhanced selectivity of heavy metal extraction in those TSILs. Protonated 1-carboxy-*N*,*N*,*N*-trimethylmethanaminium bis(trifluoromethylsulfonyl)imide, trivially known as protonated betaine bis(trifluoromethylsulfonyl)imide ($[Hbet][NTf_2]$) was reported to be a solvent for dissolving oxides of some lanthanides and actinides [4]. Harjani *et al.*[5] synthesized new class of TSILs containing aminodiacetic acid moieties and studied the separation of copper, nickel and cobalt. Monoaza-crown ether attached to imidazolium moiety was prepared by Luo *et al.*[6] and studied for the extraction of cesium(I) and strontium (II) from nitric acid medium. Ouadi *et al.*[7,8] synthesized new class of TSILs bearing 2-hydroxybenzylamine and reported extraction of americium from aqueous media. The distribution ratio of ^{241}Am(III) increased with increase of pH, reaching a maximum at ~ pH 8 – pH 10. Above pH 10, partial dissolution of ionic liquid in aqueous phase was reported. The stoichiometry of Am:TSIL was determined to be 1:2. Similarly, the extraction of U(VI) from 3 M was reported by using phosphoryl based TSIL and the preliminary extraction data indicate the potential use of these FILs for applications related to uranium separation. A general approach for the synthesis of carbamoylmethylphosphine oxide functionalized ionic liquid and its application for the extraction of actinides and lanthanides was reported by Odinets *et al.*[9]. In neutral media, these ionic liquids formed bidendate complexes of the type M-(ligand)$_2$ with europium chloride or europium nitrate. The preliminary data suggests good extraction of Pu(IV), Am(III), Eu(III), and U(VI) from 3 M nitric acid medium. Recently, Oliver *et al.*[10] synthesized diketonate functionalized ionic liquid by grafting the β - diketonate moiety with imidazolium moiety and studied the extraction of lanthanides using silica support (solid – liquid extraction).

This chapter reports the studies on the synthesis of a couple of functionalized ionic liquids containing phosphonate and amide functional groups attached to the imidazolium moiety and the extraction of actinides and fission products from nitric acid medium using these ionic liquids. This chapter also discusses the merits of functionalization to the ionic liquid moiety. The present chapter is divided in to two parts. Part "A" deals with the unusual extraction of Pu(IV) from other actinides and fission products using phosphonate based functionalized ionic liqud, diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide (ImPNTf$_2$). Part "B" deals with unusual extraction of Pu(IV) from other actinides and fission products using amide based functionalized ionic liquid,*N*,*N*-dioctyl-2-(3-methylimidazolium)acetamide bis(trifluoromethanesulfonyl)imide (DOAImNTf$_2$).

The synthesis of these FILs have been discussed in the section 2.4.4 and 2.4.5 of the chapter 2 respectively. Experimental details of this chapter has been given in the section 2.6.4 of the chapter 2 respectively.

A. Separation of plutonium(IV) from other actinides and fission products using phosphonate based functionalized ionic liquid

5.2 Results and Discussions

5.2.1 Pu(IV) extraction by RTIL diluents- Effect of [HNO_3]

Table 5.1 shows the distribution ratios of Pu(IV), U(VI) and Am(III) in $C_n$mimNTf$_2$ (n = 4, 6 and 8) at various concentrations of nitric acid. It is observed that distribution ratios of plutonium(IV) in $C_n$mimNTf$_2$ are significant, while the values observed for U(VI) and Am(III) are very less. The $D_{Pu(IV)}$ value increases with increase in the acidity and chain length of alkyl group. $D_{Pu(IV)}$ is insignificant up to 3 – 4 M nitric acid and increases with increase in the acidity. It is worthwhile to note that the distribution ratios in C_8mimNTf$_2$ are nearly an order higher than the values observed for C_4mimNTf$_2$. These observations indicate that $C_n$mimNTf$_2$ (n = 4, 6 and 8) is not an inert diluent and anion exchange of plutonium nitrate species, $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$, with NTf_2^- of ionic liquid phase is responsible for such extraction at higher acidities. On the contrary, in case of U(VI) and Am(III) distribution ratios are of the order of 10^{-2} -10^{-4} irrespective of the aqueous acidity and structure of the ionic liquid diluent. This shows that the anion exchange mechanism is not observed in case of U(VI) and Am(III) unlike Pu(IV).

Table 5.1. Variation in the distribution ratio of Pu(IV), U(VI) and Am(III) in $C_n$mimNTf$_2$ (n = 4,6 and 8) as a function of nitric acid concentration at 298 K

[HNO_3]$_{eq.}$/ M	$D_{Pu(IV)}$			$D_{U(VI)}$			$D_{Am(III)}$		
	n = 4	n-6	n=8	n=4	n=6	n=8	n=4	n=6	n=8
1	0.004	0.02	0.05	5 x 10^{-4}	10^{-4}	0.001	2 x 10^{-4}	2 x 10^{-5}	3 x 10^{-5}
2	0.06	0.15	0.73	6 x 10^{-4}	7x10^{-4}	---	---	---	---
3	0.4	2	3.9	8 x 10^{-3}	2 x 10^{-3}	0.019	2 x 10^{-4}	5 x 10^{-3}	1 x 10^{-4}
4	1.77	7.7	11.1	10^{-3}	8 x 10^{-3}	---	---	---	---
5	6.62	20	37.5	7 x 10^{-2}	0.05	0.135	2 x 10^{-4}	3 x 10^{-4}	4 x 10^{-4}

The extraction of uranium(VI) in RTILs such as $C_4mimNTf_2$ and C_4mimPF_6 and the involvement of ion exchange mechanism at higher nitric acid concentration (8.0 M) was reported by Giridhar *et al.*[11]. A distribution value of 0.05 and 0.4 were reported for the extraction of U(VI) by C_4mimPF_6 from 4.0 M and 8 M nitric acid respectively. Marginal increase in distribution ratio at 8 M nitric acid was attributed to the anion exchange of uranyl nitrate complexes, which are likely to form only at high nitric acid concentrations (>7 M), with anion of RTIL. In contrast to this, Pu(IV) forms anionic complexes at nitric acid concentrations ($\geq$ 5 M) and undergoes anion exchange with RTILs ($C_nmimNTf_2$) at lower acidities leading to high distribution ratios, as shown in table 5.1. A distribution value of 1.66, 20 and 37.5 obtained at 5.0 M equilibrium nitric acid in $C_4mimNTf_2$, $C_6mimNTf_2$ and $C_8mimNTf_2$ medium respectively and the trend observed at different acidities indeed show that Pu(IV) is extracted by anion exchange in this case also.

5.2.2 Anion Exchange

In order to support the involvement of ion exchange mechanism for the extraction of plutonium(IV) in the present case, the distribution ratios of plutonium(IV) were measured at various concentrations of NTf_2^- ion (added as $LiNTf_2$) present in aqueous phase. The probable anion exchange reactions responsible for the extraction of plutonium (IV) by $C_4mimNTf_2$ extraction are shown in equations 5.1 and 5.2.

$$[Pu(NO_3)_5(H_2O)]^-_{aq} + NTf^-_{2\,IL} \Leftrightarrow [Pu(NO_3)_5(H_2O)]_{IL} + NTf^-_{2\,aq} \qquad (5.1)$$

$$[Pu(NO_3)_6]^{2-}_{aq} + 2NTf_{2\,IL} \Leftrightarrow [Pu(NO_3)_6]_{IL} + 2\ NTf^-_{2\,aq} \qquad (5.2)$$

If the mechanisms shown in equations (5.1) and (5.2) hold good for the extraction of Pu(IV), then the plot of log $D_{Pu(IV)}$ against $\log[NTf_2^-]_{aq}$ should result in a negative slope of –1 and –2 respectively. A plot of log $D_{Pu(IV)}$ vs. log $[NTf_2^-]_{ini,aq}$. for the extraction of plutonium(IV) from 3 M and 5 M nitric acid medium by $C_4mimNTf_2$ is shown in the figure 5.1. Since, the added $LiNTf_2$ was dissolved in the ionic liquid phase to some extent, the aqueous phase concentration of $[NTf_2]^-$ ion at equilibrium was not known. In view of this, the variation in the distribution ratio of Pu(IV) as a function of initial concentration of NTf_2^- ion rather than equilibrium concentration has been plotted in the figure 5.1. A slope of –1 obtained in both cases indicates that extraction of plutonium(IV) is essentially governed by ion exchange reaction shown in equation 5.1. Similarly, a higher negative slope value of –1.43 and –1.9 obtained for the extraction of plutonium(IV) by $C_8mimNTf_2$ from 3 M and 5.0 M nitric acid respectively, shown in figure 5.1, confirms the enhancement in the formation of anionic species leading to higher extraction, when

$C_8mimNTf_2$ is used as extractant. Thus, the predominant mode of Pu(IV) transfer in to ionic liquid phase at higher nitric acid concentration is through anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ and $[Pu(NO_3)_6]^{2-}$ with NTf_2^- ion of ionic liquid. The results indicate that unlike traditional diluents, e.g. *n*-dodecane, the ionic liquid diluents are not inert [12 - 14] and depending upon the structure of ionic liquid the distribution values realized for Pu(IV) are different.

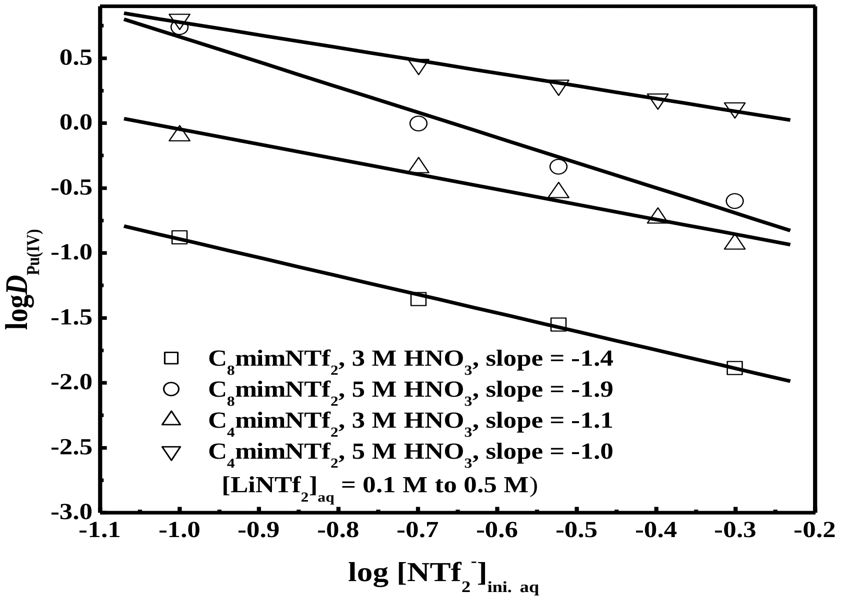


Figure 5.1. Variation of log $D_{Pu(IV)}$ with log $[NTf_2]^-_{aq.}$ for the extraction of Pu(IV) from nitric acid medium (3 & 5 M) by $C_4mimNTf_2$ and $C_8mimNTf_2$ at 298 K

5.2.3 Pu(IV) extraction by $ImPNTf_2$ - Effect of $[HNO_3]$

The distribution ratios of Pu(IV) in a solution of $ImPNTf_2$ in $C_4mimNTf_2$ at various concentrations of nitric acid are tabulated in table 5.2. The concentration of $ImPNTf_2$ in $C_4mimNTf_2$ was varied from 0.2 M to 0.5 M. It is observed that the distribution value of Pu(IV) increases with increase in the concentration of $ImPNTf_2$ in organic phase and decreases with increase in the concentration of nitric acid in aqueous phase. Considering the distribution ratios of plutonium (IV) obtained in the presence and absence of ionic liquid extractant, $ImPNTf_2$, shown in (table 5.1 and table 5.2), it is likely that of Pu(IV) is extracted by $ImPNTf_2$ by complex formation. Figure 5.2 displays the extraction of Pu(IV) in 0.4 M $ImPNTf_2/C_nmimNTf_2$ (n = 4, 5 and 6) to support the evidence for involvement of complex formation of Pu(IV) with $ImPNTf_2$. It is observed that the distribution ratio of Pu(IV) 0.4 M $ImPNTf_2/C_nmimNTf_2$ is higher in the nitric acid region 0.5 - 4 M. On the contrary, $D_{Pu(IV)}$ is insignificant in $C_nmimNTf_2$ alone (see table 5.1). This shows there is the occurrence of complex formation of Pu(IV) with $ImPNTf_2$

and $D_{Pu(IV)}$ decreases with increase in chain length of the diluent, $C_nmimNTf_2$. The metal-solvate stoichiometry of such complex formation can be determined by plotting log $D_{Pu(IV)}$ against log $[ImPNTf_2]_{org}$. Figure 5.3 shows the plot of log$D_{Pu(IV)}$ against log$[ImPNTf_2]_{org}$ for the nitric acid range 1 M to 4 M. The data obtained for 5 M nitric acid is not plotted in figure 5.3. It is observed that a slope value of ~3.0 (indicated in figure 5.3) is obtained for the extraction of Pu(IV) only at 3-4 M nitric acid concentration. The slope value differs significantly for others. Several authors have proposed wide variety of mechanisms for the extraction of target metals from aqueous phase by neutral extractants in ionic liquid medium [15 –20]. Dietz and co-workers [16 –18] studied the extraction behavior of several metal ions of nuclear interest by appropriate neutral extractants present in RTIL medium.

Table 5.2. Variation in the distribution ratio of Pu(IV) in $ImPNTf_2/C_4mimNTf_2$ as a function of nitric acid concentration, at 298 K

$[HNO_3]_{eq.}$ /M	$D_{Pu(IV)}$ in $ImPNTf_2/C_4mimNTf_2$ at				
	0.0 M	**0.2M**	**0.3M**	**0.4M**	**0.5M**
1	0.004	123	120	159	240
2	0.059	35	20	35	90
3	0.412	1.9	7	17	35
4	1.77	1.85	4	9	18
5	6.62	4.2	4.5	8	4.1

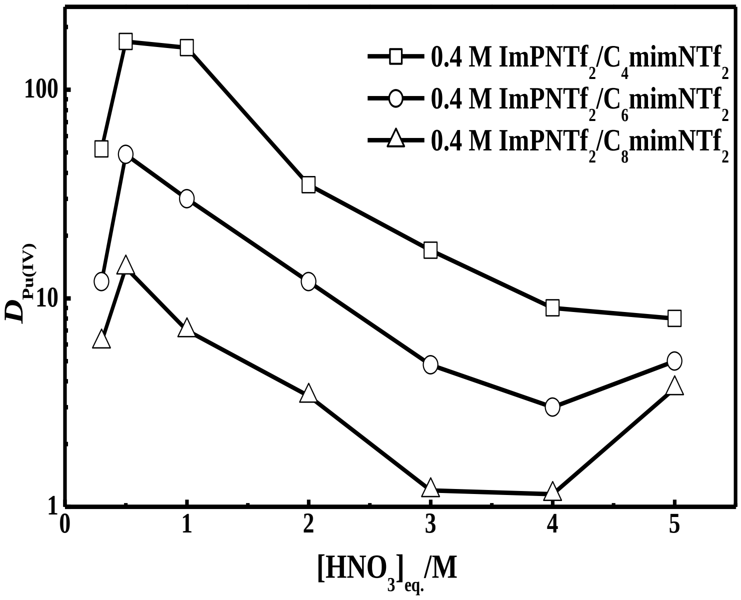


Figure 5.2. Variation in the distribution ratio of Pu(IV) as a function of nitric acid. Organic phase: 0.4 M $ImPNTf_2/C_nmimNTf_2$ (n = 4,6 and 8), Aqueous phase: 0.3 - 5 M HNO_3, Equilibration time = 1 hr, O : A = 1:1, T = 298 K

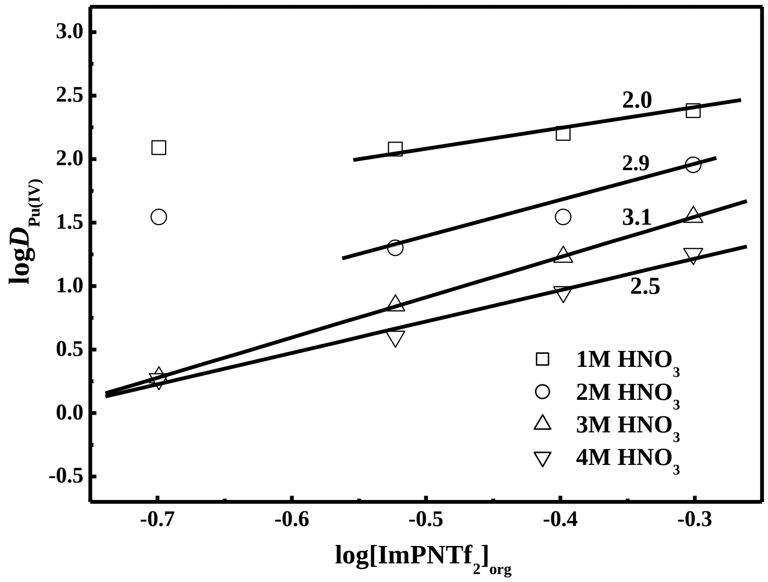


Figure 5.3. Variation of log$D_{Pu(IV)}$ with log [ImPNTf$_2$]$_{org}$ for the extraction of plutonium (IV) from nitric acid medium by ImPNTf$_2$/C$_4$mimNTf$_2$ at 298 K

Dietz *et al.* [16] proposed a couple of mechanisms for the extraction behavior of Sr^{2+} by the neutral extractant crown ether (CE) in ionic liquid medium (the extraction trend is similar to the present observation). According to them, the mechanism involves (a) formation of $Sr(NTf_2)_2$.CE complex in organic phase rather than the usual $Sr(NO_3)_2$CE, as well as (b) ion exchange with cationic part of ionic liquid explain,. However, the present system is a very unique extractant namely ionic liquid, ImPNTf$_2$, itself and the extraction behavior observed for Pu(IV) in the present study indicates the involvement of different mechanism or a combination of some mechanisms, which is not clear at the present and requires further investigation. Nevertheless, the study revealed that extraction of plutonium (IV) by ImPNTf$_2$ is through complex formation reaction from 1 – 4 M nitric acid medium.

5.2.4 Separation factor

Table 5.3 shows the distribution ratios of Am(III) and U(VI) in 0.4 M ImPNTf$_2$/C$_4$mimNTf$_2$. It is observed that distribution ratios are insignificant in these cases, when compared to the values obtained for plutonium (IV). It is worthwhile to note that the distribution data obtained for the extraction of uranium (VI) in ImPNTf$_2$/C$_4$mimNTf$_2$ are unusually low. Generally, neutral extractants containing phosphoryl group (P=O group), when used for extraction, exhibit [21, 22] a comparable distribution ratio for uranium (VI) and plutonium (IV). For example, table 5.4 shows the distribution ratios of U(VI) and Pu(IV) reported for the solutions of some trialkyl phosphates [21] and trialkyl phosphonates [22] present in *n*-dodecane. It is observed that the distribution values are quite similar. This is due to the fact that these phosphates and phosphonates are neutral extractants and extract only the neutral species such as $UO_2(NO_3)_2$ for U(VI) and $Pu(NO_3)_4$ for Pu(IV) from nitric acid medium.

