Synthesis of Mono- and Di-ionic Liquids for Extraction of Pb(II) & Co(II) from Waste water

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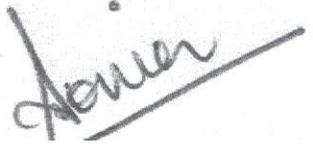
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MS THESIS WORK

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To my supervisor, Dr. Mudassir Iqbal, Family
and Friends

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ABSTRACT

Two Glycolamide based functionalized ionic liquids having imidazolium cations namely L_I (mono-ionic) and L_{II} (di-ionic) were synthesized for the extraction of Pb(II) and Co(II) from waste water. The synthesized ligands were characterized by FTIR and ^{1}H NMR spectroscopy. The extraction efficiency of both mono- and di-ionic liquid was evaluated in terms of contact time, pH of the aqueous phase and metal ion concentration. The metal extraction was performed at pH range of 2, 4, 6, 8 and 10 whereas, at contact time of 15, 30, 45, 60 and 75 mins. The optimized pH of 4 and equilibration time of 75 mins was further utilized for extraction at various metal ions concentration (50, 100, 150, 200 and 250 ppm). L_I exhibited low equilibration time as compared to L_{II} whereas, both ligand showed maximum extraction at a pH of 4. A very high extraction efficiency of upto 99% for both metals was observed with L_I and L_{II} under optimized conditions.

CHAPTER 1

1. INTRODUCTION

1.1   Ionic liquids

Ionic liquids are the liquids which are composed of ions, usually a large bulky organic cation and a smaller organic or inorganic anion. Usually ionic compounds are present in the form of solid but here the asymmetrical organic bulky cation frustrates the crystal structure which renders the lattice energies very low causing ILs to exist in the form of liquids at room temperature. Ionic liquids have have a great variety of designability because of the wide range of anions and cations. They are sometime recognized as thirds class of solvents after organic solvents and water. They possess unique set of properties, such as:

- Non flammability
- Non- toxicity
- High thermal stability
- High ionic conductivity
- Non-coordinating polar nature
- Ability to dissolve organic and inorganic compounds.

The properties of ionic liquids depend upon basicity/acidity of the anoins/cations, coulombic and wander wall interaction between ions of the ionic liquid. [3] Following is the example of some typical anions and cations. [1]

1-alkyl-3-methyl imidazolium

N-alkyl pyridinium

tetra alkyl ammonium

tetra alkyl phosphonium

$$[PF_6]^- \quad [BF_4]^- \quad [CH_3CO] \quad [CF_3CO]$$

$$[(CF_3SO_2)_2N] \quad [CF_3SO_2] \quad [Al_2Cl_7]$$

$$[NO_3] \quad Cl^{-1} \quad Br^{-1} \quad I^{-1}$$
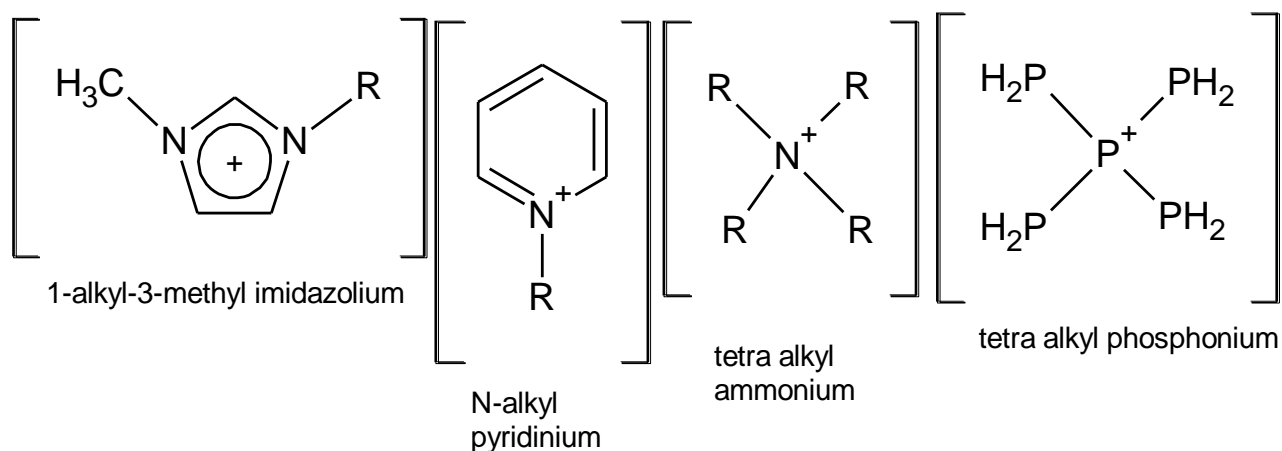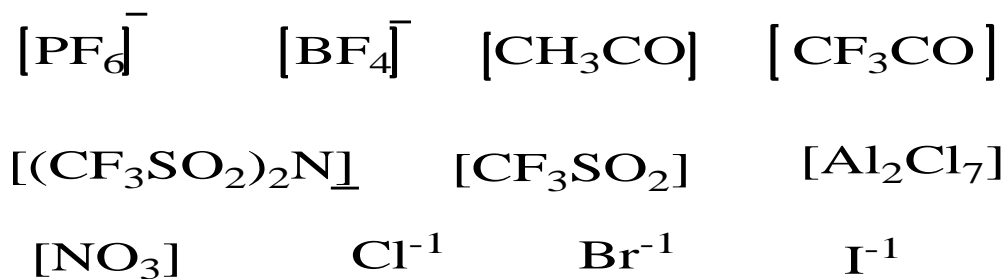
The most fascinating property of the ionic liquids is their negligible vapour pressure as compared to highly volatile organic solvents making them superior solvents than organic solvents. That is why ILs are considered green alternative to organic solvents with low volatility. The composition of ionic liquids can be selected to fine-tune their chemical and physical properties. Due to the environment friendly and versatility, ILs have replaced organic solvents in many chemical processes e.g. purification and separation, reaction media and in biochemical and chemical catalysis. [2]

Although the term of 'molten salts' was introduced in 1800s but it wasn't until 1914 when Walden first studied the properties of IL, alkylammomiun nitrates. After that Gordon also critically reviewed the ILs but it was the work of Wilkes and team which introduced the ILs to their popularity which they have today. The report of first IL as catalyst, chloroaluminates, came in 1986 but it was later dropped due to high moisture sensitivity of these ILs. In 1990, Wilkes and team solved this problem by replacing the moisture sensitive aluminium chloride with other moisture stable anions such as hexaflorophosphate or tetrafloroborate. This was a major step towards the introduction of moisture stable ionic liquids and ILs have seen burst of fame after that seminal report by Wilkes and co-workers.

Typical cations for ionic liquids includes imidazolium, thiazolium, triazolium, phosphonium, ammonium and pyridinium species. These cations are combined with weak anions to give room temperature ionic liquids, RTILs. Examples of anions include hexaflourophosphate, triflimide, tetraflouroborate and dicyanimide.

Hexaflourophosphate and tetrafloroborate have been used extensively, but great care has to be taken as they can easily go hydrolysis to give phosphoric acid and boric acid respectively. The list of possible anions is growing at a rapid rate giving scientist a wide range of anions to choose from, also the diversity of the ILs is increasing in return. With the increase in diversity of nature of ionic liquids and their properties, their applications are also varying and although much attention has been put to them as solvents in the past but their uses are much more diverse which are still to be discovered.

1.2 Task specific ionic liquids

In 1999, Davis and his team worked on functionalizing the ionic liquids by introduction of functional group into the ionic liquid molecule. The external functional group is covalently attached to either anion or cation, or both. TSILs have received much attention over the past few years due to their unique properties.

- It is possible to control the physical and chemical properties depending upon the need of user by introducing choice of functional group into the IL.
- When used in reaction media, they have the ability to covalently bind or activate the dissolved substrate catalytically.
- They also show progress in the field of catalysis as they provide large surface area and kinetic mobility as compared to solid supported catalysts.
- As ILs are used as solvents, introducing new functional groups in the molecule change the solvent parameters for the IL, making it an even better solvent for the solute.
- Example: ILs having functional group , sulfonic acids were used as a catalyst and solvent for the process of esterification, in another example, functionalized salts of immidazolium can absorb CO_2 from streams of gas.

Moreover the use of TSILs in the field of organic synthesis, chiral induction, catalysis, nanomaterials synthesis and stabilization, as modifiers and in electrochemical chemistry is also reported. [4]

1.3 Applications

Ionic liquid have been exploited for many uses, some of these are as follows:

1.3.1 Electronic applications:

Ionic liquids are used in electrochemical devices like lithium ion batteries(LIB), electric double-layer capacitors (EDLC), dye-sensitized solar cells (DSSC) electrolytes used in batteries, light emitting cells , devices for charge storage, and electrochemical cells etc. by using their attribute of non-flammability and non-volatility, they can be used as alternative of typical electrolytes. The high ion conductivity of ionic liquids can be exploited for their use in batteries resulting in better performance. ILs are used in electrodeposition as well.

1.3.2 As Solvents:

The increased demand of environment friendly alternatives for harmful, flammable and highly volatile solvents makes way for the use of ionic liquids as solvents in the field of organic synthesis, separations and purification. The non-toxicity and low volatile nature makes them better solvents for chemical processes. Moreover they can be easily recovered at the end of reaction and re-used. Due to diverse variety of anions and cations that form IL, their solvent properties are also diverse making them extremely versatile.

1.3.3 Extraction of metals:

Determination of analytes at trace levels is required for assessment or research purposes. There are only a few techniques which assess metal ions in desired samples at even trace levels. Use of ionic liquids has revolutionized the uptake of metal ions from contaminated samples through liquid-liquid extraction (LLE). This attribute of ionic liquid has benefitted the process of reducing heavy metal toxicity from water bodies, treating harmful metals from nuclear waste and uptake of toxic metals from waste produced by industries and mining activities.

1.3.4 CO_2 absorbents:

The greenhouse effect caused by the capture of CO_2 is causing the climate to change. Thus the treatment of CO_2 produced through different activities such as process of photosynthesis, combustion of fuel from industries and vehicles etc. is very important. Ionic liquids cannot be used in the gaseous phase but due to their non-inflammability, they can be used at a wide range of temperatures thus help in the absorption of CO_2.

1.3.5 Lubricants:

Lubricants are being used in many processes, especially mechanical, to reduce friction between mechanical bodies and to improve their energy efficiency. Ionic liquids also find their use as lubricants in mechanical systems due to their low vapor pressure and ability to be stable in vacuum. [9]

1.3.6 Analytical chemistry

Ionic liquids find their use in preparation of samples for chemical processes, in separations through solvent extraction, in chromatographic electrophoretic separation and detection etc.

1.3.7 Polymers:

ILs are used as grafted components of solvents for the process of polymerization, unusually as components of polymers and modifiers for morphology of polymers.

1.3.8 Nanomaterial:

Ionic liquids are used for the synthesis and stabilization of nanomaterial.

1.3.9 Bio refinery:

Ionic liquids can dissolve biological compounds such as lignin, cellulose and hemicellulose, thus making their use in the field of bio-refinery as well.

1.3.10 Spectroscopy:

Ionic liquids have been exploited as matrices for Mass spectroscopy (MALDI).

1.3.11 Utilization of biomass:

Ionic liquid is used as non-petroleum based fuel for the utilization of biomass. It is also bio-renewable.

1.3.12 Absorption refrigeration:

Ionic liquids are being used as refrigerants due to their high density, low volatility, and high chemical and thermal stability.

This list of applications does not represent the true potential of RTILs, with the ongoing progress in the field of RTILs, this list is only expected to grow further and become more diverse. [5]

1.4 Ionic liquids as metal extractants

To determine the analytes from a sample at trace level e.g. contaminated soil and water is required for the monitoring and assessment of the quality of soil and water sample, as well as, it is being done by environmental scientists for research purposes. There are only s few techniques which can sense the trace amounts of these analytes from the sample. And thus a beginning step of preconcentration is required in many cases. Ionic liquid solve this problem as well.[7]

The property of ionic liquids to extract metal from given sample when mixed with molecular diluents (ME) is very progressive in the field of metal extraction as they extract a wide range of metals from toxic heavy metal to harmful actinides/lanthanides from nuclear waste. When ionic liquid is mixed with a ME, it act as a acid/base coupling bi-functional ionic liquid (ABC-BIL) playing an active part in the extraction of metals. The separation behavior, preparation of sample and mechanism of extraction of IL-ME system can be compared to the other conventional methods. Other aspects like stripping studies, re-generation of the IL and enrichment of extraction are under study [6]

Organic analytes from aqueous samples can easily be extracted by ILs on the basis of their hydrophobicity as well as ILs hydrophobicity because they both will tend to stay in organic phase. But in the case of metals, the extraction is low if only the IL is used because IL tends to stay in organic phase and the metal tends to stay hydrated in the aqueous phase. Thus an extract molecule was required which can make complexes with the metal and staying completely in organic phase at the same time under all conditions. This problem was solved by the introduction of Task specific ionic liquids (TSILs) which make complexes with the metals but remain in the organic phase [8]

Apart from the liquid-liquid extraction(LLE) , the newest trends and innovations in liquid phase microextraction, are as follows :

- in situ solvent formation microextraction (ISFME)
- in situ sorbent formation microextraction (ISSFME)

- Solvent bar microextraction (SBME)

- single-drop microextraction (SDME)

- hollow fiber liquid-phase microextraction (HF-LPME), and

- dispersive liquid–liquid microextraction (DLLME)

- vortex assisted ionic liquid based liquid–liquid microextraction technique (VALLME)

All of these modified techniques differ from conventional methods in automation or miniaturization, the use of ultrasound or agitation and electrochemical methods. [7]

1.5   Pollution

Pollution is caused when a substance having harmful effect or toxicity enters the environment. These substances termed as pollutants can be in the form of chemicals or energy e.g. noise. Environmental pollution is the biggest challenge we are facing today as it is affecting world's air, soil and water quality drastically which indirectly affects all the living organisms including humans, animals, aquatic life and plants etc.

1.5.1 Causes

There are many causes of pollution like industrial waste in the form of effluents in water as well as gases from chimneys into the air. The combustion of organic matter as fuel consumption as well as in generation of electricity. The use of agricultural chemicals, pesticides, fertilizers etc. that cause all three types of pollution i.e. they contaminate soil and seep down to underground water storage, also harmful gases are release by their action causing air pollution. Natural causes like acid rain and natural seeping of rocks also contribute to the environmental pollution.

1.5.2 Types

There are many types of pollution of which three main types are discussed mostly;

1. Water pollution
2. Land pollution
3. Air pollution[9]

1.6　Water pollution

Water pollution is caused when harmful substances enter the water bodies like lakes, oceans etc without the adequate treatment causing harmful effects for the aquatic life and also humans and animals when they use that water.

1.6.1　Sources

They can be divided in two categories:

- **Point sources : w**here pollutants come from identifiable single, source. It is also called localized pollution such as ditches, drain from industries/houses, pipelines carrying harmful material, some channel, tunnel etc.
- **Non-point sources**: where the pollutants are introduces from dispersed, broadly distributed sources (often difficult to identify) e.g. snowmelt runoffs, rain, leaks, sediment erosion and spills etc.

1.6.2　Toxic heavy metal water pollution

Toxic heavy metals contaminates the water bodies with its potential toxicity especially when talked in context of environment. The most harmful heavy metals are **arsenic, lead, mercury and cadmium.** Following these more harmful metals are **chromium, nickel, cobalt, manganese, zinc, copper, silver, selenium, thallium and antimony.**

Sources

Metal pollution in the water is caused by the industrial waste being dumped into the water bodies, their smoke in the air, metal particles coming from coal burning power plants, etc. Mining companies also contribute to the release of heavy metals in the water by their drainage system. Their drainage system also contaminate the underground water. Natural causes like weathering of rocks also results in the addition of these metals into the water seeping through them. Another natural cause is the acid rain which bring down harmful metals along with rain on the soil and in water. [10]

Harmful effects

Heavy metal toxicity can result in

- damaged mental and central nervous function
- lower energy levels
- damage to blood composition
- lungs
- Kidneys
- Liver
- physical, muscular inactivity
- Neurological degenerative processes such as multiple sclerosis, Parkinson' disease Alzheimer's disease, and muscular dystrophy.
- Uncommon allergies
- Cancer (long exposure to certain metals) [11]

1.6.3 Cobalt

Cobalt is widely distributed in our environment and it is also needed as a micronutrient by humans as part of vitamin B. but excess quantity of cobalt is harmful for humans as well. When it is taken up by plants or animals, it is accumulated in their bodies causing following harmful effects:

- Vomiting and nausea
- Vision problems
- Heart problems
- Thyroid damage
- Pulmonary disorders (asthma, cough, shortness of breath)
- Hair loss
- Diarrhea
- Cancer (when exposed to radioactive cobalt) [14]

1.6.4 Lead

Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Although lead occurs naturally but human activities generates high concentration in the environment that is harmful. It is introduced as a result of gasoline used in cars as fuel, through the leaded pipes when their corrosion starts and also paints containing lead. The salts of lead are produced which are harmful to dispose off as metal are non-biodegradable and cannot be destroyed.

Harmful effects on lead on health are:

- Disruption of the biosynthesis of haemoglobin and anaemia

- A rise in blood pressure

- Kidney damage

- Miscarriages and subtle abortions

- Disruption of nervous systems

- Brain damage

- Declined fertility of men through sperm damage

- Diminished learning abilities of children

- Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity[13]

1.7   Heavy metal removal

Due to high toxicity and fatal hazards of the heavy metals in water, their removal has become a huge concern, different approaches are being used to process contaminated or polluted water to get rid of these metals. Some of the conventional methods are listed here:

1. Physio-chemical methods
2. Chemical precipitation

3. Solvent extraction

4. Coagulation and Flocculation

5. Electrochemical Treatments

6. Ion Exchange

7. Membrane Filtration

8. Electro dialysis

9. Biological Methods [14]

CHAPTER 2

2. LITERATURE REVIEW

2.1 Introduction
2.1.1 Ionic liquids

Chemical industry contributes to everyday life commodities from household items, plastic, detergents to life saving medicines but it also produce some harmful wastes, effluents and emissions which are highly pollution and jeopardizes the environment we are living in. From the past decades, scientists have been searching for "greener" options for synthetic as well as catalytic purposes which are environment friendly and cost effective.

Ionic liquids provided solution to these problems by providing sustainable green approaches in chemical reactions. This is because of unique physical properties such as low flammability, low volatility, non-coordinating polar nature and their ability to solubilize many inorganic and organic compounds. These properties make ionic liquids suitable green option for synthesis, separations and catalysis.

Although the term IL is recently introduced but its history goes back to 1914 when it was first reported by Walden, he reported IL [EtNH$_3$][NO$_3$]. Later on Gordon reviewed further development in the field of ILs in 1969, but it was the work of Wilkes and co-workers which lead to increase in popularity of ILs in the field of extraction media. In 1985, first successful attempt to use ILs, dialkylimidazolium chloroaluminate, as catalyst of Friedal-Crafts reaction was reported. Earle and Seddon also did the pioneering work of engraving ILs to their well-known versatility.

2.1.2 Task specific ionic liquids

It was Davis and team who first worked on designing IL in such a way that it reacts with solute differently e.g. thiazolium IL could work as solvent as well as catalyst in benzoin condensation. These ILs were named as "task specific ionic liquids" in which the cation or anion of the IL was covalently teethered with any functional group. This can be considered as solid supported catalyst but with the added benefit of large surface area and more kinetic mobility.

This class of ILs gained much popularity because it was possible to design the ionic liquid according to one's requirements with the composition of that IL depending upon desired chemical, physical and biological properties.

Moreover attaching a specific functional group to IL is also helpful as it changes the solvent parameters like polarizability, polarity basicity and acidity of that IL, making it helpful to design suitable solvent for a specific reaction.

The first detailed review on the synthesis and applications of TSILs was done by David in 2004 which explained their use in catalysis, organic synthesis, electrochemistry and separations.

