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Extraction of Some Heavy Metals Using Ionic Liquid Systems

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Declaration

I hereby certify that this Thesis is the result of my own investigation otherwise stated.

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Abstract

Since the rise of industrialization, discharging of industrial wastewater containing heavy metals, such as from mining, agricultural plants, electronic waste, and pharmaceutical industries, has raised serious concerns due to their high toxicities to environment and the human body. Further, metal-containing wastewater treatments are generally complicated, costly, and energy intensive. To combat such issues, ionic liquids have been investigated to simplify the wastewater treatment processes. The previous studies have shown potential uses of ionic liquids in separation of metal ions from aqueous solutions by means of a biphasic system.

In this project, ionic liquids with quaternary triethylammonium cation and bis(trifluoromethylsulfonyl)amide anion were synthesized and compared to extract Co(II), Cu(II), Pb(II), and Hg(II) from aqueous phase. Two groups of ionic liquids containing alkane or ethylene glycol functional group were studied. To further enhance the extraction efficiency, 2-thenoyltrifluoroacetone was added to the ionic liquid systems. The outcome of the extractions and interaction of water, ionic liquids, and 2-thenoyltrifluoroacetone were analysed by ICP-OES, UV-vis spectroscopy, TGA analysis, and ATR-FTIR spectroscopy.

Abbreviations and Acronyms

A ⁻	Anion
atm	Atmospheres
ATR-FTIR	Attenuated Total Reflection-Fourier-Transform Infrared Spectroscopy
CHN	Carbon-Hydrogen-Nitrogen Micro Elemental Analysis
C _i	Initial Concentration of Metal
C _f	Final Concentration of Metal
CF ₃	Trifluoromethane Group
D	Distribution Constant
DSC	Differential Scanning Calorimetry
E	Extraction Efficiency
ESI-MS	Electrospray Ionization Mass Spectrometer
H ⁺	Proton
HSAB	Hard and Soft Acid and Base Theory
Htta	2-thenoyltrifluoroacetone
ICP-OES	Inductively Couple Plasma-Optical Emission Spectroscopy
IC	Ion Chromatography
IL	Ionic Liquid
λ	Wavelength
L	Ligand
M ⁺	Metal Ion
M-tta, M(tta)	Metal-2-thenoyltrifluoroacetone Complex
NMR	Nuclear Magnetic Resonance
[NTf ₂] ⁻	Bis(trifluoromethylsulfonyl)imide Anion
[N ₂₂₂ R] ⁺	Triethylammonium Cation
PEG	Polyethylene Glycol

[PF ₆] ⁻	Hexafluorophosphate Anion
ppm	Parts per million
S _N 2	Nucleophilic Substitution
TGA	Thermogravimetric Analysis
TSIL	Task Specific Ionic Liquid
UV-vis	Ultraviolet-visible
V _{aq}	Volume of Aqueous Phase
V _{IL}	Volume of Ionic Liquid Phase

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1. Introduction

1.1. Water Treatment

Contamination of water sources by anthropogenic activities is a serious concern as the level of contamination of water has raised due to the increase in industrialization, population growth, and urbanization.¹ The damages to environment and human bodies by contaminated water may result in serious health defects depending on the type and concentration of the pollutants, as well as the level of water quality regulation of the region.² Of numbers of pollutants, heavy metals are especially hazardous to environment because many heavy metals are highly toxic and can cause serious direct impact on environment and human as the heavy metals can be bioaccumulated in the ecosystem because they are not biodegradable.^{3, 4} The increase in the amount of electronic waste in the recent decades is also gaining larger concerns due to the presence of hazardous chemicals and precious metals present in the waste.⁵

1.1.1. Heavy Metals

In this study, four heavy metals, copper, cobalt, lead and mercury, were subjected to be treated because of their toxicity and abundancy in industry. The characteristics and toxicity of the metals are described.

Copper

Copper is widely used in copper wire, electroplating, coins, plumbing pipes, and metal alloys due to its high thermal and electrical conductivity, ability to alloy with other metals, and high tolerance to corrosion.⁶ It is the second highest in the amount present in the e-waste water after iron and steel.⁵ Despite the popular use of copper, discharge of copper is an environmental

concern, especially when it is exposed to the environment in a high dosage, as a high dosage of copper ions can interfere with biological system.⁷ The excess intake of exposure to copper can also disturb plant growth even though copper is an essential element to many living organisms.⁸

Cobalt

Cobalt is one of the essential elements for human body as it is part of vitamin B₁₂, however, high concentration of cobalt may cause paralysis, diarrhoea, low blood pressure, lung irritation, and bone defects.⁹ In the metal industry, cobalt is used to form metal alloy, especially with nickel and iron that produce strong magnetic property.¹⁰ Cobalt is also used as a catalyst in chemical synthesis. Specifically, cobalt plays an important role in catalytic reactions such as syngas conversion,¹¹ generation of radical species¹², and petroleum refining process.¹³ Such chemical syntheses may also contribute to discharge of cobalt to the environment as a form of catalyst waste.

Lead

Like many other metals, lead can be exposed to humans and environment via industrial activities such as electro-plating, mining, lead smelting and metal finishing processes.¹⁴ A long exposure to lead can decrease muscle thickness and damage optical nerve and organs.^{15, 16} Intake of lead by ingestion through crops near electronic waste site has shown to induce cancer, especially in children.¹⁷ Additionally, excessive intake of Pb(II) may result in serious damages to the central nervous system and disturb the physical and mental development.¹⁸ In the North American countries, contamination by lead is a large concern because lead-containing water pipelines were installed in households until 1986 in the United States, of which some parts of the lead

containing pipelines were corroded and contaminated water were exposed to the community without further treatment.¹⁹

Mercury

Mercury is the only metal that is liquid in ambient room temperature and its property consists of high density, low viscosity, and good electrical conductance.²⁰ Because of its unique property, metallic mercury is widely used in thermometer, barometer, and even as the dental amalgam in many countries to this day.²¹ Mercury can be exposed to the environment via coal combustion and recycling of mercury-containing products such as fluoresce lamps.²²⁻²⁴ In the organic form, mercury can be ingested by humans and animals as methylmercury by bioaccumulation in aquatic organisms.²⁵ The accumulation of mercury in the atmosphere has been a concern for the environmental and human health due to its high toxicity and wide range of exposure.²⁶ Mercury poisoning causes severe irreversible neurotoxicity as seen in methyl mercury poisoning in Japan in the 1960's, as well as in Iraq in the 1970's.²⁷

1.2. Heavy Metal Treatment

As described, although some heavy metals are essential for living organisms, some possess a very high toxicity to many organisms and environment, and even the essential heavy metals can be toxic upon a high exposure or ingestion. Heavy metals can directly affect the living organisms via water, air, and soil contamination from anthropogenic activities and the effects of the heavy metals to the bodies and environment have been deeply concerned.²⁸

To minimize the discharge of these toxic heavy metals from the industrial and laboratorial wastes, numbers of wastewater treatment processes

have been developed. The three major treatment methods are physical, chemical, and biological methods. Each major method consists of specific processes for different treatment parameters as listed (**Table 1.1**). Of the three water treatment operations, chemical operations can target specific contaminants by using suited chemicals and appropriate processes.