Table 5.3. Variation in the distribution ratio of Am(III) and U(VI) in a solution of $ImPNTf_2$ in $C_nmimNTf_2$ (n = 4,6 and 8) as a function of nitric acid concentration, at 298 K

	Distribution ratio of					
$[HNO_3]_{eq.}$/ M	**Am(III) in 0.4 M [$ImPNTf_2$] in $C_nmimNTf_2$**			**U(VI) in 0.4 M [$ImPNTf_2$] in $C_nmimNTf_2$**		
	n = 4	**n = 6**	**n = 8**	**n = 4**	**n = 6**	**n = 8**
1	6×10^{-4}	3×10^{-4}	2×10^{-3}	0.305	0.12	0.080
3	6×10^{-4}	10^{-4}	-	0.145	0.07	0.044
5	9×10^{-4}	2×10^{-3}	2×10^{-3}	0.200	0.15	0.135

Table 5.4. Distribution ratio of U(VI) and Pu(IV) in various solvents at different nitric acid concentration and their separation factors (= $D_{Pu(IV)}/D_{U(VI)}$)

Extractant in *n*-DD	**Distribution ratio of**						**Separation factor of Pu from U at**			**Ref.**
	U(VI) in			**Pu(IV) in**						
	1M	**3M**	**4M**	**1M**	**3M**	**4M**	**1M**	**3M**	**4M**	
TBP	7.3	24.5	30.9	2.91	15.01	24.12	0.39	0.61	0.78	[21]
TiBP	6.95	24	30.3	2.64	13.35	21.92	0.38	0.55	0.723	[21]
TAP	8.76	29.7	35.2	3.36	17.01	27.69	0.38	0.57	0.787	[21]
TiAP	8.86	29.8	35.2	3.32	18.13	29.33	0.37	0.60	0.83	[21]
DAAP	43	71.2	65	56	106	112	1.3	1.48	1.72	[22]

TBP = Tri-n-butylphosphate, TiBP= Tri-n-isobutylphosphate, TAP= Tri-n-amylphosphate, TiAP = Tri-n-isoamylphosphate, DAAP =Diamylamylphosphonate

There are few factors that control the abundance of neutral species in aqueous phase. The crucial factors include (a) coordinating ability of the extractant with metal ion (b) coordinating ability of the metal ion with nitrate and (c) solvating ability of the diluent in extracted phase etc. Since the coordinating ability of these extractants with U(VI) and Pu(IV) are not very different and, moreover, the diluent *n*-dodecane is inert, the distribution of uranium(VI) and plutonium(IV) realized for phosphates and phosphonate are fairly similar. This phenomenon leads to poor separation factor (quotient of $D_{Pu(IV)}$ to $D_{U(VI)}$) tending towards the value of unity, as shown in table 5.4. However, the separation factors achieved using phosphonate based ionic liquid, $ImPNTf_2$, shown in table 5.5, are amazing as they are nearly 20 – 500 times higher than the values obtained for traditional phosphoryl based neutral extractants. This could be attributed to the extraordinary and specific solvating ability of plutonium complexes in ionic liquid phase. This behavior can be suitability exploited for separating plutonium from uranium in PUREX process streams.

Table 5.5. Separation factors of Pu(IV) to U(VI) and Am(III) at various nitric acid concentrations obtained using ionic liquids at 298 K

Solvent	Separation factor of Pu (IV) from U(VI)					Separation factor of Pu(IV) from Am(III)	
	1M	2M	3M	4M	5M	1M	5M
0.4 M $ImPNTf_2$/ $C_4mimNTf_2$	521	175	117	55	33	3×10^5	8.6×10^3
0.4 M $ImPNTf_2$/ $C_6mimNTf_2$	0.15	0.09	0.16	30	4.2	5	200
0.4 M $ImPNTf_2$ /$C_8mimNTf_2$	84	78.8	32	22.6	28	4×10^3	2.1×10^3
$C_4mimNTf_2$	8.7	35	55	80	91	20	3.3×10^4
$C_6mimNTf_2$	200	85	206	221	132	200	6.6×10^4
$C_8mimNTf_2$	50	132	205	226	277	1515	9.3×10^4

Moreover, table 5.5 also shows the separation factors achieved when RTIL diluents alone were employed for extraction. The separation factors ranging from 10 to 250 are obtained for the separation of plutonium from uranium depending upon the nature of ionic liquid and nitric acid concentration. As expected the separation factor achieved in case of $C_8mimNTf_2$ is higher than $C_4mimNTf_2$ at all nitric acid concentrations indicating that the ionic liquid $C_8mimNTf_2$ facilitates the formation of anionic plutonium species and enhances the extraction of plutonium. The separation factors determined for plutonium to americium are also shown in 5.5. Extraordinary separation factors ranging from 10^3 –10^5 are obtained using ionic liquid medium. Since Am(III) is inextractable by P=O based neutral extractants; whereas Pu(IV) is extractable, the separation factors reported [22] for Pu(IV) to Am(III) in traditional solvents are of the order 10^3. Nevertheless, the increase in separation factors with the use of $ImPNTf_2/C_4mimNTf_2$ indicates again that ionic liquid solvents are very selective in stabilizing the extracted plutonium complexes. The task specific property of $ImPNTf_2$ was further confirmed by contacting the solution of 0.4 M $ImPNTf_2/C_4mimNTf_2$ with the aqueous solution containing 3 M nitric acid spiked with HLLW (155 Gwd/Te). Figure 5.4 (A & B) shows the gamma spectra of organic and aqueous phases obtained after the extraction. The energies range from 50 to 700 keV are plotted in figure 5.4 A, and from 700 to 1200 keV are plotted in figure 5.4 B for clarity. It is observed that the extraction of fission products, such as cesium isotopes, europium isotopes, ^{144} Ce and ^{154} Mn by $ImPNTf_2$ is insignificant. From the gamma spectrum, the distribution ratio of ^{137}Cs, ^{155}Eu, ^{144}Ce were determined to be 0.19, 0.17 and 0.045 and the distribution ratio of other nuclides are much lower. This indicates the task specific property of $ImPNTf_2$.

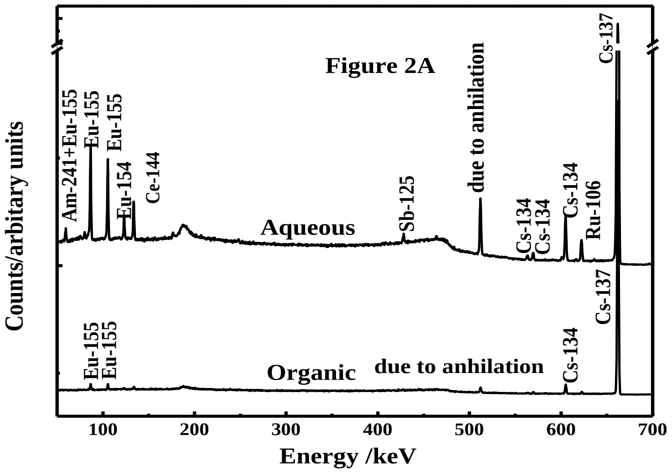


Figure 5.4A. Gamma spectrum of aqueous and organic phase. Organic phase: 0.4M $ImPNTf_2/C_4mimNTf_2$, Aqueous phase: 4M nitric acid spiked with HLLW (155 GWd/Te), Energy range : 0 - 700 KeV

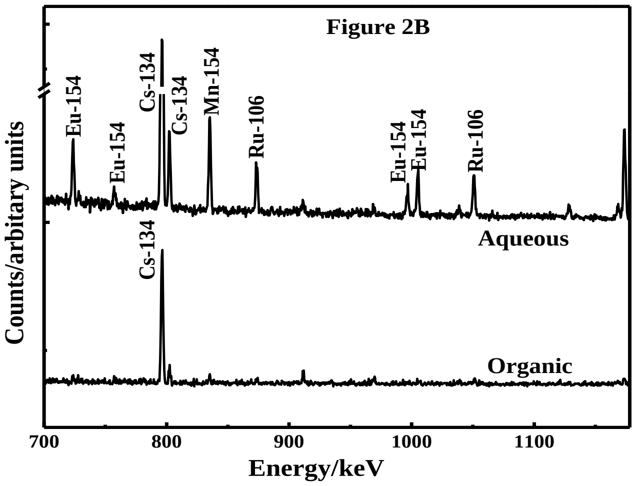


Figure 5.4B. Gamma spectrum of aqueous and organic phase. Organic phase: 0.4M $ImPNTf_2/C_4mimNTf_2$. Aqueous phase: 4M nitric acid spiked with HLLW (155 GWd/Te). Energy range : 700- 1200 KeV

5.2.5 Stripping of plutonium

A decrease in the distribution ratio of plutonium (IV) with increase in the concentration of nitric acid, as shown in table 5.2, indicates that plutonium is expected to strip to aqueous phase at higher nitric acid concentration. However, anion exchange of plutonium nitrate with NTf_2^- prevails at nitric acid concentrations more than 5 M as discussed above. Since Pu(IV) is extracted at very low nitric acid (0.35 M), the stripping of plutonium(IV) was carried out using complexing agents. Figure 5.5 shows the stripping behavior of plutonium (IV) using various reagents. It is observed that quantitative stripping of plutonium (IV) is achieved with in 10 stages with the use of acetohydroxamic acid (0.5 M) and citric acid (1 M). However, further studies are required to minimize the number of stages required for stripping.

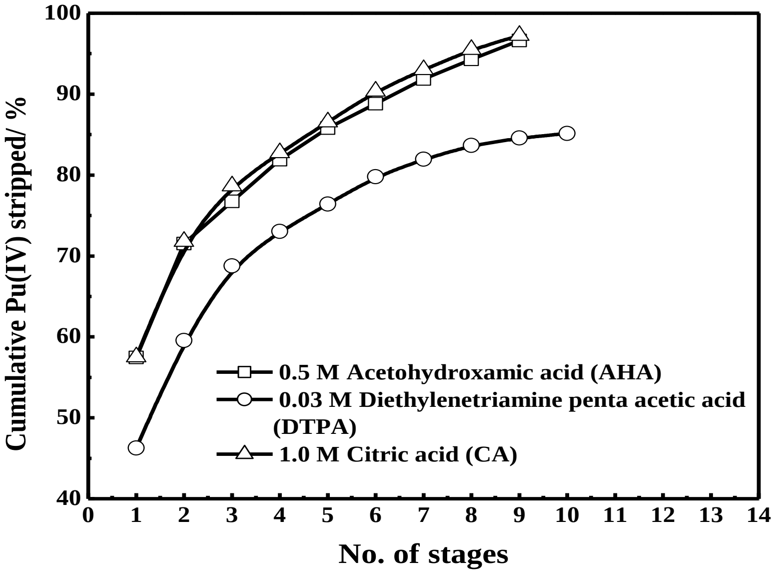


Figure 5.5. Stripping of plutonium (IV) from 0.4 M $ImPNTf_2/C_4mimNTf_2$ using various stripping agents at 298K

5.2.6 Effect of temperature

The enthalpy of Pu(IV) extraction by 0.4 M $ImPNTf_2/C_4mimNTf_2$ can be determined from van’t Hoff equation as given in the *section 2.5.16* of the chapter 2. A plot of $\ln D_{Pu(IV)}$ against 1/T for the extraction of Pu(IV) at various concentration of nitric acid by 0.4 M $ImPNTf_2/C_4mimNTf_2$ is shown in figure 5.6. It is observed that distribution ratio decreases with increase of temperature indicating the extraction reaction is exothermic. The enthalpies of extraction, determined from the slope of straight lines, are also shown in figure 5.7. It can be seen that exothermicity ($-\Delta H_{tot}$) decreases from 31.4 $\pm$ 0.075 kJ/mol to 18.9 $\pm$ 0.125 kJ/mol with the increase in the concentration of nitric acid from 1M to 4 M.

The standard deviation reported is estimated from the linear regression analysis of the fit applicable in the temperature range investigated in the present study. However, the standard deviation of 2 – 3% is usually unavoidable if enthalpy is determined from solvent extraction procedures using van't Hoff method. Burger *et al.*[23] described several factors that influence the overall enthalpy change associated with solvent extraction of metal ions from aqueous phase. The decrease in exothermicity observed in the present case could perhaps be attributed to the formation of ImPNTf$_2$---HNO$_3$ complex in organic phase, at higher nitric acid concentrations. The extraction of nitric acid by 0.4M ImPNTf$_2$/C$_4$mimNTf$_2$ increases from 0.098 M to 0.63 M when the initial concentration of nitric acid increases from 1 M to 5 M respectively. Since the ligand P=O present in ImPNTf$_2$, need to be deprotonated to form Pu–(ImPNTf$_2$)$_3$ complex for extraction, the overall exothermic enthalpy decreases with increase in the concentration of nitric acid.

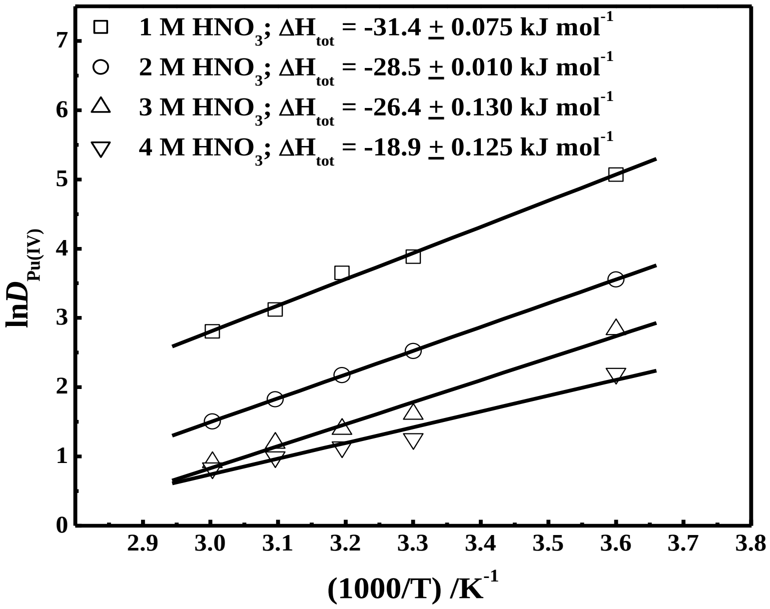


Figure 5.6. Variation of ln $D_{Pu(IV)}$ with 1/T for the extraction of plutonium (IV) from nitric acid medium by 0.4 M ImPNTf$_2$/C$_4$mimNTf$_2$

5.2.7 Viscosity measurement

Figure 5.7 shows the effect of temperature on the viscosity (η, in cP) of C$_4$mimNTf$_2$, C$_8$mimNTf$_2$ and its solution with 0.4 M ImPNTf$_2$. It can be seen that the viscosity of ionic liquids decreases with increase of temperature from 303 K to 348 K. The activation energy (E$_a$) was determined from the equation given in the *section 2.5.17* of the chapter 2. The plot of ln η against 1/T is also shown in figure 5.7. The energy of activation determined from the slope of straight line was in the range ~30 kJ/mol.

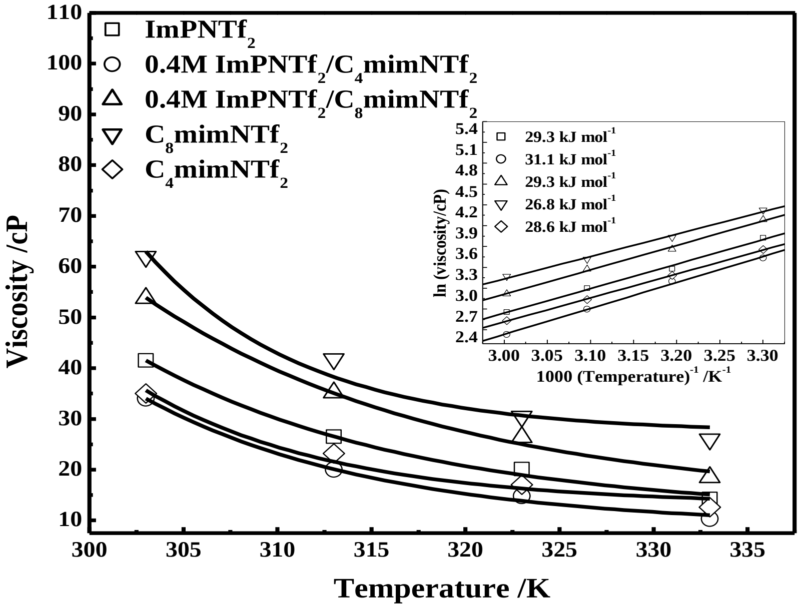


Figure 5.7. Variation of viscosity of $C_4mimNTf_2$, $C_8mimNTf_2$ and $ImPNTf_2$ and their solutions as a function of temperature. Inset: Arrhenius Plot

5.3 Conclusions

Extraordinary extraction of Pu(IV) over U(VI), Am(III) and fission products was achieved with the use of phosphonate based ionic liquid-extractant, $ImPNTf_2$, in ionic liquid diluents ($C_nmimNTf_2$). The extraordinary separation factors of plutonium (IV) achieved could be attributed to the rejection of U(VI), Am(III) and fission products by ionic liquid phase rather than to the selective extraction of plutonium and to the stabilization of Pu(IV) complex in ionic liquid phase. This task specific property was dependent on the concentrations of nitric acid, concentration of $ImPNTf_2$ and the nature of diluent-ionic liquid used. Dual nature of the RTIL phase enables plutonium (IV) to get extracted predominantly through complex formation from 1 – 4 M nitric acid medium and through anion exchange by the ionic liquid-diluent, $C_4mimNTf_2$ or $C_8mimNTf_2$, at higher nitric acid concentrations ($\geq$ 5). The stripping of plutonium (IV) was possible within 10 stages using citric acid and acetohydroxamic acid as the complexing agents. Extraction of plutonium (IV) by ionic liquid phase was accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration.

B. Separation of plutonium(IV) from other actinides and fission products using amide based functionalized ionic liquid

5.4 Results and Discussions

5.4.1 Pu(IV) extraction in $C_n$mimNTf$_2$

The extraction behavior of Pu(IV) in $C_n$mimNTf$_2$ (n = 4 and 6) is reported in the *section 5.2.1 and 5.2.2* described above and the data are presented in figure 5.8 for comparison purposes. The distribution ratio of Pu(IV) increases with the increase in the concentration of nitric acid. At nitric acid concentrations < 2 M, the extraction of Pu(IV) in $C_n$mimNTf$_2$ is negligible ($D < 10^{-2}$). However, gradual increase in $D_{\text{Pu(IV)}}$ is observed above 3 M nitric acid and the extraction increases in the order C_4mimNTf$_2$ < C_6mimNTf$_2$. The extraction of Pu(IV) in $C_n$mimNTf$_2$ was attributed to the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species present in aqueous phase with the NTf_2^- ion of ionic liquid phase, as reported above in the *section 5.2.1 and 5.2.2* of the part "A".

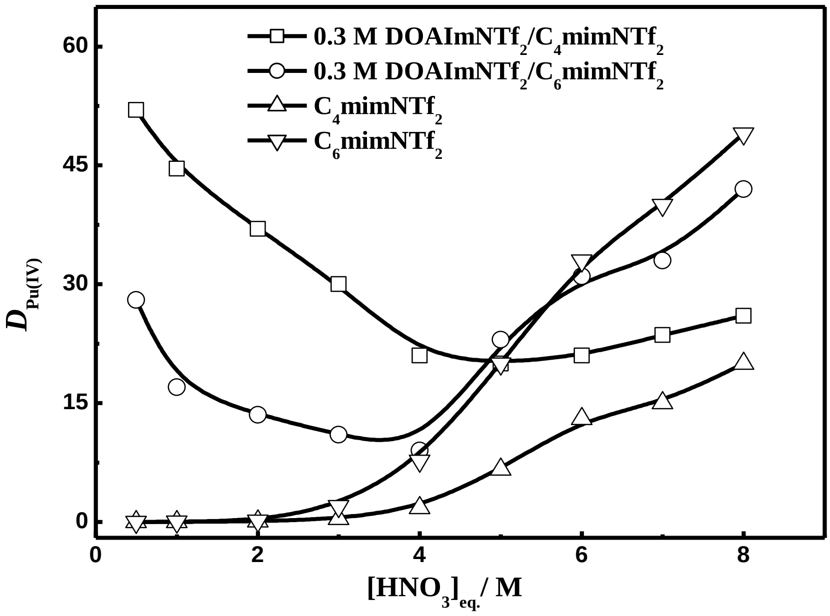


Figure 5.8. Variation in the distribution ratio of Pu(IV) in $C_n$mimNTf$_2$ and 0.3 M DOAImNTf$_2$/$C_n$mimNTf$_2$ as a function of nitric acid concentration. Equilibration time = 1hr, T = 298 K. O/A = 1

5.4.2 Pu(IV) extraction in DOAImNTf$_2$/$C_n$mimNTf$_2$

Figure 5.8 also shows the variation in the distribution ratio of Pu(IV) in 0.3 M DOAImNTf$_2$/$C_n$mimNTf$_2$ as a function of nitric acid concentration. It is observed that the distribution ratio of Pu(IV) initially decreases with increase in the concentration of nitric acid. The distribution ratio reaches a minimum value at 4 –5 M in nitric acid followed by an increase. The trend observed in the presence of 0.3 M DOAImNTf$_2$ shows that there could be a couple of modes through which plutonium (IV) is extracted in $DOAImNTf_2/C_nmimNTf_2$ phase. The extraction trend observed above 4 M nitric acid in 0.3 M $DOAImNTf_2/C_nmimNTf_2$ compares well the trend observed for $C_nmimNTf_2$ (figure 5.8). This indicates that plutonium (IV) could be extracted by the anion exchange of $[Pu(NO_3)_5(H_2O)]^-$ or $[Pu(NO_3)_6]^{2-}$ species with NTf_2^- of ionic liquid phase. To confirm this, the variation in the distribution ratio of Pu(IV) in 0.3 M $DOAImNTf_2/C_nmimNTf_2$ was studied as a function of $[NTf_2]^-_{aq}$ at 5 M nitric acid. The results are shown in the figure 5.9. It is observed that the distribution ratio of plutonium (IV) decreases with increase in the concentration of NTf_2^- ion in aqueous phase as expected. A slope of unity observed in the present case compares well with the slope obtained for the extraction of plutonium(IV) in $C_4mimNTf_2$ (figure 5.9). This observation confirms that the predominant mode of plutonium (IV) extraction in 0.3 M $DOAImNTf_2/C_nmimNTf_2$ above 4 M nitric acid is through anion exchange (see equation 5.1 & 5.2).

