Synthesis of Task Specific Ionic Liquids for Extraction of Lanthanides/Actinides from Nuclear Waste

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To my mother for her unconditional love, inspiration, and support.

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Words are bound and knowledge is limited to praise Almighty ALLAH. The beneficent, and the merciful who created the universe and ability to think into His secrets. Peace and blessings of ALLAH upon Holy prophet Muhammad (peace be upon him) the everlasting source of guidance and knowledge for humanity.

I would like to thank my mother, for her limitless support, love, and encouragement. Without her being there for me when things got tough, this never could have been possible. She has been there for me since the beginning, and I know she always will be.

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ABSTRACT

Two DGA based extractants were synthesized and functionalized with imidazolium and ammonium cations. These DGA functionalized ionic liquid were named as L_I and L_{II}. The prepared functionalized ionic liquid were characterized using different spectroscopic techniques FTIR and NMR. The NMR spectroscopic analysis confirm the synthesis of diglycolamate based extractants. The extraction efficiencies of both the extractants were evaluated for the extraction of Eu(III), Sm(III) and UO_2^{2+} from the acidic aqueous phase. The experiments were carried out to optimize the equilibrium time, initial pH of the aqueous phase and the ligand concentration in the organic phase, to determine extraction stoichiometry. The metal to ligand ratio was found to be 1:3 for Eu(III), Sm(III) and 1:2 for the UO_2^{2+}. The extraction study at various nitrate ion concentration, suggest the involvement of NO_3^- in the complex formation. Both the ligands were found better extractants for trivalent Eu^{3+}, Sm^{3+} in comparison with the hexavalent uranyl ion.

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Abbreviations

HLW	High Level Waste
SNF	Spent Nuclear Fuel
PUREX	Plutonium URanium Reduction Extraction
DIAMEX	DIAMide Extraction
SANEX	Selective ActiNide Extraction
DGA	DiGlycolAmide
Ln(III)	Lanthanide
An(III)	Actinide
TBP	Tri-*n*-Butyl Phosphate
TRPO	TRialkylPhosphine Oxides
CMPO	octyl(phenyl)-*N,N* -diisobutylCarbamoyMethyl Phosphine Oxide
DMDBTTDMA	*N,N’*-DiMethyl-*N,N’*- DiButylTetraDecylMalonAmide
DMDOHEMA	*N,N’*-DiMethyl-*N,N’*- DiOctyl-2-(2-HexylOxyEthyl)MalonAmide
TODGA	*N,N,N’,N’*-TetraOctyl DiGlycolAmide
TREN	TRis(2-aminoEthyl)amine
EDC	1-Ethyl-3-(3-Dimethylaminopropyl) Carbodiimide hydrochloride
DCC	DiCyclohexylCarbodiimide
HOBt	1-HydrOxyBenzotriazole
FTIR	Fourier Transform Infrared spectroscopy
NMR	Nuclear Magnetic Resonance
HRMS	High Resolution Mass Spectrometry

Chapter 1

1. INTRODUCTION

1.1. Nuclear energy

With a steadily growing human population in the world, the demand for energy is constantly increasing. The nuclear power is inescapable to fulfil the increasing energy demand around the world, especially in the south Asian region.[1] It has indeed attracted the world due to several important aspects includes; the increase in fossil fuel prices and environmental problems related to fossil fuel consumption and resulting emission of greenhouse gases.[2]

Nuclear energy is one of the most economical and environment friendly energy source. In comparison with other energy sources the lowest greenhouse gases emission is recorded for nuclear power.[3] Fission and fusion reactions can be used for power generation from nuclear resources, but mostly fission reaction is used by power generators. In fission reaction enormous amount of energy is produced by splitting the heavy nucleus into fragments of smaller nuclei by capturing the neutron. The heat energy provided by the reaction is used to produce steam from the water which is used to run turbines for electrical power generation.[4][5]

Currently around 19% of the world energy requirements are fulfilled by the use of nuclear energy. About 375,000 MWe of energy is produced by nuclear energy in 31 countries having more than 450 commercial power generator units in operation.[6][1]

The access to clean air as well as electricity is vital for every human being, as every year more than 7 million people die due to air pollution and about 1.2 billion people cannot afford electricity for their house hold. Current practice to control emission of carbon dioxide are not enough, much more efforts are required to meet the Paris Agreement objective of keeping the average global temperature change to well below 2°C, therefore action plan must be followed with great intensions. [7]

By 2050 the demand of electricity will be double as of today due to increase of industrialization by many countries to improve life quality of common man. To cope with environmental challenges there is need for production of 80% electricity from low carbon sources and currently we are at 34%.Currently 31 countries use nuclear energy which is about 13% of the total energy consumed.[1][7] To balance the climate change there is need for producing at least 25% nuclear energy with the introduction of low carbon energy sources.[8]

1.2. Radioactive waste

Spent nuclear fuel (SNF) is the byproduct of nuclear power production which is highly radioactive and can be considered as high level radioactive waste (HLW). Use of nuclear energy in the fields of medicine, research and industry produce radioactive waste, this type of waste is considered as low level waste. The high level radioactive waste must be handled with cooling and shielding. Nuclear energy waste also contains enormous amount of long lived isotopes (if not reprocessed) which need proper dispose of. [2]

1.3. High level waste

During the spent nuclear fuel reprocessing steps, a significant amount of radioactive waste is generated, which is major concern for environment and need to be processed. It contains unextracted Uranium, Plutonium, and lanthanides, some actinides such as Am , Cm and Np, fission and corrosion product elements such as Pd, Tc, I, Zr, Sr and Cs, transition metal elements including Ni, Zr and Co, and salts of Na, Fe, and Al.[9]

The decay heat of the HLW is large enough to increase the temperature of the surroundings elevated degrees, therefore its shielding and cooling is essential. HLW is generated when the spent nuclear fuel is partitioned through PUREX process. The uranium and plutonium is separated from the spent fuel and available for reuse as nuclear fuel.[10]

Short and long-live both components are present in HLW, their management and disposal depends upon the separation of short lived fission products from that of long-lived actinides.[7] Their disposal is managed on the basis of time they required for radioactivity to decrease to level which is considered as non-hazardous for life.[11]

1.4. Volume of produced waste

The civil nuclear industry produces small amount of HLW as compared to nuclear power plants for electricity generation. According to IAEA calculations about 370,000 tons of heavy metals is produced to date since the operation of first nuclear plant. 120,000 tons of the heavy metals produced have been reprocessed. According to the estimates which are given by IAEA, approx. 22,000m^3 current disposal volume is produced in the form of solid high level waste.[2][5]

This information is provided by all the states account for almost 95% nuclear energy generators of the world. The data given above about spent fuel and reprocessed spent fuel is according to provided data, there is approximately 35million m^3 of solid radioactive waste from which 82% (28.5 million m^3) has been permanently disposed of and remaining 18% (6.3 million m3) is in storage for final disposal. 98% above solid waste is termed as very low in terms of volume, and mostly the remainder waste level is intermediate. While talking about radioactivity, the situation is completely opposite because more than 98% of radioactivity is associated with intermediate and high level waste. [4]

1.5. Safety standards

Radioactive waste must be managed safely for protection of environment and human health. With the experience of years gained by working with radioactive waste, IAEA has adopted certain safety standards. Standards include some general principles and some are directly related to radioactive waste management. [12] The safety standards of IAEA are developed by international consensus for the protection of environment and people from the harmful effects of ionizing radiation. [2] Fukushima accident highlights the importance of nuclear waste management for development and safety of nuclear power.[9]

1.6. Reprocessing waste

One of the important process of nuclear power is nuclear fuel cycle (NFC). The reprocessing of the spent fuel is done by its solution extracted with the TBP. For recycling of spent fuel, Plutonium and uranium are collected separately for reuse. The remaining HLW solution contains the active waste products. Long lived radioactive actinides remains in the solution after the PUREX, thus need to be separated or managed to reduce the radioactivity and disposed of properly and for the protection of environment from their lethal effects.[13] [9]

1.7. Classification of reprocessing methods

Lanthanides and actinides present is the radioactive waste belong to f-block elements, hence possess the same chemical and physical properties. The actinides must be separated from lanthanides by effective methods due to their importance in nuclear fuel cycle. As the REEs reflects the same chemical properties, so their separation is quite difficult [14]. Several techniques are used for this separation based on different principles.[9] These processes are classified as follows:

1. **Dry processes**
    a) Ion exchange
    b) Precipitation
    c) Solvent extraction.
2. **Wet processes**
    a) Pyrochemical / Pyrometallurgical
    b) Halide volatilization

Ion exchange, evaporation, and precipitation are the conventional ways to deal with radioactive waste and these methods have many draw backs. These draw backs include: high energy consumption and formation of secondary wastes, like the slop from sediment chambers, ion exchange adsorbents and regeneration solutions. [5]These processes have many limitations as well which include, production of secondary waste in solvent extraction, loss of solvents, foaming and drop entrainment in evaporators, or bed clogging in ion exchange columns.[9][15]

The process of reprocessing includes the separation of uranium and plutonium by dissolving spent fuel. High-level and heat generating waste includes the bulk amount of fission products in the spent fuel.[9]

1.8. Solvent extraction

Solvent extraction by using the different organic extractants, is found a most reliable and efficient separation method for this hard task. The most remarkable advances in industrial solvent extraction that occurred in the last fifty years have been undoubtedly driven by requirements imposed by nuclear science and technology, as nuclear applications always involve costly materials with a high degree of purity.[16] The reprocessing of spent nuclear fuels usually requires approximate quantitative recovery and separation of fissile uranium and plutonium from dozens of products of fission involving several chemical elements. For separating f-block elements and nuclear fuel cycle industries, perhaps the most effective technology is solvent extraction. Solvent extraction is advantageous because of its simple operation, good separating effect high treatment capacity, and quick reaction rate.[9]

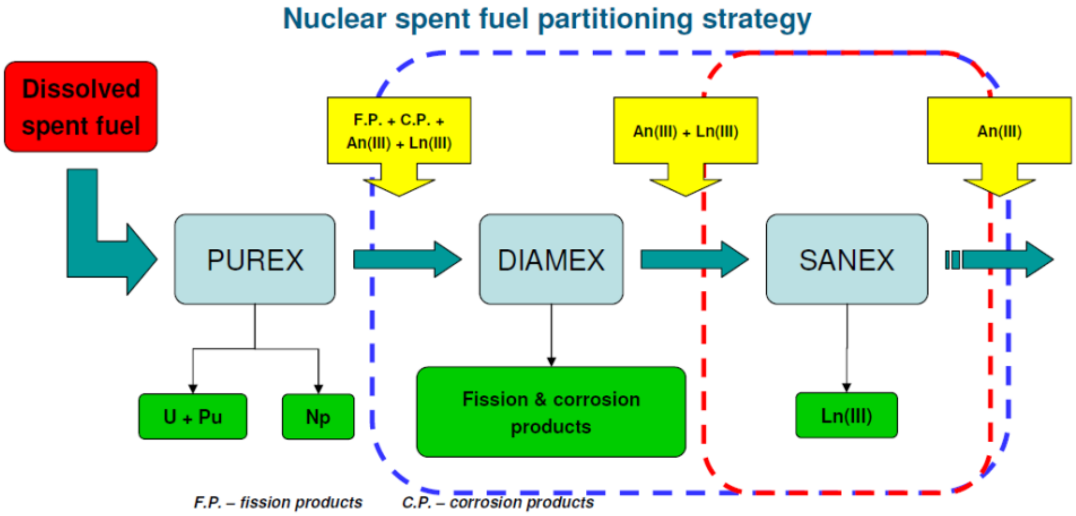


Figure 1. 1. Partitioning process of actinides.[9]

Liquid-liquid solvent extraction method is used for separation and recovery of uranium and plutonium in a closed nuclear fuel cycle. PUREX process employed to separate plutonium and uranium from SNF. Aqueous phase formed in liquid-liquid solvent extraction by dissolving SNF in nitric acid, organic phase is consist of tributylphosphate and a hydrocarbon solvent (often kerosene). After the separation of uranium and plutonium, minor actinides americium and curium remain unextracted in aqueous phase and different ways are used to separate them from lanthanides.

Chapter 2

2. Literature Survey

Nuclear waste processing is mostly done by solvent extraction method. Lot of research has been done in past few years and different classes of ligands are produced for collective extraction of lanthanides and actinide and their mutual separation within the group. This chapter includes an overview about the designed ligands current ongoing research on ligand development for the separation of lanthanides and actinides for aqueous phase.

Organic Extractants for Nuclear Waste Processing.

2.1. Ligands for solvent extraction of actinides/ lanthanides.

According to the HSAB theory, both series of lanthanides and actinides are considered as hard acids. However, the 5f orbitals of actinides elements are found to be more expended in the space that creates difference between the reactivity of actinides and lanthanides. The actinides can be separated from lanthanides, by the introduction of soft donor atom(N and S) into the organic extractants. The An(III) and Ln(III) reacts differently towards complex formation between metal and ligands, due to the varied binding ratios and structure of the extractant.

2.2. CO-Extraction of lanthanides/actinides.

Organic extractants having oxygen donor atom do not any discrimination in reactivity towards the An(III) and Ln(III) for complexation. They can be termed as classes as organophosphorus ligands, malonamides, and glycolamides. They are usually used for extraction actinides and lanthanides, fission and corrosion products remains unextracted.

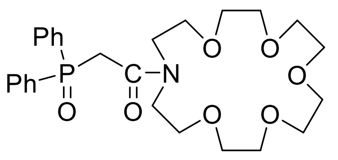
2.3. Actinide/lanthanide separation

SANEX process by means of N, S donor ligands is utilized for the separation of actinides. One of the most challenging issues is the separation of An(III) from the Ln(III), However, soft donor atoms(N, S) containing ligand possess the efficacy to extract them separately.[9]

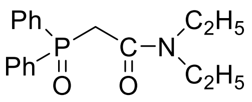
2.3.1. Conventional ligands

Panja *et al*. reported extraction of tera valent Pu^{4+} from nitric acid medium into two diluents: n-dodecane and a RTIL, 1-butyl-3-methylimidazolium bis(trifluoromethane-sulphonyl)imide (C_4mimTf_2N). The study was performed by using TBP as extractant. The D value using RTIL was >20 while it was around 16 when n-DD was used. The analysis revealed that kinetics for RTIL equilibrium was slow as compared to n-DD. Also the mechanism in case of lower acidity was cationic exchange whereas at higher acidity (1M and above) it switched to neutral complex formation. Stripping of Pu (IV) was done by mixture of EDTA and guanidine carbonate.[17]

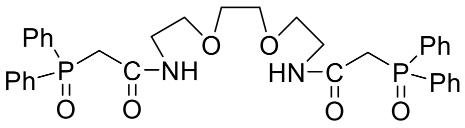
Turanov *et al*. studied extraction of rare earth metals into an organic phase from nitric acid medium using $[C_4mim][Tf_2N^-]$, and *N,N*'-bis(diphenylphosphinylmethylcarbonyl)-diaza-18-crown-6 as extractant, its efficiency was compared to *N*-(diphenyl-phosphinylmethylcarbonyl)aza-18-crown-6 and diphenyl *N,N*-diethylcarbamoylmethyl-phosphine oxide. The conc.of IL in organic layer, amount of extractant and HNO_3 in aqueous phase was considered during the experimentation. The D_{Ln} with the IL was calculated to be upto 1000 as compared to D_{Ln} in some conventional organic solvents which were upto 0.01, 0.17 and 10 for chloroform, 1,2-dichloroethane and nitrobenzene respectively. A synergistic effect due to a neutral organophosphorus ligand in the organic phase containing IL was reported. The hydrophobic nature of the ionic liquid's anion was connected to this synergistic behavior. This study demonstrates the potential applications of ionic liquid impregnated polymeric resins in for lanthanide's extraction from aqueous acidic phase.[18]



N-(diphenylphosphinylmethylcarbonyl)aza-18-crown-6



N,N-diethylcarbamoylmethyl-phosphine oxide



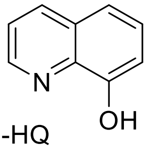
N,N-bis(diphenylphosphinylmethylcarbonyl)diaza-18-crown-6

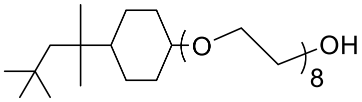
G. Pribylova investigated the extraction of Pu(IV), Am(III), and U(VI) on the addition of extra amount of ionic liquid. The D_{Am} value increased 126 fold by adding 50% of [C_4mim][PF_6] to 0.1 mol/L diphenyl(dibutyl)carbamoylmethyl phosphine oxide (Ph_2iBu_2-CMPO) in dichloroethane and 1040 fold by adding 50% of [PH_4][PF_6] (phosphoniumhexafluorophosphate). The D_{U} and D_{Pu} values were found to be increased by 272 and 135 times, respectively, when 50% of [C_4mim][PF_6] to 0.001 mol/L Ph_2iBu_2-CMPO was used in dichloroethane. [19]

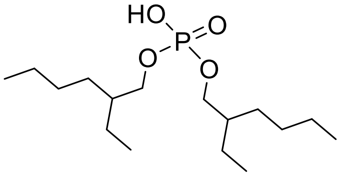
Turanov et. al. carried out the extraction study for the evaluation of tetraphenylmethylenediphosphine dioxide, dibutyl(diethylcarbamoylmethyl)phosphine oxide and diphenyl(diethylcarbamoylmethyl)phosphine oxide for Y nitrates and various lanthanides, and found a considerably increased efficiency by using [C_4mim][PF_6] as ionic liquid as compared to that of *n*-dodecane. A copolymer, based on macroporous styrene- divinylbenzene, impregnated with a mixture of tetraphenylmethylenediphosphine oxide and [C_4mim][PF_6] was effective for the extraction of Th(IV), U(VI) and REEs elements from HNO_3 acidic aqueos phase.[20]

