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Development of functional ionic liquids for separation and recovery of rare earth elements

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DEVELOPMENT OF FUNCTIONAL IONIC LIQUIDS FOR SEPARATION AND

RECOVERY OF RARE EARTH ELEMENTS

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ABSTRACT

This research focused on the design and synthesis of task-specific ionic liquids for enhanced extraction and separation of rare earth elements (REEs). Two novel ammonium-based functional ionic liquids (FILs) with oxygen donating groups: trioctyl(2-ethoxy-2-oxoethyl)ammonium dihexyl diglycolamate, [OcGBOEt][DHDGA], and tricaprylmethylammonium dihexyl diglycolamate, [A336][DHDGA] were synthesized and tested for the recovery and separation of selected REEs from aqueous solutions. Functionalities with different denticities were incorporated into both anionic and cationic parts of ionic liquids, which are solely composed of incinerable atoms including C, H, O, and N. The structural, physical, and chemical properties of the synthesized FILs were studied using nuclear magnetic resonance (^{1}H- and ^{13}C-NMR), Fourier transform infrared spectroscopy (FTIR), high-resolution mass spectrometry (HRMS), thermal gravimetric analysis (TGA), disc scanning calorimetry (DSC) in addition to density and viscosity analysis.

The influence of key process parameters on the extraction efficiency of the synthesized FILs was examined in detail using europium as an example of REEs. The extraction mechanism of the synthesized FILs was systematically investigated using FTIR and NMR spectroscopies in addition to the slope analysis approach.

The better extractability, enhanced selectivity towards heavy rare earth, and improved loading capacity of the new FILs are the key advances of this research which will immensely contribute to the field of hydrometallurgical separation of REEs.

ACKNOWLEDGMENTS

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NOMENCLATURE

Symbol	Description
REE	Rare Earth Element
IL	Ionic Liquid
FIL	Functional Ionic Liquid
PIL	Protic Ionic Liquid
HREE	Heavy Rare Earth Element
LREE	Light Rare Earth Element
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric Analysis
DCS	Differential Scanning Calorimetery
HRMS	High Resolution Mass Spectrometery
ICP	Inductively-Coupled Plasma
MDS	Molecular Dynamics Simulation
D	Distributio ratio
S.F.	Separation Factor
E%	Extraction percentage
K_{ex}	Extraction constant
A/O	Aqueous-to-Organic ratio
[A336]	Tricaprylmethyl ammonium
DHDGAA	Dihexyldiglycolamic acid

[DHDGA]   Dihexyldiglycolamate

[OcGBOEt]   Trioctyl[2-ethoxy-2-oxoethyl]ammonium

D2EHPA   Di-(2-ethylhexyl)phosphoric acid

PC88A   2-ethylhexylphosphonic acid mono-2-ethylhexyl ester

TODGA   N,N,N',N'-tetraoctylglycolamide

THDGA   N,N,N',N'-tetrahexylglycolamide

TBP   Tri-n-butylphosphate

PAA   Poly(acrylic acid)

1. INTRODUCTION

1.1. PROBLEM STATEMENT

Rare earth elements (REEs) have been identified as critical elements that are needed to secure a sustainable source of energy in the future. Increasing the demand for REEs has led to a worldwide interest in the development of novel technologies to separate them. However, the separation of these elements and their compounds has been very challenging due to their complex chemistries. Among the different separation and purification techniques, the separation and extraction of REEs is heavily relied on solvent extraction, due to several advantages such as suitability over a wide range of operation scales and the relatively simple equipment design. However, the existing separation technologies that primarily use solvent extraction process, suffer from low separation efficiency, poor stability of separation materials, limited selectivity and production of huge amount of waste materials. Furthermore, the types of solvents used in the extraction processes over the last century have generated fears about their hazardous impact on the environment. Development of safer and more efficient processes that rely on the design of green and highly selective extractants has been the focus of rare earth research in the last decade and is the major motivation of this research study.

1.2. OBJECTIVES OF THE PRESENT RESEARCH

The goal of this research was to develop a novel type of ionic liquids for the recovery and separation of rare earth elements. This study used novel in-house synthesized functional ionic liquids (FILs) with different cations and tridentate oxygen-

donor coordinating ligands. Therefore, complexing functionalities have been incorporated into both anionic and cationic parts of the FILs. Both anions and cations of ionic liquids are composed of only C, H, O, and N atoms, which are incinerable, therefore, could help to reduce the amount of solid wastes produced at plant operations. The inner synergistic effect provided by both cation and anion helped to improve the loading capacity and kinetics of the extraction process. The diglycolamide-based ligand on the anionic component enhanced the extraction efficiency, due to the presence of three oxygen atoms in the ligand structure. Incorporating a bi-dentate betaine derivative ligand with two oxygen donating atoms to the cationic component could help to reduce reagents' consumption and make the extraction process very efficient and fast. Easy synthesis and benign nature of degradation products are some of the advantages of the proposed FILs.

The specific objectives of this study were as follows:

- Investigations on the effect of the structural characteristics of the synthesized FILs on the extraction efficiency and selectivity. These structural properties include: 1) integration of a tridentate O-donor ligand into the anionic part of FIL molecular architecture; 2) changing the length of the non-polar alkyl chain; and 3) functionalization of the cationic component with a bi-dentate O-donor ligand;

- Examining the effect of diluent type on the extraction efficiency;

- Investigations on the extraction kinetics and thermodynamics;

- Feasibility of metal stripping from the FIL/diluent phase; and

- Investigations on the complexation mechanism and identification of different species formed during the extraction process and their relative stabilities.

1.3. RESEARCH OUTLINE

Research objectives had been accomplished through the implementation of three research phases. The goals or tasks of each phase are explained briefly here.

1.3.1. Phase 1: Synthesis and Characterization of Functionalized Ionic Liquids. During this phase, two types of functionalized ionic liquids were synthesized through alkylation, neutralization and metathesis reactions. The synthesized FILs were characterized using advanced diagnostic tools to reveal structural characteristics and physical properties such melting point, thermal stability, electrochemical properties, viscosity, density, water content, and the different functional groups. These tools include: nuclear magnetic resonance (^{1}H and ^{13}C NMR), Fourier transform infrared spectroscopy (FTIR), high-resolution mass spectrometry (HRMS), thermal gravimetric analysis (TGA), disc scanning calorimetry (DSC) in addition to density and viscosity analysis.

1.3.2. Phase II: Investigations on the Extraction Efficiency of FILs and the Relevant Kinetic and Thermodynamic Aspects. Bench scale extraction tests were carried out using the synthesized FILs and selected REEs from the three primary groups of REEs: heavy REEs; light REEs and medium REEs (Europium is taken as an example). This classification of REEs is based on the electron configuration of each rare earth element, which will affect the physiochemical properties and the complexation mechanism between REE and FILs. Process kinetics and extraction thermodynamics were investigated by studying the influence of extraction time and temperature on the extraction efficiency. A competitive extraction study of ten rare earth elements by the synthesized FILs was carried out to assess the separation selectivity. The effect of diluent

type on the extraction efficiency was investigated. Stripping of the REEs from the loaded FILs was also studied.

1.3.3. Phase III: Complexation and Extraction Mechanism. The primary objective of this phase was to understand the REE-FIL complexation behavior and extraction mechanism. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the REE-FIL complexes, and identify the possible loss of FIL components, if existed, to the aqueous phase. The stoichiometry of complexation was determined using slope analysis approach and the extraction mechanism and possible reactions were proposed based on the FTIR and NMR analyses of the organic and aqueous phases before and after extraction. scale extraction tests were carried out using the synthesized FILs and selected REEs from the three primary groups of REEs: heavy REEs; light REEs and medium

1.4. INTELLECTUAL MERITS AND BROADER IMPACTS

The merits and impacts of this research are summarized in the following sections.

1.4.1. Intellectual Merits. This work introduces novel functionalized ionic liquids that were successfully used to enhance the selective separation and recovery of rare earth elements from aqueous solutions. Important contributions of this research to the advancements in science are highlighted as follows:

1.4.1.1. Material science. This study used, for the first time, new types of ammonium-based functionalized ionic liquids that possess functionalities in both cationic and anionic components which improved the separation efficiency of rare earth elements. By demonstrating methodologies to synthesize and use these novel FILs, this study charts

new pathways for rational design of other classes of "task-specific" FILs for use in other applications such as biotechnology, nanotechnology and alternative energy.

1.4.1.2. Separation science/Hydrometallurgy. The systematic investigations carried out in this study to reveal the fundamental structure-performance (cause-effect) links can be applied to better understand and describe sub-processes involved in particulate and metal separation processes. Such understanding will open new frontiers in the field of separation science and hydrometallurgy, wherein molecular architecture of FILs can be tailored for a myriad of applications such as extraction of critical metal, separation of strategic minerals, water purification, and wastewater treatment.

1.4.1.3. Coordination chemistry. Spectroscopic investigations on the complexation mechanism revealed valuable information about the coordinating sites and bonding features of each ionic liquid, in addition to the stability of complexes formed by FILs. Therefore, the coordination chemistry of FIL-based systems was better understood to further improve the extraction process. Better understanding of the effect of functionalization, denticity, and functional groups on the complexation behavior can help to develop other separation systems based on functional ILs.

1.4.1.4. Physical chemistry. Although understanding the surface chemistry and thermodynamics has been identified as future cutting-edge research in the field of process separation, current research on rare earth extraction by functionalized ILs lacks major fundamental areas of investigation such as: 1) detailed knowledge of the role of solution chemistry in metal uptake and release in IL-based systems and 2) development of a reliable thermodynamics and kinetics model for REE/IL complex formation. This research studied the thermodynamic aspects of the FIL-based extraction system and the

factors involved in solution chemistry, which can be useful from the operational and environmental points of view.

1.4.2. Broader Impacts. This research could have a broader impact regarding the sustainability and environment, which is discussed below.

1.4.2.1. Societal benefits. This project addresses our generation's grand challenge to integrate sustainability into the separation and purification processes of rare earth as ones of the most critical elements. Using task specific ILs as alternative extractants will lead to improved separation efficiency due to their unique physicochemical properties, superior loading capacity, and enhanced selectivity. The new types of ILs developed here will allow the use of smaller quantities of ILs compared to the amounts of conventional extractants used in solvent extraction processes. In addition, the proposed ILs are composed of only C, H, O, and N atoms, which are incinerable and therefore reduce the amount of solid wastes. Thus, the use of IL should minimize the disposal cost since these materials are more environmentally friendly and less toxic. Also, the saponification process in traditional rare earth extraction technologies leads to the consumption of tons of ammonia, which results in the production of massive amount of wastewater containing nitrogen. Treatment of wastewater produced in REE solvent extraction accounts for 20–30% of total cost [1]. For example, over 20 million tons of wastewater are produced annually from the REE industry in china with ammonia level up to 5000 ppm and requires 0.24 Billion USD annually to deal with environmental pollution. Therefore, the proposed ILs can serve as potential alternatives to commercial extractants ensure sustainable separation of critical metals, especially rare earth elements and their compounds.

1.4.2.2. Knowledge dissemination/outreach. Technical outcomes of this research have been published in top peer-reviewed journals and will be presented at national and international conferences [e.g., Society of Mining, Metallurgy and Exploration (SME) annual conferences, the American Chemical Society (ACS) regional and national meetings, and the International Mineral Processing Congress Conference (IMPC)]. Moreover, a patent of this invention has been filed (U.S. Patent Application No. 62/849,244, Unpublished, filed on May 17, 2019).

1.5. CLAIM OF NOVELTY AND ORIGINALITY

This research is an original and independent work seeking for the goals, objectives and impacts mentioned in Sections 1.2 to 1.4. The work introduces a novel type of functionalized ionic liquids (FILs) for enhanced recovery and separation of REEs from aqueous solutions. The better extractability, enhanced selectivity towards heavy rare earth, and improved loading capacity of the new FILs are the key advances of this research which will immensely contribute to the field of hydrometallurgical separation of REEs. In addition to the technology advancement, this research provides a better understanding of the extraction of lanthanides using ammonium-based ionic liquids which is essential to design more robust separation technologies in the future.

2. LITERATURE REVIEW

2.1. INTRODUCTION TO RARE EARTH ELEMENTS

Critical materials such as rare earth elements have become the foundation in several technologies and have been used extensively in many industries such as modern electronics, green energy, health care, transportation, and defense. The criticality of materials is usually evaluated in terms of supply risk, environmental implications, strategic applications, and security concerns in terms of economic prosperity and possible political tensions. US Department of Energy and European Union have published separate lists of critical elements [2, 3]. Among all the critical materials listed, the most critical situation seems to be that of REEs.
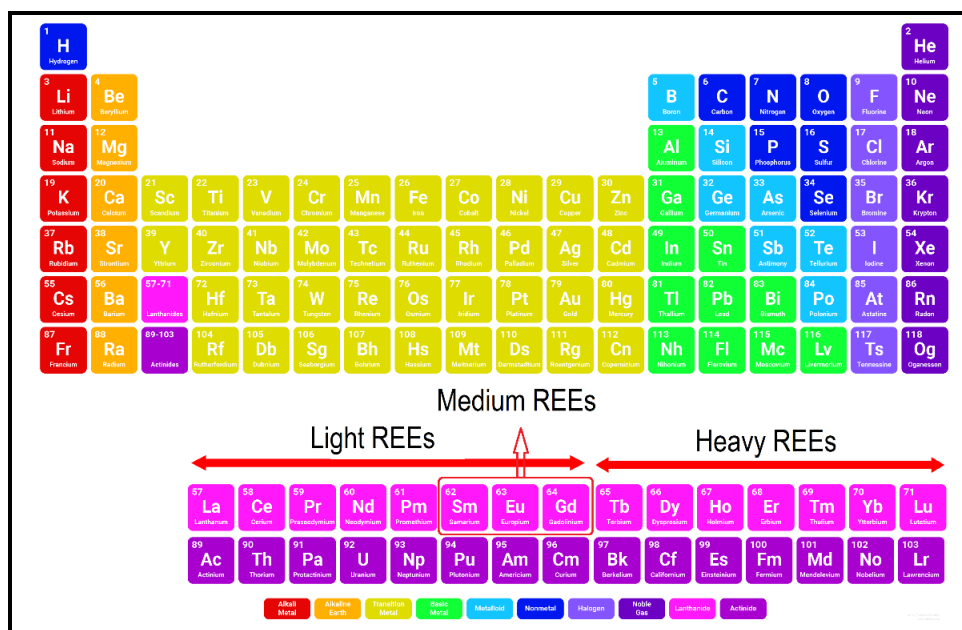
Figure 2.1. Rare earth elements in the periodic table and their classification

Rare earth elements represent a group of 17 elements in the periodic table as shown in Figure 2.1. REEs group comprise the lanthanides from lanthanum to lutetium, plus scandium and yttrium. The discovery of REEs began in the late eighteenth century and continued for 150 years (Figure 2.2). First REEs were discovered in a black mineral "Ytterbite" consisting of lanthanum, cerium and yttrium. Promethium was the last element identified through the nuclear reaction in 1947 [4].

Rare earth elements are classified based on the differences in their chemical and physical properties such as atomic number, electron configuration and double-salt solubility [5-7]. In one classification, REEs are categorized into two groups namely light REEs (LREEs) (form lanthanum to europium) and heavy REEs (HREEs) (from gadolinium to lutetium). Yttrium is considered as a heavy rare earth element due to its co-occurrence with HREEs in same ore deposits and it also exhibits similar properties to those of HREEs. Scandium is considered as a light rare earth element in some references but in others, it is considered neither light nor heavy REE [8]. In another common classification, REEs are categorized into three groups based on the difference in their double-salt solubility [8]. Samarium, europium, and gadolinium are considered as medium REEs (MREEs) since their sodium double sulfates are more soluble than those of LREEs but less soluble as compared to those of HREEs.

2.1.1. Sources. Rare earth elements can be found in primary and secondary sources.

2.1.1.1. Primary sources. There are about 200 minerals containing one or more REEs [10]. These minerals include phosphates, carbonates, oxides, silicates, and halides. Despite the wide range and the large number of rare earth minerals, a few of them is

commercially significant. Most of the primary REE resources are associated with three major minerals namely bastnaesite, monazite, and xenotime. Bastnaesite and monazite are the primary sources for light REEs while xenotime is dominated by the heavier REEs [11]. In Table 2.1, REEs content of the major rare earth deposits is presented. Rare earth minerals are found in association with different forms of rocks including igneous, sedimentary, and metamorphic rocks [12]. A simple classification of RE deposits is presented in Figure 2.3. The global distributions of rare earth deposits and rare earth reserves are shown in Figure 2.4 and Figure 2.5, respectively.
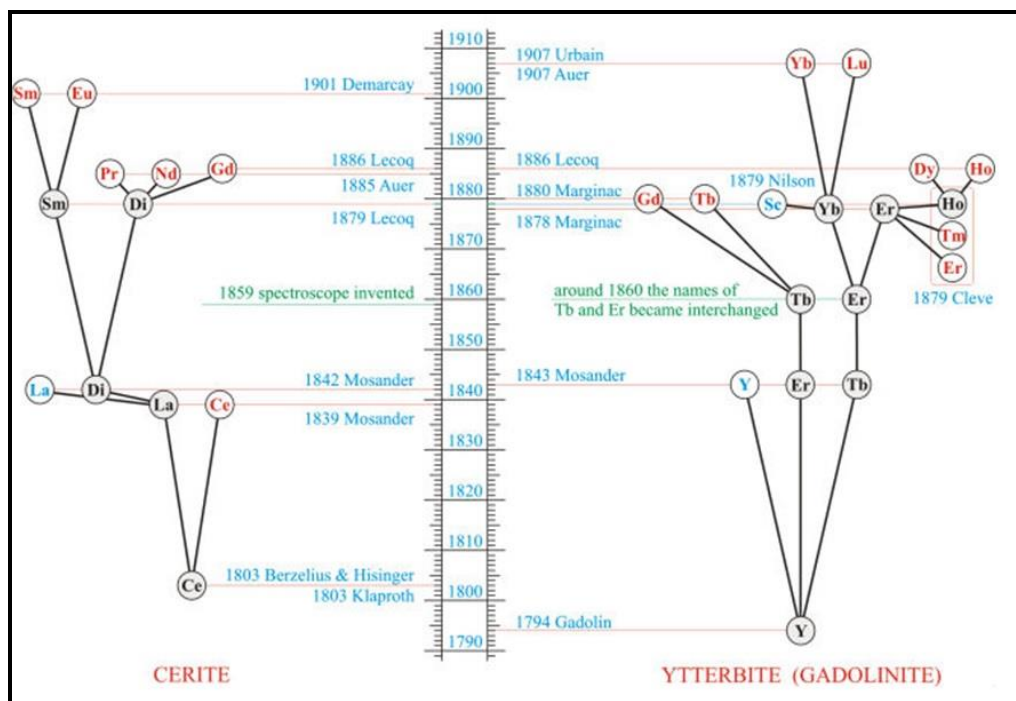
Figure 2.2. History of the discovery of rare earth elements [9]

Table 2.1. REEs content in major rare earth deposits [13]

REE	Mixed ore	Bastnasite	Monozite	Ion-adsorbed RE deposits	
	Bayan Obo (China)	Mountain Pass (USA)	Mount Weld (Australia)	Xunwu (China)	Longnan (China)
Y	0.27	0.09	Trace	8	65
La	27.27	32.25	26.00	43.4	1.82
Ce	48.73	49.17	51.00	2.40	0.4
Pr	5.13	4.35	4.00	9.00	0.7
Nd	16.63	12.02	15.00	31.70	3.00
Sm	1.24	0.79	1.80	3.90	2.80
Eu	0.21	0.12	0.4	0.5	0.10
Gd	0.4	0.17	1.00	3.00	6.90
Tb	Trace	Trace	0.1	Trace	1.30
Dy	0.1	Trace	0.2	Trace	6.70
Ho	Trace	Trace	0.1	Trace	1.60
Er	Trace	Trace	0.2	Trace	4.90
Tm	Trace	Trace	Trace	Trace	0.7
Yb	Trace	Trace	0.1	0.3	2.50
Lu	Trace	Trace	Trace	0.1	0.4
Total	100	100	100	100	100
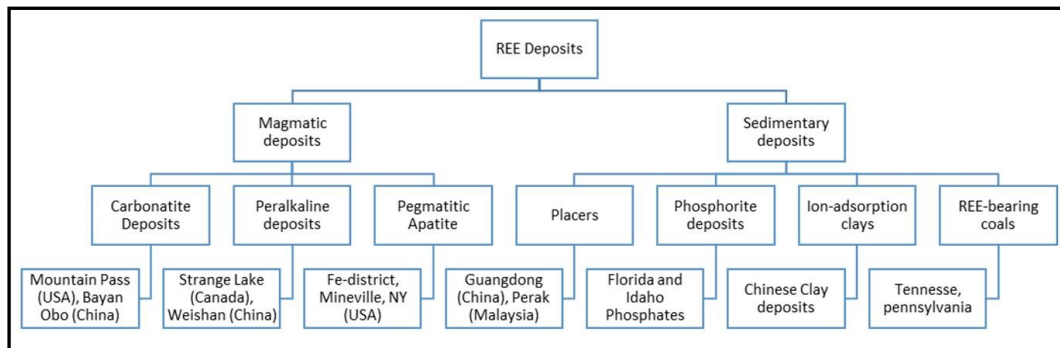
Figure 2.3. Classification of rare earth deposits [12]
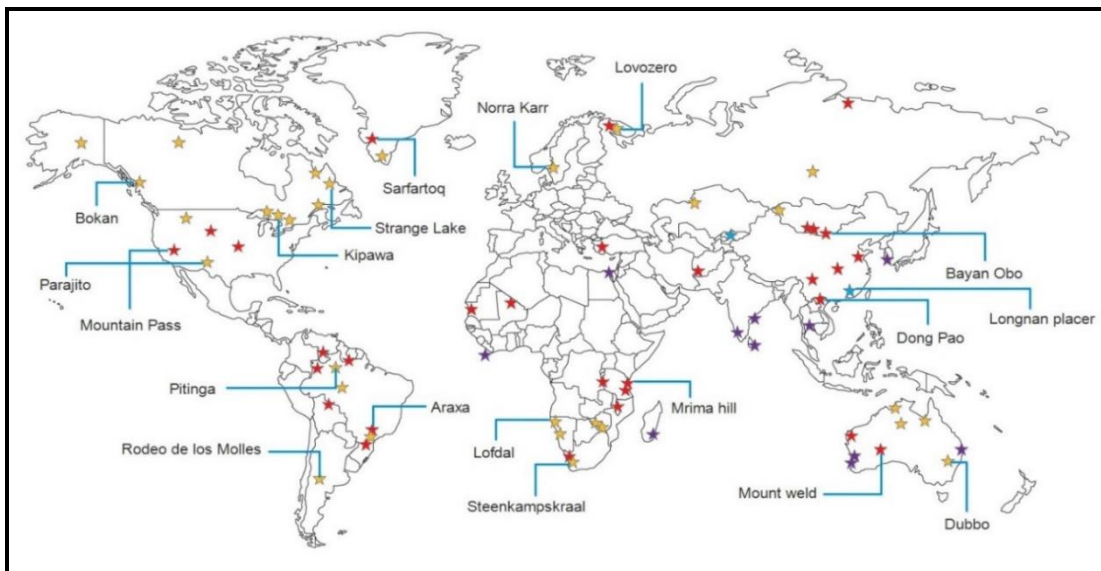
Figure 2.4. Global distribution of rare earth deposits [14]

2.1.1.2. Secondary sources. Secondary sources of rare earth elements have attracted more attention due to their dramatically increasing number of applications and significant growth in global consumption [16-18]. In-use stocks such as catalysts and magnets in automobiles and wind turbines are considered as alternative sources of rare

earth elements. As shown in Figure 2.6, light REEs are more abundant in secondary

sources than the heavy REEs.
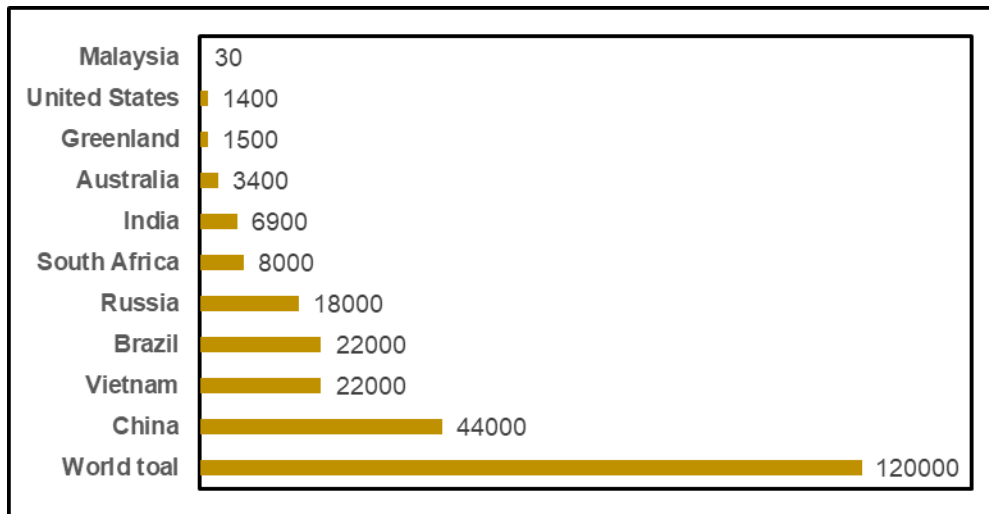
Figure 2.5. Global distribution of rare earth reserves as of 2017 (in 1000 metric tons REO) [15]
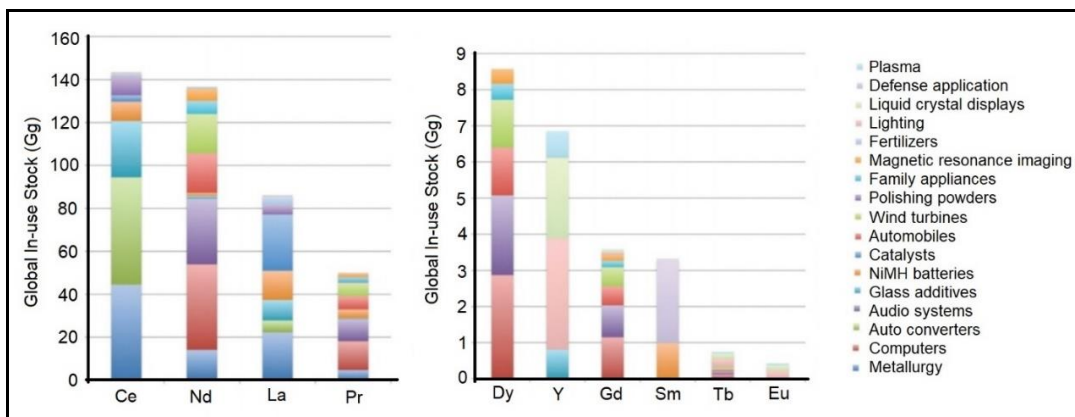
Figure 2.6. Global in-use stocks of selected rare earth (2007) [18]

Current recycling rate of REEs is estimated to be less than 1%, and assessments show that it is increasing particularly from sources like used magnets, batteries, and lamps [19]. The concentration of REEs in secondary sources is varied in a wide range from 0.1 to 30 % [20]. Absence of radioactive elements is an advantage of secondary sources but the less abundance of heavy REEs is a challenge [21]. Electronic wastes, tailings from iron, lead, zinc, sulfurs, phosphate (phosphogypsum), alumina (red mud) mining and processing are considered as potential secondary sources of rare earth elements [22-24].

2.1.2. Properties. Rare earth elements have several physical and chemical properties that make them attractive for many applications.

2.1.2.1. Physical and chemical properties. Rare earth elements are typically silvery-white or silvery-gray metallic elements, with the exception of promethium and neodymium, which are pale yellow [25]. The color of REE ions are controlled by their electron configuration [26]. Some of the physical characteristics of REEs are presented in Table 2.2. Boiling point and melting points are key factors when considering pyrometallurgical techniques for REE processing [27]. According to these two key properties, REEs can be categorized into four groups: 1) Yb, Eu, Sm, Tm; 2) Dy, Ho, Sc, Er; 3) Tb, Gd, Y, Lu; and 4) Ce, La, Pr, Nd. The melting and boiling points of REEs within each of these four categories are close to each other. The high thermal neutron absorption of Sm, Eu, and Gd makes them good candidates for neutron capture reaction in nuclear reactors. Sc, Y, La, and Lu are diamagnetic due to the unpaired electrons in their 3d, 4d and 4f orbitals. Gd, Tb, Dy, and Tm are ferromagnetic while the rest of REEs are paramagnetic. The REE cations are good luminescent materials with long afterglow

due to their long average life of excited state. Ce-based rare earth materials have low ignition point and are widely used for making flints. REEs are very reactive and can easily react with water and inorganic acids [26]. They form stable compounds when react with oxygen, nitrogen, halogens and carbon [8]. Intermetallic compounds of rare earth elements are widely used in several high-tech applications [28, 29].

2.1.2.2. Lanthanide contraction. Lanthanide contraction is a phenomenon that describes the decrease in the atomic size and ionic size with the increase in atomic number through the lanthanide series while the valence shell remains unchanged. According to this phenomenon, as the atomic number increases the size of the atoms and ions of REEs decreases (Figure 2.7). The contraction is due to the weak shielding of nuclear charge by the electrons in 4f orbital that result in an increase of attraction between the outer shell (6s electrons) and the nucleus. The order for the shielding effects of electrons is: $s > p > d > f$.

The lanthanide contraction leads to a regular change of the physicochemical properties of lanthanides through the series [30]. The changes of these properties make it possible to separate REEs. As the ionic radii of REEs change, their coordination ability with different ligands changes. This provides a mean for separation technologies to produce pure single REEs.

2.1.3. Applications. The distinctive properties of REEs make them essential additives to highly-demanded materials in different applications. Around 55% of the total worldwide production of rare earth elements is consumed in the market of catalysts, magnets and metallurgy [31-34]. Some of important applications of REEs are summarized in In Table 2.3.