Table 1.1: *The list of wastewater treatment processes are categorized into physical, chemical, and biological methods.*

Physical unit operations	Chemical unit operations	Biological unit operations
Screening	Chemical precipitation	Activated sludge process
Comminution	Adsorption	Aerated lagoon
Slow equalization	Disinfection	Trickling filters
Sedimentation	Dechlorination	Rotating biological contactors
Flotation	Other chemical applications	Pond stabilization
Granular-medium filtration		Anaerobic digestion
		Biological nutrient removal

For treatment of heavy metals, the purification processes include: chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, and electrochemical treatment.²⁹ Although these processes may efficiently separate contaminants from water, there are some drawbacks. Chemical precipitation, coagulation, and flocculation produces further byproduct wastes in the form of sludge or flocs, adsorption may result in low purification efficiency due to limited adsorbing surface area, and electrochemical treatments rely on electricity and type of cathodes and anodes, which may be costly.³⁰ Further, the treatment of heavy metals depends on the initial concentration of the metals in the wastewater, flexibility of the treatment, simplicity, reliability, and environmental impact of

the performance, as well as economics parameter such as capital investment, energy consumption, and maintenance cost.³¹ To improve the treatment processes, these drawbacks must be considered.

1.3. Ionic Liquids

1.3.1. Definition

Ionic liquids (ILs) have been studied widely in industrial applications, including separation chemistry. ILs possess unique properties such as negligible vapour pressure, low flammability, thermal stability, wide electrochemical window, low melting point, as well as tuneable characteristics such as polarity, hydrophobicity, density, and viscosity.³² ILs consist of organic and/or inorganic cationic and anionic component that make up an entirely ionic molecular interaction, whose properties can be modified for specific tasks.³³ Some of the well-known cations include imidazolium, pyrrolidinium, sulfonium, ammonium, and phosphonium, and anions include halides, nitrate, acetate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide (**Figure 1.1**).³⁴

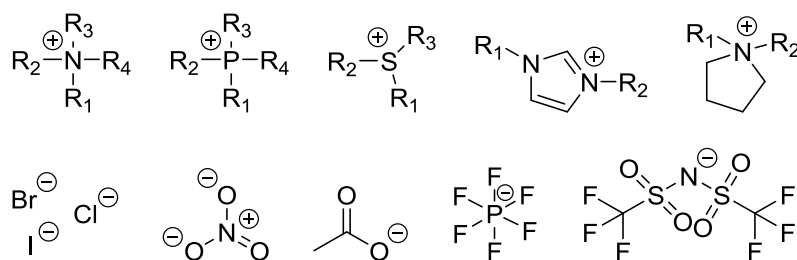


Figure 1.1: Examples of cations and anions of ILs. From left to right: top row: ammonium, phosphonium, sulfonium, imidazolium, and pyrrolidinium cations; bottom row: halide, nitrate, acetate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide.

1.3.2. Properties

The properties of ILs depend on the molecular structure of anion and cation. The viscosity of ILs can be increased by increasing the length of non-polar alkyl chain of the cation, which enhances van der Waals' force within the ionic system.³⁵ Similarly, the density, polarity and hydrophobicity can be tuned by the length and bulkiness of the IL components.

Low melting point can be achieved by depression of lattice energy governed by Born-Landé equation whereby the lattice energy depends on geometry, size of the charge, and spacing of ions. For example, a hydrophobic anion bis(trifluoromethylsulfonyl)imide ($[\text{NTf}_2]^-$) consists of bulky structure caused by partial delocalization of negatively charged central nitrogen atom, as well as shielding effect by the oxygen atoms and terminal CF_3 group.³⁶ Such a structure reduces the overall lattice energy of the system, and due to the reduction of negative charge, the increased hydrophobicity is achieved.

Also, because ILs are composed entirely by ionic interaction, their vapour pressure is almost negligible. This property is especially advantageous in the practical and industrial applications because release of solvent into the atmosphere is a seriously concerning issue as some conventional solvents used in the industry can be dangerous to aqueous and atmospheric environment. Due to these properties, ILs are considered as “green” solvents for many applications such as catalytic reactions, electrochemistry, separation chemistry, metal-ligand chemistry and material chemistry.³⁷

1.4. Application of ILs in Wastewater Treatment

Because some ILs possess hydrophobic properties, they are one of the promising candidates of optimizing heavy metal treatment. To overcome the

challenges such as generation of byproduct waste, energy consumption, and complexity of water treatment, ILs have been studied for simple biphasic liquid-liquid separation. Some of the recent advances are elaborated.

1.4.1. Previous Studies

TSILs are especially advantageous in homogeneous biphasic extraction processes because they are tuneable and can target specific molecules to extract.^{38, 39} Studies have shown that many TSILs act as promising extractants for extracting both organic and inorganic compounds.⁴⁰ Of many possible combination of ILs, ammonium-based ionic liquids are more ideal for biphasic extraction due to their quaternary structure because the hydrophobicity and viscosity can be tuned by varying the maximum of four functional groups than can be attached to the core nitrogen atom.³⁶ Some examples of ammonium-based TSIL used for liquid-liquid extraction includes A336, TOMAS, CTMA, TMA, and [Hbet][Tf₂N].

TOMAS is extensively studied to extract cadmium, mercury other heavy metal complexes from aqueous solutions with high extraction efficiencies. Fischer *et. al.* used four A336-based ILs with varying anion and effectively extracted Ag, Hg, Pt, and Ni metal(iod)s.³⁹ Kogelnig *et. al.* also synthesized A336-based ILs through “deprotonation-metathesis” methods with the use of Brønsted acid to compare the extraction efficiency of Cd. The study showed that tricaprylmethylammonium thiosalicylate, [A336][TS] was the best extractant with the extraction efficiency above 99%.⁴¹ In a study of TOMAS by Egorov *et. al.*, an IL synthesized from A336, was used test extractability of Fe³⁺, Cu²⁺, Ni²⁺, and Mn²⁺ and concluded that thiocyanate component of the IL, whose stability constant directly corresponds to the extraction efficiency, is

responsible for extractability.⁴² This study showed that the extraction efficiency depends on the stability of the system of the ionic liquids and the metal ions. Vergara *et. al* investigated the extraction efficiency of Cd^{2+} , Cu^{2+} , and Pb^{2+} by CTMA and TMA, as well as recycling of ILs by conventional solvents. They achieved 76-81% extraction efficiency and recyclability up to 5 times without decreasing the extraction efficiency.⁴³

In contrast to ILs whose hydrophobicity is achieved by the long-chain cations, Hbet-based ILs contains short cation chains with hydrophobic anion such as $[\text{NTf}_2]^-$. Hoogerstraete *et. al.* used $[\text{Hbet}][\text{Tf}_2\text{N}]$ to extract lanthanides by achieving a homogenous system by heating the IL and aqueous phase above the IL's upper critical solution temperature and re-establishing a biphasic system by cooling it down. With this system, as well as use of an extractant, zwitterionic betaine, which forms metal complex with lanthanides, they have effectively extracted Sc^{3+} , Ga^{3+} , and In^{3+} , as well as Cu^{2+} .³⁸ The study showed a potential application of ammonium ionic liquids with $[\text{Tf}_2\text{N}]^-$ anion.