Then functionalized imidazolium TSILs were investigated by Lee. and Winkel et al. Much work has been done on the TSILs in last 5-7 years enlightening more applications of TSILs everyday. [4]

2.2   Ionic liquids for heavy metal extraction

Raphlin Leymaa and coworkers studied extraction efficiencies of novel phosphonium and ammonium ionic liquids' derivatives with thiosalicylate. The extraction of cadmiuim, zinc and copper was evaluated with the help of six ILs. Flame absorption spectroscopy (F-AAS) was used to investigate the extraction efficiency using model solutions (pH 7; 0.1 M $CaCl_2$). Higher efficiency was observed with the phosphonium based ILs i.e trihexyltetradecylphosphonium 2-(propylthio)benzoate [P66614][PTB] for copper, 2-(benzylthio)benzoate [P66614][BTB] for cadmium and [P66614][BTB] for zinc.[15]

Sonja Platzer *et. al* evaluated time-resolved extraction effeciency of eight thioglycolate based task-specific ionic liquids (TSILs) for the heavy metals, cadmium and copper. Distribution ratio for these metals was studied which was as high as 1200. Leaching behavior of these hydrophobic TSILs was also studied by TOC (total dissolved organic carbon) measurements. Recyclability was ensured for both metals by successful recovery process. [16]

Sonja Platzer *et. al.* also studied extraction of nickel, cobalt and zinc with the help of two thioglycolate-based ionic liquids (ILs); methyltrioctylphosphonium S-hexyl thioglycolate [P1888][C6SAc] and methyltrioctylammonium S-hexyl thioglycolate[N1888][C6SAc]. They

showed very good extractability for these metals and distribution ratio was highest for zinc i.e. 2000. Stripping studies showed that the compounds could be recycled. [17]

Mohammad Reza Jamali and associates studied in situ solvent formation microextraction (ISFME) methodology for the preconcentration of cobalt in trace amount. 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) was complexed with cobalt and extracted into ionic liquid phase. FAAS was used to determine the final efficiency. The conditions were optimized and limits for detection and enrichment factor and detection was evaluated i.e. .97μg per liter and 50. RSD (relative standard deviation) was obtained as 2.4%. [18]

They also evaluated the cobalt amount in food by using 2-nitroso-1-naphthol as a complexing agent, perchlorate ion as an ion-pairing agent, and bromide as cationic surfactant. FAAS was used here to determine extraction ability and conditions were optimized. The limit for detection was 0.8μg per liter and preconcentration was 50 with RSD value of 2.3%.

The applicability and accuracy of this method was evaluated by comparing cobalt concentration with food and water samples having certified reference for cobalt. [19]

Mahmoud Chamsaz and coworkers proposed liquid–liquid microextraction technique (VALLME) which was vortex assisted for preconcentration of cadmium using ionic liquids. Ionic liquid, 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF6]) and the 8-hydroxyquinoline(oxine) reagent was used as chelating agent. The study was done using many variable such as volume of [Omim][PF6], pH of sample and concentration of oxine. Optimum conditions were obtained and LOD (limit of detection) was 2.9μg per liter with RSD of 4.1%. This method was used to determine the cadmium level in rice, tap water and apple samples. [20]

Maria Fuerhacker *et. al.* investigated the removal of heavy metals (Cu, Cr, Cd, Ni, Zn and Pb) from standard solutions as well as samples of real waste water and activated sewage sludge with the help of phosphonium and ammonium based ionic liquids. The ionic liquids used were [PR4][MTBA], [A336][MTBA], [A336][TS] and [PR4][TS]. The efficiency was negligible with the standard solutions but removal of these metals from waste water and activated sludge was successful with up to 90% for Zn, Ni and Cu. This method was also more successful as compared to conventional methods such as acid extraction, incineration and thermal treatment, etc. [21]

Pape Diaba Diabate and his team evaluated the extraction of Co, Ni, Pb, Cd and Cu with room temperature ionic liquids,RTILs. These Ionic liquids were TSILs which were generated by association between coordinating inorganic anions i.e. saccharinate (sac), chlorosalycilate (ClSal) and dicyanamide (Dca) and derivative of cationic ester of betaine. The results showed that the ILs containing Clsal anions extracted Ni, Cu and Cd with higher efficiency while dicyanamide IL efficiently extracted Ni, Cu, Cd and Cd. The ILs with saccharinate anions selectively extracted Cd. The mechanism if extraction showed involved of both ion pairing and cation exchange processes. The coordination studies for metals was studied with UV-VIS spectrometry. The reusability of the IL was very high as it can be recycled to the extinct of fresh mixture. [22]

Philip Pirkwieser and group investigated the extraction of Ag, Cu, Cd and Pb from sea water and waste water samples which were more successful than from that of aqueous samples. They used TSILs i.e. methyltrioctylammonium 3-hydroxy-2-naphthoate and trihexyltetradecyl-phosphonium-, methyltrioctylphosphonium in two-phase solvent bar micro-extraction (SBME). Different factors like pH, stirring rate, time, volume of IL, organic additives etc. were also studied. A pH of 8.0 gave highest extraction effceincy for all metals. The leaching of ionic liquids in aqueous phase was very minimal. Salanity of the sample also had a positive effect on extraction effeciency especially for Cd. The extraction of Cu and Ag was achieved upto 85% from drinking water whereas natural sea water and hypersaline water gave better extractability for Cd and Ag. This method was proposed as efficient SBME for heavy metals without modify in or pretreating the sample. [23]

Daniel kogelnig and team studied hydrophobic ILs for extraction of Cd. A thiol containing TSIL, tricaprylmethylammonium thiosalicylate, [A336][TS], was synthesized with the help of bronsted acids using cost saving, simple and sustainable route of deprotonation-metathesis and tricaprylmethylammonium chloride. Different aqueous solutions were used and higher efficiency as well as selectivity was achieved from natural river water as compared to standard solutions. [24]

Belen herce sesa and coworkers evaluated the extraction of Ag and Cd from natural saline water with a hollow fiber liquid micro-extraction (HFLPME) system configured by 2SBME . The IL used was liquid N-methyl-N, N, N-trioctylammonium chloride and extractant was kerosene. This system proposed to get higher efficiency for these metals from saline water which was limited before for HFLPME. [25]

They also examined the 3SBME system for preconcentration of Cd from sea water with the IL trioctylmethylammonium chloride, because it has the ability to form $CdCl_n^{(n-2)-}$ through ion exchange. The conditions were optimized at the pH of sea water so that the system can be applied to real samples. The system contained IL dissolved in kerosene with dodecan-1-ol (0.25 M), acceptor solution was 1.5 M HNO_3, and extraction time was 60 mins with the stirring speed of 800 rpm. GF-AAS was used to determine the preconcentration i.e. 65 times and LOD was 0.04nM. [26]

Lisa Fischer *et. al.* investigated the use of phosphonium and ammonium cation based ionic liquids for the treatment of sewage. The removal of the cancerostatic platinum compounds carboplatin and cisplatin, as well as, metal(oids) Zn, Sn, Pt, Pb, Ni, Cr, Cu, Hg, Cd, As, Ag was observed through micro extraction. The results were evaluated using LC-ICP-MS and ICP-FSMS. The extraction efficiency for Cu, Hg, Ag and Pt were more than 95% using both ammonium and phosphonium based ILs, whereas all the other metals gave extraction efficiency between 7-79%. [27]

Belen Herce sesa and team worked on the extraction of Ag, Pb and Cd from natural saline water and standard aqueous samples. They used HFLPME with configuration of SBME using the IL trihexyltetradecylphosphonium chloride. Optimum conditions of 800rpm stirring rate, 30 min extraction time and 50% IL in organic solution were established. Leaching of IL into aqueous phase was minimal, as low as 0.1%. F-AAS was used to determine metallic concentrations. The extraction efficiency from saline was very good i.e. 93-95% for Ag, ≈100% for Cd for saline water samples and more than 90% for Pd in all cases.[28]

Masami kumano *et. al.* investigated the extraction of heavy metals such as Cu, Mn, Zn and Cd with the help of IL N,N,-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethansulfonyl)imide. The effect of volume ratio, shaking time and added

chelationg agent; 8-hydroxyquinoline was also studied. Studies revealed that 8-HQ significantly increased the extraction efficiency of these metals as it was well soluble in the IL. When 100 µl of ionic liquid was used, it gave 5 µmol of heavy metals, showing that this system gives good extractability. [29]

Belen herce sesa and team evaluated the extraction of $AgCl_n^{(n-1)-}$ from organic silver in samples from marine water using HFLPME with configuration of SBME using the IL trihexyltetradecylphosphonium chloride. They used 2.5% trihexyltetradecylphosphonium chloride in kerosene inside the fibre with 10% dodecan-1-ol. Stirring time was 30 mins with 800 stirring rate. GF-AAS was used for result determination presenting LOD 0.4ngL^{-1} and linear response of 500 ngL^{-1}. [30]

José A. Lopez-lopez examined the abilities of N-Methyl-N,N,N-trioctylammonium chloride and its 2-(methylthio)benzoate ([A336][MTBA]) and thiosalicylate ([A336][TS]) derivatives, as well as trihexyl(tetradecyl)phosphonium chloride salicylate ([C101][Sal]) and anthranilate ([C101][Ant]) for micro-extraction of Pb, Cu, Cr, Cd, Ag, Pt and Ni from aqueous solutions. Phosphonium based ionic liquids showed higher extraction effeciency in every case except Ag, for which N-Methyl-N,N,N-trioctylammonium chloride showed more extractability i.e. 97%. Leaching was reduced upto 60% by using SBME. [31]

2.3   Conventional ionic liquids

Mark P. Jensen and coworkers studied extraction of lanthanides using ionic liquid 1-butyl-3-methylimidazolium nonafluoro-1-butanesulfonate and extractant 2-thenoyltrifluoroacetone (Htta) in the aqueous medium containing 1M NaClO$_4$. At lower concentration of the extractant, no coordination of lanthanides and extractant was observed but as the concentration of extractant was increased, the cation complexes of lanthanides with Htta(La:tta) species were observed in the ratio of 1:2 and 1:3, and were thus extracted. Whereas in the case of [Cnmim]+Tf2N-, the complex ratio of La:tta as 1:4 as recorded making [Cnmim]+NfO- better solvent for extraction.[32]

Htta
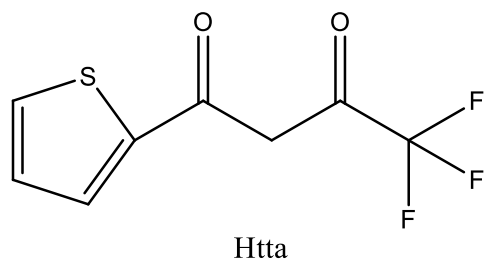
A. N. Turanov and his team studied extraction of rare earth metals into an organic phase from nitric acid medium . the ionic liquid they used was 1-butyl-3- methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (BMImTf2N), and the extractant was *N,N_*-bis(diphenylphosphinylmethylcarbonyl)diaza-18-crown-6, whose efficiency was compared to *N*-(diphenylphosphinylmethylcarbonyl)aza-18-crown-6 and diphenyl *N,N*diethylcarbamoylmethylphosphine oxide . The concentration of IL in organic phase, concentration of extractant and nitric acid in aqueous phase was considered during the study. The D_{Ln} with the IL was calculated to be up to 1000 as compared to D_{Ln} in some conventional organic solvents which were up to .01, .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 IL impregnated polymeric resins in the extraction of lanthanides from nitric acid medium.[33]
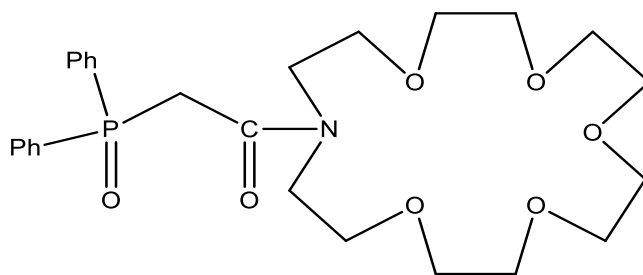
N-(diphenylphosphinylmethylcarbonyl)aza-18-crown-6
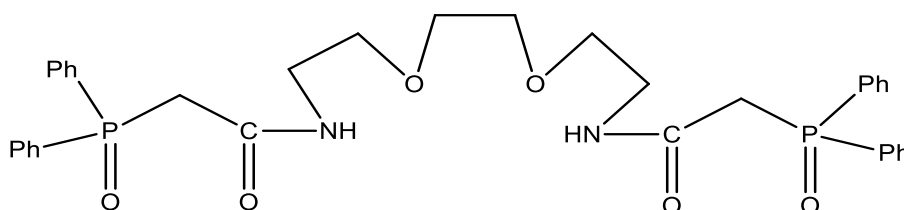
N,N_-bis(diphenylphosphinylmethylcarbonyl)diaza-18-crown-6
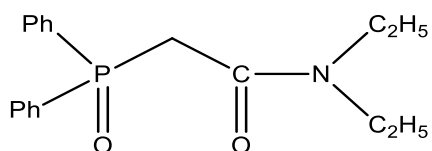


(BMImTf2N

Song Gao and team investigated the addition of ionic liquids in Triton X-114 (TX-114)micellar solution with several anions such as tetrafluoroborate (BF4−), hexafluorophosphate (PF6−) ,bromide(Br−) and bis[(trifluoromethyl)sulfonyl]imide(NTf2−) for cloud point extraction (CPE) of UO_2^{2+} and other lanthanides. The extractants used were 8-hydroxyquinoline (8-HQ), bis(2-ethylhexyl)phosphoric acid (HDEHP), both of which were acidic, and a neutral extractant i.e. tri-octylphosphine oxide (TOPO) was used. The addition of ionic liquid in TOPO showed significant increase in the extraction of target metal at highly acidic 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 C4mimNTf2 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 NTf2- forms a

soft template for UO_2^{2+} ion thus providing a supramolecular assembly to separate UO_2^{2+} selectively and effectively. [34]

Triton X-114

TOPO

8-HQ HDEHP
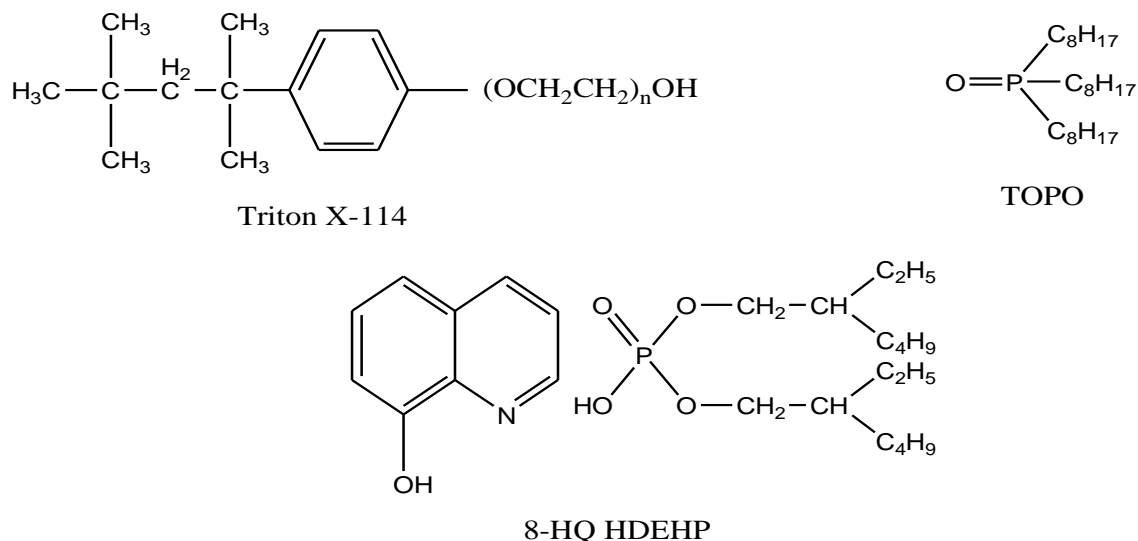
Jing Fu et al reported the extraction of Th by the β-diketone extractant 2-thenoyltrifluoroacetone (HTTA) in aqueous medium by adding the ionic liquid 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides (CnmimNTf2, n = 2, 4, 6, 8). Ion chromatograph and log-log plot analysis suggested a neutral complex extraction system. Stripping of the extracted ion was done by supercritical carbon dioxide (CO_2) by monitoring the temperature and pressure of carbon dioxide, polarity and volume of modifiers and extraction time required for efficient stripping.[35]


Htta
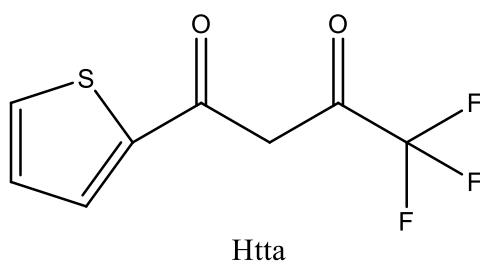
Prasanta K. Mohapatra and team used Diglycolamide-functionalized calix[4]arenes with various modifications in structure for the extraction of actinides such as as UO_2^{2+} , Pu^{4+} , PuO_2^{2+} and Am^{3+} in RTIL 1-n-octyl-3-methylimidazolium bis(trifluoromethane)sulfonamide (C8mimNTf2). The distribution values for Am, Eu, UO_2^{2+} , Pu^{4+} , PuO_2^2 were ranging from 9.37-748, 143-879, .07-.41, 2.88-6.17, and ,1-.60 respectively depending upon the nature of ligand on the extractant. The formation of metal ligand complex was affected by the nature and size of substituents on the

extractant calix[4]arenes (C4DGAs) , the spacer length and acidity of the medium. Lower acidity favored the ligand metal complex formation whereas the high acidity caused ligand crowding at liganding site which lead to less extraction efficiency. Again here the Am showed more symmetrical complex formation with ligands as compared to Eu and hence giving more extraction efficiency. [36]

K. V. Lohithakshan and his team extracted Pu(IV) and Am(III) from nitric acid medium to RTIL by the use of an acidic extractant HDEHP (di-2-ethyl hexyl phosphoric acid) . the 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 °C. At 21°C, 7.2-25.2 for HDEHP/HMIIM and 1.47-19.12 for HDEHP/DMPIIM when the concentration of extractant was varied. The distribution ratios for Pu(IV) were substantial but Am (III) showed poor extraction at higher acidity of aqueous medium(1M HNO3) whereas at pH=3, the extraction of Am(III) was improved. Thermodynamic parameters were also calculated by carrying out the procedure at various temperatures. [37]


Kotoe Sasaki and fellows reported on the extraction of uranyl ions from nitric acid media by two ionic liquids i.e. [Hbet][Tf$_2$N] (Hbet: Betainium, Tf$_2$N: bis(trifluoromethylsulfonyl)imide)) and [TMPA][Tf$_2$N] (TMPA: N,N,N-trimethyl-N-propylammonium). The results showed a 62% extraction from 0.01M HNO$_3$ to ionic phase [Hbet][Tf$_2$N] but U(IV) was not extracted into [TMPA][Tf^{2}N] phase. This was explained by the complex formation of UO_2^{2+} with COO group of deprotonated betaine (bet). [38]

[Hbet][NTf$_2$]   [TMPA][NTf$_2$]
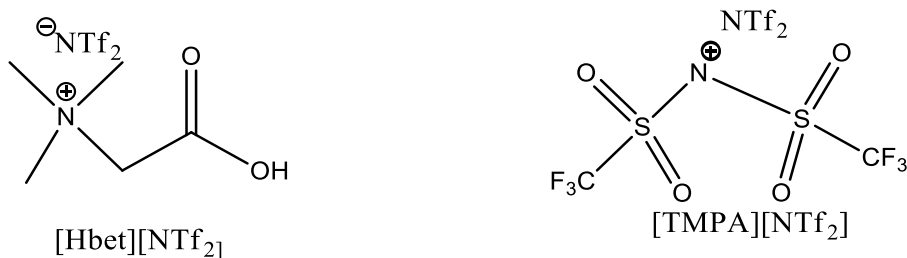
Youwen Zhang *et. al.* studied the extraction of Th^{4+} and UO_2^{2+} from nitric acid medium by using the extractant TODGA and the ionic liquid -alkyl-3-methylimidazolium hexafluorophosphate ([C$_n$ mim][PF6], n = 6 or 8) . The results showed that extraction of these

metals was higher in this IL system as compared to n-DD. The D values for Th^{4+} were around 30 with n-DD and around 55 when the ionic liquids were used. The increase in D values for UO_2^{2+} could also be seen as they rose from around 7 to 13 on the use of ionic liquids. The slope analysis suggested that the extraction was increased by increasing acidity of the medium. The ratio for metal ligand complex was 1:2 at lower acidity while it became 1:1 at higher value of acidity. Stripping of the metals was also done by sodium salt of EDTA. The thermodynamic studies reported the process as exothermic. [39]