Table 2.2. Physical properties of rare earth elements [25]

REE	Density (g/cm^3)	Boiling point (^{0}C)	Melting point (^{0}C)	Resistivity (25 ^{0}C) ($\times10^{-4}$ Ω cm)	Thermal neutron absorption capture cross section (b)
Sc	2.98	2730	1538	66	24
Y	4.47	2630	1502	53	1.31
La	6.16	3470	920	57	9.3
Ce	6.77	3468	793	75	0.73
Pr	6.47	3017	935	68	11.6
Nd	7.00	3210	1024	64	46
Sm	7.53	1670	1072	92	5600
Eu	5.24	1430	826	81	4300
Gd	7.88	2800	1312	134	46000
Tb	8.25	2480	1356	116	46
Dy	8.55	2330	1407	91	950
Ho	8.78	2490	1461	94	65
Er	9.05	2420	1497	86	173
Tm	9.32	1720	1545	90	127
Yb	6.97	1320	824	28	37
Lu	9.84	3330	1652	68	112
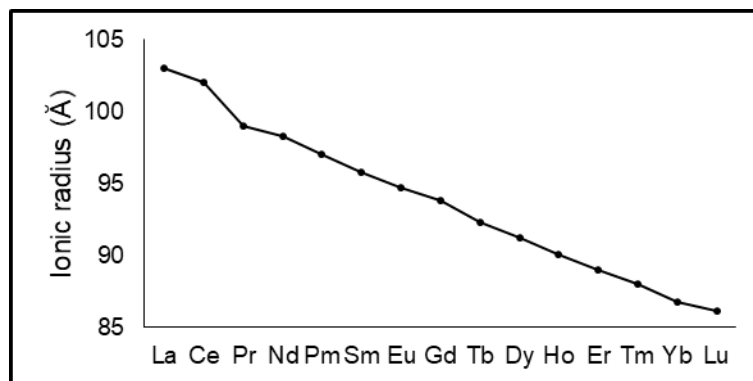
Figure 2.7. Ionic radius decrease in lanthanides with increasing atomic number

Lanthanum and cerium are the mostly-used REEs in the production of catalysts, glass and metallurgical products. Neodymium, praseodymium and dysprosium are used in the production of magnets and ceramics. Due to their unique chemical and physical properties, REEs are also used in advanced technologies including energy technology (e.g., batteries, lighting, hydrogen storage, electric and hybrid vehicles, etc.), computing and information technology (smart phones, hard drives, digital cameras, etc.), and security and defense technologies [35, 36].

2.1.4. Supply Risk. The According to the U.S. department of energy (DOE) criticality matrix (Figure 2.8), rare earth elements are among the most critical elements in the medium-term (2015-2025). This criticality assessment is based on the increasing demands of key materials and supply-demand mismatches. The key point about REEs is that the demands of different elements is not uniformly growing [39]. The current global REE demand is estimated to be 105,000 tons of rare earth oxides per annum with an expected annual growth of 5.6%. This will result in a demand of approximately 210,000 tons of total REEs in the year 2025 [38, 40].

Table 2.3. REEs and their applications [37, 38]

REE	Application and products
Sc	Aerospace framework, lasers, magnets, lighting, baseball bats
Y	Cancer treatment drugs, ceramics, LED lights, fuels additive, jet engine turbines, televisions, satellites
La	Catalyst, television, fuel cells, night vision instruments, rechargeable batteries
Ce	Catalytic converters, catalysts in petroleum refining, glass, polishing agents
Pr	Aircraft engine alloys, catalyst, ceramics, fiber optic cables, magnets, wind turbines
Nd	Cell phones, electric vehicles, lasers, MRI machines, magnets, wind turbines
Pm	Laser for submarines, nuclear powered battery
Sm	Missile/radar system, magnets, stealth technology
Eu	Fluorescent glass, lasers, televisions, control rods in nuclear reactors
Gd	Microwave applications, MRI machines
Tb	Solar systems, electric vehicles, fuel cells, televisions, optic data processing, magnets, wind turbines
Dy	Electric vehicles, home electronics, permanent magnets, wind turbines, lasers
Ho	Microwave equipment, glass coloring
Er	Glass, metallurgical uses, fiber optic data transmission, lasers
Tm	X-ray machines, high temperature superconductors
Yb	Improving stainless steel, stress gauges
Lu	Catalysts, positron emission tomography detectors

As mentioned in previous sections, REEs are of a great importance in different technology sectors including green and alternative energy, water purification,

papermaking, metal extraction, mining, medicine, microelectronics, etc. As these industry

sectors are growing, the global consumption of REEs is going to increase dramatically

while the supply is diminishing. The consumptions of REE worldwide and in the USA

are presented in Figure 2.9(a-b), respectively.
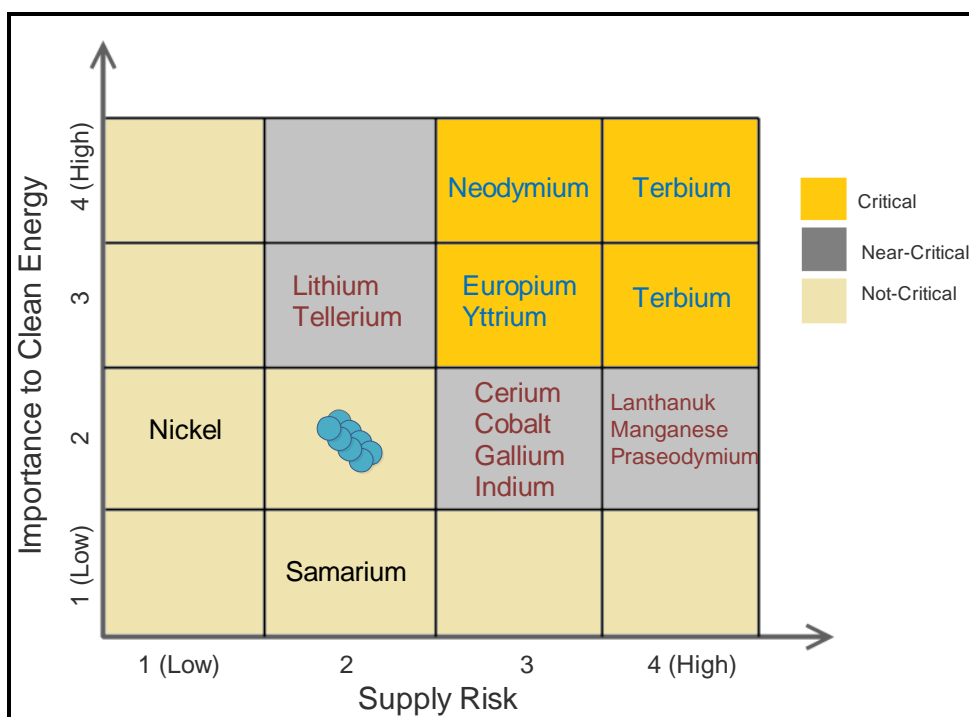
Figure 2.8. Rare earth criticality matrix (2015–2025) [2]

Currently, China is controlling the rare earth market with about 90% of the

world's mine production. This lack of supply diversity could result in supply disruption

on the long term. As shown in Figure 2.9 (c-d), China is the largest producer and

consumer of the REEs. The USA is not among the largest REE producers but is one of the main consumers.

2.2. SEPARATION AND RECOVERY OF RARE EARTH ELEMENTS

Separating REEs from natural resources is a complicated process due to the relative low concentration of these elements and the complex nature of the host rock. Moreover, REEs have similar physiochemical properties which makes the separation of individual elements very challenging. Physical separation and chemical dissolution following by solvent extraction are the most common techniques used for REEs extraction and enrichment. A brief discussion of these techniques is provided in the following subsections.

2.2.1. Physical Processes. The REE bearing minerals are usually beneficiated based on the differences among their physical properties (e.g. gravity, magnetic, electrical, and surface chemistry). Gravity separation is considered as a suitable beneficiation technique due to the relatively large specific gravity of REE bearing minerals as compared to associated gangue minerals (mainly silicates) [42, 43]. Gravity concentration technique is usually employed to separate monazite from sand. Beach sand is initially treated by a cone concentrator and a pre-concentrate containing 20–30% heavy minerals is produced. A product containing 80–90% heavy minerals can be obtained thereafter by using spiral concentrators.

Other physical processes such as magnetic and electrostatic operations are also used for further beneficiation. For example, in the processing circuit of Egyptian beach

sands, gravity separation is initially utilized to separate low gravity minerals, then the

ferromagnetic minerals are removed using low intensity magnetic separator [44].
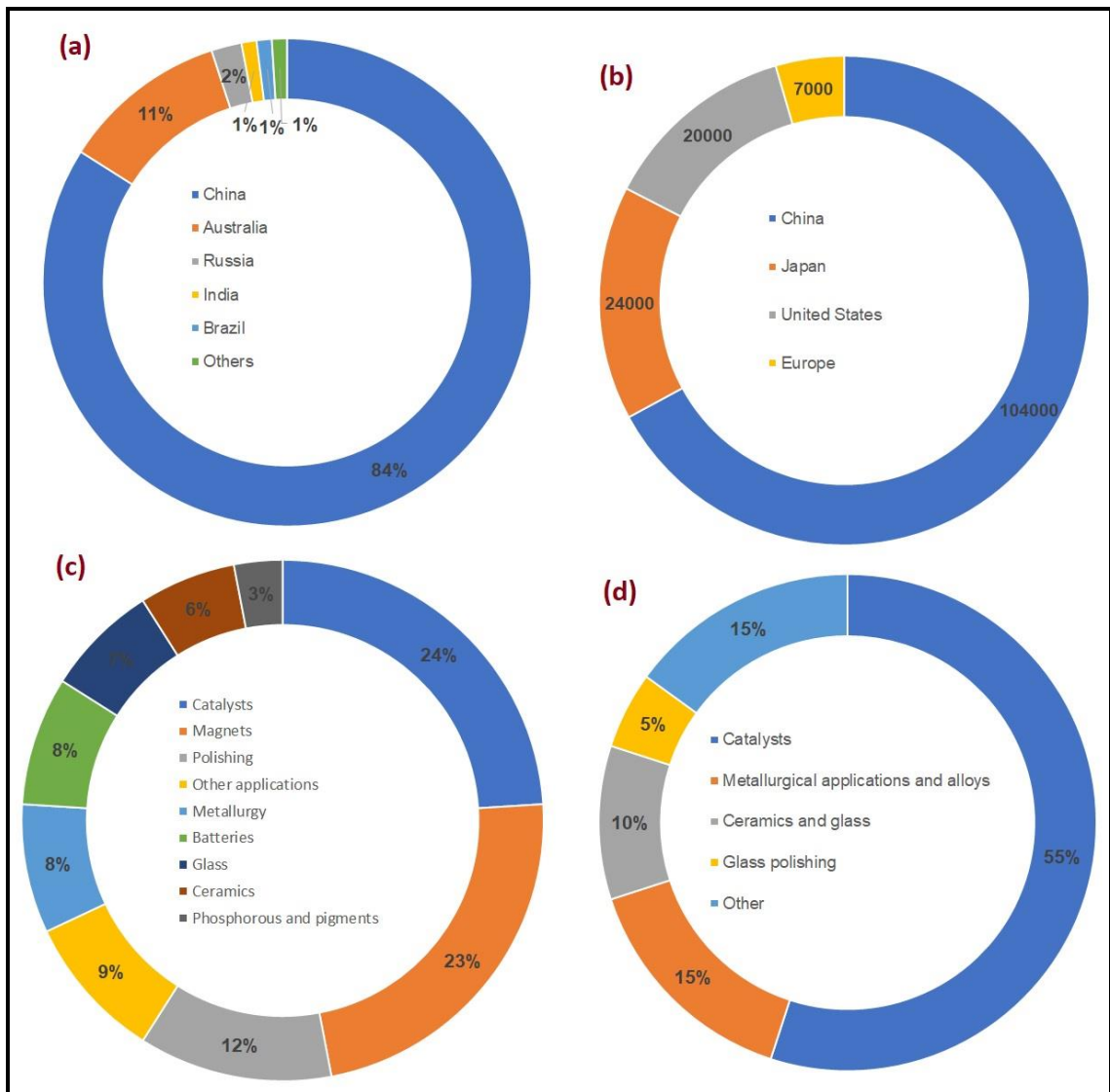
Figure 2.9. Major producing and consuming countries, and major demands of REEs (2016) (a) Major producing countries, (b) major consuming countries, (c) global demand, and (d) U.S. demand of REEs as of 2017 (data acquired from [32, 33, and 41])

Magnetic separation is a common technique for rare earth processing to discard magnetic gangue minerals (e.g. zircon and rutile) and concentrate paramagnetic REEs [45]. Paramagnetic rare earth minerals pose ferromagnetic nature when exposed to magnetic fields at low temperatures. The magnetic susceptibility and magnetic properties of rare earth minerals are calculated based on the susceptibility of individual REEs [46]. The calculations indicate that Gd, Dy and Er have the highest magnetic susceptibilities in comparison with other lanthanides, therefore, the xenotime containing these elements has higher magnetic susceptibility compared to monazite [47]. In the processing of Egyptian beach sands, electrostatic separation is employed after the magnetic separation to remove the rutile from monazite and zircon as non-conductive minerals [44]. The electrostatic separation is based on the difference in conductivity of the minerals and is usually utilized when the other alternative techniques cannot be used, since the moisture is harmful for electrostatic separation [55]. This technique is typically used when the specific gravity and magnetic properties of the minerals are similar. A specific example is the separation of monazite from ilmenite by electrostatic separation after they are removed from xenotime via magnetic separation [45]. Physical beneficiation of monazite in beach sands using the combination of the gravity, magnetic and electrostatic techniques is shown in Figure 2.10.

2.2.2. Froth Flotation. Froth flotation is a common separation technique which utilizes the differences in surface wettability of minerals as established by the interaction with various reagents at different interfaces. In this process, the hydrophobic solids attach to air bubbles and float leaving behind the hydrophilic ones in the aqueous suspension. A large number of research studies have been conducted on the flotation of rare earth

minerals compared to other beneficiation methods. The studies focused on the flotation of

bastnasite and monazite as they are major components of large rare earth deposits (e.g.

Bayan Obo and Mountain Pass) [48, 49]. Various types of flotation surfactants have been

developed to enhance the selective flotation of rare earth minerals [50-53]. For example,

flotation collectors such as hydroxamates, fatty acids, phosphoric acids, and carboxylic

acids have been intensively tested in many studies to improve the recovery and grade of

the rare earth flotation concentrates.
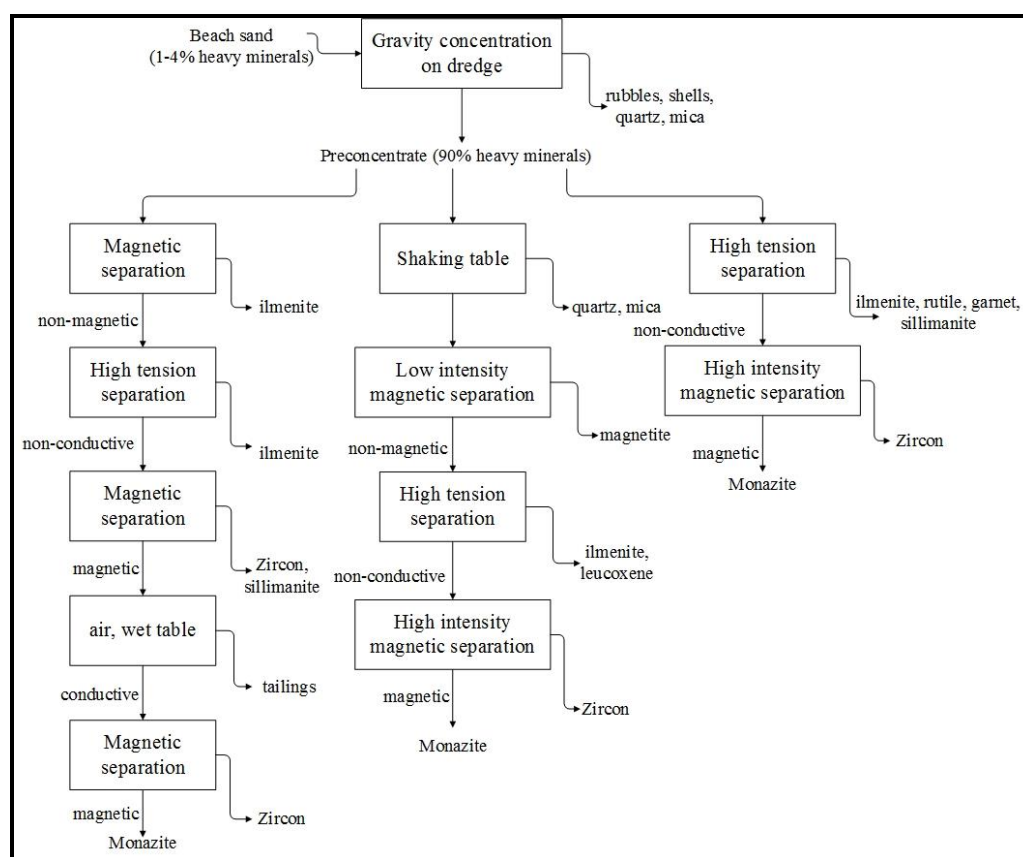
Figure 2.10. Physical beneficiation of monazite in beach sands using the combination of the gravity, magnetic and electrostatic techniques [26]

The common collectors used in rare earth flotation is summarized in Table 2.4. Flotation depressants such as sodium silicate, sodium hexafluorosilicate, lignin sulfonate, and sodium carbonate are also utilized in the flotation process of rare earth minerals to suppress the flotation of the associated minerals. [54, 55]. A simplified flowsheet of the flotation process of Mountain Pass mine is shown in Figure 2.11.

Table 2.4. Types and examples of collectors used in rare earth flotation [56]

Mineral	Collector type	Example	pH range
Bastnasite	Hydroxamic acid	Hydroxamate H_2O_5	8-8.5
Bastnasite	Alkyl phosphoric acid	Alkyl phosphate Easter	4-5
Bastnasite	Aromatic phosphoric acid	Styrene phosphoric acid	6-10
Bastnasite	Aromatic amide	-	5-6
Bastnasite	Aromatic carboxylic acid	O-phthalic acid	5
Bastnasite or Monozite	Alkyl carboxylic acid	Fatty acid, oleate, tall oil	6-9

2.2.3. Hydrometallurgical Processes. Hydrometallurgical processes are one of the major parts in rare earth production facilities.
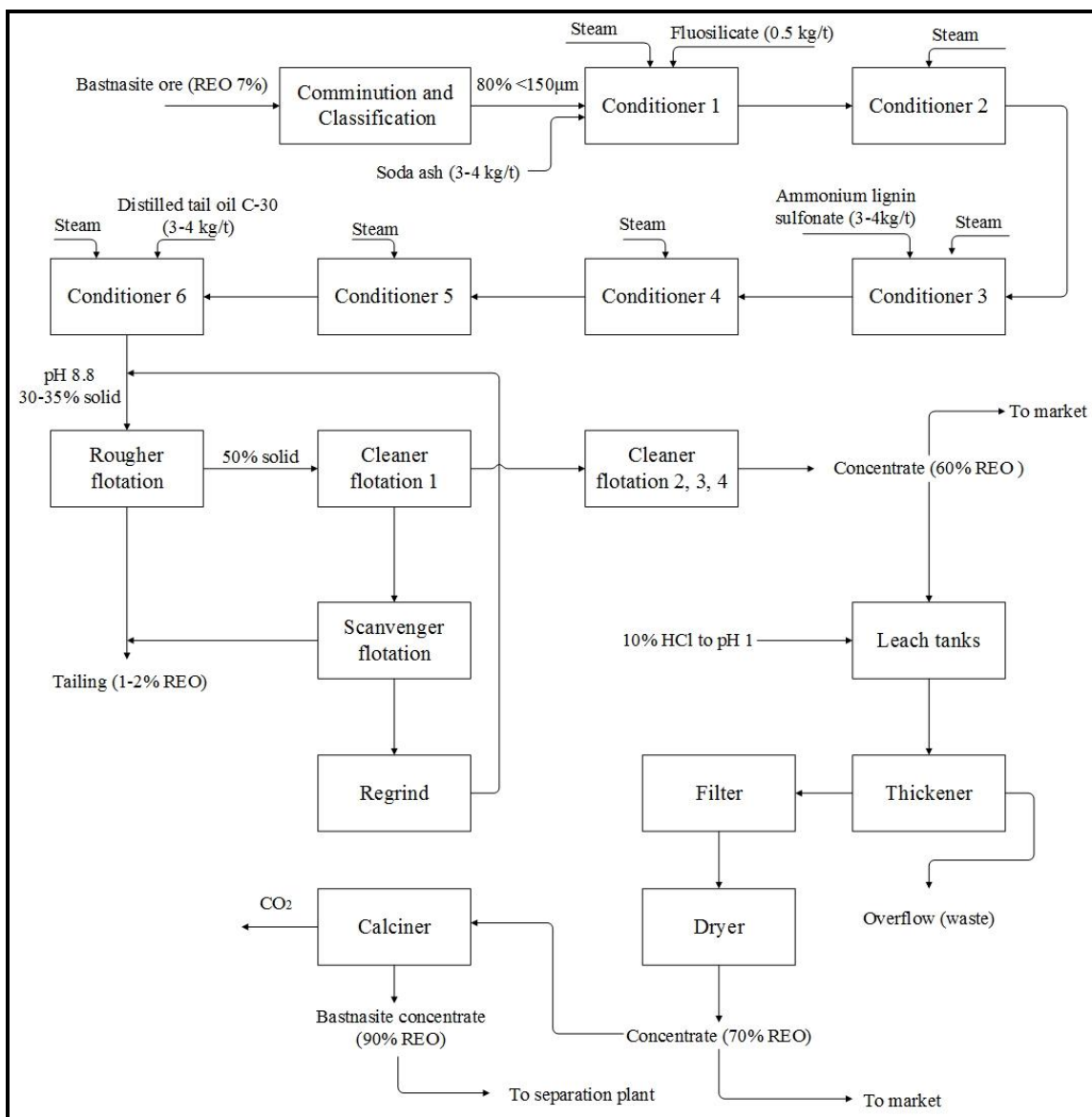
Figure 2.11. Flowsheet of bastnaesite beneficiation at Mountain Pass using froth flotation (bastnaesite is the rare earth mineral and barite, calcite, strontianite, and quartz are the gangue minerals) [26]

2.2.3.1. Chemical dissolution and thermal decomposition. Rare earth concentrates obtained from the aforementioned physical beneficiation techniques can be further processed using various chemical and thermal processes such as acid roasting,

chlorination, and caustic decomposition. The reagents used in these processes include

chlorine gas, electrolytes (e.g. NaCl, NH₄Cl, and (NH₄)₂SO₄), alkalis (e.g. NaOH and

Na₂CO₃) and inorganic acids (e.g. HCl, H₂SO₄, and HNO₃) [57-61].

The acid-roasting of rare earth is mostly performed at high temperatures [62, 63].

The process at high temperature is simple, however, it emits some toxic gases (e.g. HF,

SO₂, SO₃ and SiF₄), which are normally captured by a water scrubber [64, 65]. A general

scheme of acid-roasting and water leaching of   astnaesite and monazite is shown in

Figure 2.12. The concentration of the acid depends on the grade of the ore and the type of

gangue minerals present in the ore.

Hydrochloric acid (HCL) is a common reagent that is used to leach carbonate-rich

bastnaesite. Rare earth fluorides, which do not dissolve in concentrated HCl, can be

leached using sodium hydroxide (NaOH). Chlorination process is used sometimes to

decompose rare earth minerals using chlorine gas in the presence of carbon. This process

can effectively decompose various rare earth minerals such as   astnaesite, monazite,

xenotime, allanite, cerite, euxenite, fergusonite, and gadolinite, but there is no industrial

application for this process yet [25].
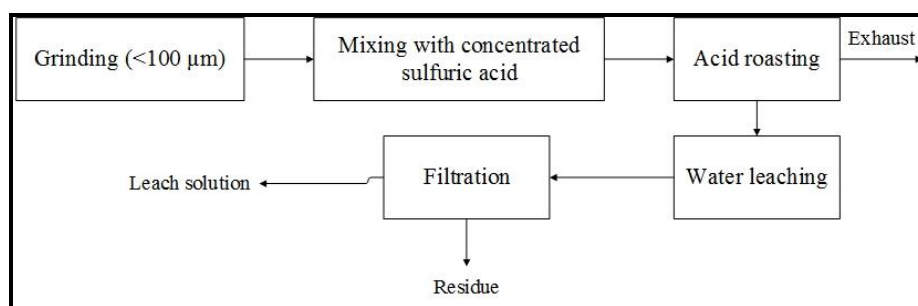
Figure 2.12. General scheme of acid-roasting and water leaching of bastnaesite and
monazite [25]

2.2.3.2. Ion exchange. Ion exchange technology have played a significant role in the development of separation and purification systems. This technology is based on the exchange of ions of the same charge between a liquid phase in contact with a solid phase. Ion exchange techniques have not only been applied for hydrometallurgical processes but also are used in water treatment, food, oil and pharmaceutical industries.

Extraction of REEs by ion exchange was first applied in nuclear process to separate fission products [66]. A citric acid–ammonium citrate solution was successfully used at Ames and at Oak Ridge National Laboratory to separate rare earth elements. Since then, ion exchange replaced the crystallization process for separation and purification of REEs. Ion exchange technique was the dominant technology for separation of rare earth elements until 1960s, before solvent extraction process was highly developed. However, many ion exchange resins with different chelating agents and functional groups have been designed and tested for REE extraction and separation (Table 2.5).

Table 2.5. Some ion exchange resins recently used for REE extraction
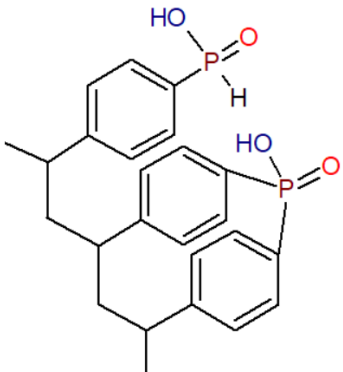
Resin name	Composition	Application	Year	Ref
Tulsion CH-96		Extraction of heavy rare earth elements from phosphoric acid	2010	[67]

Table 2.5. Some ion exchange resins recently used for REE extraction (Cont.)

Resin name	Composition	Application	Year	Ref
D151	Macroporous weak acid resin with functional group of (–COOH)	Adsorption of Cerium from aqueous solution	2010	[68]
D113-III	Polymeric material containing a functional group (–COOH)	Adsorption of erbium(III) from aqueous solution	2007	[69]
XAD-4		Adsorption of La(III), Nd(III) and Sm(III) from aqueous solution	2005	[70]
Tertiary pyridine type resin		Separation of rare earth elements from nitric acid solution	2006	[71]
Amberlite XAD-4 resin with azacrown ether		Preconcentration and separation of La(III), Nd(III) and Sm(III) in hydrochloric acid solution	2010	[72]
N-methylimida zolium resin		Adsorption of Ce(IV) in nitric acid medium	2011	[73]

2.2.3.3. Crystallization and precipitation. In crystallization process, a chemical or metallic compound in solution is converted into a solid state by a change in temperature. The separation between species occurs via precipitation, freezing, or deposition. Crystallization has been considered as one of the important conventional separation procedures for producing highly pure individual elements. Several salts and double salts have been tested for fractional crystallization of rare earth elements [25]. The double ammonium nitrates $REE(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ have been used for the removal of lanthanum and separation of praseodymium and neodymium [74]. The double magnesium nitrates $2REE(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ have been used for producing the medium rare earth elements as well as separation of the ceric group [75]. The bromates $REE(BrO_3)_3 \cdot 9H_2O$ and ethyl sulfates $REE(C_2H_5SO_4)3 \cdot 9H_2O$ have been successfully employed for the separation of the yttric group [76].

Precipitation denotes the formation of a less soluble compound by the addition of a chemical reagent to separate the metal ions from aqueous solution. Several reagents have been employed for precipitation of rare earth elements as oxalate, hydroxide, or other compounds. The hydroxides, oxalic acid, and double salts have been widely used for precipitation of rare earth elements.

Separation of rare earth elements from each other has also been conducted through precipitation of rare earth double chromate [77]. Lanthanum gets hydrolyzed less extensively, in comparison with other rare earth elements. Ammonia has been used for separation of yttrium and heavy rare earth elements from the nitrate or chloride solutions [78]. The sodium sulfate is used to precipitate rare earth elements as a double sulfate $REE_2(SO_4)_3 \cdot Na_2SO_4 \cdot nH_2O$ [79]. The light and medium rare earth elements such as La,

Ce, Pr, Nd, Sm, Eu, Gd, and Dy form low-soluble double sulfates, which are separable from solution. Oxalic acid is another widely used reagent developed in Ames National Laboratory for precipitation of rare earth elements [80]. Oxalic acid is considered as a better reagent as it can produce concentrates free of troublesome compounds like sulfates and phosphates. However, some ions such as iron can inhibit the precipitation of rare earth elements and hence decrease the efficiency of process. In general, precipitation is used to fractionate rare earth elements into two or three groups and is not considered as an efficient method for producing rare earth elements in high purity.

  2.2.3.4. Solvent extraction. Demands for more effective, efficient, and cheaper processes have led to the use of solvent extraction as a simple and fast process with wide scope. Solvent extraction, also known as liquid-liquid extraction, has been widely used at industrial scale for the extraction and separation of different elements including REEs and other critical metals [81-83]. The basic principle of solvent extraction is shown in Figure 2.13. In this technique, the aqueous solution that contains metal ions is mixed (contacted) with an immiscible non-polar organic liquid, also called a diluent, containing an "extractant". Metal ions bind to extractant molecules and form an "ion complex". The ion complex is then transferred to the organic phase until equilibrium state is reached. The extraction is then followed by a phase separation step. Scrubbing, also called washing, is performed after extraction to remove the undesirable impurities in the loaded organic phase. Water and weak acids or bases are common scrubbing reagents. The loaded organic phase is then stripped by a stripping solution, such as concentrated acids, bases, and salt, to back-extract the target metal ions into the aqueous solution. It is

important to mention that the composition and the nature of the solution feed can affect the efficiency of the entire solvent extraction process.
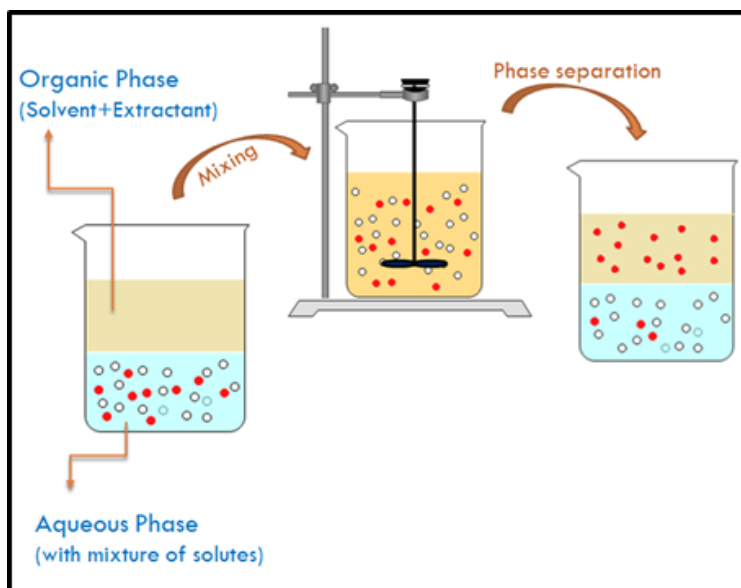
Figure 2.13. Simplified principle of solvent extraction process

Table 2.6 shows examples of commercial extractants that are used in solvent extraction process of rare earth elements. The flowsheet of the extraction of europium from the leach solution in the Mountain Pass is shown in Figure 2.14.