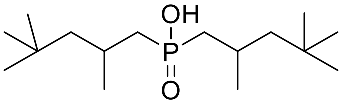
Pribylova and coworkers studied the extraction for the REEs by adding 1–5 wt% of RTILs [C_4mim][Tf_2N], [C_4mim][PF_6], and trihexyl(tetradecyl)phosphonium to a diphenyl(dibutyl)carbamoylmethylphosphine oxide (Ph_2Bu_2) solution. It was recorded that this system increased the extraction coefficient of Am from acidic phase. The distribution coefficients of Am were recorded as high as 748, 793, and 38.8 for above RTILs respectively. The use of [C_4mim][Tf_2N] made the extraction possible at as high conc. of nitric acid as 8 M. This renders this extraction system very important as most of the solid samples in radiochemical analysis of environmental and technological solutions are transferred to an 8 M HNO_3 solution.[21]

Gao and coworkers investigated the addition of ionic liquids in Triton X-114 solution using several anions *viz.* BF_4^-, PF_6^-, Br^- and NTf_2^- for cloud point extraction (CPE) of UO_2^{2+} and other lanthanides.[22] The acidic extractants used were 8-hydroxyquinoline (8-HQ), bis(2-ethylhexyl)phosphoric acid (HDEHP), a neutral ligand was tri-octylphosphine oxide (TOPO). The addition of ionic liquid in TOPO showed significant increase in the extraction of target metal at highly acidity as well as neutral conditions. However, cloud point extraction with acidic extractions was not improved by the addition of ILs. The extraction efficiency calculated was up to 90% when $C_4mimNTf_2^-$ was used. This study also revealed that the combination of TOPO and IL increased the separation of uranyl ions from other lanthanides ions, the reason for this was explained as that the TOPO micelle and NTf_2^- forms a soft template for UO_2^{2+} ion thus providing a supramolecular assembly to separate UO_2^{2+} selectively and effectively.[23]


8-HQ


Triton X-114


HDEHP

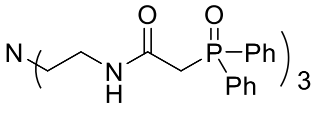

CYANEX-272

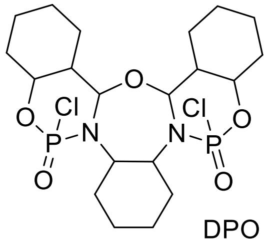
Mohapatra et al. studied the uranyl ions extraction from acidic aqueous phase by using tri-n-octyl phosphine oxide (TOPO) in ionic liquids such as [C_4mim][PF_6], [C_6mim][PF_6], [C_8mim][PF_6], [C_4mim][NTf_2], [C_6mim][NTf_2], [C_8mim][NTf_2]. The conclusion says that the extractions carried out with ionic liquids carrying C_8mim^+ as counter cation showed higher distribution ratio for the extraction whereas the ionic liquids carrying PF_6^- as counter anion reflects the quicker as well as high efficiency for extraction. The distribution ratios obtained by using [C_n mim][PF_6] and[C_n mim][NTf_2] were as high as 12.1 and 18.2 respectively at 0.01M acidity and dropped to 0.01 as the acidity increased to 2M. The observations from the extraction studies proposed a solvation mechanism for extraction. The mixture of TOPO with solutions of D2EHPA was also utilized for uranyl extraction of U(IV) in acidic media (both HNO_3 and H_3PO_4) in ionic liquids but there were no appreciable extraction.[24]

Lohithakshan *et al.* studied the extraction ability of Pu(IV) and Am(III) from nitric acid aqueous phase to RTIL by the use of an acidic extractant HDEHP. RTILs used were 1,2-dimethyl-3-propylimmidazolium bis(trifluoromethyl sulphonyl)imide (DMPIIM), N-butyl-3-methyl pyridinium bis(trifluoromethyl sulphonyl) imide (BMPIM), and 1-hexyl-3-methylimidazolium bis (trifluoromethyl sulphonyl)imide (HMIIM). The distribution ratios for Pu in different RTILs were ranging between 20.5-69 for HDEHP/BMPIM and 0.65-16.2 for HDEHP/DMPIIM at 25 ^oC. At 21 ^oC, D values of 7.2-25.2 for HDEHP/HMIIM and 1.47-19.12 for HDEHP/DMPIIM. The distribution ratios for Pu(IV) were substantial but Am (III) showed poor extraction at higher acidity of aqueous medium (1M HNO_3) whereas using pH=3, the extraction of Am(III) was enhanced. Thermodynamic parameters were also calculated by carrying out the extractions at various temperatures.[25]

Elena V. Sharova investigated a ligand system for metal extraction by complexation from acidic and neutral mediums; this ligand system consists of a central nitrogen atom surrounded by tripodal platform to which three CMPO moieties are attached. This extractant showed significant increase in distribution ratio of rare earth metals as compared to similar tripodands with one or two CMPO moieties. The system worked even better with the IL [C_4mim][Tf_2N] in 3M nitric acid medium. The effective extraction of anionic complexes occurred due to nitrogen atom protonate in acidic media.[26]

The extraction of Eu(III) and Th(IV) using bis(chlorophosphoryle)decahydro-2,4-di(2-hydroxyphenyl)benzo[d][1,3,6]oxadiazepine was also carried out from nitric acid medium into an IL medium,1 -hexyl-3-methylimidazolium hexafluorophosphate. It was observed that Eu(III) was extracted through solvation mechanism while Th(IV) followed the pathway of ion exchange. The results revealed that the D value of Eu(III) was lower and appreciable extraction was not occurred as compared to Th(IV) proposing this solvent system as a selective extraction media for Th extraction. [27]

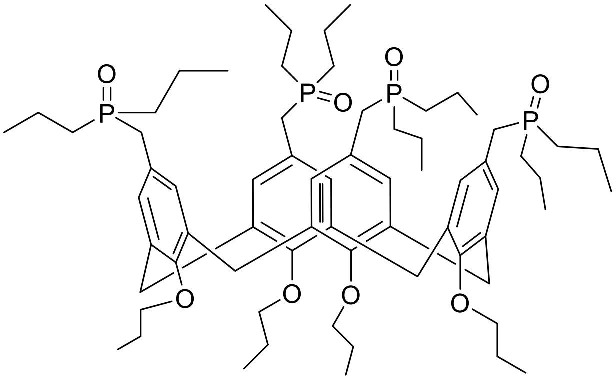

tris-CMPO Ligand


DPO

Turanov et. al. investigated the extraction for all the elements of Ln series from aqueous solutions of HCl, and distribution between solutions of various carbamoyl methyl phosphine oxides

(CMPOs) in of the [C_4mim][Tf_2N] ionic liquid. The selectivity and efficiency of REEs (III) extraction by CMPO solutions increase considerably as the ionic liquid is present in organic layer. The extraction stoichiometry in complexes was calculated; the effects of the IL cation, organic solvent, CMPO structure, and aqueous HCl concentration on the efficiency of REEs(III) recovery was investigated.[28]

Gorbacheva *et al*. studied the impact of ILs on the extraction of Eu and Am using an upper rim phosphorylated calixarene. It was shown that this calixarene can extract the metals without the ionic liquid from nitric acid medium to organic phase by forming 1:1 complex with metals. The distribution coefficients were good but the isolation of the extracted metals was insufficient thus rendering this method not fit for extraction. The results showed the extraction efficiency of Am(III)/ Eu(III) increased by the factor of 2 times and 25 times respectively when 50% ionic liquid was added.[29]



2.3.2. Malonamide based ligands

The extraction of Am(III), U(IV) and Pu(IV) in ionic liquid 1–butyl–3–methylimidazolium bis(trifluoromethanesulfonyl)imide (C_4mimNTf_2) by a solution of N,Ndimethyl- N,N-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA) using nitric acid as medium was studied. The distribution of the actinides in this system was recorded as a function of parameters such as alkyl chain length of IL, and concentration of IL, nitirc acid and solution used. The results showed that extraction was significantly better with the use of DMDOHEMA in conjunction with C_4mimNTf_2.Although the mechanism for extraction of metal ions varied when the nitric acid concentration was increased. Below 4 M nitric acid, the mechanism followed was cation exchange whereas it was anion exchange above 4 M nitric acid. Also the separation of these metals was done and the separation factor was >1000 for these metals from many other fission products.[30]

The extraction of tetra valent Th was done using N,N-dialkyl aliphatic amides containing different substitution of alkyl *viz.* di-butyl-3,3-dimethylbutanamide (DBDMBA), N,N-di-sec-butyl pentanamide (DBPA), N,N-dihexyl octanamide (DHOA), N,N-dibutyl-2-ethyl hexanamide (DBEHA) and N,N-dibutyl octanamide (DBOA). The solvent extraction was done from nitric acid medium into an ionic liquid, 1-butyl-3-methyl imidazolium hexafluorophosphate [bmim][PF_6]. D_{Th} were found significantly lower with the use n-hexane as compared to those of ionic liquid. The D values ranging from 0.08 to 13.5 when the conc. of nitric acid was varied from 0.2 M - 4M. The highest ratio was obtained by DBOA when the acidity was low, and the lowest ratio at low acidity was given by DBEHA. The extraction behavior of RTIL was also different than n-hexane in terms of kinetics, complex formation and acidity of the medium. Stripping of the extracted specie was done by supercritical carbon dioxide.[31]

N,N-dihexyloctanamide (DHOA) belong to the class of monoamide, extraction studies were performed in same ionic liquid, trioctylmethylammonium nitrate ([N1888][NO_3]) was used for the extraction of Pu(IV) . The extraction efficiency of this DHOA/[N1888][NTf_2] system was compared with DHOA in a conventional organic diluent i.e. n-DD and an IL such as [$C_n$mim][NTf_2]. DHOA in [N1888][NTf_2] showed excellent extractability for Pu(IV) as compared to n-dodecane or [Cnmim][NTf_2]. The D value for Pu(IV) in 0.5 M DHOA/ [N1888][NTf_2] was <1 at lower acidity but it increase to >80 as the acidity increases to 8 M HNO_3. DHOA was also compared with TBP however, the D_{Pu} was reduced by using TBP.[32]

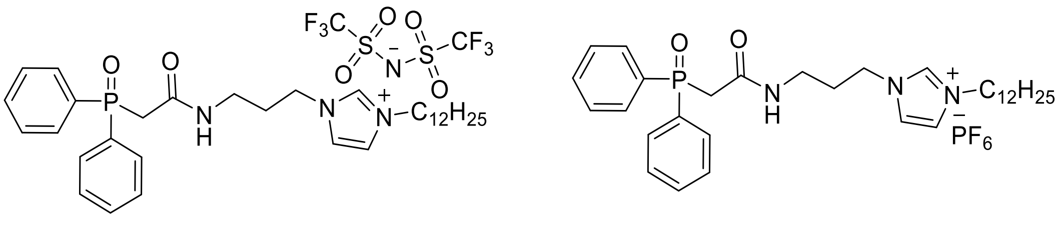
2.4. Task-specific ionic liquids

Recently, development of taskspecific ionic liquids based extractants, due to their chemical and physical properties have received much consideration. They are consist for the main functional extracting moiety as their anionic and/or cationic part and serve as the extracting agent as well as an organic phase.

The extractant molecule dehydrates the metal ion to provide it with hydrophobic environment which enables it to move to organic phase. The extractant can be made by substitution of alkyl chains as integral part of ionic liquid or organic phase in order to increase the hydrophobicity. This decreases the chances of back movement towards aqueous phase by attaching metal-complexing functionalities to imidazolium ion. This enables the examination of the application for the extraction metal ions by using the ionic liquid concept .[33] [34]

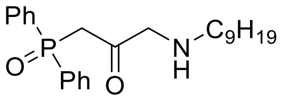
2.4.1. CMPO based functionalized ionic liquids.

Mohapatra and his team synthesized functionalized ionic liquid L_I and L_{II} with PF_6^- anion and NTf_2^- counter anions based on carbamoylmethylphosphine oxide (CMPO) and their solutions of room temperature ionic liquids i.e. as $C_n$minPF$_6$ and $C_n$mimNTf$_2$ were used for the extraction of actinide / lanthanide using 3M HNO_3 aqueous phase. The results were compared with extraction data obtained with carbamoylmethylphosphine oxide in the same set of room temperature ionic liquids and n-dodecane. The D_{Am} found with 0.03 M L_I and 0.1 M L_{II} in C_8mimPF$_6$ and C_8mimNTf$_2$ were 0.16 and 16 respectively. The extraction kinetics for the CMPO-TSIL L_{II} decreased with the increased alkyl chain, and follows order such as C_4minNTf$_2^-$ > C_6minNTf$_2^-$ > C_8minNTf$_2^-$ which showed that the metal ion extraction is based on cation exchange extraction mechanism. Both CMPO task specific ionic liquid L_I and L_{II} reflects lower distribution ratio of Am^{3+} and Eu^{3+}, while CMPO-TSIL L-II showed significantly larger extent of UO_2^{2+} as compared to that obtained with CMPO in same set room temperature ionic liquids. Higher extraction was observed using TSIL-CMPO L_{II} in C_4mimNTf$_2$ for partitioning of Pu^{4+} than CMPO in C_4mimNTf$_2$, while in other two ionic liquids it showed opposite trend. Various spectroscopic UV-visible and FTIR spectroscopy indicated the complexes with inner sphere for Uranium and Neodymium and coordination through carbonyl oxygen atom.[35]

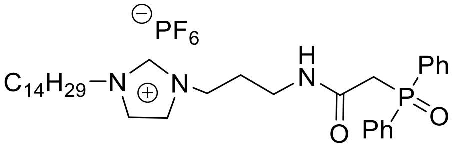


CMPO-TSIL

Turanov *et al*. investigated extraction of uranium, thorium and other lanthanides from nitric acid medium into organic molecular diluents with the help of CMPO functionalized ionic liquid (FIL), 1-[3[[(diphenylphosphinyl)acetyl]amino] propyl]-3-tetradecyl-1H-imidazol-3-ium hexafluorophosphate. This CMPO-FIL depicted better extractability for lanthanides than its non-functionalized equivalent, diphenylphosphorylacetic acid N-nonylamide. This difference can be attributed to the FIL's partition in between the organic and aqueous phases. The distribution ratio for lanthanides when simple CMPO was used, was 0.3, it rose to around 3 when it was functionalized to give CMPO-FIL and further rose to nearly 8-10 when ionic liquids such as $[C_4mim][PF_6]$ or $[C_4mim][Tf_2N]$ were added.[34]

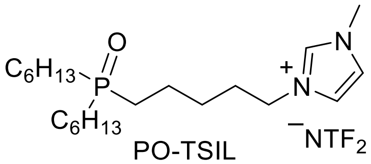


CMPO-Analogue



CMPO-FIL

M paraminik et al. studied trialkylphosphine oxide functionalized task specific ionic liquid (PO-TSIL) with a NTf_2^- counter anion was estimated for the extraction efficiency for actinide ions UO_2^{2+} and Pu^{4+} from nitric acid feed solutions using RTILs viz $[C_nmim][NTf_2^-]$ (where, n = 4, 8) as the diluents.[36] The extraction results were equated with its analog extractant tri-*n*-octylphosphine oxide (TOPO) keeping all other extraction conditions constant. The mechanism of extraction determined by slope analysis, was found to be cation exchange mechanism.[37]

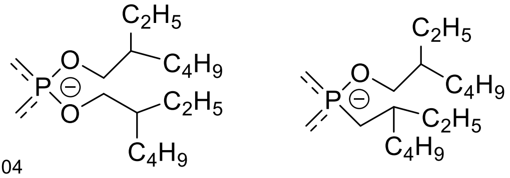


PO-TSIL

Mohapatra and coworkers reported of carbamoylmethylphosphine oxide (CMPO) based functionalized ionic liquid having PF_6^- and NTf_2^- anions in room temperature ionic liquids (RTILs) such as C_nminPF_6 and $C_nmimNTf_2$ for the partitioning of lanthanides and actinide from 3M HNO_3 solutions. The extraction kinetics for the CMPO-TSIL decreased with the increase in the length of alkyl substituent, and following order was found; $C_4minNTf_2^- > C_6minNTf_2^- >$

$C_8minNTf_2^-$ which suggested that the metal ion extraction is based on cation exchange extraction mechanism. Both CMPO task specific ionic liquid showed lower extraction for Am(III) and Eu(III), while CMPO-TSIL with NTF_2^- showed significantly larger extent of UO_2^{2+} and Pu^{4+} than CMPO in $C_4mimNTf_2$.[35]

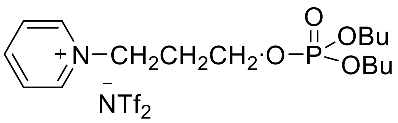
In another study extraction of rareearth metals from nitricacid medium by using bi-functional ionic liquid extractants (Bif-ILEs) such astrialkylmethylammonium][di-2-ethylhexylphosphate] [A336][P204] and [trialkylmethylammonium][di(2-ethylhexyl)orthophosphinate] ([A336]-[P507]) using n-heptane was studied. The extraction efficiency was quite significant and was found to be 100% for La and above 80% for Eu. The studies depicted that these bi-functional ionic liquids are suitable to extract heavy metals in nitrate ions medium and light metals in chloride ions medium. The separating factor values in chloride media, using[A336][P507] as extractant were Sm/Nd (4.70), and Nd/Pr (9.52). Whereas in nitrate medium, by using extractant [A336][P204] the SF values were Yb/Tm (7.92), Tm/Er (3.36), and Lu/Yb (8.55).[38]