Further, Lu *et. al.* used $[\text{NTf}_2]$ -based imidazolium ionic liquids with a ligand prepared from 1,3-diethylimidazolium acetate, 1,3-diethylimidazole-2-thioneto ($\text{C}_2\text{C}_2\text{ImT}$), to extract $\text{Hg}(\text{II})$ and concluded that when the anion is hydrophobic, the extractability depends on the hydrophilicity of the cation and the hydrophobicity of the complex of $\text{Hg}(\text{II})$, ($\text{C}_2\text{C}_2\text{ImT}$), and $[\text{NTf}_2]^-$, as the cation leaves to the aqueous phase and the complex remains in the IL phase.⁴⁴ Another candidate of hydrophobic anion is hexafluorophosphate ($[\text{PF}_6]^-$). However, $[\text{PF}_6]^-$ is less stable than $[\text{NTf}_2]^-$ as $[\text{PF}_6]^-$ is more easily degraded and less hydrophobic because PF_6^- lacks the bulkiness of $[\text{NTf}_2]^-$.⁴⁵ Also use of

$[\text{PF}_6]^-$ is not an ideal anion because it generates HF upon contact with water by hydrolysis.⁴⁶

2. Theory and Experimental

2.1. Biphasic Extraction Theory

As partially described in Section 1.4.1., biphasic extraction requires two phases that are insoluble to one another. Traditionally, extraction of solutes in a biphasic system is done by using conventional solvents such as hexane and dichloromethane. Factors involved in biphasic separation of metals are described.

2.1.1. Hard and Soft Lewis Acids and Bases

A factor determining the metal-ligand complexation process is the hardness and softness of metal ions and ligands, which is explained by Lewis acid base concepts. Generally, soft base atoms are considered to be polarizable and hard atoms are nonpolarizable. These properties are due to the individual atom's internuclear distance and the absolute electronegativity. In order for two atoms to interact and form a stable metal-ligand complex, atoms must interact in a way such that the interaction of the molecules gives the maximum overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the two molecules. Because of these factors influencing the interaction of metal and ligand, the similar hardness/softness of electron donor and acceptor of metal ions and ligands are preferred to form a stable complex.^{47, 48} In a treatment of aqueous solution with different metal ions present, softness and hardness of the different metals must be considered in order to optimize the separation the metals.

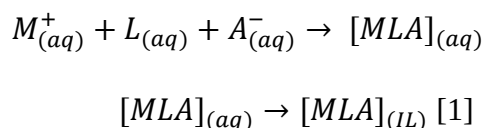
2.1.2. Extraction Mechanism

In order to improve the efficiency and selectivity of extraction by IL, the coordination chemistry of the ionic liquids, metals, and ligand must be

understood. The mechanism of metal extraction with ILs is complicated and differs with the types of ILs, ligands, and metals in the system. The three of the most studied metal extraction mechanisms using ILs are 1) neutral extraction, 2) the ion exchange extraction, 3) neutral coextraction.⁴⁹

The Neutral Extraction Mechanism

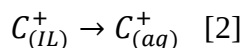
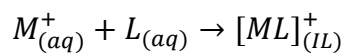
In neutral extraction system, neutral coordination complex forms with metal, ligand, and an ion in the aqueous phase, which partition into the IL phase as the complex forms:



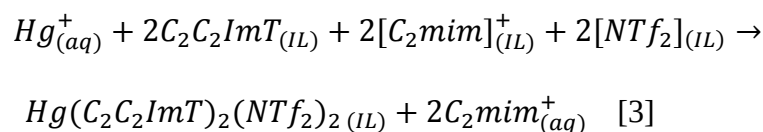
Where M^{+} is a metal ion, L is a ligand, and A^{-} is an anion in the system.⁵⁰ The rate of partition is depended on the solvation factors of the complex including hydrophobicity of the anion.⁵¹ For example, if the cationic component of IL is weakly hydrophobic, some portion of metal-ligand-anion complex will stay in the aqueous phase, rather than going into the IL phase.⁵² However, the neutral extraction mechanism is difficult to be the sole extraction mechanism due to the cationic ion exchange that may occur while neutral extraction takes a place. In order for neutral extraction to be the only extraction mechanism the ion exchange mechanism must be fully suppressed, such as in a case of using strongly hydrophobic cation.⁴⁹

The Ion Exchange Mechanism

Ion exchange mechanism is the most studied metal extraction mechanism of the three. Generally, ion exchange involving IL is as follows:⁴⁹



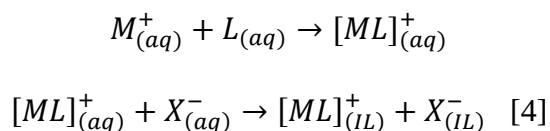
Where C^+ is the cationic component of IL as A^- indicates the anionic component. The first step of Equation 2 may be energetically less unfavourable because some metal cation and ligand are hydrophilic, thus it is difficult for the complex to partition into the IL phase. Consequently, the next step is energetically favourable if the cation of IL is relatively more hydrophilic.⁵³ An example of such a mechanism is illustrated by a study of mercury extraction using 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulphonamide ($[C_2mim][NTf_2]$) and an thione extractant, 1,3-diethylimidazole-2-thione (C_2C_2ImT):⁴⁴



In this example, as the complex of $[MLA]$ forms, the cationic component of IL escapes into the aqueous phase, which leads to a contamination of water by IL. This problem can be prevented by the use of “sacrificial ion” that is hydrophilic and environmentally benign, which allows the more toxic ion to remain in the IL phase and nontoxic ion in the aqueous phase.⁴⁹ Also, as seen in the Equation 3, as the concentration of the partitioned IL component in the aqueous phase increases, which is depended on the solvation ability of the IL, the reaction proceeds backwards. This results in inhibition of metal extraction from the aqueous phase.

The Neutral Coextraction Mechanism

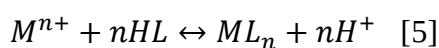
In contrast to neutral extraction, neutral coextraction involves a formation of positively charged metal-ligand complex, which then partitions into the IL phase with a presence of an anion.⁴⁹



This process is largely depended on the ligation properties of the metal and ligand, and the anion is preferably hydrophobic for the complex to form a heterogeneous ionic system with the available anion from the aqueous phase. The excess of anions added to the aqueous phase also prevents the ILs to partition into the aqueous phase. This is an advantage over neutral extraction and ion exchange because it prevents the contamination of water by IL. However, the if anion is added with a presence of its counter-cation such as use of Li[NTf₂] in an application of [NTf₂]-based ILs, the cationic component - lithium in this case - will remain in the aqueous phase or form another ionic system, which ultimately leads to contamination of the IL phase.⁵⁴

Dependence of pH

Because ligands and metals behave differently in varying pH levels, known as amphoteric properties of metals, the role of pH must be considered in aqueous metal treatment. Similarly, investigating the pH-depended chelate complexation---effect of pH in aqueous solution on metal extraction efficiency---allows determining the extraction mechanism. First, the general chemical equation of ligation is presented as:



Where M is the metal ion in the aqueous phase and L is the ligand. From this equation, the extraction constant (K_{ex}) can be expressed as:

$$K_{ex} = \frac{[ML_n][H^+]^n}{[M^{n+}][HL]^n} \quad [6]$$

By neglecting the generation of side products and presence of the competing reagent in the aqueous phase, Equation [6] can be simplified to:

$$K_{ex} = D \frac{[H^+]^n}{[HL]^n} \quad [7]$$

And

$$\log(D) = \log(K_{ex}) + npH + n\log[HL]^n \quad [8]$$

Where D is the distribution coefficient,⁵⁵ which can be determined by

$$D = \frac{C_i - C_f}{C_i} \times \frac{V_{aq}}{V_{IL}} \quad [9]$$

Where C_i and C_f are the initial and final concentration of metal in the aqueous phase before and after the extraction treatment, respectively, and V_{aq} and V_{IL} are the volumes of aqueous phase and IL phase, respectively.⁵⁶ The volume ratio of aqueous phase and IL phase are incorporated to account for the difference in the volume of the two phases. Furthermore, by keeping the molar concentration and determining the distribution experimentally, a curve of distribution coefficient vs pH can be determined, whose linear slope is the value of n.⁵⁷ By knowing the value of n, extraction mechanism using ILs may be explained.