2.2.3.5. Problems with conventional solvents and extractants. Organic diluents (or solvents) are usually used to dissolve the extractants and reduce the viscosity of the metal-extractant complexes. Kerosene, n-heptane, hexane, and toluene are common non-polar solvents used in rare earth solvent extraction process [98-100]. The most challenging problem with organic solvents is that they are volatile and flammable. This results in issuing tough standards and strict cautions in workplace. Despite all these

standards, tragedies are still occurring. For example, Inner Mongolia Baotou Steel Rare-Earth's metallurgical facility caught fire on June 7. 2007 and it took about 4 months to get back the normal operation [102]. In addition to safety and environmental concerns, evaporation of organic solvents leads to increasing consumption, cost, and health issues [103, 104].

Table 2.6. Conventional organic extractants for separation and recovery of rare earth elements
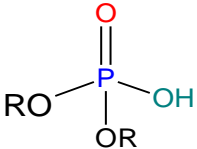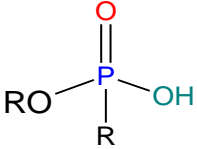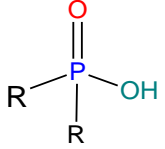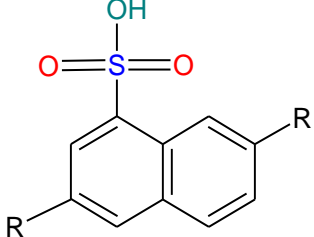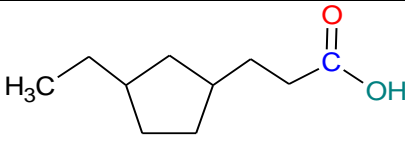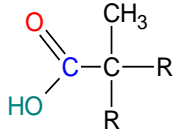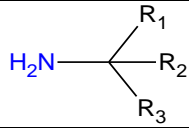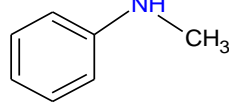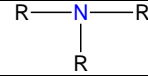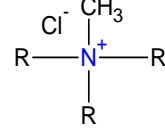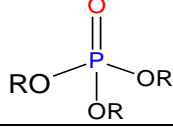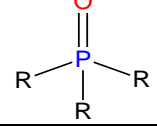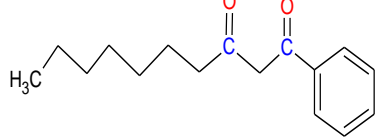
Class of extractant	Type	Example	Structure	Ref.
Acidic extractants	Phosphoric acids	D2EHPA		[84]
	Phosphonic acid	PC88A		[85]
	Phosphinic acids	Cyanex 272		[86]
	Sulphonic acids	Dinonylnaphthalene sulfonic acid		[87]
	Carboxylic acids	Naphthenic acids		[88]

Table 2.6. Conventional organic extractants for separation and recovery of rare earth elements (Cont.)

Class of extractant	Type	Example	Structure	Ref.
		Versatic acids		[89]
Basic extractants	Primary amines	Primene JMT		[90, 91]
	Secondary amines	N-ethylaniline		[92]
	Tertiary amines	Alamines		[93]
	Quaternary amines	Aliquat336		[94]
Neutral extractants	Phosphorous -based	TBP		[95]
		(TOPO) CYANEX 923		[96]
Chelating extractants	Beta diketones	LIX 54		[97]

Over the last six decades, numerous investigations have been made seeking for effective extractants for the recovery and separation of rare earth elements. Table 2.6 shows selected examples of four categories of extractants that are currently used in rare earth extraction.
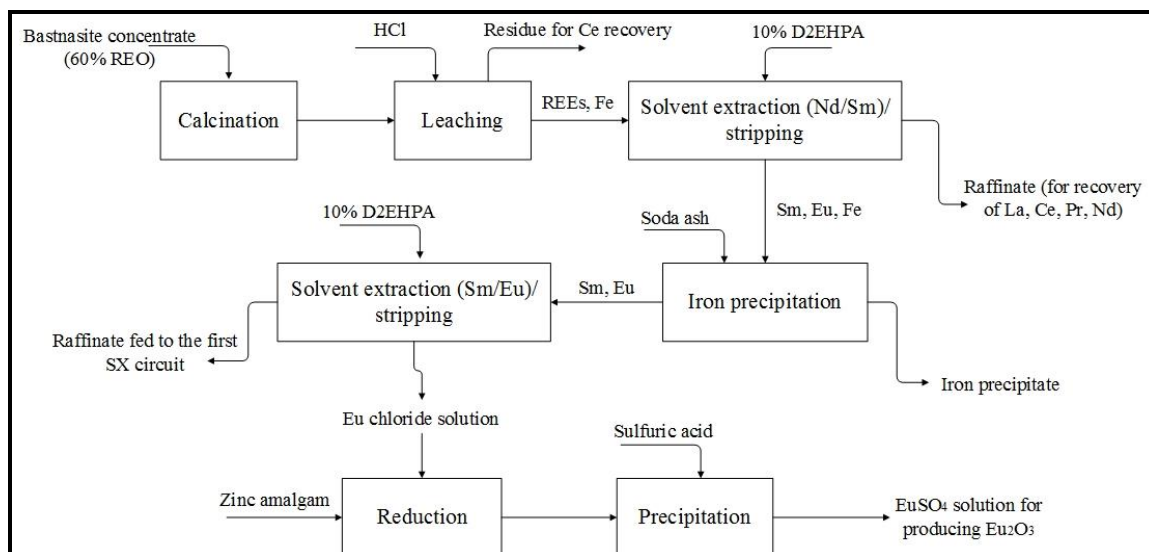
Figure 2.14. Molycorp process for producing europium oxide from the bastnaesite concentrate [26]

Commercial acidic organophosphorus extractants have been widely used for the recovery of lanthanides. They are often used in synergistic mixtures [104, 105] and the active extracting sites are the ionizable protons. Their donor atoms can be altered to suit the ionic properties of metals. D2EHPA (also denoted by HDEHP and P204) is one of the most investigated extractants in rare earth extraction. Extraction in low pH, difficult stripping, gel formation and phase separation problems are undesirable issues of the extraction by D2EHPA. PC88A (also known as HEHEHP, P507, and Ionquest 801) has gained more attention in rare earth extraction due to its higher stripping ability at low acidity as compared with D2EHPA [107]. PC88A behaves as a chelating and a solvating extractant in low and high acidic environments, respectively. At lower acidity PC88A, extracts the rare earth ions through the cation exchange reaction, which leads to the formation of H^+ ions and thus increase of acidity of the solution. On the other hand, increasing the pH of the solution results in a decrease of the

extraction percentage due to the competition between metal ions and H^+ ions for the ligand. To overcome this issue, saponification is required, which is considered as a major disadvantage of extraction by acidic extractants, since the saponification process produces a large amount of wastewater [108]. Cyanex 272 has two P−C bonds with bulky alkyl groups, which gives it higher thermal and chemical stability. However, the low lipophilicity of the complexes formed during the extraction limits the practical application of this extractant [109]. Carboxylic acids, unlike the organophosphorus acids, have a tendency to associate in non-polar solvents but are weaker pH swing extractants [88, 89]. The association of carboxylic acids in low polarity solvents leads to complicated speciation which results in lower selectivity. Low cost and easy stripping of naphthenic acid, as a weak organic acid belonging to carboxylic acid, is the major advantage over D2EHPA and PC88A. However, extraction by naphthenic acid requires the use of some organic additives (e.g. ethers, alcohols, petroleum sulfoxide) to avoid emulsification and disengagement problems [109, 110]. Urbanski et al. and Arichi et al. examined the chelating extractants in the solvent extraction process of europium from nitrate solution, and cerium and lanthanum from chloride solution [111, 112]. Results showed that their performance is unfavorable compared with acidic extractants. The Neutral organophosphates such as Tributylphosphate (TBP) extract the rare earth ions in the form of ion-pairs and neutral complexes [93]. One disadvantage of TBP is that it extracts acid and water molecule as well as rare earth ions, leading to the decrease in the loading efficiency. Cyanex 923 is another example of solvating neutral extractant. Commercial Cyanex 923 usually contains impurity acids and should be purified before extraction to avoid metal reduction effects [113]. The extraction by unpurified Cyanex 923 can follow different mechanism depending on the extraction system. Ma et al. reported that Y^{3+} and La^{3+} are

extracted in the form of $REE(OH)^{2+}$ in unpurified Cyanex 923-n-octane-HNO_3 system. Panda et al. showed that the promethium is extracted in terms of Pr^{3+} in Cyanex 923-kerosene-HNO_3 system and showed that the H^+ has negligible effect on the rare earth extraction. This was confirmed by El-Nadi et al. work on extraction of light REEs by Cyanex 923 [114, 115].

Amines have been proposed as alternatives to the phosphorus-containing extractants for the recovery and separation of rare earth elements [116, 117]. The innocuous nature and incincerability are their principal advantages over organophosphorus compounds. Liu investigated the extractability of different metals with amines and concluded that rare earth ions can be extracted by primary amines, while their extraction is difficult by secondary amines and negligible with tertiary amines [118]. Cuillerdier et al. investigated the substituted malonamides, as bidentate diamide ligands, for the extraction of lanthanides and actinides [119]. A proper selection of alkyl groups increased the selectivity of malonamides. Substitution of malonamides with oxyalkyl group at the central methylene carbon showed higher extraction efficiency than non-substituted and alkyl group substituted malonamides. In pursuit of new extractants, diglycolamides (tridentate diamide ligands) have been investigated, and they exhibited higher extraction efficiency in solvent extraction of rare earth elements [120]. Easy synthesis and benign nature of degradation products are some of the evident advantages of diglycolamide-based extractants over phosphorus-containing extractants [121]. Amongst derivatives of diglycolamide with different alkyl chain length, N,N,N′,N′-tetraoctyl diglycolamide (TODGA) exhibits higher efficiency in solvent extraction of lanthanides [120]. However, studies show that the aggregation of TODGA increases with acid concentration, regardless of the type of acid and diluent [122]. Several investigations

have been carried out to explain the unusual complexation behavior of diglycolamides with f-block elements [123-125]. Metwally et al. studied the extraction of europium by TODGA and THDGA, and showed that the extraction is insufficient at low acidity but increases drastically as the acidity increases to 8M HCl [126].

The modification of the structure of the extractants allows us to alter selectivity, loading capacity and consumption rate. Finding out suitable replacements for conventional extractants is not an easy task, owing to the challenges in synthesis, preparation and evaluation process.

2.3. NEW REAGENTS FOR RARE EARTH RECOVERY

Among the many topics in area of rare earth extraction, designing new chemicals and complexing agents for separation of rare earth elements from leach solutions is of special importance [127]. Numerous chemicals have been used in cutting-edge separation applications. Recently, polymeric materials such as chitosan, polyethyleneimine, polyvinylamine, carboxylic acid-based polymers, etc. have been proposed as efficient materials for recovering rare earth elements and other metals from leach solutions [128-131]. Stimuli-responsive polymers are polymers that respond to changes in physical or chemical conditions by applying external or internal stimulus such as pH, temperature, ionic strength, light, electric or magnetic field. These polymers can be designed to respond to multiple stimulus as well as single stimuli. This ability allows stimuli-responsive polymers to be used for a wide range of applications which are usually in an aqueous environment. For most applications, the polymer's response to the stimulus should be reversible upon the removal of the stimulus. These materials have immense

capability in different advanced industries. Weak electrolyte groups such as a carboxylic acid group, or an amino group are main parts of pH-responsive polymers [132]. Ionization degree of these groups change and can accept or donate protons in response to a change in the charge of the solution. In addition to the charge of solution, pH-responsive polymers can respond to changes in ionic strength and electrostatic interactions of solution. Poly(acrylic acid) (PAA) is a weak polyelectrolyte and water soluble pH-responsive polymer that has been used in various applications such as ion exchange resins, adhesives, thickening and dispersing agents [133, 134]. PAA can lose its protons and acquire a negative charge and can provide carboxylate groups which are appropriate ligands for lanthanides ions. The ionization degree of PAA plays significant role in chain mobility in aqueous solution. Increasing pH value will enhance the ionization of PAA and hence increase the interaction with rare earth ions. Some studies have been performed to investigate the interaction of PAA and rare earth ions [135].

Seeking for green and more efficient reagents with higher potential for separation processes has led to a new class of chemicals called ionic liquids (ILs). ILs have continually received significant attention not only because of their unique physicochemical properties but also their potential of tuning their properties by modification of cationic or anionic components. Their ability to be functionalized makes them promising candidates adjusted for separation and purification applications. Low vapor pressure, low flammability, high radiation stability, higher thermal and chemical stability, tunability, broad electrochemical window, conductivity, and capability to extract in low acidity environment are some of the main advantages of ionic liquids over

other conventional organic compounds. ILs will be discussed in more detail in the

following sections.

2.4. IONIC LIQUIDS FOR HYDROMETALLURGICAL PROCESSING OF RARE EARTH

Coordination ability and adjustable physicochemical properties make ILs suitable

candidates for hydrometallurgy of rare earth elements.

2.4.1. Introduction to Ionic Liquids. ILs are classically defined as molten salts

with melting temperature below $100\,^0C$. Though the discovery of ILs goes back to over

100 years ago, most of developments in this area have been obtained in the past three

decades. They have recently gained a considerable attention by academia and industry

due to their unique physicochemical properties. Various fields of science and engineering

are focusing on ionic liquids to develop new task-specific chemicals for various

applications. The number of research publications on the topic of ionic liquids has

exponentially grown in the past 20 years (Figure 2.15). These articles are from several

areas of science and technology such as separation, polymers, materials, energy,

catalysis, electrochemistry, and environment.

Numerous cations and anions with various functional groups have been designed

for the synthesis of ionic liquids. Ionic liquids with specific tasks and physicochemical

properties can be synthesized by modifying and functionalizing the cationic and/or the

anionic components. In Figure 2.16, examples of conventional cations and anions that are

common in metal extraction processes are presented.
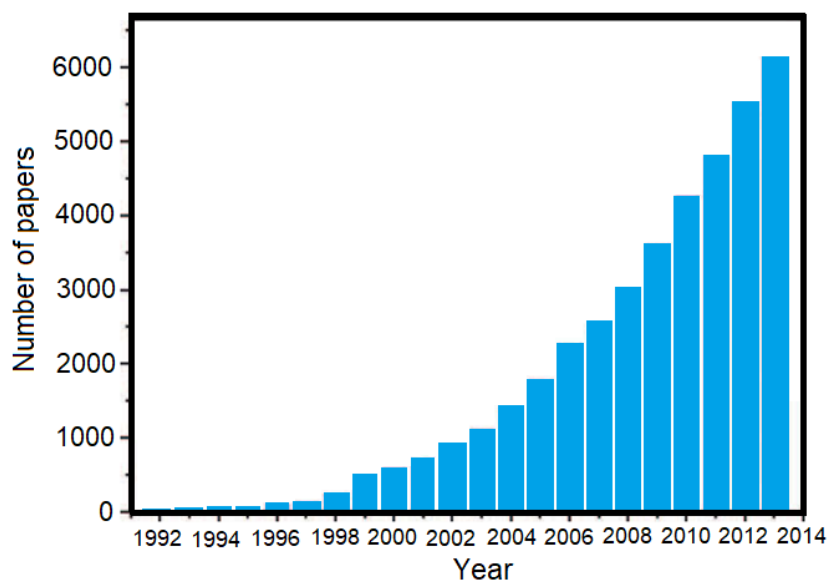
Figure 2.15. The trends of publications on ionic liquids over years [136]

2.4.2. Physics and Chemistry of Ionic Liquids. The properties of ionic liquids can vary in a wide range; however, they own some common characteristics such as low volatilities, low melting point, high thermal stability, and wide electrochemical window that make them suitable candidates for different applications. One important advantage of ILs is their physiochemical flexibility, which makes it possible to tune their structures to target specific applications and technical requests. For example, ILs with specific hydrophobic/hydrophilic balance can be designed or specific functional groups can be integrated into the cationic and/or anionic components. In addition, other physical and chemical properties such as viscosity, density, optical properties, conductivity, surface tension, electrophilicity, coordination properties, acidity, and basicity can be modified. Therefore, a thorough understanding of the physical and chemical properties of ionic

liquids is essential for the development of more selective types for a myriad of applications.
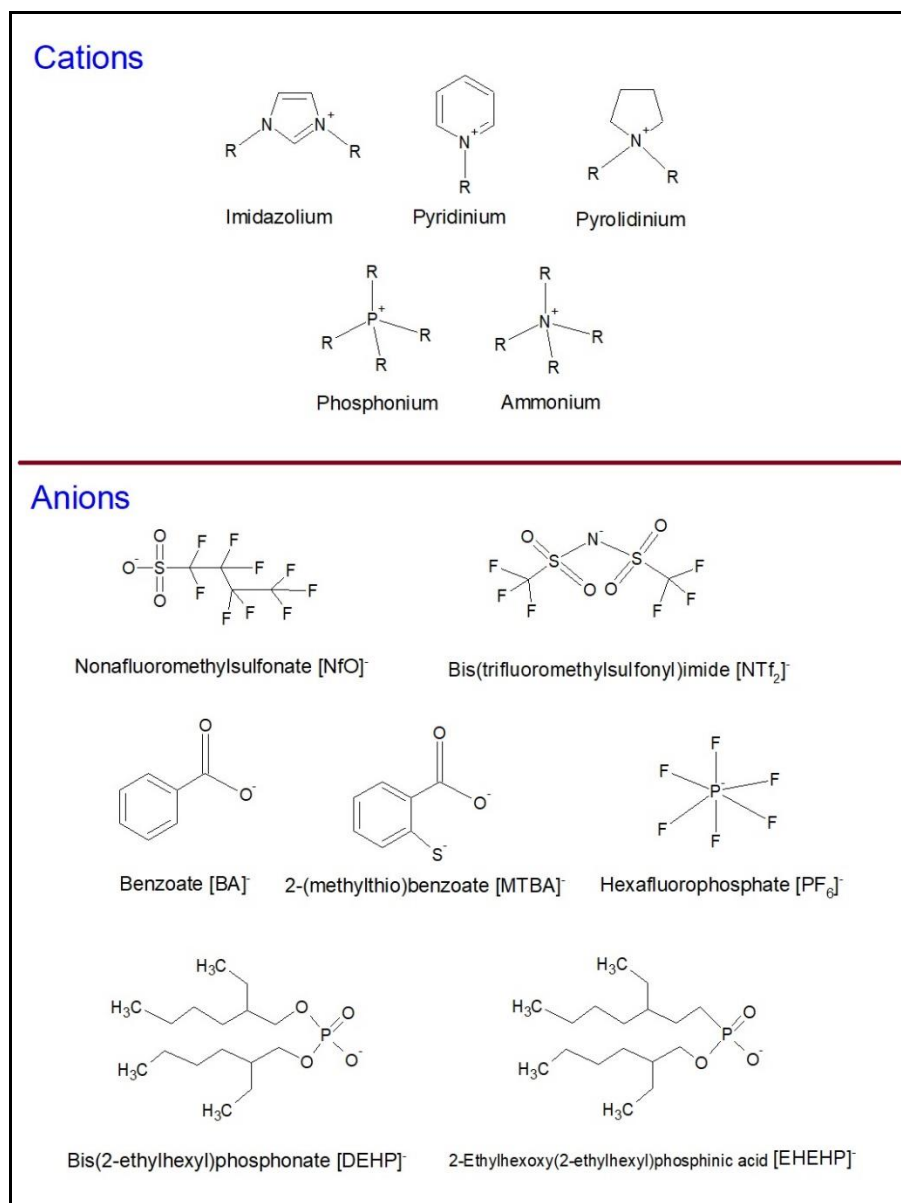
Figure 2.16. Common cations and anions used in preparation of IL-based extractant

The melting point of ILs strongly depends on the nature of the cationic and anionic components [137]. Any slight change in the cation or the anion constituent can result in a large change in the melting point. Therefore, the prediction of the melting point of ionic liquids is difficult as different anion-cation combination can lead to different melting points. However, some general changes may be applied to modify the melting point. For example, asymmetrical cation and/or anion can decrease the melting point. The length of the alky chain and the type of anion are other parameters determining the melting point of ILs (Table 2.7&2.8). The length of the alkyl chain does not only change the melting point, but also other physicochemical properties such hydrophobicity and miscibility with other solvents. For example, $[C_1C_1im][BF_4]$ is soluble in water at room temperature while $[C_8C_1im][BF_4]$ becomes soluble in water at 80 ^{0}C [138].

Table 2.7. Melting points of 1-alkyl-3-methylimidazolium tetrafluoroborate salts

Ionic liquid	Melting point (^{0}C)	Ref
$[C_1C_1im][BF_4]$	10	[139]
$[C_2C_1im][BF_4]$	6	[140]
$[C_4C_1im][BF_4]$	-81	[141]
$[C_6C_1im][BF_4]$	-82	[140]
$[C_8C_1im][BF_4]$	-78	[140]
$[C_{10}C_1im][BF_4]$	-4	[140]

Table 2.8. Melting points of 1-butyl-3-methylimidazolium salts

Ionic liquid	Melting point (^{0}C)	Ref
[C$_4$C$_1$im][Cl]	41	[141]
[C$_4$C$_1$im][PF$_6$]	-64	[141]
[C$_4$C$_1$im][BF$_4$]	-81	[141]
[C$_4$C$_1$im][Tf$_2$N]	-4	[142]
[C$_4$C$_1$im][Otfl]	16	[142]

Viscosity is another important property of ILs. It is usually high; however, it can be markedly decreased by increasing temperature [143]. Some studies have shown that using less symmetric anions may reduce the viscosity of ionic liquids. In Table 2.9, the viscosity of some common ionic liquids with different cations and anions are presented.

Table 2.9. Viscosity of some common solvents and ionic liquids

Liquid	Viscosity (cP)	Temperature (^{0}C)	Ref
H$_2$O	0.890	25	[144]
CH$_3$OH	0.544	25	[144]
CH$_2$Cl$_2$	0.413	25	[144]
DMSO	1.987	25	[144]
Ethylene glycol	16.1	25	[144]
[(C$_6$H$_{13}$)(C$_2$H$_5$)$_3$N][Tf$_2$N]	167	25	[145]

Table 2.9. Viscosity of some common solvents and ionic liquids (Cont.)

Liquid	Viscosity (cP)	Temperature (^{0}C)	Ref
[C$_4$Py][BF$_4$]	103	25	[146]
[C$_4$Py][Tf$_2$N]	57	25	[146]
[C$_2$C$_1$im][BF$_4$]	32	25	[146]
[C$_4$C$_1$im][BF$_4$]	154	20	[147]
[C$_4$C$_1$im][PF$_6$]	371	20	[147]
[C$_4$C$_1$im][Tf$_2$N]	52	20	[142]
[C$_4$C$_1$im][CF3COO]	73	20	[142]
[C$_6$C$_1$im][BF$_4$]	314	20	[147]
[(CC=C)C$_1$im][BF$_4$]	6110	20	[148]
[(CC=C)C$_1$im][BF$_3$CHCH$_3$CH$_2$CN]	25	20	[148]
[C$_2$C$_1$im][BF$_4$][BF3CF3]	26	25	[149]
[C$_4$C$_1$im][BF$_4$] [BF3CF3]	49	25	[149]

As shown in Figure 2.17, the melting point and the viscosity of ionic liquids are sensitive to the content of impurities.

The densities of ionic liquids are usually higher than that of molecular solvents. Although the higher density can lead to faster phase separation, the mixing efficiency may decrease when IL is used as solvent.

The polarity of ILs is also essential to assess the ability of ionic liquids to solvate a solute. The polarity of ILs is difficult to measure since different forces such as electrostatic, dispersion, inductive, and hydrogen bonding forces are playing role.

However, several methods, such as studying the spectral properties and studying the equilibrium and kinetic rate constants of chemical reactions have been devised to quantify the polarity of ILs [150].
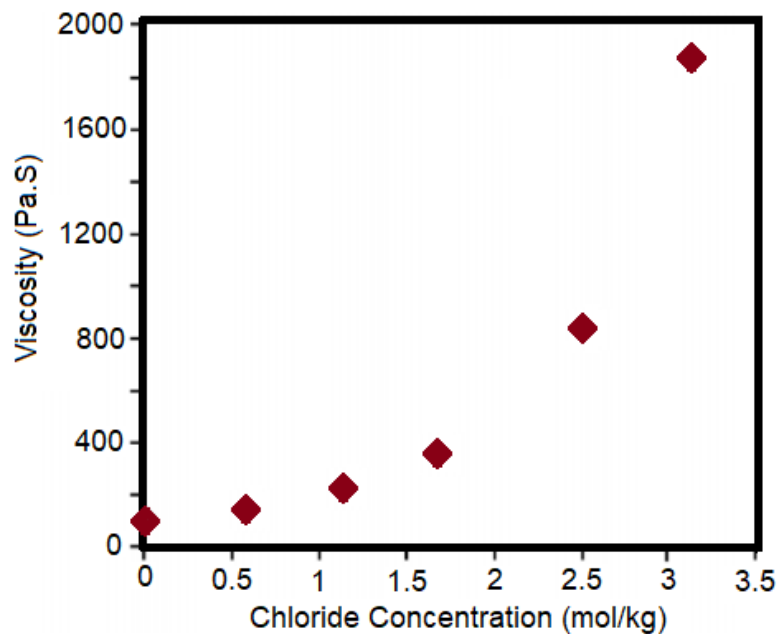
Figure 2.17. Graph of chloride concentration versus viscosity for [C4C1im][BF4] [151]

Thermodynamic properties of ILs such as vapor pressure and vaporization enthalpy have been systematically investigated. Various methods such as microcalorimetry, thermogravimetric analysis, and molecular dynamics simulation have been used to screen the vapor pressure of ILs [152, 153]. The vapor pressure of ionic liquids is challenging to measure at ambient temperature and pressure since it is very low. Experimental data shows that many ILs can evaporate and condensed at low pressure and 200-300 ^{0}C [154]. However, at higher temperatures, ILs may start to decompose.

Although the ILs do not boil, it is essential to know the temperature range that they can work without decomposition.

The heat capacity of ionic liquids is an important property for the calculation of energy transfer in engineering applications. There is a reasonable amount of data available on the heat capacity of ionic liquids [155, 156]. However, the discrepancies in the reported data are observed due to the presence of impurities in ILs (Table 2.10). Studies showed that the heat capacity of ILs is comparable to that of other molecular solvents, but lower than that of solvents with strong hydrogen bonding interactions. The heat capacities of several ILs at 298.15 K are reported in Table 2.11.

2.4.3. Applications of Ionic Liquids. The application of IL in science and technology is continually expanding due to their unique and flexible physicochemical properties. ILs have been used in a myriad number of applications as solvents, catalysts and electrolytes in electrochemical devices [157, 158].

ILs have been employed in the area of polymer engineering as polymerization media, morphology modifiers, grafted components, plasticizers, porogenic agents, etc. [159, 160]. Recently, chemically bonded ionic liquid moieties with polymers have been studied and their applications have been explored.

In addition to polymer science, ILs are being increasingly employed in the area of nanomaterials [161, 162]. ILs have been used as synthesis media, templates, and precursors to produce functional nanomaterials. Furthermore, ILs have been used as synthesis environment to prevent the aggregation of nanoparticles and modify their physicochemical properties.

Table 2.10. Effect of 0.01 Mass Fraction of Impurity on the Specific Heat Capacity of [C4mim]BF4 at T : 298 K [155]

Impurity	$Cp(J.K^{-1}.g^{-1})$
[C4Mim][Cl]	1.815
[C4Mim][Br]	1.421
1-bromobutane	1.185
1-chlorobutane	1.720
1-methylimidazole	1.794
Sodium tetrafluoroborate	1.095
Water	4.189
Acetonitrile	2.233
Acetone	2.191
Ethyl acetate	1.904
Toluene	1.706
1,1,1-trichloroethane	1.321
Methanol	2.533
Dichloromethane	1.189
Trichloromethane	0.954

The other most common and important application of ionic liquids is their use as solvents in different types of reactions [163, 164]. ILs are considered as green solvents in organic reactions and have been widely used to improve the recovery, enhance the

reactivity, and control the purity and distribution of products. They are also applied as solvent in biochemical processes such as extraction of proteins and enzymes. In recent years, several applications of ionic liquids in the pharmaceutical industry have been reported, however, the viability of using ILs in food and pharmaceutical applications requires clear understanding of toxicological properties of ionic liquids [165].