P_{204} P_{507}

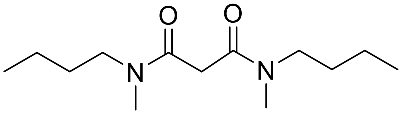
Bif-ILEs

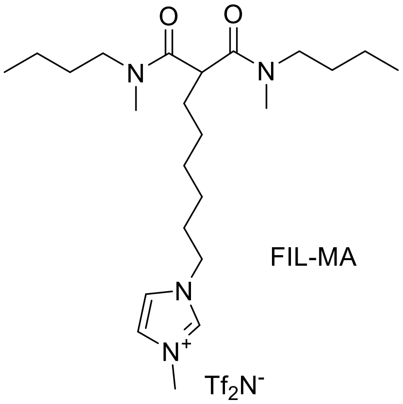
Hongyu Li et. al designed a pyridine-based task-specific ionic liquid [Phos-C_3-Pyr] [NTf_2] with tributyl phosphates (TBP) functional group for the extraction of uranyl ion from acid feed solutions. The synthesis was carried out by reacting 1-dibutylphosphoryl-3-bromopropane with pyridine, reaction mixture was stirred at room temperature for 3-4 days. The spectroscopic studies such as FTIR, NMR and elemental analysis were carried out to confirm the structure. The compound was thermally stable up to 200 ˚C. They reported excellent extraction of U(VI) from nitric acid medium at room temperature, where pyridine-based task specific ionic liquid was used as extractant as well as a diluent.[39]



2.4.2. Malonamides-based task specific ionic liquid.

Marieke et al carried out the extraction experiments to study the comparison between the functionalized malonamide based extractants having imidazolium cation and Tf_2N^- as anion, and its classical analog malonamide, N, N′-dimethyl-N,N′-dibutylmalonamide (DMDBMA). The study showed 12 times higher extraction by using the functionalized extractant having imidazolium cation and Tf_2N^- as anion, for the $UO_2^{2+}$from aqueous phase. The conventional malonamide ligand N,N′-dimethyl-N,N′-dibutylmalonamide (DMDBMA) was found less efficient and lower distribution ratio was observed.[40]


DMDBMA

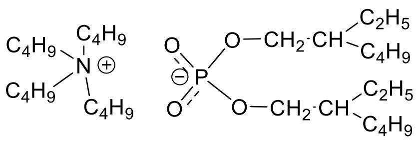


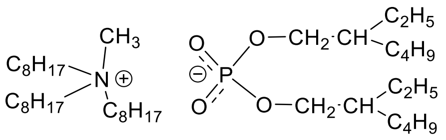
FIL-MA

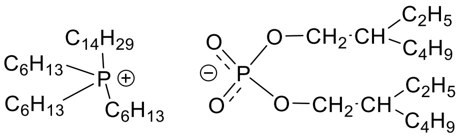
2.4.3. Phosphonium and Ammonium based functionalized ionic liquids.

Xiaoqi et. al. evaluated the extractions of rare earth metals by using ionic liquids as both the extractants as well as diluents. They synthesized phosphonium and ammonium based functionalized ionic liquids, tetrabutylammonium di(2-ethylhexyl)phosphate, trioctylmethylammonium di(2-ethylhexyl)phosphate and trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate. These DEHP functionalized ionic liquids were used as extractants in 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6mim][NTf_2]$) and diisopropylbenzene to study the extraction behavior of rare earth elements series.[41] The extraction results of DEHP-based ionic extractants were also compared with their analogous acid i.e. di(2-ethylhexyl)phosphoric acid (HDEHP) in same set of ionic liquid and molecular diluent. Due to better solubilities in $[C_6mim][NTf_2]$, the distribution coefficients of all the extractants were

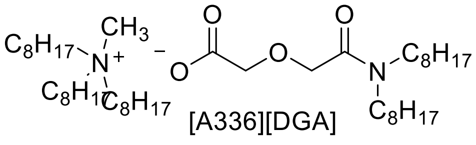
6 times higher than those in diisopropylbenzene. The D_{IL}/D_{DIPB} values for Lu^{3+} from [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] were 3.95×10^{2}, 6.04×106, and 2.16×103 ,respectively. Thermal gravimetric analysis showed all functionalized ionic liquids were thermally stable up to ~250°C, [THTP][DEHP] was more stable than [TOMA][DEHP]) and ([TBA][DEHP]. The study report using the synthesized functionalized ionic liquids better extractabilities and selective separation of rare earth elements was achieved.[42]


[TBA][DEHP]

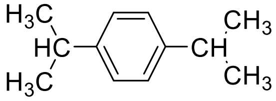

[TOMA] [DEHP]


[THTP] [DEHP]

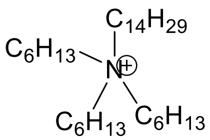
Rout *et al.* investigated extraction of lanthanides particularly Nd^{3+} from nitricacid aqueous phase by using functionalized ionic liquid trioctylmethylammonium dioctyl diglycolamate, [A336][DGA] in a non-fluorinated diluent i.e. trioctylmethylammonium nitrate, [A336][NO3]. The distribution ratios obtained by extraction were compared to the precursor of this functionalized ionic liquid in same diluent i.e. HDGA in [A336][NO$_3$]. The results showed that the derived FIL [A336][DGA] gave better extraction results ; D value at 5M acidity at around 28 as compared to around 8 when HDGA was used. This extraction was performed as function of many parameters such as concentration of acidic aqueous feed, concentration of salting-out agent, concentration of the extractant, pH and temperature. Thermodynamic parameters, stripping of Nd(III) and reusability of FIL was also studied.[43]


[A336][DGA]

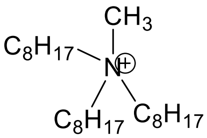
Sun *et al*. studied Three di(2-ethylhexyl)phosphate (DEPH) based functinalized ILs for the separation of rare earth metals. They prepared trioctylmethylammonium (TOMA) tetrabutylammonium (TBA) trihexyl(tetradecyl)ammonium (THTA) analogues of DEHP . The solvent system that was used in this process consisted of diisopropylbenzene (DIPB; Chart 37) along with di(2-ethylhexyl)phosphoric acid (HDEHP) and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6mim][NTf_2]$) . They concluded that DEHP-based ionic extractants are more soluble in [C6mim][NTf2] than in DIPB. Also the distribution ratio for REEs in ionic liquid was higher by the magnitude of 6 orders than in DIPB. The synthesized ionic extractants also showed better D_{IL}/D_{DIPB} ratio than HDEHP as the D_{IL}/D_{DIPB} for [TBA][DEHP], [TOMA][DEHP], and[THTP][DEHP] for Lu^{3+} are 3.95×10^2, 6.04×10^6, and 2.16×10^3, respectively whereas it is 1.3 for Lu^{3+} from HDEHP.[42]



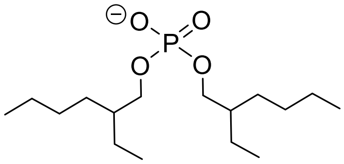
DIBP



THTA

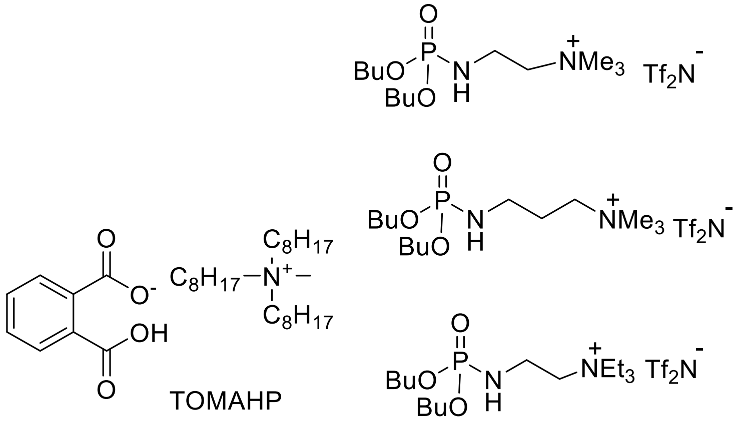


TOMA



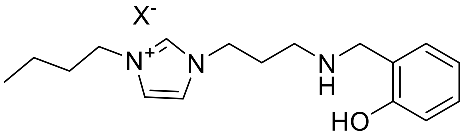
DHEP

Sujoy Biswas and Co reported a tetralkyl ammonium hydrogen phthalate based task specific ionic liquid (TSIL). Trioctylmethylammonium hydrogen phthalate (TOMAHP) was synthesized via metathesis route using Aliquat^R 336 (trimethylammonium chloride) and potassium hydrogen phosphate. TOMAHP was characterized using techniques such as ^{1}H NMR, ESI-MS infra-red etc. TSIL was evaluated for extraction of lanthanides, actinides and transition metal ions such as U(VI), Th(IV), La(III), Nd(III), Y(III), Fe(III) from HNO_3 acidic aqueous solutions at different pH. The carboxylic group present in TOMAHP act as functional group for the binding of metal ion. TOMAHP has shown better extraction of uranium than the other metal ions in the following: U(VI) >Th(IV) > Fe(III) > Y(III) >>Nd(III) > La(III). In case of U(VI), Th(IV) and Fe(III) the extraction was very efficient.[44]



TOMAHP

The extraction of Pu(IV), U(VI), and Am(III) by a solution of [diethyl-2-(3-methylimidazolium)ethylphosphonate][NTf$_2$] ([ImP][NTf$_2$]) in [Cnmim][NTf$_2$] (n = 4, 8) was studied as a function of the HNO$_3$ concentration. The distribution ratios of Am(III) and U(VI) were significantly lower both in [ImP][NTf$_2$]/[C$_n$mim][NTf$_2$] and [C$_n$mim][NTf$_2$] at all HNO$_3$ concentrations, but unusually high separation factors for Pu(IV) from other actinides were obtained.[45]

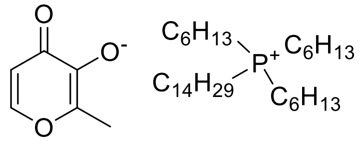


2-hydroxybenzylamine imidazolium

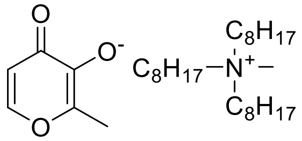
X= Tf_2N^-

PF_6^-

The extraction of various radionuclides viz. ^{238}U and ^{234}U, ^{234}Th, ^{226}Ra, ^{210}Pb and also its descendants ^{210}Bi and ^{210}Po was carried by platzer *et al*. Maltolate based room temperature task specific ionic liquids namely Tricaprylmethylammonium maltolate and tetradecyltrihexylphosphonium maltolate . The TSILs exhibited high extraction efficiency towards these radionuclides due to their high affinity for various metal ions. Both of these ionic liquids completely extracted the Uranium using various acidic feeds, and results showed that the pH of solution has no effect the extraction of U(IV).[46]

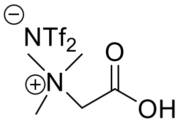


Tetradecyltrihexylphosphonium maltolate



trioctylmethylammonium maltolate

Mori *et al*. worked on solid wastes for its purification from uranium by using ionic liquid, betainium bis(trifluoromethylsulfonyl) imide [Hbet] [Tf_2N] for this purpose. The observations showed that uranium was extracted very efficiently i.e. D>1 at lower acidities even without the addition of an extractant suggesting that this ionic liquid also behaves as an extractant. The complex formation of U (IV) with ligand of the IL liquid was the reason for good extraction. Recovery of U(IV) was also studied and reported by using H_2O_2. The conventional (CLLE) as well as homogenous liquid extraction (HLLE) showed almost same pattern.[47]

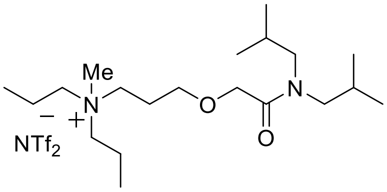


[Hbet][NTf_2]

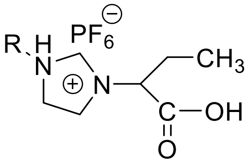
Mohapatra and his team synthesized carbamoylmethylphosphine oxide (CMPO) based task specific ionic liquid L-I and L-II with PF_6^- and NTf_2^- counter anions respectively and their solutions in room temperature ionic liquids (RTILs) such as $C_n$minPF$_6$ and $C_n$mimNTf$_2$ were used for the extraction of actinide and lanthanide from 3M HNO_3 solutions. The results were compared with the extraction data obtained with carbamoylmethylphosphine oxide in the same set of room temperature ionic liquids and n-dodecane. The D_{Am} value obtained with 0.03 M L-I and 0.1 M L-II in C_8mimPF$_6$ and C_8mimNTf$_2$ were 0.16 and 16 respectively. The extraction kinetics for the CMPO-TSIL L_{II} decreased with the increase in alkyl chain length, and followed the order i.e. C_4minNTf$_2^-$ > C_6minNTf$_2^-$ > C_8minNTf$_2^-$ which showed that the metal ion extraction is based on cation exchange extraction mechanism. Both CMPO task specific ionic liquid L_I and L_{II} showed lower extraction for Am^{3+} and Eu^{3+}, while CMPO-TSIL L-II showed significantly larger extent of UO_2^{2+} as compared to that obtained with CMPO in same set room temperature ionic liquids. Higher extraction was observed using CMPO-TSIL L-II in C_4mimNTf$_2$ for extraction of Pu^{4+} than CMPO in C_4mimNTf$_2$, while in other two ionic liquids it showed opposite trend. Various spectroscopic techniques such as FT-IR and UV-visible spectroscopy indicated the formation of inner sphere complexes for Uranium and Neodymium and coordination through carbonyl oxygen atom.[35]

2.4.4. Glycolamide based task specific liquid

Dhaval R. Raut et. al reported the synthesis of glycolamide based task specific liquid, and its extraction studies for the actinide ions and various fission products such as Am^{3+}, $UO2^{2+}$, Pu^{4+}, Eu^{3+}, Sr^{2+} and Cs^{+} using $3.43x10^{-2}$ M G-FIL in $[C_4mim][TNf_2]$. The extraordinarily higher extraction of trivalent lanthanide and actinide ions at low acid feed was reported which decreases at higher acidity. The other metal ions such as mono-, bi-, tetra- and hexavalent ions were not significantly extracted. According to thermodynamics studies the reactions were highly endothermic due to dehydration of metal ions before the complex formation. Stripping was done using higher HNO_3 concentration, quantitatively more than 99 percent stripping of Am^{3+} was achieved at 2 M HNO_3. Limited radiolytic stability of the extractant was reported indicating that recycling of G-FIL cannot be achieved in high level nuclear waste containing highly radioactive species.[48]



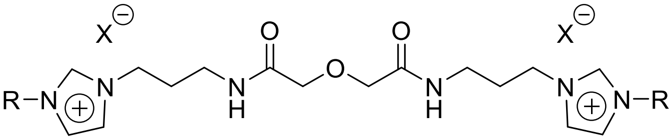
A hydrophobic ionic liquid $[1\text{-alkyl-3-(1-carboxylpropyl)im}][PF_6]$,having R= butyl, hexyl, octyl, and its extraction properties were studied in nitric acid medium for the extraction of Y(III). The extraction was studied by keeping the factors of concentration, pH and temperature in control. They concluded that this type of TSIL should be used after saponification as the extraction is acid dependent moreover the stripping of loaded organic phase was very easy and over 95 % yield was obtained.[49]



[1-hexyl-3-(1-carboxylpropyl)im][PF6]

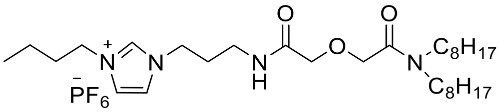
2.4.5. Diglycolamide-functionalized task specific ionic liquids.