2.2. Metal Extraction Procedure

The metal extraction procedure was adapted and modified from the literature.³⁹ In a 20 mL test tube (Carousel 12 Plus Reaction Station™, Radleys), magnetic stirrer was placed and 0.75 mL of ILs was injected using 1 mL plastic syringe (Injekt®, BRAUN) and needle. To the system, 15 mL of

prepared metal salt aqueous solution (50 mg/L) was poured by using 15 mL plastic syringe and needle. After all systems were prepared, the mixture of IL and aqueous metal salt solution was stirred at 115 rpm at room temperature (23 to 24 °C) for two hours. After the treatment, the stirring was stopped and the mixture was settled for 15 minutes to let the two layers to separate. The aqueous layer was carefully extracted by using glass pipette and transferred to 10 mL volumetric flask (TC 20 °C borosilicate glass) containing 200 µL of nitric acid (Assay 68.5-69.5%, ARISTAR) in order to prepare a solution containing 2% nitric acid solution for ICP-OES analysis. The aqueous solution was shaken well and transferred into a 15 mL plastic test tube (Sarstedt Tube Conical Base 120mm x 17mm). The experiment was repeated three times for each IL-metal combination. The extraction efficiencies (E) of ILs were calculated:

$$E = \frac{C_i - C_f}{C_i} \times 100 \quad [10]$$

Where C_i and C_f are the concentration of metal in aqueous phase before and after the extraction process, respectively.

2.2.1. Analytical Instrumentation

2.2.1.1. ICP-OES

Inductively coupled plasma – optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 2000) was used for determination of metal chloride solution after the treatment. The calibration curve was obtained by preparing a standard solution of 5, 10, 20, 30, 40, and 50 ppm of metal salt containing 2% by volume nitric acid. Two recommended wavelengths (λ) were selected in order to monitor the consistency of the analysis: 228.616 and 238.892 nm for

cobalt, 327.393 and 324.752 nm for copper, 220.353 nm and 217.000 nm for lead, and 194.168 and 253.652 nm for mercury analysis. All measurements were repeated three times and done by axial detection mode. The washing time between each measurement was 30 seconds for CuCl_2 and CoCl_2 and 60 seconds for PbCl_2 and HgCl_2 . The results were reported in the unit of mg/L. The standard deviation and mean value of the repeated measurement of a sample is calculated by the program. The standard deviation, mean value, and standard error of the samples of the IL-metal combinations were calculated manually.

2.2.1.2. UV-vis Spectroscopy

UV-vis-NIR spectrophotometer (Cary WinUV) was used for UV-vis spectroscopic measurements. The single-front measurement from 800 nm to 200 nm was applied and the lamp switches occurred at 350 nm. The scan rate was set to be 600 nm/min with the data interval of 1 nm. Prior to the measurement, dark background and baseline with acetonitrile in 5 mm quartz cuvette were taken. The samples were prepared by dissolving approximately 100 mg of IL phase in acetonitrile in 10 mL volumetric flask. The spectra were normalized to 1 mg of the sample because the density and the weight of IL phase changed after saturated by water and metal salts, and a precise molar concentration was difficult to determine. The results were reported as arbitrary absorbance value and wavelength in nm.

2.2.1.3. Ion Chromatography

Ion chromatography was recorded by DIONEX ICS-5000 (Thermo SCIENTIFIC) fitted with DIONEX AS-AP and DIONEX ICS-5000⁺ DP. The eluent consisting of water (60%), acetonitrile (25%) and an aqueous 100 mM

NaOH solution (15%) was used. The column was kept at 35 °C during analysis. The flow rate was 0.25 mL/min and the duration was 35 minutes. The aqueous samples from the extraction treatment were used without any further dilution.

2.3. Synthesis of ILs

2.3.1. Design of ILs

In this study, ammonium-[NTf₂]⁻ based ILs were chosen because many literatures used imidazolium as cation and [NTf₂]⁻ as anion, or hydrophobic alkylammonium cation and halide anion. To investigate hydrophilic, short-chain ammonium cation, widely studied [NTf₂]⁻ anion were chosen. Alkyl or ethylene glycol functional chains were added to the cationic component to study the difference in extraction efficiency in the varying functional groups.

2.3.2. Material

ILs synthesized for this project were prepared by modifying literature procedures. The chemical precursors were obtained from commercial suppliers without further purification unless stated otherwise. Water used in this project was Millipore Milli-Q 18 MΩ ultrapure and deionized. All solvents were analytical reagent grade.

2.3.3. Instrumentation

2.3.3.1. NMR Analysis

All ILs were dried in vacuum prior to NMR analysis. All NMR experiments were recorded by Bruker DPX-300 spectrometer. The frequencies of measurements were 400 MHz for ¹H, 101 MHz for ¹³C, and 377 MHz for ¹⁹F. The chemical shifts (δ) are reported in parts per million (ppm).

Commercial deuterated solvents, DMSO- d_6 (δ_H 2.50 and δ_C 39.51 ppm), and $CDCl_3$ (δ_H 7.27 and δ_C 77.0 ppm), were used as reference. Coupling constants (J) are reported in Hz whose multiplicities were labelled as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), triple triplet (tt), double quartet (dq), and multiplet (m). The chemical shifts are assigned to the structure. ^1H -NMR and ^{19}F -NMR chemical shifts are presented together in the same IL compound structure. ^{13}C -NMR chemical shifts are presented separately.

2.3.3.2. Mass Spectrometry

Electrospray ionization mass spectrometer (ESI-MS) was recorded on Bruker micrOTOF II. Both the molecular mass of anion and cation were obtained. All samples were prepared by diluting the sample in analytical reagent grade methanol, following the procedure provided by the University of Nottingham, School of Chemistry.

2.3.3.3. CHN Elemental Analysis

CHN elemental analysis was done by the University of Nottingham, School of Chemistry Analytical Service. Each analysis was done at least twice and the result closest to the calculated values were reported.

2.3.3.4. Viscosity and Density Measurements

Prior to the density and viscosity measurements, IL were dried under vacuum at 60 °C overnight. The densities of ILs are measured by weighing out the mass of 1 mL IL using 1 mL syringe. The measurement was carried out four times and the average values are reported. The viscosities of ionic liquids were measured by automated microviscometer (AMVn, Anton Paar), using 4.0 mm diameter capillary and 3.0 mm steel ball. The measurements were taken at

20 °C and at the angle of 70°. Four measurements were taken per IL and standard deviation of the measurement was calculated by the instrument.