Table 2.11. The thermal properties of some ILs [155]

Ionic liquid	M (g.mol^{-1})	T$_{fus}$ (K)	Δ_{fus}H (KJ.mol^{-1})	m$_{sample}$ (g)
[C$_2$mim][EtSO$_4$]	236.29	N/A	N/A	0.9887
[C$_3$mim][Br]	205.10	309.56	19.2	0.9719
[C$_4$mim][N(CN)$_2$]	205.26	270.83	17.8	0.9325
[C$_4$mim][BF$_4$]	226.02	N/A	N/A	1.0248
[C$_4$mim][Otf]	288.29	290.98	19.4	0.9922
[C$_8$mim][BF$_4$]	282.13	245.75	14.7	0.9481
[C$_{14}$mim][NTf$_2$]	559.63	308.72	39.9	0.6503
[BuMe$_3$N][NTf$_2$]	396.37	290.23	11.4	1.1131
[C$_4$MePrl][NTf$_2$]	422.41	265.65	21.9	0.8403

ILs have been widely used in analytical chemistry techniques including gas and liquid chromatography, mass spectrometry, capillary electrophoresis, electrochemistry, and sensors [166-168]. Unique physicochemical properties of ILs have made it possible to use them in biosensors and electrochemical sensors. In addition to analytical

separations, ILs have attracted attention in other field of separations such as gas separation, metal recovery, and liquid-liquid extraction [169, 170]. In Figure 2.18, the application of ILs in different area is presented.
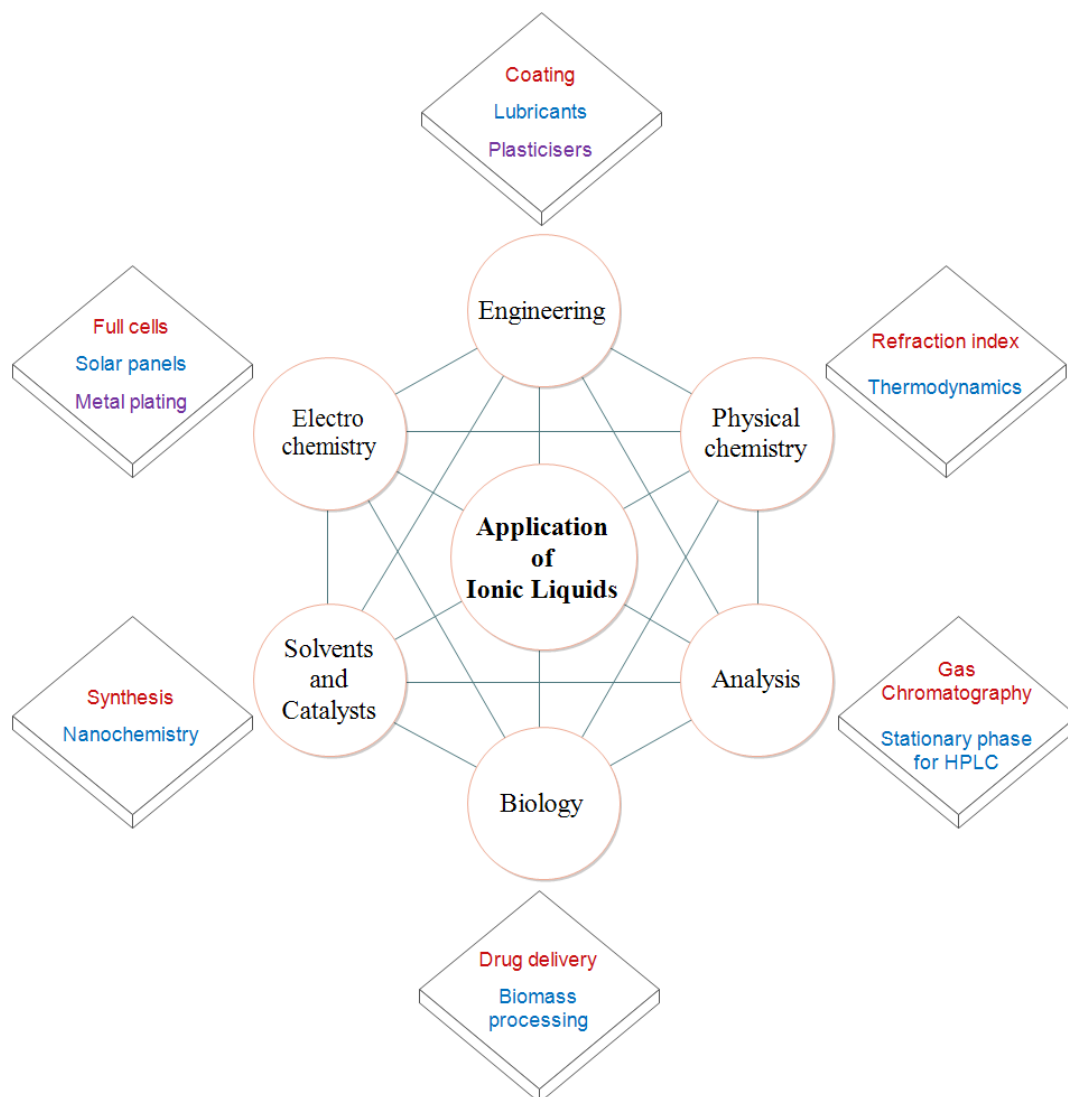
Figure 2.18. Applications of ionic liquids

2.4.4. Ionic liquids for Metal Recovery. As mentioned earlier, ionic liquids have gained considerable attention due to their unique structural properties [171, 172] such as low melting point, biodegradability, non-flammability, negligible vapor pressure and most important is the flexibility in structural design which allows to tailor their structures [173]. This unlimited potential of tunability makes them potential candidates for selective separation and purification of metals. In the field of REE recovery, imidazolium, phosphonium and ammonium based ILs are used as solvents and extractants [100]. Acid−base coupling ionic liquid extractant have shown inner synergistic effect when used for rare earth extraction [174]. Acid−base coupling ionic liquids are usually made of a quaternary ammonium cation and a deprotonated organic anion. Table 2.12 shows example applications of ILs in the rare earth separation. The advantages of using ILs as alternative extractants and solvents to replace the conventional extractants and molecular solvents are listed below.

- Physiochemical properties of ILs can be tuned to enhance the extraction of target metal ions. Below are some examples of physiochemical flexibility of ILs.
    - Interaction of ligand with aqueous and organic phases can be simply controlled and altered by tuning the hydrophobicity and hydrophilicity of its components [127-129].
    - Polarity of ILs can be modified based on the solutes present in the feed aqueous solution, and the extraction medium. Solvation ability of the ILs can also be changed by changing the polarity [130-132].
    - The coordination chemistry of ILs and metal ions in solution can be altered by introducing task-specific functional groups. Thus, the affinity of

ILs to metals ions can be changed based on the physical and chemical properties of the metal such as size and charge density. [133-135 & 174-178].

  o Diffusivity of ILs can be altered by changing their geometries and structural configurations which provides, with their ionic nature, a unique mass transfer environment [179, 180].

- Ionic liquids have the potential to be used as both solvent and extractant at the same time.

- The unique electrochemical properties of ILs can make the extraction process more thermodynamically favorable and thus enhance the separation efficiency [181].

- More diverse metal-ligand complexes can be present in ILs, in comparison with molecular solvents where only neutral complexes are soluble [182].

- Low vapor pressure, non-flammability, and thermal stability which create a safer working environment.

- The use of ILs can help to minimize the disposal cost since these materials are more environmentally friendly and less toxic.

Table 2.12. Recent research articles on the recovery and separation of rare earth elements using ILs

Target ions	Extractants	Diluent	Year	Ref.
Sc, Y, Eu, Ce	[A336][CA-100]	[A336][CA-100]	2009	[183]
U, Eu, Pu, Am	CMPO-modified IL	CMPO-modified IL	2010	[184]
Y, Dy, Ho, Er, Yb	Cyphos IL 104	$[C_nmim][PF_6]$, Cyphos IL104	2009	[185]

Table 2.12. Recent research articles on the recovery and separation of rare earth elements using ILs (Cont.)

Target ions	Extractants	Diluent	Year	Ref.
Nd	[T$_{66614}$][BA], [T$_{66614}$][TFSA]	Toluene, [T$_{66614}$][BA], [T$_{66614}$][TFSA]	2016	[186]
Nd	[Ph$_3$PC$_3$P(Oet)$_2$][PF$_6$], [Ph$_3$PC$_3$P(Oet)$_2$][NTf$_2$]	[C$_6$mim][NTf$_2$]	2016	[187]
Nd	[A336][DGA]	[A336][NO3]	2014	[188]
Y, Eu, Gd, Ce, Tb	[A336][P$_2$O$_4$], [A336][P$_5$O$_7$]	n-heptane	2011	[189]
Lanthanides	[TBA][DEHP], [TOMA][DEHP], [THTP][DEHP]	[C$_6$mim][NTf$_2$] and diisopropylbenzene	2012	[190]
Lu and HREEs	[N$_{1888}$][EHEHP],	n-heptane	2015	[191]
Y and lanthanides	([N$_{1888}$][CA12]	kerosene	2016	[192]
Pr and lanthanides	[A336][NO$_3$]-DEHEHP, [P$_{66614}$][Cl]-DEHEHP	No diluent	2017	[193]
Ce	[A336][P507], [A336][P204], [A336][C272]	n-heptane	2012	[194]
La, Nd, Eu, Dy, Er	[N$_{2222}$][DEHP], [N$_{4444}$][DEHP], [N$_{6666}$][DEHP], [N$_{8888}$][DEHP], [N$_{2222}$][EHEHP]	n-heptane	2014	[195]
Sc	[Hbet][Tf$_2$N]	No diluent	2015	[196]
Sc, La, Ce, Y, Nd, Sm, Gd, Dy, Ho, Yb, Lu	[PEGm(mim)$_2$][NTf$_2$]$_2$ (m=200, 400, 600)	No diluent	2017	[197]
Heavy lanthanides	[N$_{4444}$][BTMPP], [N$_{4444}$][EHEHP]	n-heptane	2015	[198]
Lu	[P$_{66614}$][EHEHP] and [N$_{1888}$][BTMPP] (mixed together)	toluene	2017	[199]
Y, Lu, Dy, Nd, La	[N$_{888}$C$_3$SO$_3$H][Tf$_2$N]	No diluent	2015	[200]
Eu	[A336][DEHP], [A336][DGA]	n-dodecane, tetradecane, hexadecane	2012	[201]

2.4.5. Challenges of Existing IL-based Separation Technologies. Most separation technologies associated with ILs, including solvent extraction of metals, use "non-functional ILs, which do not possess metal-coordinating groups. Despite the fact that the non-functional ILs have shown higher efficiency in comparison with conventional organic solvents as mentioned earlier, using non-functional ILs as extractant is scarce due to their non-coordination property. Studies show that non-functional ILs cannot be considered as green solvents since they extract metals by ion exchange mechanism and hence release the cationic or anionic components of the ILs into the aqueous phase. Thus, the loss of ILs as a result of ion exchange mechanism will result not only in environmental issues but also in cost increase which is considered a major barrier for the implementation of ILs at large scale.

Functionalization of ILs seems to be a good solution to address the aforementioned challenges. Functional ionic liquids are a class of ILs which have task specific coordination ligands that facilitate metal extraction by solvation mechanism rather than ion exchange mechanism, thus it will increase the life time of the extractant and eliminate the requirement for the costly process of saponification. Furthermore, functional ILs can serve as both extractant and diluent if their physical and chemical properties (e.g. viscosity) are modified to act so. Recently, fluorinated anions such as hexafluorophosphate [PF6]⁻ and bis(trifluoromethylsulfonyl)imide [Tf2N]⁻ anions have been proposed to serve as coordination ligands in functionalized ILs since they possess enough hydrophobicity and less viscosity [201]. However, the fluorinated anions are subject to hydrolysis and can produce hydrofluoric acid, which causes environmental and technical problems.

Finding new functional cations and anions with higher binding efficiency and less environmental impact and integrate them into the molecular structure of ionic liquids was the main motivation of this work. Therefore, the current work and the future research proposed here focus on the development of new functional ILs and understanding the extraction mechanism and the relevant fundamental features of ion-complex formation.

3. SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL IONIC LIQUIDS

3.1. INTRODUCTION TO FILs

Since the first room temperature ionic liquid [EtNH$_3$][NO$_3$] was synthesized in 1914 [202], families of ILs with combination of complex cations and anions have been developed. The synthesis of ILs generally include quaternization, ion exchange, and acid-base neutralization. Several alkylammonium halides are available for producing ILs through ion exchange reaction, however, alkylation reaction is usually used for the synthesis of organic halide salts. In Figure 3.1, a general synthetic scheme of imidazolium ionic liquids through alkylation reaction is shown.
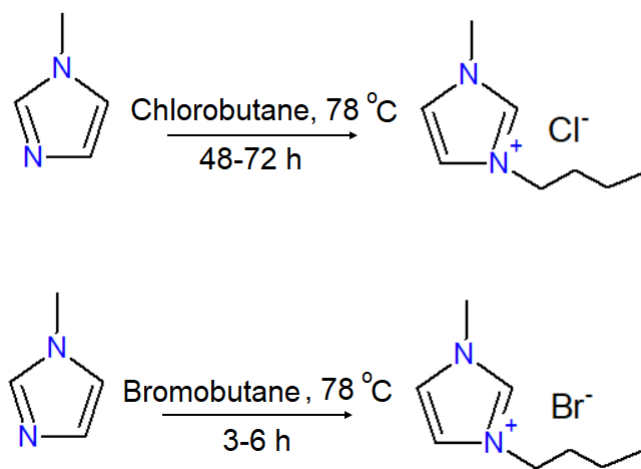
Figure 3.1. Synthetic scheme of imidazolium ionic liquids (ILs) using alkylation [203]

Ion exchange reactions are usually used to prepare free-halide ILs from halide salts. Figure 3.2 shows selected examples of ionic liquids synthesized through ion exchange mechanism.
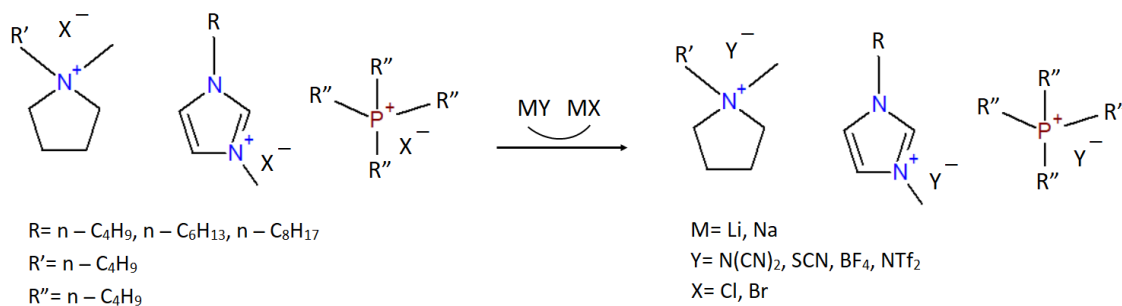
Figure 3.2. Examples of ILs synthesized through ion exchange reactions

Despite the simplicity of ion exchange reactions, there are some challenges such as the contamination with traces of halide ions, which can affect the properties and efficiency of ionic liquids. Another problem of ion exchange reactions is that there are not many available salts suitable for ion exchange with organic ILs.

The problem with contamination can be addressed using the acid-base neutralization procedure. It is a simple method that can avoid the formation of by-products. In this process, protic ionic liquids (PILs) are synthesized through proton exchange between a Brønsted acid (A) and a Brønsted base (B):

$$B + HA \rightarrow HB^+ + A^-$$
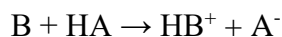
Angell et al. have prepared a series of protic ionic liquids with equimolar mixing of acids and bases (Figure 3.3). In addition, a series of protic ionic liquids containing complex heterocyclic cations have been recently synthesized by neutralization of amines with organic or inorganic acids (Figure 3.4).

The possibility of proton transfer from an acid to a base depends mainly on the acidity and basicity of acids and bases. Stronger acids and bases can promote the proton transfer process.
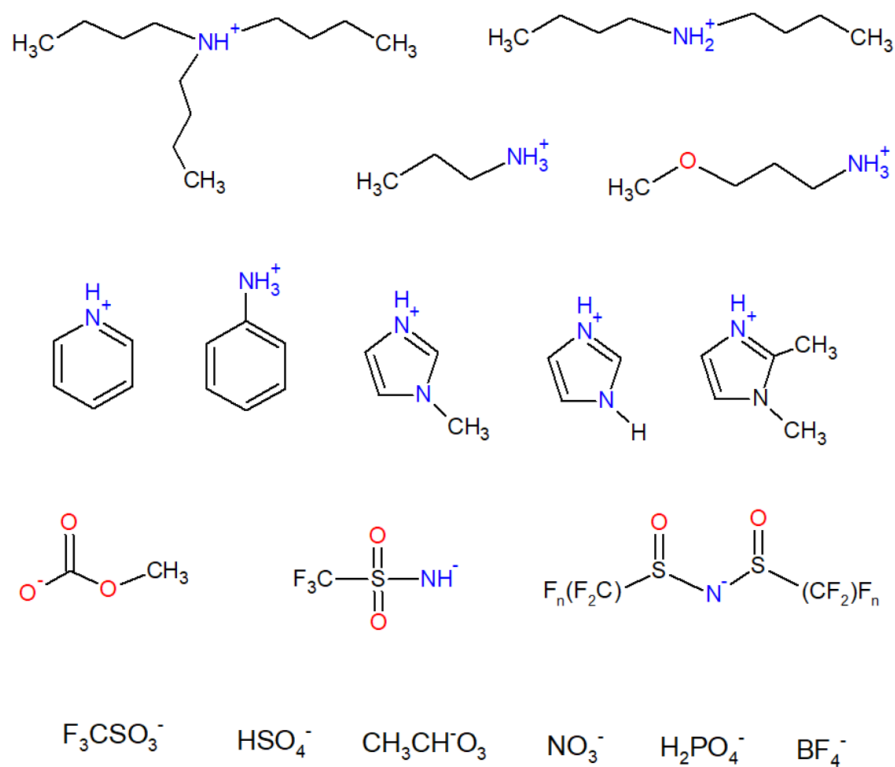
Figure 3.3. Representative anions and cations of protic ionic liquids (PILs) prepared by Angell et al. [204]
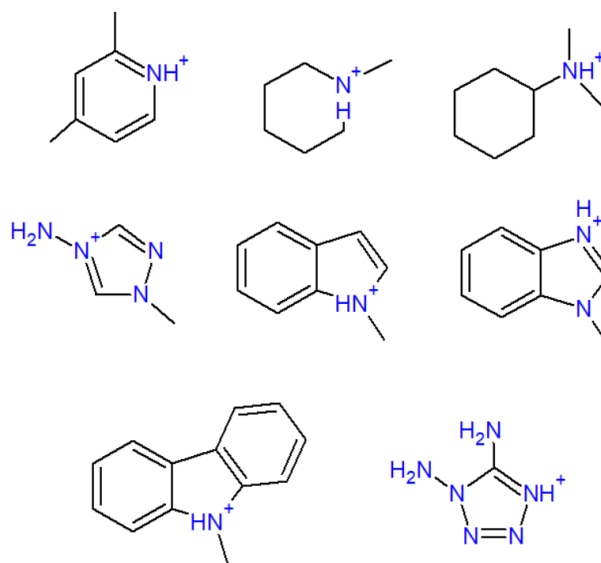
Figure 3.4. Examples of cation of protic ionic liquids (PILs) [205-208]

Ammonium, phosphonium, pyridinium, imidazolium, and sulphonate ions are the most frequently used ions for producing the ILs. In Figures 3.5-3.9, synthetic schemes of imidazolium, pyridinium, ammonium, phosphonium, and sulfur-based ionic liquids using alkylation, ion exchange, and neutralization are presented.
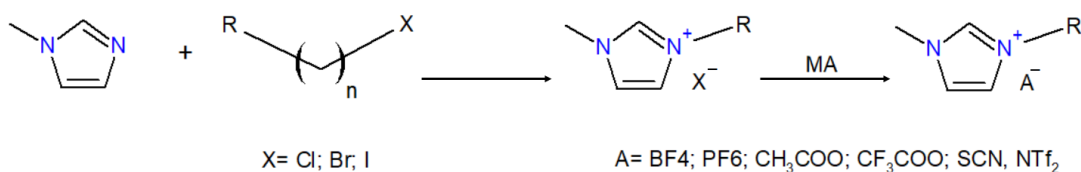
Figure 3.5. Synthesis of imidazolium-based ionic liquids [209-211]
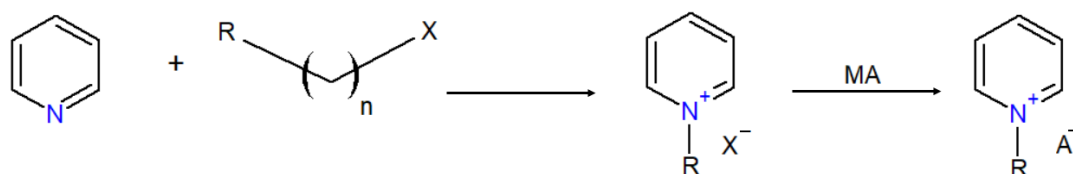
Figure 3.6. Synthesis of pyridinium-based ionic liquids [212-214]
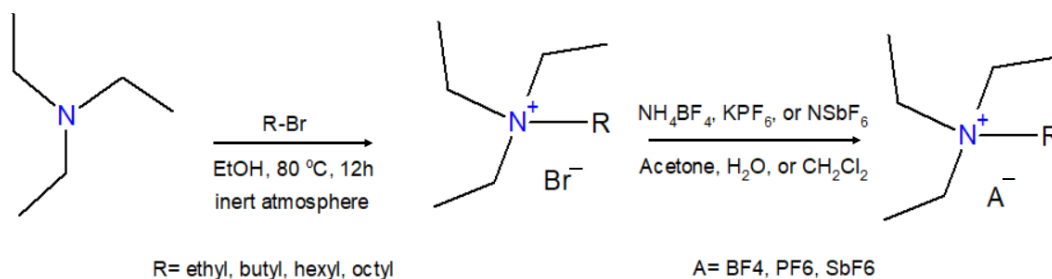
Figure 3.7. Synthesis of ammonium-based ionic liquids [215]

$$PR'_3 \quad + \quad HA \longrightarrow$$

A= BF_4, PF_6, CH_3COO, CF_3COO, CSN, Tf_2N
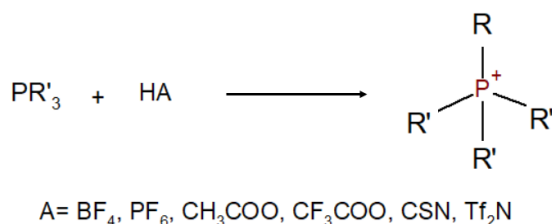
Figure 3.8. Synthesis of phosphonium-based ionic liquids [216]

R^3= Me, n-Bu, 2-Bu, Et
R^2= Me, n-Bu, $(CH_2)_2OMe$

X= BF_4, PF_6, $PF_3(CF_2CF_3)_3$,
CF_3SO_3, $N(CF_3SO_2)_2$
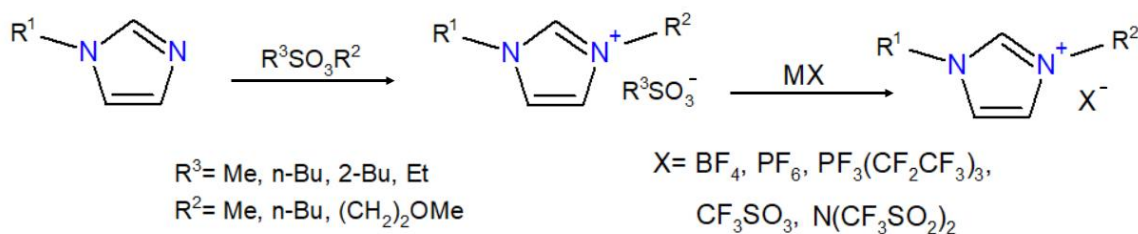
Figure 3.9. Synthesis of sulfur-based ionic liquids [216]

In functionalized ILs a functional group is incorporated into the cation or anion. The functional group typically contains coordinating moieties. The functionality can be incorporated by ion exchange reaction (Figure 3.10).

+ X-$(CH_2)_n$-FG $\longrightarrow$

FG= -OH, -SH, OR, NH_2, PPh_2, $Si(OR)_3$, SO_3H, SO_3Cl,...
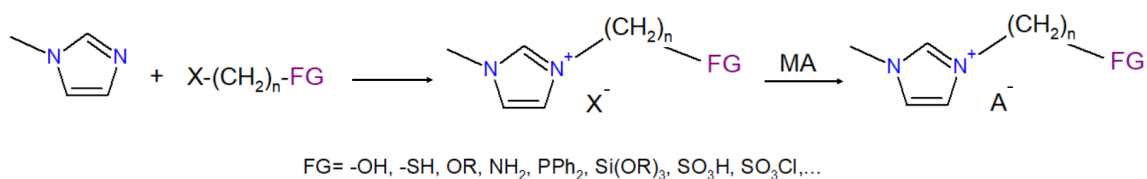
Figure 3.10. Synthesis of functionalized ionic liquids [217-219]

Recently, many new functional ILs have been synthesized by the combination of quaterinization, ion exchange, and neutralization techniques.

In Figure 3.11, the synthesis approach of a polyethylene glycol (PEG)-functionalized ILs is presented.
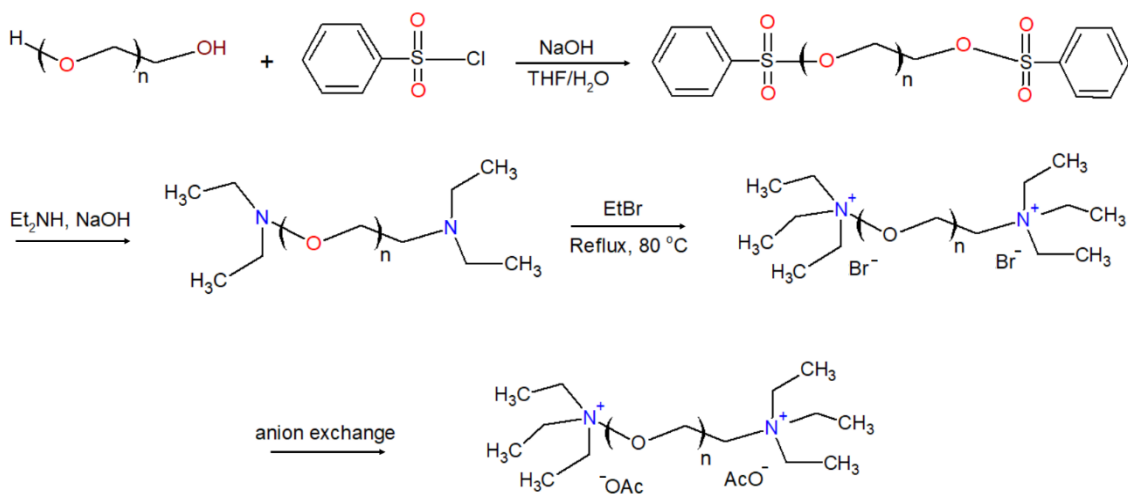
Figure 3.11. Synthesis of poly ethylene glycol (PEG)-functionalized ionic liquids [220]

Regardless of the type of the IL, it is likely to contain some impurities due to the multiple chemical reactions involved. Water is the most common impurity found in ILs. Although water may not affect many of the IL applications, the characterization of ILs need to be conducted on dry samples [221]. Drying ILs in a vacuum oven for several hours can effectively remove most of the water content. However, this method is not appropriate for some protic ionic liquids, which contain volatile species.

Unreacted organic chemicals and reaction solvents are other common impurities found in ILs [221]. Vacuum evaporation can usually be effectively applied for the removal of these types of impurities. Washing ILs with an immiscible organic solvent can also be used to remove them. Suspended particles are other sort of impurities formed as by-products. Sorbents such as activated carbon and silica, molecular sieves, drying

agents, and distillation method are common techniques that are used for the purification of ILs [222].

3.2. SYNTHESIS OF PROPOSED FUNCTIONAL IONIC LIQUIDS

Two types of functionalized ionic liquids were synthesized through alkylation, neutralization and metathesis reactions. The synthesized FILs were characterized using nuclear magnetic resonance (^{1}H and ^{13}C NMR), Fourier transform infrared spectroscopy (FTIR), high-resolution mass spectrometry (HRMS), thermal gravimetric analysis (TGA), disc scanning calorimetry (DSC) in addition to density and viscosity analysis. The structures of the synthesized FILs used in this study are shown in Figure 3.12. Below are the details about the different steps of the synthesis.