Zhao Long and *et. al.* investigated extraction of lanthanides(La^{3+}, Eu^{3+}, Lu^{3+}) using a novel extractant ,6-bis(5,6-dihexyl-1,2,4-triazin-3-yl) pyridine (*iso*hexyl-BTP) in ionic liquid, 1-alkyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide ([C*n*mim][NTf2]). It was observed by slope analysis that the mechanism was cation exchange at lower acidity whereas it shifted to neutral species extraction at higher acidity. Moreover the extractant worked better with shorter alkyl chain of the ionic liquid and lower acidity as the extraction efficiency was 80-100% when the acidity was <0.5 and it decreased as the acidity increased. [40]
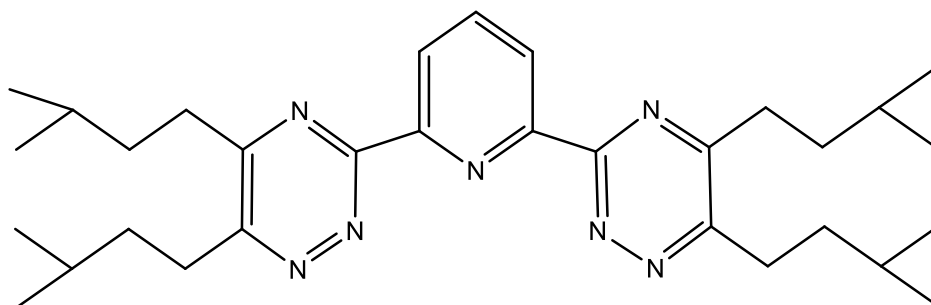

isohexyl-BTP

R.B. Gujar *et. al*. introduced the extraction chromatographic resins for the extraction of actinides/lanthanides. The extractant used was TODGA and the ionic liquid was [C$_4$mim][NTF$_2$]. Three sets of chromatographic resins were prepared in which the composition of extractant and ionic liquid was varied. In the first set, the XC had varying fractions of TODGA (10–30% (w/w)) whereas the fraction of IL (10% (w/w)) was constant. In the second step, the fraction for IL was varied(10–30%(w/w)) whereas the fraction for extractant was kept constant(10% (w/w)) and in the third set, both the IL and TODGA had varying fractions(10–30%(w/w)) . The loading of Europium (III) increased from 8.74 mg/g to 23.66 mg/g when the TODGA conc. was increased from 10-30% but there was no change in loading of the metal when the conc. of ionic

liquid was increased. The distribution coefficients showed that trivalent *f*-elements showed selective sorption over hexavalent *f*-elements over a wide range of pH i.e. 0.01-6M. [41]

Takahiro Mori *et. al.* worked on decontamination of solid wastes from uranium and they used a thermomorphic ionic liquid, betainium bis(trifluoromethylsulfonyl) imide ([Hbet][Tf$_2$N]) 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 conventional (CLLE) as well as homogenous liquid extraction (HLLE) showed almost same pattern. 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$_2$O$_2$. [42]

S. Panja and team reported a novel and selective extractant for extraction of Pu(IV) i.e. bis-(2-ethylhexyl) carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide (BenzoDODA). The extractant behaves differently in RTIL 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imide {[Cnmim][Tf$_2$N] as compared to conventional diluent n-dodecane as the extraction was significantly better in the presence of RTIL. In the care of ionic liquid the mechanism is cationic exchange upto 3M acidity and anionic exchange above 3M. Whereas in n-dodecane the mechanism at all acidities is anion-assisted neutral complex formation. Also the mechanism involves formation of di-solvate specie in RTIL and mono-solvate specie in N-DD. The results are selective at higher pH values, at lower acidities, the selectivity is lost. The distribution values for Pu(IV) in IL with extractant(BenzoDODA) were around 50 and 58 for HNO$_3$ and HCl respectively whereas in n-DD they were <.01 and <10 for HCl and HNO$_3$ respectively.[43]
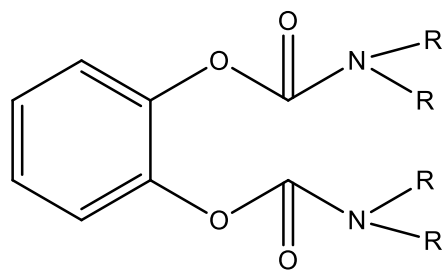

BenzoDODA

Xin Wu *et.al.* worked on the extraction of Uranyl ions with the help of extractant N,N,N',N'-tetrabutylsuccinamide (TBSA) from nitric acid medium into an ionic liquid, [Bmim][NTf2]. At lower acidities, this system showed distribution ratios 20 times larger than obtained in common organic solvents, the D value for UO_2^{2+} is >100 when the HNO_3 is 0.01M and the ratio decreases to <0.1 when the acidity increases to 1M HNO3. This efficiency is however drastically decreased when acidity of the medium increases.[44]


TBSA
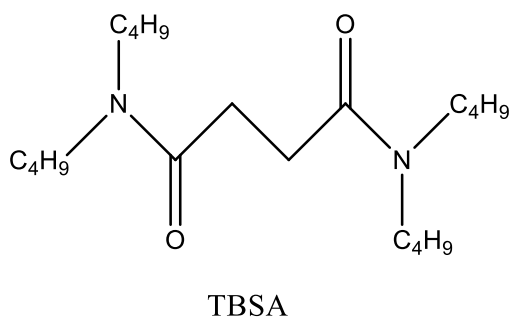
Ajay B. Patil and team used a substituted dipicolinamide extractant, N,N'-diethyl-N,N'-di(para)fluorophenyl-2,6-dipicolinamide(DPA), to extract Am(III), Pu(IV) and Eu(III) from nitric acid medium into ionic liquid([Cnmim][NTf2], n=4,6,8).the D_{Eu} and D_{Am} values were recorded from 0.37-9.45 and 1.22-15.5 respectively. The highest D value for both metals was obtained by using ([C4mim][NTf2]. Further when chlorinated cobalt dicarbollide (CCD) was added into this system then the D value rose to 15.95 and 12.58 for Am (III) and Eu(III) respectively. This was an efficient solvent system as compared to conventional diluents used. [45]
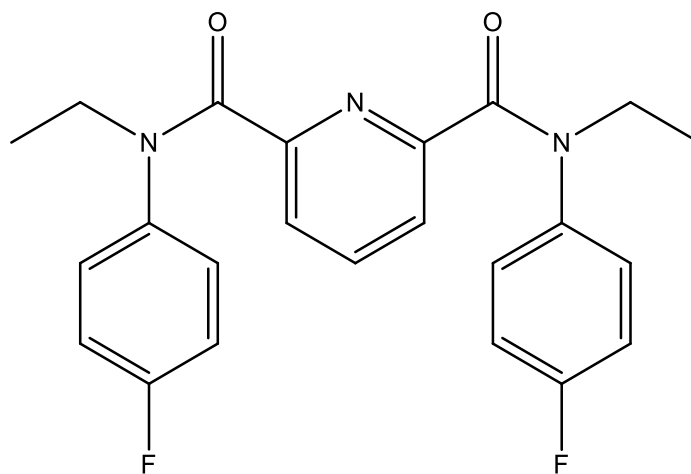
DPA

Hongyu Li *et. al.* synthesized a pyridine based TSIL(1-dibutylphosphorylpropyl-3-pyridine bis (trifluoromethanesulfonyl) imide ([Phos-C3-Pyr] [NTf2])) to extract uranyl ion from acidic medium. This was synthesized by introducing tri-butyl phosphates (TBP) functional structure in cationic part of the Task-specific ionic liquid. The D value for U (IV) rose from 0.7 to 17 as the conc. of nitric acid was increased from 0.1 to 5M. The results showed that this TSIL provides excellent results for the extraction of uranyl ions from acidic medium as the extraction rate and distribution ratios can be obtained more than 90% and 10 respectively. [46]
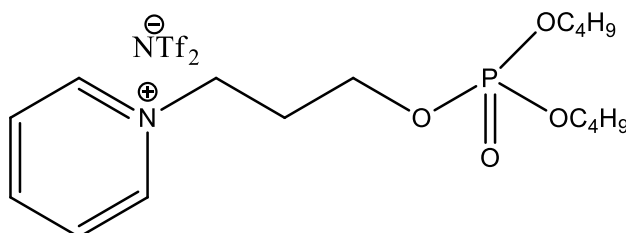
[Phos-C3-Pyr] [NTf2]

Arunasis Bhattacharyya et al attempted to separate trivalent actinides and lanthanides by using ligands such as (bis- (5,6-dialkyl-1,2,4-triazinyl)pyridine (R-BTP)) at room temperature by using an ionic liquid $[C_nmim]\cdot[NTf_2]$ as the diluents (where n = 2, 3, 4, 6 or 8). The D values for Am were very high, 231 and >2000, when Me-BTP was used in $[C_4mim]\cdot[NTf_2]$and $[C_8mim]\cdot[NTf_2]$ respectively. The distribution ratios with Et-BTP were <3 and with *n*Pr-BTP were <1 .A spectacular separation factor of >3000 for Am^{3+} over Eu^{3+} was reported, which was more than any comparable figure obtained from other molecular diluents. This high selectivity for Am^{3+} over Eu^{3+} was attributed to the higher metal orbital (d and f orbital) participation in the

bonding with R-BTP for Am^{3+} as compared to Eu^{3+} which led to selectivity between these metals. [47]
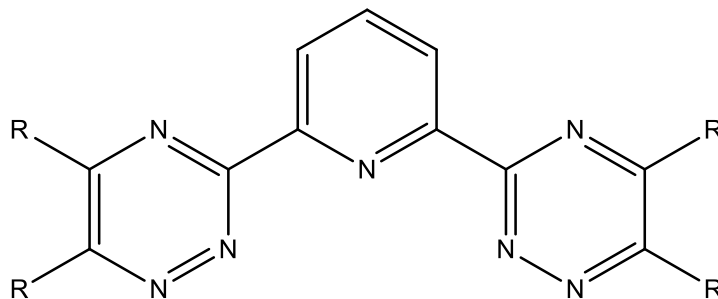
R-BTP

In another work by A. Rout and team, extraction of Am (III) was done from nitric acid into 1-butyl-1-methylpyrrolidinium bis(trifluoro-methanesulfonyl)imide ([C$_4$mpyr][NTf$_2$]) ionic liquid using 1-Phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one (HPMBP) solution as extractant. The distribution ratio of Am (III) in this system was significantly greater than conventional diluent n-DD and any other diketone based extractant as well, as it was also compared to the MPP(3-methyl -1-phenyl-2- pyrazolin-5-one) from which HPMBP was derived, And the result was better with HPMBP. The D value for Am(III) was <10 at 1M HNO_3 concentration but it rose to >1000 when the conc. of nitric acid reached 3M although as comparison to n-DD, the d value for Am(III) was still <100 at 3M. The slope analysis suggested that the mechanism for Am extraction in IL and in n-DD was different. [48]
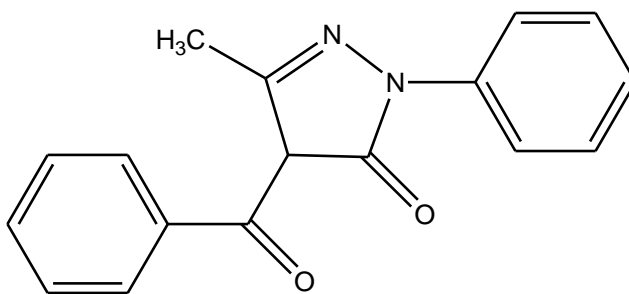

HPMBP

A.N. Turanov and team studied the extraction of uranium(IV) with the help of extractant TODGA as well as a mixture of TODGA with ionic liquid , 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_4$mim][Tf$_2$N]), in the organic molecular diluent, 1,2-dichloroethane. Results showed that the extractability was significantly enhanced when a small

amount of ionic liquid was added along with the extractant. This increase in extraction can be explained by partitioning of the Tf2N_ anions in both aqueous and organic phases. [49]

R. Rama and team synthesized a novel TSIL, diethyl-3-(-3-butylimidazolium)propylphosphoramide bis(trifluoromethanesulfonyl)imide ([BuImPA][NTf$_2$]), and used it to extract Am(III), U(IV), and Pu(IV) from nitric acid media into an RTIL , 1-butyl-3- methylimidazolium bis(trifluoromethanesulfonyl)imide ([C$_4$mim][NTf$_2$]). The study of extraction was measure as function of various parameters such as extractant conc., alkyl chain length of imidazolium group of RTIL, temperature and conc. of nitric acid. The results showed that the extraction of Pu(IV) was increased with increase in the acidity up to 5M then it turned into a plateau. Whereas the extraction of uranium (IV) showed decrease and the extraction of Am(III) was negligible. The slope analysis and study to determine stripping of extracted metals from loaded organic phase was also done. [50]

S. Priya et al worked on sulphoxides with modifications in structure as extractant for the extraction of uranyl ions in ionic liquid, 1-Ethyl- 2,3-dimethylimidazolium chloride and 1-Ethyl-2,3-dimethylimidazolium bis (trifluoromethylsulfonyl)imide. These modified sulphoxides were allyl phenyl sulphoxide (APSO), Benzyl methyl sulphoxide (BMSO), di hexyl sulphoxide (DHSO), and di isobutyl sulphoxide (DISO). These extractants in RTIL were highly efficient for the extraction of target metal as the steric crowding and extended resonance increases the formation of complexes between ligands and uranyl ions. Thermodynamic studies revealed the reaction of be spontaneous, endothermic, and kinetically slow which was due to the viscosity of the liquid. [51]
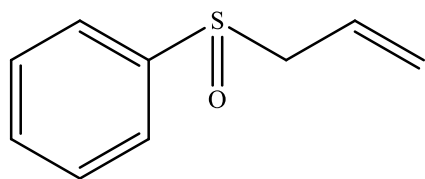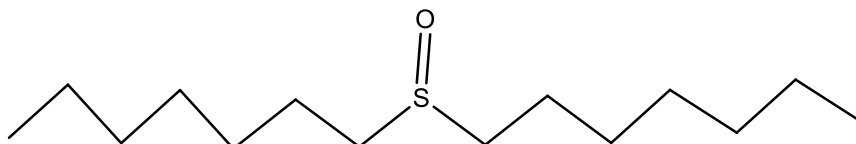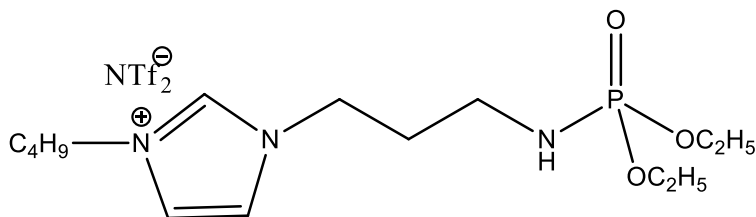
APSO
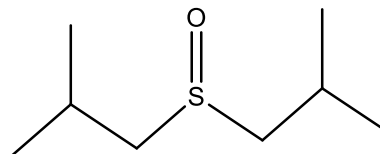
DISO
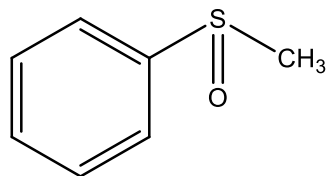
BMSO

BMSO

TSIL- [BuImPA][NTf$_2$]

Manpreet Singh and co-workers reported a selective solvent system for extraction of Thorium(IV). The extractants used were Cyanex-272 (Bis(2,4,4-trimethyl) pentyl phosphinic Acid, Cyanex-923 (tri-n-alkyl phosphineoxide), TBP(tri-n-butyl phosphate) and DHOA(di-n-hexyl octanamide) in ionic liquid, C$_8$mimNTf$_2$ (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide). The extraction studies proposed a solvation mechanism in the case of extractants TBP and DHOA, whereas, cation exchange mechanism was found to proceed in case of Cyanex-923 and 272. The reaction was energetically favorable but kinetically slow. Oxalic acid showed good results for stripping of extracted thorium. [52]
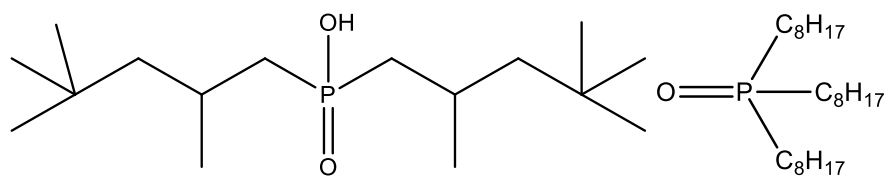
Cyanex-272   Cyanex-923

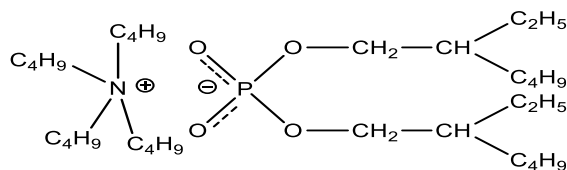## 2.4   DEPH- based ionic liquids

Xiaoqi Sun *et. al.* studied DEPH- based ionic extractants for the separation of rare earth metals. They prepared three functionalized ILs ;   trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][DEHP]),   tetrabutylammonium di(2-ethylhexyl)phosphate ([TBA][DEHP]) and   and trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][DEHP]). The solvent system that was used in this process consisted of diisopropylbenzene (DIPB) 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 [C_6mim][NTf_2] than in DIPB. Also the distribution factor 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. This study developed a potential ionic liquid based extractant system for separation of REEs, where ionic liquid was used as extractant as well as a diluent .[53]
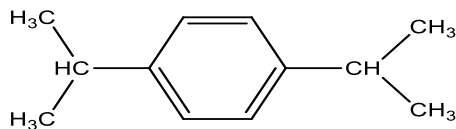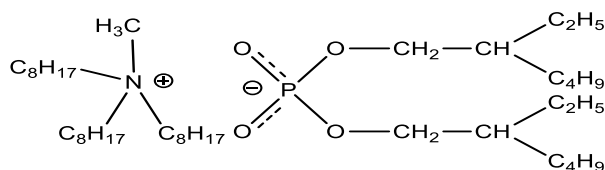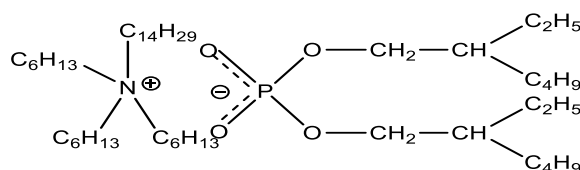
DIBP
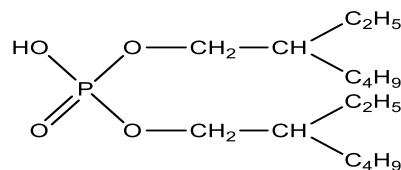
HDEHP

[TBA][DEHP]

[TOMA][DEHP]

[THTP][DEHP]