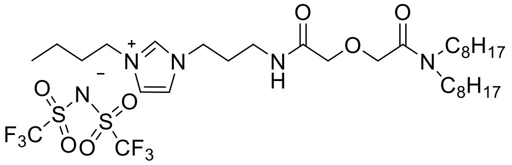
Wu Yun et al. synthesized imidazolium based task-specific ionic liquids containing drafted diglycolamide moieties. The solid phase extraction was carried out to study complexation capabilities of the synthesized TSILs. Long alkyl chain TSILs were used as component in siliceous mesostructured cellular foams to prepare solid phase to adsorbed trivalent lanthanide ions (Lu^{3+}, Eu^{3+}, and La^{3+}) from aqueous phase. Lanthanide complexes were water soluble and no extraction of lanthanide ions to 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_6mim][NTf_2]) from aqueous phase at various PH. TSILs as ligand showed efficient stripping for lanthanides (Lu^{3+}, Eu^{3+}, and La^{3+}) in solvent extraction system having N, N, N`, N`-tetraoctyl-3-oxapentanediamide in [C_6mim][NTf_2] and 0.01 M HNO_3 aqueous solutions indicating that it can be used to transfer lanthanides to aqueous phase from organic phase. [10]



TSIL

P K. Mohapatra et al. first time reported the synthesis of diglycolamide based tasks specific ionic liquids (DGA-TSILs) and studied the extraction behavior of actinides such as (Pu^{4+}, Np^{4+}, Am^{3+}, UO_2^{2+}), lanthanides along with fission product ions i.e. (Sr^{2+},Eu^{3+}, Cs^{+}) from acid feed solutions. The extraction results were equated through that of N,N,N,N-tetra-n-octyl diglycolamide using molecular organic diluents and in ionic liquids. Highly exceptional abilities towards trivalent actinide ion (Am^{3+}) and about 5-10 times lanthanide ion Eu^{3+}were shown. The $SF_{Eu/Am}$ for TSIL-DGA with PF_6^- and NTf_2^- counter anions values were 8.88 and 4.89 respectively which were double than that were obtained for TODGA in C_4mimPF_6, $C_4mimNTf_2$ and n-dodecane. These results showed the no special acid feed adjustment was required for more effective extraction of decontaminated minor actinide products, previously in order to achieve better decontamination acid feed was adjusted to 6 M HNO_3.[50] Diluted solutions of DGA-TSILs in ionic liquids $C_4mim^+PF_6^-$ and $C_4min^+NTf_2^-$ were used for the extraction, due to their lower viscosity as compared with their octyl derivatives. The ionic liquid based solvent systems showed significantly higher D_M values as compared to those in n-dodecane. The following distribution-ratio trend was obtained; Eu^{3+} > Am^{3+} >> Pu^{4+} > Np^{4+} >> UO2^{2+} >> $Sr^{2+} \approx Cs^{+}$. Slope analysis was carried out to determine the nature of extracted species. The extracted species contain two DGA-TSILs molecules along with one nitrate anion. Time resolved laser induced fluorescence studies indicated strong complexation without inner sphere water molecules in metal-TSIL-DGA complexes. Radiolytic stability was tested by irradiating the TSILs-DGA to an absorbed gamma-ray dose of 100 MRad, high radiolytic degradation showed that the DGA-TSILs solvent systems were the most suitable for recycling and radioactive waste remediation applications.[51]



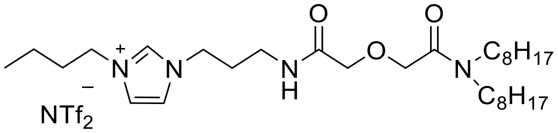


Arijit Sengupta and co studied the extraction behavior of diglycolamide functionalized task specific ionic liquid (TSIL) for the several actinides such as Am^{3+}, Np^{4+}, UO_2^{2+}, Pu^{4+}, , PuO_2^{2+} and NpO_2^{2+} from nitric acid medium. The extraction was carried out by using 3.6 × 10^2 M Diluted solution of the DGA-TSIL in C_4mim.NTf_2. The resulting trend was as followed: Am^{3+}> Pu^{4+} >Np^{4+} >>$UO_2^{2+,}$ >NpO_2^{2+} > PuO_2^{2+} .The distribution ratios of various ions at 3 M HNO_3 were reported as 34,5.9, 3.5, 0.44, 0.38 and 0.32 for Am^{3+}, Pu^{4+} ,Np^{4+} ,$UO_2^{2+,}$, NpO_2^{2+} and PuO_2^{2+} respectively. The extraction efficiency of the DGA-based TSIL for trivalent actinide ions was reported one order of magnitude higher than the tetravalent ions, which was sequentially one order of magnitude higher than analogous hexavalent ions. The extraction system was operated through ion-exchange mechanism, which was reflected by the decreased trend in extraction of actinide ions at higher acidity.[52] According to the slope analysis all the actinide ions form 1:1 the metal-ligand stoichiometry with extractants solution in C_4mim.NTf_2. The thermodynamic parameters such as enthalpy, entropy and Gibb’s free energy were obtained by temperature variation studies. All the extraction process were spontaneous and exothermic in nature, reflected by the high D_M values for the tri- and tetravalent ions, which decreases with the increase in temperature. Stripping studies of actinides at various oxidation states from the solutions of DGA-TSIL in C_4mimNTf_2 indicated good stripping percentages. The effective strippants for the trivalent actinide ions were DTPA and

EDTA in guanidine carbonate, while oxalic acid and sodium carbonate are good for stripping hexavalent and tetravalent actinide ions.[53]

T. Prathibha et al. repoted the modifier free solvent extraction system containing monoglycolamide derivative, N,N-di-octyl-2-hydroxyacetamide (DOHyA) in n-dodecane for the extraction Am(III) and different metal ions from the fast reactor simulated high- level liquid waste. (DOHyA) was synthesized by alkaline hydrolysis of N,N-di-octyl-2- acetoxyacetamide. The extraction studies of trivalent metal ions from nitric acid medium were carried out without formation of third phase. co-extraction of Am(III) and all lanthanides was carried out through batch studies and quantitative extraction was obtained in the first five run of a twenty-stage mixer-settler. For each batch extraction 1: 1 ratio of aqueous and organic phase was equilibrated for an hour at 298 K. The radioactivity of Am(III) was analyzed by scintillation detector, where as concentrations of other metal as obtained by ICP-AES. Stripping studies were also carried out and the loaded Ln(III), Y(III) and Am(III). metal ions were efficiently recovered by using 0.5 M nitric acid solution in three stripping runs, while the other metal ions were retained in organic phase.[54]

Arijit Sengupta and his team evaluate potential of DGA-based task specific ionic liquid for the extraction of metal ions present in the simulated high level nuclear waste. The trivalent lanthanide and actinide ions were selectively extracted along with various co-extracted metal ions such as Pd(II), La(III), Pr(III), Nd(III), Zr(IV), Sm(III), Ce(IV), and Y(III). Relatively higher extraction such as 99, 97, and 45% was showed by Ce(IV), Zr(IV), and Pd(II) respectively. The higher extraction efficiency for Eu^{3+} has confirmed the similar mechanism shown by the other GDA based extractants.[55]. The distribution ratio values of tri and tetravalent actinides ions were affected by the presence of various metal ions in SHLW and decreases significantly. In pure tracer at optimum acidity feed Eu^{3+} and Am^{3+} showed higher extraction efficiency as compared to those obtained in simulated high level waste. Structural information was obtained from the analysis of the luminescence data of the Eu^{3+} DGA-TSIL complex by calculating the Judd–Ofelt parameters. The formed complexes showed S_4 symmetry. The nature of extracted species was determined by using slope analysis method, ligand concentration was taken as function to measure the distribution ratios, higher distribution ratio values at increased ligand concentration showed the direct participation of ligand molecule in complex formation. The increased concentration of DGA-TSIL molecules in complexes resulted in increased lipophilicity hence showed high D values.[56]



Aims and Objectives

This study focuses the preparation of task specific ionic liquids for the extraction of various actinides/ lanthanides.

- To synthesize two diglycolamide based ionic liquid extractant having two different cationic parts i.e. imidazolium cation and tetraoctylammonium cation.
- To characterize the functionalized ionic liquid by FTIR, NMR.
- To evaluate the synthesized extractant for the extraction capability for U(VI), Eu(III) and Sm(III).
- Extraction studies will be carried out by using different parameters i.e. pH of aqueous phase, contact time, and concentration of ligands, NO_3^- ions concentration and stripping of metal ions.

Chapter 3

3. EXPRIMENTAL

3.1. Chemicals

Diglycolic anhydride, tetrahydrofuran, dioctylamine, 1-methyl imidazole, 1-bromooctane, acetonitrile, methanol, chloroform, sodium hydride, benzophenone, sodium metal, dichloromethane, n-hexane, ethyl acetate, deionized water, nitric acid, sodium nitrate, hydrochloric acid, anhydrous magnesium sulfate.

3.2. Glassware and Apparatus

3.2.1. Glassware

Distillation assembly, three necked round bottom flasks, conical flasks, , beakers , graduated cylinders, volumetric cylinders, spatula, reagent bottles, condenser, thermometer, pipettes, micropipettes, measuring cylinder, funnel, sample vials, rubber septa, nitrogen balloons, magnetic bar, syringes, oil bath etc.

3.2.2. Apparatus

Magnetic stirrer hot plate, weighing balance, melting point apparatus, vacuum pump, pH meter, UV lamp, and vacuum oven, stands etc.

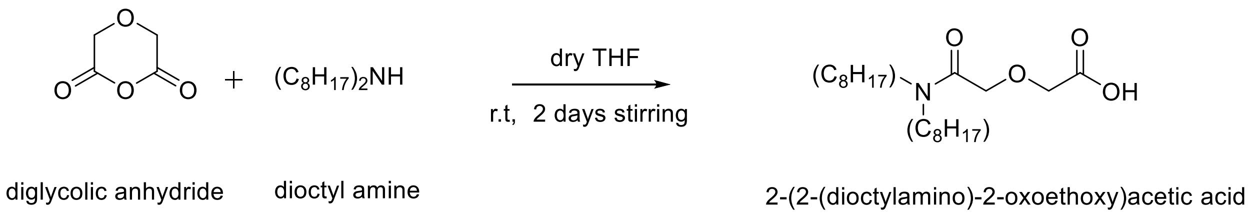
3.3. Experimental Procedure

Synthesis of task specific ionic liquids involves following steps.

1. All the solvents were distilled or dried before use.
2. Synthesis of N, N'-di-n-octyldiglycolamic acid.
3. Synthesis of 1-methyl-3-octyl imidazolium bromide.
4. Synthesis of trioctylamine.
5. Synthesis of tetraoctylammonium bromide.
6. Synthesis of diglycolamide functionalized ionic liquids.

3.3.1. Synthesis of 2-(2-(di-n-octylamino)-2-oxoethoxy)acetic acid.

2-(2-(di-n-octylamino)-2-oxoethoxy)acetic acid (1) was prepared by mixing diglycolic anhydride (0.5 g, 4.3 mmol) and dioctylamine (1.04 g,4.3 mmol) into 50 ml dry THF in three necked round bottom flask. The resulting mixture was stirred for 48 hours at room temperature. The reaction progress was monitored by TLC using 2% methanol in chloroform, after the completion of reaction, the reaction mixture was concentrated on rotary evaporator to afford yellowish semi liquid product.

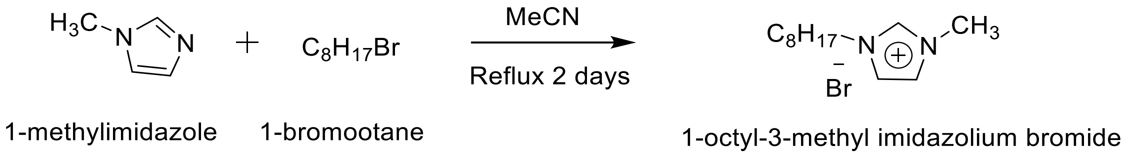


(1)

Scheme 3. 1

3.3.2. Synthesis of 1-methyl-3-octyl imidazolium bromide.

1-methylimidazole (5 g, 60.9 mmol) and 1-bromooctane (11.76 g, 60.9 mmol) were mixed in 80 ml acetonitrile. The reaction mixture was refluxed for 48 hours. After the completion of reaction (as monitored by TLC using 5% methanol in chloroform), the solvent was rotary evaporated from the reaction mixture to afford 1-methyl-3-octyl imidazolium bromide (2) as light yellow viscous liquid. The obtained ionic liquid was dried under vacuum oven at 40 ^{o}C for 4 hours.

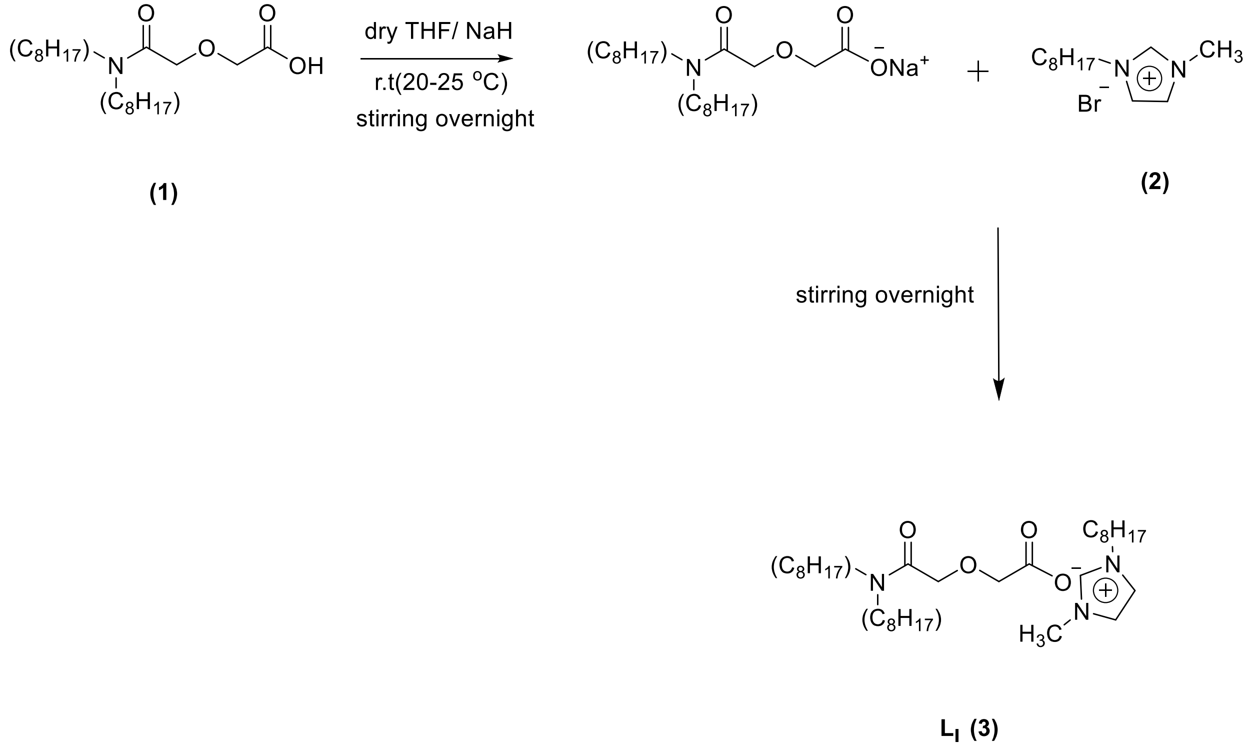


(2)

Scheme 3. 2

3.3.3. Synthesis of 1-methyl-3-octyl imidazolium dioctyl diglycolamate ($\mathrm{L_I}$).

The synthesis of diglycolamide based task specific ionic liquid involved ion exchange of tetra octylammonium bromide with dioctyl diglycolamic acid under argon atmosphere. 2-(2-(di-n-octylamino)-2-oxoethoxy) acetic acid (1.5 g, 4.2 mmol) was dissolved in dry THF. The reaction mixture was placed on ice bath and evacuated the reaction flask with the help of vacuum pump. Sodium hydride (0.252 g, 2.37 mmol) was gradually added at 0 °C on continuous stirring under argon environment. The reaction mixture was allowed to stir overnight, after 12 hours 1-methyl-3-octyl imidazolium bromide (1.16 g, 4.2 mmol) was added and resulting reaction mixture was stirred overnight at room temperature. After the completion of reaction, the solvent was rotary evaporated to collect the yellow viscous liquid as product. The synthesis of functionalized ionic liquid 1-methyl-3-octyl imidazolium dioctyl diglycolamate (3) is summarized in scheme 3.3.



(1)

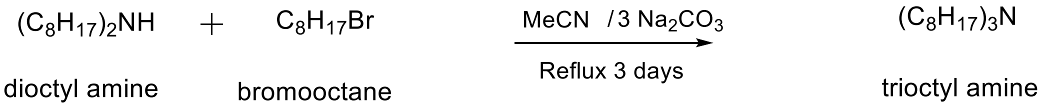
(2)

$\mathrm{L_I}$ (3)

Scheme 3. 3

3.3.4. Synthesis of trioctyl amine.

Dioctylamine (2 g, 8.28mmol) and 1-bromooctane (1.6 g, 8.28mmol) were mixed into 100 ml acetonitrile in a round bottom flask. Sodium bicarbonate (2.63 g, 24.8 mmol) was added in the mixture with continuous stirring. The reaction mixture was refluxed for 3 days. After the completion of reaction (as monitored by TLC using 2% methanol in chloroform), the solvent was rotary evaporated from the reaction mixture. The residue was dissolved in chloroform and filtered. The filtrate was washed with 0.5 N HCl and water. The chloroform layer was dried over anhydrous magnesium sulphate Mg(SO$_4$) and rotary evaporated. The obtained residue was purified through silica gel column chromatography by using 5% methanol in dichloromethane as mobile phase. The clear oily liquid of trioctylamine (4) was obtained as intermediate in 79% yield.

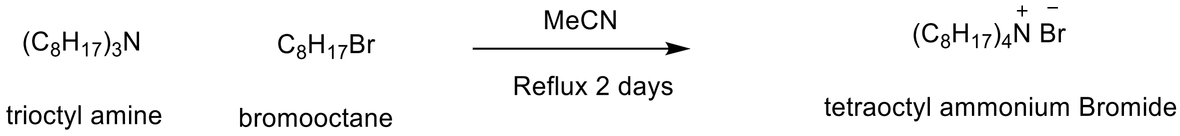


(4)

Scheme 3. 4

3.3.5. Synthesis of tetraoctyl ammonium bromide.

Trioctylamine (2.32 g, 6.57 mmol) and 1-bromooctane (1.27 g, 6.57 mmol) were mixed into 80 ml acetonitrile in a round bottom flask. The reaction mixture was refluxed for 4 days. After the completion of reaction (as monitored by TLC using 5% methanol in chloroform), the solvent was rotary evaporated from the reaction mixture. The residue was dissolved in 50 ml n-hexane and decanted to remove the excess of 1-bromooctane. Repeated the decantation process three time to afford the pure tetraoctyl ammonium bromide (5) as white flakes. The obtained product was dried under vacuum for 12 hours.