Below 4 M nitric acid, the enhancement in distribution ratio in the presence of $DOAImNTf_2$ (figure 5.8) indicates the involvement of $DOAImNTf_2$ for extraction. In this range (0.5 – 4 M), the extraction of Pu(IV) could occur by ion exchange or by metal –solvate formation with $DOAImNTf_2$ ionic liquid. The possibility of anion exchange is unlikely to occur in this region, since the abundance of anionic plutonium (IV) species is negligible in the acid range 1 –3 M. It is well-known that plutonium (IV) is purified by anion exchange method only from 5 – 7 M nitric acid. Moreover, in $C_nmimNTf_2$ medium, the extraction of plutonium (IV) by anion exchange is observed only above 4 M (figure 5.8). These characteristics indicate that the abundance of plutonium (IV) anionic species, below 4 M, is insignificant and it is unlikely that plutonium (IV) is extracted by anion exchange in this region (0.5 - 4 M). Nevertheless, the effect of $[NTf_2^-]_{aq}$ on the extraction of Pu(IV) in 0.3 M $DOAImNTf_2/C_4mimNTf_2$ from 1 M nitric acid medium was studied and the results are shown in figure 5.10. It is observed that the distribution ratio of Pu(IV) increases with increase in the concentration of $[NTf_2]^-_{aq}$. This result is inconsistent with the anion exchange observed at 5 M HNO_3 (figure 5.9). This indicates that more studies are needed to understand the extraction behavior of Pu(IV) below 4 M nitric acid.

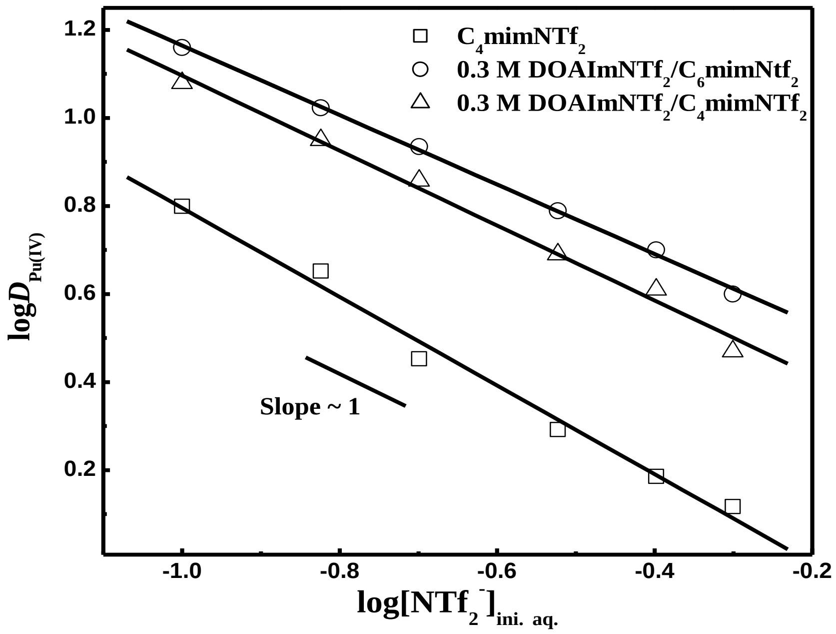


Figure 5.9. Variation of log $D_{Pu(IV)}$ with log $[NTf_2]^-$ for the extraction of Pu(IV) in $C_4mimNTf_2$ and 0.3M $DOAImNTf_2$/ $C_nmimNTf_2$ (n = 4 and 6). Aqueous phase: 5M nitric acid + varied concentration of NTf_2^- ion, Equilibration time = 1 hr, O/A = 1, T = 298 K

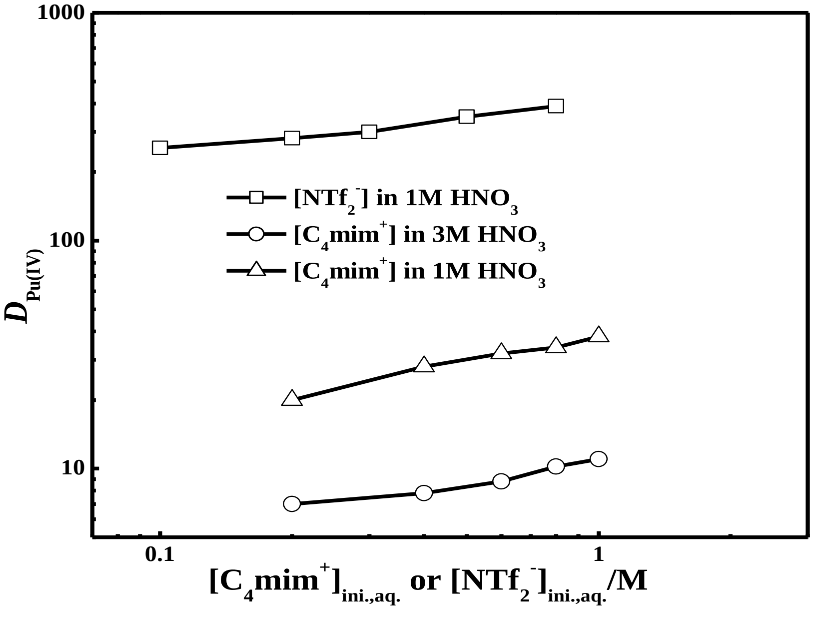


Figure 5.10. Variation in the distribution ratio of Pu(IV) with the concentration of NTf_2^- or C_4mim^+ ion in aqueous phase. Organic phase = 0.3 M $DOAImNTf_2/C_4mimNTf_2$, Aqueous phase = 1 M (or 3 M HNO_3 + varied concentration of C_4mim^+ ion (or NTf_2^- ion), Equilibration time = 1hr, T = 298 K, O/A = 1

5.4.3 Effect of $[C_4mimNO_3]_{aq}$

Ion exchange is being reported as the primary mode of metal ion transfer in ionic liquid media [17,18,24,25]. For instance cation exchange is the predominate mode of metal ion transfer in systems such as Sr^{2+} in crown ether/ionic liquid [18], Pu(IV) in

CMPO/ionic liquid [24], lanthanides in diglycolamide/ionic liquid [25] etc. However, the cation exchange of Pu(IV) with C_4mim^+ ion is unlikely to occur in this region (0.5 – 4 M), since the extraction of plutonium is negligible when $C_4mimNTf_2$ is used for extraction (Figure 5.8). Nevertheless, the effect of $[C_4mim^+]_{aq}$ on the extraction of Pu(IV) in 0.3 M $DOAImNTf_2/C_4mimNTf_2$ from 1M nitric acid medium was studied and the results are also shown in figure 5.10. If the extraction of Pu(IV) in $DOAImNTf_2/C_4mimNTf_2$ is assumed to be governed by the cation exchange mechanism shown in equation 5.3, then the distribution ratio of Pu(IV) should decrease with increase in the concentration of C_4mim^+ ion in aqueous phase. The concentration of $[C_4mim^+]_{aq}$ was varied by adding aqueous soluble, C_4mimNO_3. It is interesting to observe from figure 5.10 that the distribution ratio of Pu(IV) increases marginally with increase of $[C_4mim^+]_{aq}$, instead of the expected decrease. This behavior could perhaps be attributed to the association of nitrate ion with Pu(IV) leading to the formation of anionic plutonium nitrate complexes such as $[Pu(NO_3)_6]^{2-}$ upon adding C_4mimNO_3 in aqueous phase. Since these anionic species are easily extracted through anion exchange (figure 5.8), the distribution ratio of Pu(IV) seems to increase with increase in the concentration of $[C_4mim^+]_{aq}$. A similar behavior is also observed in 3 M nitric acid, as shown in figure 5.10. This indicates that higher concentration of nitrate ion facilitates the formation of anionic plutonium nitrate complexes and increases the extraction. All these observations excludes the possibility of cation exchange of Pu(IV) with C_nmim^+ ion, during extraction.

$$M^{n+}_{aq} + m\, DOAImNTf_{2\,IL} + n\, C_4mim^+_{IL} \Leftrightarrow \{M(DOAImNTf_2)_m\}^{n+}_{IL} + n\; C_4mim^+_{aq} \qquad (5.3)$$

The other possibility for the extraction of Pu(IV) (below 4 M) could be the cation exchange of Pu^{4+} or $[Pu(NO_3)_n]^{(4-n)+}$ (n = 1-3) species with $DOAIm^+$ cation. However, such possibility is unlikely to occur, since $DOAIm^+$ is more organophilic than the C_nmim^+ cation. Since the cation exchange of C_nmim^+ with Pu(IV) species is not favourable in this acid range (1- 4 M), as discussed above, it is unlikely that the organophilic $DOAIm^+$ cation could be exchanged for Pu(IV) species. Nevertheless, the cation exchange of Pu(IV) with $DOAIm^+$ was ruled out by measuring the absorbance of $DOAIm^+$ cation (300 – 260 nm) in the aqueous phase after extraction. Figure 5.11 shows the UV-visible absorption spectrum of $DOAImNTf_2$ (8 x 10^{-4} M in $CHCl_3$) and the aqueous phase obtained after the extraction of plutonium (IV) (2 x 10^{-4} M). The absorbance of the aqueous phase is negligible after Pu(IV) extraction. This indicates that $DOAIm^+$ cation is not exchanged for Pu(IV) from the aqueous phase. In view of these reasons, the most plausible explanation that emerges out for the extraction of plutonium (IV) from 0.5 – 4 M nitric acid medium is formation of metal-solvate (Pu(IV) –$(DOAImNTf_2)_n$) complex in organic phase. The initial decrease in the distribution ratio of Pu(IV) with increase in nitric acid concentration could be attributed to the protonation of $DOAImNTf_2$.

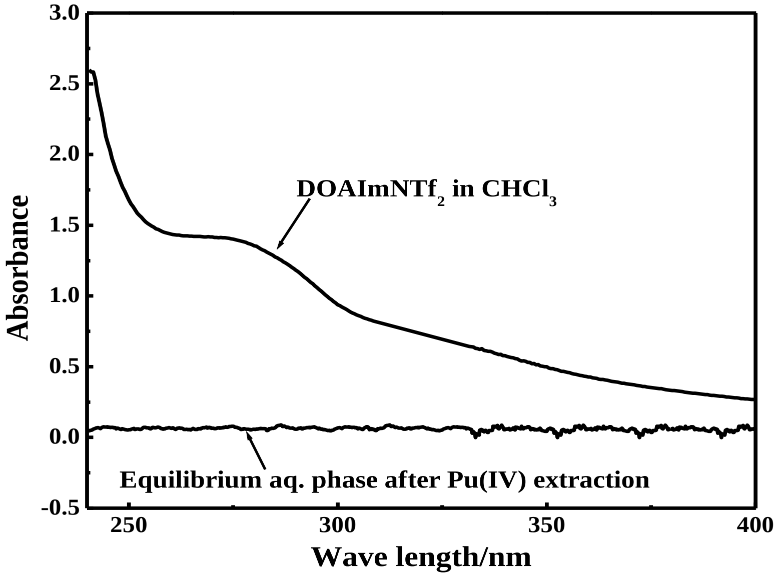


Figure 5.11. UV - VIS absorption spectrum of amide functionalized ionic liquid (8 x 10^{-4} M $DOAImNTf_2$ in $CHCl_3$ and the aqueous phase after Pu(IV) extraction. Organic phase = 0.3 M $DOAImNTf_2/C_4mimNTf_2$, Aqueous phase = 2 x 10^{-4} M Pu(IV) + 1M nitric acid, Equilibration time = 1hr, O/A=1

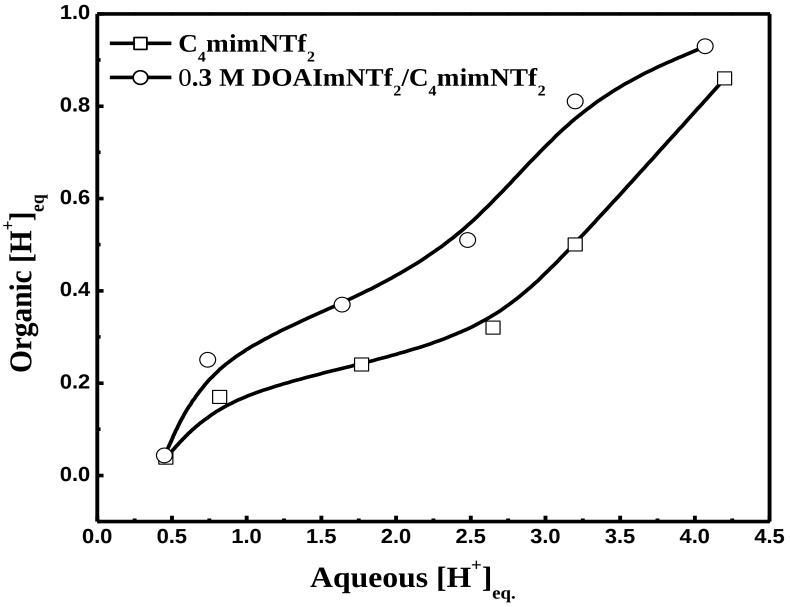


Figure 5.12. Acid extraction isotherm of $C_4mimNTf_2$ and 0.3 M $DOAImNTf_2/C_4mimNTf_2$. Aqueous phase = 0.5 - 5 M nitric acid, Equilibration time = 1hr, T = 298 K, O/A = 1

Figure 5.12 given above, shows the extraction of nitric acid in $C_4mimNTf_2$ and 0.3 M $DOAImNTf_2/C_4mimNTf_2$. Higher extraction of nitric acid observed in the presence of $DOAImNTf_2$ indicates the protonation of $DOAImNTf_2$. The extractant ionic liquid when protonated by nitric acid is less available for Pu(IV) extraction. Therefore, the distribution ratio of plutonium (IV) decreases with increase in the concentration of nitric acid. The metal-solvate stoichiometry for the extraction of plutonium (IV) in $DOAImNTf_2$ was investigated by the slope analysis of extraction data. The variation of $D_{\mathrm{Pu(IV)}}$ with $[\mathrm{DOAImNTf_2}]_{\mathrm{IL}}$ is shown in the figure 5.13. Linear regression analysis of the extraction data results in a slope of 3, indicating that three molecules of $DOAImNTf_2$ are involved in the extraction step.

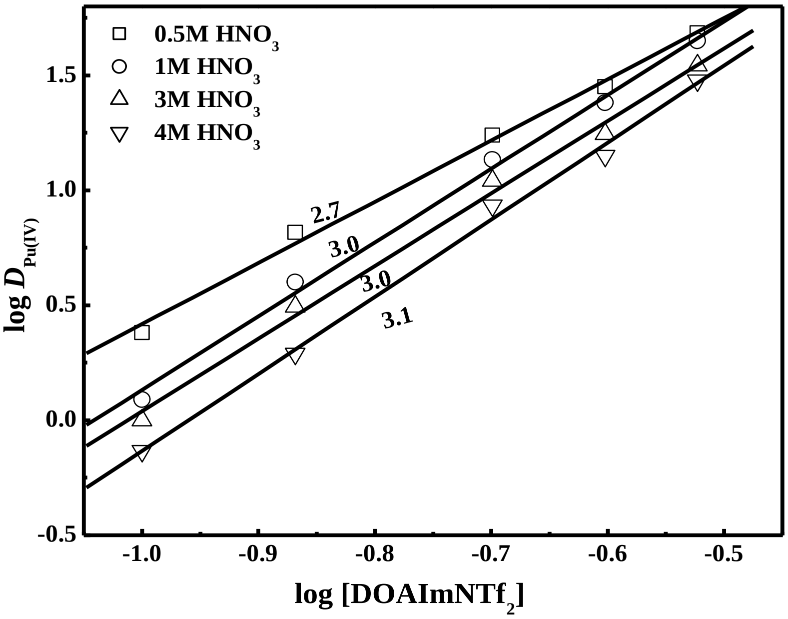


Figure 5.13. Variation of log $D_{\mathrm{Pu(IV)}}$ with log $[\mathrm{DOAImNTf_2}]$ for the extraction of Pu(IV) from nitric acid medium. Organic phase = 0.1 - 0.3 M $DOAImNTf_2$, Aqueous phase = 0.5 - 4 M HNO_3, Equilibration time = 1 hr, T = 298 K, O/A = 1

5.4.4 Separation factor

Table 5.6 shows the distribution ratios of U(VI) and Am(III) in 0.3 M $DOAImNTf_2/C_4mimNTf_2$. It is interesting to obverve that the distribution data obtained for the extraction of uranium (VI) in $DOAImNTf_2/C_4mimNTf_2$ are unusually low. Table 5.7 compares the distribution ratio of U(VI) and Pu(IV) in a solution of some amide based extractants namely, dioctylbutaramide (DOBA), dioctyloctanamide (DOOA) and dioctylethylhexanamide (DOEHA) in molecular diluents [26, 27]. It is observed that the distribution ratios of Pu(IV) and U(VI) are similar in all cases. Therefore the separation factor (SF = $D_{\mathrm{Pu(IV)/U(VI)}}$) obtained using amides/molecular diluents are in the range of 0.3 – 4 in all cases. However, the separation factors of plutonium (IV) from other actinides achieved with the use of amide functionalized ionic liquid, DOAImNTf$_2$, shown in table 5.8, are remarkable. The SF varies from the value of 40 to 3400 depending upon the concentration of nitric acid employed for extraction. The SF of Pu(IV) over U(VI) decreases with increase in the concentration of nitric acid. This is due to the decrease of $D_{\mathrm{Pu(IV)}}$ and increase of $D_{\mathrm{U(VI)}}$ with increase in the concentration of nitric acid.