2.3.4. Synthetic Procedure

The general procedure of ILs are adapted and modified from literature.⁵⁸ A scheme of general synthesis of ILs is illustrated (**Figure 2.1**)

Synthesis of [N₂₂₂EG₃C₂][MeSO₃] and its precursor methane sulfonyl tri(ethylene)glycol ether were synthesized by following the literatures by Schrekker *et. al.* (**Figure 2.2**).⁵⁹

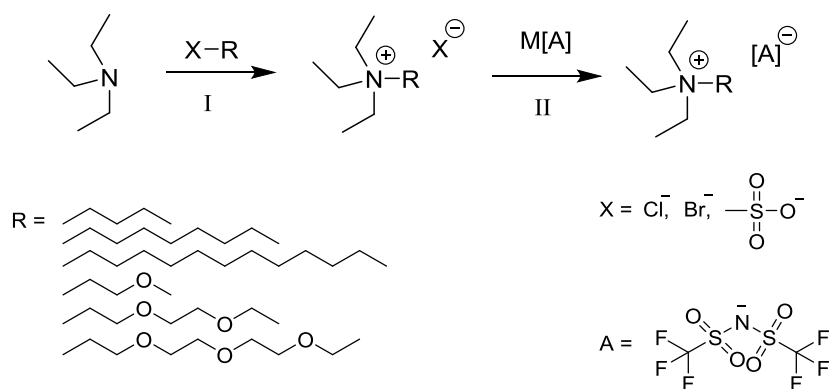


Figure 2.1: The synthetic methods of ammonium ILs where R is the functional group, X is a halide molecule, and A is anion. Reaction I is the alkylation step and reaction II is the metathesis step.

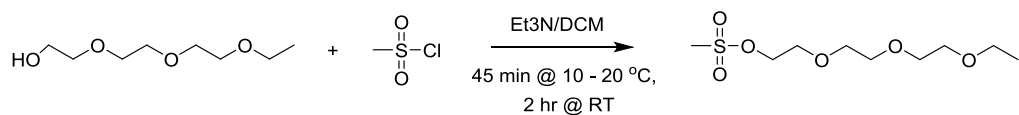
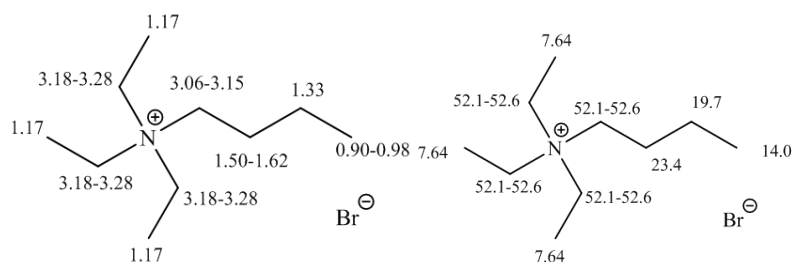


Figure 2.2: synthesis of methane sulfonyl tri(ethylene glycol) monoethyl ether from tri(ethylene glycol) monoethyl ether.

2.3.4.1. Triethylbutylammonium bromide, [N₂₂₂₄]Br

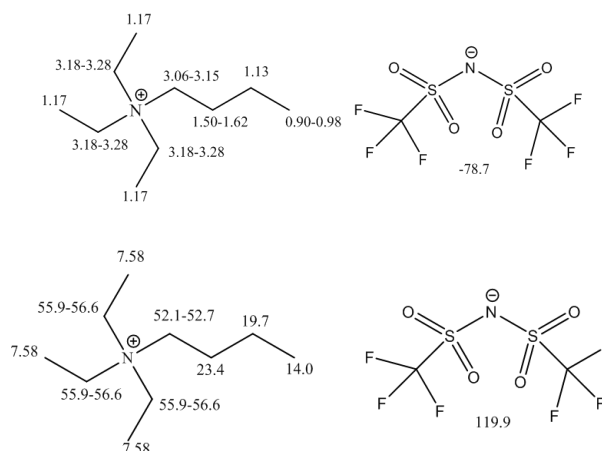


Bromobutane (24.2 g, 176 mmol, 1.20 eqv) was placed in a 250 ml double-neck round bottom flask equipped with a condenser and magnetic stirrer in the presence of acetonitrile (20.0 ml) under inert atmosphere by argon, enclosed by suba seal. A corresponding amount of triethylamine (14.9 g, 147 mmol, 1.00 eqv) was added dropwise at 60 °C while stirring. After 72 hours, yellow transparent mixture was obtained and cooled to room temperature. The solvent was evaporated and the product was re-dissolved in a minimum amount of acetonitrile. Diethyl ether was added until the formation of fine white solid was no longer observed. The solid was recrystallized from acetonitrile and diethyl ether one more time. White solids were vacuum dried at 70 °C overnight and collected (32.1g, 91.8%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 0.83 - 0.91 (m, 3 H) 1.16 (tt, *J*=7.28, 1.76 Hz, 9 H) 1.22 - 1.36 (m, 10 H) 1.51 - 1.63 (m, 2 H) 3.07 - 3.14 (m, 2 H) 3.23 (q, *J*=7.19 Hz, 6 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.66 (s, 3 C) 14.44 (s, 1 C) 21.41 (s, 1 C) 22.53 (s, 1 C) 26.29 (s, 1 C) 28.96 (d, *J*=2.93 Hz, 2 C) 31.64 (s, 1 C) 51.73 - 53.00 (m, 3 C) 55.84 - 57.01 (m, 1 C).

**2.3.4.2. Triethylbutylammonium bis(trifluoromethylsulfonyl)amide,
[N₂₂₂₄][NTf₂]**



[N₂₂₂₄]Br (13.6 g, 57.0 mmol, 1.00 eqv) was dissolved a minimum amount of ultrapure water in a 100 ml around bottom flask. A corresponding amount of Li[NTf₂] (19.6 g, 68.4 mmol, 1.20 eqv) was dissolved in a minimum amount of ultrapure water and was added to the aqueous solution of [N₂₂₂₄]Br dropwise while stirring by magnet stirrer at room temperature. After 17 hours, the lower organic layer was washed with ultrapure water 5 times and vacuum dried at 70 °C overnight. A yellow transparent oil was obtained (19.6 g, 78.5%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 0.90 - 0.98 (m, 3 H) 1.17 (tt, *J*=7.28, 1.88 Hz, 9 H) 1.33 (dq, *J*=14.71, 7.39 Hz, 2 H) 1.50 - 1.62 (m, 2 H) 3.06 - 3.15 (m, 2 H) 3.18 - 3.28 (m, 6 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.58 (s, 3 C) 13.96 (s, 1 C) 19.67 (s, 1 C) 23.38 (s, 1 C) 52.14 - 52.65 (m, 3 C) 55.90 - 56.62 (m, 1 C) 119.9 (q, *J*=321.8 Hz, 1 C)

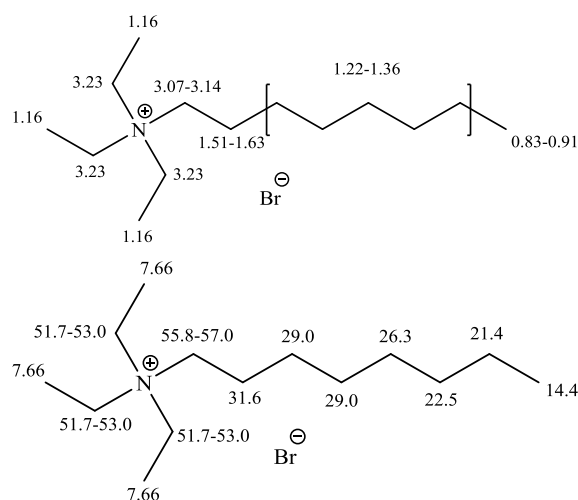
¹⁹F NMR (377 MHz, DMSO-*d*₆): δ ppm -80.92 - -76.47 (m, 6 F).

ESI-MS (+ve) [C₁₀H₂₄N₁]⁺: calculated 158.3085, found 158.1911.