Trioctylmethylammonium dihexyldiglycolamate
[A336][DHDGA]

Trioctyl[2-ethoxy-2-oxoethyl]ammonium dihexyldiglycolamate
[OcGBOEt][DHDGA]
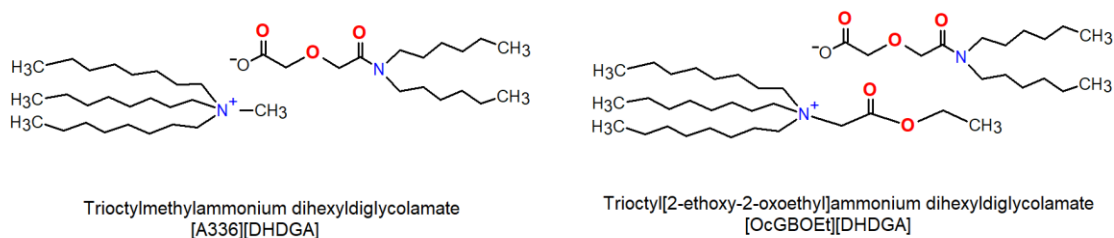
Figure 3.12. Structures of functionalized ionic liquids used in this study

3.2.1. Preparation of Dihexyldiglycolamic Acid, [DHDGAA]. Dihexylamine (40 mmol, 7.4g) dissolved in 10 mL of dichloromethane was added dropwise in an ice-bath to diglycolic anhydride (40 mmol, 5.8g) dispersed in 40 mL of dichloromethane. The ice bath was then removed, and the reaction was allowed to continue at room temperature for further 20 hours. The resulting solution was then washed four times with

deionized water and the organic layer was decanted and dried with anhydrous sodium
sulfate. The solvent was evaporated under vacuum, and the residue was recrystallized
from hexane as a white powder ($\approx$ 83% yield). The synthesis procedure for DHDGAA is
schematically shown in Figure 3.13.

$$C_4H_4O_4 + (CH_3(CH_2)_5)_2NH \rightarrow (CH_3(CH_2)_5)_2N(C_4H_4O_4)$$
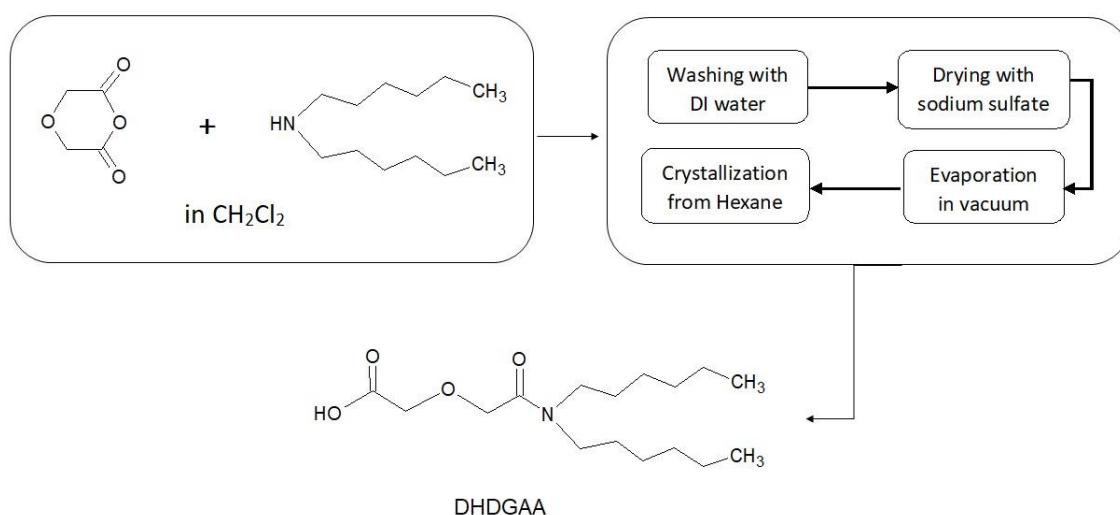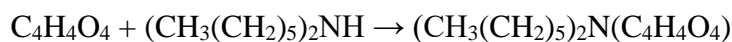
Figure 3.13. Scheme of the synthesis route for DHDGAA

3.2.2. Preparation of Tricaprylmethylammonium Dihexyldiglycolamate,
[A336][DHDGA]. To prepare tricaprylmethylammonium hydroxide, [A336][OH], 20
mmol (8.1g) of tricaprylmethylammonium chloride was dissolved in 30 mL of
chloroform and then reacted with 20 mL of 4M sodium hydroxide solution in deionized
water. The reaction was carried out for approximately one hour, and then the organic
phase was decanted and equilibrated with a fresh 4M NaOH solution. This procedure was
repeated for eight times and the chloride content was tested with an acidified silver nitrate

solution to assure that the chloride content is negligible. The resulting organic layer was washed with deionized water, and the solvent was evaporated under vacuum to yield a viscous [A336][OH] liquid. The [A336][OH] and DHDGAA were then dissolved in dichloromethane (molar ratio 1:1) and refluxed for 12 h. The solvent was rotary evaporated followed by heating the remaining residue at 70 °C in vacuum oven for 7-8 h to yield the yellowish viscous [A336][DHDGA] (≈ 90% yield). The synthesis procedure for [A336][DHDGA] is schematically shown in Figure 3.14.

$$(CH_3(CH_2)_7)_3NCH_3Cl + NaOH \rightarrow (CH_3(CH_2)_7)_3NCH_3OH + NaCl$$

$$(CH_3(CH_2)_7)_3NCH_3OH + (CH_3(CH_2)_5)_2N(C_4H_4O_4) \rightarrow$$
$$CH_3(CH_2)_7)_3NCH_3((CH_3(CH_2)_5)_2N(C_4H_3O_4)) + H_2O$$
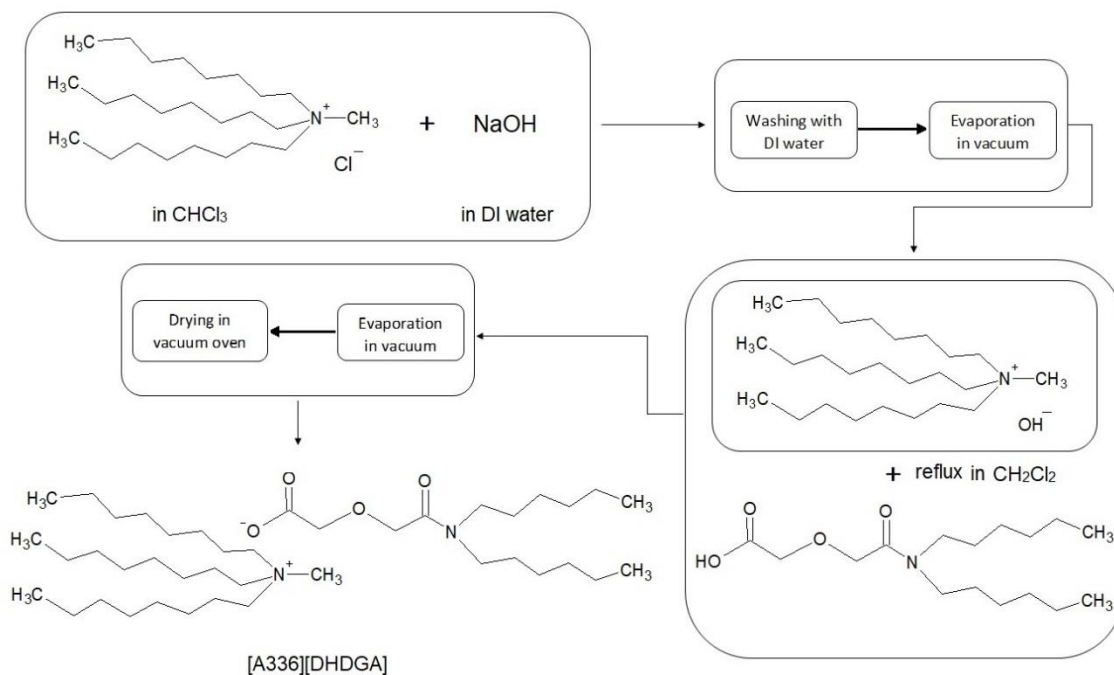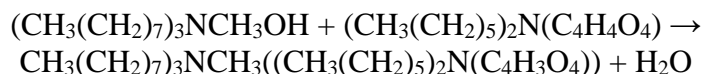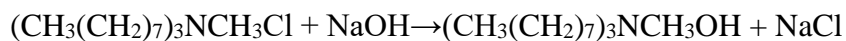
Figure 3.14. Synthetic scheme of [A336][DHDGA]

3.2.3. Preparation of Trioctyl[2-ethoxy-2-oxoethyl]ammonium

Dihexyldiglycolamate, [OcGBOEt][DHDGA]. Trioctylamine (25.5 mmol, 9g) was

dissolved in ethyl acetate (50 mL), and then was added dropwise to bromoacetic acid

ethyl ester (20 mmol, 3.3g) in an ice-bath. The mixture was stirred at room temperature

for 24 h. The solution was then evaporated under vacuum to give a clear greenish

trioctyl(2-ethoxy-2-oxoethyl)ammonium bromide, [OcGBOEt][Br]. 5.8 mmol (3g) of

[OcGBOEt][Br] was dissolved in ethanol (15 mL), and then reacted with 6.9 mmol (3.9g)

of potassium hydroxide dissolved in 25 mL of ethanol. The mixture was stirred for 24 h

followed by solid-liquid separation by centrifugation. The ethanol was evaporated

thereafter under vacuum, and the [OcGBOEt][OH] was synthesized as the intermediate

product (97 % yield). The subsequent step involved dissolving [OcGBOEt][OH] and

DHDGAA in dichloromethane (molar ratio 1:1) and refluxing for 18 h. The solvent was

then removed under vacuum and the final product was completely dried at 70 °C using a

vacuum oven for about 7-8 h. The final product, [OcGBOEt][DHDGA], was obtained

with yield of 93.13%. The synthesis procedure for [OcGBOEt][DHDGA] is

schematically shown in Figure 3.15.

$$(C_8H_{17})_3N + C_4H_7O_2Br \rightarrow (C_8H_{17})_3NC_4H_7O_2Br$$
$$(C_8H_{17})_3NC_4H_7O_2Br + KOH \rightarrow (C_8H_{17})_3NC_4H_7O_2OH + KBr$$
$$(C_8H_{17})_3NC_4H_7O_2OH + (CH_3(CH_2)_5)_2N(C_4H_4O_4) \rightarrow$$
$$(C_8H_{17})_3NC_4H_7O_2(CH_3(CH_2)_5)_2N(C_4H_3O_4) + H_2O$$
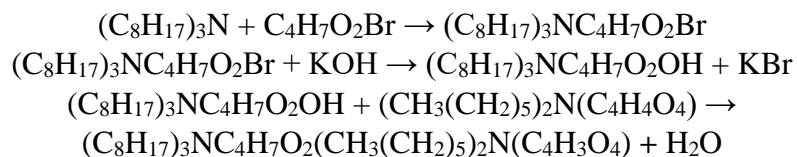
3.3. CHARACTERIZATION OF FUNCTIONAL IONIC LIQUIDS

The synthesized FILs were characterized by NMR, FTIR, HRMS, TGA, and DSC

analysis in addition to viscosity and density measurements.

3.3.1. Nuclear Magnetic Resonance and Infrared Spectroscopy. The Nuclear

Magnetic Resonance (NMR) spectroscopy is essential in organic synthesis as it can

reveal important information about the structure, cation-anion interaction, and purity. It is

a good common technique for characterization of FILs, even though the difficulty of

NMR analysis of FILs due to their large viscosity and less deuterated form. NMR

analysis has been mostly employed for the identification of cationic components of FILs

since the anionic components of many FILs, like PF_6 and BF_4, are difficult or impossible

to be identified by NMR spectroscopy. The chemical shift in NMR measurement of FILs

can be influenced by type of cation and anion, the alkyl chain length and structure,

interaction with solvent, and the presence of impurities. In addition to NMR

spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy was used as an important

supportive tool to investigate the structures and composition of FILs.

The FILs synthesized in this work were characterized by FTIR, ^{1}H and ^{13}C NMR

spectroscopies. The chemical shifts were interpreted carefully to identify the groups in

both cation and anion of FILs. The NMR and FTIR spectra are presented in Appendix A.

FTIR signals and the NMR chemical shift values and related groups are as follows:

3.3.1.1. IR and NMR analysis of DHDGAA. ^{1}<u>H NMR</u> (400 MHz, CDCl$_3$, δ

ppm): 0.67–0.98 (m, 6H), 1.12–1.41 (m, 12H), 1.41–1.70 (m, 5H), 2.94–3.18 (m, 2H),

3.20–3.52 (m, 2H), 3.99–4.26 (m, 2H), 4.28–4.55 (m, 2H).

^{13}<u>C NMR</u> (101 MHz, CDCl$_3$, δ ppm): 13.88, 13.94 ($-CH_3$ groups), 21.95, 22.46,

26.33, 27.39, 28.91, 31.5 (various $-CH_2-$ groups), 45.93, 46.85 (CH$_2$-N groups), 69.63

($-CH_2O-$), 69.86 ($-OCH_2-$), 168.94 ($-CON$), 172.53 (COOH).

<u>IR (cm^{-1})</u>: 3409 (OH), 2960−2862 (CH$_2$), 1712, 1628 (C=O), 1460 (−CH$_2$−CO), 1258 (C−N), 1063 (C−O ether linkage).
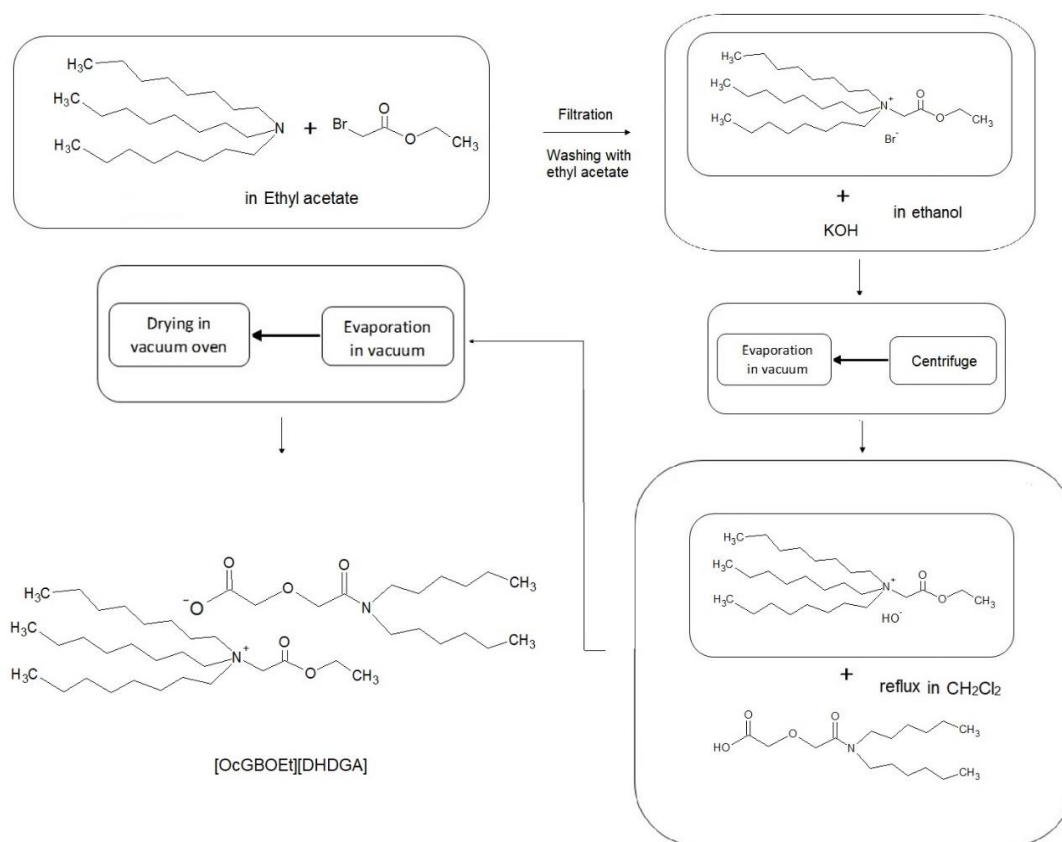
Figure 3.15. Synthetic scheme of [OcGBOEt][DHDGA]

3.3.1.2. IR and NMR analysis of [A336][DHDGA]. <u>^{1}H NMR</u> (400 MHz, CDCl$_3$, δ ppm): 0.67–0.89 (m, 15H), 1.09–1.33 (m, 44H), 1.39–1.51 (m, 5H), 1.54–1.67 (m, 5H), 2.97–3.09 (m, 2H), 3.18–3.22 (m, 2H), 3.23–3.29 (m, 2H), 3.31–3.43 (m, 5H), 4.07–4.18 (m, 2H), 4.25–4.37 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$, δ ppm): 14.01, 14.11 (−CH$_3$ groups), 22.46, 22.57, 22.63, 26.53, 26.4, 27.46, 29.08, 29.24, 29.43, 29.48, 31.56, 31.7, 31.89 (various −CH$_2$− groups), 46.68 (CH$_3$N), 46.98 (2×CH$_2$N of [DHDGA]$^−$), 61.55 (3×CH$_2$N of [A336]$^+$), 70.9 (−CH$_2$O−), 72.01 (−OCH$_2$−), 170.24 (−CON), 171.89 (−COO−).

IR (cm^{-1}): 2957−2856 (CH$_2$), 1709, 1625 (C=O), 1465 (−CH$_2$−CO), 1258 (C−N), 1063 (C−O ether linkage).

3.3.1.3. IR and NMR analysis of [OcGBOEt][DHDGA]. ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 0.67–0.99 (m, 16H), 1.12–1.42 (m, 45H), 1.44–1.54 (m, 4H), 1.56–1.73 (m, 6H), 2.87–2.98 (m, 1H), 3.01–3.19 (m, 2H), 3.21–3.36 (m, 2H), 3.39–3.53 (m, 6H), 3.59–3.75 (m, 2H), 4.07–4.20 (m, 2H), 4.26–4.37 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$, δ ppm): 14.13, 14.18, 14.20 (−CH$_3$ groups), 22.23, 22.70, 22.74, 23.33, 26.60, 26.67, 27.12, 27.66, 28.95, 29.14, 29.18, 31.74, 31.83 (various −CH$_2$− groups), 46.17 (CH$_3$N), 47.02 (2×CH$_2$N of [DHDGA]$^−$), 51.66, 59.05 (2×CH$_2$ of betaine in [OcGBOEt]$^+$), 59.82 (3×CH$_2$N of [OcGBOEt]$^+$), 69.55 (−CH$_2$O− of [DHDGA]$^−$), 70.46 (−OCH$_2$− of [DHDGA]$^−$), 165.06 (−COO− of [OcGBOEt]$^+$), 169.05 (−CON), 173.90 (−COO− of [DHDGA]$^−$).

IR (cm^{-1}): 2957−2856 (CH$_2$), 1734, 1644 (C=O), 1468 (−CH$_2$−CO), 1378 (C−N), 1129 (C−O linkages).

3.3.2. High Resolution Mass Spectrometry. Mass spectrometry is a powerful technique that provides a better understanding and deeper insights on the entire structure of FILs. In this study high-resolution mass spectrometry (HRMS) was employed for structural characterization of FILs. The ionic liquids were diluted (1:100) in acidified acetonitrile (99.9% OCCURRED, 0.1% v/v formic acid), loaded into a static nanospray

ECONO 12 tip (Proxeon) and analyzed by nano-electrospray ionization in positive-ion

mode on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Fourier transform

MS data were collected in the Orbitrap (60,000 resolving power, 100-2000 m/z for

[A336][DHDGA] and 400-2000 m/z for [OcGBOEt][DHDGA], 1 microscan, maximum

inject time of 100ms, AGC= 5e5) over 1 min of direct infusion. The cations of both ionic

liquids and different combination of clusters were observed in the HRMS spectrums. In

the case of [OcGBOEt][DHDGA], the cationic component was evident at m/z 440.4, and

the ionic liquid was observed at m/z 765.8 with a possible Na or K adduct. The analysis

of [A336][DHDGA] revealed that the [A336] cation consisted of a mixture of C8 to C10

alkyl chains. According to the HRMS spectrums, dioctyldecylmethyl ammonium (m/z =

396.4) and trioctylmethyl ammonium (m/z = 368.4) were the predominating components

of $[A336]^+$.

     3.3.3. Thermal Analysis. The thermal stability of the functionalized ionic liquids

was analyzed using a thermogravimetric analyzer (TA Instruments Inc., STD Q600). The

samples were heated under nitrogen gas from 20 to 700 °C with a heating rate of 10

°C/min. Thermogravimetric analysis (TGA) show that both ionic liquids undergo one

step decomposition behavior. The onset decomposition temperatures of [A336][DHDGA]

and [OcGBOEt][DHDGA] were ~213 and 218 °C, respectively.

     Two different transitions were observed for both of ionic liquids probably due to

the decomposition of different components of ionic liquids at various temperatures. The

TGA thermograms showed that the decomposition of [OcGBOEt][DHDGA] was faster

than that of [A336][DHDGA]. Results indicated that [OcGBOEt][DHDGA] fully

decomposed at   330 °C while the complete decomposition of [A336][DHDGA] occurred

at ~ 356 °C. The solid-liquid phase transition was studied by differential scanning calorimeter (TA Instruments Inc., DSC2010) with a heating rate of 10 °C/min. The analysis was done under a nitrogen atmosphere in the temperature range of -100 to 30 °C. DSC analysis showed that both ionic liquids presented a very weak tendency to crystallize. Results indicated that ionic liquids transferred to a supercooled liquid state as they cooled down. The glass transition temperatures of [A336][DHDGA] and [OcGBOEt][DHDGA] were found to be -63 and -56 °C, respectively, which demonstrated that the [OcGBOEt][DHDGA] ions need more energy to move around.

3.3.4. Viscosity and Density Measurement. Densities of the synthesized ionic liquids were measured at room temperature using a standard 2 mL specific gravity bottle. The density of [A336][DHDGA] was found to be 1.19 g/mL, slightly larger than the density of [OcGBOEt][DHDGA] which was 1.14 g/mL. Functionalization of [A336]$^+$ increased both the mass and volume of ionic liquid, however, the density measurement demonstrated that the increase in volume had a larger contribution to the overall density value of [OcGBOEt][DHDGA].

Two different tests were conducted to measure the viscosities of the synthesized ionic liquids. The tests were performed using a Haake Mars rheometer with cone-plate measuring system (cone angle 1º). In the first test, the shear rate was increased from 0 to 500 s^{-1} and the flow curve was obtained. In the second test, the shear rate was ramped stepwise from 1 to 200 s^{-1} with shearing maintained for 30 s for each shear rate. The viscosity of [OcGBOEt][DHDGA] was 5.85 Pa.s, which was ~ 2.2 times greater than the viscosity of [A336][DHDGA] which was found to be 2.68 Pa.s.

4. RECOVERY AND SEPARATION OF RARE EARTH ELEMENTS

4.1. EXPERIMENTAL

Solvent extraction experiments were conducted, and key process parameters were investigated.

4.1.1. Materials and Methods. Hexane, toluene, chloroform, nitric acid, and ammonium hydroxide were purchased from Sigma Aldrich (USA). All chemicals and solvents were of analytical reagent grade and used without further purification unless otherwise stated. All rare earth nitrates used in this study were purchased from the Alfa Aesar (USA). Stock solutions of REEs were prepared by dissolving their hydrated nitrates (>99 %) in deionized water and the pH of aqueous solution was adjusted using nitric acid and ammonium hydroxide.

Inductively coupled plasma-atomic emission spectrometer (Avio 200 ICP-AES) was used to determine the concentrations of REEs in the aqueous phase. 1% HNO_3 solution were used as a wash solution in ICP analysis. For method validation first standards, samples, duplicate sample, spike sample and QC were run. 10ppm and 1ppm QC were passed and the spike recovery was 99.76%. ^{1}H-nuclear magnetic resonance (NMR) spectra of the aqueous phases before and after extraction were obtained in deuterated acetone using a Bruker BioSpin GmbH NMR spectrometer, operating at 399.79 MHz. Further investigations on the structures of REE-FIL complexes were performed using Fourier transform infrared spectroscopy (Nicolet iS50 FT-IR).

4.1.2. Extraction Tests. Extraction experiments were performed by mixing equal volumes of FILs (diluted in chloroform) and aqueous solutions of rare earth elements.

The phase separation was carried out using a separatory funnel. The aqueous phase was further diluted for ICP analysis if necessary. In the stripping experiments, 2 ml of loaded organic phase was mixed with 2 ml HNO_3 solutions of different concentrations, followed by stirring for 75 min to reach equilibrium. The extraction efficiency (%E), distribution ratio (D) stripping percentage (S) and separation factors (SF) were used as performance indicators and were obtained using the following equations:

$$\%E = \left(1 - \frac{C_a}{C_t}\right) \times 100\% \tag{4.1}$$

$$D = \frac{E}{(100-E)} \times \frac{V_W}{V_O} \tag{4.2}$$

$$S = \left(\frac{C_{aq}}{C_{org}}\right) \times 100\% \tag{4.3}$$

$$SF = \left(\frac{D_1}{D_2}\right) \tag{4.4}$$

where C_t and C_a are the initial and equilibrium concentrations of rare earth ions in aqueous phase, respectively; V_w and V_o are the volumes of aqueous and organic phases, respectively; C_{aq} is the equilibrium concentration of rare earth ions in stripping acid and C_{org} is the initial concentration of rare earth ions in organic phase. All the extraction tests were duplicated, and the concentration of rare earth ions was measured in aqueous phase using ICP-AES. All determinations were performed in duplicate to get the average and the relative error as low as possible.

4.2. RESULTS AND DISCUSSION

Extraction efficiency, selectivity, kinetic, and thermodynamic parameters are discussed in the following sections.

4.2.1. Synergistic Effect of Cationic-Anionic Components of FILs. To investigate the synergistic effect of cationic and anionic components of the synthesized FILs on their overall performance, extraction efficiency of Eu^{3+} from nitrate solution using [OcGBOEt][DHDGA] and [A336][DHDGA] was examined and compared to their precursors. As shown in Figure 4.1(a), the extraction efficiencies of [OcGBOEt], [A336], and [DHDGA] were 4.2%, 3.7%, and 76%, respectively as compared to 98.5% and 86% for [OcGBOEt][DHDGA] and [A336][DHDGA], respectively.
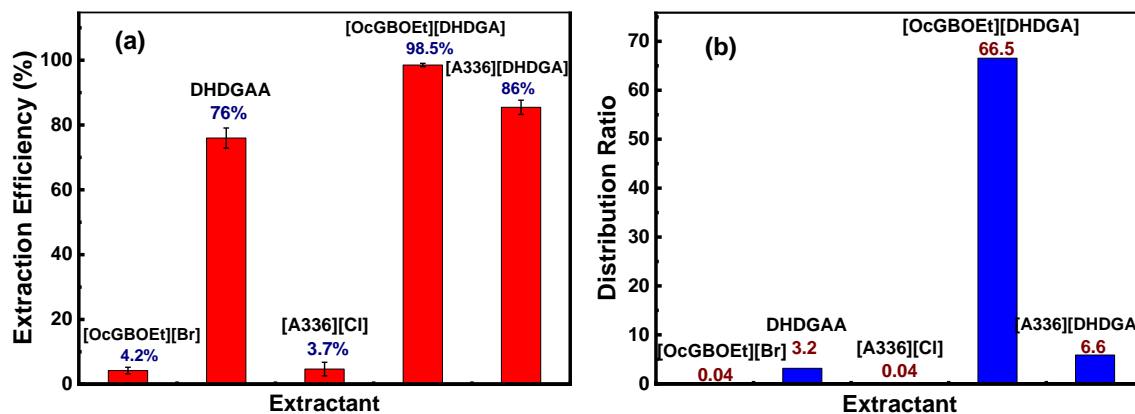
Figure 4.1. Comparison of the extraction performance of FILs and their precursors: (a) Extraction efficiency and (b) Distribution ratio (pH= 4, time= 90 min, temperature: =32 °C, Eu^{3+}= 0.001 $molL^{-1}$, extractant concentration= 0.04 $molL^{-1}$, diluent= chloroform)

Figure 4.1(b) shows the distribution coefficients of Eu^{3+} in the two FIL and in their anionic and cationic precursors. As indicated, the D value of Eu^{3+} reached as high as

45 and 6.6 in [OcGBOEt][DHDGA] and [A336][DHDGA], respectively. This enhanced extraction by the two FILs was probably due to the inner synergistic effect of both the acidic and basic components. Both the cation and the anion would involve in the extraction process and could form coordination bonds with REE^{3+} which would help to increase the capacity of IL-system and reduce the loss of cation and anion to the aqueous phase.

4.2.2. Influence of Solution Acidity. To investigate the effect of solution acidity on the extraction behavior of the functionalized ionic liquids, the recoveries of europium ions (Eu^{3+}) extracted using [OcGBOEt][DHDGA] and [A336][DHDGA] were determined at different initial pH values of 1, 2.5, 4 and 6. As can be seen in Figure 4.2, the extraction efficiency of Eu^{3+} decreased as the acidity of the aqueous phase increased. Extraction efficiency at pH 1 was ~55% and 4.3% for [OcGBOEt][DHDGA] and [A336][DHDGA], respectively, and increased to 98.5% and 85.7 % at pH 4. This indicated that high acidity has a negative effect on the extraction efficiency of FILs. As shown, %E values displayed a slow increase in the pH range of 2.5-4, however at pH > 4, the extraction efficiency dropped to 70-80%.

As shown, %E values display a slow increase between pH 2.5–4, however at pH > 4, the extraction efficiency dropped to less than 75%.

By comparing the %E values of [OcGBOEt][DHDGA] and [A336][DHDGA] at different solution acidities, it is clear that the extractability of [OcGBOEt][DHDGA] was much better than that of [A336][DHDGA] at high and medium pH values. These results therefore indicated that the [OcGBOEt] cations are more likely to form complexes with metal ions than the [A336] anion.

The pH dependency of the extraction process can be explained by the competition between H^+ and Eu^{3+} ions on the ligand. Extraction of H^+ ions leads to a decrease in the effective ligand concentration in the organic phase, thereby decreasing extraction efficiency. The decrease in the extraction efficiency at pH 6 may be due to the hydrolysis of Eu^{3+} and formation of $Eu(OH)_3$ species. The Eh-pH diagram Eu-NO_3-H_2O system at 32 °C is shown in Figure 4.3. The diagram helps to identify the nature and the stability of each species by determining the domain of un-complexed and hydrolytic species of rare earth ions. As shown, the hydrolysis of Eu^{3+} is not significant until the pH value is greater than 4.5. As it is evident, the formation and precipitation of $Eu(OH)_3$ was the major factor affecting the solubility of europium ion under low acidic and alkaline conditions. Authors are aware that changing the temperature, europium concentration, and considering the other ions present in the solution can change the domains and forms of different species.
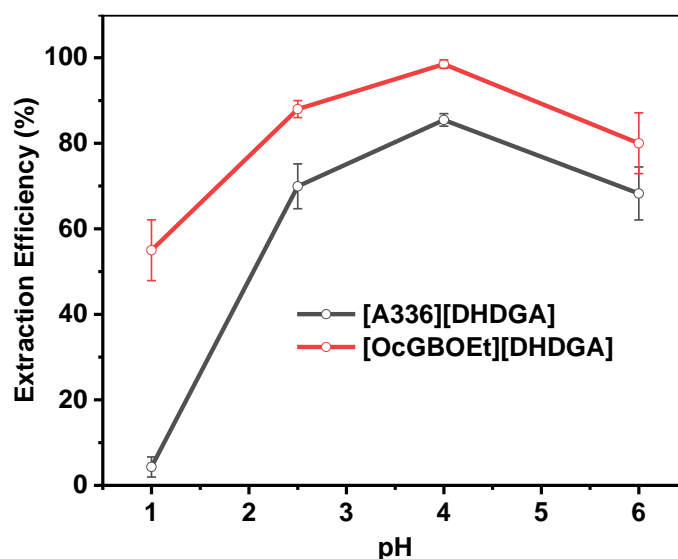
Figure 4.2. Effect of the acidity of aqueous phase (pH) on the extraction efficiency of Eu^{3+}. ([OcGBOEt][DHDGA] = [A336][DHDGA]= 0.04 molL^{-1}, Eu^{3+}= 0.001 molL^{-1}, time= 90 min, temperature= 32 °C)
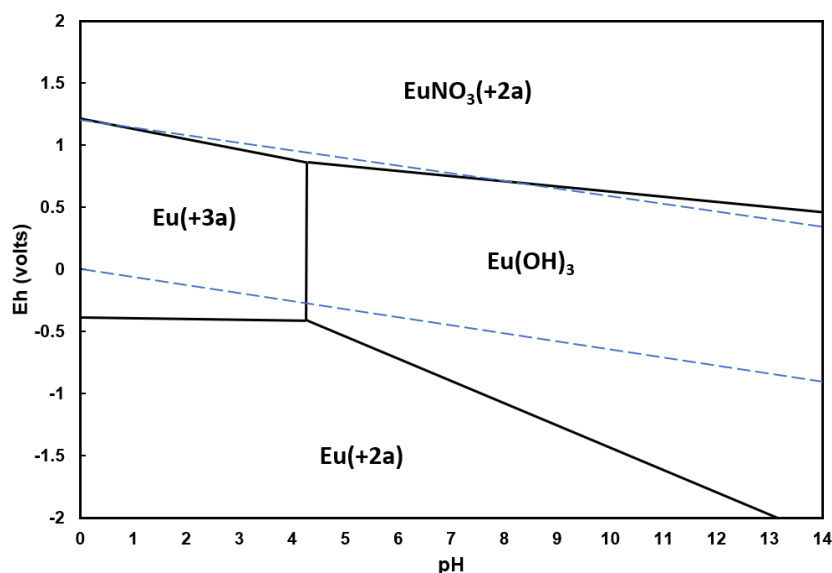
Figure 4.3. Eh-pH diagram of europium species in nitric acid medium (temperature= 32 °C, Eu^{3+}= 0.001 $molL^{-1}$)

4.2.3. Effect of REE Concentration. Extraction efficiency of europium was investigated using different initial concentrations of Eu^{3+} ions in feed solution. The Eu^{3+} concentrations ranged from 0.0005 to 0.01 $molL^{-1}$. The concentration of FILs in all the tests performed in this task was kept at 0.04 M in chloroform.

As shown in Figure 4.4a, in the case of [OcGBOEt][DHDGA], the extraction percentage remained constant (~98%) as a function of europium ion concentration between 0.5 and 5 mM. As indicated, at low Eu^{3+} concentrations, the ionic liquid was present in a large excess, and loading of the ionic liquid phase with metal ions did not influence the distribution of Eu^{3+}. At higher Eu^{3+} concentrations, the ionic liquid was no longer in excess and the extraction equilibrium was shifted due to the loading effects.