Alok Rout et al synthesized An Aliquat-336 based ionic liquid i.e., tri-n octylmethylammonium bis(2-ethylhexyl)phosphate ([A3636]$^+$[DEHP]$^-$) and observed its extractive properties for U(IV), Pu(IV) and Am(III). The medium was nitric acid and as the ionic liquid was miscible with n-dodecane, it was used in combination with n-dodecane and 1M TBP (tri-n-butylphosphate) as well, which made a PUREX solvent. It was observed that extraction of Pu decreased with increase in acidity of the medium, the extractability reached a maximum in higher acidic medium as high as 4M, followed by decrease in extraction. They concluded that the distribution ratio of these Pu increased by adding ionic liquid in TBP/n-DD system as compared to simple TBP/n-DD system. On the other hand, the extrability of uranium decreased with addition of IL and Am(III) could not be extracted significantly even with ionic liquid.[54]
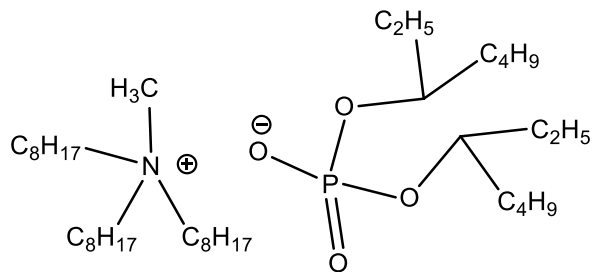
[A336][DEHP]
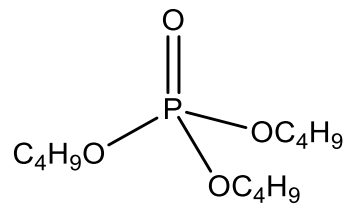
TBP

Arijit Sengupta *et. al.* worked on the extraction of uranyl ions from nitric acid feeds by using tri-n-octyl phosphine oxide (TOPO) in several room temperature ionic liquids such as [C$_4$mim][PF$_6$], [C$_6$mim][PF$_6$], [C$_8$mim][PF$_6$], [C$_4$mim][NTf$_2$], [C$_6$mim][NTf$_2$], [C$_8$mim][NTf$_2$]. The conclusion says that the extractions carried out with ionic liquids carrying C8mim+ as counter cation showed higher extraction while the ionic liquids carrying PF6- as counter anion showed faster as well as high extraction efficiency. 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 they dropped to .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 used for extraction of U (IV) from acidic media (both HNO$_3$ and H$_3$PO$_4$) in ionic liquids but there were no appreciable results.[55]

TOPO   D2EHPA
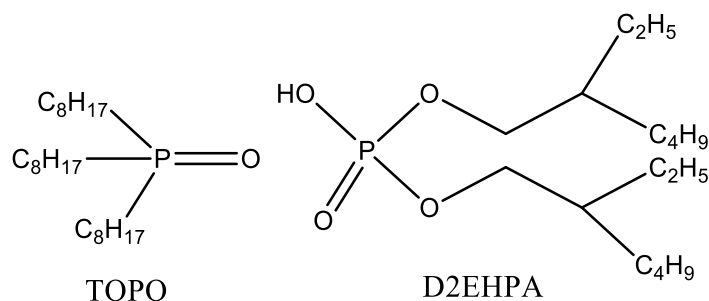
Xiaoqi Sun and coworkers synthesized five new functionalized ionic liquids i.e. tetraethylammonium bis(2,4,4-trimethylpentyl)phosphinite ([N2222][BTMPP]), tetraethylammonium di(2-ethylhexyl)phosphate ([N2222][DEHP]), tetraethylammonium bis(2,4,4-trimethylpentyl)dithiophosphinite ([N2222][BTMPDTP]), tetraoctylammonium di(2-ethylhexyl)phosphate ([N8888][DEHP]) and tetrahexylammonium di(2-ethylhexyl)phosphate ([N6666][DEHP]). The FILs were used as extractants in ionic liquid 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide/ bis(perfluoroethanesulfonyl)imide ([C$_{10}$mim][NTf$_2$]/[BETI]) for the extraction of rare earth metals. The study illustrated their applications in in an IL-based TALSPEAK-like process as they can optimize the process of extraction by adjusting the anions and cations and concentration of FILs in IL, also by varying the acidities of aqueous phase. [56]
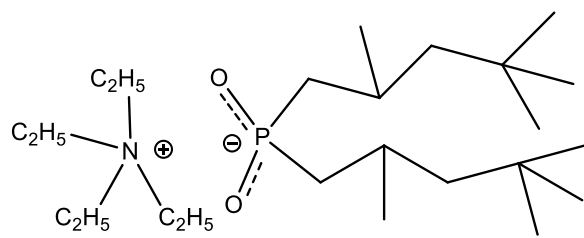
[N2222][BTMPP]
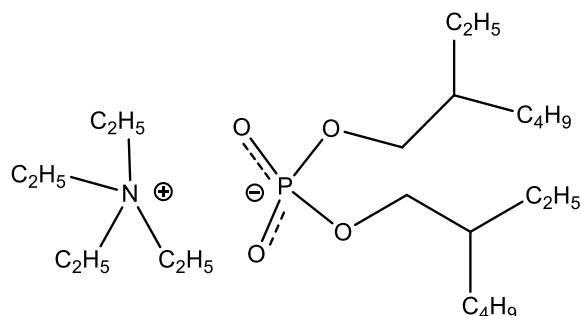
[N2222][DEHP]
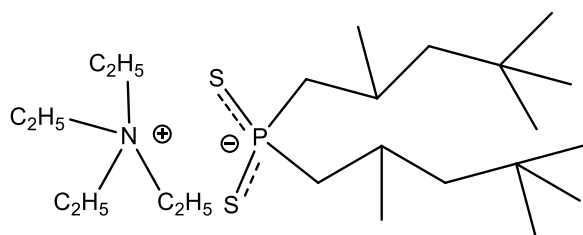
[N2222][BTMPPTP]
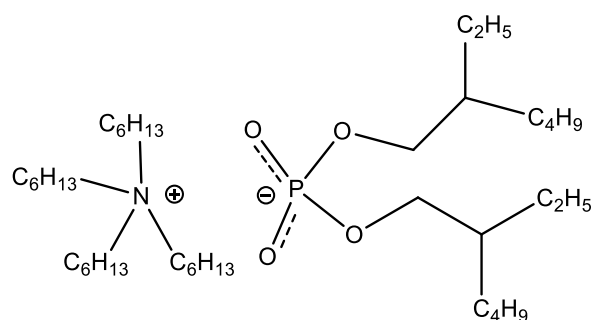
[N6666][DEHP]
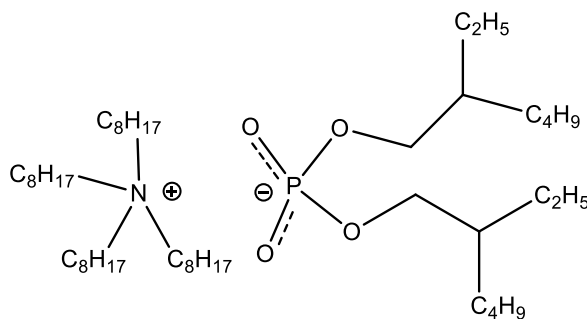
[N8888][DEHP]

2.5 Ammonium based ionic liquids

In another study conducted by Alok Rout and his cworkers , the extraction of Eu(III) was studied in ionic liquids tri-noctylmethylammonium bis(2-ethylhexyl)diglycolamate ([A336]$^+$[DGA]$^-$) and tri-n-octylmethylammonium bis(2-ethylhexyl)phosphate ([A336]+[DEHP]$^-$) and their precursors as well in different molecular diluents as a function of various parameters such as nature of diluent, pH and conc. of ionic liquid . The extraction of Eu(III) was depicted dependence on nature of diluent, as the carbon chain length increases the distribution coefficient decreases. Also the distribution of Eu(III) increased in the ionic liquids as the pH increased and it was significantly higher at pH>2. The separation factor for Eu(III) and

Am(III) remained constant at all pH values. Diethylenetriaminepentaacetic acid (DTPA) was also used to separate Am(III) and Eu(III), SF increased with the increase in concentration of DTPA but after a certain concentration i.e. 10^{-4} M , it started decreasing . These new ionic liquids showed good separation of target metals in conventional molecular diluents. [57]

[A336][DGA]

DTPA

[A336][DEHP]
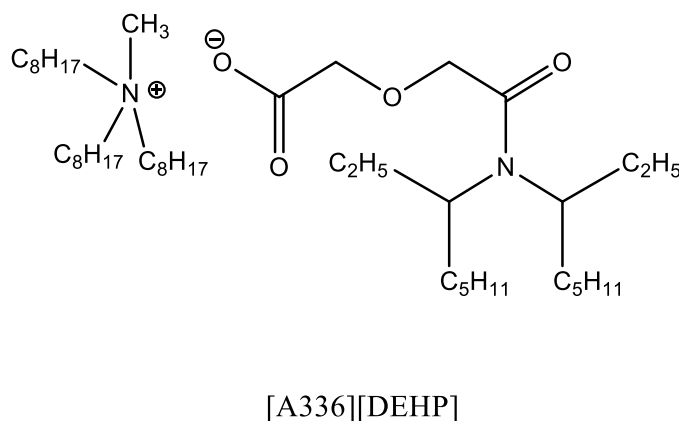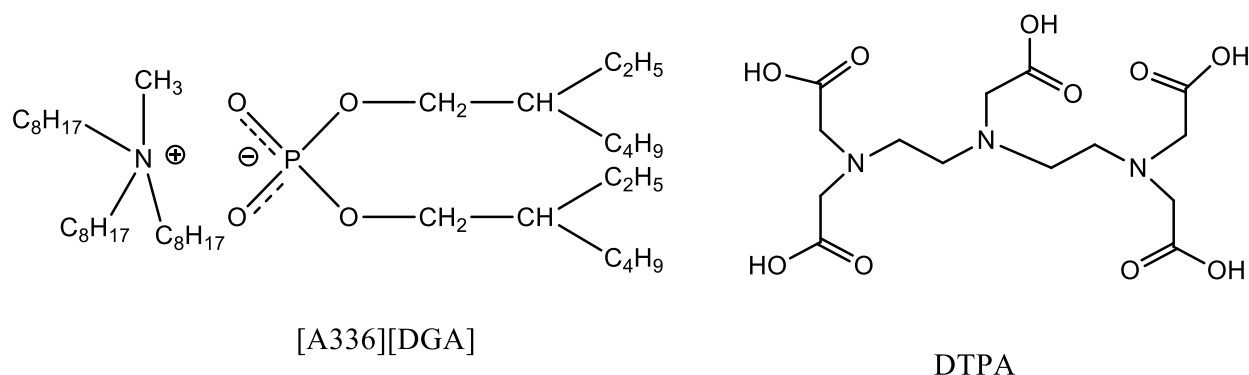
Lin Guo *et. al.* investigated the extraction of rare earth metals from nitric acid medium by using bi-functional ionic liquid extractants (Bif-ILEs) such as   trialkylmethylammonium][di-2-ethylhexylphosphate]   ([A336][P204])   and   [trialkylmethylammonium][di(2-ethylhexyl)orthophosphinate] ([A336]-[P507]) in n-heptane. The extraction efficiency was quite significant and even close to 100% for La and above 80% for Eu. The separation factor depicted that these bi-functional ionic liquids are suitable to extract heavy metals in nitrate medium and light metals in chloride 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 values were Yb/Tm (7.92), Tm/Er (3.36), and Lu/Yb (8.55). [58]

[A336][P204]

[A336][P507]
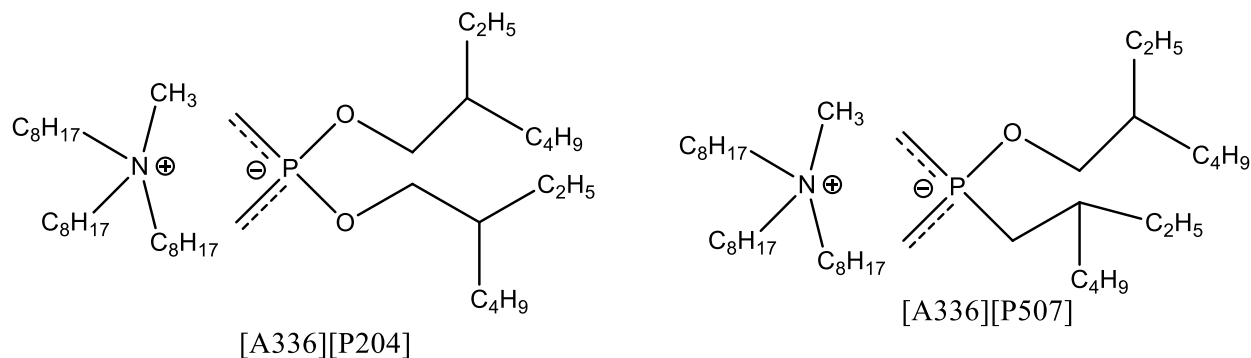
2.6 Malonamide based ionic liquids

Alok Rout and his team also worked on 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. 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, nitric 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 4M nitric acid, the mechanism followed was cation exchange whereas it was anion exchange above 4m nitric acid concentration. . Also the separation of these metals was done and the separation factor was >1000 for these metals from many other fission products. [59]
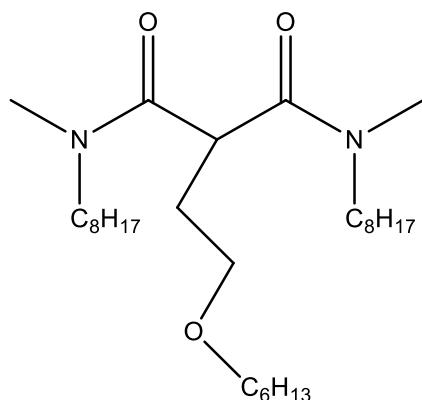
DMDOHEMA

2.7   Amide based ionic liquid

A. Sengupta and coworkers synthesized tripodal diglycolamide (T-DGA) and studied its extraction properties in three RTILs viz. C_4mim^+ NTf_2^-, C_6mim^+ NTf_2^-, and C_8mim^+ NTf_2^-. These results were then compared to extraction results of N, N, N, N'-tetra-n-octyl diglycolamide (TODGA) and it was found that (T-DGA) gave significantly higher distribution ratios. The effect of equilibration time, T-DGA concentration variation and aqueous phase acid concentration variation was studied in these distribution studies. Longer equilibrium time was reported for (T-DGA) which was due to viscous RTIL and slow conformations of (T-DGA) during complex formation with metals. The distribution ratio for Am, when T_DGA was used was 1518 as compared to 208 obtained with TODGA at acidity $1.0x\ 10^{-2}$. The Dam ratio decreased to 0.6 for T-DGA and 0.25 for TODGA as the acidity was increased to 3M. Extraction of Pu^{4+}, Sr^{2+}, Cs^+, UO_2^{2+}, Eu^{3+} and Am^+ was studied with this system. Stripping was done up to .99% in three stages when 0.5 M EDTA in 1 M guanidine carbonate was used. The extraction of 1: 1 complexed species of Am(III) with T-DGA was reported by slope analysis. The extraction was done at various temperatures and thermodynamic parameters were calculated. [60]

R$_1$ =

R$_2$ = C$_8$H$_{17}$

T-DGA
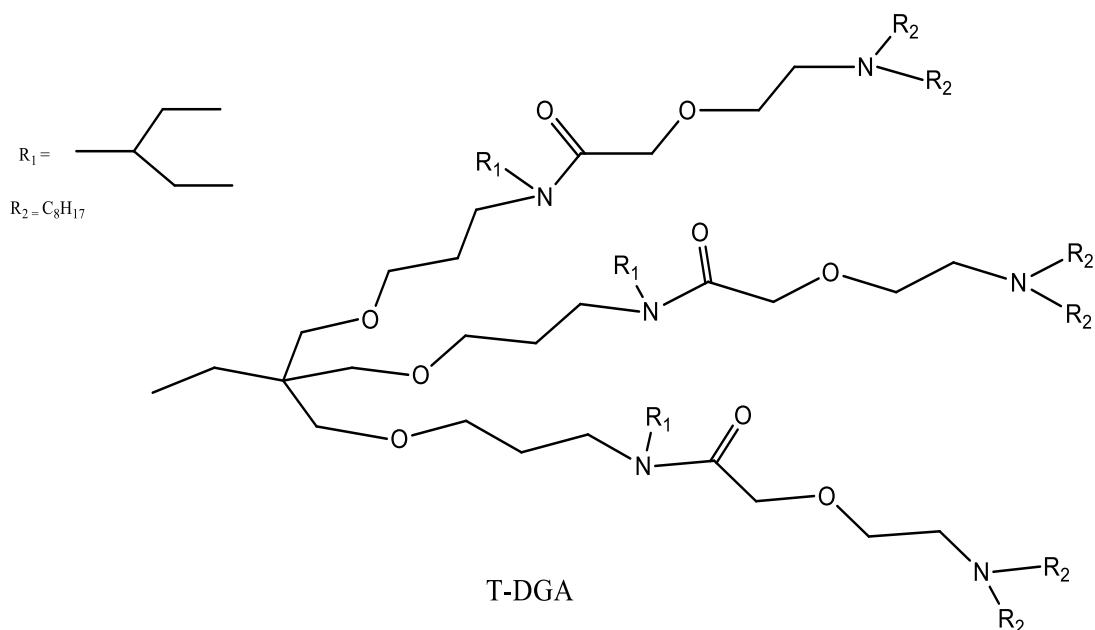
M. E. Mincher *et. al.* reported the extraction as well as separation of lanthanide specifically Am in both molecular diluent and RTIL using diglycolamide N,N,N ,N-tetrabutyldiglycolamide (TBDGA) as extractant . The RTIL used was [C$_4$mim][Tf$_2$N] which showed high extraction efficiency of Am from low acidic concentration whereas the molecular diluent, 1-octanol, showed high efficiency at higher acidic concentrations. This difference was explained by the fact that RTIL extracted ionic nitrate complexes whereas neutral nitrate complexes were extracted by 1-octanol. The distribution ratio for lanthanides from RTIL was recorded up to 50-60 while the D value with 1-octanol reached 90. As far as the separation is concerned 1-octanol showed higher separation coefficient as compared to RTIL. [61]
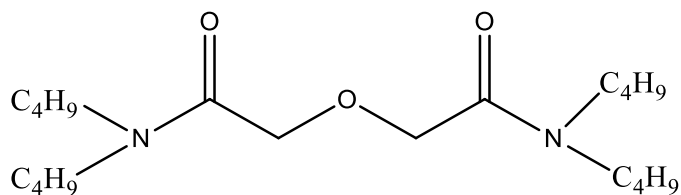
TBDGA

Arijit Sengupta and his fellow scientists worked on the diglycolamide functionalized task specific ionic liquids for the extraction of various actinides such as Pu^{4+}, Am^{3+} , UO$_2^{2+}$, Np^{4+}, PuO$_2^{2+}$ and NpO$_2^{2+}$. They concluded that extraction efficiency for trivalent ions was one order of

36

magnitude higher than tetravalent ions which consequently was higher than hexavalent ions with the same order of magnitude. The D values were .34, 5.9, 3.5, .44, .38 and .32 for Am^{3+}, Pu^{4+} , Np^{4+} , $UO_2^{2+,}$, NpO_2^{2+} and PuO_2^{2+} respectively.   It was also reported that as the acidity of aqueous phase was increased, there was a decrease in the extraction for actinides which supported that there was an ion-exchange mechanism operating in this process. The reaction was rendered spontaneous due to negative ΔG values, which also resulted in high D values. [62]

DGA-TSIL
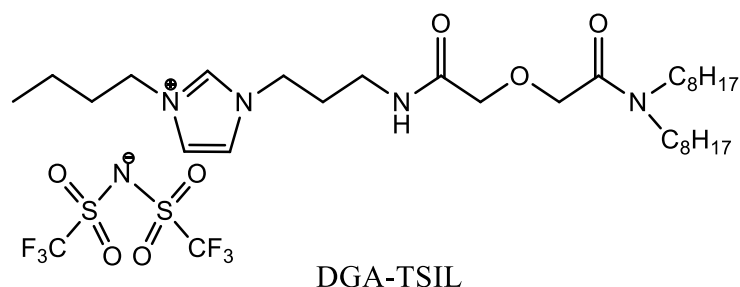
Arijit Sengupta and team also compared the efficiency of TODGA in RTIL for the extraction of Am and Eu. TODGA showed low efficiency for Eu as compared to Am *viz* 1:1 for Eu and TODGA as compared to 1:2 for Am and TODGA. The D values for Am and Eu were 32 and 11 respectively at 3m acidity with the formation constant for Am-TODGA complex to be $4.18x10^8$ M^{-1} whereas $3.31X10^8$ M^{-1} for Eu-TODGA. The slow kinetics for the reaction was attributed to the high viscosity of the RTIL as compared to other molecular diluents. The formation constant and activation energy for complex formation of Am with RTIL was also measured which was comparatively higher than that of Eu explaining the extraction efficiency difference. [63]]