Table 5.6. Distribution ratio of U(VI) and Am(III) in C$_4$mimNTf$_2$ and 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ as function of nitric acid concentration. Aqueous phase = 0.5 – 5 M HNO$_3$, Equilibration time = 1hr, T = 298K, O/A = 1

[HNO$_3$]$_{\mathrm{eq.}}$/M	Distribution ratio of			
	U(VI) in		Am(III) in	
	C$_4$mimNTf$_2$	0.3 M DOAImNTf$_2$ in C$_4$mimNTf$_2$	C$_4$mimNTf$_2$	0.3 M DOAImNTf$_2$ in C$_4$mimNTf$_2$
0.5	10^{-4}	0.015	10^{-4}	0.07
1	10^{-4}	0.02	10^{-4}	0.03
3	10^{-3}	0.13	10^{-4}	0.01
4	10^{-3}	0.2	10^{-4}	0.008
5	0.07	0.4	10^{-4}	0.005
6	0.07	----	10^{-5}	----
8	0.06	0.5	10^{-4}	0.001

Table 5.7. Distribution ratio of U(VI) and Pu(IV) in various amides present in different molecular diluents. Organic phase = DOBA/DOOA/DOEHA in *n*-DD, Aqueous phase = 0.5 – 5M nitric acid, Equilbration time = 1hr, T = 298K, O/A = 1

[HNO$_3$]$_{\mathrm{eq}}$ /M	0.5 M DOBA /*n* – DD [26]		SF	0.5M DOOA / *n*- DD [27]		SF	0.5 M DOEHA /*n*-DD [27]		SF
	$D_{\mathrm{Pu(IV)}}$	$D_{\mathrm{U(VI)}}$		$D_{\mathrm{Pu(IV)}}$	$D_{\mathrm{U(VI)}}$		$D_{\mathrm{Pu(IV)}}$	$D_{\mathrm{U(VI)}}$	
0.5	0.5	0.5	1	0.1	0.2	0.5	0.05	0.1	0.8
1	1.5	0.75	2	0.25	0.5	0.5	0.1	0.2	0.6
3	5.5	1.5	3.6	1.8	2.8	0.6	0.5	0.62	0.8
4	10	2.5	4	3.5	3.8	0.9	0.5	0.6	0.4
5	12.5	3.5	3.4	4.8	4	1.2	0.6	1.8	0.3

Table 5.8. Distribution ratio of Pu(IV), U(VI) and Am(III) in 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ as a function of nitric acid concentration and their separation factors, at 298 K. Organic phase = 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$, Aqueous phase = 0.5 – 5M nitric acid, Equil. time = 1 hr, T = 298 K, O/A = 1

[HNO$_3$]$_{eq.}$ /M	**Distribution ratio in 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$**			**SF**	
	Pu(IV)	U(VI)	Am(III)	Pu over U	Pu over Am
0.5	52	0.015	0.07	3466	743
1	44	0.02	0.03	2200	1466
3	30	0.13	0.01	230	3000
4	21	0.2	0.008	105	2625
5	20	0.49	0.005	41	4000

5.5.5 Task specific property

Table 5.9 shows the comparison in the extraction behavior of Pu(IV) over U(VI) observed in the solution of a amide based molecular extractant, DOBA present in C$_4$mimNTf$_2$ and in 0.3M DOAImNTf$_2$/C$_4$mimNTf$_2$. DOBA is an amide based molecular extractant and DOAImNTf$_2$ is the amide functionalized ionic liquid, as indicated above. It is observed that the distribution ratio of Pu(IV) in 0.5 M DOBA/C$_4$mimNTf$_2$ increases from 0.02 to 5 with the increase in the concentration of nitric acid from 0.5 M to 5 M. In contrast, the distribution ratio of Pu(IV) in 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ is much higher and the $D_{\mathrm{Pu(IV)}}$ decreases with increase in the concentration of nitric acid, as discussed above. Since the diluent, C$_4$mimNTf$_2$, is same in both cases, higher extraction of Pu(IV) observed in DOAImNTf$_2$/C$_4$mimNTf$_2$ could be attributed to the task specific nature of the extractant ionic liquid, DOAImNTf$_2$, towards plutonium. Moreover, the functional group that extracts Pu(IV) from nitric acid medium is amide in both cases. Inspite of this, higher extraction of Pu(IV) is observed only in DOAImNTf$_2$. This indicates that the amide becomes task specific upon its functionalization on imidazolium cation. In view of this, the separation factor of Pu(IV) over U(VI) varies from 3400 to 40 in 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ system, where as the SF varies from 0.1 to 10 in 0.5 M DOBA/C$_4$mimNTf$_2$ system, depending upon the concentration of nitric acid employed for extraction. The task specific property of DOAImNTf$_2$ was further confirmed by contacting the aqueous solution of 3 M nitric acid spiked with HLLW (155 Gwd/Te), with 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$. Figure 5.14 shows the gamma spectra of the organic and aqueous phases obtained after the extraction. From the gamma spectrum the distribution ratio of ^{137}Cs, ^{155}Eu, ^{144}Ce, ^{106}Ru etc. were determined to be 0.18, 0.01, 0.08 and 0.01 and the distribution ratio of other nuclides are much lower. All these observations confirm the task specific property of DOAImNTf$_2$.

Table 5.9. Comparision in the distribution ratio of Pu(IV) and U(VI) in 0.5 M DOBA/C$_4$mimNTf$_2$ and 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$, Aqueous phase = 0.5 – 5 M nitric acid, Equilibration time = 1hr, T = 298K, O/A = 1

[HNO$_3$]$_{eq}$ /M	Distribution ratio in 0.5M DOBA in C$_4$mimNTf$_2$		SF = $D_{Pu(IV)}/D_{U(VI)}$	Distribution ratio in 0.3M DOAImNTf$_2$/ C$_4$mimNTf$_2$		SF = $D_{Pu(IV)}/D_{U(VI)}$
	Pu(IV)	U(VI)		Pu(IV)	U(VI)	
0.5	0.03	0.23	0.13	52	0.015	3466
1	0.05	0.15	0.33	44	0.02	2200
3	1	0.13	7.7	30	0.13	230
4	3	0.15	20	21	0.2	105
5	5	0.4	12.5	20	0.49	41

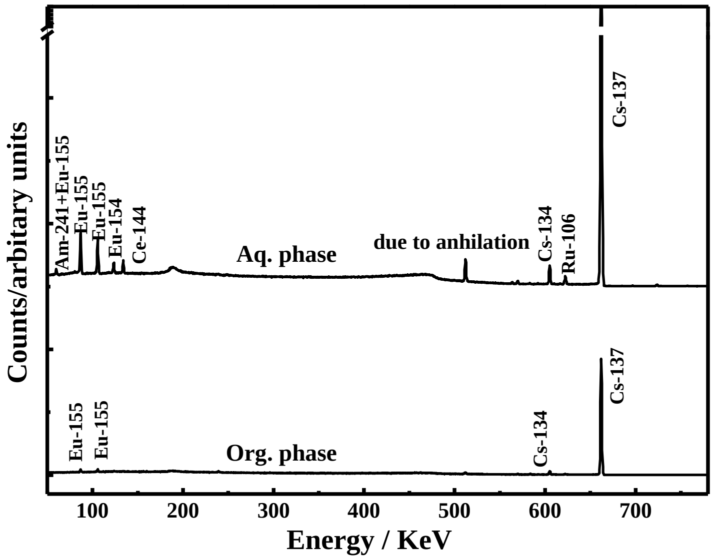


Figure 5.14. Gamma spectrum of aqueous and organic phases obtained after the extraction of radioisotopes present in 3M nitric acid medium spiked with HLLW (155GWd/Te). Organic phase = 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$, Aqueous phase = 3 M nitric acid spiked with high level liquid waste (155 GWd/Te), Equilibration time = 1 hr, T = 298 K, O/A = 1

5.5.6 Stripping of plutonium

The stripping of plutonium (IV) from 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ in dilute nitric acid is difficult due to the high distribution ratio of Pu(IV) observed at low nitric acid concentration (figure 5.8). Therefore, the complexing agents such as citric acid (CA) and acetohydroxamic acid (AHA) have been used for stripping of Pu(IV) from ionic liquid phase. Figure 5.15 shows the stripping behavior of plutonium(IV) from 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ using the complexing agents such as 0.5 M CA (or 0.5 M AHA) in 0.3 M nitric acid. It is observed that quantitative stripping of plutonium (IV) is achieved within 10 stages. However, further studies are required to minimize the number of stages required for stripping.

The reusability of the solvent, 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$, was investigated by measuring the distribution ratio of Pu(IV) in ionic liquid phase after each cycle. The experiment involved extraction of Pu(IV) using 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ followed by stripping with 0.5 M AHA in 0.3 M nitric acid (8 times). The ionic liquid phase thus obtained was taken for second cycle of extraction. The results, shown in table 5.10, indicate that the $D_{\mathrm{Pu(IV)}}$ decreases marginally from 30 to 26.2 upon recycling the ionic liquid phase four times. This confirms that 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ can be reused at least five times without much change in the efficiency of the process.

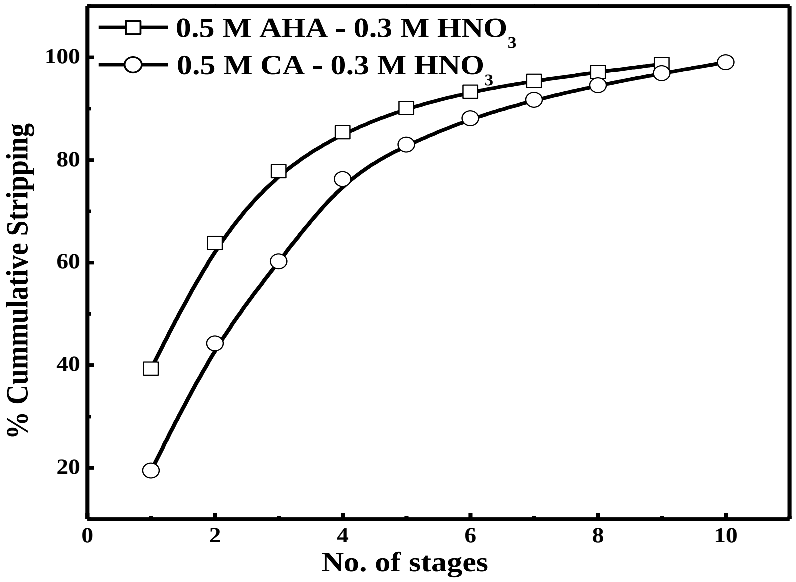


Figure 5.15. Stripping of plutonium (IV) from 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ using 0.5 M acetohydroxamic acid (AHA) and 0.5 M citric acid (CA). Organic phase: 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$ loaded with Pu(IV), Aqueous phase: 0.5 M AHA (or 0.5 M CA) in 0.3 M nitric acid, Equilibration time = 1hr, T = 298K, O/A = 1

Table 5.10. Variation in the distribution ratio of Pu(IV) upon recycling the ionic liquid phase. Organic phase: 0.3 M DOAImNTf$_2$/C$_4$mimNTf$_2$, Aqueous phase: 3 M HNO$_3$ spiked with ^{239}Pu(IV) during extraction. Aqueous phase: 0.5 M AHA in 0.3 M nitric acid during stripping

Recycle number	$D_{Pu(IV)}$
1	30
2	28
3	26.8
4	26.2

5.5.7 Effect of temperature

The enthalpy Pu(IV) extraction by 0.3M DOAImNTf$_2$/C$_4$mimNTf$_2$ was determined from van't Hoff equation given in *section 2.5.16* of the chapter 2. A plot of ln$D_{Pu(IV)}$ against 1/T for the extraction of Pu(IV) at various concentration of nitric acid by 0.3M DOAImNTf$_2$/C$_4$mimNTf$_2$ is shown in figure 5.16. Analogous to the result obtained in the part "A", the extraction reaction is exothermic here also as the distribution ratio decreases with increase of temperature. Figure 5.16 shows that exothermicity ($-\Delta H_{tot}$) decreases from 46 ± 0.1 kJ/mol to 39 ± 0.06 kJ/mol with the increase in the concentration of nitric acid from 1 M to 4 M. Even though the decreasing trend is not sharp, still the trend refers the exothermicity of the extraction. The standard deviation reported is estimated from the linear regression analysis of the fit applicable in the temperature range investigated in the present study.

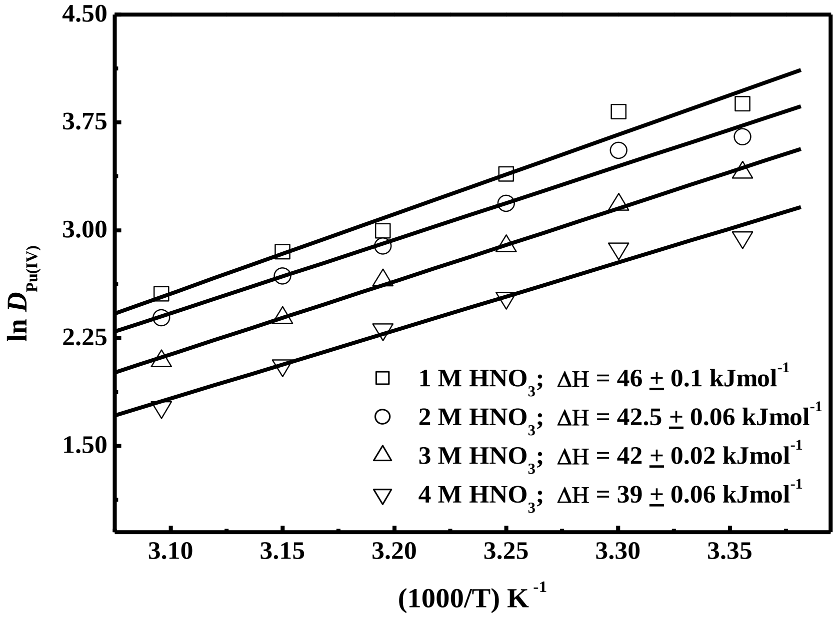


Figure 5.16. Variation of ln $D_{Pu(IV)}$ with 1/T for the extraction of plutonium (IV) from nitric acid medium by 0.3M DOAImNTf$_2$/C$_4$mimNTf$_2$

The decrease in exothermicity observed in the present case could perhaps be attributed to the formation of $DOAImNTf_2$---HNO_3 complex in organic phase, at higher nitric acid concentrations. The extraction of nitric acid by 0.3 M $DOAImNTf_2/C_4mimNTf_2$ increases from 0.043 M to 0.93 M when the initial concentration of nitric acid increases from 1 M to 5 M respectively. Thus the overall exothermic enthalpy decreases with increase in the concentration of nitric acid as some energy is necessary for the deprotonation of HNO_3 ---- $(DOAImNTf_2)_3$ complex.

5.5.8 Viscosity measurement

Figure 5.17 shows the effect of temperature on the viscosity (η, in cP) of $C_nmimNTf_2$ and 0.3 M $DOAImNTf_2/C_nmimNTf_2$ ionic liquids. It is observed as expected that the viscosity of ionic liquid decreases with increase of temperature. The viscosity of 0.3 M $DOAImNTf_2/C_nmimNTf_2$ is determined to be ~70 cP at 298 K. The viscosity of $C_4mimNTf_2$ is given for comparison. Addition of $DOAImNTf_2$ to $C_nmimNTf_2$ increases the viscosity of the resultant solution.

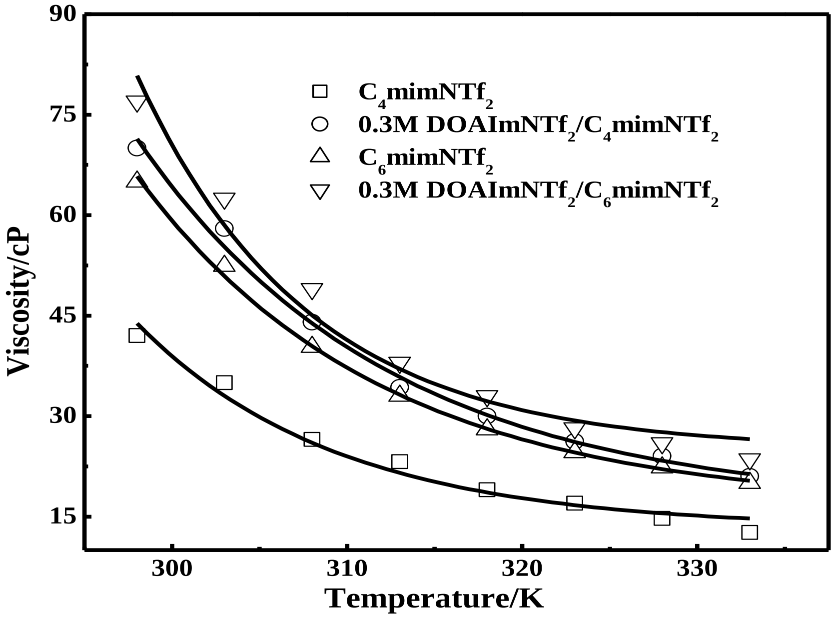


Figure 5.17. Variation of the viscosity of $C_4mimNTf_2$, $C_6mimNTf_2$ and their solution with $DOAImNTf_2$

5.5.9 Conclusions

A new amide functionalized ionic liquid, $DOAImNTf_2$, was prepared and studied for the extraction of Pu(IV), U(VI), Am(III) and fission products from nitric acid medium. Above 4 M nitric acid, the primary mode of plutonium(IV) transfer in ionic liquid phase was determined to be anion exchange. Below 4 M, the present investigation indicates the possibility of metal solvate complex ($Pu(IV)-(DOAImNTf_2)_3$) formation in ionic liquid phase. However, more studies are needed to bring out the insights of Pu(IV) extraction. Unlike the traditional systems, the ionic liquid extractant, $DOAImNTf_2$, was selective for plutonium (IV) over other actinides and fission products. The separation factor of Pu(IV) over U(VI) was found to vary from 40 to 3400 depending upon the concentration of nitric acid employed for extraction. Moreover, selectivity was observed only upon functionalization of the amide moiety on imidazolium cation. Plutonium(IV) was back extracted from the organic phase using complexing agents within 10 contacts. The ionic liquid, $DOAImNTf_2$ can be used atleast five times without any change in the efficiency of the process.

5.6. References

1. J.H. Davis Jr., Task-Specific Ionic Liquids. Chemistry Letters 33 (9) (2004) 1072 - 1077.
2. A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S.A. Sheff, Wierzbicki, J.H. Davis Jr. and R.D. Rogers, Task Specific Ionic Liquids Incorporating Novel Cations for the Coordination and Extraction of Hg^{2+} and Cd^{2+} : Synthesis, Characterization and Extraction Studies. Envir. Sci. Technol. 36 (11) (2002) 2523 - 2529.
3. A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S.A. Sheff, Wierzbicki, J.H. Davis Jr. and R.D. Rogers, Task-specific ionic liquids for the extraction of metal ions from aqueous solutions. Chem. Commun. (2001) 135 -136.
4. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K.V. Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, Task-Specific ionic liquid for solubilizing metal oxides. J.Phys.Chem.B. 110 (42) (2006) 20978 - 20992.
5. R.J. Harjani, T. Friscic, R. Leonard, MacGillivary, and D. Singer, Removal of metal ions from aqueous solutions using chelating task specific ionic liquids. Dalton Trans. 34 (2008) 4595 - 4601.
6. H. Luo, S. Dai, P.V. Bonnesen, A.C. Buchanan, Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an aza-crown ether fragment. J. Alloys and Compds. 418 (1-2) (2006) 195 – 199.
7. A. Ouadi, B. Gadenne, P. Hesemann, J.J.E. Moreau, I. Billard, C. Gaillard, S. Mekki, G. Moutiers, Task specific ionic liquids bearing 2- hydroxybenzylamine units: Synthesis and americium extraction studies. Chem. Eur. J. 12 (11) (2006) 3074 -3081.
8. A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, Solvent extraction of U(VI) by task specific ionic liquids bearing phosphoryl groups. Green Chem. 9 (11) (2007) 1160 – 1162.
9. I. L. Odinets, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. Nelyubina, V. Myasoedova, V. Galina, N. P. Molochnikova, E. A. Zakharchenro, Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery. Dalton Trans. 39 (2010) 4170-4178.
10. J. H. Olivier, F. Camerel, R. Ziessel, Lanthanide Ion Extraction by Trifluoromethyl-1,3-diketonate-Functionalised Ionic Liquids Adsorbed on Silica. Chem. Eur. J. 17 (33) (2011) 9113 – 9122.
11. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P.R. Vasudeva Rao, Extraction of uranium (VI) from nitric acid medium by 1.1 m tri-n-butylphosphate in ionic liquid diluent. J. Radioanal. Nucl. Chem. 265 (1) (2005) 31 - 38.

12. S. Dai, Y. H. Ju, C.E. Barnes, Solvent extraction of strontium nitrate by crown ether using room – temperature ionic liquids. J.Chem.Soc, Dalton Trans. 9 (1999) 1201-1202.
13. T. J. Bell, Y. Ikeda, The application of novel hydrophobic ionic liquids to the extraction of uranium(VI) from nitric acid medium and a determination of the uranyl complexes formed. Dalton Trans. 40 (2011) 10125-10130.
14. C. Xu, L. Yuan, X. Shen, M. Zhai, Efficient removal of caesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism radiation effect. Dalton Trans. 39 (2010) 3897–3902.
15. A.E. Visser, R. P. Swatloski, W. M. Reichert, S.T. Griffin, R.D. Rogers, Traditional extractants in non-traditional solvents: Group 1 and 2 extractions by crown ethers in room temperature ionic liquids. Ind. Eng. Chem. Res., 39 (10) (2000) 3596 - 3604.
16. M. L. Dietz, J.A. Dzielawa, I. L. Blake, A. Young, M. P. Jensen, Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. Green Chem. 5 (6) (2003) 682 - 685.
17. M.L. Dietz, D. C. Stepinski, Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. Talanta 75 (2) (2008) 598 - 603.
18. D. C. Stepinski, M. P. Jensen, J. A. Dzielawa, M. L. Dietz, Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids. Green Chem. 7 (2005) 151 – 157.
19. K. Nakashima, F. Kubota, T. Maruyama, M. Goto, Feasibility of ionic liquids as alternative separation media for industrial solvent extraction process. Ind. Eng. Chem. Res. 44 (12) (2005) 4368 - 4372.
20. I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg, Understanding the extraction mechanism in ionic liquids: $UO_2^{2+}/HNO_3/TBP/C_4mimNTf_2$ as a Case Study. Solvent Extr. Ion Exch. 29 (4) (2011)577-601.
21. A. Suresh, PhD Thesis: The effect of altering the structure of trialkyl phosphates on actinide separations by solvent extraction for nuclear fuel materials processing.University of Madras, 2009.
22. Brahmananda Rao, C.V.S., Srinivasan,T.G., Vasudeva Rao, P.R.: Studies on the extraction of actinides by diamylamyl phosphonate. Solvent Extr. Ion Exch. 25 (6) (2007) 771 - 789.
23. L.L. Burger, The neutral organophosphorous compounds as extractants. Nucl. Sci. Eng. 16 (1963) 428 – 439.