In the case of [A336][DHDGA], at an initial Eu^{3+} concentration of 0.0005 $molL^{-1}$ in the aqueous phase, around 80% of the Eu^{3+} ions were extracted. However, the

maximum extraction efficiency by [A336][DHDGA] was observed at 0.001 molL^{-1} (%E ~ 85%). With increasing the initial concentration to more than 0.001 molL^{-1}, the extraction efficiency dropped sharply due to the decrease in the loading capacity of [A336][DHDGA].
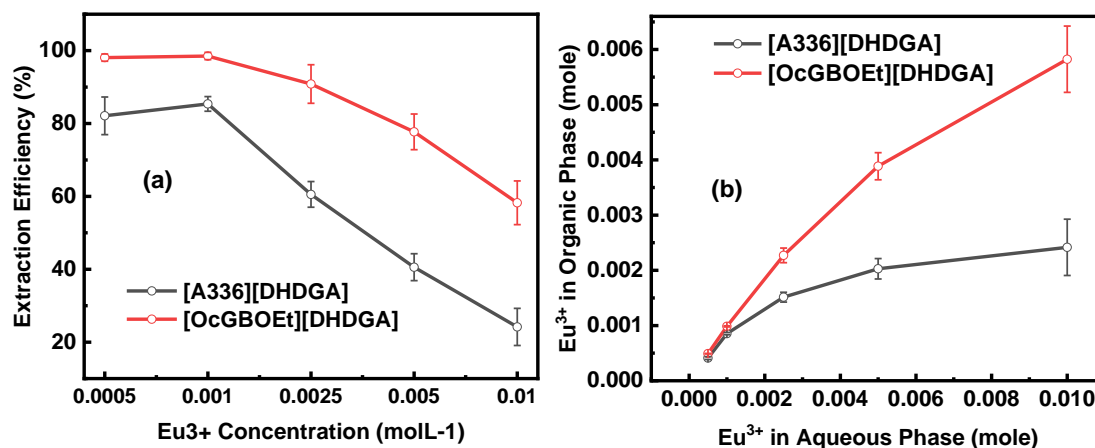
Figure 4.4. Influence of the initial Eu^{3+} concentration on %E (O/A= 1; time= 90 min; temperature= 32 $^{\circ}$C; pH= 4; FIL concentration= 0.04 molL^{-1})

In Figure 4.4(b), the loading capacities of 0.04 molL^{-1} FILs is presented. It was found that the concentration of Eu^{3+} in organic phase increased with increasing the concentration of Eu^{3+} in aqueous phase. As it is evident, the loading capacity of [OcGBOEt][DHDGA] was about three times higher than the loading capacity of [A336][DHDGA]. Although the comparison between the FILs used in this study and other extractants used in other works should be made with caution due to the differences in experimental condition, the FILs used in this study show better performance in terms of loading capacity and extraction efficiency, compared to the conventional extractants.

For example, Mishra and Devi reported that 0.01 M D2EHPA in chloroform could extract 30.6% of ~0.001 molL^{-1} Eu^{3+} (0.002 molL^{-1} EuCl$_3$), while with the same concentration of [A336][DHDGA] and [OcGBOEt][DHDGA] in chloroform could extract 55% and 80% of 0.001molL^{-1} Eu^{3+}, respectively [223]. The saturation loading capacities (as determined using Fig. 4.4b) were ~0.0045 mol and ~0.01 mol of Eu^{3+} for 0.04 mol of [A336][DHDGA] and [OcGBOEt][DHDGA], respectively. As expected, the functionalization of the cationic component resulted in a larger loading capacity of [OcGBOEt][DHDGA]. Even though the [OcGBOEt][DHDGA] is a single compound, its components can, in fact, have separate binding properties.

4.2.4. Effect of Diluent Type. The effect of diluent type on the extraction of europium ions from aqueous nitrate feed solution by the synthesized FILs was also investigated. Three diluents were used: hexane, toluene, and chloroform. Both [OcGBOEt][DHDGA] and [A336][DHDGA] were well miscible in all diluents. As results indicated (Figure 4.5), lower values of %E were obtained with toluene (dielectric constant ~ 2.3). It was also observed that [OcGBOEt][DHDGA] could efficiently extracts Eu^{3+} ions with all three types of diluents but the % E is a little bit higher with chloroform (dielectric constant ~ 4.8). As shown in Figure 4.5, the extraction efficiency of [A336][DHDGA] in hexane diluent (dielectric constant ~ 1.9) was higher than that of [OcGBOEt][DHDGA]. In addition to the influence of dielectric constant, the interaction between the diluent and ILs could largely impact the extraction efficiency. A weaker interaction between extractant and diluent would result in a higher extraction capacity.

4.2.5. Effect of FIL Concentration. The extraction of 0.001 molL^{-1} Eu^{3+} from nitrate solution using various concentrations of FILs (0.005 to 0.1 molL^{-1}) in chloroform

was investigated. As shown in Figure 4.6, the extraction percentage increased with the

increase in concentration of FILs. In the case of [OcGBOEt][DHDGA], 0.04 molL^{-1} was

enough to recover about 98% of the Eu^{3+} ions, while the maximum recovery achieved by

[A336][DHDGA] was 92% which reached with 0.1 molL^{-1} ionic liquid. The result here

was in agreement with the results achieved by studying the effect of Eu^{3+} concentration,

approving the higher loading capacity of [OcGBOEt][DHDGA].
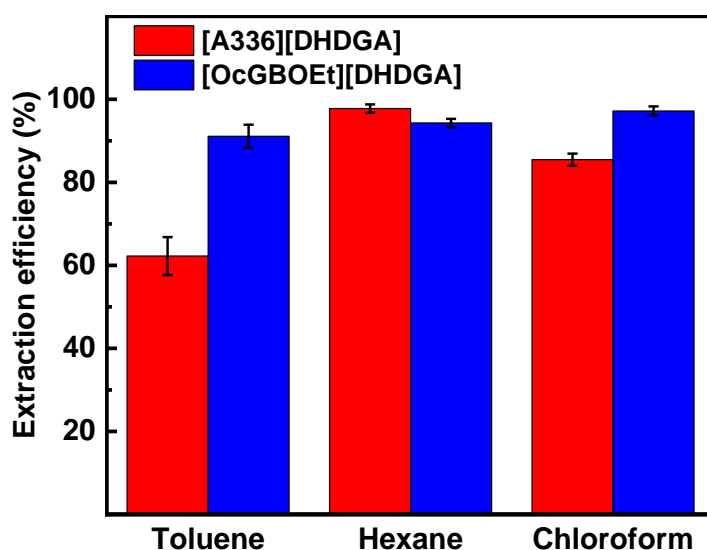
Figure 4.5. Influence of diluent type on the extraction efficiency (%E) of Eu^{3+}. (time= 90 min; temperature= 32 °C; pH= 4; Eu^{3+}= 0.001 molL^{-1}; FIL concentration= 0.04 molL^{-1})

4.2.6. Kinetic Studies. The extraction kinetics was evaluated based on the time of

contact of aqueous phase containing europium ions with the organic phase containing

FILs. The results indicated that the extraction kinetic was relatively fast. Fast extraction

is mainly important for processing radio toxic elements, such as f-block elements, which

continuously emit particle radiation like alpha and beta, and electromagnetic radiation like gamma.
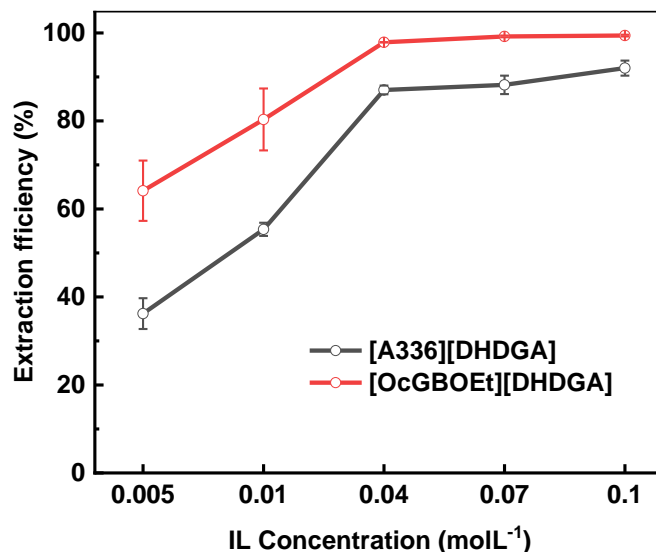
Figure 4.6. Effect of ionic liquid concentration on Eu^{3+} extraction (Eu^{3+} concentration= 0.001 $molL^{-1}$; time= 90 minutes; temperature= 32 °C; pH= 4)

The organic phase is exposed to such radiations and longer contact time could lead to larger chances of radiolytic degradation [78]. In this study, about 88% of europium ions were extracted in first 2 minutes using [OcGBOEt][DHDGA] while ~55% were extracted using [A336][DHDGA]. As it is shown in Figure 4.7, the extraction efficiency of [OcGBOEt][DHDGA] slightly increased to 97.4% when the extraction time increased to 5 minutes, and then reached a plateau (E% ~98-100%) as time increased to 120 minutes. About 75% of Eu^{3+} was extracted by [A336][DHDGA] in 5 minutes and then was continuously increased to ~90% as the extraction time increased to 120 minutes.

4.2.7. Investigations on Extraction Thermodynamics. To calculate the key thermodynamic parameters of the extraction process of REEs by [OcGBOEt][DHDGA] and [A336][DHDGA], extraction experiments of Eu^{3+} were carried out over a temperature range of 23-47 °C. As shown in Figure 4.8, temperature did not have a significant effect on the extraction efficiency of [OcGBOEt][DHDGA] as the extraction process was highly efficient at room temperature. However, it was evident that an increase in temperature from 23 to 47 °C lead to an increase in %E of [A336][DHDGA] from 79.8% to 96.4%, respectively.
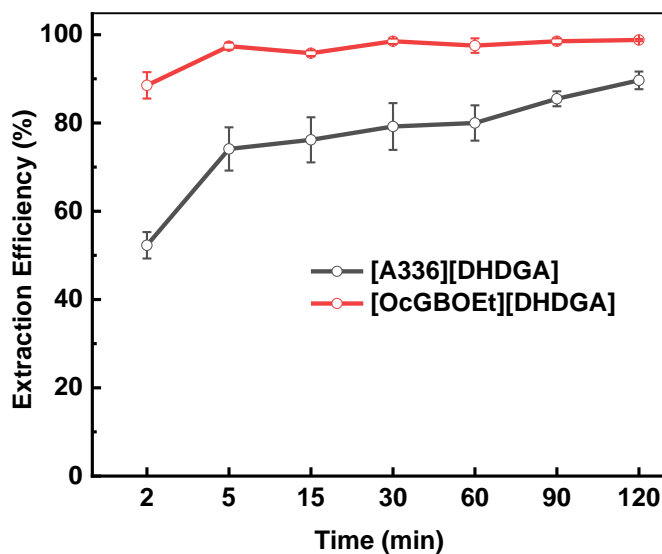
Figure 4.7. Effect of time on the extraction of Eu^{3+}.
([OcGBOEt][DHDGA]=[A336][DHDGA]= 0.04 $molL^{-1}$, Eu^{3+}= 0.001 $molL^{-1}$, pH= 4, temperature= 32 °C)

According to the van't Hoff Equation, enthalpy change of the reaction ($\Delta H°$) can be obtained by the following equation:

$$\log D = -\frac{\Delta H}{2.303R}\frac{1}{T} + C \tag{4.5}$$

where R is the gas constant and C is the integration constant.
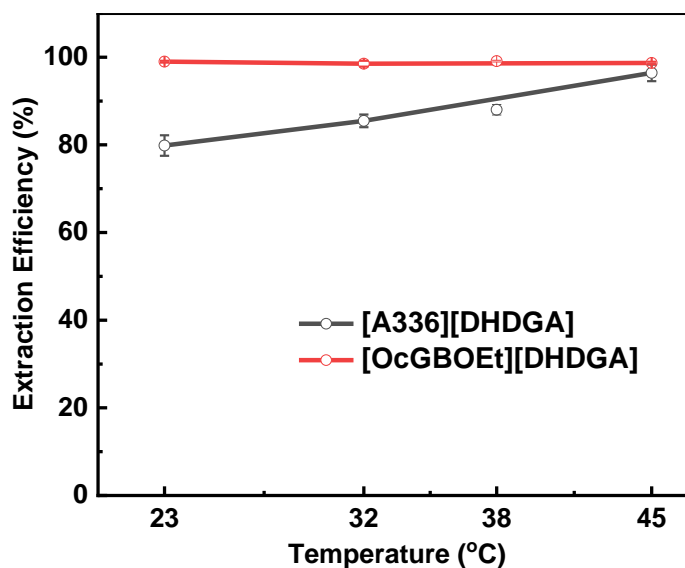
Figure 4.8. Effect of temperature on the extraction of Eu^{3+} (FIL concentration= 0.04 molL^{-1}, Eu^{3+}concentration= 0.001 molL^{-1}, time= 90 min; pH= 4)

As shown in Figure 4.9, plotting log D versus 1000/T resulted in a straight line with a slope of 0.25 and -3.3 for [OcGBOEt][DHDGA] and [A336][DHDGA], respectively. As presented in Table 4.1, ΔH value for [A336][DHDGA] was positive which means that the extraction of europium ions was endothermic. The ΔH value for [OcGBOEt][DHDGA] was negative showing the exothermic nature of the extraction by [OcGBOEt][DHDGA].

The change in Gibbs free energy ($\Delta G°$) was calculated using the eq 4.6:

$$\Delta G = -RT \ln K_{ex} \tag{4.6}$$

K_{ex} is the extraction equilibrium constant and can be calculated using 5.16 and from the intercept of the plot of log D versus log [IL]. The change in entropy ($\Delta S°$) at a particular temperature can be calculated using following equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$ (4.7)

Table 4.1. Thermodynamic parameters of Eu^{3+} extractions in nitric acid medium
(temperature= 298.15 K; time=90 min.; pH=4)

[A336][DHDGA]			[OcGBOEt][DHDGA]		
ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
63.2	-10.8	248.3	-4.8	-22.8	59.2
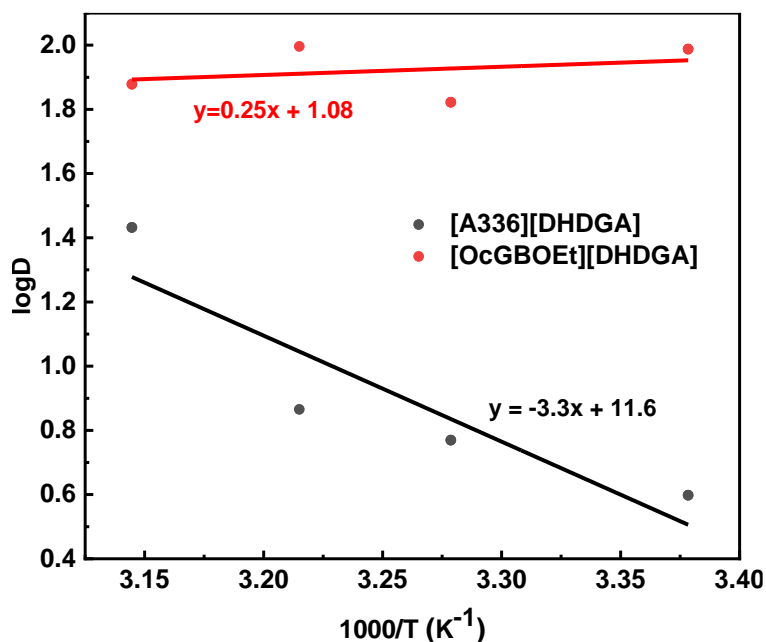
Figure 4.9. Van't Hoff plot correlating the distribution ratio (D) with the extraction temperature (T)

The positive values of $\Delta S°$ suggest that the degree of disorder increased upon the Eu^{3+} extraction. The negative values of Gibbs free energy confirmed the feasibility of the process and the favorable nature of the extraction reactions. As presented in Table 4.1, the extraction by [OcGBOEt][DHDGA] was more favorable than the extraction by [A336][DHDGA].]. However, it should be noted that the enthalpy and related thermodynamic parameters obtained by Van't Hoff method may not be ideally reliable due to the experimental uncertainties. This is a reason for inconsistency between the results obtained by Van't Hoff and calorimetric methods.

4.2.8. Studies on the Extraction Selectivity. Affinity of FILs towards light and heavy rare earth elements was investigated by studying the solvent extraction of La^{3+} and Lu^{3+}.

4.2.8.1. Light and heavy REEs. Extraction of La^{3+} and Lu^{3+}, as representatives of light and heavy REEs, using [OcGBOEt][DHDGA] and [A336][DHDGA] was studied separately to find out the affinity of the synthesized FILs to heavy and light REEs. As it is shown in Figure 4.10, [A336][DHDGA] obviously had much more affinity to heavy REEs, while [OcGBOEt][DHDGA] was less selective.

4.2.8.2. Mixture of REEs. A competitive extraction of ten rare earth elements using [OcGBOEt][DHDGA] and [A336][DHDGA] was carried out to assess the separation efficiency and the selectivity of the proposed FIL systems. The extraction efficiencies are plotted in Figure 4.11. The [OcGBOEt][DHDGA] could effectively extract all the REEs, however, it showed more affinity to middle and heavy REEs. On the other hand, [A336][DHDGA] had a higher selectivity for heavy REEs. The distribution ratios and the separation factors calculated using Eqs. 4.2 and 4.4, are tabulated in Tables

4.2 and 4.3, respectively. As indicated, the separation efficiency of [A336][DHDGA] was much higher than that of [OcGBOEt][DHDGA].
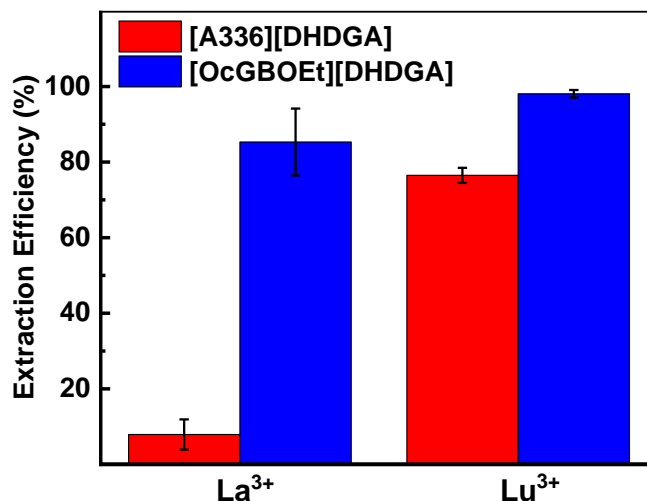
Figure 4.10. Affinity of the synthesized FILs to the light and heavy REEs (REE concentration= 0.001 molL^{-1}; time= 90 min; temperature= 32 $^\circ$C; pH= 4; FIL concentration= 0.04 molL^{-1})

As shown in Figure 4.11 and Tables 4.2 and 4.3, it was evident that La^{3+}, Pr^{3+} and to a smaller extent Nd^{3+}, were much less efficiently extracted than the middle and heavy rare elements. This suggests that [A336][DHDGA] could be used to separate light rare earth elements from the heavier ones. Yttrium behaved like heavy REEs in nitrate media, but the extraction percentage was clearly less than the adjacent heavy REEs with closer ionic size. The separation study was conducted using 0.07 molL^{-1} FILs, however, the separation efficiency was studied by 0.04 molL^{-1} FILs. Results showed not a considerable change in the selectivity of [A336][DHDGA] but an increase in the selectivity of [OcGBOEt][DHDGA] towards heavier rare earth elements.

Figure 4.11. Extraction efficiencies of rare earth ions from nitrate aqueous solution. (REE concentration= 100 mg/l; FIL concentration= 0.07 molL^{-1}; temperature= 32 $^{\circ}$C; time= 90 min; pH= 4)

Table 4.2. Separation factors (SF) of REEs in [OcGBOEt][DHDGA] + Chloroform system

	Pr	Nd	Sm	Eu	Tb	Dy	Y	Er	Lu
La	2.2	1.9	2.4	6.95	15.1	16.6	7.4	16.0	12.9
Pr		0.8	1.1	3.2	6.9	7.7	3.4	7.4	5.9
Nd			1.2	3.6	7.8	8.5	3.8	8.2	6.7
Sm				2.9	6.4	7.0	3.1	6.8	5.5
Eu					2.2	2.4	1.1	2.3	1.9
Tb						1.1	0.5	1.1	0.9
Dy							0.4	0.9	0.8
Y								2.2	1.7
Er									0.8

Table 4.3. Separation factors (SF) of REEs in [A336][DHDGA] + Chloroform system

	Pr	Nd	Sm	Eu	Tb	Dy	Y	Er	Lu
La	10.8	42.6	228.5	450.4	877.5	1149.3	484.6	1266.2	1006.6
Pr		3.9	21.1	41.5	80.9	105.9	44.7	116.8	92.8
Nd			5.4	10.6	20.6	27.0	11.4	29.7	23.7
Sm				1.9	3.8	5.0	2.1	5.5	4.4
Eu					1.9	2.6	1.1	2.8	2.2
Tb						1.3	0.6	1.4	1.1
Dy							0.4	1.1	0.9
Y								2.6	2.0
Er									0.8

4.2.9. Back-Extraction and Reusability Studies. Back-extraction (also known as stripping) studies are important for evaluating the suitability of an extractant for industrial operations. One of the challenges facing the industrial implementation of ionic liquids as extractants is the feasibility of stripping of metal ion from the ionic liquid phase. In some cases, since the extraction of metal ion by FILs may not be very sensitive to pH, stripping the loaded phase by adjusting the pH may not work efficiently. To overcome this problem, some aqueous soluble complexing agents are usually used to facilitate stripping. In the present investigation, nitric acid solutions with different concentrations were used without any complexing agent to examine the back-extraction feasibility. Results (Figure 4.12) showed that the stripping amount of [OcGBOEt][DHDGA] was very high at nitric acid concentrations above 0.1 molL^{-1} (pH < 1). Approximately 95, 99.7, and 100% of the europium ions were extracted using 0.1, 0.3 and 0.5 molL^{-1} nitric acid. As shown in Figure 4.12, the europium extracted from

[OcGBOEt][DHDGA] by 0.001 and 0.01 $molL^{-1}$ nitric acid was not considerable, while about 20% and 53% of europium was extracted from [A336][DHDGA] with 0.001 and 0.01 $molL^{-1}$ HNO_3, respectively. The stripping efficiency could increase to 66, 83, and 100% for [A336][DHDGA] by using 0.1, 0.3, and 0.5 $molL^{-1}$ nitric acid.

The stability and reusability of functional ionic liquids are essential from a practical point of view. The reusability of [A336][DHDGA] and [OcGBOEt][DHDGA] was studied by stripping of loaded FILs with 0.3 and 0.1 $molL^{-1}$ nitric acid, respectively, and then re-loading with 0.001 $molL^{-1}$ Eu^{3+} aqueous feed. The extraction was performed at pH 4 and 32 °C for 90 minutes. The results indicated that the extractability of both ionic liquids after being stripped remained as high as the extractability of fresh FILs. The extraction efficiencies of stripped 0.04 $molL^{-1}$ [A336][DHDGA] and [OcGBOEt][DHDGA] were ~86% and 95%, respectively.
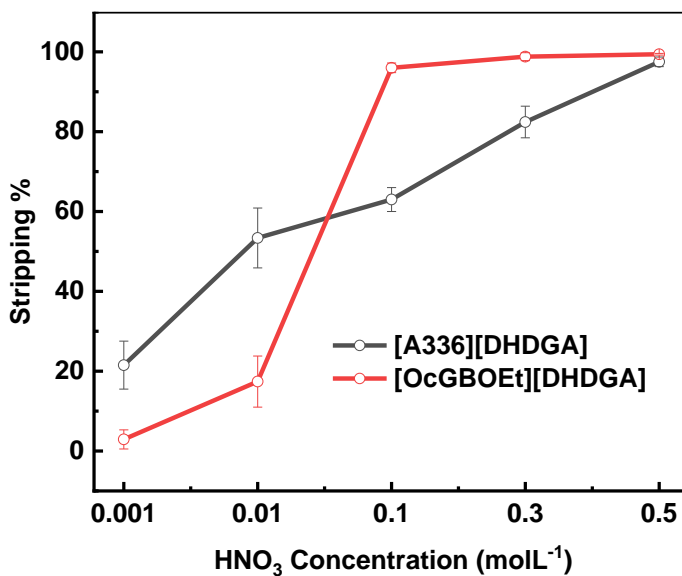
Figure 4.12. Stripping of the loaded [OcGBOEt][DHDGA] and [A336][DHDGA] with different concentrations of nitric acid (temperature= 23 °C; time= 75 min)

5. STUDY OF EXTRACTION MECHANISM

5.1. INTRODUCTION TO SOLVENT EXTRACTION MECHANISM

The complex chemistry of metal extraction processes, specially the extraction of critical metals, is still not completely understood. The behavior of metal ions in extraction systems is very dependent on the experimental circumstances and the type of applied extractants and solvents. Metal extraction using acidic extractants (cation exchangers) is supposed to takes place through a stepwise process comprised of extractant partitioning between the organic and aqueous phases, ionization in the aqueous phase and reaction between the metal ion with the anion of acidic extractant, and finally the partitioning of the neutral complexes between organic and aqueous phases [224]. The extraction mechanism depends on chemical reactions in the aqueous phase, and the interaction between the extractant in organic phase and the metal ions in aqueous phase. However, reactions between metal ions and extratant molecules rather than extractant anions are also possible, depending on the acidity of the extractant. Solution diffusion is a common mechanism proposed for metal solvent extraction. Although the solution diffusion can occur with or without chemical reactions, some chemical changes are always present due to the coordination, association, dissociation, and aggregation of complexes [225, 226]. The complexation reactions can be presented by following equations

$$M + L = ML \quad K_1 = \frac{[ML]}{[M][L]} \tag{5.1}$$

$$ML + L = ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]} \tag{5.2}$$

$$ML_{n-1} + L = ML_n \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{5.3}$$
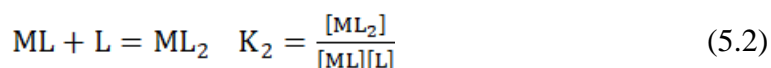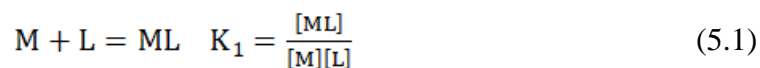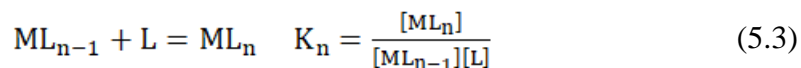
M denotes metal cation and L represents ligand anion. K_n is formation constant, which determines the extent of complexation. Complexation proceeds until reaching the coordination number (n).

In the case of solvent extraction by anion exchangers, negatively charged complexes are formed by reaction between metal ions and inorganic ligands with large organic cations. Amine salts are examples of anion exchangers, however, although the formation of negatively charged complexes by amine salts is well explained, it is difficult to obtain a simple mathematical model that is in agreement with the experimental results [227, 228]. The other difficulty is the identification of the species formed in organic phase, which may contain free, monomeric, and polymeric amine salts as well as metal complexes. The metal extraction by amine salts is presented in the following equations [224]

$$ML_n^{-q} + qRNH^+L_{(O)}^- \leftrightarrow ([RNH^+]_q^q[ML]_n^{-q})_{(O)} + qL^- \tag{5.4}$$

and/or

$$ML_n + R_4NL \leftrightarrow RN^+ML^- \tag{5.5}$$
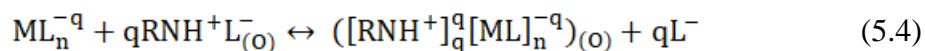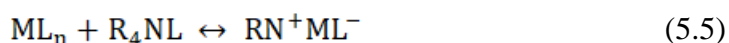
so, the extraction constant can be defined as

$$K_{ex} = \frac{[(RNH)_q^{+q}]_{(O)}[L_{\bar{n}}]^q}{(ML_n^{-q})(RNH)_{(O)}^q} \tag{5.6}$$

If the aqueous phase contains all the stepwise complexes, then the distribution ratio will be

$$D = \frac{[(RNH)_q^{+q} ML_n^{-q}]_{(O)}}{\Sigma[ML_n^{z-n}]} \tag{5.7}$$

The distribution ratio depends on both the concentration of free ligand in the aqueous phase and concentration of amine in the organic phase. To have the negatively charged complexes, the concentration of ligand in the aqueous phase must be high. The nature of anionic complexes that can be extracted have been investigated with different types of ligands. Oxyanions are common complexes occurring for group VI metals [224, 229]. The anions of mineral acids, such as ClO_4^-, NO_3^-, Cl^-, and SO_4^{2-} can also form anionic complexes with metal ions. The extent of extraction and complexation of metal ions with quaternary ammonium salts is in order of $ClO_4^- < NO_3^- < Cl^- < SO_4^-$ [224]. Although the metal nitrate complexes are not strong, there are few elements such as some of the lanthanides and some transition elements can be extracted in the form of nitrate complexes [230].

In addition to extraction through cation or anion exchange mechanism, the extraction of metal ions can occur through H-bonding and solvation. In this extraction mechanism, neutral species are transferred to the organic phase by solvation of neutral species of metal ions or solvation of the hydrogen ions in metal acid species [231]. If the neutral metal-ligand complexes are unsaturated, then $ML_z(H_2O)_x$ complexes can get formed until reaching the maximum coordination number [224]. The presence of solvating organic solvent can increase the distribution constant by making more lipophilic complexes through replacement of organic molecules with the hydrating water

molecules. Different types of complexes can be formed, depending on the extent of complex formation in the aqueous phase and the type of ligand.

Extraction occurs through solvation of either the central metal atom of the complex or the proton in the case of formation of a complex acid species [224]. The complex formation can be expressed as

$$[ML_z]_{(O)} + bE \leftrightarrow [ML_zE_b]_{(O)} \tag{5.8}$$

or

$$HML_{z+1} + pE_{(O)} \leftrightarrow [(HE_b)^+(ML_{z+1})^-]_{(O)} \tag{5.9}$$
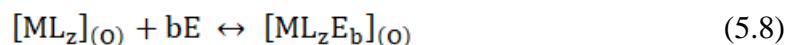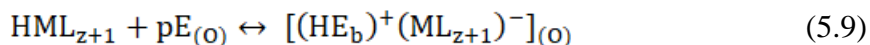
In the case of ionic liquids, the extraction mechanism depends on the role of ILs in the extraction process. When ILs are used as solvents, the extraction of metal ions can occur through ion exchange mechanism [232, 233]. Both cation and anion exchange can happen since both the cationic and anionic components of ILs can transfer into the aqueous phase. Therefore, understanding the extraction mechanism in IL-based extraction systems is essential to carefully design the right components for ILs. Since the non-functional ILs do not have coordination property, organic extractants must be used to chelate with metal ions to solubilize the metal complexes in IL phase. When ILs are used as solvent, the hydrophobicity of IL components is key factor suppressing or promoting the ion exchange process [234]. The cation exchange mechanism in IL-based extraction systems can be written as Equation 5.10, where L denotes the extractant, M is the metal ion, and C is the cationic component of IL:

$$M^{m+} + mL + mC_{IL}^+ \leftrightarrow ML_{m,IL}^{m+} + mC^+ \tag{5.10}$$
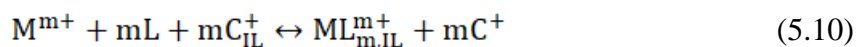
As expressed in Equation 5.10, cation exchange mechanism leads to the loss of cationic part of IL, which restricts the application of ILs as solvent in extraction systems. Anion exchange is also a possible mechanism for solvent extraction of metal ions with ILs. Although this mechanism is not well understood, the transfer of anionic component to the aqueous phase still occurs [235].