Xiaohong Huang and team investigated the extraction of Pu(IV) from nitric acid medium with the extractant TODGA and ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C_6mimTf_2N). The log D_{Pu} increased till 6.5M acidity then decreased. The highest value for log D_{Pu} obtained was 5.0k at 6.5M HNO_3. The cation exchange mechanism was suggested for this process and thermodynamic parameters were calculated by monitoring the effect of extractant concentration and acidity. [64]

Alok Rout and team worked on the extraction of lanthanides particularly Nd (III) from nitric acid media by using functionalized ionic liquid trioctylmethylammonium dioctyl diglycolamate, [A336][DGA] in a non-fluorinated diluent i.e. trioctylmethylammonium nitrate, [A336][NO_3]. 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 carried as function of many parameters such as concentration of the 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.[65]

[A336][DGA]
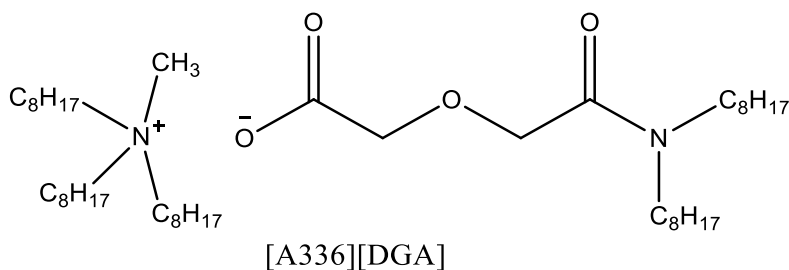
R. Rama and coworkers investigated the extraction of Eu(III) into ionic liquid 1-methyl-3-octylimidazolium bis(trifluormethanesulfonyl)imide ([C8mim][NTf2]) and by using extractant N,N,N',N'-tetra-noctyldiglycolamide (TODGA). The results were compared to the D value obtained in n-DD by the same extractant. At lower acidity D value obtained in IL was nearly equal to 1000 whereas the D values in n-DD were <0.1 but as the acidity increased, the D values in IL decreased to <10. The extraction of the Eu(III) was studied as function of different parameters such as Eu(III) ion in aqueous phase, nature of extractant, nature of ionic liquid, concentration of nitric acid, TODGA, and phase modifiers etc. the results showed that Eu could be extracted in ratio of 1:3 without leading to undesirable phase formation.[66]

R. B. Gujar and his team used several diglycolamide ligands to extract Am(III) and Cm (III) from nitric acid medium to ionic liquid. The ligands containing extractant, N, N, N', N'-tetraethyldiglycolamide (TEDGA), and the ionic liquid, [C4mim][Tf$_2$N], was impregnated on the extraction chromatograph resin and the metal uptake was calculated for this process. The maximum capacity for metal uptake was estimated to be 20.05 ± 0.73 mg/g. another finding of this study was that the D value increased as the carbon number of the alkyl substituent increased up to 4 then decreased as the carbon number increased further, thus deducing that tetrabutyl-DGA was most efficient in extraction of metals(Am(III), Cm(III)). Separation factor D_{Cm}/D_{Am} was also >1 by using these substituted diglycolamides in ionic liquid. [67]

Alok Rout et al studied the extraction of U(IV) from nitric acid into 1-butyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide ($[C_4mpip][NTf_2]$) ionic liquid. The extractants used were N,N-dimethyl-N,N-dioctyl- 2-(2-hexyloxylethyl)malonamide (DMDOHEMA), di-n-hexyloctanamide (DHOA), and N,N,N',N' tetra(ethylhexyl)diglycolamides(T2EHDGA). The extraction was measured as function of various parameters such as concentration of aqueous phase feed acid, temperature and duration of equilibrium, ionic liquid cation, extractant etc. the distribution ratios for all the extractants were different , decreasing in the order T2EHDGA > DMDOHEMA > DHOA. The values for distribution ratios for U (IV) were 57, 7.5, 0.06 for T2EHDGA, DMDOHEMA, and DHOA respectively at 3M HNO_3. The slop analysis was done to find out the mechanism of the process i.e. cation exchange. [68]
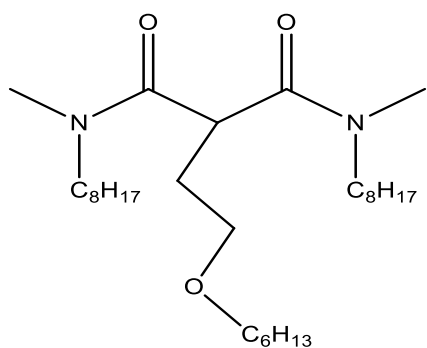
DMDOHEMA

T2EHDGA

DHOA
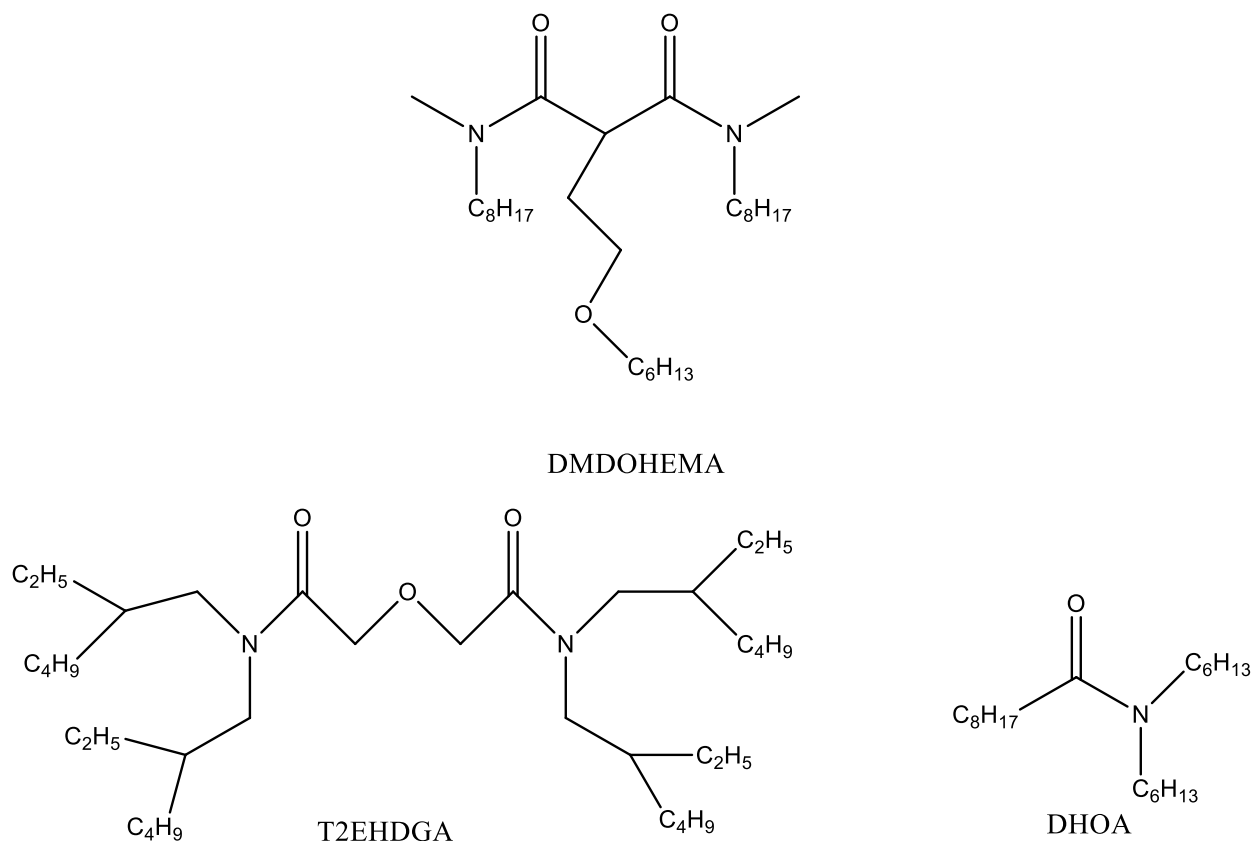
In another extraction chromatography done by R.B. Gujar and team, the extractant ligands as well as the ionic liquid was impregnated on the Chromosorb-W(inert solid support). The

extractants used were tripodal diglycolamide (T-DGA) and diglycolamide-functionalized calix[4]arene (C4DGA) which were dissolved in ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide(RTIL: C4mim Tf2N). The sorption of the metals on the surface by using C4DGA and T-DGA was 2 and 3 times greater than TODGA, when 10% of each was impregnated on the surface. The K_d values were also >10 times when 50% of each of these three extractants were used rendering C4DGA and T-DGA better extractants than TODGA. Also by the addition of IL the sorption increased by 5 times proving that presence of ionic liquids has enhancing effects on the extraction of the metals. The selectivity of resins for actinides was noticeable as distribution coefficients showed selective sorption of Am (III) on these resins as compared to Eu (III).[69]

Alok Rout and team reported a novel ionic liquid, trioctylmethylammonium nitrate ([N1888][NO3]). The extractants used were N, N, N', N'-tetra (ethylhexyl)diglycolamide (T2EHDGA). Two neutral extractants to compare the results of T2EHDGA were also used which were, N,N-dimethyl-N,N-di-octyl-2-(2-hexyloxylethyl)malonamide (DMDOHEMA) and octylphenyl(N,N-diisobutylcarba moylmethyl)-phosphinoxide (CMPO). The D values using these extractants were <10 when acidity was low (<1M HNO_3) whereas they increased to <100 for T_2EHDGA as the acidity increased (8M HNO_3) while the D values for DMDOHEMA and CMPO did not show appreciable increase. T_2EHDGA was found to have better efficiency in extraction as compared to other two extractants in this particular ionic liquid. This extraction was measure as function of several parameters such as, extractant concentration, aqueous phase acidity, temperature and isomeric forms of extractant. The isomeric forms of extractant had no significantly different effect than T_2EHDGA. The analysis revealed a neutral solvation pathway. Stripping of extracted Am (III) was done by dil. Nitric acid.[70]

DMDOHEMA
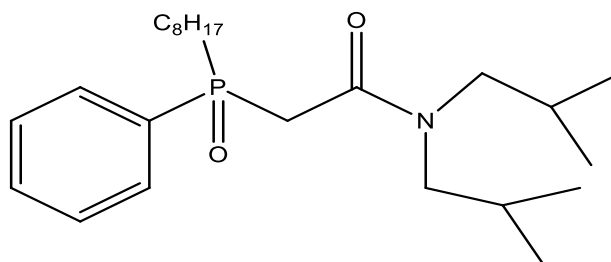
CMPO
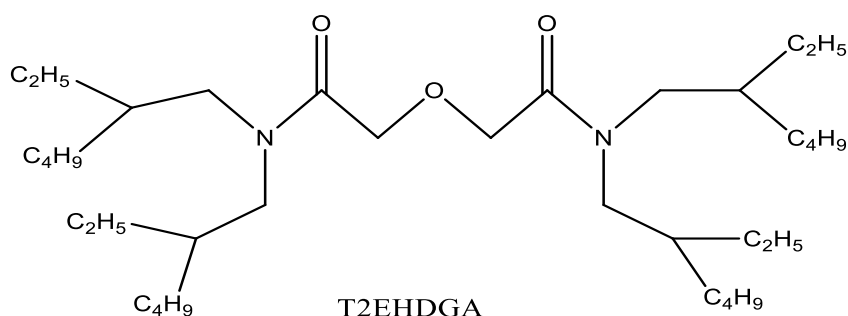
T2EHDGA

Alok Rout et al used the same ionic liquid, trioctylmethylammonium nitrate ([N1888][NO$_3$]), for the extraction of Pu(IV) with another extractant, a monoamide, N, Ndihexyloctanamide (DHOA). The extraction efficiency of this DHOA/[N1888][NTf2] system was compared with DHOA in a conventional diluent i.e. n-DD and an IL such as ([Cnmim][NTf$_2$]). DHOA in [N1888][NTf$_2$] showed excellent extractability for Pu(IV) as compared to n-DD or ([Cnmim][NTf$_2$]). The D value for Pu(IV) in 0.5M DHOA/ [N1888][NTf$_2$] was <1 at lower acidity but it increase to >80 as the acidity increases to 8M HNO$_3$. Moreover the extract was also switched with TBP but it reduced the distribution ratio of Pu (IV). The extraction was done as function of many parameters such as ionic liquid and extractant concentration, feed acid concentration, equilibrium time, temperature and type of extractants. Stripping of extracted specie in this case was also done by dilute nitric acid. [71]

DHOA
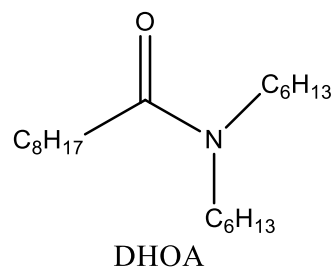
In a study conducted by Ankita Rao and team , the extraction of Th(IV) was done by the help of N,N-dialkyl aliphatic amides which were carrying different alkyl groups viz. N,N-dibutyl-3,3-dimethyl butanamide (DBDMBA), N,N-di-sec-butyl pentanamide (DBPA), N,N-dihexyl octanamide (DHOA), N,N-dibutyl-2-ethyl 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][PF6]. Distribution ratios were significantly higher with the use of ionic liquid as compared to the ratios obtained by using n-hexane. The D values ranging from 0.08 to 13.5 when the conc. of nitric acid was varied between 0.2m to 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. [72]

DBDMBA

DBPA

DHOA

DBEHA

DBOA
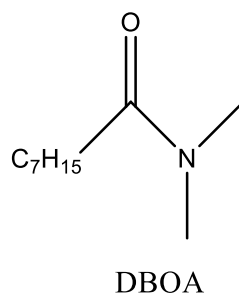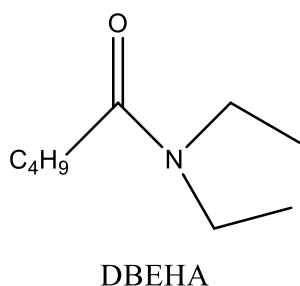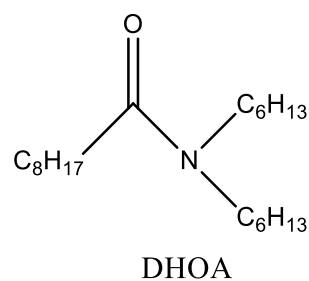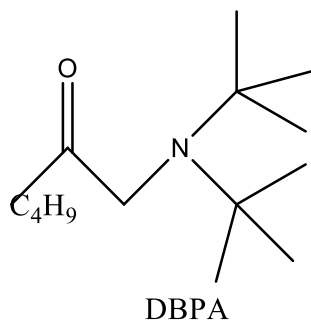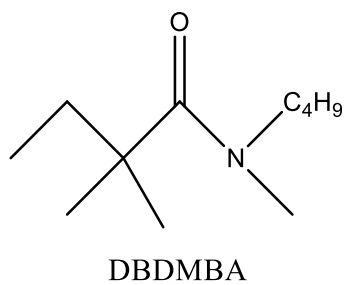
2.8   Phosphinium based ionic liquids

Wang Wei and his team synthesized a hydrophobic ionic liquid [1-alkyl-3-(1-carboxylpropyl)im][PF$_6$], where 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. They also advised a possible cation-exchange mechanism whereas the slope technique analysis was done to obtain results. [73]
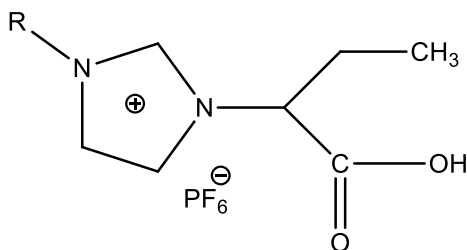
[1-hexyl-3-(1-carboxylpropyl)im][PF6]

Sena Murakami and his team studied the extraction of trivalent rare earth metals by using extractant ,N,N,N',N'-tetraoctyl diglycolamide (TODGA) in ionic liquid, triethylpentylphosphonium bis(trifluoromethylsulfonyl) amide ([P2225][TFSA]). The metals, Pr(III), Nd(III) and Dy(III) were obtained from their metallic salts with bis (trifluoromethylsulfonyl)amide (TFSA). The results revealed a cation exchange mechanism for this process. The stoichiometry for RE: TODGA was observed as 1:2 for Dy, and 1 :(2–3) for Pr and Nd according to slope analysis. [74]

[P2225][TFSA]   TODGA
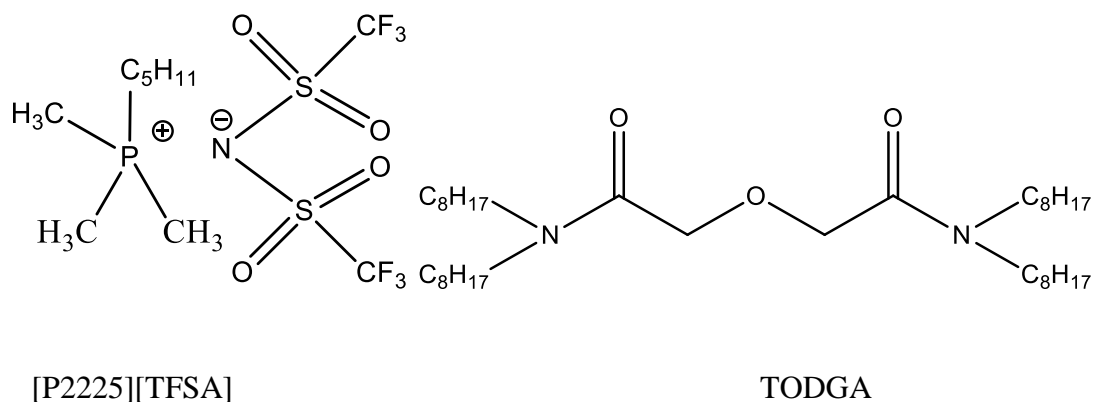
2.9   CMPO based ionic liquids

Elena V. Sharova and team synthesized a ligand system for metal extraction by complexion 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 ([bmim][Tf$_2$N]) in 3M nitric acid medium. The protonation of central nitrogen atom in the acidic media lead to effective extraction of anionic complexes. The complexes of Eu (III) and Tb (III) showed strong luminescence at 300K. [75]
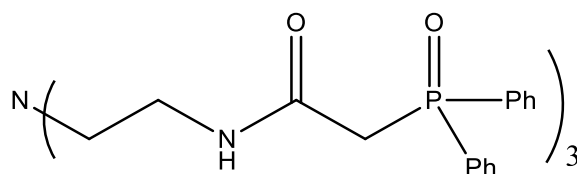
tris- CMPO ligand

A. N. Turanov and his team worked on extraction of uranium, thorium and other lanthanides from nitric acid medium into organic molecular diluents with the help of 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 analog, diphenylphosphorylacetic acid N-nonylamide. This difference can be

attributed to the partition of this FIL between the aqueous and organic 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 [C4mim][PF6] or [C4mim][Tf2N] were added.[76]

CMPO-FIL

CMPO-ANALOG
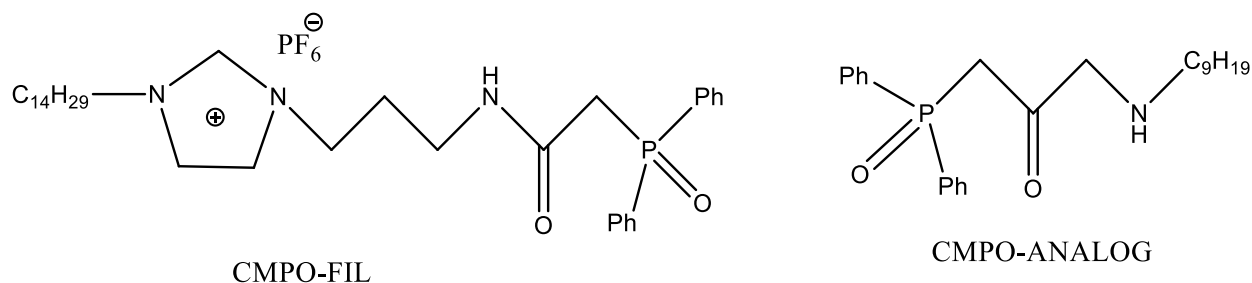
Maria A. Petrova studied the extraction of lanthanides (Lu^{3+}, Ce^{3+}, and Eu^{3+}) into four ionic liquids of imidazolium family i.e. [C1Cnim][Tf$_2$N], (n = 4, 6, 8, and 10). The extract used was 3-methyl-4-(4-methylbenzoyl)-1- phenyl-pyrazol-5-one (HL) in addition with N, N-diisobutyl-2-(octylphenylphosphoryl)acetamide (CMPO). The studies showed that the *log*D values for the lanthanide ions decreased as function of the 'n' value of IL in the order of hydrophobicity of their cations i.e. 4>6>8>10. They also studied the effect of para-substituted 4-acylpyrazolone on the extractant and its synergistic effects were discussed. [77]

HL
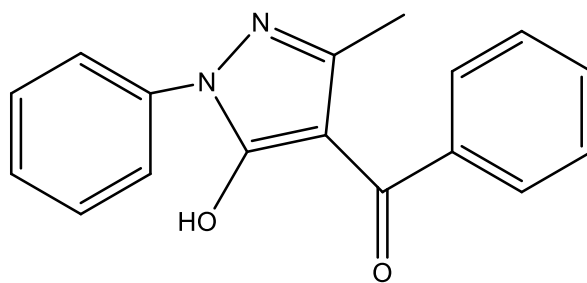
CHAPTER 3

3. EXPRIMENTAL WORK

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

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.