24. K. V. Lohithakshan, S. K. Aggarwal, Solvent extraction studies of Pu(IV) with CMPO in 1-octyl 3-methyl imidazolium hexa fluorophosphate (C8mimPF6) room temperature ionic liquid (RTIL). Radiochim. Acta 96 (2) (2008) 93-97.
25. Y. Shen, X. Tan, L. Wang, W. Wu, Extraction of the uranyl ion from the aqueous phase into an ionic liquid by diglycolamide. Separation Purification Technol. 78 (3) (2011) 298–302.
26. G. M. Nair, G. M. Mahajan, D. R. Prabhu., Extraction of Uranium(VI) and Plutonium(IV) with some high molecular weight monoamides from nitric acid medium. Journal of radioanal chem.191 (2) (1995) 323-330.
27. G. M. Nair, G. M. Mahajan, D. R. Prabhu, Dioctyl butyramide and dioctyl isobutyramide as extractants for uranium(VI) and plutonium(IV) 204 (1) (1996) 103-111.

Chapter - 6

CHAPTER – 6

Ionic liquids in molecular diluents: Extraction behavior of plutonium(IV) and europium(III) in ionic liquids with strongly coordinating anions

This chapter describes the application of ionic liquids with strongly coordinating anions for the separation of plutonium (IV) and europium (III) from the nitric acid medium. The ionic liquids reported in the present chapter contain 1, 3 – diketonate or alkyl phosphate or diglycolamate anions associated either with alkylquaternaryammonium or imidazolium cations. The ionic liquids containing β–diketonate anion are alkylquaternaryammonium thenoyltrifluoroacetonate (R_4NTTA) and 1-alkyl-3-methylimidazolium thenoyltrifluoroacetonate, $C_n$mimTTA (n = 4, 6 and 8). Similarly, the ionic liquids with alkylphosphate and diglycolamate anions are tri-*n*-octylmethylammonium di(2-ethylhexyl)phosphate ($[A336]^+[P204]^-$) and tri-*n*-octylmethylammonium bis(ethylhexyl)diglycolamate ($[A336]^+[DGA]^-$).

6.1 Introduction

Room temperature ionic liquids with strongly coordinating anions [1 - 4] are becoming popular in addition to the functionalized ionic liquids that contain cations tethered with organic functionalities [5 - 9]. The advantages of such ionic liquids over functionalized ionic liquids are simple method of preparation, higher loading of metals, excellent miscibility with non-polar diluents such as toluene etc. Mehdi *et al.*[1] synthesized a new family of ionic liquids containing strongly coordinating β - diketonate anion and reported their solubility in aromatic diluents such as toluene and xylene. Yet, such ionic liquids were insoluble in paraffins.

Aliquat-336 is regarded as a versatile and affordable cation source for the synthesis of new family of hydrophobic ionic liquids [10]. The cation present in Aliquat-336, tricaprylmethylammonium cation ($[A336]^+$) can be combined with a number of anions by means of simple replacement of the chloride anion in Aliquat-336. The ionic liquids obtained by such procedure are strongly hydrophobic and have density lower than 0.9 g/mL. Low density of organic phase is necessary for adapting the ionic liquids in counter current extractions; whereas the higher density of ionic liquid could result in phase inversion during solvent extraction, as described elsewhere [11]. In addition, these Aliquat-336 based ionic liquids were reported to be completely soluble in aromatic diluents and some were also soluble even in paraffins, e.g., in hexane [10]. The solubility in molecular diluents is necessary for probing the role of ionic liquids in extraction procedures. In view of these unique advantages of aliquat-336 ionic liquids over imidazolium ionic liquids, Sun *et al.* [2] and Ling *et al.*[3] synthesized the several $[A336]^+$ based ionic liquids and studied for the extraction of rare earths from aqueous medium. The solubility of ionic liquids in *n*-DD is imperative for studying the applications of ionic liquids in nuclear fuel reprocessing and waste management.

In view of these, the present chapter details the preparation of few β-diketonate based hydrophobic ionic liquids with quaternary ammonium and imidazolium ions as cationic moieties, and studies on the extraction of plutonium(IV) in the part “A”. In part “B”, it deals with the unusual miscibility of $[A336]^+$ based ionic liquids containing 2-ethylhexylphosphate ($[P204]^-$) or 2-ethylhexyldiglycolamate ($[DGA]^-$) anions in paraffinic diluents and the application of such ionic liquids for the extraction of europium(III) from nitric acid.

The synthesis of these types ionic liquids have been detailed in the section 2.4.6 and 2.4.7 of the chapter 2 respectively. The experimental part has been described in the section 2.6.5 and 2.6.6 of the chapter 2 respectively.

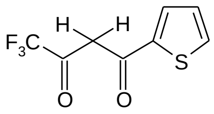
A. Ionic liquid extractants in molecular diluents: I. Extraction behavior of plutonium(IV) in 1,3-diketonate based ionic liquids

6.2 Results and Discussions

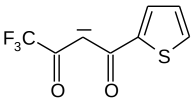
6.2.1 Structure of 1, 3-diketonate based ionic liquids

The structures, and abbreviations of the β-diketonate ionic liquids, and other ionic liquids used in the present study are tabulated in table 6.1 for convenience. General synthesis procedure of all ionic liquids and their precursors along with characterization is given in the *section 2.4.6* of the chapter 2.

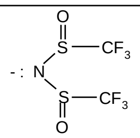
Table 6.1. Precursors and some TTA^- and NTf_2^- based ionic liquids and their abbreviations



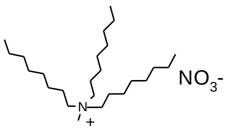
Thenoyltrifluoroactonate (HTTA)



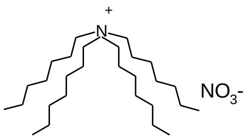
Thenoyltrifluoroactonate (TTA^-)



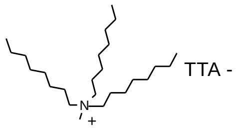
Bis(trifluoromethanesulfonyl)imide ion (NTf_2^-)



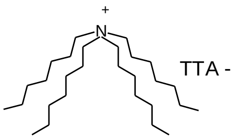
Trioctyloctylmethyl ammoniumnitrate (TOMAN)



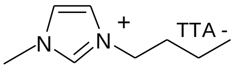
Tetraheptylammoniumnitrate (THEPAN)



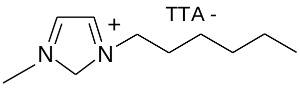
Trioctyloctylmethylammonium thenoyltrifluoroacetonate (TOMATTA)



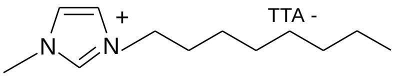
Tetraheptylammonium thenoyltrifluoroacetonate (THEPATTA)



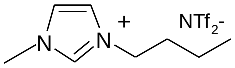
1-butyl-3-methylimidazolium thenoyltrifluoroacetonate (C_4mimTTA)



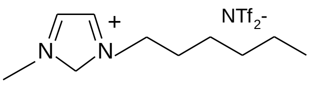
1-hexyl 3-methylimidazolium thenoyltrifluoroacetonate (C_6mimTTA)



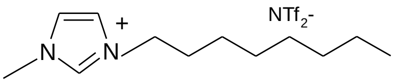
1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C_8mimTTA)



1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_8mimNTf_2$)



1-hexyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide ($C_6mimNTf_2$)



1-octyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide ($C_8mimNTf_2$)

6.2.2 Extraction of Pu(IV) in TOMATTA/TOMANTf$_2$

The ionic liquid, TOMANTf$_2$ was used as a diluent in the present study, and thus the extraction behavior of plutonium(IV) in TOMANTf$_2$ was studied initially to understand and the implications of using TOMANTf$_2$. The distribution ratio of Pu(IV) ($D_{Pu(IV)}$) in TOMANTf$_2$ at various concentration of nitric acid is shown in table 6.2. It is observed that the distribution ratio of plutonium(IV) increases with increase in the concentration of nitric acid. The extraction of Pu(IV) is less ($D_{Pu(IV)}$ = 0.15 to 0.4) when the concentration of nitric acid is 0.5 – 1 M, and it increases significantly at higher nitric acid concentrations. This indicates that the diluent, TOMANTf$_2$ is not "inert". A similar behavior has been reported in several cases when ionic liquid acted as diluent [12 - 14]. The observed extraction behavior in TOMANTf$_2$ could be attributed to the anion exchange of $[Pu(NO_3)_{5+x}]^{-(1+x)}$ species from aqueous phase with NTf_2^- of TOMANTf$_2$, as discussed elsewhere for imidazolium-NTf$_2$ based ionic liquids [9]. Table 6.2 also shows the distribution ratio of plutonium (IV) in a solution of 0.2 M TOMATTA/TOMANTf$_2$. $D_{Pu(IV)}$ values are much higher in this case even at nitric acid concentrations 0.5 – 1 M. This indicates that extraction of plutonium(IV) is essentially accomplished by the ionic liquid-extractant, TOMATTA, in this nitric acid range, and the presence of TOMATTA in TOMANTf$_2$ aids further extraction of plutonium(IV) at higher nitric acid concentrations (>1 M).

Table 6.2. Extraction of ^{239}Pu(IV) from nitric acid medium using 0.2 M TOMATTA/TOMANTf$_2$, A : O = 1 : 1 mL , T = 298 K, Equilibration time = 1hr

$[HNO_3]_{eq.}$ / ±0.05 M	**Distribution ratio of ^{239}Pu(IV) in**	
	TOMANTf$_2$	**0.2M TOMATTA in TOMANTf$_2$**
0.5	0.15	45
1	0.4	91
3	11	122
4	24	143
5	48	160

Since TOMATTA is composed of a tri-*n*-octylmethylammonium cation, which does not contain any functional group for extraction, associated with a derivative of β-diketonate anion, the extraction of plutonium(IV) in TOMATTA would be expected to be governed by the β-diketonate anion. In such case, the extraction of plutonium(IV) in

TOMATTA should decrease with increase of nitric acid concentration, which is characteristic to β-diketone extractants [15]. However, the extraction trend observed in the present study (table 6.2) indicates that the mechanism of plutonium extraction in TOMATTA is not simple, and requires more detailed investigations.

6.2.3 Extraction of Pu(IV) in TOMATTA/xylene

The β-diketonate based ionic liquids are the rare type of RTILs that are miscible in molecular diluents like toluene, and xylene. This unique property can be exploited to unravel the complex extraction behavior exhibited by TOMATTA/TOMANTf$_2$. Table 6.3 shows the extraction behavior of Pu(IV) in a solution of 0.2 M TOMATTA in xylene. It is observed that the distribution ratio of Pu(IV) increases with increase in the concentration of nitric acid, reaches a maximum at 4 M followed by decrease in $D_{\mathrm{Pu(IV)}}$ values. Again, this behavior is uncharacteristic to the extraction of plutonium(IV) in β-diketone extractants [15]. Since, the TOMATTA consists of tri-*n*-octylmethylammonium cation, and β-diketonate anion, it is likely that TOMATTA in the presence of aqueous nitric acid medium is converted to tri-*n*-octylmethylammonium nitrate (TOMAN), and theonyltrifluoroacetone (HTTA) by the reaction shown in equation 6.1.

$$\mathrm{TOMATTA} \; + \mathrm{HNO_3} \Leftrightarrow \mathrm{TOMAN} + \mathrm{HTTA} \tag{6.1}$$

The extraction of nitric acid in TOMATTA/xylene phase is verified in the nitric acid extraction isotherm shown in figure 6.1. It is observed that extraction of nitric acid in 0.2 M TOMATTA/xylene increases with increase in its concentration in aqueous phase. Nearly ~0.2 M nitric acid is extracted by organic phase even at the equilibrium concentration of 1 M. Thus, it is likely that TOMATTA in organic phase could exist in the form of TOMAN, and HTTA according to the reaction shown in equation 6.1; however, the extent of such conversion is not known. In view of this, the extraction of plutonium observed in 0.2 M TOMATTA/xylene can be visualized to consist of extractions contributed by the components namely 0.2 M TOMAN/xylene as well as 0.2 M HTTA/xylene. Therefore, the extraction behavior of Pu(IV) was studied, independently, in 0.2 M HTTA/xylene, and 0.2 M TOMAN/xylene, and the results are tabulated in table 6.3. It is observed that the extraction of Pu(IV) in 0.2 M HTTA/xylene decreases with increase in the concentration of nitric acid as expected for β-diketone extractants [15]. The $D_{\mathrm{Pu(IV)}}$ in 0.2 M TOMAN/xylene increases with increase in the concentration of nitric acid, reaches a maximum around 4 M followed by decrease in $D_{\mathrm{Pu(IV)}}$ values. This behavior is also characteristic to the extraction of Pu(IV) in alkyl quaternary ammonium nitrates [16].

Table 6.3 also shows the distribution ratio of plutonium(IV) in a solution of 0.2 M TOMAN-0.2 M HTTA in xylene. It is worthwhile to observe that these values are comparable with the data obtained in 0.2 M TOMATTA/xylene, even though TOMAN, and HTTA are added independently in xylene to make the solution of 0.2 M TOMAN-0.2 M HTTA in xylene. This indicates that TOMAN, and HTTA in 0.2 M TOMAN-0.2 M HTTA/xylene seem to react together, and exist predominantly as TOMATTA in organic phase. In addition, similar extraction trend of 0.2 M TOMAN/xylene with 0.2 M TOMATTA/xylene systems, and higher $D_{\mathrm{Pu(IV)}}$ in 0.2 M TOMAN/xylene obtained in the present study does not exclude the fact that TOMATTA reacts with nitric acid during extraction leading to the formation of TOMAN, and HTTA. However, such reaction seems to occur to a lesser extent, otherwise, TOMAN/xylene would have controlled the extraction of Pu(IV). The study, thus, shows that extraction of plutonium(IV) in TOMATTA/TOMANTf$_2$ (table 6.2) seems to be governed by TOMAN in the nitric acid concentration range 1 – 4M, even though TTA$^-$ contains the β-diketonate functional group. Perhaps at much lower acidities (< 0.5 M) TTA$^-$ may be controlling extraction. Above 4M, the extraction is aided by the anion exchange [9, 17] of $[\mathrm{Pu(NO_3)_{5+x}}]^{-(1+x)}$ species from aqueous phase with NTf$_2^-$ of TOMANTf$_2$ as discussed above.

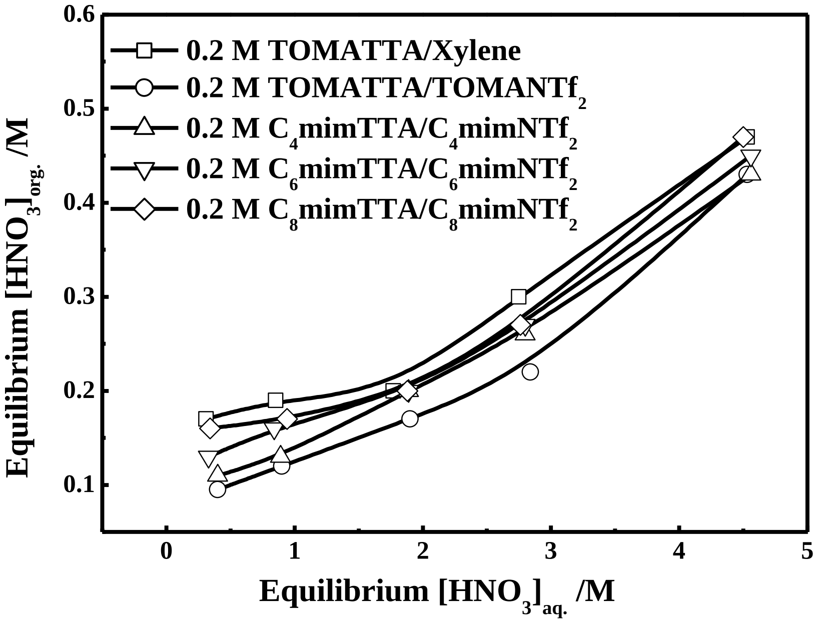


Figure 6.1. Nitric acid extraction isotherm in various systems. T = 298 K. O : A = 1:1

Table 6.3. Extraction of ^{239}Pu(IV) from nitric acid medium in TOMA-systems. A: O = 1: 1, T = 298K, Equilibration time = 1hr

$[HNO_3]_{eq}$ / $\pm$0.05M	Distribution ratio of ^{239}Pu(IV) in			
	0.2 M TOMATTA/ Xylene	0.2 M HTTA/ Xylene	0.2 M TOMAN/ Xylene	0.2 M TOMAN- 0.2 M HTTA/ Xylene
0.5	55	83	100	60
1	107	60	145	95
3	175	0.6	190	161
4	200	0.11	250	210
5	158	0.027	210	161

From the above discussions, it is clear that the components of the ionic liquid seems to control the extraction behavior of Pu(IV). Consequently, the study allows a method for predicting the extraction behavior of metal ions in β-diketonate based ionic liquids, by simply studying their extraction behavior in the components of ionic liquid. For instance, table 6.4, shows the extraction behavior of Pu(IV) in 0.2 M HTTA/benzene, and 0.2 M tetraheptylammonium nitrate (THEPAN) in benzene. The extractants, HTTA, and THEPAN, are the components of the ionic liquid, THEPATTA. As expected, the distribution values obtained for Pu(IV) are typical for HTTA, and quaternaryammonium salt extractants.

Table 6.4. Extraction of ^{239}Pu(IV) from nitric acid medium in THEA-systems.
A : O = 1 : 1 ,T = 298K, Equilibration time = 1hr

$[HNO_3]_{eq}$ / $\pm$0.05M	Distribution ratio of ^{239}Pu(IV) in			
	0.2 M HTTA/ benzene	0.2 M THEPAN/ benzene	0.2 M THEPAN-0.2 M HTTA/ benzene	0.2 M THEPATTA/ benzene
0.5	120	100	72	78
1	76	140	103	114
3	1.3	200	142	153
4	0.2	225	162	177
5	0.09	142	130	132

Table 6.4 also shows the distribution values in a solution of 0.2 M THEPAN – 0.2 M HTTA in benzene, and 0.2 M THEPATTA/benzene. Comparable distribution

values obtained in these cases confirm the hypothesis that the distribution ratio of Pu(IV) in β-diketonate ionic liquid can be predicted from the extraction behavior of its components.

6.2.4 Extraction of Pu(IV) in imidazolium-TTA based RTILs

Figure 6.2 shows the extraction behavior of Pu(IV) in a solution of imidazolium-TTA ionic liquids diluted in the respective $C_n$mimNTf_2 (alkylmethylimidazolium-NTf_2) ionic liquids. In contrast to the quaternary ammonium-TTA ionic liquid, the distribution ratio of Pu(IV) decreases initially with increase in nitric acid concentration reaches a minimum value followed by increase in $D_{Pu(IV)}$ values. Moreover, the distribution values increase in the order C_4mimTTA < C_6mimTTA < C_8mimTTA. It is interesting to note that the extraction behavior of Pu(IV) changes significantly by simply substituting the alkylimidazolium cation in place of alkylquaternary ammonium ion, while the β-diketonate anion remains the same. To understand this contrasting behavior, the extraction of Pu(IV) in the diluent $C_n$mimNTf_2 as a function of concentration of nitric acid was studied, and the $D_{Pu(IV)}$ values are plotted in figure 6.3. As described in the chapter 3 & 5, the distribution ratio is insignificant up to 2 M followed by increase in $D_{Pu(IV)}$ values in the order C_4mimNTf_2 < C_6mimNTf_2 < C_8mimNTf_2. The $D_{Pu(IV)}$ are given in the figure 6.3 for comparison with that of HTTA/$C_n$mimNTf_2.