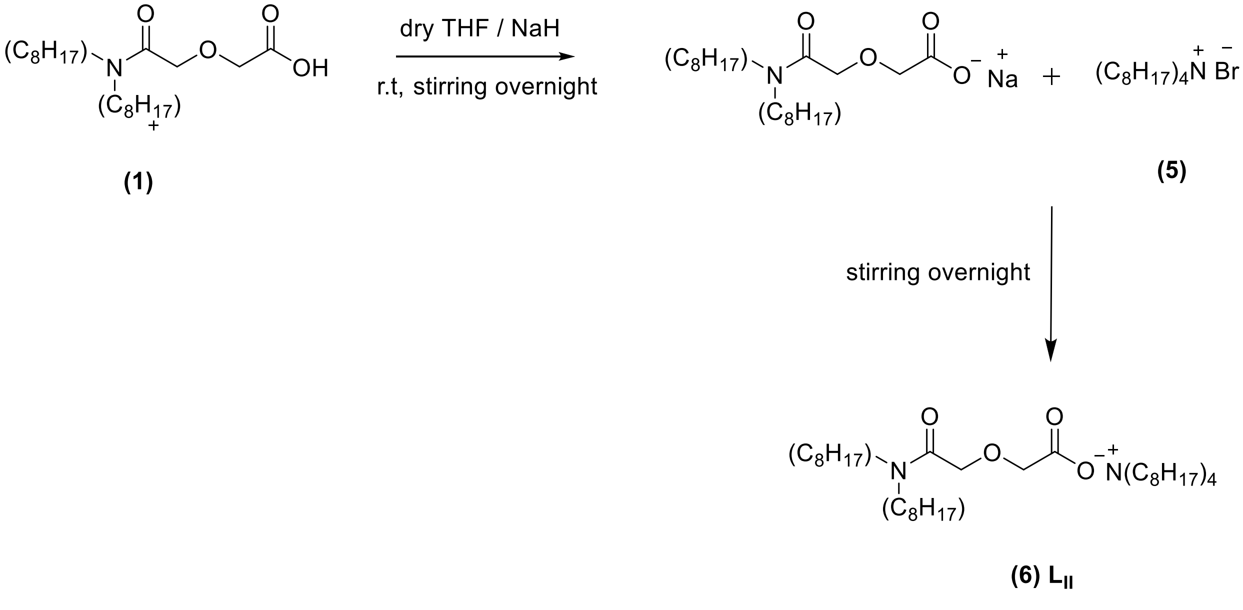


(5)

Scheme 3. 5

3.3.6. Synthesis of tetraoctyl ammonium dioctyl diglycolamate. (L_{II}).

The synthesis of diglycolamide based task specific ionic liquid involved ion exchange of tetra octylammonium bromide with dioctyl diglycolamic acid under argon atmosphere. 2-(2-(di-n-octylamino)-2-oxoethoxy) acetic acid (1.52 g, 4.26 mmol) was dissolved in dry THF. The reaction mixture was placed on ice bath and evacuated the reaction flask with the help of vacuum pump. Sodium hydride (0.255 g, 2.41 mmol) was gradually added at 0 °C on continuous stirring under argon environment. The reaction mixture was allowed to stir overnight, after 12 hours tetraoctylammonium bromide (2.32 g, 4.26 mmol) was added and resulting reaction mixture was stirred overnight at room temperature. After the completion of reaction, the solvent was rotary evaporated to get the orange viscous liquid as product. The synthesis of functionalized ionic liquid tetraoctyl ammonium dioctyl diglycolamate (6) is summarized in scheme 3.6.



Scheme 3. 6

The FIL ionic liquid extractant L_I and L_{II} were used for the extraction of Ln/An.

Chapter 4

4. RESULTS & DISCUSSION

This chapter includes the detailed results and discussions of synthesis of functionalized ionic liquids, characterization of the synthesized extractant and their application for the extraction of various lanthanides/actinides. To understand the structure of synthesized extractants characterization techniques viz. Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR) were employed.

4.1. Fourier Transform Infrared Spectroscopy (FTIR)

The infra-red spectroscopy is technique that involves the vibration motion of molecules or functional groups when beam of light in infra red region of electromagnetic spectrum (400 cm^{-1} to 4000 cm^{-1}) strikes the molecules. Some of the light is absorbed by the molecules of organic compound and some inorganic compounds, and those molecules whose dipole moment varies display IR band in characteristic region [16]. To measure the absorbance capacity, corresponding to each absorbance the detector receives signals. In the ATR-FTIR spectroscopy, the sample is directly applied for the analysis. The resulting IR characteristic band provide us data for the structure elucidation of unknown molecules. ATR-FTIR was performed on Bruker Alpha platinum-ATR. Spectra of synthesized products are given below:

4.1.1. FT-IR analysis of 2-(2-(di-n-octylamino)-2-oxoethoxy)acetic acid.

Figure 4.1. shows the FTIR spectrum of dioctyl diglycolic acid (1). The conversion of diglycolic anhydride into dioctyl diglycolic acid is confirmed by presence of characteristic band of carbonyl of carboxylic acid (C=O) at 1720 cm^{-1}. The band for carbonyl C=O of diglycolic anhydride is disappeared, which was present at 1824 cm^{-1}. The following absorption band are shown in the spectrum: a strong absorption band due to stretching vibration of carbonyl C=O for amide is present at 1630 cm^{-1}, the strong bands at 2854 cm^{-1} and 2923 cm^{-1} corresponds to the C-H stretching vibrations in sp^3 CH_2. Bending vibrations of CH_2 is present at 1431 cm^{-1}, a band at 1120 cm^{-1} reflects the presence of C-O linkage, band present at 750cm^{-1} depicts the rocking bending vibrations of CH_2 group present in long chain of octyl groups.

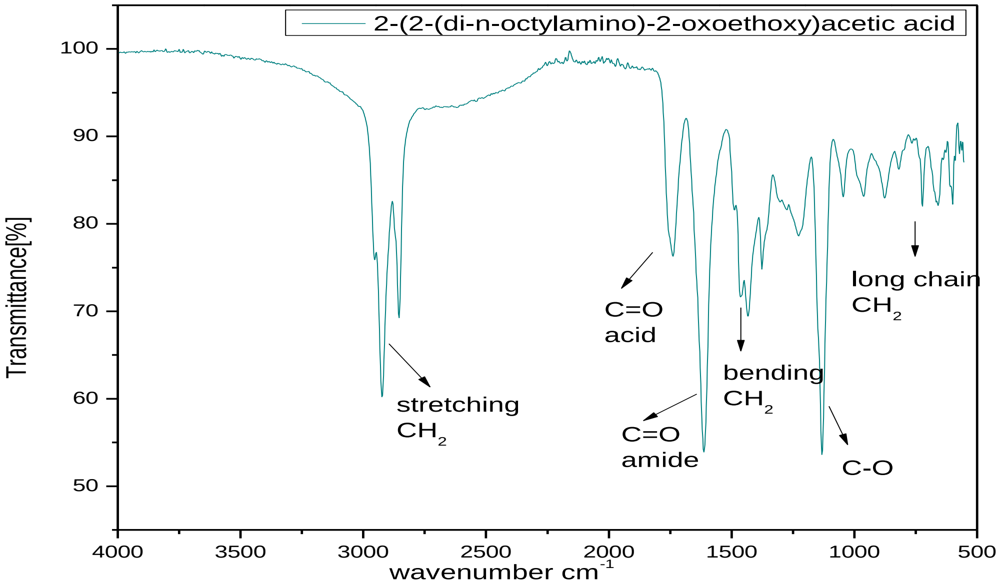


Figure 4. 1. FTIR analysis dioctyl diglycolic acid.

4.1.2. FT-IR analysis of 1-methyl-3-octyl imidazolium bromide.

The FTIR analysis of 1-methyl-octylimidazolium bromide is shown in Figure 4.2. The presence of broad bell shaped O-H like band reflects the stretching vibration of C=N of aromatic ring present in imidazole. The band appeared at 3120 cm^{-1} is assigned to C-H stretching of sp^2 C=C present in aromatic ring. The strong bands at 2854 cm^{-1} and 2923 cm^{-1} corresponds to the C-H stretching vibrations in sp^3 CH_2. A band at 1569 cm^{-1} is due to stretching vibrations of C=C group. Bending vibrations of CH_2 and CH_3 are present at 1463 cm^{-1} and 1379 cm^{-1} respectively. A strong band present at 750cm^{-1} reflects the rocking bending vibrations of CH_2 group present in long chained octyl group.

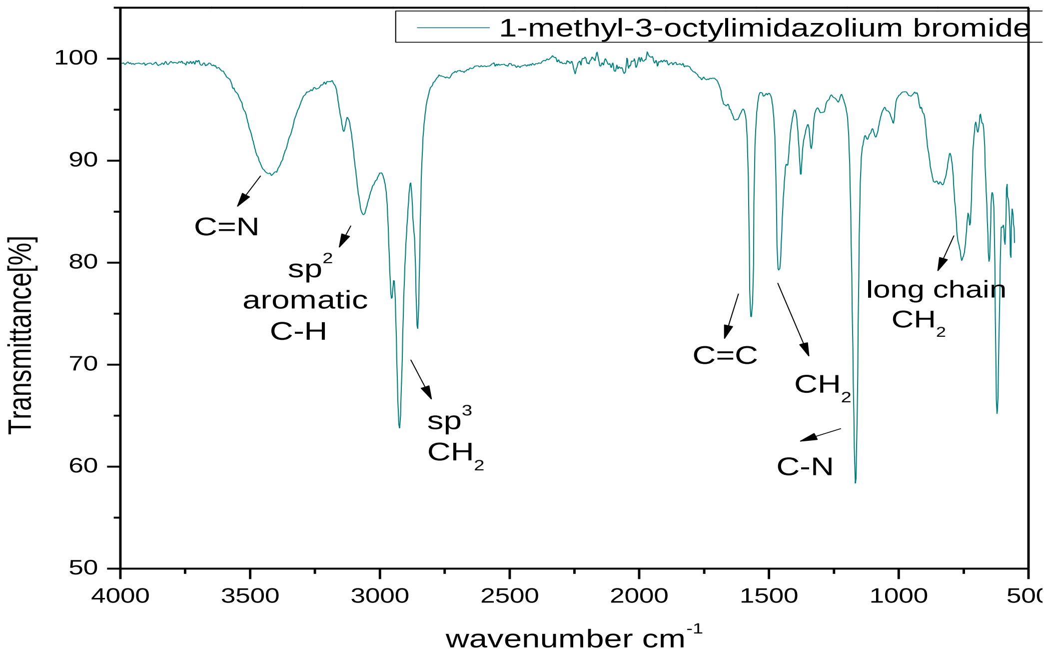


Figure 4. 2. FTIR analysis of 1-methyl-octylimidazolium bromide

4.1.3. FT-IR analysis of 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L$_I$).

Figure 4.3. shows the FT-IR of analysis of the functionalized dioctyl diglycolamate. The characteristic broad band is appeared at 1612cm^{-1}, due to exchange of cation ion with 1-methyl-3-octylimidazolium.

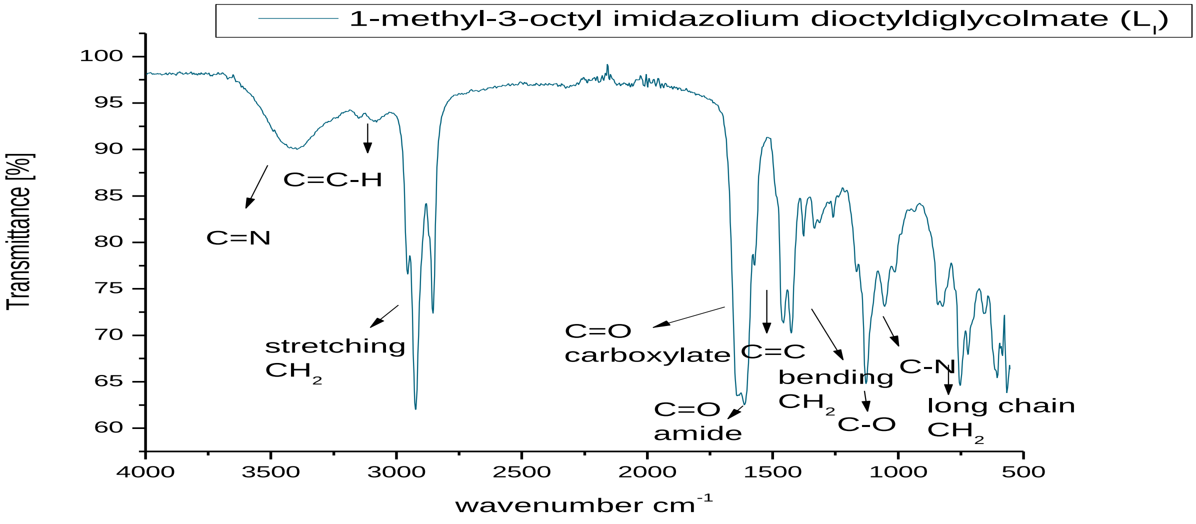


Figure 4. 3. FTIR spectrum of 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L$_I$)

The characteristic band of carbonyl group C=O which was present at 1720cm^{-1} in carboxylic acid is shifted towards lower value, due to increase in single bond character and a broad band of carboxylate ion of functionalized DGA is found to be merged with C=O carbonyl of amide group. The presence of broad bell shaped O-H like band reflects the stretching vibration of C=N of aromatic ring present in imidazole. The band appeared at 3122 cm^{-1} is assigned to C-H stretching of sp^2 C=C present in aromatic ring. The strong bands at 2852 cm^{-1} and 2924 cm^{-1} corresponds to the C-H symmetric stretching vibrations in sp^3 CH_3 and CH_2 respectively. A band at 1509 cm^{-1} is due to stretching vibrations of C=C group. A band appeared at 1127cm^{-1} reflects the presence of C-O bond. Band present at 750cm^{-1} is appeared due to the rocking bending vibrations of CH_2 group present in long chain of octyl groups.

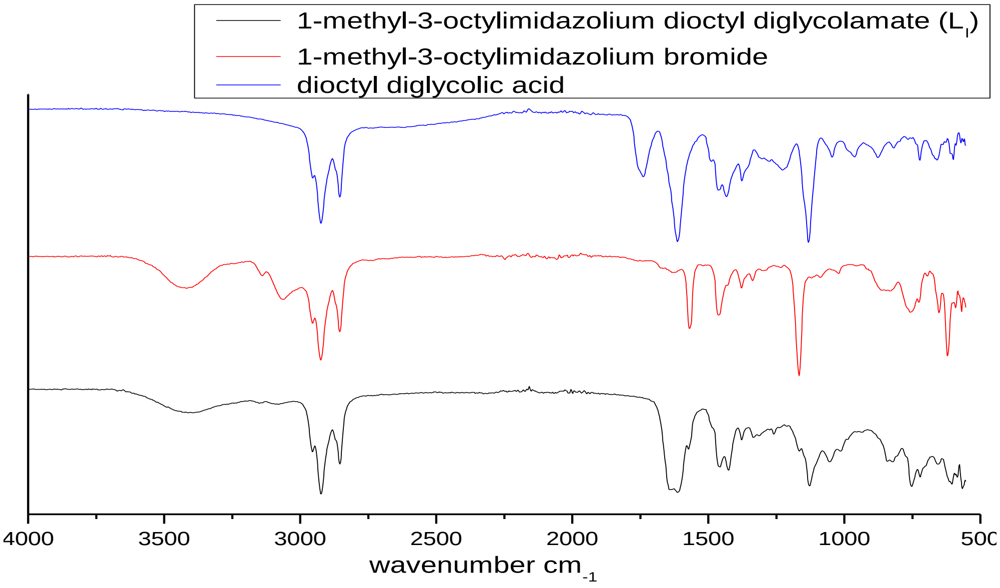


Figure 4. 4. FTIR analysis of L_I

4.1.4. FT-IR analysis of tetraoctylammonium bromide.

The FTIR analysis of 1-methyl-octylimidazolium bromide is shown in Figure 4.5. . The strong bands at 2852 cm^{-1} and 2924 cm^{-1} corresponds to the C-H symmetric stretching vibrations in sp^3 CH_3 and CH_2 respectively. Bending vibrations of CH_2 and CH_3 are present at 1466 cm^{-1} and 1384 cm^{-1} respectively. A strong band present at 750cm^{-1} is appeared due to the rocking bending vibrations of CH_2 group present in long chain of octyl groups.

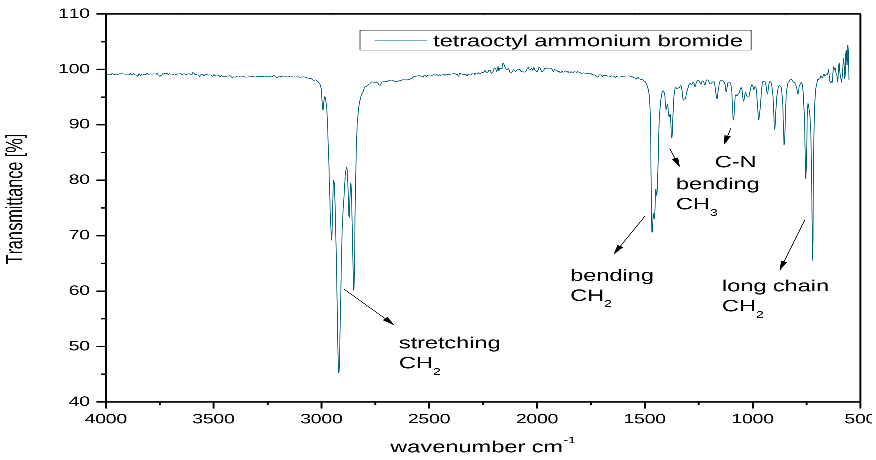


Figure 4. 5. FTIR spectrum of tetraoctylammonium bromide

4.1.5. FT-IR analysis of tetraoctylammonium dioctyl diglycolamate (L_{II}).

Figure 4.6. shows the FT-IR of analysis of the ammonium functionalized dioctyl diglycolamate. The strong bands at 2852 cm^{-1} and 2924 cm^{-1} corresponds to the C-H stretching vibrations in sp^3 CH_2.