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. Synthesis of 1-methyl-3-octyl imidazolium bromide.
2. Synthesis of 2-(2-(di-n-octylamino)-2-oxoethoxy) aceticacid.
3. Synthesis of 2,2'- oxydiacetic acid
4. Synthesis of functionalized ionic liquids.
5. All the solvents were distilled or dried before use.

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(1.07 g, 9.2 mmol)   and dioctylamine (2.2 g, 9.2 mmol) in 50 mL dry THF in round bottom flask. The resulting mixture was stirred for 48 hours at room temperature. The reaction progress was monitored by TLC using 2-4% methanol in chloroform, after the completion of reaction, the reaction mixture was concentrated on rotary evaporator to obtain yellowish semi liquid product.

1,4-dioxane-2,6-dione   Dioctyl amine   2-(2-(dioctylamino)-2-oxoethoxy)acetic acid

(1)
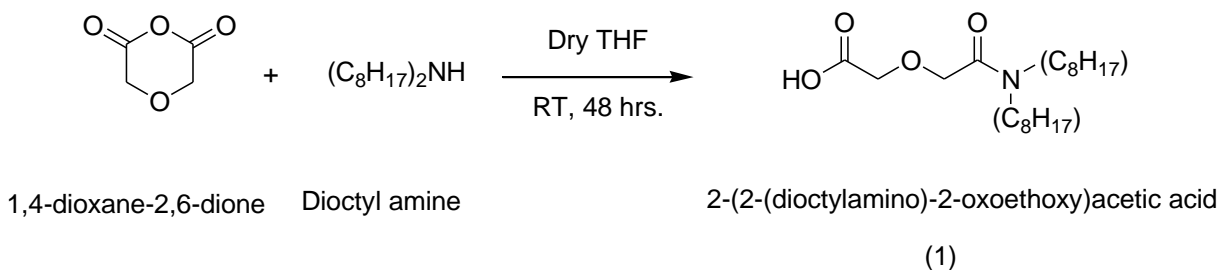
Scheme 3. 1

3.3.2 Synthesis of 2,2'-oxydiacetic acid

2,2'-oxydiacetic acid(2) was synthesized by the reaction of diglycolic anhydride(1.3 g, 11.1 mmol)   with water(0.2 g, 11.1 mmol) , using dry THF in round bottom flask. The reaction mixture was kept on stirring for 48 hrs at room temperature. The solvent was evaporated through rotary evaporator to get the white solid i.e. diacid. It was then put in vaccum oven for 24 hrs at 50 °C under reduced pressure to get rid of all the moisture in the system as extra dry conditions were required for the next step.

Scheme 3.2

3.3.4 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, the solvent was rotary evaporated from the reaction mixture to obtain 1-methyl-3-octyl imidazolium bromide (3) as light yellow viscous liquid. Progress of the reaction was monitored by TLC using 5% methanol in chloroform. The obtained ionic liquid was dried under vacuum oven at 40 °C for 4 hours.

Scheme 3. 3

3.3.5 Synthesis of 1-methyl-3-octyl imidazolium dioctyldiglycolamate (L$_I$)

Task specific ionic liquid, 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L$_I$), was synthesized in two step reaction. In the first step, 2-(2-(di-n-octylamino)-2-oxoethoxy)aceticacid(was treated with NaH under inert atmosphere of N$_2$ and extra dry conditions to obtain salt of salt of the acid. 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 nitrogen 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 (L_I) (4) is summarized in scheme 3.4
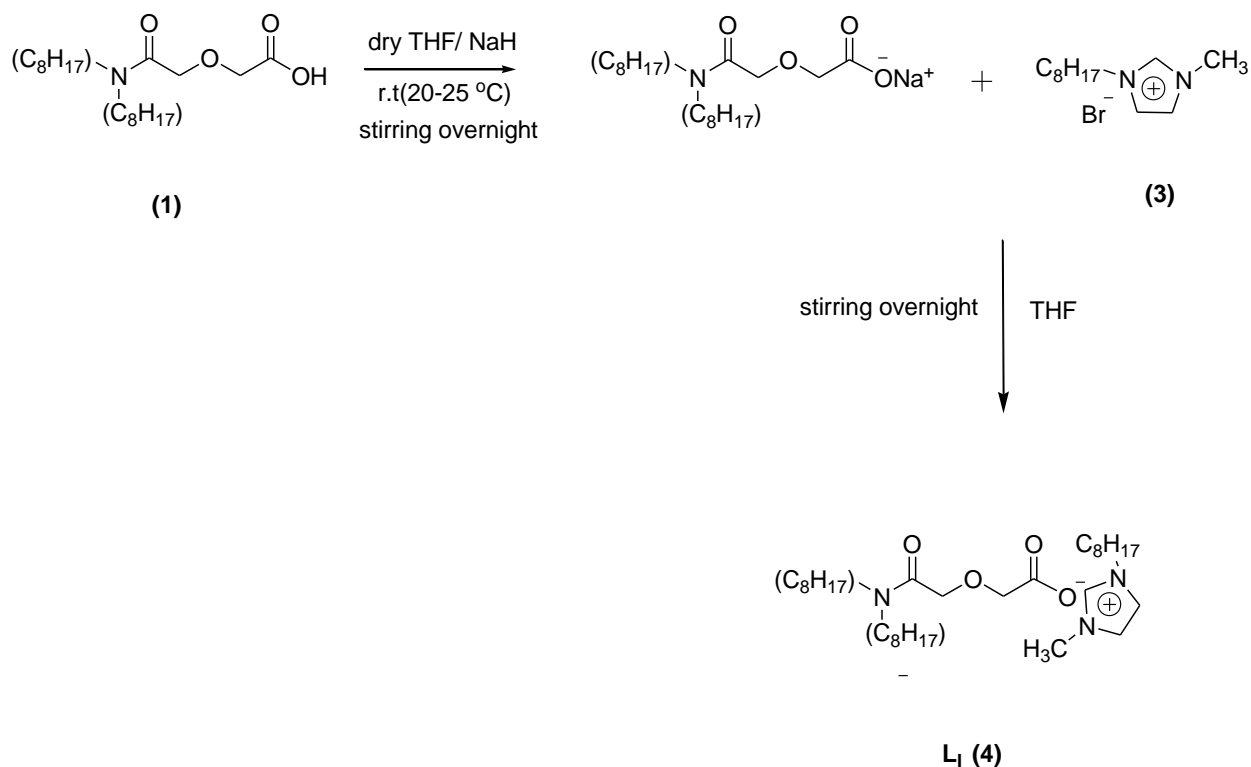
Scheme 3. 4

3.3.6 Synthesis of 2,2'-bis(1-methyl-3-octylimidazolium) oxydiacetate(L_{II}).

Task specific ionic ligand was also synthesized in two steps. Salt of the 2,2'-oxydiacetic acid was obtained by the reaction of acid with sodium hydride, NaH, under extra dry and inert atmosphere of nitrogen(N_2). The reaction mixture was placed on ice bath and inert environment

was created by the introduction of nitrogen gas and evacuation of air through vacuum pump. Sodium hydride (0.252 g, 2.37 mmol) was gradually added at 0 °C with continuous stirring under nitrogen 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 2,2'-di(1-methyl-3-octylimidazolium) oxydiacetate(L_{II}) (5) is summarized in scheme 3.5
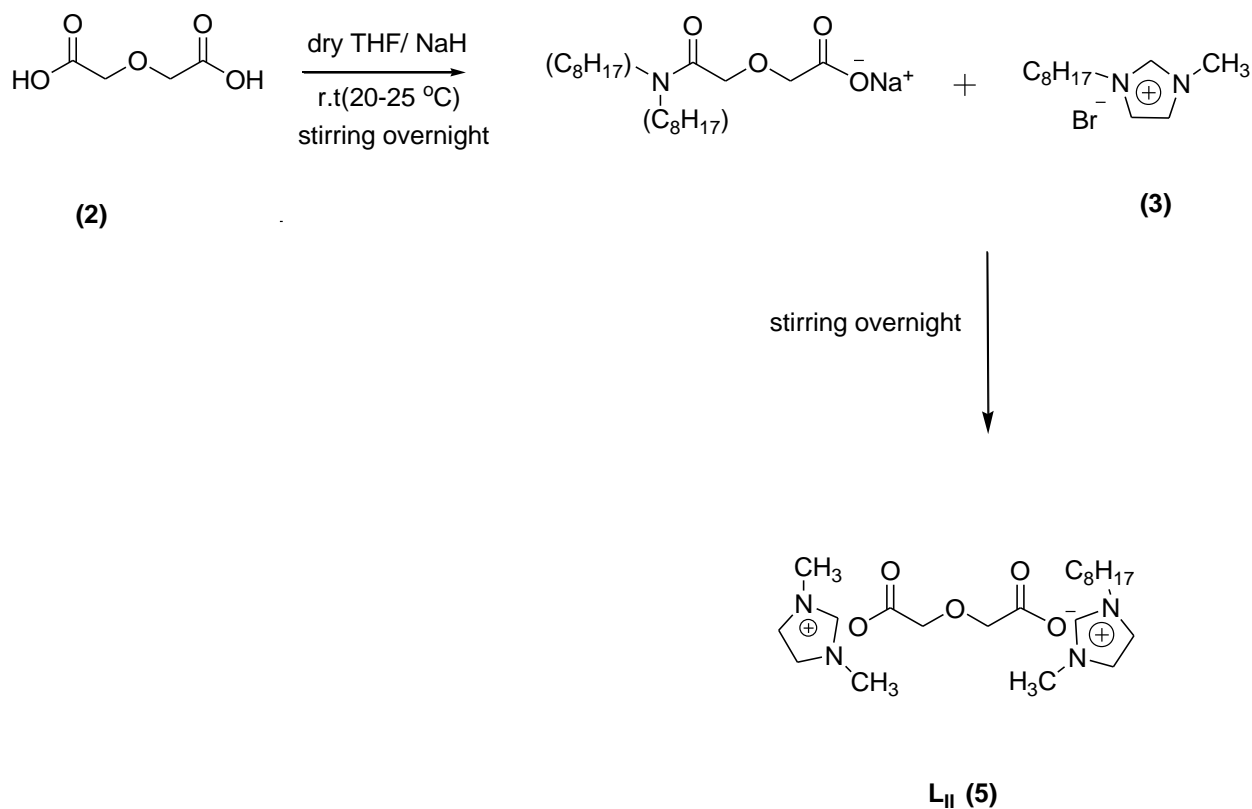

Scheme 3.5

CHAPTER 4

4. RESULTS & DISCUSSION

In this chapter, detailed discussion about the results of synthesis of functionalized task specific ionic liquids, their characterization and application to extract heavy metals is included. The structural elucidation of the synthesized compounds was done by the techniques Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (NMR).

4.1   Fourier Transform Infrared Spectroscopy (FTIR)

In the Fourier Transform infrared spectroscopy, the light beam is passed through the sample, the wavelength of the beam lies in the infrared region of the electromagnetic spectrum (400 cm^{-1} to 4000 cm^{-1}). When the light strikes the molecules, some of it is absorbed and it excites the molecules of the compound which produces an absorption/emission spectrum in the IR region. Different types of bonds respond differently to this IR radiation and thus their bands appear in their characteristic region making it possible to recognize the type of bond e.g. carbonyl bond absorb differently as compared to C=C bond. Similarly, C-C bond absorbs at lower frequency than C=C bond. All these bonds have their characteristic regions. Spectra of the synthesized TSILs are given below:

4.1.1.1   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.
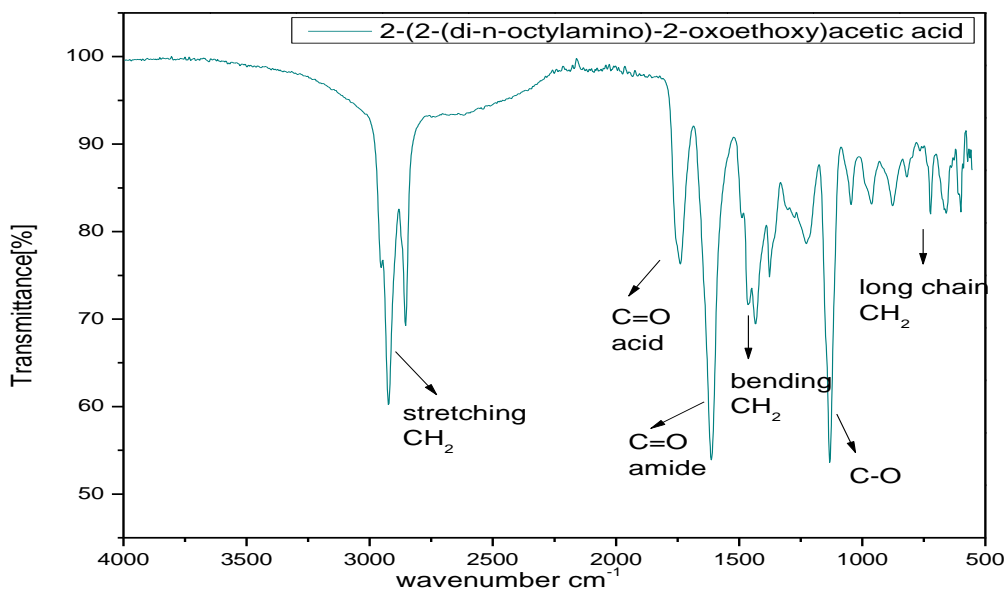
Figure 4. 5. FTIR spectrum dioctyl diglycolic acid.

4.1.1.2 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.
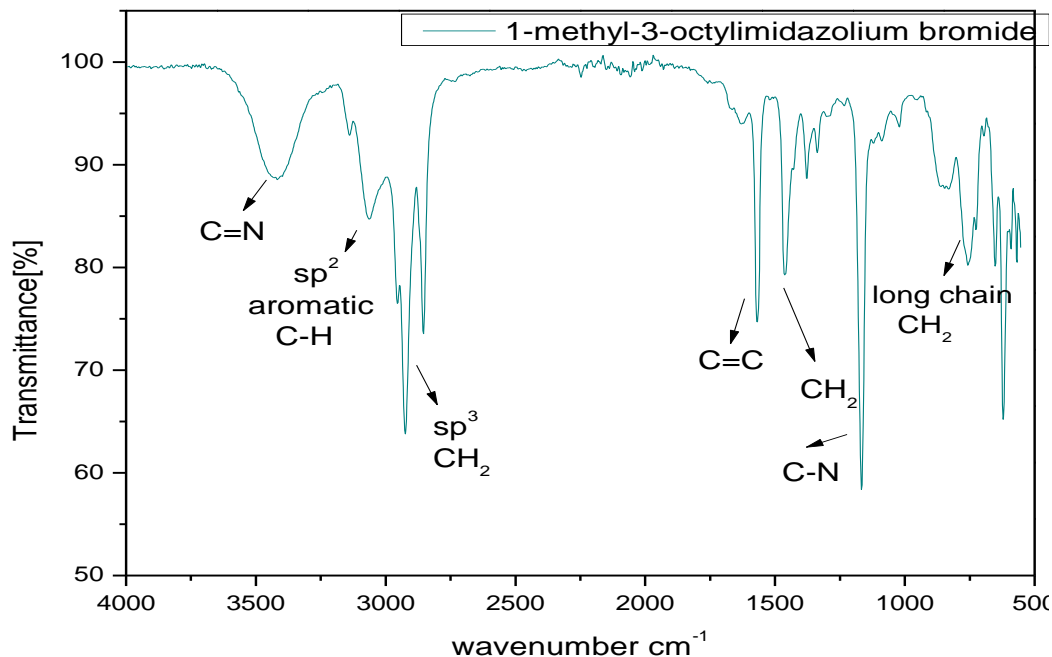
Figure 4. 6. FTIR spectrum of 1-methyl-octylimidazolium bromide

4.1.1.3   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.
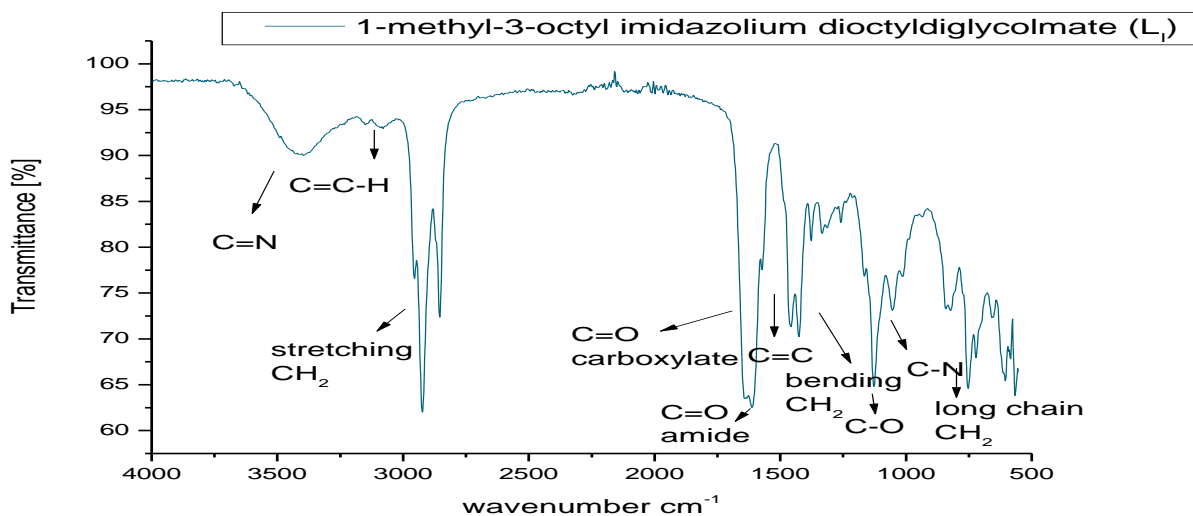
Figure 4. 7. FTIR spectrum of 1-methyl-3-octyl imidazolium dioctyl diglycolamate (L_I)