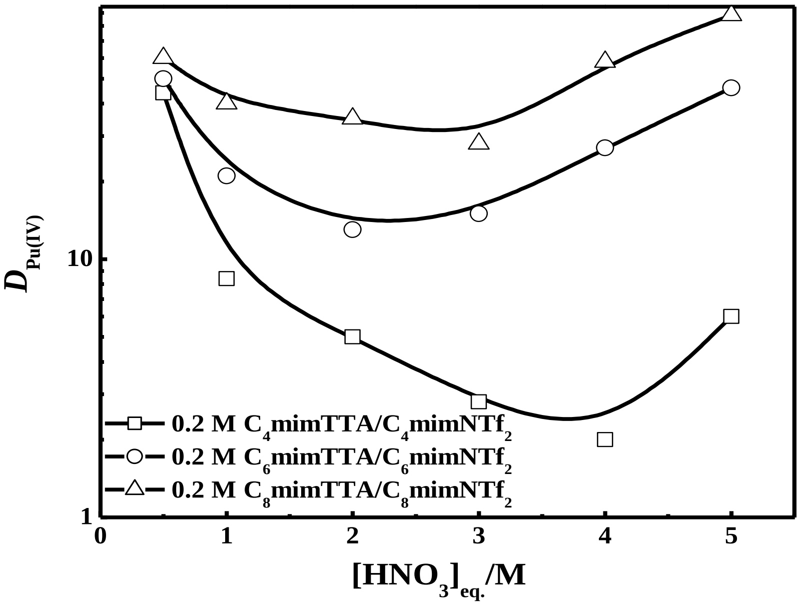


Figure 6.2. Variation in the distribution ratio of plutonium (IV) with concentration of nitric acid in imidazolium - TTA based systems. O : A = 1, T = 298 K, Equilibration time = 1 hr

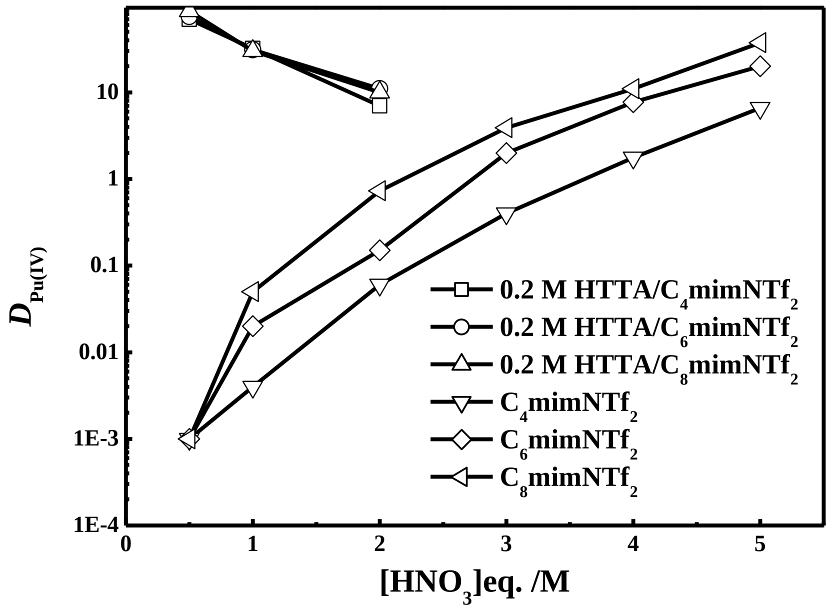


Figure 6.3. Variation in the distribution ratio of plutonium (IV) with concentration of nitric acid in alkylmethylimidazolium-NTf$_2$ based diluents. O : A = 1, T = 298 K, Equilibration time = 1 hr

The extraction of Pu(IV) above 2 M could be attributed to the anion exchange of $[Pu(NO_3)_{5+x}]^{-(1+x)}$ species from aqueous phase with NTf_2^- of $C_n$mimNTf$_2$ as reported in the chapter 5. Increasing the chain length of alkyl group attached to imidazolium cation favours anion exchange. However, the poor extraction of Pu(IV) at nitric acid concentrations lower than 2M observed in the present case, excludes the anion exchange mode of extraction (at < 2 M) not only from $C_n$mimNTf$_2$ (n = 4, 6 and 8) but also from their components $C_n$mimNO$_3$, which is expected to be formed upon nitric acid extraction. Since the extractant $C_n$mimTTA consists of an $C_n$mim$^+$ cation, and TTA$^-$ anion, and upon nitric acid extraction it is likely that TTA$^-$ may get associated with H$^+$ as discussed above. Therefore, the extraction behavior of HTTA/$C_n$mimNTf$_2$ was studied, and the results are shown in figure 6.3. It is observed that the distribution ratio decreases in all cases with increase of nitric acid concentration as expected for HTTA extractants [15]. The distribution values observed in this case are higher than those observed for 0.2 M $C_n$mimTTA/$C_n$mimNTf$_2$ (n = 4, 6 and 8). This could perhaps be attributed to lower extraction of nitric acid in 0.2 M $C_n$mimTTA/$C_n$mimNTf$_2$ resulting in lesser extent of conversion of TTA$^-$ to HTTA. This can be verified from figure 6.1 that 0.2 M $C_n$mimTTA/$C_n$mimNTf$_2$ extracts about 0.1 –0.15 M nitric acid when the concentration of nitric acid in aqueous phase is lower than 2 M, where as 0.2 M HTTA in $C_n$mimNTf$_2$ was employed for extraction. Moreover it is likely that all the extracted acid may not lead to the formation of HTTA. Thus, the extraction of Pu(IV) by HTTA/$C_n$mimNTf$_2$ indicates the extraction is essentially governed by HTTA at lower nitric acid concentrations (< 2 M), and by the anion exchange of $C_n$mimNTf$_2$ at higher nitric acid concentrations.

6.2.5 Separation factors

Table 6.5 compares the distribution ratio of Pu(IV) with U(VI), and Am(III) in all TTA – based ionic liquids. It is interesting to observe that the $D_{\mathrm{Pu(IV)}}$ values are quite significant as compared to $D_{\mathrm{U(VI)}}$, and $D_{\mathrm{Am(III)}}$. Therefore, the separation factors (SF), which is the quotient of $D_{\mathrm{Pu(IV)}}$ to D_{M} (M = U(VI) or Am(III)), achieved with the use of β-diketone extractants are remarkably high. This could be attributed to the extraordinary, and specific solvating ability of plutonium complexes in ionic liquid phase. This behavior can be suitability exploited for separating plutonium from uranium, and americium in various process streams.

Table 6.5. The distribution ratio of ^{239}Pu(IV), ^{233}U(VI) and ^{241}Am(III) in various ionic liquid systems as a function of nitric acid concentration and their separation factors (SF = $D_{\mathrm{Pu(IV)}}/D_{\mathrm{M}}$ (M = ^{233}U or ^{241}Am))

$[HNO_3]_{eq.}$ $/\pm 0.05$ M	Pu(IV)	U(VI)	Am(III)	SF of Pu(IV) from U(VI)	SF of Pu(IV) from Am(III)
Distribution ratios in 0.2 M TOMATTA / TOMANTf$_2$					
0.5	45	0.8	5×10^{-4}	56	$> 10^{4}$
1	91	1.2	3×10^{-3}	76	$> 10^{4}$
3	122	1.3	2×10^{-3}	99	$> 10^{4}$
5	160	2.5	10^{-3}	64	$> 10^{5}$
Distribution ratios in 0.2 M C_4mimTTA / C_4mimNTf$_2$					
0.5	44	2×10^{-3}	2×10^{-4}	$> 10^{4}$	$> 10^{4}$
1	8.4	3×10^{-3}	2×10^{-3}	$> 10^{3}$	$> 10^{3}$
3	2.8	10^{-2}	9×10^{-4}	$> 10^{3}$	$> 10^{3}$
5	6	0.1	7×10^{-4}	60	$> 10^{3}$
Distribution ratios in 0.2 M C_6mimTTA / C_6mimNTf$_2$					
0.5	50	0.08	10^{-3}	625	$>10^{4}$
1	21	0.06	1.2×10^{-3}	350	$> 10^{4}$
3	15	0.14	2.5×10^{-3}	107	$> 10^{3}$
5	46	0.36	1.5×10^{-3}	128	$> 10^{4}$
Distribution ratios in 0.2 M C_8mimTTA / C_8mimNTf$_2$					
0.5	60	0.35	2×10^{-4}	171	$> 10^{5}$
1	40	0.3	7×10^{-4}	133	$> 10^{4}$
3	28	0.49	2×10^{-3}	57	$> 10^{4}$
5	88	0.86	6×10^{-3}	102	$> 10^{4}$

6.3 Conclusions

Some new room temperature ionic liquids containing theonyltrifluoroacetonate anion were synthesized, and studied for Pu(IV) extraction. The distribution ratio of plutonium(IV) in 0.2 M TOMATTA/TOMANTf$_2$ increased with increase in the concentration of nitric acid, and the $D_{\mathrm{Pu(IV)}}$ values were much lower in the absence of TOMATTA. The unique property of these β-diketonate ionic liquid to dissolve in molecular diluents was exploited to elucidate the mechanism of Pu(IV) extraction. The study revealed that extraction was essentially controlled by the constituents of TOMATTA namely TOMAN, and HTTA, which could form upon nitric acid extraction. In addition, the study established a means of predicting the extraction behavior of metal ions in β-diketonate based ionic liquids, by simply studying their extraction in the components of ionic liquid. Unlike alkylquaternary ammonium –TTA ionic liquids, the extraction of Pu(IV) in imidazolium based ionic liquid (C$_n$mimTTA) was essentially governed by the component HTTA at lower nitric acid concentrations (<2 M), and by the anion exchange of C$_n$mimNTf$_2$ at higher nitric acid concentrations.

B. Ionic liquid extractants in molecular diluents: II. Extraction behavior of europium(III) in quarternary ammonium based ionic liquids

6.4 Results and Discussions

The structure of ionic liquids and their precursors used in this study are given in the *figure 2.2* of the chapter 2.

6.4.1 Miscibility of $[A336]^+[P204]^-$ in paraffin

n-Dodecane (*n*-DD) is extensively used as a diluent for solvent extraction applications in nuclear fuel cycle. Since the ionic liquids are composed entirely of ions, they are generally soluble in polar diluents and immiscible in paraffinic diluents like *n*-DD. However, Mehdi *et al.*[1] synthesized a new family of ionic liquids containing strongly coordinating anions such as diketonate. Interestingly, these ionic liquids were reported to dissolve in aromatic diluents like toluene, xylene etc. However, these ionic liquids were immiscible in paraffinic diluents. Mikkola *et al.* [10] reported the synthesis of $A336^+$ based ionic liquids and indicated the solubility of some $A336^+$ based ionic liquids in paraffin diluents like n-hexane. Sun *et al.* [2] synthesized the ionic liquid containing $A336^+$ cation and $P204^-$ anion was reported and studied the extraction behavior of some rare earths in $[A336]^+[P204]^-$ present in cyclohexane and heptane. In the present study, the unusual solubility of the ionic liquids, $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ in *n*-DD and higher homologues of *n*-DD were studied. These ionic liquids were found to be completely soluble in all paraffinic diluents, ranging from *n*-hexane (C6) to hexadecane (C16). However, it was interesting to note that the precursor, $[A336]^+[NO_3]^-$, was insoluble in paraffins. In addition, the precursor of the anion, HP204, though it was soluble in *n*-DD, but incompatible upon contacting HP204/*n*-DD solution with aqueous phase. It was found that the time required for the phase separation of organic phase (HP204/*n*-DD) from aqueous phase was very long. In view of this, the TALSPEAK process [18] developed for the separation of lanthanides from actinides, use HP204 in aromatic diluent rather than paraffin diluent. However, the present study showed that the ionic liquid containing $A336^+$ cation and $P204^-$ (or DGA^-) anion was completely miscible in paraffins and underwent phase disengagement in less than 30 seconds. Since, *n*-DD was used as diluent for the solvent extraction application in nuclear fuel cycle, the miscibility of $[A336]^+$ - based ionic liquid in paraffin was exploited for the extraction of Eu(III) and Am(III) from the aqueous solution as discussed below.

Figure 6.4 shows the variation in the distribution ratio of Eu(III) in a solution of $[A336]^+[P204]^-$ in different paraffin diluents as a function of pH. It is observed that the distribution ratio of Eu(III) is very less when the pH of the aqueous phase is less than 2. The $D_{\mathrm{Eu(III)}}$ increases with increase of pH thereafter. It is interesting to observe that the distribution ratio of Eu(III) decreases with increase in the chain length of the paraffin diluent in the order C_{12} > C_{14}> C_{16}. Dietz *et al.* [13] studied the extraction of U(VI) in a solution of tri-*n*-butyl phosphate (TBP) in 1-alkyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide based ionic liquids ($C_n$mimNTf$_2$, n = C_4 – C_{10}). The data were compared with those obtained in a paraffin diluent. As expected, the distribution ratio of U(VI) in TBP did not change with the nature of paraffinic diluent. Therefore, the paraffin diluent was regarded as “inert”. However, Dietz *et al.*[13] also reported that the distribution ratio of U(VI) changed with the increase in the chain length of alkyl group attached to the alkyl imidazolium ionic liquid. The present study also shows that the distribution ratio of Eu(III) varied significantly with the nature of paraffin diluents. Therefore, comparision of the present extraction trend, with the work of Dietz *et al.* [13] and others [19, 20] indicate that the distribution ratio of the metal ions could vary if one of the component in the solvent is ionic liquid irrespective of the nature of other component.

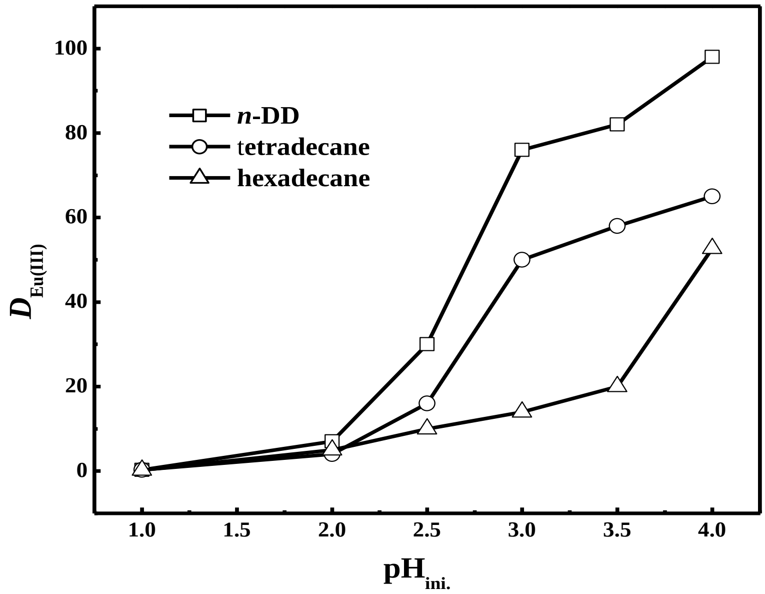


Figure 6.4. Variation in the distribution ratio of Eu(III) as a function of pH. Organic phase: 0.04 M $[A336]^+[P204]^-$/*n*-DD (or tetradecane or hexadecane), Aqueous phase: HNO_3, Equilibration time = 1hr, Temp = 298 K, O/A = 1

6.4.2 Extraction of Eu(III) in $[A336]^+[P204]^-$ in *n*-DD

The distribution ratio of Eu(III) in 0.04 M $[A336]^+[P204]^-$ in *n*-DD as a function of initial pH (pH$_{\mathrm{ini}}$) of the aqueous phase is shown in figure 6.5. The data are compared with its precursor solution containing 0.04 M $[A336]^+[NO_3]^-$ and 0.04 M HP204 in *n*-DD. It is observed that the distribution ratio of Eu(III) increases with increase of pH$_{\mathrm{ini}}$ in both cases.

At $pH_{ini} < 2$, the distribution ratio of Eu(III) is low. However, at $pH_{ini} > 2$, it is interesting to observe that the distribution ratio of Eu(III) in $[A336]^+[P204]^-$/*n*-DD is much higher than those observed in the precursor solution, under similar condition. The difference in the extraction observed in these cases could be due to the variation in the equilibrium pH that is likely to occur upon equilibration. Figure 6.5 also shows the pH of the aqueous phase obtained at equilibrium (values given in paranthesis) in each case. It is interesting to observe that the equilibrium pH of the aqueous phase decreases significantly in the case of 0.04 M $[A336]^+[NO_3]^-$ - 0.04 M HP204/*n*-DD and the pH increases marginally, in $[A336]^+[P204]^-$/*n*-DD system. This indicates that $[A336]^+[P204]^-$ extracts HNO_3 from aqueous phase and converted to $[A336]^+[NO_3]^-$ and HP204 by the reaction shown in the equation 6.2. Therefore, the $pH_{eq.}$ of the aqueous phase increases in case of $[A336]^+[P204]^-$/*n*-DD. Similarly, 0.04 M $[A336]^+[NO_3]^-$ - 0.04 M HP204/*n*-DD releases HNO_3 to aqueous phase by the reaction shown in equation 6.3. This leads to the decrease of equilibrium pH upon equilibration. Since the equilibrium pH is decreased, the distribution ratio of Eu(III) in 0.04 M $[A336]^+[NO_3]^-$- 0.04 M HP204/*n*-DD is lower. However, the extent to which the reactions shown in equation (6.2) and (6.3) are proceeding is not known in the present study.

$$[A336]^+[P204]^-_{org} + HNO_{3\,aq.} \Leftrightarrow [A336]^+[NO_3]^-_{org} + HP204_{org} \qquad (6.2)$$

$$[A336]^+[NO_3]^-_{org.} + HP204_{org.} \Leftrightarrow [A336]^+[P204]^-_{org.} + HNO_{3aq.} \qquad (6.3)$$

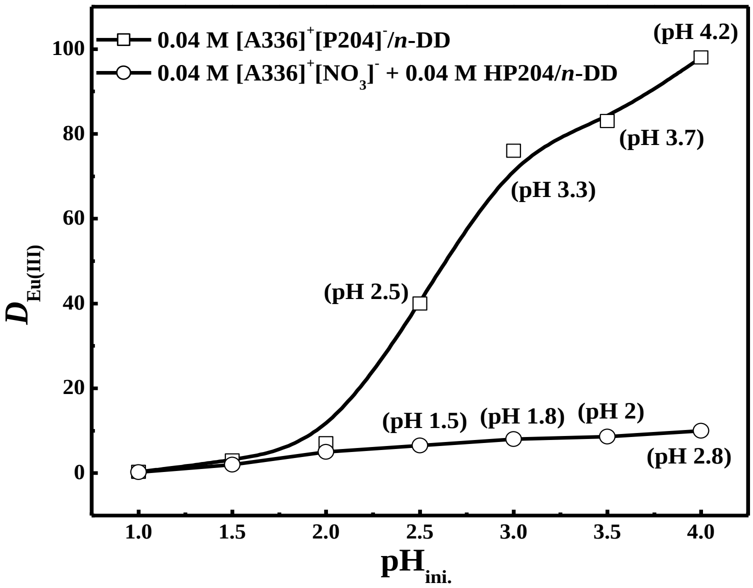


Figure 6.5. Variation in the distribution ratio of Eu(III) as a function of pH of the aqueous phase. Organic phase: 0.04 M $[A336]^+[P204]^-$/*n*-DD (or 0.04 M $[A336]^+[NO_3]^-$ + 0.04 M HP204 in *n*-DD, Aqueous phase: HNO_3, Equilibrium time: 1 hr, T = 298 K, O/A = 1

The reaction shown in equation 6.2 indicates that $[A336]^+[P204]^-$ associates with HNO_3 during equilibration and converted to the solution of $[A336]^+[NO_3]^-$ - HP204 in *n*-DD phase. From figure 6.5, the distribution ratio of Eu(III) in a solution of $[A336]^+[NO_3]^-$ - HP204/*n*-DD is lower. Therefore it is likely that the distribution ratio of Eu(III) in $[A336]^+[P204]^-$/*n*-DD may be reduced upon recycling the solvent phase.