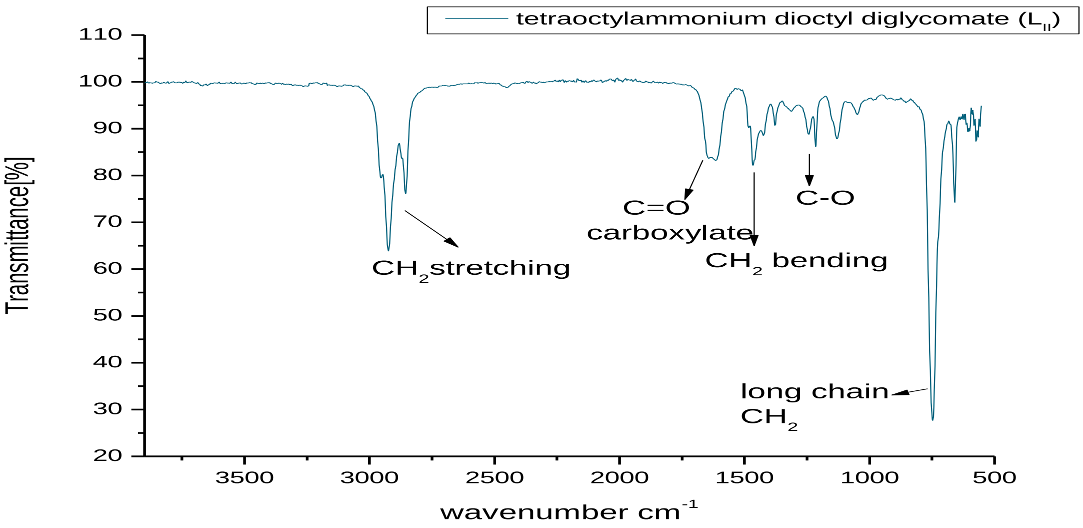


Figure 4. 6. FTIR spectrum of tetraoctylammonium dioctyl diglycolamate (L_{II})

The characteristic broad band is appeared at 1615cm^{-1}, due to exchange of cation ion with tetra octyl ammonium. The characteristic band of carbonyl group C=O which was present at 1722cm^{-1} in carboxylic acid is shifted towards lower value, due to increase in single bond character and a broad band of carboxylate ion of functionalized DGA is found to be merged with C=O carbonyl of amide group. A band appeared at 1133cm^{-1} reflects the presence of C-O bond. Band present at 747 cm^{-1} is appeared due to the rocking bending vibrations of CH_2 group present in long chain of octyl groups.

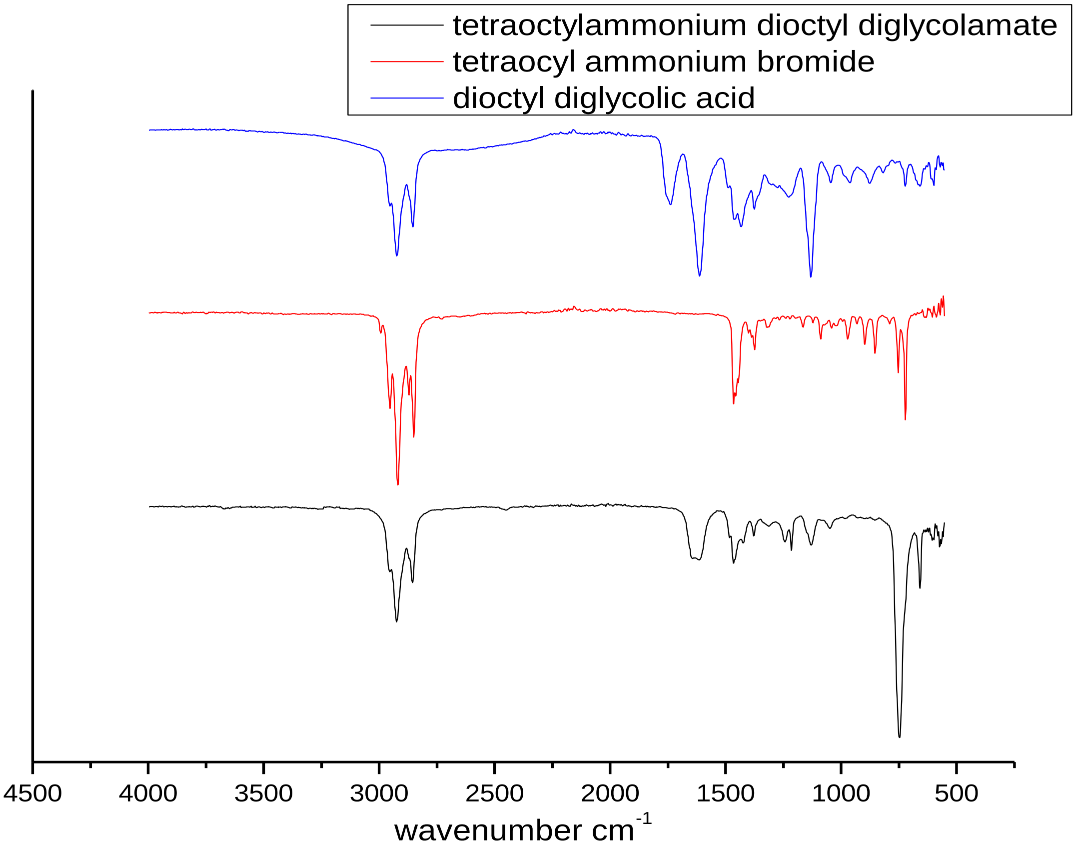


Figure 4. 7 FTIR analysis of L_{II}

4.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were determined at 500 MHz on Bruker by using $CDCl_3$ as solvent.

4.2.1. Structure elucidation of 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L_I).

^{1}H NMR spectrum of functionalized dioctyl diglycolamate (L_I) confirm the synthesis of (**3**).

^{1}H NMR ($CDCl_3$, δ ppm): 0.9-1 (m, 9H; C**H**$_3$), 1.26-1.35 (m, 36H, $3(CH_2)_6$), 3.1, 3.3 (t, 2H, NCH_2), 3.9, 4.2 (s, 2H, C**H**$_2$CO), 4.1 (s, 3H, CH_3N) 4.3 (t, 2H, NCH_2), 7.4 (s, 1H; Im C**H**), 7.50 (s, 1H; Im C**H**), 10.40(s, 1H; Im NC**H**N).

Protons	**Chemical Shift values ppm**	**Multiplicity**
C**H**$_3$	0.85 - 0.9	m
C**H**$_2$	1.26 - 1.33	m
CONC**H**$_2$	3.1 , 3.3	t
OC**H**$_2$CO	3.9 , 4.2	s
NC**H**$_3$	4.1	s
NC**H**$_2$	4.3	t
C**H**=C**H**	7.4 ,7.5	s
NC**H**N	10.4	s

Table 4. 1 ^{1}HNMR data of 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L_I).

4.2.2. Structure elucidation of tetraoctylammonium dioctyl diglycolamate (L_{II}).

^{1}H NMR spectrum of functionalized dioctyl diglycolamate (L_I) confirm the synthesis of (**6**).

^{1}H NMR ($CDCl_3$, δ ppm): 0.8-0.89 (m, 18H; C**H**$_3$), 1.22-1.35 (m, 72 H, $6(CH_2)_6$), 3, 3.2 (t, 2H, NCH_2), 3.7 (t, 8H, CH_2N) 3.9, 4.1 (s, 2H, C**H**$_2$CO).

Protons	**Chemical Shift values ppm**	**Multiplicity**
C**H**$_3$	0.86 - 0.89	m

C**H**$_2$	1.22 - 1.35	m
CONC**H**$_2$	3 , 3.2	t
C**H**$_2$N	3.7	t
OC**H**$_2$CO	3.9 , 4.1	s

Table 4. 2. ^{1}HNMR data of tetraoctylammonium dioctyl diglycolamate (L_{II})

4.3. Extraction study for Ln/An

The extraction efficiency of synthesized functional ionic liquids as extractants were evaluated for the extraction of trivalent Europium (III) and uranium (VI) from acidic aqueous phase. The study was carried out for various parameters like extraction time for equilibrium kinetics, pH, ligands concentration and nitrate ion concentration. To optimize the several parameters, the extraction study was performed in batches in order to get maximum extraction efficiency.

4.3.1. Preparation of aqueous phase

$7x10^{-4}$ M solutions of Eu(III) and U(VI) were prepared by using nitric acid medium. The salts of Eu_2O_3 and $UO_2 (NO_3)_2$. $6H_2O$ were dissolved in nitric acid. Different solution of Varying pH value range from 1-6 were prepared by using metrohm pH meter. The pH of solution was adjusted by using sodium hydroxide as base.

4.3.2. Preparation of organic phase

The functionalized ionic liquids L_I and L_{II} as extractant were dissolved in chloroform to prepare solution of various concentration ranges from 0.005 to 0.1 M ligand concentration.

4.3.3. Extraction procedure

For the extraction study, both the organic and aqueous phases were equilibrated in equal 1:1 volume ratio. 1 ml of aqueous phase along with 1 ml of organic phase was taken in 4 ml vial. The sample vials are equilibrated at 600 rpm on flask shaker. After the intensive shaking, phases were allowed to separate, and aqueous layer was taken out with the help of micropipette. The aqueous phase was analyzed by inductively coupled plasma optical emission spectroscopy.

Distribution Ratio

Distribution ratio is the activity per unit volume of the organic to that of aqueous phase. The extent of metal extraction was measured by calculating the distribution ratio (D) by using the following equation.

$$D = \frac{C_i - C_f}{C_f}$$

Where C_i and C_f represents the concentration of metal ions present in the aqueous phase before and after extraction respectively.

4.3.4. Effect of initial pH of aqueous phase

pH effects strongly on the extraction efficiency of the ligands. The extraction experiments were carried out as function of initial pH of various metals solution using nitric acid medium. Both the extractant showed varied extraction at different pH values. The extraction studies at various pH range (1 – 6) of the aqueous phase were carried out. The organic phase was consist of 2.5×10^{-2} M for both DGA- functionalized ionic liquids extractants.

The extraction experiments were carried out by using different aqueous phases having pH in the range or (1 -6). L_I extractant showed better extraction efficiency for Eu(III) and U(VI) ions at pH range between 2 to 3. The maximum distribution ratio was obtained at pH =2. Increase in the pH of initial aqueous phase above 2 pH results showed decrease in the extraction of metal ions. DGA based task specific ionic ligands mostly shows the better extraction at lower concentration of nitric acid ranges from 0.01 M to 1 M. At higher concentration of HNO3, DGA.HNO_3. In DGA based extractant, experimental pH greatly affects the extraction of the metals ions. Increase in pH results in a steadily decease in distribution ratio of Eu(III), Sm(III) and U(VI) Figure 4.8, 4.9 and 4.10 represents the extraction of L_I ionic liquid extractant at various pH values.

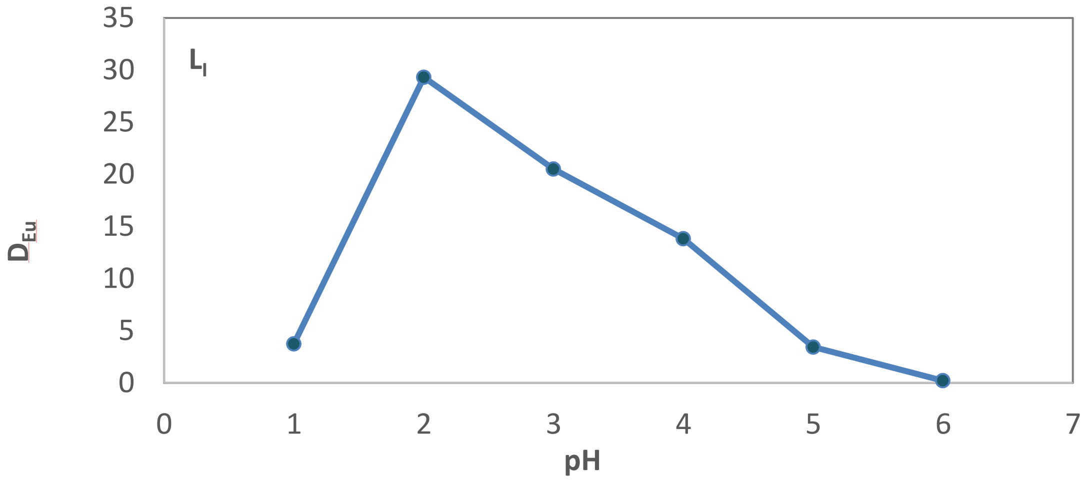


Figure 4. 8 . Distribution ratio of Eu^{3+} Vs pH using L_I

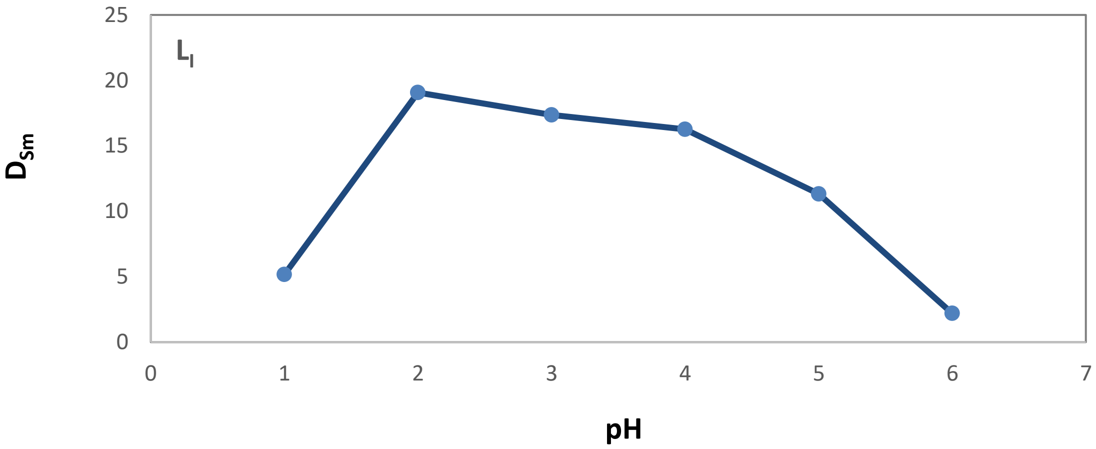


Figure 4. 9. Distribution ratio of Sm^{3+} Vs pH using L_I

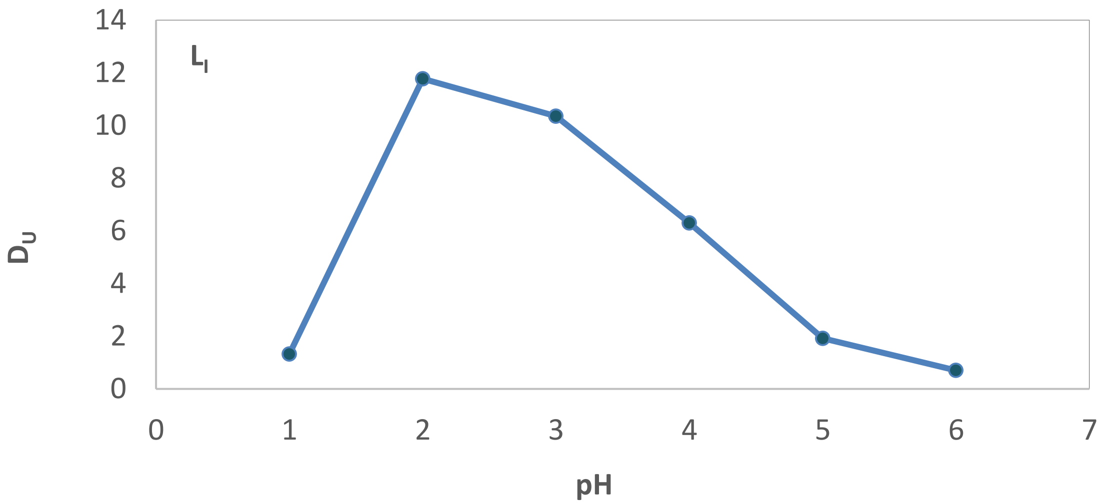


Figure 4. 10. Distribution ratio of Uo_2^{2+} Vs pH using L_I

L_{II} extractant showed better extraction efficiency for Eu(III) and U(VI) ions at pH range between 3 to 5 pH. The distribution ratio increases with increase in the pH of initial aqueous phase above 2 pH. This trend is found comparable with ammonium based diglycolic acid ligands in molecular diluent as acidic extractant system. At higher pH of the aqueous phase, there is lesser competition occurs between the metal ions and HNO_3 extraction. Due to the lower PK_a of the DGA based extractant, experimental pH greatly affects the extraction of the metals ions. The maximum extraction was found to be taken place at pH 4 -5, and further increase in pH results in a quick drop in the metal extraction trend, because of the hydrolysis of the metal ions. Figure 4.11, 4.12 and 4.13 represents the extraction of L_{II} ionic liquid extractant at various pH values.