A way to change the extraction mechanism in IL-based systems is to functionalize the ionic components of the ILs so that the metal ions can be extracted through neutral mechanism, which avoids the loss of IL components to the aqueous phase. Several studies have shown that the extraction mechanism totally changes when functionalized ILs are used as extractants [236-238]. Studying the complexation between Eu(III) and [A336][P204] by extended X-ray absorption fine structure and FTIR analysis showed that both cation and anion of the FILs participated in extraction process and unlike the acidic extractants, the extraction mechanism was concluded to be neutral [236]

$$Eu^{3+} + 3[A336][P2O4]_{IL} + 3NO_3^- \leftrightarrow Eu(NO_3)_3.3[A336][P2O4]_{IL} \qquad (5.11)$$
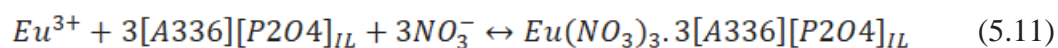
As obvious in Equation 5.11, no ammonium ions is released to the aqueous phase which could reduce the production of ammonia- contaminated wastewater and thus can help to eliminate the need for the costly saponification process.

In this study, the mechanism of europium (as an example of rare earth elements) extraction by [A336][DHDGA] and [OcGBOEt][DHDGA] was investigated using NMR and FTIR spectroscopies by analyzing the organic and aqueous phases before and after europium extraction. In addition, slope analysis approach was used to determine the stoichiometry of FILs/ europium ions complexation.

5.2. EXPERIMENTAL

To study the extraction mechanism, the aqueous and organic phases before and after extraction experiments were analyzed by different techniques. ^{1}H NMR analysis was used to see if any components of FILs were released to the aqueous phase. FTIR analysis was employed to investigate the composition of Eu-FIL complexes. Also, the stability of the complexes was evaluated by ^{1}H NMR analysis of the organic phases after the extraction. Slope analysis was used to investigate the stoichiometry of Eu-FIL complexation. This was obtained by measuring the distribution ratio of europium as a function of FILs concentration in organic phase and plotting the logarithmic value of the measured distribution ratio against logarithm of FILs. RESULTS AND DISCUSSION

5.3. RESULTS AND DISCUSSION

Understanding the extraction mechanism of FILs is vital to develop more selective IL-based reagents for the extraction and recovery of rare earth and other critical metals. In this work, the extraction mechanism of the synthesized FILs was investigated using FTIR spectroscopy by analyzing the organic and aqueous phases before and after europium extraction. In addition, slope analysis approach was used to determine the stoichiometry of FILs/ europium ions complexation. This was obtained by measuring the distribution ratio of europium as a function of FILs concentration in organic phase and plotting the logarithmic value of the measured distribution ratio against logarithm of FILs concentration.

The possible loss of the cations in the synthesized FILs to the aqueous phase was initially examined by ^{1}H NMR and FTIR analysis of the aqueous phases after the

extraction process to investigate the possibility of ion exchange mechanism. As shown in Figure 5.1, no peak other than the peaks for water and acetone as solvent were observed in NMR analysis of the aqueous phases before and after extraction. Figure 5.2, showed the FTIR spectra of the three aqueous phases: the feed solution, the aqueous phase after extraction of Eu^{3+} with [A336][DHDGA], and the aqueous phase after extraction of Eu^{3+} with [OcGBOEt][DHDGA] . As indicated, no change in the peaks of the aqueous phases was observed after extraction. The bands around 1400 cm^{-1} corresponded to the N−O bands of NO_3^- ions and the −OH group was present at 3450 cm^{-1}. This observation suggested that Eu^{3+} was not extracted through cation exchange mechanism. In fact, the long alkyl chains of the cationic components are the key factors preventing the cation exchange across the aqueous/organic phases.

Further investigations using FTIR was conducted thereafter to analyze the organic phases before and after Eu^{3+} extraction and to study the composition of the extracted complexes. As shown in Figure 5.3, the C=O stretching vibrations were present at 1628 and 1712 cm^{-1} in the spectra of [A336][DHDGA]. The shift of C=O stretching vibrations in IR spectra of loaded [A336][DHDGA] demonstrated the interactions between C=O groups from [A336][DHDGA] and europium ions.

Also, the C−N stretching vibration at 1258 cm^{-1} in IR spectra of [A336][DHDGA] was shifted to 1261 cm^{-1} in the spectra of loaded [A336][DHDGA], showing the participation of [A336]$^+$ in the extraction mechanism. As indicated in Figure 5.4, the C=O stretching vibration at 1644 cm^{-1} in the spectra of [OcGBOEt][DHDGA] was decreased to 1640 cm^{-1} in the spectra of loaded [OcGBOEt][DHDGA] which

demonstrated the interaction between the C=O band from [OcGBOEt][DHDGA] and Eu^{3+}.
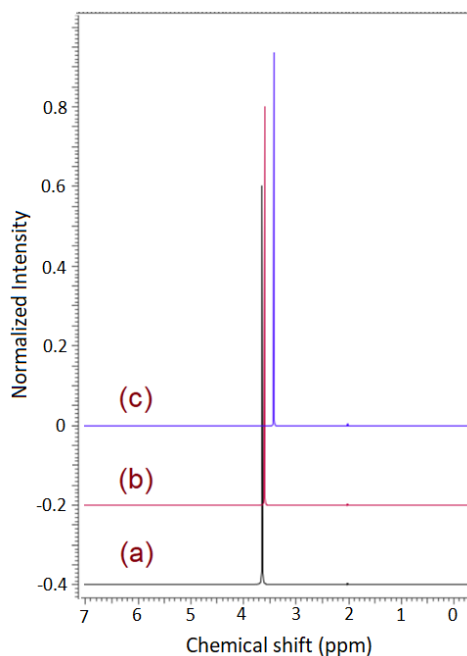
Figure 5.1. ^{1}H NMR spectra of (a) aqueous 0.001 molL^{-1} feed solution (b) aqueous phase after extraction of Eu^{3+} with [A336][DHDGA], and (c) aqueous phase after extraction of Eu^{3+} with [OcGBOEt][DHDGA] (NMR solvent: acetone)
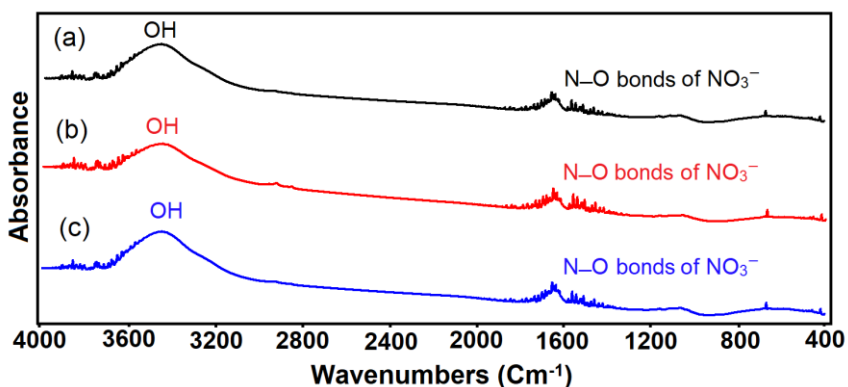
Figure 5.2. FT-IR spectra of (a) aqueous 0.001 molL^{-1} feed solution (b) aqueous phase after extraction of Eu^{3+} with [A336][DHDGA], and (c) aqueous phase after extraction of Eu^{3+} with [OcGBOEt][DHDGA]
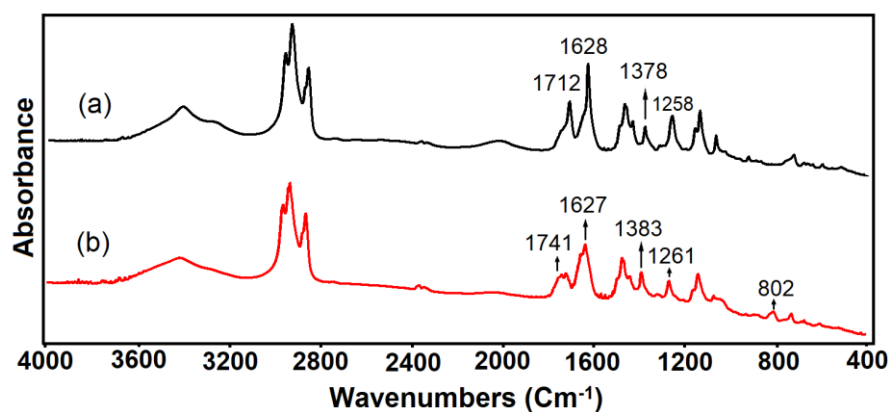
Figure 5.3. FT-IR spectra of (a) [A336][DHDGA] and (b) [A336][DHDGA] loaded with Eu^{3+}
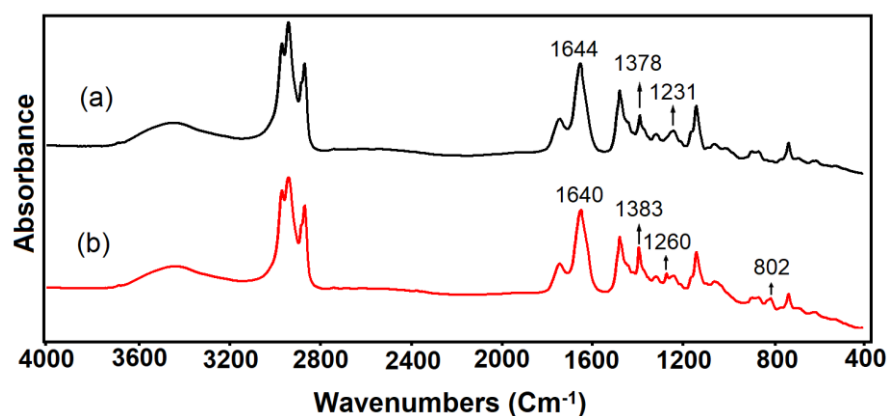
Figure 5.4. FT-IR spectra of (a) [OcGBOEt][DHDGA] and (b) [OcGBOEt][DHDGA] loaded with Eu^{3+}

The ^{1}H NMR analysis of the organic phases loaded with Eu^{3+} showed higher stability of complexes for [OcGBOEt][DHDGA] as compared to [A336][DHDGA]. Actually, no change was observed in the chemical shifts after the extraction process (Figures. 5.5&5.6). The chemical shift at around 2ppm in the NMR spectrums of loaded organic phases could be due to the extraction of hydrated europium ions.
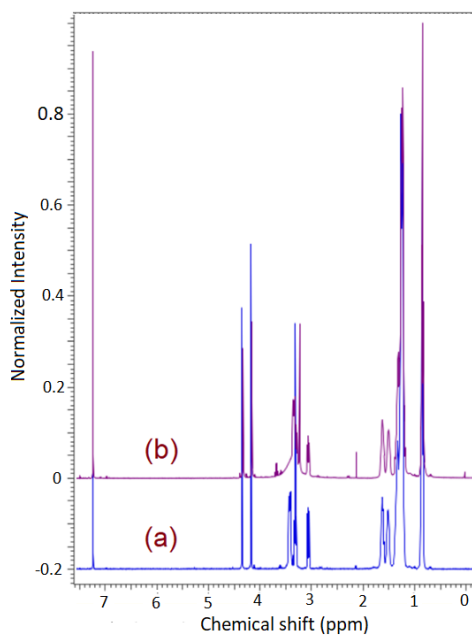
Figure 5.5. ^{1}H NMR spectra of (a) [A336][DHDGA] and (b) [A336][DHDGA] loaded with Eu^{3+} (NMR solvent: deuterated chloroform)
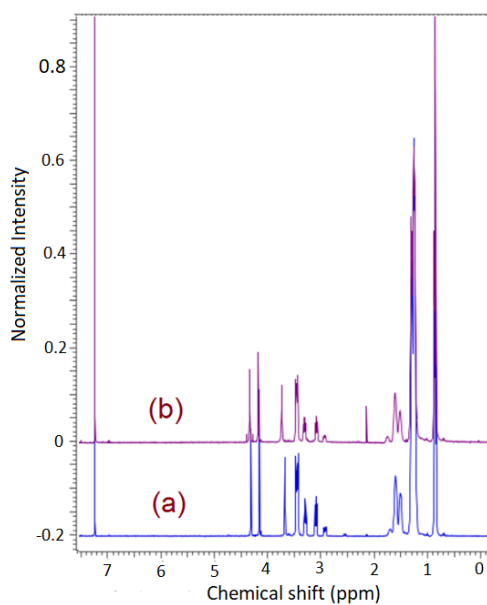
Figure 5.6. ^{1}H NMR spectra of (a) [OcGBOEt][DHDGA] and (b) [OcGBOEt][DHDGA] loaded with Eu3+ (NMR solvent: deuterated chloroform)

Based on the FTIR and NMR analysis, the extraction of Eu^{3+} by both ionic liquids possibly occurred through ion association mechanism. The driving force for ion exchange mechanism is different from that for solvation and ion association mechanism. While the driving force for ion exchange is the partitioning of the cationic part of ionic liquids, the driving force for solvation is the ionic interactions between ionic liquid and extracting complexes. The extraction equilibrium between Eu^{3+}, nitrate ion, and FILs maybe be stated by Equation 5.12

$$M_{aq}^{3+} + x[Cn][An]_{org} + y(NO_3^-)_{aq} \overset{K_{ex}}{\rightleftharpoons} [Cn]_x M[An]_x (NO_3)_y \qquad (5.12)$$
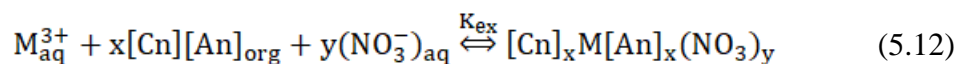
where M represents Eu, the subscripts "org" and "aq" denote organic phase and aqueous phase, respectively. Cn and An represent the cation and anion of the FILs, respectively. D and the extraction equilibrium constant (K_{ex}) can be expressed by Equations 5.13 and 5.14

$$D = \frac{[Cn]_x M[An]_x [NO_3]_y}{[M^{3+}]_{aq}} \qquad (5.13)$$

$$K_{ex} = \frac{[Cn]_x M[An]_x [NO_3]_y}{[M^{3+}]_{aq}[Cn][An]_{org}^x [NO_3^-]_{aq}^y} \qquad (5.14)$$

Applying the Equation 5.13 in Equation 5.14 yields the Equation 5.15

$$K_{ex} = \frac{D}{[Cn]_x [An]_{org}^x [NO_3^-]_{aq}^y} \qquad (5.15)$$

Then the Equation 5.16 can be concluded for the calculation of log D

$$\log D = \log K_{ex} + x\log[Cn][An]_{org} + y\log[NO_3^-]_{aq} \qquad (5.16)$$

For further investigation of the extraction mechanism, the stoichiometry of complexation was determined using slope analysis method by plotting the log D versus

log [IL] at a constant pH. As shown in Figure 5.7, a higher [OcGBOEt][DHDGA] concentration contributed to the extraction of 0.001 molL^{-1} Eu^{3+} when the initial pH value of the aqueous phase was 4. The linear relationship between the log D and log [IL] was obtained with a slope of 1.6 for [OcGBOEt][DHDGA] and 0.9 for [A336][DHDGA] when the concentration of ionic liquids was changed from 0.0005 to 0.1 molL^{-1}.
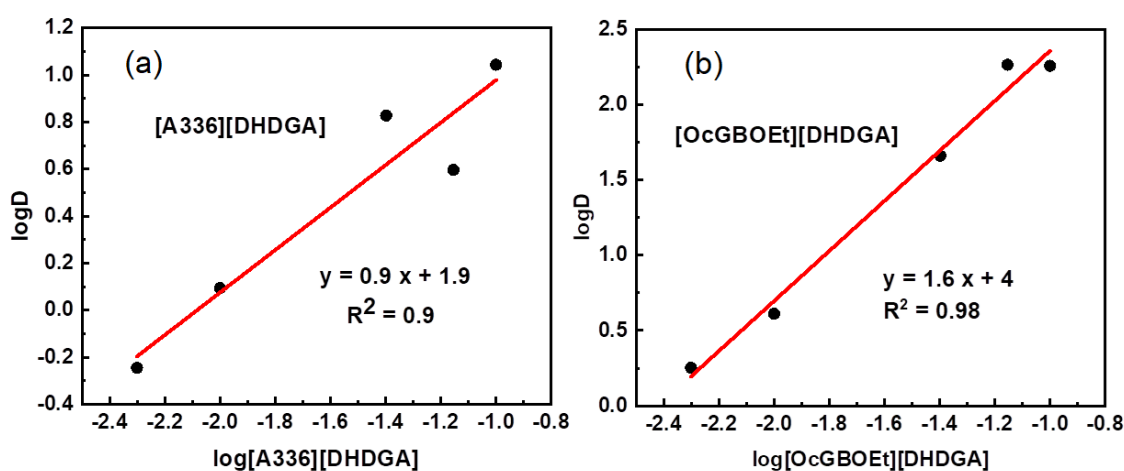
Figure 5.7. Linear relationship between log D$_{Eu}$ and log [IL] in Eu^{3+} extraction by (a) [A336][DHDGA] and (b) [OcGBOEt][DHDGA]

The slopes revealed that the stoichiometry of [OcGBOEt][DHDGA] with Eu^{3+} was approximately 2:1, and the stoichiometry of [A336][DHDGA] with Eu^{3+} was about 1:1. The stoichiometry of nitrate ions can be considered to be 3 due to the electroneutrality principle. Thus, the extraction mechanism of Eu^{3+} by [A336][DHDGA] and [OcGBOEt][DHDGA] can be represented by the following equations

$$Eu_{aq}^{3+} + [A336][DHDGA]_{org} + 3(NO_3^-)_{aq} \leftrightarrow [A336]Eu[DHDGA](NO_3)_3 \quad (5.17)$$

$$Eu^{3+}_{aq} + 2[OcGBOEt][DHDGA]_{org} + 3(NO_3^-)_{aq} \leftrightarrow [OcGBOEt]_2 Eu[DHDGA]_2(NO_3)_3 \quad (5.18)$$
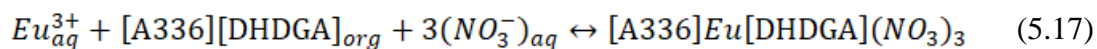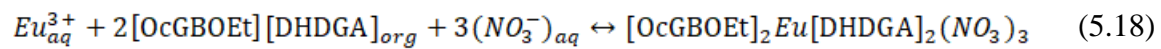
It should be noted that the stoichiometric values obtained by slope analysis are specific to the experimental conditions used in this study and changing the condition can result in a different stoichiometry.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. GENERAL FINDINGS

In this study, two novel ammonium-based functional ionic liquids: trioctyl(2-ethoxy-2-oxoethyl) ammonium dihexyldiglycolamate, [OcGBOEt][DHDGA], and tricaprylmethyl ammonium dihexyldiglycolamate, [A336][DHDGA] were synthesized and tested, for the first time, for the recovery and separation of europium and other selected rare earth elements (heavy and light REEs) from nitric acid solutions.

TGA analysis showed that both ionic liquids undergo a one-step decomposition behavior. The onset decomposition temperatures of [A336][DHDGA] and [OcGBOEt][DHDGA] were 213 and 218 °C, respectively. Two different transitions were observed for both ionic liquids probably due to the decomposition of different components at various temperatures. The TGA thermograms showed that the decomposition of [OcGBOEt][DHDGA] was faster than that of [A336][DHDGA]. Results indicated that [OcGBOEt][DHDGA] fully decomposed at ~330 °C while the complete decomposition of [A336][DHDGA] occurred at ~356 °C.

DSC analysis showed that both ionic liquids presented a very weak tendency to crystallize. Results indicated that ionic liquids transferred to a supercooled liquid state as they cooled down. The glass transition temperatures of [A336][DHDGA] and [OcGBOEt][DHDGA] were found to be -63 and -56 °C, respectively, which demonstrated that [OcGBOEt][DHDGA] ions need more energy to move around when not diluted.

The density of [A336][DHDGA] was found to be 1.19 g/mL, slightly larger than the density of [OcGBOEt][DHDGA] which was 1.14 g/mL. Functionalization of [A336]$^+$ increased both the mass and volume of ionic liquid, however, the density measurement demonstrated that the increase in volume had a larger contribution to the overall density value of [OcGBOEt][DHDGA]. The viscosity of [OcGBOEt][DHDGA] was 5.85 Pa.s, which was 2.2 times greater than the viscosity of [A336][DHDGA] which was found to be 2.68 Pa.s.

Extraction experiments using europium, as an example of REEs, revealed the enhanced extraction efficiency of the synthesized FILs as compared to their precursors. The extraction percentage of the precursors, [OcGBOEt][Br], [A336][Cl], and [DHDGAA], were 4.2%, 3.7%, and 76%, respectively as compared to 98.5% and 86% for [OcGBOEt][DHDGA] and [A336][DHDGA], respectively. This enhanced extraction is due to the inner synergistic effect of both the acidic and basic components. Both the cation and the anion possibly involved in the extraction process and formed coordination bonds with REE^{3+} ions which would help to increase the capacity of ILs and reduce the loss of cation and anion to the aqueous phase. It was also observed that the functionalization of both cation and anion in [OcGBOEt][DHDGA] resulted in higher loading capacity compared to [A336][DHDGA], where only the anionic component was functionalized. The loading capacity of [OcGBOEt][DHDGA] was found to be about three times higher than the loading capacity of [A336][DHDGA].

Results indicated that high acidity had a negative effect on the extraction efficiency of FILs. Extraction efficiency (%E) values displayed a slow increase in the pH range of 2.5-4, however at pH > 4, the extraction efficiency dropped to 70-80%.

It was observed that both FILs were miscible in the tested organic diluents namely hexane, chloroform, and toluene, however, the values of %E obtained with toluene were lower. The [OcGBOEt][DHDGA] could efficiently extracts metal ions with all three types of diluents but the % E was a little bit higher with chloroform. The extraction efficiency of [A336][DHDGA] could be effectively increased when diluted in hexane.

Studies on the extraction kinetics indicated that the extraction process was relatively fast. About 88% of metal ions (europium as an example of REEs) were extracted in first 2 minutes using [OcGBOEt][DHDGA] while ~55% were extracted using [A336][DHDGA] in the same time. The extraction efficiency of [OcGBOEt][DHDGA] slightly increased to 97.4% when the extraction time increased to 5 minutes, and then reached a plateau (E% ~98-100%) as time increased to 120 minutes. About 75% of Eu^{3+} was extracted by [A336][DHDGA] in 5 minutes and then was continuously increased to ~90% as the extraction time increased to 120 minutes.

Results showed that temperature did not have a significant effect on the extraction efficiency of [OcGBOEt][DHDGA] as the extraction process was highly efficient at room temperature. However, in the case of [A336][DHDGA], increasing the temperature from 23 to 45 °C lead to an increase in the %E of Eu^{3+} from ~80% to 96%, respectively. The extraction of europium ions by [A336][DHDGA] was found to be endothermic, while the ΔH value for [OcGBOEt][DHDGA] was negative showing the exothermic nature of the extraction by [OcGBOEt][DHDGA]. The positive values of ΔS° suggested that the degree of disorder increased upon the Eu^{3+} extraction by both the FILs. The negative values of Gibbs free energy confirmed the feasibility of the process and the favorable nature of the extraction reactions.

It was found that the [A336][DHDGA] had much more affinity to heavy REEs, while [OcGBOEt][DHDGA] was less selective. The %E of [A336][DHDGA] was much higher than that of [OcGBOEt][DHDGA]. It was observed that La^{3+}, Pr^{3+} and to a smaller extent Nd^{3+}, were much less efficiently extracted than the middle and heavy rare elements. This suggests that [A336][DHDGA] could be used to separate light rare earth elements from the heavier ones. Yttrium behaved like heavy REEs in nitrate media, but the extraction percentage was clearly less than the adjacent heavy REEs with closer ionic size.

Back-extraction studies using eurpium indicated that [OcGBOEt][DHDGA] had better stripping properties compared to [A336][DHDGA]. Approximately 95, 99.7, and 100% of the europium ions were extracted using 0.1, 0.3 and 0.5 $molL^{-1}$ nitric acid. The amount of europium extracted from [OcGBOEt][DHDGA] by 0.001 and 0.01 $molL^{-1}$ nitric acid was not considerable, while about 20% and 53% of europium was extracted from [A336][DHDGA] with 0.001 and 0.01 $molL^{-1}$ HNO_3, respectively. The stripping efficiency increased to 66, 83, and 100% for [A336][DHDGA] by using 0.1, 0.3, and 0.5 $molL^{-1}$ nitric acid.

Re-loading the stripped FILs showed that both FILs could be effectively reused for extraction of rare earth elements. The results indicated that the extractability of both ionic liquids after being stripped remained as high as the extractability of fresh FILs.

Slope analysis indicated the formation of the 1:1 metal-ligand complex for [A336][DHDGA] and ~1:2 metal-ligand ratio for [OcGBOEt][DHDGA].   NMR and FTIR analyses of the aqueous phases after extraction revealed that there is no loss of FIL components to the aqueous phase. This observation suggested that Eu^{3+} was not extracted

through ion exchange mechanism. The FTIR analysis of the loaded organic phases revealed the interaction between Eu^{3+} and C=O groups. The shift of C−N stretching vibration in IR spectra of loaded [A336][DHDGA] indicated the participation of $[A336]^+$ in the extraction mechanism. The ^{1}H NMR analysis of the organic phases loaded with Eu^{3+} showed higher stability of complexes for [OcGBOEt][DHDGA]. The chemical shift at around 2ppm in the H NMR spectrums of loaded organic phases showed the extraction of hydrated europium ions.

Although the comparison between the FILs used in this work and other extractants used in other studies should be made with caution due to the differences in experimental condition, the FILs used in this study showed better performance in terms of loading capacity and extraction efficiency, compared to the conventional extractants such as D2EHPA.

6.2. SUGGESTED FUTURE WORK

It will be useful to analyze the structure of REE-FIL complexes by extended X-ray absorption fine structure analysis to have a better insight about the complexation process. Other suggestion is to alter the hydrophobicity of FILs to increase the interaction between the organic and the aqueous phases. Studying the polarity of complexes formed by FILs with different hydrophobic characters can be helpful to improve the transfer of metal ions from the aqueous phase to the organic phase. It is also recommended to study the separation efficiency of FILs in other operational conditions since the selectivity of FILs may change under different experimental conditions. Kerosene is another organic solvent which is suggested to be examined for diluting the synthesized FILs. Moreover,

molecular dynamics simulation (MDS) is recommended to study the geometry of complexes, the effect of denticity, and the influence of donating groups, in addition to distinguishing the role of cations and anions, separately. MD calculations are also useful to study the interaction between FILs and both the aqueous and organic phases. This is of great importance which will help to optimize the FILs systems to minimize the loss of FILs to the aqueous phase. The behavior of synthesized FILs in practical systems in the presence of other ions has not been investigated in this research. It is suggested to study the effect of common impurities such as calcium and iron on the efficiency of FILs.

Also, structural alteration may help to improve the physical properties such as viscosity of FILs. Incorporation of size-responsive functionalities into anionic and cationic components can produce smarter and more selective FILs for the separation of adjacent rare earth elements.

From the application point of view, it is recommended to apply the FILs synthesized in this study in membrane systems for the separation of critical metals. . It is also highly recommended test these novel reagents in the separation of lanthanides from actinides. It could be helpful to test their potential for separating fission products in nuclear process.