ESI-MS (-ve) [C₂F₆N₁O₄S₂]⁻: calculated 279.9178, found 279.9181.

CHN Analysis: calculated C, 32.87; H, 5.52; N, 6.39, found C, 33.51; H, 4.96; N, 5.70.

2.3.4.3. Triethyloctylammonium bromide, [N₂₂₂₈]Br

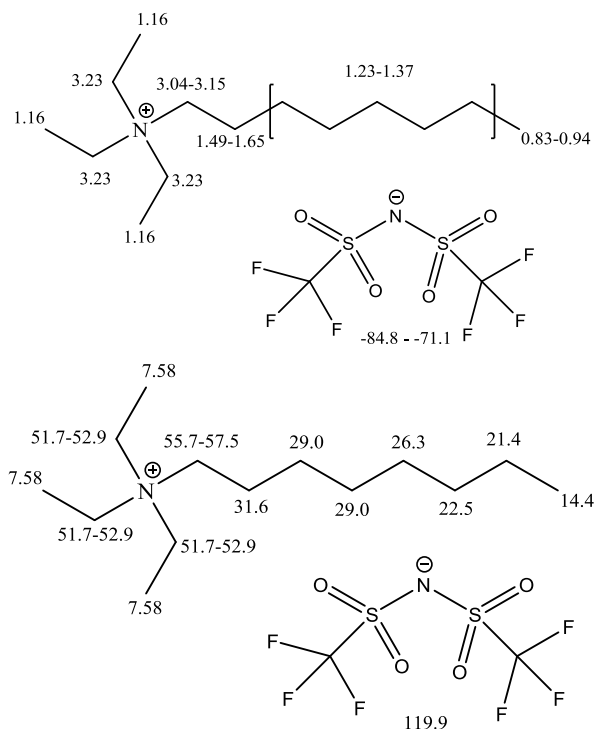


Bromooctane (31.5 g, 163 mmol, 1.20 eqv) was placed in a 250 ml double-neck round bottom flask equipped with a condenser and magnetic stirrer in the presence of acetonitrile (20.0 ml) under inert atmosphere by argon, enclosed by suba seal. A corresponding amount of triethylamine (13.8 g, 136 mmol, 1.00 eqv) was added dropwise at 65 °C while stirring. After 96 hours, an orange transparent mixture was obtained and cooled to room temperature. The solvent was evaporated and the product was re-dissolved in a minimum amount of acetonitrile and diethyl ether was added until the formation of fine white solid was no longer observed. The solid was recrystallized from acetonitrile and diethyl ether. The obtained white solid was vacuum dried at 70 °C overnight and collected (35.3 g, 88.2%).

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 0.83 - 0.91 (m, 3 H) 1.16 (tt, *J*=7.28, 1.76 Hz, 9 H) 1.22 - 1.36 (m, 10 H) 1.51 - 1.63 (m, 2 H) 3.07 - 3.14 (m, 2 H) 3.23 (q, *J*=7.19 Hz, 6 H).

^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 7.66 (s, 3 C) 14.44 (s, 1 C) 21.41 (s, 1 C) 22.53 (s, 1 C) 26.29 (s, 1 C) 28.96 (d, $J=2.93$ Hz, 2 C) 31.64 (s, 1 C) 51.73 - 53.00 (m, 3 C) 55.84 - 57.01 (m, 1 C).

2.3.4.4. Triethyloctylammonium bis(trifluoromethylsulfonyl)amide, [N₂₂₂₈][NTf₂]



[N₂₂₂₈]Br (30.0 g, 102 mmol, 1.00 eqv) was dissolved a minimum amount of ultrapure water in a 100 ml around bottom flask. A corresponding amount of Li[NTf₂] (32.2 g, 112 mmol, 1.10 eqv) was dissolved in a minimum amount of ultrapure water and added to the aqueous solution of [N₂₂₂₈]Br dropwise while stirring by magnet stirrer at room temperature. After 17 hours, the lower organic layer was washed with ultrapure water 5 times and vacuum dried at 70 °C overnight. An orange transparent oil was obtained (38.1 g, 75.7%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 0.83 - 0.94 (m, 3 H) 1.16 (m, *J*=7.28, 7.28, 1.76, 1.76 Hz, 9 H) 1.23 - 1.37 (m, 10 H) 1.49 - 1.65 (m, 2 H) 3.04 - 3.15 (m, 2 H) 3.23 (q, *J*=7.11 Hz, 6 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.58 (s, 3 C) 14.41 (s, 1 C) 21.38 (s, 1 C) 22.52 (s, 1 C) 26.28 (s, 1 C) 28.95 (d, *J*=2.93 Hz, 2 C) 31.64 (s, 1 C) 51.72 - 52.90 (m, 3 C) 55.72 - 57.51 (m, 1 C) 119.9 (d, *J*=321.31 Hz, 1 C).

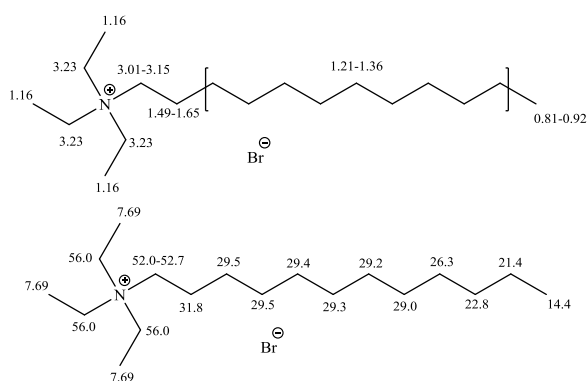
¹⁹F NMR (377 MHz, DMSO-*d*₆): δ ppm -84.78 - -71.06 (m, 6 F).

ESI-MS (+ve) [C₁₄H₃₂N₁]⁺: calculated 214.2529, found 214.2531.

ESI-MS (-ve) [C₂F₆N₁O₄S₂]⁻: calculated 279.9178, found 279.9187.

CHN Analysis: calculated C, 38.86; H, 6.51; N, 5.66; found C, 40.12; H, 7.01; N, 5.03

2.3.4.5. Triethyldodecylammonium bromide, [N₂₂₂₍₁₂₎]Br



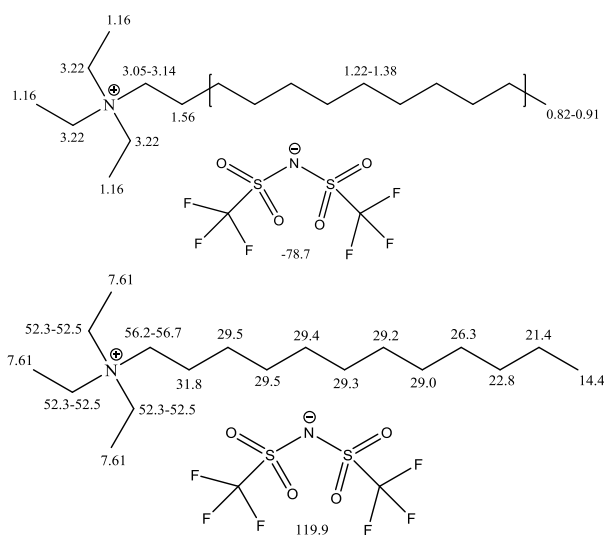
Bromododecane (25.6 g, 103 mmol, 1.20 eqv) was placed in a 250 ml double-neck round bottom flask equipped with a condenser and magnetic stirrer in the presence of acetonitrile (20.0 ml) under inert atmosphere by argon, enclosed by suba seal. A corresponding amount of triethylamine (8.60 g, 85.6 mmol, 1.00 eqv) was added dropwise at 65 °C while stirring. After 96 hours, a dark yellow transparent mixture was obtained and cooled to room