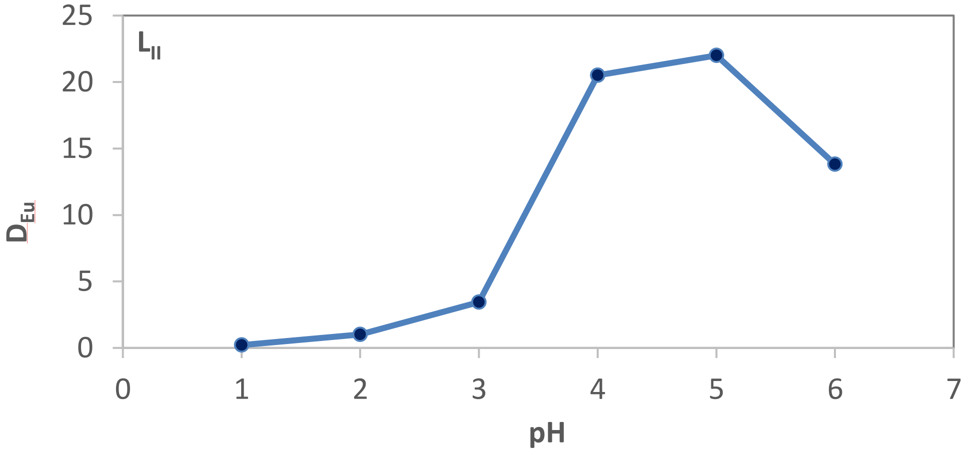


Figure 4. 11. Distribution ratio of Eu^{3+} Vs pH using L_{II}

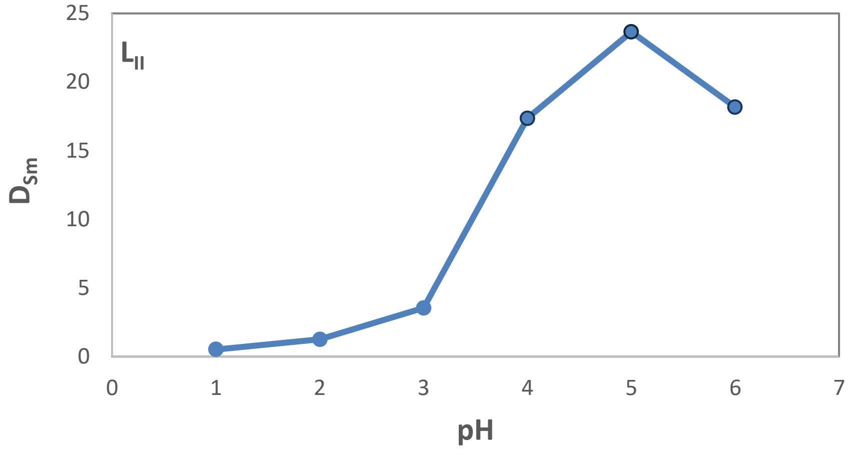


Figure 4. 12. Distribution ratio of Sm^{3+} Vs pH using L_{II}

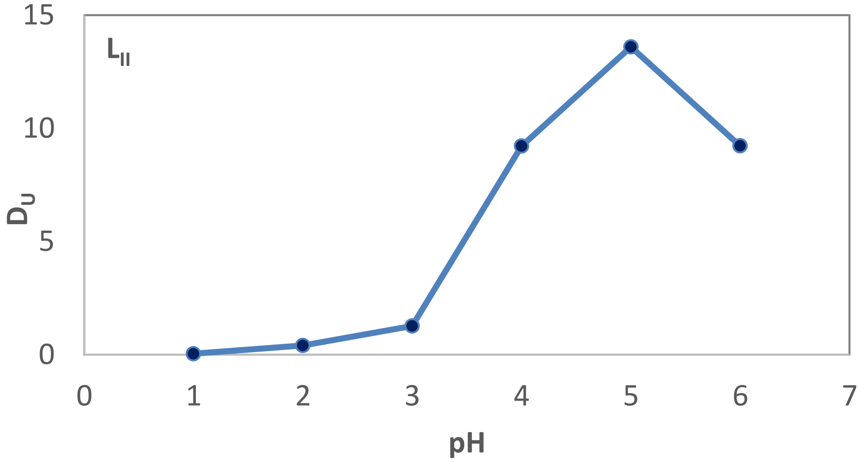


Figure 4. 13. Distribution ratio of UO_2^{2+} Vs pH using L_{II}

4.3.5. Extraction Kinetics

The effect of equilibration time on extraction of Eu(III) and U(VI) was estimated. In order to optimize the time required for maximum extraction 7x 10^{-4} M solutions of Eu(III) and U(VI) were used, The initial pH of the solutions were adjusted at 2 in case of L_I extractant and for the extraction study of L_{II}, pH of aqueous phase was kept at 4.5, which was found to be optimum pH for L_{II}. The organic phase was consist of 2.5 x 10^{-2} M for both DGA- functionalized ionic liquids extractants. Both the organic and aqueous phases were equilibrated in equal 1:1 volume ratio. 1 ml of aqueous phase along with 1 ml of organic phase was taken in 4 ml vial. In order to get the equilibrium time both phases were vigorously shaken, and duration of the contact time was noted from 5 minutes to an hour.

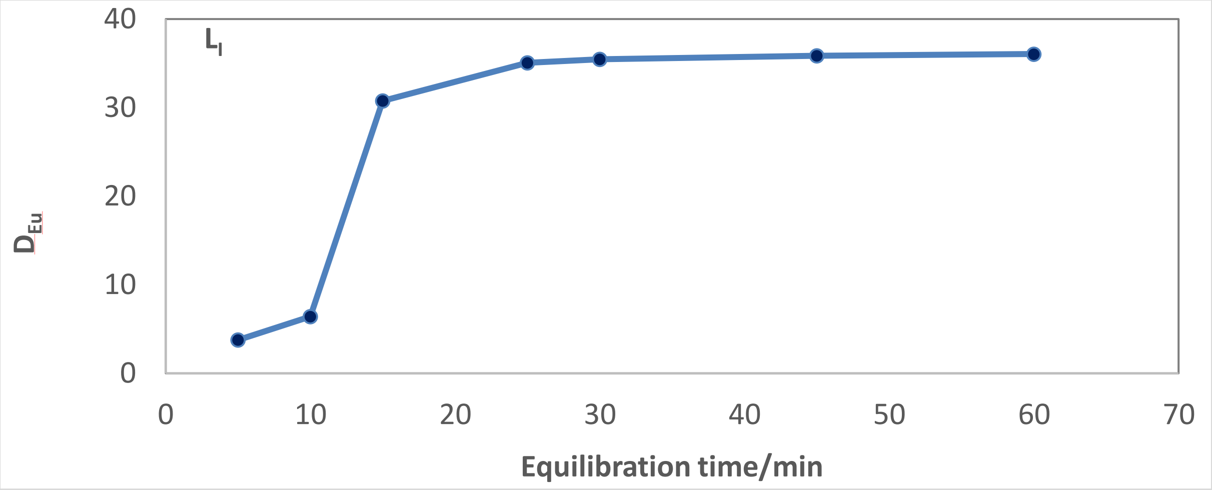


Figure 4. 14. Trend of D_{Eu} as function of equilibrium time

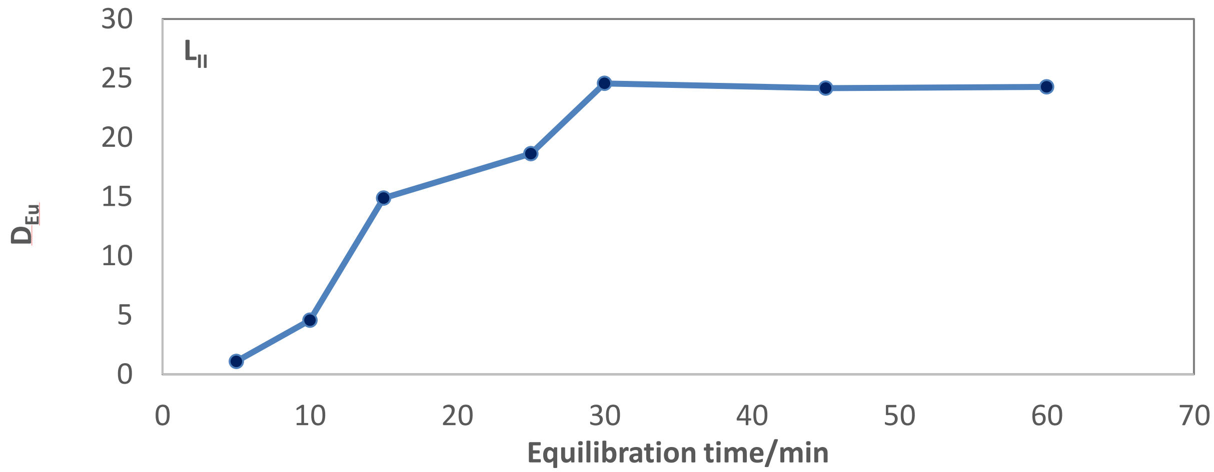


Figure 4. 15. Trend of D_{Eu} as function of equilibrium time

The sample vials were equilibrated at 600 rpm on flask shaker, phases were separated, and aqueous layer was separated and analyzed by inductively coupled plasma optical emission spectroscopy. It can be seen in the results of both L_I and L_{II} extractants, the extraction increases exponentially in the first 15 minutes contact time, and reaches its maximum after 25 to 30 minutes and plateau in plot of D_M as function of equilibration time was observed after 30 minutes.

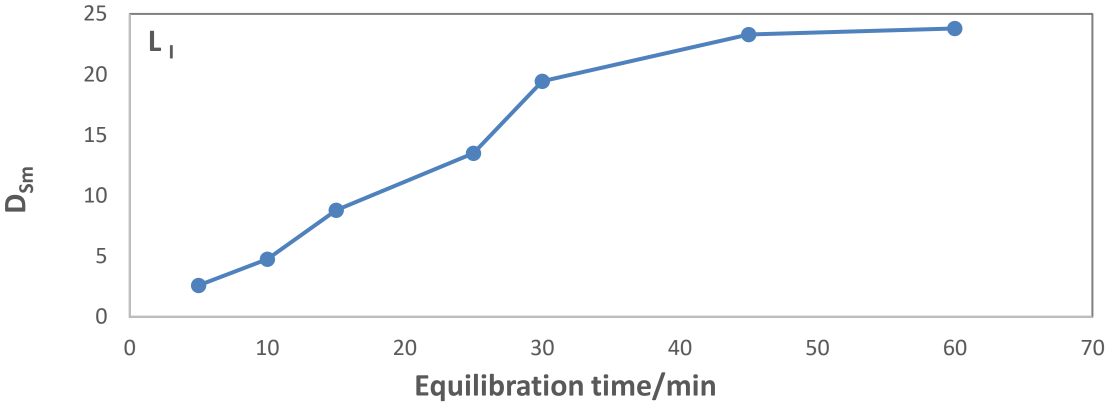


Figure 4. 16. Trend of D_{Sm} as function of equilibrium time

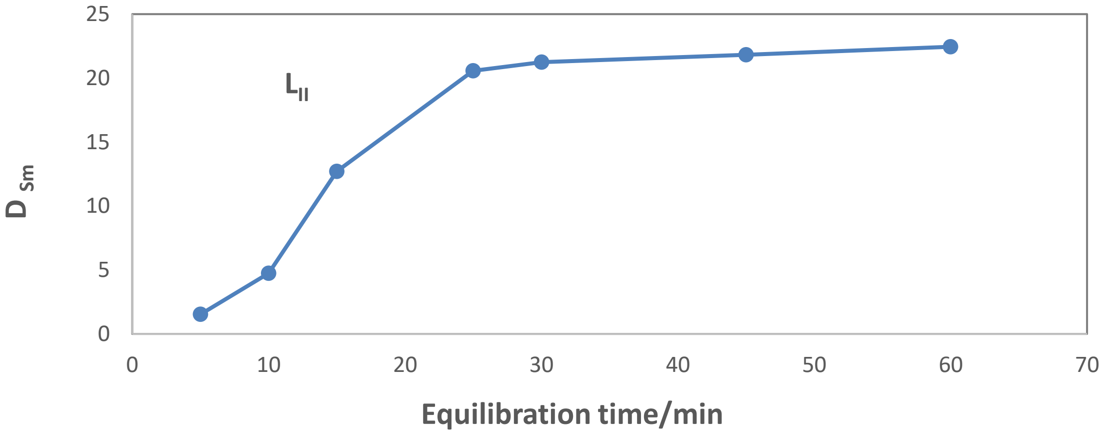


Figure 4. 17. Trend of D_{Sm} as function of equilibrium time

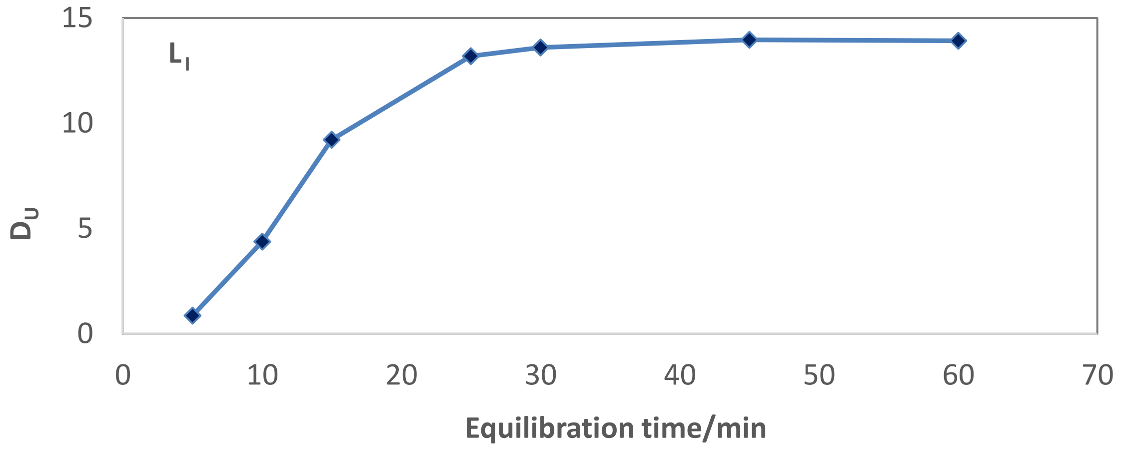


Figure 4. 18 Trend of D_U as function of equilibration time

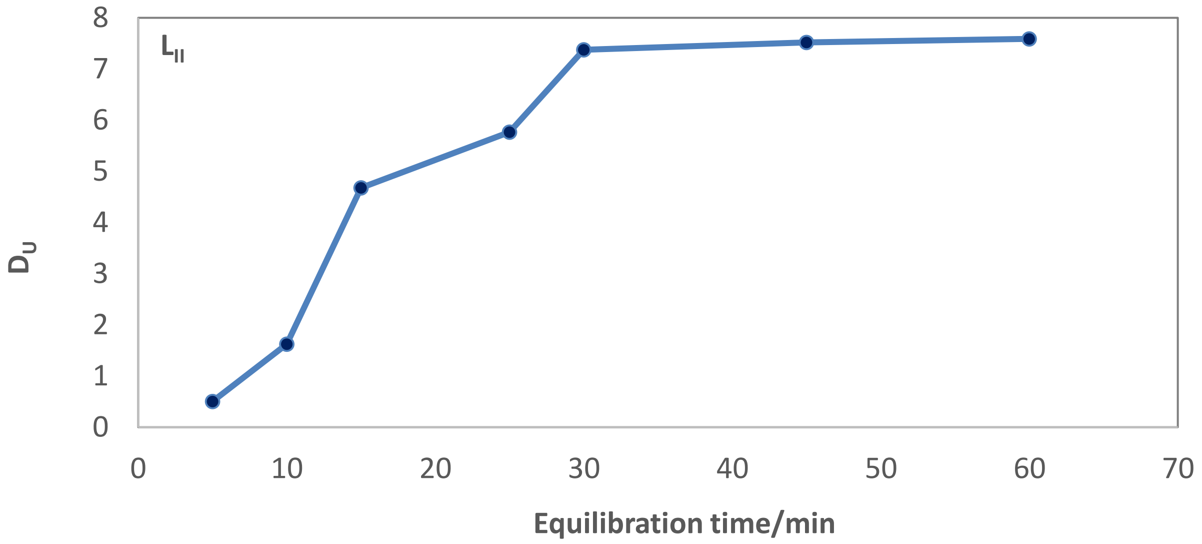


Figure 4. 19 Trend of D_U as function of equilibrium time

4.3.6. Extraction Stoichiometry

In solvent extraction, metal to ligand ratio is always important to determine the extraction stoichiometry. The effect of ligand concentration on the metal extraction was studied at various concentration of organic phase ranges 0.005 – 0.1 M solution of extractants. The distribution ratio of both the metal increases with the increase in the concentration of organic phase containing ligands. The slope analysis defines the metal extraction mechanism. The experimental results for extraction of Eu(III) and UVI) suggest the involvement of number ligands for complex formation.