To confirm this, the variation in the distribution ratio of Eu(III) upon recycling the organic phase (0.04 M $[A336]^+[P204]^-$/*n*-DD) was studied. The organic phase was pre-equilibrated with the aqueous phase at a particular pH. The aqueous phase was removed and the organic phase was contacted again with the fresh aqueous phase at that pH. This procedure was repeated up to 5 times. After each pre-equilibrations, the distribution ratio of Eu(III) in the organic phase was measured. The results are shown in figure 6.6. It is observed that the $D_{Eu(III)}$ decreases with increase in the number of pre-equilibrations. This confirms that the ionic liquid present in organic phase is converted to $[A336]^+[NO_3]^-$ and HP204 (by equation 6.2) upon equilibration. Since the solution of $[A336]^+[NO_3]^-$ - HP204 in *n*-DD exhibits lower distribution ratio for Eu(III) than $[A336]^+[P204]^-$/*n*-DD, the distribution ratio of Eu(III) decreases with increase in the number of pre-equilibrations as shown in figure 6.6. The study therefore indicates the requirement of a treatment procedure for converting back to $[A336]^+[P204]^-$/*n*-DD for recycling.

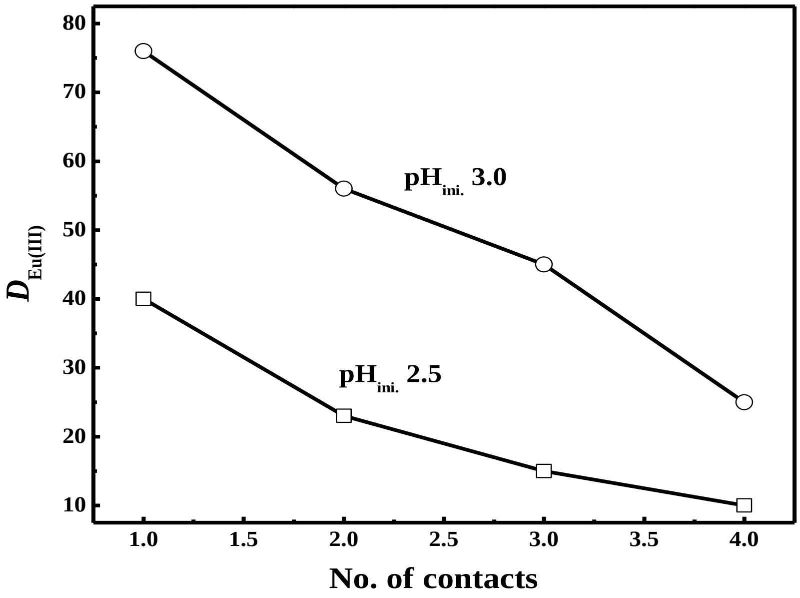


Figure 6.6. Variation in the distribution ratio of europium(III) upon recycling the solvent. Organic phase: 0.04 M $[A336]^+[P204]^-$/*n*-DD, Aqueous phase: pH = 3 or 2.5 (HNO_3), Equilibration time = 1 hr, T =298 K, O/A =1

6.4.3 Extraction of Eu(III) in other systems

The ionic liquid $[A336]^+[P204]^-$ is also soluble in aromatic diluents. Therefore, the distribution ratio of Eu(III) in $[A336]^+[P204]^-$/toluene (or xylene) was measured and compared with those obtained in a solution of $[A336]^+[NO_3]^-$ - HP204 in toluene (or xylene), in figure 6.7. Similar to the previous case, the distribution ratio of Eu(III) in $[A336]^+[P204]^-$ is much higher than its precursor solution. Figure 6.8 shows the variation in the distribution ratio of Eu(III) in a diglycolamate based ionic liquid $[A336]^+[DGA]^-$. This ionic liquid was soluble in *n*-DD. Therefore the extraction behavior of Eu(III) in $[A336]^+[DGA]^-$/*n*-DD is compared with those obtained in the precursor solution $[A336]^+[NO_3]^-$ - HDGA in *n*-DD in figure 6.8. It is observed that the distribution ratio of Eu(III) in $[A336]^+[DGA]^-$/*n*-DD is higher than the precursor solution in this case also. Therefore, the present study indicates that the cation $[A336]^+$, when combined with the conjugate base of high molecular acid, the resultant ionic liquid is soluble in paraffins and aromatic diluents. The ionic liquid obtained from such cation-anion combination exhibits excellent extraction of metal ion as compared to that obtained in the precursor solution. Sun *et al.*[2] attributed such extra ordinary extraction to the inner synergistic effect by ionic liquids.

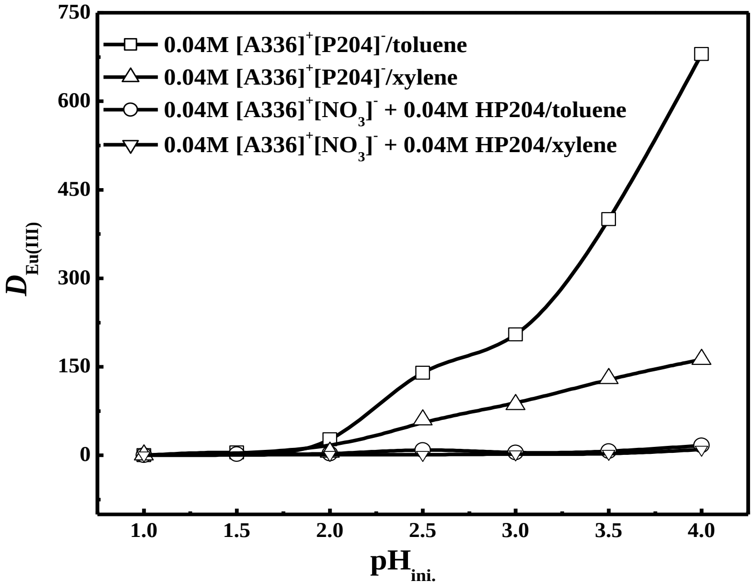


Figure 6.7. Variation in the distribution ratio of Eu(III) as a function of pH of the aqueous phase. Organic phase: 0.04 M $[A336]^+[P204]^-$ or (0.04 M $[A336]^+[NO_3]^-$ + 0.04 M HP204) in aromatic diluents, Aqueous phase: HNO_3, Equilibration time = 1hr, T = 298K, O/A = 1

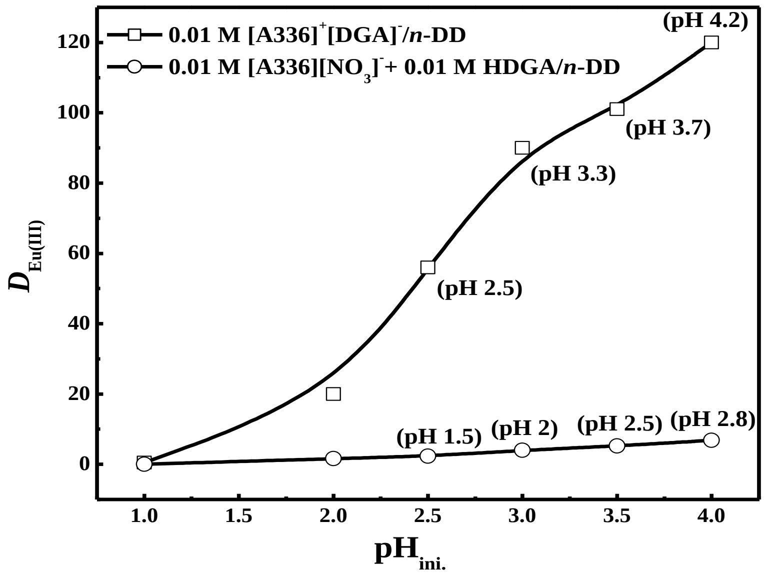


Figure 6.8. Variation in the distribution ratio of Eu(III) as a function of pH_{ini}. Organic phase: 0.01 M $[A336]^+[DGA]^-$/*n*-DD (or 0.01 M $[A336]^+[NO_3]^-$ + 0.01 M HDGA in *n*-DD), Aqueous phase: HNO_3, Equilibration time: 1 hr, T = 298 K, O/A = 1

6.4.4 Stoichiometry of Eu(III) extraction

Figure 6.9 shows the variation in the distribution ratio of Eu(III) as a function of ionic liquid concentration in organic phase at pH 3. It is observed that the distribution ratio of Eu(III) increases with increase in the concentration of ionic liquid. Linear regression analysis of the extraction data results in a slope of 3 in both ionic liquids, which is in good agreement with the value reported by Sun *et al.* [2] for the extraction of Eu(III) in $[A336]^+[P204]^-$. In addition, Sun *et al.*[2] proposed equation 6.4 for the extraction of Eu(III) in $[A336]^+[P204]^-$. A similar mechanism could be applicable to $[A336]^+[DGA]^-$ also, as shown in the equation 6.5.

$$Eu^{3+}_{aq.} + 3NO^-_{3\,aq.} + 3\{[A336]^+[P204]^-\}_{org.} \Leftrightarrow [Eu(NO_3)_3.\{[A336]^+[P204]^-\}_3]_{org.} \quad (6.4)$$

$$Eu^{3+}_{aq.} + 3NO^-_{3\,aq.} + 3\{[A336]^+[DGA]^-\}_{org.} \Leftrightarrow [Eu(NO_3)_3.\{[A336]^+[DGA]^-\}_3]_{org.} \quad (6.5)$$

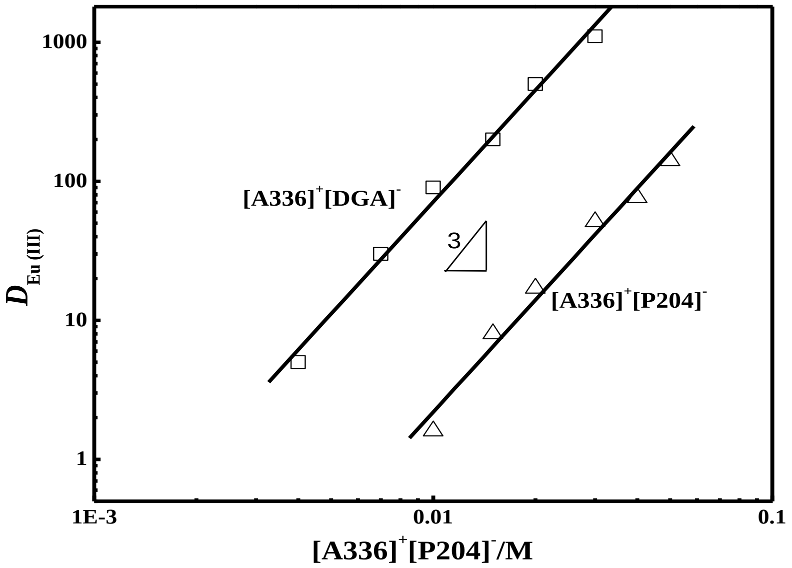


Figure 6.9. Variation in the distribution ratio of Eu(III) as a function of [A336]$^+$[P204]$^-$ or [A336]$^+$[DGA]$^-$ in *n*-DD. Aqueous phase: pH = 3, Equilibrium time = 1 hr, T = 298 K, O/A = 1

6.4.5 Separation of Eu(III) from Am(III)

Table 6.6 shows the distribution ratio of Eu(III) and Am(III) and their separation factors as a function of pH_{ini} achieved with the use of 0.04 M [A336]$^+$[P204]$^-$/*n*-DD or 0.01 M [A336]$^+$[DGA]$^-$/*n*-DD. It is observed that $D_{Eu(III)}$ and $D_{Am(III)}$ increases with increase of pH_{ini}. However, the separation factor of Eu(III) over Am(III) remains almost constant (1 - 2) irrespective of the pH. DTPA is the aqueous soluble complexing agent usually added to the aqueous phase for the separation of lanthanides from actinides [18]. Table 6.6 also shows the variation in the distribution ratio of Eu(III) and Am(III) as a function of DTPA concentration at a fixed pH_{ini}. of 3. It is observed that the distribution ratio decrease with increase in the concentration of DTPA in both ionic liquid systems. This could be attributed due to the increase in the formation of Metal-DTPA complex in aqueous phase that lowers the distribution values. However, it is interesting to observe that the separation factor of Eu(III) over Am(III) (SF = $D_{Eu(III)}/D_{Am(III)}$) increases with increase of [DTPA] concentration, and reaches a maximum in both cases at a particular DTPA concentration (10^{-4}M). This is followed by decrease of SF with further increase in the DTPA concentration. A similar behavior has been reported in *the section 4.4.3* of the chapter 4. This behavior was attributed to the differences in the complexing abilities of DTPA and the ionic liquid towards the metal ion under the given conditions. The SF achieved with the use of [A336]$^+$[DGA]$^-$ is higher than that observed for [A336]$^+$[P204]$^-$.

Table 6.6. Distribution ratios of Eu(III) and Am(III) and their separation factors in various ionic liquid systems. Organic phase: 0.04 M $[A336]^+[P204]^-$/*n*-DD or 0.01 M $[A336]^+[DGA]^-$/*n*-DD. Aqueous phase: $pH_{eq.}$ ~ 2 - 4, DTPA = 0 – 10^{-3} M. Equilibrium Time = 1 hr. O/A = 1. T = 298 K

Distribution ratio and the SF achieved using 0.04 M $[A336]^+[P204]^-$/n-DD								
$pH_{ini.}$	$D_{Eu(III)}$	$D_{Am(III)}$	SF	$pH_{ini.}$	DTPA/M	$D_{Eu(III)}$	$D_{Am(III)}$	SF
2.0	7	5	1.4		10^{-5}	5	0.61	8.12
3.0	76	64	1.2	3.0	10^{-4}	3.5	0.2	17.5
4.0	98	82	1.2		10^{-3}	1	0.08	12.5
Distribution ratio and the SF achieved using 0.01 M $[A336]^+[DGA]^-$/n-DD								
2.0	20	8	2.5		10^{-5}	30	3	10
3.0	90	65	1.4	3.0	10^{-4}	4	0.1	40
4.0	120	102	1.17		10^{-3}	2	0.066	30

6.5 Conclusions

The paraffin soluble ionic liquids, $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ were prepared and studied for the extraction of Eu(III) and Am(III) from the aqueous solutions. The extraction of Eu(III) and Am(III) increased with increase of pH and decreased with increase in the chain length of paraffin diluents. Usually the distribution ratio observed in the ionic liquid was always much higher than that obtained in the solution of ionic liquid precursors. These ionic liquids extract the trivalents as neutral metal (III) nitrate complex. Even though the ionic liquid extracted Eu(III) and Am(III) to the same extent from the aqueous phase, it was possible to separate Eu(III) from Am(III) by adding DTPA to the aqueous phase. The distribution ratio and the SF achieved with the use of $[DGA]^-$ based ionic liquid were higher than $[P204]^-$ ionic liquid under similar conditions. Since the ionic liquid was converted to its precursor during equilibration with HNO_3, the study therefore indicates the requirement of a treatment procedure for converting back to $[A336]^+[P204]^-$ or $[A336]^+[DGA]^-$ for recycling.

6.6. References

[1]. H. Mehdi, K. Binnemans, V. Hecke, L.V. Meervelt, P. Nockemann, Hydrophobic ionic liquids with strongly corodinating anions. Chem. Commun. (2010) 234-236.

[2]. X. Sun, Y. Ji, F. Hu, Bo. He, Ji. Chen, D. Li, The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. Talanta 81 (4-5) (2010)1877–1883.

[3]. Y. H. Ling, W. Wei, C. H. Min, Ji Chen, Extraction mechanism of rare earths with bifuncional ionic liquids (Bif-ILs) [A336][CA-12]/[A336][CA-100] in nitrate medium. Chin J Anal Chem. 39 (10) (2011)1561–1566.

[4]. V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, I. I. Torocheshnikova, S. V. Smirnova, I. V. Pletnev, Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. Talanta 80 (3) (2010) 1177-1182.

[5]. A. Ouadi, O. Klimchuk, C. Gaillard, I. Billard, Solvent extraction of U(VI) by task specific ionic liquids bearing phosphoryl groups. Green Chem. 9 (11) (2007) 1160 – 1162.

[6]. I. L. Odinets, E. V. Sharova, O. I. Artyshin, K. A. Lyssenko, Y. V. Nelyubina, G. V. Myasoedova, N. P. Molochnikova, E. A. Zakharchenro, Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery. Dalton Trans. 39 (17) (2010) 4170 – 4178.

[7]. A. E. Visser, R. P. Swatloski, W.M. Reichert, R. Mayton, S.A. Sheff, Wierzbicki, J.H. Davis Jr., Rogers, R.D. Task Specific Ionic Liquids Incorporating Novel Cations for the Coordination and Extraction of Hg^{2+} and Cd^{2+}. Synthesis, Characterization and Extraction Studies. Envir. Sci. Technol. 36 (11) (2002) 2523 - 2529.

[8]. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K.V. Hecke, L. Van Meervelt, B. Kirchner, K. Binnemans, Task-Specific ionic liquid for solubilizing metal oxides. J.Phys.Chem.B 110 (42) (2006) 20978 – 20992.

[9]. A. Rout, K. A. Venkatesan, T.G. Srinivasan, P. R. Vasudev Rao, Unusual extraction of plutonium(IV) from uranium(VI) and americium(III) using phosphonate based task specific ionic liquid. Radiochim. Acta 98 (8) (2010) 459-466.

[10]. J. P. Mikkola, P. Virtanen, R. Sjoholm, Aliquat 336 - A versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids. Green Chem. 8 (3) (2006) 250-255.

[11]. P. Giridhar, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao, Comparison of Diluent Characteristics of Imidazolium Hexafluorophosphate Ionic Liquid with *n*-Dodecane. J. Nucl. Radiochem. Sci. 5 (2) (2004)17 – 20.

[12]. L. Dietz, J.A. Dzielawa, Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the ‘greenness’ of ionic liquids as diluents in liquid–liquid extraction. Chem. Commun. (2001) 2124 - 2125.

[13]. M. L. Dietz, D. C. Stepinski, Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids. Talanta 75 (2) (2008) 598 - 603.

[14]. M. L. Dietz, J. A. Dzielawa, I. L. Blake, A. Young, M. P. Jensen, Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids. Green Chem. 5 (6) (2003) 682 – 685.

[15]. J. G. Cuninghame, G. L. Miles, The separation of plutonium by extraction with thenoyltrifluoroacetone (TTA), J. Inorg. Nucl. Chem. 3 (1) (1956) 54 –63.

[16]. G. Koch, Reprocessing by quarternary ammonium nitrates: laboratory studies, In: Solvent Extraction Chemistry of metals. H.A.C. McKay, T.V. Healy, I.L. Jenkins (Eds.), McMillan, 1958, pp. 247 – 266.

[17]. J. L. Ryan, E. J. Wheelwright, Recovery and Purification of Plutonium by Anion Exchange, Ind. Eng. Chem. 51 (1) (1959) 60 – 65.

[18]. M. Nilsson, K. L. Nash, A Review of the development and operational characteristics of the TALSPEAK Process. Solvent Extr. Ion Exch. 25 (6) (2007) 665–701.

[19]. Y. Shen, X. Tan, L. Wang, W. Wu, Extraction of the uranyl ion from the aqueous phase into an ionic liquid by diglycolamide. Sep. Purif. Technol. 78 (3) (2011) 298–302.

[20]. K. Shimojo, K. Kurahashi, H. Naganawa, Extraction behavior of lanthanides using a diglycolamide derivative TODGA in ionic liquids. Dalton Trans. 37 (2008) 5083–5088.

Chapter - 7

CHAPTER - 7

Summary and Conclusions

This chapter deals with the summary of studies and the future scope of the present work. The work reported in the thesis is aimed at explorimg the feasibility of using ionic liquids for the separation of actinides and fission products from aqueous solutions. The ionic liquid was employed both as diluent and extractant in the study.

7.1 Extraction behavior of actinides in RTIL diluents

The extraction behavior of Am(III) in CMPO – 1.2 M TBP/$C_4mimNTf_2$ was studied. Extraordinary extraction of americium was facilitated by the presence of $C_4mimNTf_2$ and the process required only 0.05 M CMPO in RTIL medium instead of 0.2 M CMPO employed in conventional TRUEX systems for comparable extraction behavior. The stoichiometry of americium extraction in CMPO-TBP/$C_4mimNTf_2$ resembled that of TRUEX solvent, wherein three molecules of CMPO were involved in co-ordination. However, the studies also showed that the ion exchange mechanism for the extraction of americium (III) could not be excluded. The extraction of americium (III) by RTIL solution is accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration.

The extraction behavior of some actinides (Pu(IV), U(VI) and Am(III)) in DMDOHEMA in ionic liquid diluent ($C_nmimNTf_2$; n = 4, 5 and 6) exhibited excellent selectivity for U(VI) and Pu(IV), whereas in *n*-DD medium, Am(III) was also co-extracted. Above 4 M nitric acid, the primary mode of Pu(IV) transfer in ionic liquid phase was found to be anion exchange. Below 4 M nitric acid, the investigations showed that the most plausible mechanism of actinide transfer in ionic liquid phase could be the cation exchange of metal – solvate complex with C_4mim^+ cation of ionic liquid. The distribution ratio of actinides decreased with increase of alkyl chain length of $C_nmimNTf_2$. The separation factor (SF) of > 1000 was obtained for U(VI) and Pu(IV) from Am(III) and many fission products.