temperature. The solvent was evaporated and the product was re-dissolved in a minimal amount acetonitrile and recrystallized with diethyl ether once. The obtained white solids were filtered, vacuum dried at 70 °C overnight, and collected (23.23 g 77.4%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 0.81 - 0.92 (m, 3 H) 1.16 (tt, *J*=7.15, 1.63 Hz, 9 H) 1.21 - 1.36 (m, 18 H) 1.49 - 1.65 (m, 2 H) 3.01 - 3.15 (m, 2 H) 3.23 (q, *J*=7.28 Hz, 6 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.69 (s, 3 C) 14.44 (s, 1 C) 21.42 (s, 1 C) 22.57 (s, 1 C) 26.29 (s, 1 C) 29.01 (s, 1 C) 29.18 (s, 1 C) 29.33 (s, 1 C) 29.41 (s, 1 C) 29.49 (s, 2 C) 31.78 (s, 1 C) 52.03 - 52.72 (m, 3 C) 55.97 - 56.90 (m, 1 C).

2.3.4.6. Triethyldodecylammonium bis(trifluoromethylsulfonyl)amide, [N₂₂₂(12)][NTf₂]



[N₂₂₂(12)]Br (20.0 g, 350 mmol, 1.00 eqv) was dissolved a minimum amount of ultrapure water in a 100 ml around bottom flask. A corresponding amount of Li[NTf₂] (19.7 g, 287 mmol, 1.20 eqv) was dissolved in a minimum amount of ultrapure water and was added to the aqueous solution of

[N₂₂₂(12)]Br dropwise while stirring by magnet stirrer at room temperature.

After 17 hours, the lower organic layer was collected and washed with ultrapure water 5 times and vacuum dried at 70 °C overnight. A yellow transparent, viscous oil was collected (22.9 g, 72.8%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 0.82 - 0.91 (m, 3 H) 1.16 (tt, *J*=7.15, 1.76 Hz, 9 H) 1.22 - 1.38 (m, 18 H) 1.56 (d, *J*=7.03 Hz, 2 H) 3.05 - 3.14 (m, 2 H) 3.22 (q, *J*=7.11 Hz, 6 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.61 (s, 3 C) 14.44 (s, 1 C) 21.38 (s, 1 C) 22.57 (s, 1 C) 26.28 (s, 1 C) 28.99 (s, 1 C) 29.18 (s, 1 C) 29.31 (s, 1 C) 29.40 (s, 1 C) 29.49 (s, 2 C) 31.78 (s, 1 C) 52.32 - 52.48 (m, 3 C) 56.24 - 56.65 (m, 1 C) 119.95 (d, *J*=322.05 Hz, 1 C).

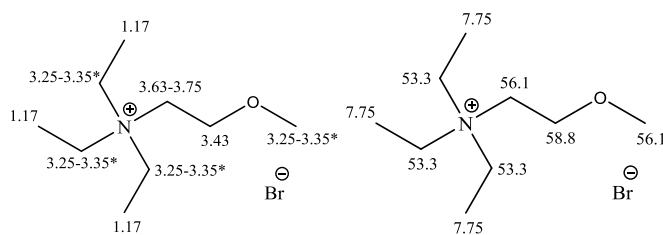
¹⁹F NMR (377 MHz, DMSO-*d*₆): δ ppm -78.71 (s, 6 F).

ESI-MS (+ve) [C₁₈H₄₀N₁]⁺: calculated 270.3189, found 270.3160.

ESI-MS (+ve) [C₂F₆N₁O₄S₂]⁻: calculated 279.9178, found 279.9186.

CHN Analysis: calculated C, 43.62; H, 7.32; N, 5.09, found C, 44.18; H, 7.30; N, 5.10.

2.3.4.7. 2-Ethoxymethyltriethylammonium bromide, [N₂₂₂EG₁C₁]Br



2-bromoethyl methyl ether (25.0 g, 180 mmol, 1.40 eqv) was placed in a 250 ml double-neck round bottom flask equipped with a condenser and magnetic stirrer in the presence of acetonitrile (20.0 ml) under inert atmosphere by argon, enclosed by suba seal. A corresponding amount of

triethylamine (13.0 g, 129 mmol, 1.00 eqv) was added dropwise at 50 °C while stirring. After 72 hours, a light-brown, transparent mixture was obtained and cooled to room temperature. The product was dissolved in a minimum amount of acetonitrile and diethyl ether was added until the formation of fine white solid was no longer observed. The solid was recrystallized from acetonitrile and diethyl ether two more times. White solids were vacuum dried at 70 °C overnight and collected (27.4 g, 88.9%).

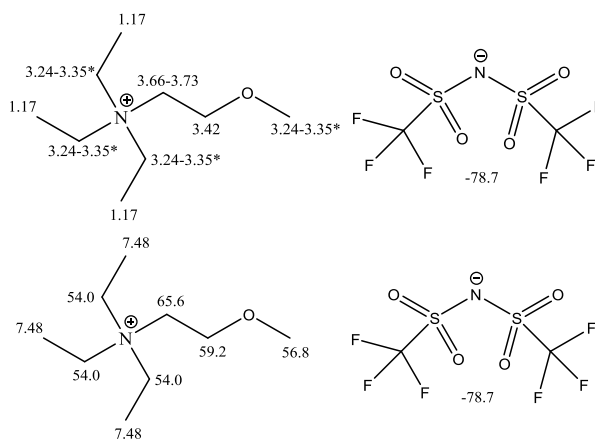
¹H NMR (400 MHz, DMSO-d₆): δ ppm 1.17 (t, J=7.22 Hz, 9 H) 3.25 - 3.35 (m, 10 H)* 3.43 (dd, J=5.58, 4.20 Hz, 2 H) 3.63 - 3.75 (m, 2 H).

¹³C NMR (101 MHz, DMSO-d₆): δ ppm 7.75 (s, 3 C) 53.28 (br s, 3 C) 56.09 (s, 1 C) 58.82 (s, 1 C) 65.51 (s, 1 C).

*Overlapping of signals observed with HDO (3.30 ppm).⁶⁰

2.3.4.8. 2-Ethoxymethyltriethylammonium

bis(trifluoromethylsulfonyl)amide, [N₂₂₂EG₁C₁][NTf₂]



[N₂₂₂EG₁C₁]⁺Br⁻ (9.8 g, 240 mmol, 1.00 eqv) was dissolved a minimum amount of ultrapure water in a 100 ml round bottom flask. A corresponding amount of Li[NTf₂] (14.1 g, 287 mmol, 1.20 eqv) was dissolved in a minimum amount of ultrapure water and was added to the aqueous solution of [N₂₂₂EG₁C₁]⁺Br⁻ dropwise while stirring by magnet stirrer at room temperature.

After 17 hours, the lower organic layer was dissolved in a minimum amount of dichloromethane and washed with ultrapure water 5 times and vacuum dried at 70 °C overnight. A light yellow transparent, viscous oil was collected (16.0 g, 88.7%).

¹H NMR (400 MHz, DMSO-d₆): δ ppm 1.17 (t, J=7.22 Hz, 9 H)* 3.24 - 3.35 (m, 9 H) 3.42 (dd, J=5.52, 4.14 Hz, 2 H) 3.66 - 3.73 (m, 2 H).