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.
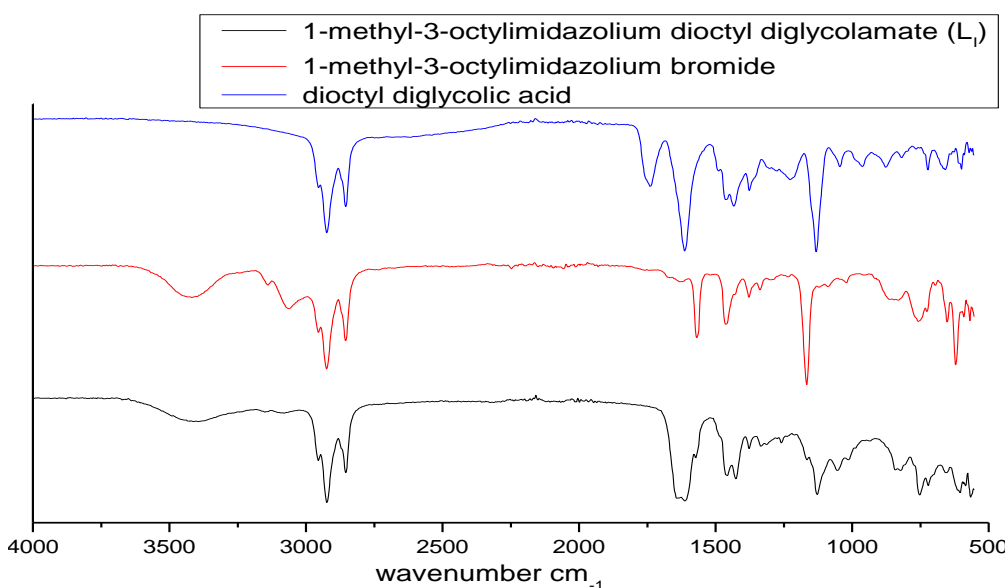
Figure 4. 8. FTIR spectrum of L$_I$

4.1.1.4   FT-IR analysis of 2,2'-oxydiacetic acid

FTIR analysis of 2,2'-oxydiacetic acid shows characteristic bell shaped peak of acid in the shape of broad bell from 2500-3500cm^{-1}. C=O peak is also present at 1690 cm^{-1}. Characteristic stretching peak of C-O can be seen at 1138 and 1240cm^{-1}. O-H bending peak can be seen at 1414cm^{-1}.
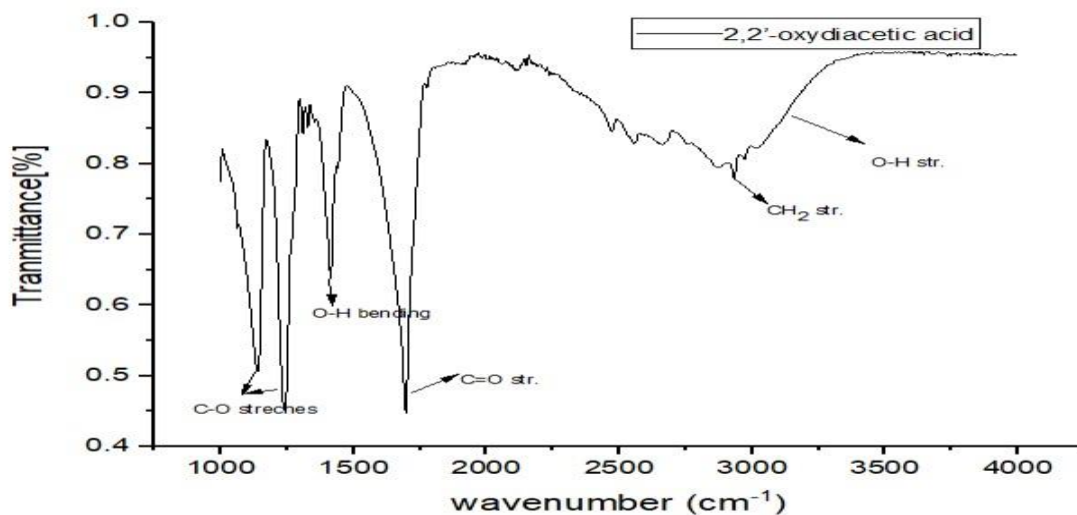
Figure 4.5. FTIR spectrum of 2,2'-oxydiacetic acid.

4.1.1.5 FT-IR analysis of 2,2'-bis(1-methyl-3-octylimidazolium) oxydiacetate(L_{II}).

Figure 4.6. shows the FT-IR of analysis of the ammonium functionalized dioctyl diglycolamate. The strong bands at 2850 cm^{-1} and 2920 cm^{-1} corresponds to the C-H stretching vibrations in sp^3 CH_2 and CH_3. Peaks for C=O and C-O can also be seen at 1728 and 1140 cm^{-1} respectively. The C=C bond shows absorption at 1563 cm^{-1}.
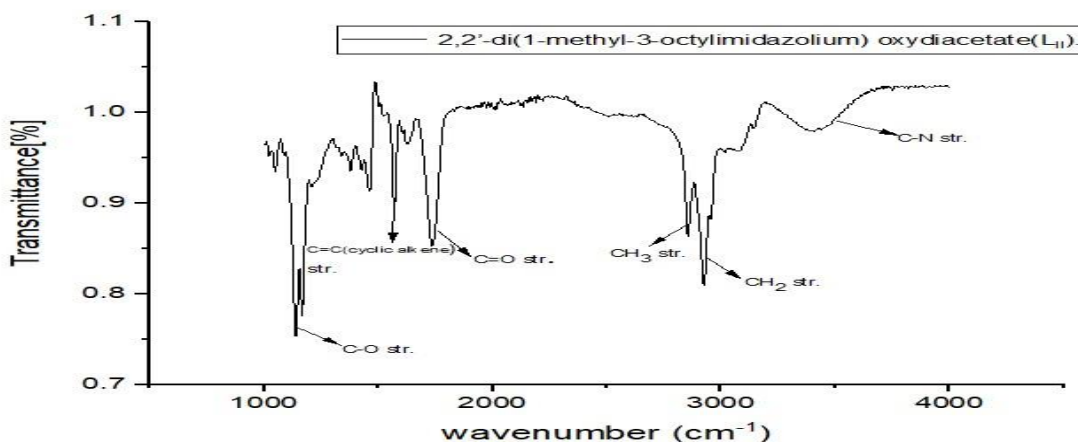
Figure 4. 6. FTIR spectrum of 2,2'-di(1-methyl-3-octylimidazolium) oxydiacetate(L_{II})

By the comparison of three spectra, it can be seen that characteristic band of C=O from 2,2'-oxydiacetic acid has moved towards higher wavelength in L_{II} due to increase in conjugation. Peak for C-N can also be seen in the spectra of L_{II} along with characteristic peaks of sp^3 CH_2 and CH_3.
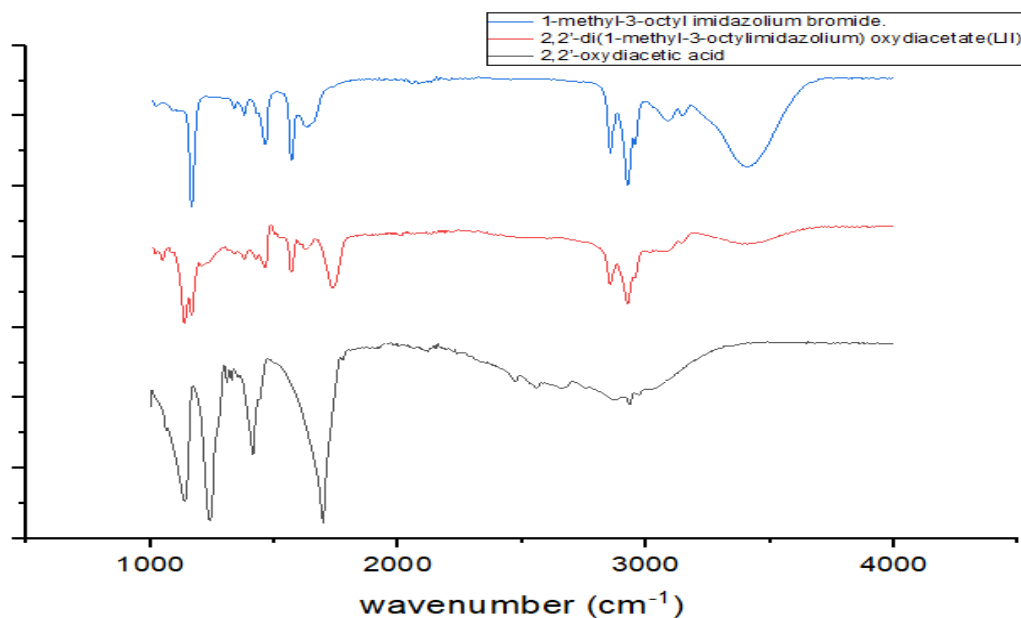
Figure 4.7. FTIR spectrum of L_{II}

4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

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

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

Protons	Chemical Shift values ppm	Multiplicity
CH_3	0.85 - 0.9	m
CH_2	1.26 - 1.33	m
$CONCH_2$	3.1 , 3.3	t
OCH_2CO	3.9 , 4.2	s
NCH_3	4.1	s
NCH_2	4.3	t
$CH=CH$	7.4 ,7.5	s
$NCHN$	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 2,2'-di(1-methyl-3-octylimidazolium) oxydiacetate(L_{II}).

^{1}H NMR (CDCl$_3$, δ ppm): 0.64-0.74 (t, 6H; **CH**$_3$), 1.06-1.76 (m, 20H; (CH$_2$)$_6$), 3.86 (s, 6H; N**CH**$_3$), 4.10-4.19 (t, 4H, N**CH**$_2$), 4.08 (s, 4H; O**CH**$_2$CO), 7.34-7.55 (d, 4H; **CH=CH**)**,** 9.42 (s, 2H, NC**H**N).

Protons	Chemical Shift values ppm	Multiplicity
CH_3	0.64-0.74	t
CH_2	1.06-1.76	m
NCH_3	3.86	s
NCH_2	4.10-4.19	t
OCH_2CO	4.08	s
$CH=CH$	7.34, 7.55	d
$NCHN$	9.42	s

Table 4. 2. ^{1}HNMR data of 2,2'-di(1-methyl-3-octylimidazolium) oxydiacetate(L_{II}).

4.3. Extraction study for Heavy metals

Extraction efficiency of functionalized ionic liquids was investigated for the extraction of heavy metals; Lead (Pb) and cobalt (Co) from aqueous solution of their salts. Various parameters like pH of the metal solution, extraction time for equilibration kinetics and concentration of the metal solutions were used to evaluate the extraction efficiency. Optimized conditions were also achieved to obtain maximum efficiency of the ionic liquids.

4.3.1. Preparation of aqueous phase

100ppm aqueous solution of $PbCl_2$ and $Co(NO_3)_2$ was prepared at varying pH i.e. 2,4,6,8, and 10. The pH was adjusted using buffer solutions of pH value 4.0 and 10 and pH was monitored with the help of pH paper. Concentration of metal solutions was also varied to 50,100,150,200 and 250ppm after achieving the optimum pH of 4.

4.3.2. Preparation of organic phase

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

4.3.3. Extraction procedure

Both the organic and aqueous phases were equilibrated in equal 1:1 volume ratio for the extraction study. 1 ml of organic solution along with 1 ml of aqueous solution was taken in 10 ml vial. Both layers were allowed to shake at 300rpm in a shaking incubator at 25 °C for different time intervals. After the thorough shaking, both layers were allowed to equilibrate and then the aqueous layer was taken out with help of a micropipette. This aqueous layer was subjected to FAS; Flame absorption spectroscopy to analyze the concentration of metal ions left in the solution. This in turn gives the concentration of metal ions taken up by the functionalized ionic liquids.

Percentage Extraction efficiency

Percentage Extraction efficiency of the ionic liquids was calculated with the help of following formula:

$$\text{Percentage Extraction efficiency} = \frac{C_i - C_f}{C_f} \times 100$$

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

The extraction studies were carried out as function of initial pH of the metal solutions of Pb and Co as pH of the aqueous phase affect the extraction efficiency of the functionalized ionic liquid significantly. Thus the study of extraction was carried out at different pH (2, 4, 6, 8 and 10) to achieve optimum conditions for the IL. The concentration of metal solution was kept same for these extraction experiments i.e. 100ppm, for both ionic liquids, L_I and L_{II}. After carrying out experiments with aqueous solutions of different pH, it was observed that the ionic liquid was achieving better extraction efficiency in acidic range as compared to basic medium. As the basicity of the metal solution was increased, the extraction efficiency of the ionic liquid

gradually decreased. This trend of better extractability in acidic medium is observed in case of DGA based ionic liquids mostly.

In the case of L_I, the maximum extraction for Pb was shown at pH 4 and the efficiency gradually decreased but not so much, whereas, maximum Co was also extracted at acidic pH of 4 with the value drastically decreasing as basic media was introduced. Figure 4.8 and 4.9 represents the extraction of L_I ionic liquid extractant at various pH values.
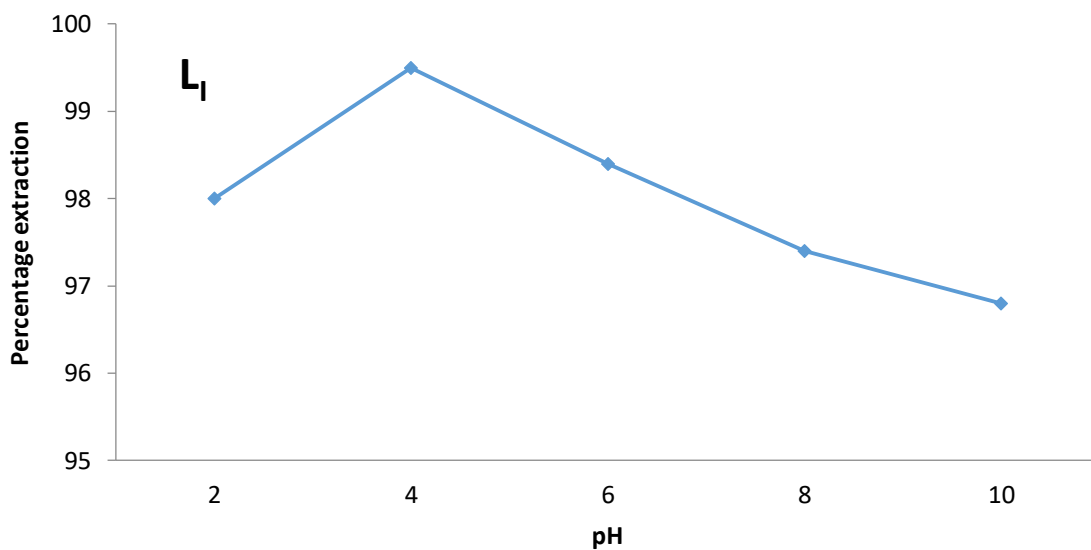
Figure 4.8. Extraction efficiency of L_I vs. pH for Pb(II)
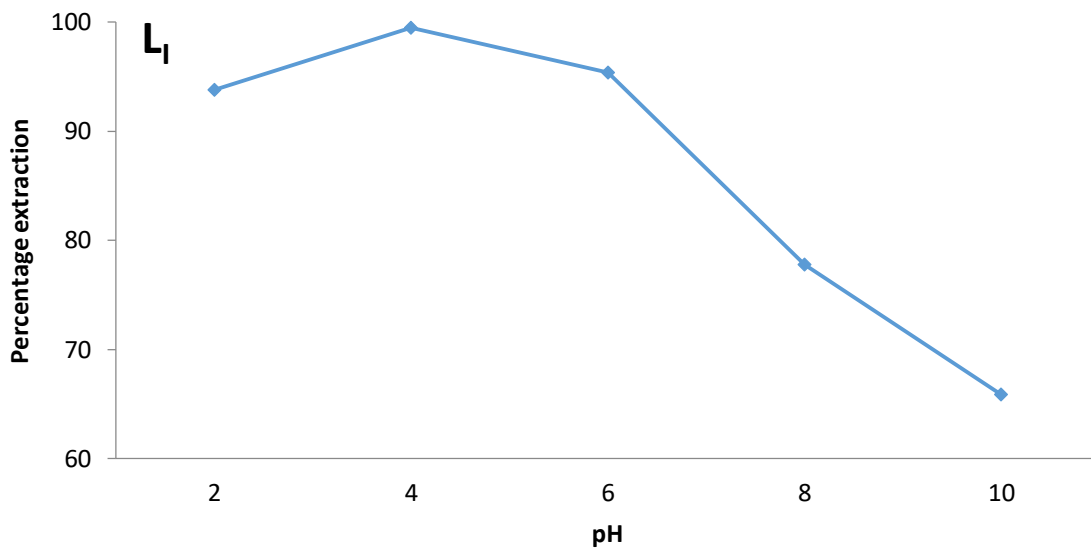
Figure 4.9. Extraction efficiency of L_I vs. pH for Co(II)

In case of $L_{II,}$ maximum extraction of Pb was also achieved at acidic pH ranging from 2-6 and it decreased to a much lower value at basic pH of 8 and 10. For Co, the extraction efficiency was better only at 2 and 4 , and decreased at pH 6, 8 and 10.
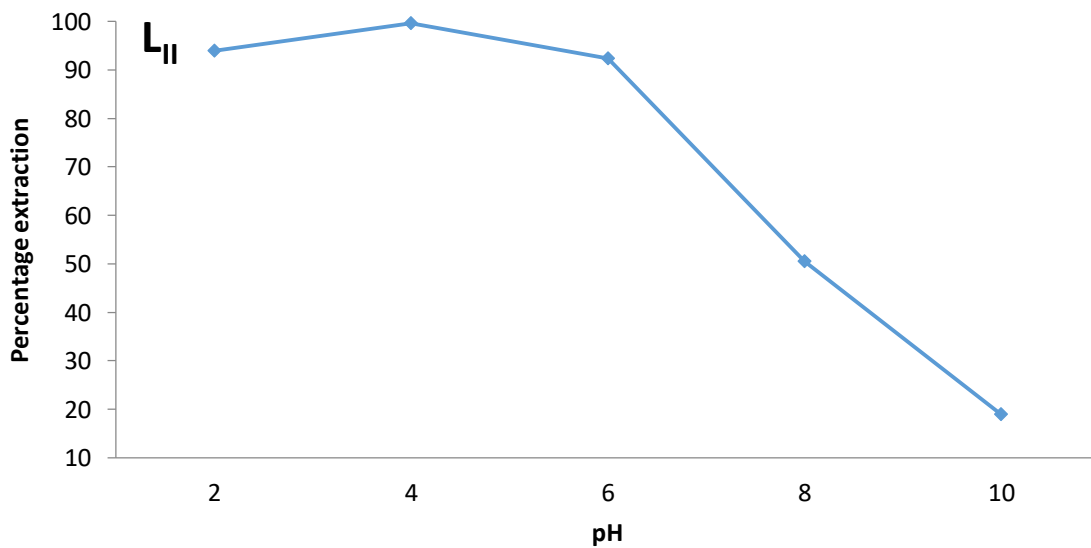
Figure 4.10. Extraction efficiency of L_{II} vs. pH for Pb(II)
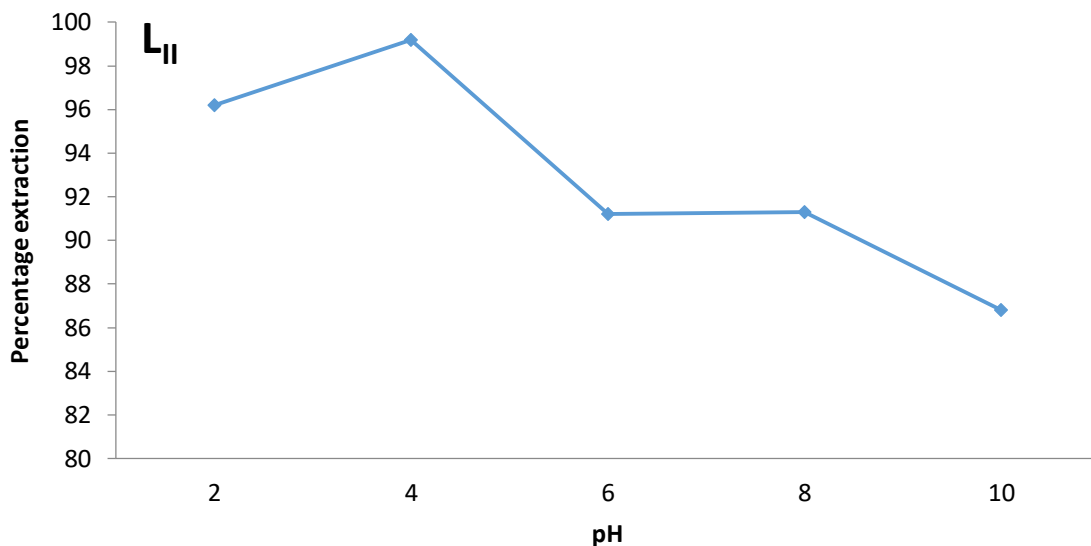
Figure 4.11. Extraction efficiency of L$_{II}$ vs. pH for Co(II)

4.3.5. Extraction Kinetics

The extraction time for the equilibration process of aqueous and organic phase was investigated for both functionalized ionic ligands. 0.1M solution of both L$_I$ and L$_{II}$ extractants was prepared and 1mL was taken into the 10mL glass vial. 100 ppm solution of both metals, Pb and Co, was prepared and their pH was kept constant at 7. 1mL of aqueous phase was also added into the glass vial and both aqueous and organic phases were allowed to vigorously shake at 300rpm in a shaking incubator for time starting from 15 mins to 75 mins, at the interval of 15 minutes each.