7.2 Extraction -Third phase formation behavior of Eu(III) in ionic liquid medium and its mutual separation from Am(III)

The extraction and third phase formation behavior of Eu(III) in 0.2 M CMPO – 1.2 M TBP in *n*-DD and in 0.2 M CMPO – 1.2 M TBP in $C_4mimNTf_2$ were compared. While the limiting organic concentration (LOC) of Eu(III) in 0.2 M CMPO – 1.2 M

TBP/*n*-DD was only ~9 mg/mL, about ~ 40 mg/mL could be loaded with the use of C_4mimNTf$_2$ without any third phase formation. The study revealed that the use of RTIL in place of *n*-DD prevents the undesirable third phase formation. The stoichiometry of Eu : CMPO in RTIL phase was found to vary depending upon the loading, from 1:3 at tracer levels to ~1:1 at higher metal loadings. In the absence of TBP, i.e, 0.2 M CMPO/C_4mimNTf$_2$, the extraction of Eu(III) results in a “crud type-precipitate” at the interphase and it disappeared with the addition of TBP to the extent of 0.2 M. The study indicated, that of TBP in C_4mimNTf$_2$ is essential to modify the RTIL phase. The extraction of europium(III) by RTIL solution was accompanied by the release of energy and the exothermicity decreased with increase in nitric acid concentration.

The extraction behavior of Am(III) and Eu(III) in the solution of bis(2-ethylhexyl)phosphoric acid (D2EHPA) or bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) in room temperature ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (C_8mimNTf$_2$) confirmed that these extractants in conjunction with the present ionic liquid provide extraordinary extraction of Am(III) and Eu(III) from aqueous solutions of widely differing compositions. The differential complexing ability of the extractant present in ionic liquid phase and diethylenetriaminepentaaceticacid (DTPA) in aqueous phase was exploited to optimize the conditions needed for effective separation of trivalent lanthanides from actinides. The stoichiometry of metal – solvate was found to be 1: 3. HDEHDGA was found to be superior to D2EHPA for efficient separations. At pH 3 and using 0.005 M DTPA, D2EHPA gave a SF of ~35, however, HDEHDGA required only 10^{-4} M DTPA for achieving a SF of ~150.

7.3 Unusual separation of plutonium (IV) from other actinides and fission products using novel task specific ionic liquids (TSILs)

Two new functionalized ionic liquids, namely, diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethane sulfonyl)imide (ImPNTf$_2$) and *N,N*–dioctyl-2-(3-methyl imidazolium) bis(trifluoromethane sulfonyl)imide (DOAImNTf$_2$) were prepared and studied for the extraction of Pu(IV), U(VI), Am(III) and fission products from nitric acid medium. The extraction of U(VI), Am(III) and fission products was insignificant. However extraordinary extraction of Pu(IV) was achieved with the use of these ionic liquid-extractants (ImPNTf$_2$ and DOAImNTf$_2$), in ionic liquid diluents ($C_n$mimNTf$_2$; n = 4, 6 and 8 depending on the experimental conditions). Above 4 M nitric acid, the primary mode of plutonium(IV) transfer in ionic liquid phase was determined to be anion exchange. Below 4 M, the present investigation indicates the possibility of metal solvate complex (Pu(IV) –$(DOAImNTf_2)_3$) or (Pu(IV) –$(ImPNTf_2)_3$) formation in ionic liquid phase. However, more studies are needed to bring out the insights of Pu(IV) extraction. Unlike the traditional systems, the ionic liquid extractant, $ImPNTf_2$ (or $DOAImNTf_2$), was selective for plutonium (IV) over other actinides and fission products. Moreover, the task speficic property was observed only upon functionalization of the phosphonate or amide moiety on to the imidazolium cation. The extraordinary separation factor of 20 – 250 for plutonium (IV) over uranium (VI) and 10^3 –10^5 for plutonium (IV) over americium (III) were achieved by using $ImPNTf_2/C_n mimNTf_2$ (n = 4 and 8) depending upon the concentration of nitric acid. Similarly, the separation factor of Pu(IV) over U(VI) was found to vary from 40 to 3400 in $DOAImNTf_2$ solution depending upon the concentration of nitric acid employed for extraction. The stripping of plutonium (IV) from both the TSIL phase was possible within 10 stages using citric acid and acetohydroxamic acid as the complexing agents. Extraction of plutonium (IV) by ionic liquid phase was observed to be exothermic and the exothermicity decreased with increase in nitric acid concentration.

7.4 Extraction behavior of actinides ionic liquids with strongly coordinating anions

Some new room temperature ionic liquids containing theonyltrifluoroacetonate anion such as alkylquaternaryammonium thenoyltrifluoroacetonate (R_4NTTA), and 1-alkyl-3-methylimidazolium thenoyltrifluoroacetonate ($C_n mimTTA$), with methyl, butyl, hexyl, heptyl and octyl moieties were synthesized, and studied for Pu(IV) extraction. The $D_{Pu(IV)}$ in 0.2 M TOMATTA/$TOMANTf_2$ increased with increase in the concentration of nitric acid, and were much lower in the absence of TOMATTA. The unique property of these β-diketonate ionic liquid to dissolve in molecular diluents was exploited to elucidate the mechanism of Pu(IV) extraction. The study revealed that the extraction was essentially controlled by the constituents of TOMATTA namely TOMAN, and HTTA, which could form upon nitric acid extraction. In addition the study established a means of predicting the extraction behavior of metal ions in β-diketonate based ionic liquids, by simply studying their extraction in the components of ionic liquid. Unlike alkylquaternary ammonium –TTA ionic liquids, the extraction of Pu(IV) in $C_n mimTTA$ ionic liquid was essentially governed by the component HTTA at lower nitric acid concentrations (< 2 M), and by the anion exchange of $C_n mimNTf_2$ at higher nitric acid concentrations. The separation factors (SF) of Pu(IV) over other actinides (U(VI) and Am(III)) using these ionic liquids was quite high.

The miscibility of aliquot-336 based ionic liquids such as $[A336]^+[P204]^-$ and $[A336]^+[DGA]^-$ in the paraffinic diluent (*n*-DD) was explored for the mutual separation of Eu(III) and Am(III). The extraction of Eu(III) and Am(III) increased with increase of pH and decreased with increase in the chain length of paraffin diluents. Usually the distribution ratio observed in the ionic liquid was always much higher than that obtained in the solution of ionic liquid precursors. These ionic liquids extract the trivalents as neutral metal (III) nitrate complex. Even though the ionic liquid extracted Eu(III) and Am(III) to the same extent from the aqueous phase, it was possible to selectively strip Eu(III) from Am(III) with DTPA in the aqueous phase. The distribution ratio and the SF achieved with the use of $[DGA]^-$ based ionic liquid were higher than $[P204]^-$ based ionic liquid under similar conditions. Since the ionic liquid was converted to its precursor during equilibration with HNO_3, the study therefore indicates the requirement of a treatment procedure for converting back to $[A336]^+[P204]^-$ or $[A336]^+[DGA]^-$ ionic liquid for recycling.

7.5 Future scope of the present work

i) Extraction behavior of Am(III) and Eu(III) in CMPO – TBP extractant (TRUEX extractant) in ionic liquid diluent with remarkably higher distribution ratio has been reported in this thesis observed in ionic liquid medium. Further studies on the extraction behavior of Am(III) and Eu(III) could be carried out by using different extractants other than TRUEX extractant in ionic liquid medium and the suitability of ionic liquid diluent over molecular diluents could be brought out.

Similarly, different malonamides other than DMDOHEMA are suggested to be used as the extractant for the actinides (Pu(IV), U(VI) and Am(III)) in ionic liquid medium in order to evaluate their suitability for the metal extraction in ionic liquid diluent and compare the extraction behavior with that of traditional diluents. Further studies are needed to establish the nobility of ionic liquid extraction system by changing either the extractant types in ionic liquid medium or using one extractant in different ionic liquid medium.

ii) The third phase formation of Eu(III) in the ionic liquid medium has been reported in this thesis. It was observed that there was no third phase formation observed even with $[Eu]_{ini}$ ~ 300 mg/mL in the aqueous phase. Third phase formation in the solvent extraction of actinides and other fission products could be studied in detail by changing different parameters in ionic liquid medium which would solve the problem that is encountered in the conventional diluents (e.g., *n*-DD).

Similarly, the mutual separation of Eu(III) and Am(III) in ionic medium is reported for the first time and thus the study suggests to extend this idea for the group separation of lanthanides from actinides in real TALSPEAK process using suitable ionic liquid diluent to achieve excellent separation factors.

iv) The unusual separation of Pu(IV) over other actinides and fission products has been reported using phosphonate and amide based functionalized ionic liquids. Further studies are required to ascertain the application of functionalized ionic liquids in the target specific separation of actinides and fission products by preparing several types of hydrophobic task specific ionic liquids with suitable target specific moiety.

v) The study of "ionic liquids in molecular diluents" suggests the synthesis of ionic liquids with different anions for the application in the back end of the fuel cycle. By selecting proper extractant moiety for ionic liquid anion, it is possible to dissolve such ionic liquids in different paraffinic liquids as described in this thesis. This important property of ionic liquids would help in altering the behavior of extracting phase in liquid-liquid extraction of actinides and fission products.

vi) One of the major studies required in solvent extraction process while dealing with ionic liquid as medium is to study carefully the mechanism associated with the extraction. The coordination environment of metal ions in the ionic liquid phase need to be investigated properly in order to bring out the insight of the proper mechanism.

vii) The fundamental properties of ionic liquids that govern solubility in aqueous phase, hydrophobicity, viscosity, density etc. need more understanding to enable the design of RTIL/FILs having the required properties for hydrometallurgical applications.

viii) Different physicochemical properties of ionic liquids need to be investigated to suit them for the robust applications in reprocessing and waste management.

It can be anticipated that the use of room temperature ionic liquids, as diluent as well as extractant would definitely solve many of the underlying issues in the back end of the nuclear fuel cycle.

Glossary

Abbreviations	Full Name
AHA	Acetohydroxamic acid
AHWR	Advance heavy water reactor
Aliquat336 (TOMAC)	Tri-*n*-octylmethylammonium chloride
$[A336]^+[P204]^-$	Tri-*n*-octylmethylammonium di (2-ethylhexyl)phosphate
$[A336]^+[DGA]^-$	Tri-*n*-octylmethylammonium bis(ethylhexyl)diglycolamate
An	Actinides
$BETI^-$	Bis(perfluoroethanesulfonyl)imide
BF_4^-	Tetrafluoroborate
CAC	Critical aqueous concentration
CMPO	*n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyphosphine oxide
$C_n$mimNTf_2	1-alkyl-3-methylimidazoliumbis(trifluoromethanesulfonyl)imide
cP	Centipoise
Cyanex 272	Bis (2,4,4-trimethylpentyl) phosphinic acid
D_M	Distribution ratio of metal ion
DAAP	Diamylamylphosphate
DCH18C6	Di-cyclohexano- 18 -crown 6
DIDPA	Diisodecylphosphoric acid
DIAMEX	Diamide extraction
DGA	Diglycolamide
D2EHPA	Di(2-ethylhexyl)phosphate
DMDBTDMA	*N,N'*-DiMethyl-DiButyl-TetraDecylMalonamide
DMDOHEMA	*N,N'*-DiMethyl-*N,N'*-Di-Octyl-2-(2-(hexyloxy)ethyl)Malonamide
DOAImNTf_2	*N*,*N*-Dioctyl-2(3-methylimidazolium)bis(trifluoromethanesulfony)limide
DOBA	Dioctylbutyramide
DOEHA	Dioctylethylhexanamide
DOOA	Dioctyloctanamide
DTPA	Diethylenetriamine-*N,N,N',N",N'"*-pentaacetic acid
EDTA	Bis(ethylenediamine)tetraacetic acid
FBTR	Fast breeder test reactor
FILs	Functionalized ionic liquids

HLLW	High level liquid waste
$[\mathrm{Hbet}]^+[\mathrm{NTf_2}]^-$	1-Carboxy-*N*,*N*,*N*-trimethylmethanammonium bis(trifluoromethylsulphonyl)imide
HDEHDGA	Bis(2-ethylhexyl)diglycolamic acid
HDODGA	*N*,*N*-Dioctyldiglycolamic acid
IL	Ionic liquid
$\mathrm{ImPNTf_2}$	Diethyl-2-(3-methylimidazolium)ethylphosphonate bis(trifluoromethansulfonyl)imide
LOC	Limiting organic concentration
Ln	Lanthanides
MBDA	Tetramethyldiglycolamide
$\mathrm{MeBu_3NTf_2}$	Tri-*n*-butylmethylammonium bis(trifluoromethansulfonyl)imide
n-DD	*n*-Dodecane
$\mathrm{NTf_2^-}$	Bis(trifluoromethansulfonyl)imide
$\mathrm{OTf^-}$	Trifluoromethanesulfonate
$\mathrm{PF_6^-}$	Hexafluorophosphate
PHWR	Pressurized heavy water reactor
PFBR	Prototype fast breeder reactor
POPOP	1,4-Bis (5-phenyloxazol-2-yl) benzene
PPO	2,5-Diphenyl Oxazole
PUREX	Plutonium Uranium Reduction Extraction (or Plutonium Uranium Recovery by Extraction)
$\mathrm{R_4NTTA}$	Alkylquaternaryammonium theonyltrifluoroacetonate
RTIL	Room temperature ionic liquid
SF	Separation factor
SETFICS	Separation of trivalent f-element introroup by CMPO solvent
TALSPEAK	Trivalent actinides and lanthanide
TAP	Tri-*n*-amyl phosphate
TBDA	Tetrabutyldiglycolamide
TIAP	Tri-*n*-isoamyl phosphonate
TIBP	Tri-*n*-isobutyl phosphonate
THEPAN	Tetraheptylammonium nitrate
THEPATTA	Tetraheptylammonium theonyltrifluoroacetonate
TOMAN	Tri-*n*-octyl-methylammonium nitrate
$\mathrm{TOMANTf_2}$	Tri-*n*-octyl-methylammonium bis(trifluoromethansulfonyl)imide

TOMATTA	Tri-*n*-octyl-methylammonium theonyltrifluoroacetonate
TOPO	Tri-*n*-octyl phosphinoxide
TPEN	Tetrakis-(2-pyridylmethyl)ethylenediamine
TRPO	Trialkylphosphinoxide
TRUEX	Trans Uranium EXtraction
TSIL	Task specific ionic liquid
TTA^-	Theonyltrifluoroacetonate
VOCs	Volatile organic compounds

List of publications

I. List of publications in peer – reviewed journals and conference proceedings

A. Peer – Reviewed Journals

1. **A. Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Extraction of americium(III) from nitric acid medium by CMPO-TBP extractants in ionic liquid diluent. Radiochimica Acta 97(12) (2009) 719-725.

2. **A. Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Unusual extraction of plutonium(IV) from uranium(VI) and americium(III) using phosphonate based task specific ionic liquid. Radiochimica Acta 98 (8) (2010) 459 - 466.

3. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Extraction and third phase formation behavior of Eu(III) in CMPO - TBP extractants present in room temperature ionic liquid. Separation and Purification Technology 76 (3) (2011) 238 – 243.

4. **A. Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Ionic liquid extractants in molecular diluents: Extraction behavior of plutonium (IV) in 1, 3- diketonate ionic liquids. Solvent Extraction and Ion Exchange 29 (4) (2011) 602 – 618.

5. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Room temperature ionic liquid diluent for the mutual separation of europium (III) from americium (III). Separation and Purification Technology 81(2) (2011) 109 – 115.

6. **A. Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Room temperature ionic liquid diluent for the extraction of Eu(III) using TRUEX extractants. Journal of Radioanalytical and Nuclear Chemistry 290 (2011) 215 – 219.

7. **A. Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Separation of plutonium(IV) from uranium(VI) using phosphonate based task specific ionic liquid. Desalination and water treatment. 38 (2012) 179–183.

8. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Extraction behavior of actinides and fission products in amide functionalized ionic liquid. Separation and Purification Technology. DOI; 10.1016/j.seppur.2012-01.020.

9. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Liquid – Liquid extraction of Pu(IV), U(VI) and Am(III) using malonamide in room temperature ionic liquid as diluent. Journal of Hazardous Material. 221-222 (2012) 62 - 67.

10. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Ionic liquid extractants in molecular diluents: II. Extraction behavior of europium (III) in quarternary ammonium-based ionic liquids. Separation and Purification Technology 95 (2012) 26 -31.

11. P. R. Vasudeva Rao, K. A. Venkatesan, **Alok Rout**, K. Nagarajan, T. G. Srinivasan, Potential Applications of Room Temperature Ionic Liquids for fission products and actinides separation. Separation Science and Technology 47 (2012) 204–222.

12.**Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Tuning the extraction behavior of actinides in PUREX solvent using room temperature ionic liquid. Separation and Purification Technology (Under Review and not included in chapters).

13.**Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Extraction behavior of Am(III) and Eu(III) using ionic liquids with strongly coordinating anions. (MS to be submitted and not included in chapters).

B. Conferences and symposia papers

International

1. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Extrcation behavior of actinides and fission products using amide functionalized ionic liquid. 1st international conference on ionic liquids in separation and purification technology, ILSEPT, Sitges, Spain, 4th – 7th sep., **2011 (Keynote lecture)**.

2. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Extraction behavior of Eu(III) in CMPO-TBP-Ionic liquid system. 2nd International conference on application of radioisoptopes in chemical, environmental and biological science, ARCEBS 2010, Saha Institute of Nuclear physics, Bidhan Nagar, Kolkata, India, November 7 – 13, **2010**.

3. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Unusual miscibility of ionic liquid in paraffinic diluents. International Conference on Vistas in Chemistry (ICVC 2011), Oct 11 – oct 13, **2011**, IGCAR, India.

National

1. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Extraction and stripping of Neodymium (III) and Dysprosium (III) by TRUEX solvent. Nuclear and Radiochemistry Symposium, NUCAR 2009, SVKM Mithibai College, Vile Parle, Mumbai, India, January 7-10, **2009** (not included in chapters).

2. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Comparison in the extraction behavior of Am(III) from nitric acid medium by TRUEX extractants in molecular and ionic liquid diluent. Emerging Trends in Separation Science and Technology, SESTEC 2010, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, March 1-4, **2010 (Best Paper award).**

3. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Separation of Plutonium(IV) from Uranium(VI) by Phosphonate based Task specific Ionic Liquid. Emerging Trends in Separation Science and Technology, SESTEC 2010, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, March 1-4, **2010**.

4. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Extraction behavior of Pu(IV) by 1,3-diketonate based ionic liquid. Nuclear and Radiochemistry Symposium, NUCAR 2011, GITAM University, Visakhpatanam, India, February 22 – 26, **2011**.

5. **Alok Rout**, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Ionic liquid extractant in molecular diluents. Chemistry Research Scholars Meet, CRSM 2011, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, July 14-15, **2011**.

II. Awards / Recognitions of thesis work

1. **Best paper award** - Alok Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao. Comparison in the extraction behavior of Am(III) from nitric acid medium by TRUEX extractants in molecular and ionic liquid diluent. Emerging Trends in Separation Science and Technology, SESTEC 2010, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, March 1-4, **2010**.

2. **Among top 4 article and most downloaded article in Radiochimica Acta from Feb-2011 to Oct- 2011**. Unusual extraction of Plutonium(IV) from Uranium(VI) and Americium(III) using phosphonate based ionic liquid. Radiochimica Acta, 98(8)(2010) 459-466 by Alok Rout, K. A. Venkatesan, T. G. Srinivasan, P. R. Vasudeva Rao

3. **Most read article in Solvent Extraction and Ion Exchange from July 2011 - today**. Ionic Liquid Extractants in Molecular Diluents: Extraction Behavior of Plutonium (IV) in 1,3-Diketonate Ionic Liquids. Solvent Extraction and Ion exchange 27(4)(2011)602-618 by Alok Rout, K. A. Venkatesan, T. G. Srinivasan & P. R. Vasudeva Rao

4. **Given a keynote lecture and chaired a session** in the “1st International conference on Ionic Liquids in Separation and Purification Technology (ILSEPT)” held at Sitges, Spain on 4th Sep – 7th Sep 2011.