APPENDIX
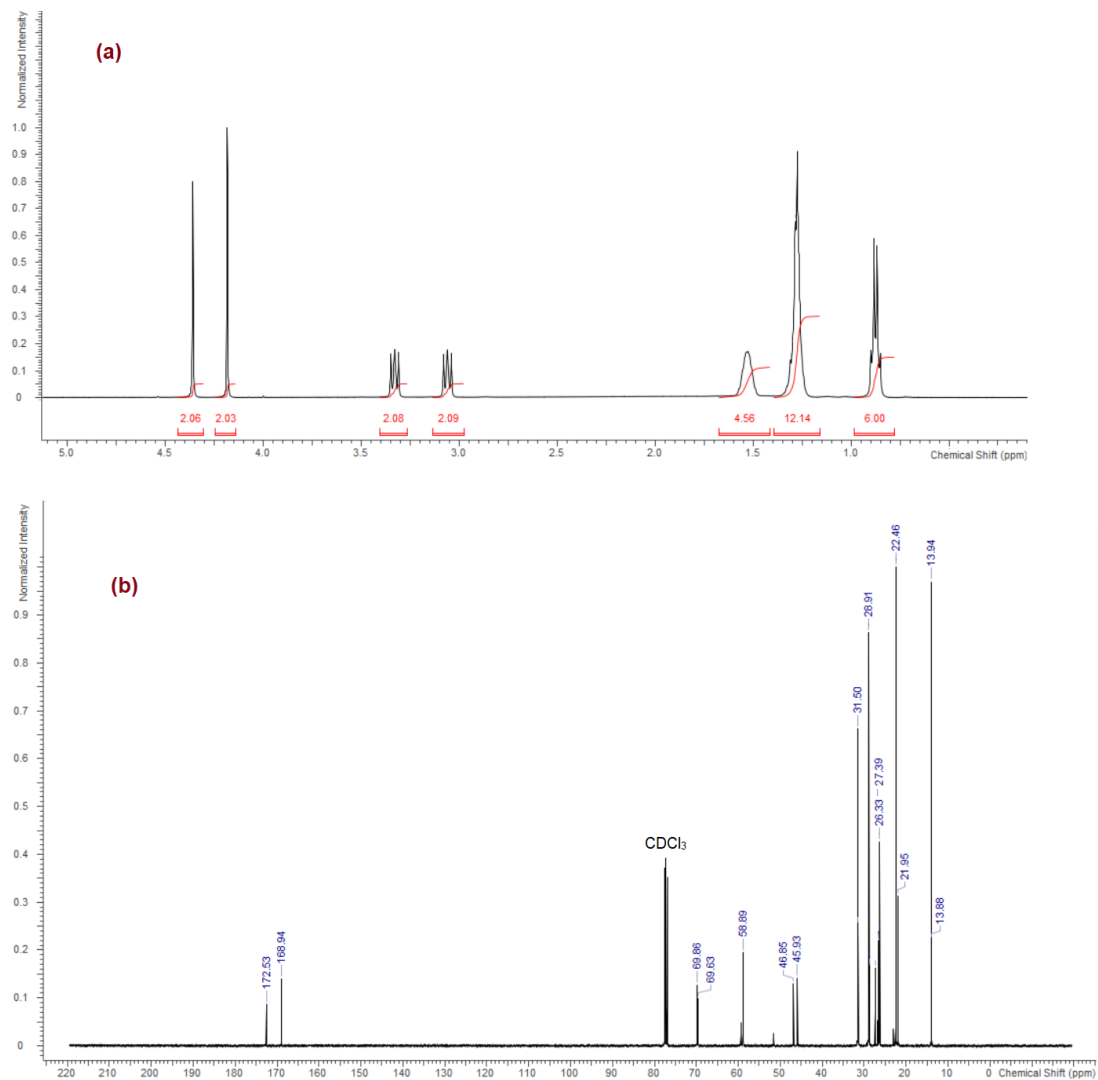
Figure A1. (a) H NMR and (b) C NMR spectra of DHDGAA

Figure A2. (a) H NMR and (b) C NMR spectra of [A336][DHDGA]

Figure A3. (a) H NMR and (b) C NMR spectra of [OcGBOEt][DHDGA]
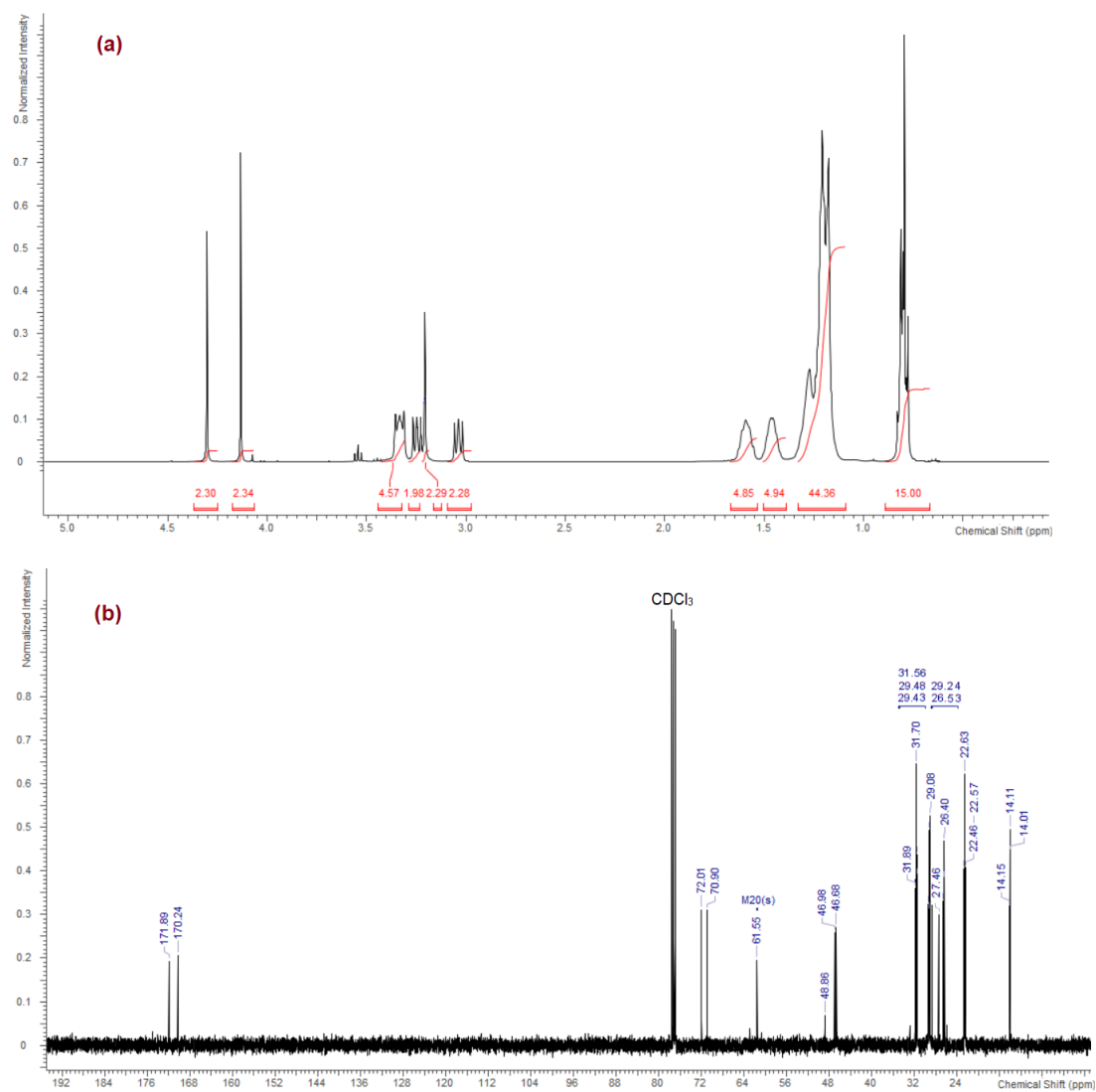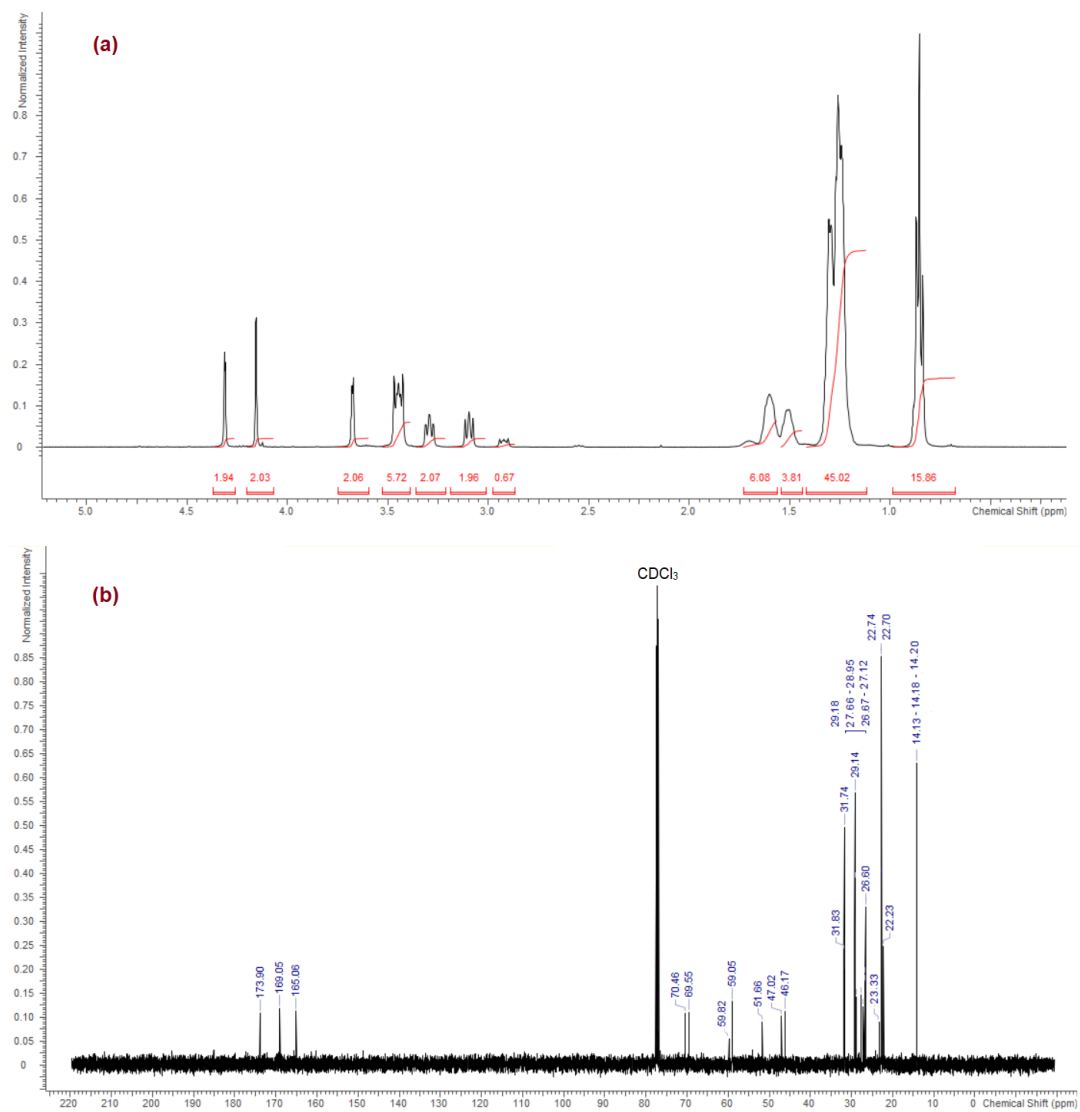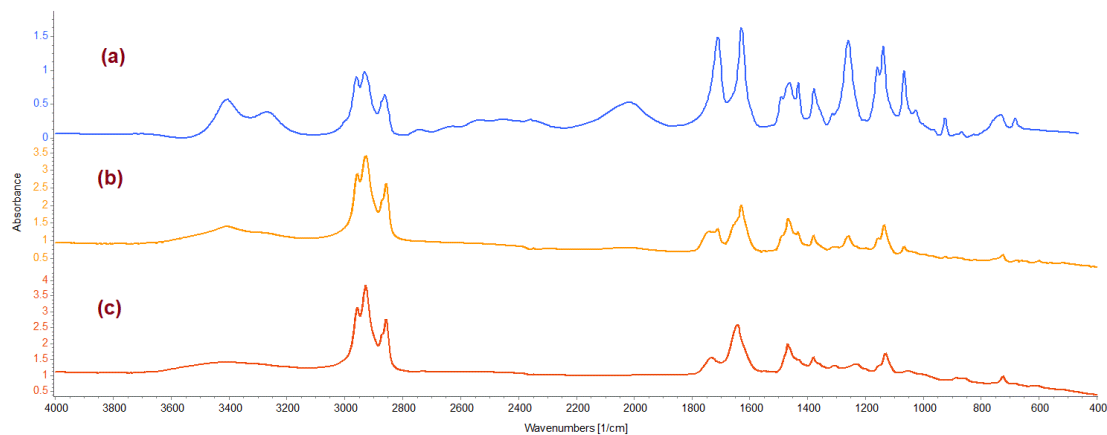
Figure A4. FTIR spectra for (a) DHDGAA, (b) [A336][DHDGA], and (c) [OcGBOEt][DHDGA]
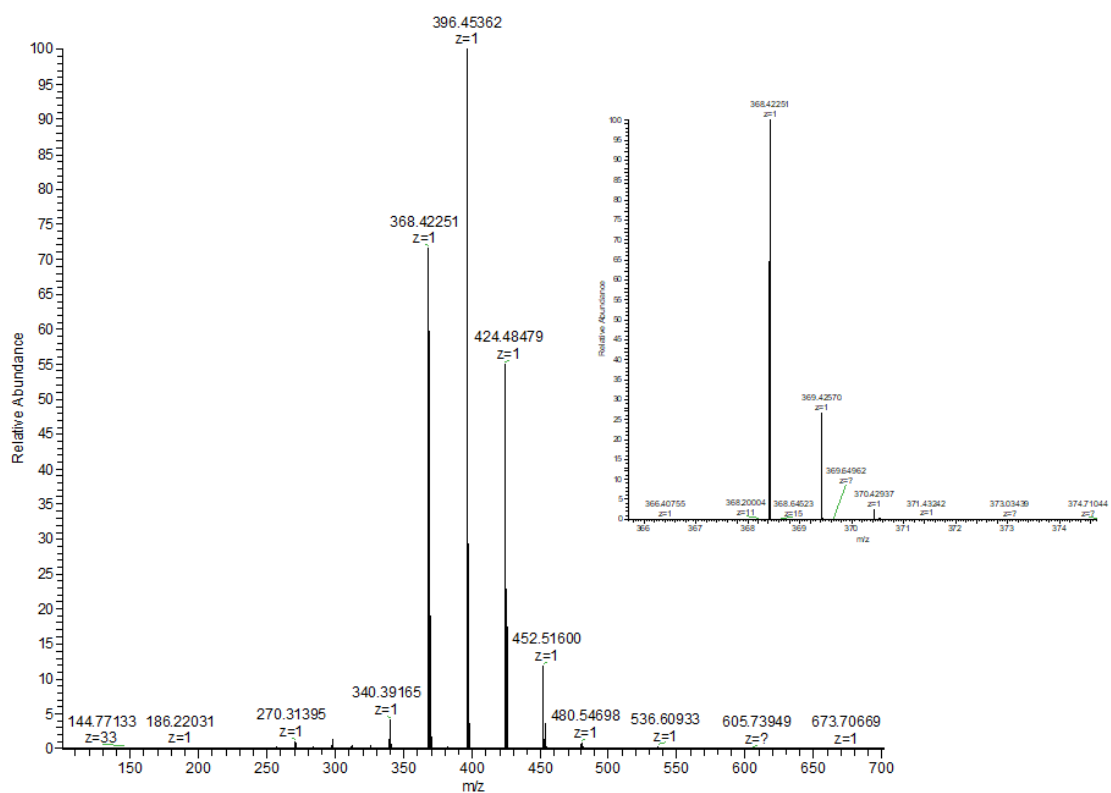
Figure A5. ESI-MS spectra for [A336][DHDGA] (100-700 m/z)
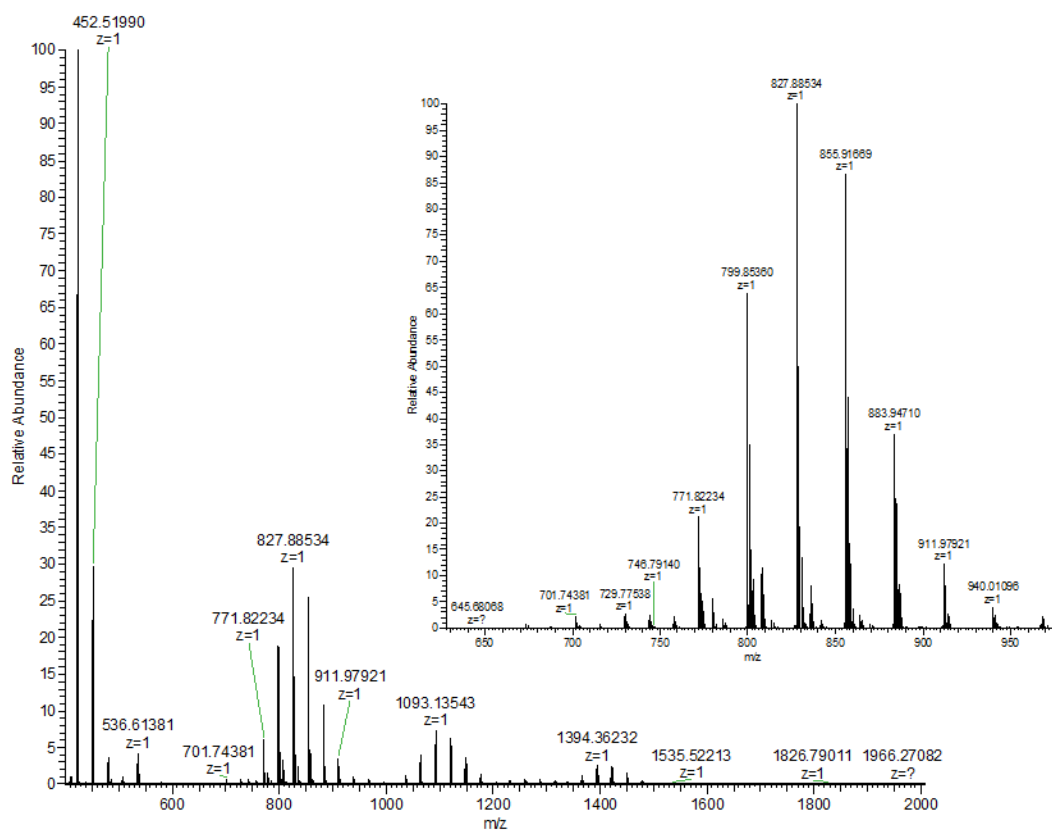
Figure A6. ESI-MS spectra for [A336][DHDGA] (400-2000 m/z)
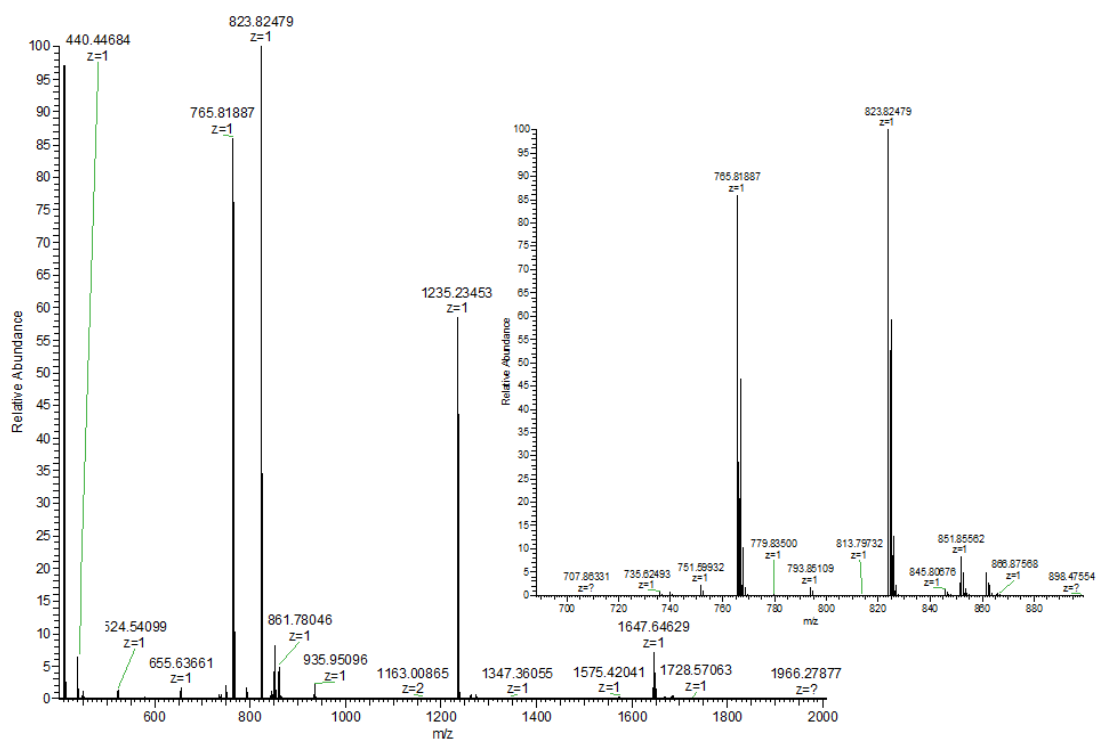
Figure A7. ESI-MS spectra for [OcGBOEt][DHDGA] (400-2000 m/z)
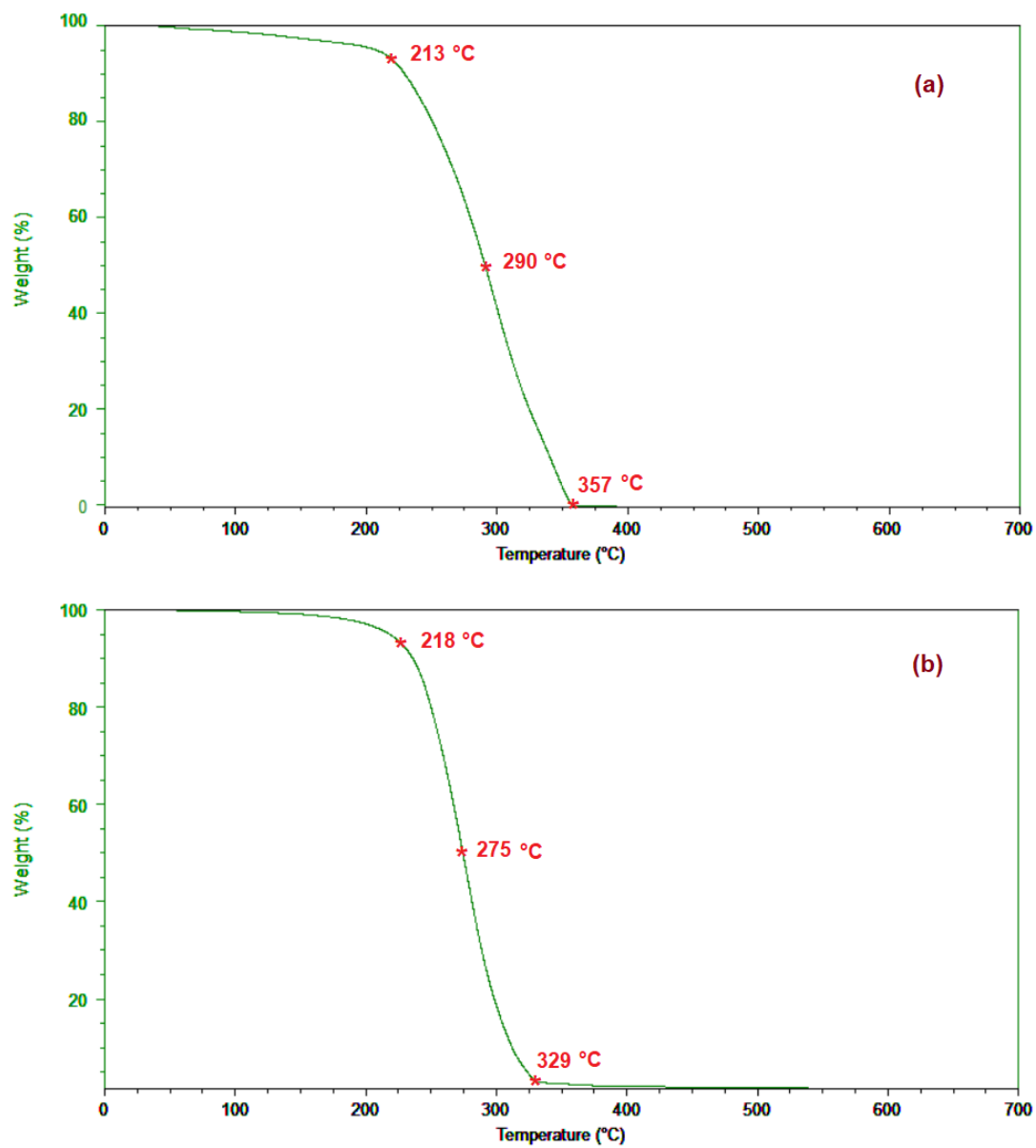
Figure A8. TGA graph for (a) [A336][DHDGA] and (b) [OcGBOEt][DHDGA]
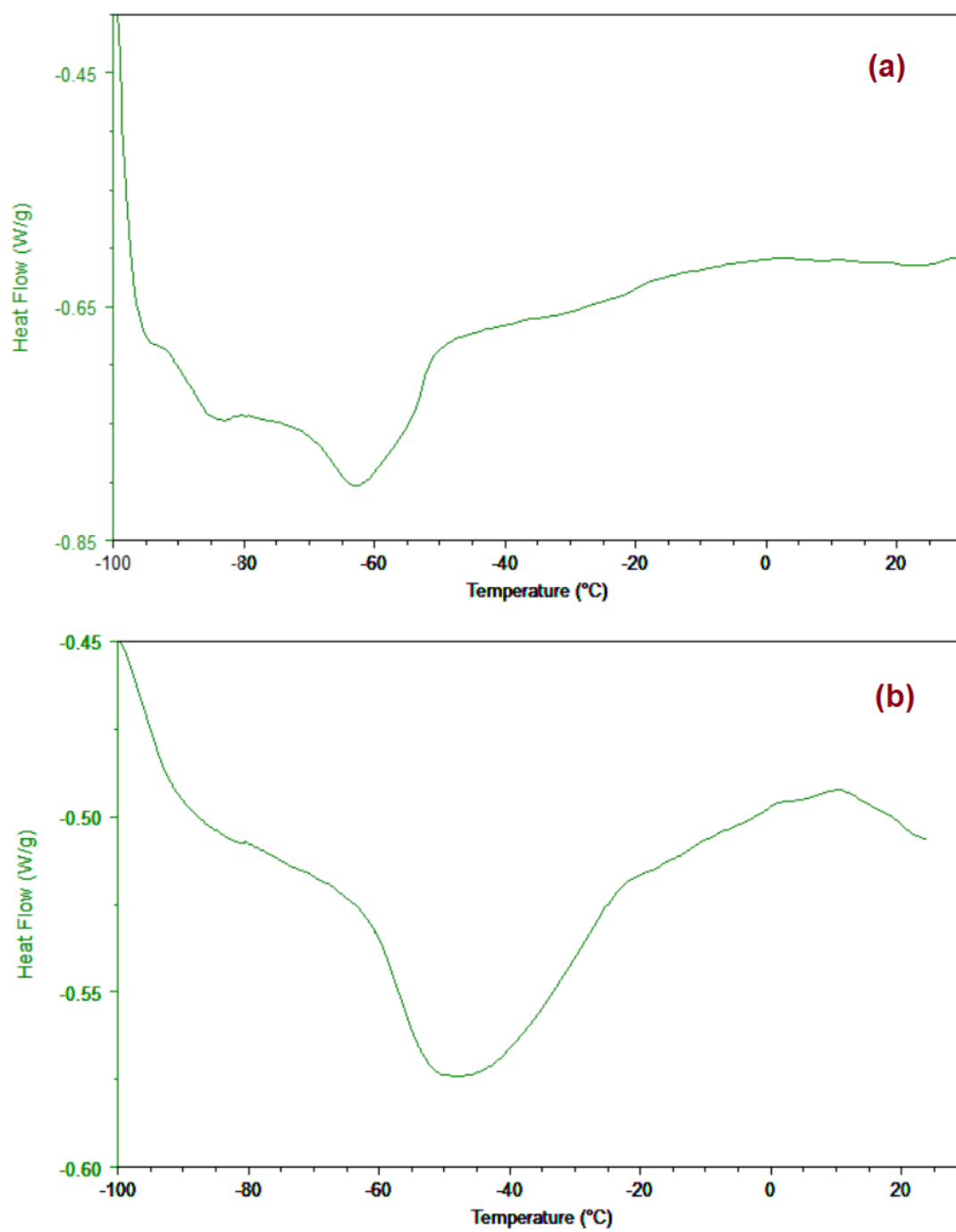
Figure A9. ADSC curve for (a) [A336][DHDGA] and (b) [OcGBOEt][DHDGA]
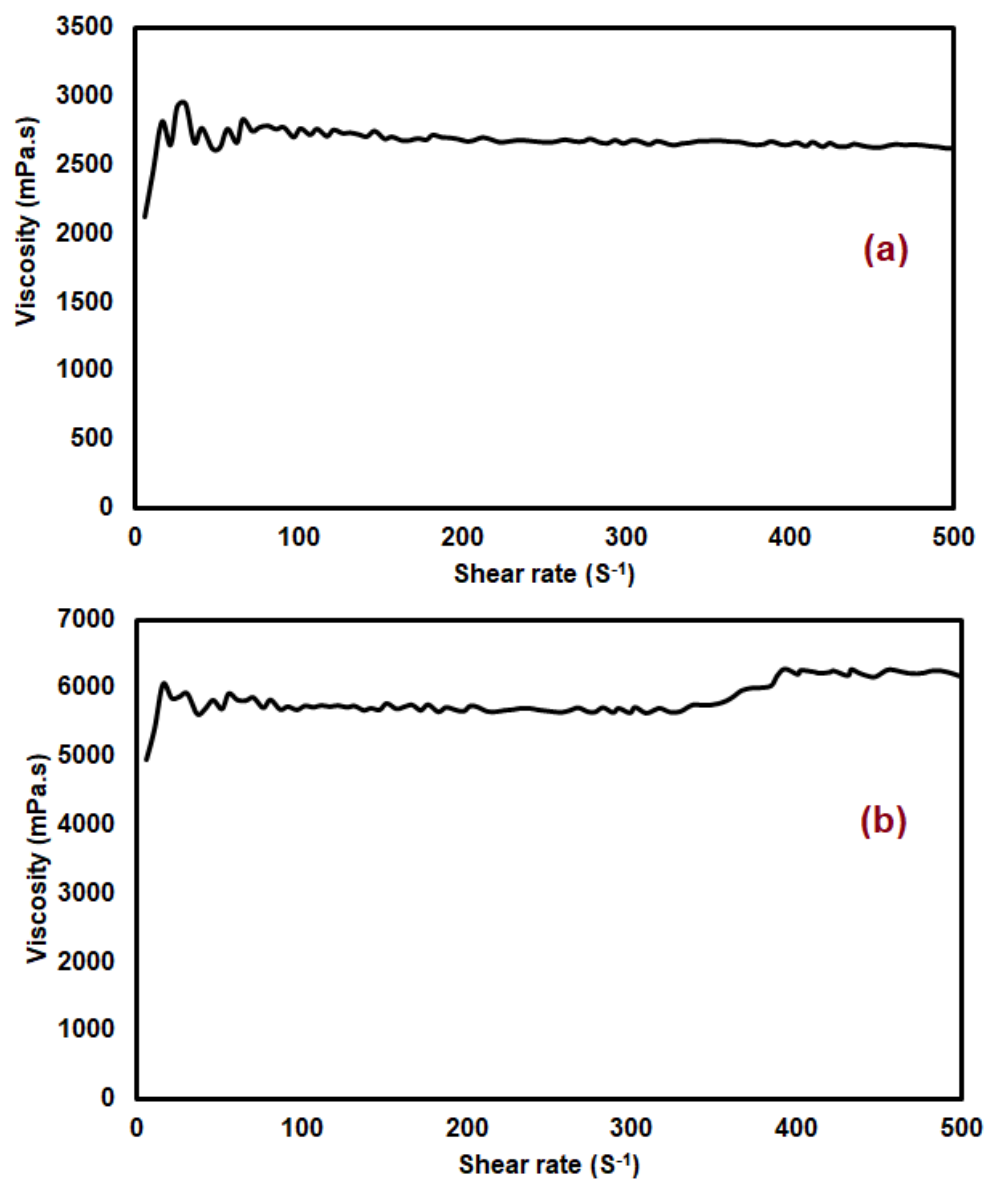
Figure A10. Viscosity curve for (a) [A336][DHDGA] and (b) [OcGBOEt][DHDGA]

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