It was observed that the extraction efficiency gradually increased in the start and reached its maximum at 45 mins for L$_I$ in case of Pb. In case of Co, maximum extraction was achieved at 60 mins and after that it was a plateau.
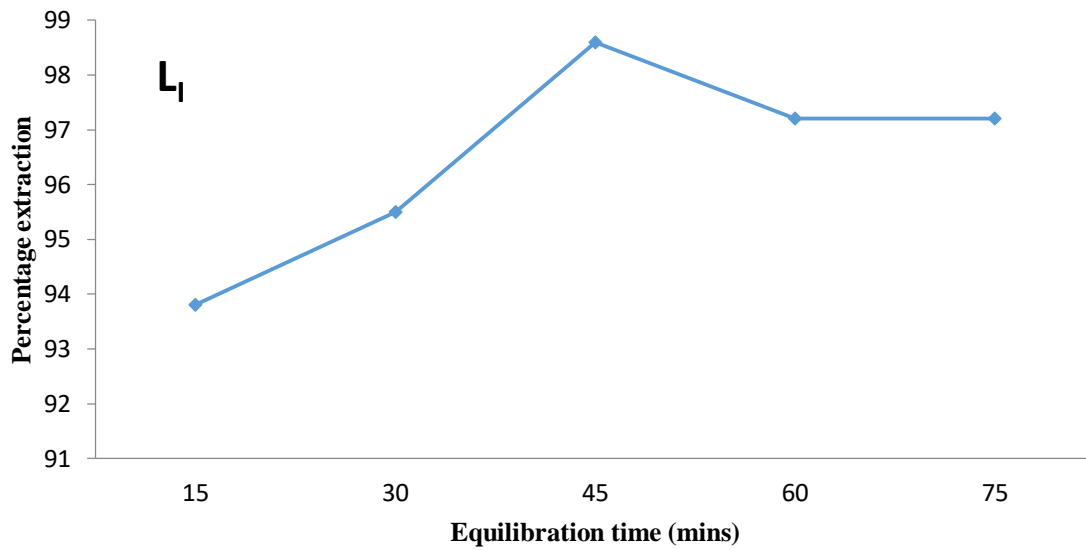
Figure 4.12. Extraction efficiency of L_I vs. time for Pb(II)
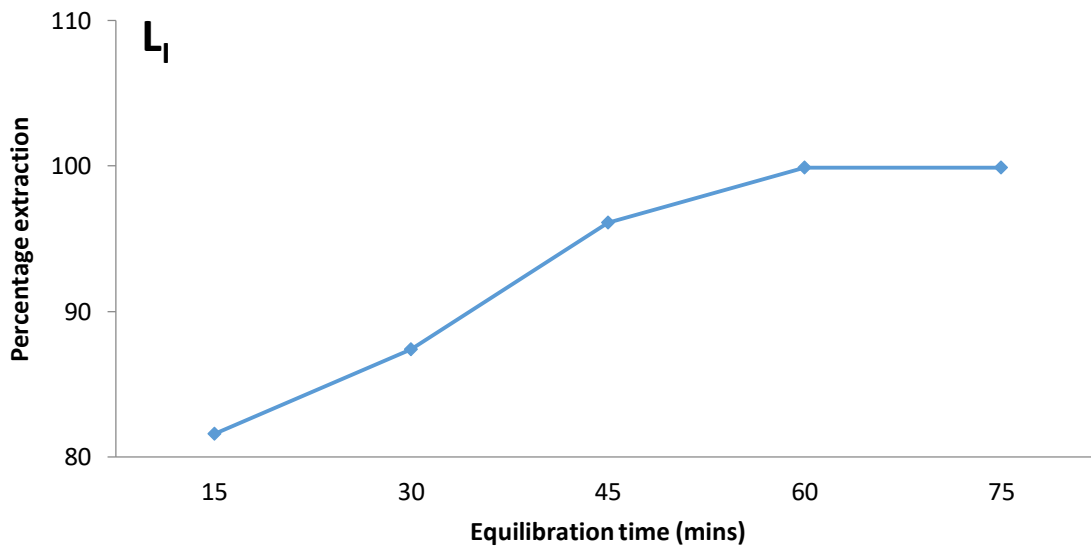
Figure 4.13. Extraction efficiency of L_I vs. time for Co(II)

In the case of L_{II}, the extraction efficiency increased gradually and maximum extraction was achieved at 75 mins for Pb as well as Co but the trend was different as evident from the figures below.
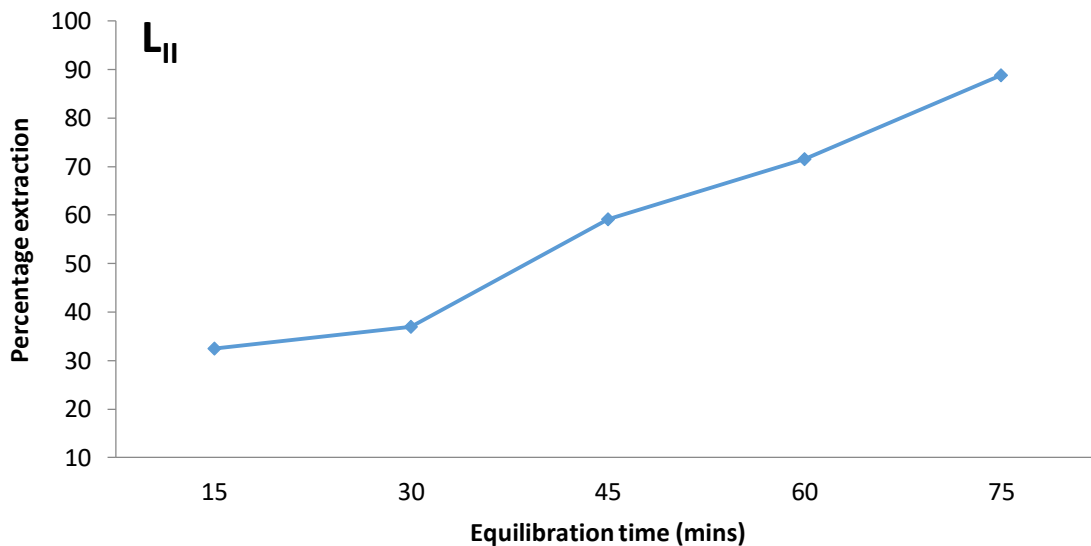
Figure 4.14. Extraction efficiency of L_{II} vs. time for Pb(II)
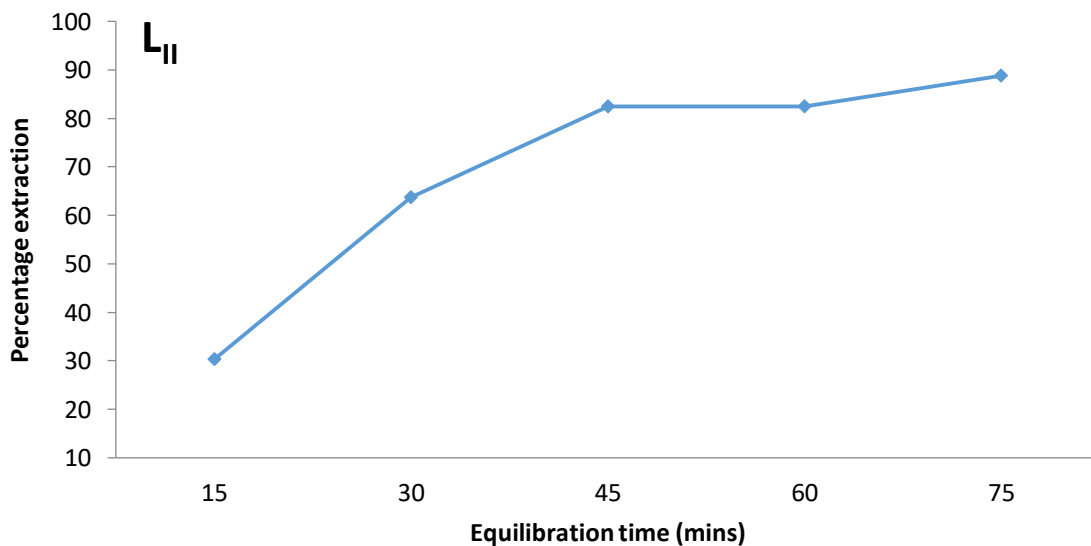
Figure 4.15. Extraction efficiency of L_{II} vs. time for Co(II)

4.3.6. Effect of metal ion concentration

The effect of metal ion concentration was studied   for extraction efficiency of L_I and L_{II} by varying the concentration of aqueous solutions of Pb(II) and Co(II) to 50, 100, 150, 200 and 250 ppm at optimum time and pH.

The results showed that the extraction by L_I was 99.9% for Co(II) and 99.8% for Pb(II) till 100ppm but it decreased when the metal ion concentration was increased further, showing more L_I was needed for the complexation of increased metal ion concentration .
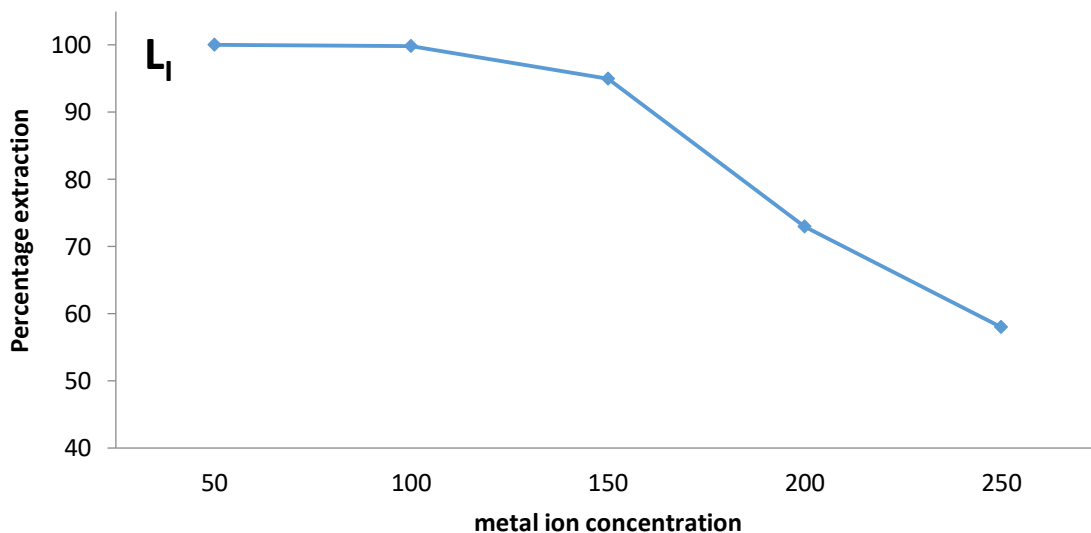
Figure 4.16. Extraction efficiency of L_I vs. metal ion conc. of Pb(II)
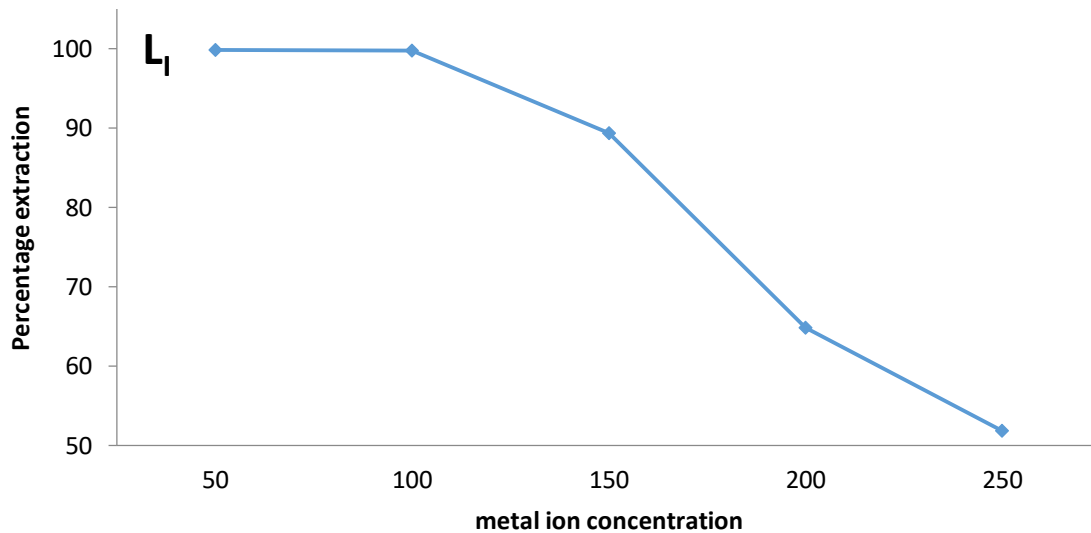
Figure 4.17. Extraction efficiency of L_I vs. metal ion conc. of Co(II)

In the case of L_{II}, it was observed that extraction efficiency was 99.8% for Co(II) and 99.9% for Co(II) while it decreased to 42.3% and 49.5% respectively when the metal ion concentration was increased to 250ppm.
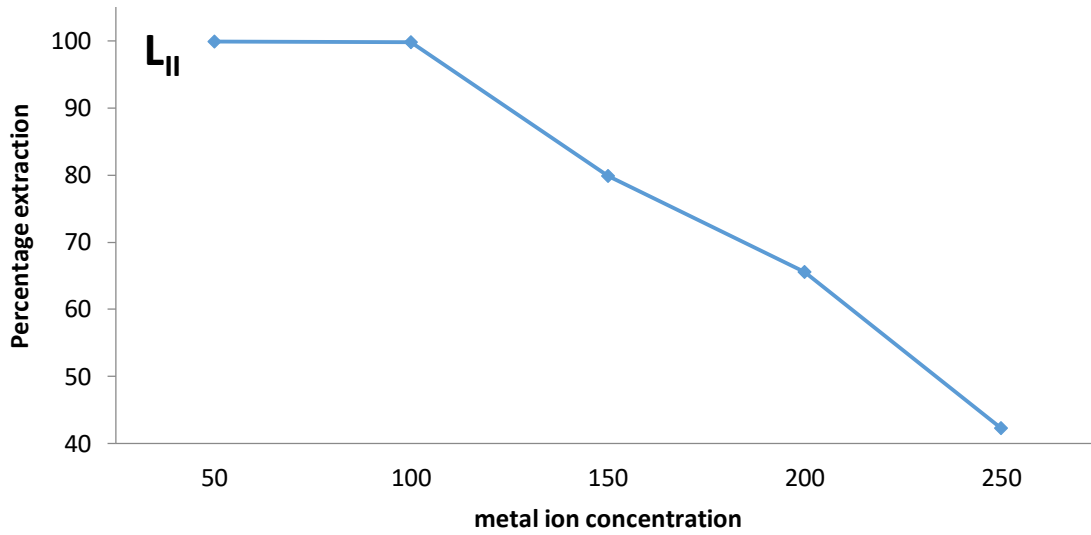
Figure 4.18. Extraction efficiency of L$_{II}$ vs. metal ion conc. of Pb(II)
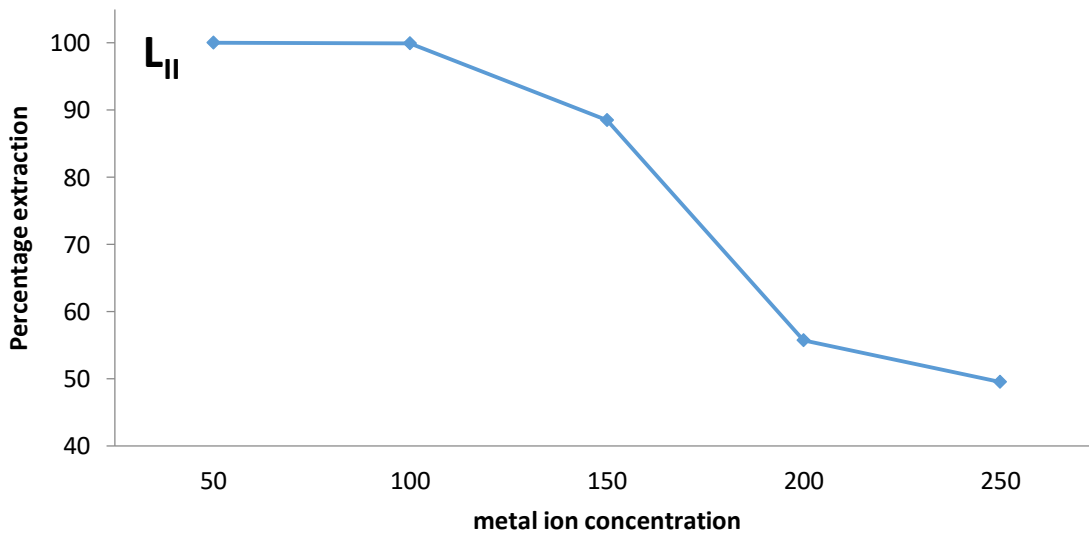
Figure 4.19. Extraction efficiency of L$_{II}$ vs. metal ion conc. of Co(II)

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4.3.7. Comparison of extraction efficiency of L_I and L_{II}

When the comparison of the extraction efficiencies of both ionic liquids was being made, it was observed that the mono-ionic liquid L_I showed better extraction for both metals , Pb and Co, as compared to the di-ionic liquid L_{II}.

This was attributed to the fact that mono-ionic liquid, L_I, had one ionic site thus its interaction with water was lesser than di-ionic liquid, L_{II}, which had two ionic sites which could interact with aqueous phase more rendering less extraction of the metal ion.

Secondly, two imidazolium groups in L_{II} as compared to one imidazolium group in L_I could also contribute to the lesser efficiency of L_{II} due to steric hindrance caused by bulky imidazolium groups.

CONCLUSION

- Two different types functionalized ionic liquid were successfully synthesized.

- These extractants were characterized by FTIR and ^{1}H NMR Spectroscopy.

- Extraction study was carried out by using these task specific ionic liquids, for the extraction of Pb(II) and Co(II).

- Extraction studies shows that these TSILs work better at acidic pH for both metals, Pb(II) and Co(II).

- The extraction time for L_I was 45 mins where as it took 75 mins for L_{II} to achieve maximum extraction.

- Extraction efficiency of both ionic liquids is almost 100% till 100ppm which gradually decreases with increase in metal ion concentration.

- The extraction efficiency of mono-ionic liquid (L_I) proved to be better than di-ionic liquid (L_{II}).

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