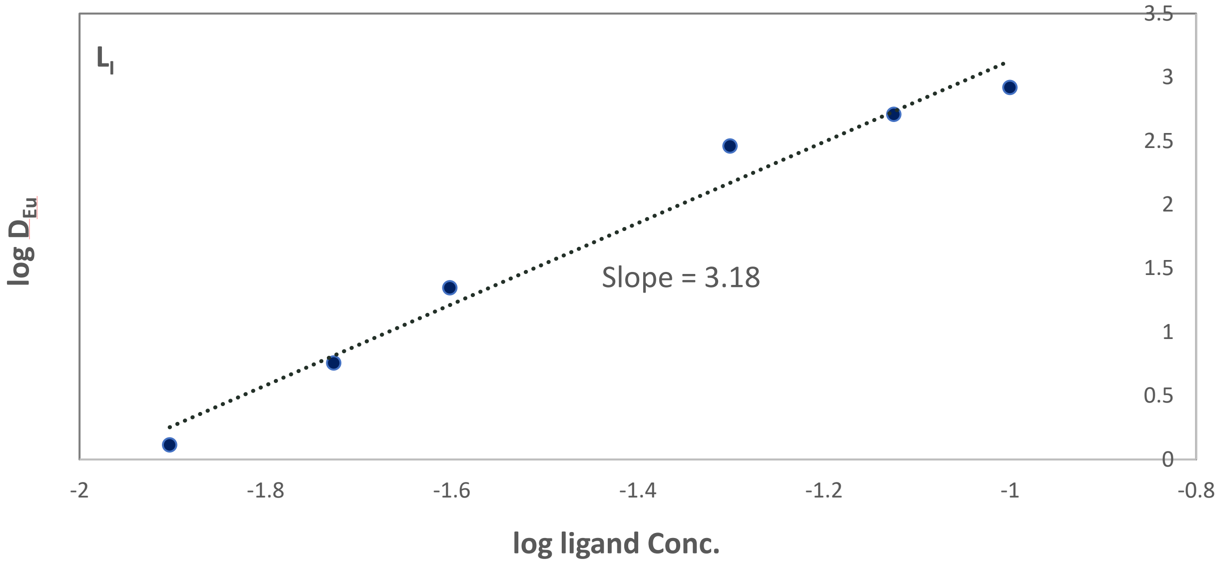


Figure 4. 20. plot of logD$_{Eu}$ vs log ligand concentration L$_I$

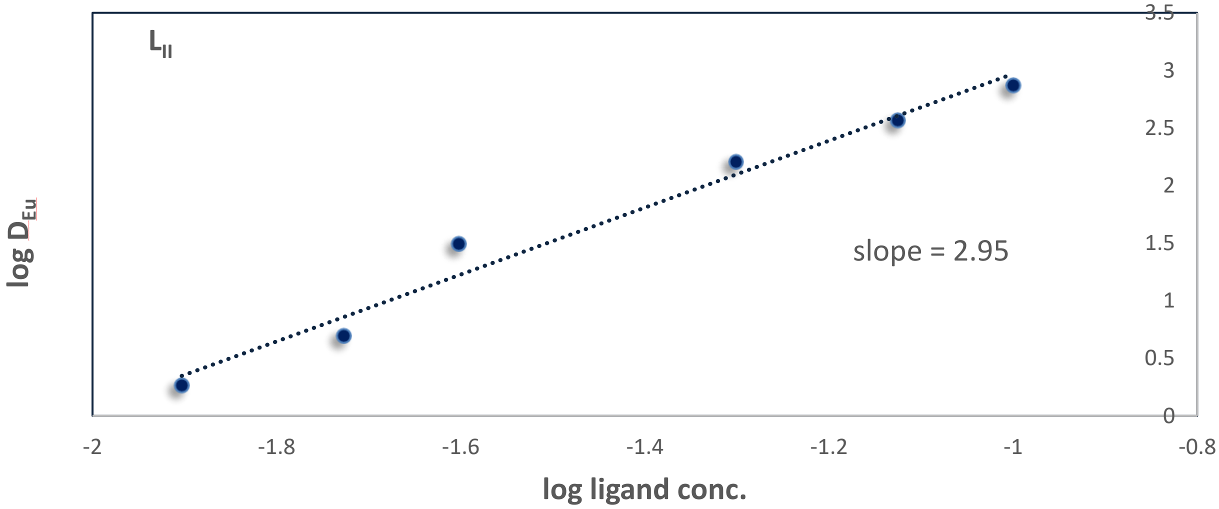


Figure 4. 21.plot of logD$_{Eu}$ vs log ligand concentration L$_{II}$

It was observed from the plot logD$_M$ as function of log of initial concentration of extractant that the trivalent europium and hexa valent uranium showed varied slope values. The straight line having slope of 3 was found and suggest the participation of 3 ligand molecules for the extraction of one Eu(III) ion from the aqueous phase. The slope analysis suggest the solvation mechanism was involved for the metal extraction.

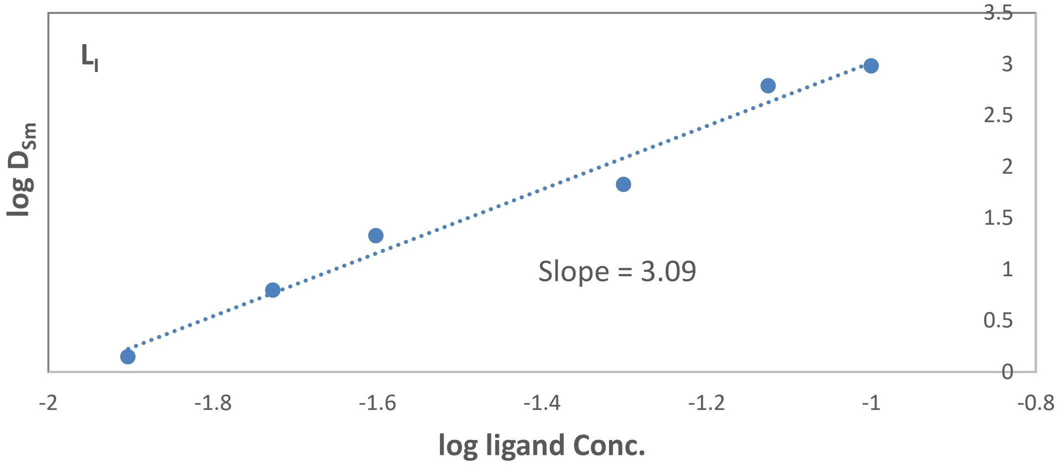


Figure 4. 22. plot of logD$_{Sm}$ vs log ligand concentration L$_I$

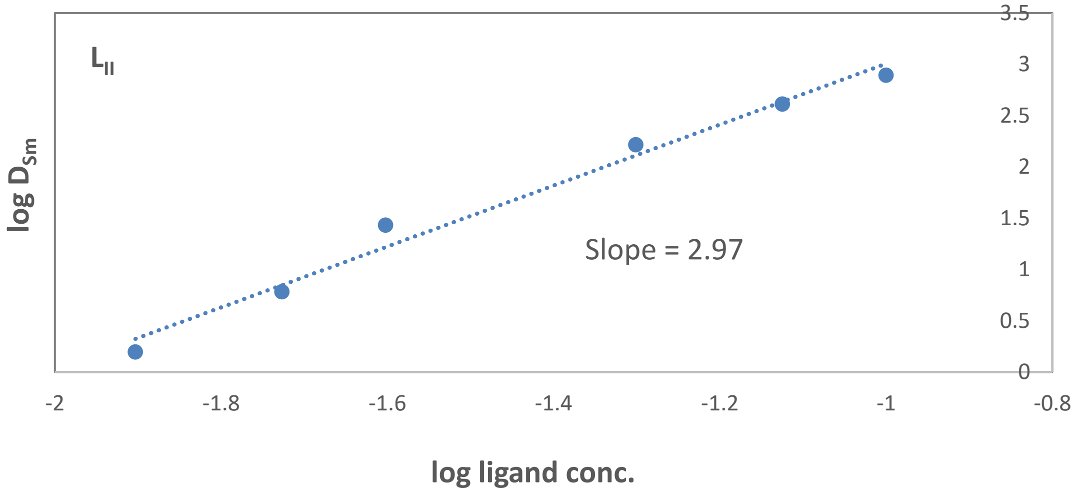


Figure 4. 23. plot of logD$_{Sm}$ vs log ligand concentration L$_{II}$

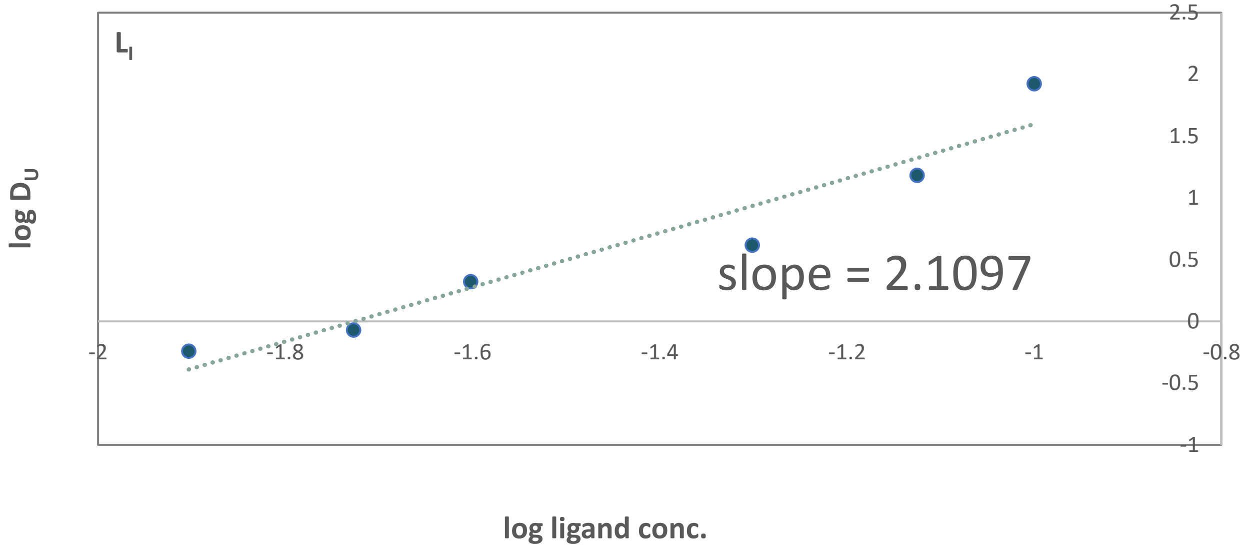


Figure 4. 24. plot of log D_U vs log ligand concentration using L_I

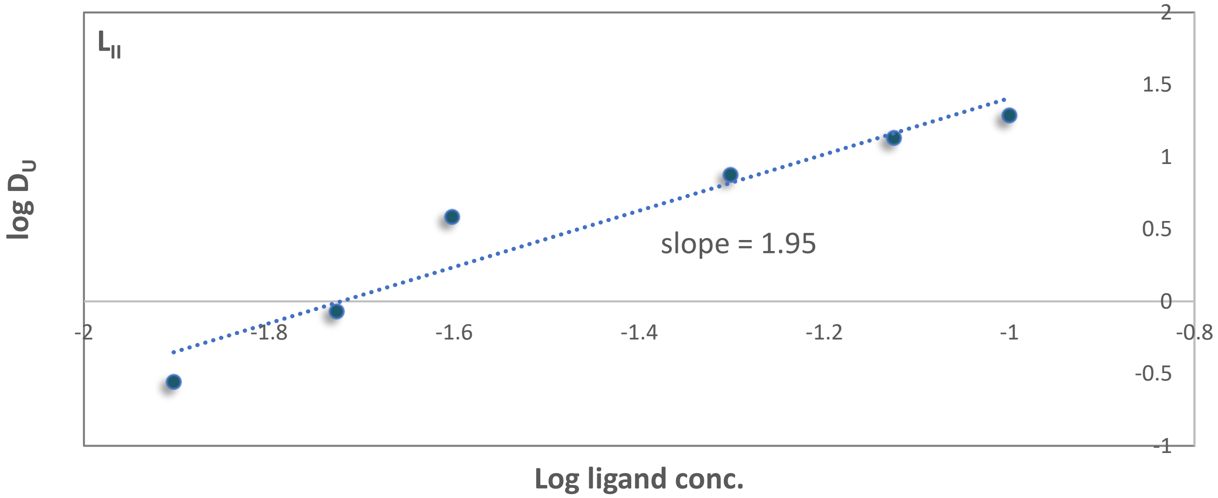


Figure 4. 25. plot of logD_U vs log ligand concentration using L_{II}

The slope of 2 was observed in case of uranyl (VI) and suggest the participation of 2 ligand molecules for the extraction of one UO_2^{2+}(VI) ion from the aqueous phase. In task specific ionic liquids, where both the cation and anion are the component of the extractants. The possible extraction mechanism could be solvation process.

4.3.7. Effect of Nitrate Ions Concentration.

The nitrate ions concentration plays important part in the extraction of metal from the acidic aqueous phase. The effect of nitrate ions on the extraction efficiency was determined to explain the extraction mechanism. The experimental study was carried out by using the various concentrations ranges from 0.01 to 3 M $NaNO_3$ in aqueous phase at fixed metal ratio at pH=2, and 4.5 for extraction using L_I and L_{II} respectively. The increase in D_M was observed with the increase in $NaNO_3$ concentration.

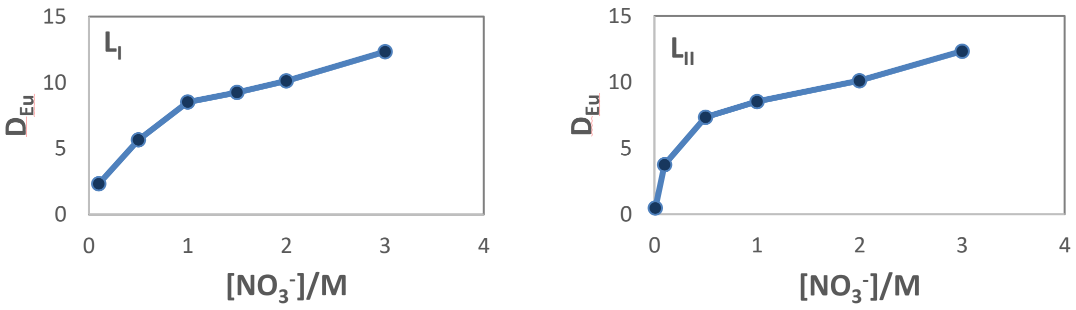


Figure 4. 26 trends of variation in D_{Eu} as function of NO_3^- ion concentration

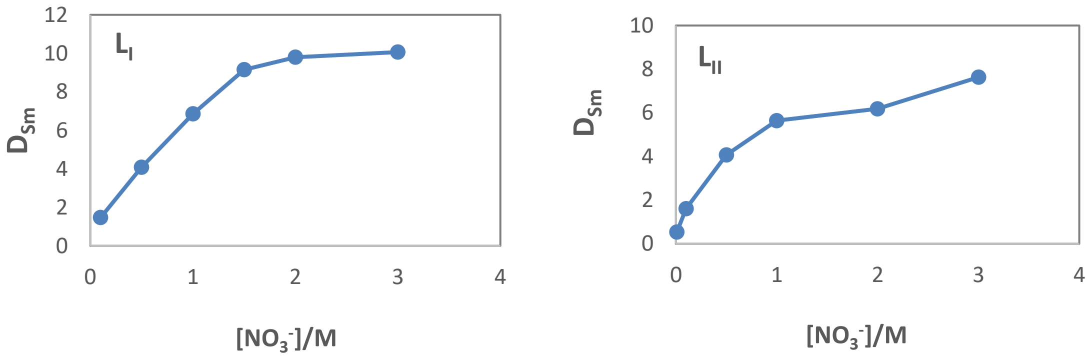


Figure 4. 27. trends of variation in D_{Sm} as function of NO_3^- ion concentration

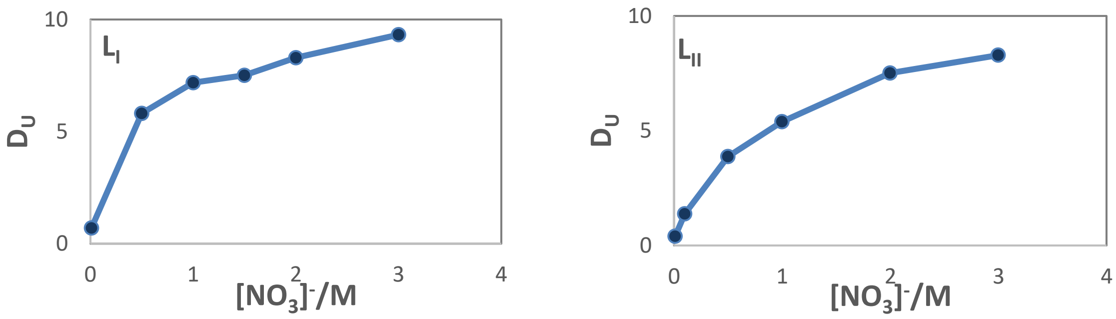


Figure 4. 28 trends of variation in D_U as function of NO_3^- ion concentration

4.3.8. Stripping Studies

The reusability of the extractants is always important for the effective use of extraction system for the radioactive waste management. The loaded organic phases of both the extractants i.e. L_I and L_{II} were equilibrated with equal volume ratio of nitric acid solutions ranging from 0.5 to 4 M.

- The efficient stripping of metal ions from loaded organic phases of extractant was observed at 0.5 M HNO_3 aqueous phase concentration. The complete back extraction was carried out in four stages.

Chapter 5

5. Conclusion

- Two different types functionalized ionic liquid were successfully synthesized.
- These extractants were characterized by FTIR and NMR.
- Extraction study was carried out by using these task specific ionic liquids, for the extraction of Ln(III) and Uranyl ions (VI).
- The Extraction stoichiometry indicates the formation of 1:3 complex for Eu(III), Sm(III), and 1:2 complexes for U(VI) ions.
- Efficient Stripping of the loaded ionic liquids was carried out by using 0.5M HNO_3 aqueous phase.

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