¹³C NMR (101 MHz, DMSO-d₆): δ ppm 7.68 (s, 3 C) 53.27 (br s, 3 C) 52.62 - 53.10 (m, 1 C) 55.52 - 56.73 (m, 1 C) 58.18 - 59.64 (m, 1 C) 64.72 - 66.42 (m, 1 C) 119.95 (q, J=321.56 Hz, 1 C).

¹⁹F NMR (377 MHz, DMSO-d₆): δ ppm -78.72 (s, 6 F).

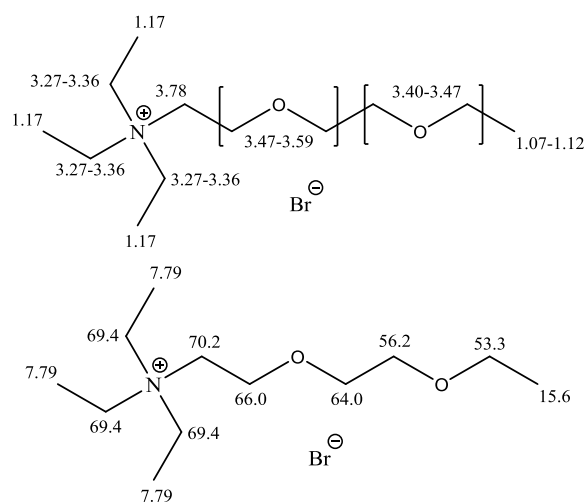
ESI-MS (+ve) [C₉H₂₂N₁O₁]⁺: calculated 160.1696, found 160.1702.

ESI-MS (-ve) [C₂F₆N₁O₄S₂]⁻: calculated 279.9175, found 279.9183.

CHN Analysis: calculated C, 29.99; H, 5.03; N, 6.36, found C, 31.06; H, 4.25; N, 5.96.

*Overlapping of signals observed with HDO (3.30 ppm).⁶⁰

2.3.4.9. 2-Ethoxyethoxyethyltriethylammonium bromide, [N₂₂₂EG₂C₂]Br



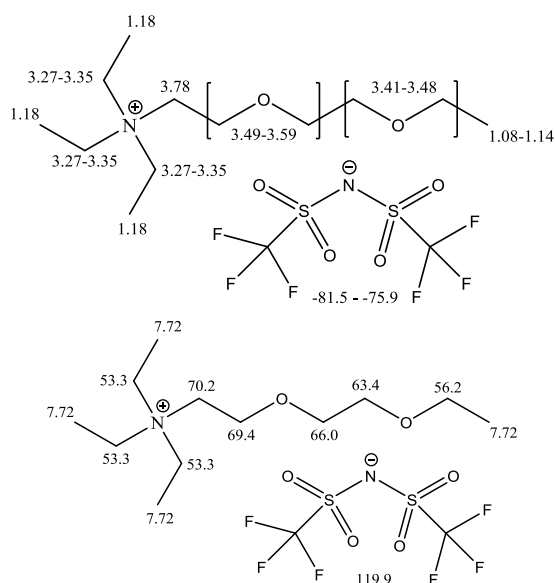
2-(2-ethoxyethoxy)ethyl bromide (31.7 g, 197 mmol, 1.20 eqv) was placed in a 250 ml double-neck round bottom flask equipped with a condenser

and magnetic stirrer in the presence of diethyl ether (20.0 ml) under inert atmosphere by argon, enclosed by suba seal. A corresponding amount of triethylamine (13.6 g, 101 mmol, 1.00 eqv) was added dropwise at 80 °C while stirring. After 72 hours, a light-brown transparent mixture was obtained and cooled to room temperature. The product was dissolved in a minimum amount of acetonitrile and diethyl ether was added until the formation of fine white solid was no longer observed. The solid was recrystallized from acetonitrile and diethyl ether twice. The obtained white solid was vacuum dried at 70 °C overnight and collected (18.7 g, 46.8%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 1.07 - 1.12 (m, 3 H) 1.17 (t, *J*=7.15 Hz, 9 H) 3.27 - 3.36 (m, 6 H) 3.40 - 3.47 (m, 4 H) 3.47 - 3.59 (m, 4 H) 3.78 (d, *J*=4.27 Hz, 2 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.79 (s, 3 C) 15.62 (s, 1 C) 53.28 (s, 3 C) 56.20 (s, 1 C) 63.97 (s, 1 C) 66.00 (s, 1 C) 69.40 (s, 1 C) 70.16 (s, 1 C).

**2.3.4.10. (2-(2-ethoxyethoxy)triethylethanammonium
bis(trifluoromethylsulfonyl)amide, [N₂₂₂EG₂C₂][NTf₂]**



[N₂₂₂EG₂C₂]Br (15.0 g, 298 mmol, 1.00 eqv) was dissolved a minimum amount of ultrapure water in a 100 ml round bottom flask. A corresponding amount of Li[NTf₂] (17.3 g, 287 mmol, 1.20 eqv) was dissolved in a minimum amount of ultrapure water and was added to the aqueous solution of [N₂₂₂EG₂C₂]Br dropwise while stirring by magnet stirrer at room temperature. After 17 hours, the lower organic layer was washed with ultrapure water 5 times and vacuum dried at 70 °C overnight. An orange transparent, oil was collected (16.7 g, 66.5%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 1.08 - 1.14 (m, 3 H) 1.18 (t, *J*=7.15 Hz, 9 H) 3.27 - 3.35 (m, 6 H) 3.41 - 3.48 (m, 4 H) 3.49 - 3.59 (m, 4 H) 3.78 (d, *J*=4.27 Hz, 2 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.72 (s, 3 C) 15.58 (s, 1 C) 53.25 (s, 3 C) 56.17 (s, 1 C) 63.96 (s, 1 C) 66.00 (s, 1 C) 69.38 (s, 1 C) 70.17 (s, 1 C) 119.87 (d, *J*=322.05 Hz, 1 C).

¹⁹F NMR (377 MHz, DMSO-*d*₆): δ ppm -81.50 - -75.89 (m, 6 F).

ESI-MS (+ve) [C₁₂H₂₈N₁O₂]⁺: calculated 218.2115, found 218.2116.

ESI-MS (-ve) [C₂F₆N₁O₄S₂]⁻: calculated 279.9178, found 279.9183.

CHN Analysis: calculated C, 33.36; H, 5.66; N, 5.62, found C, 34.30; H, 5.54; N, 4.78.

2.3.4.11. Methane sulfonyl tri(ethylene glycol) monoethyl ether

For synthesis of Methane sulfonyl tri(ethylene glycol) monoethyl ether, two different purification methods were used, following the same synthetic method.

Method #1

In a 500 mL triple-neck round bottom flask connected to a bleach system and condenser, tri(ethylene glycol) monoethyl ether (13.3 g, 74.4 mmol, 1.00 eqv), triethylamine (7.52 g, 74.4 mmol, 1.0 eqv) and 100 mL of dichloromethane were stirred with a magnetic stirring bar at 500 rpm under Ar atmosphere. The solution temperature was brought down to 0-10 °C by means of an external ice bath and methansulfonyl chloride (9.37 g, 81.4 mmol, 1.10 eqv) was slowly added dropwise with a syringe. The reaction temperature was maintained between 0 to 10 °C for 45 minutes, then brought up to room temperature for 2 hours. After reaction was complete, the mixture was washed with brine solution and the organic layer was collected and solvent was evaporated by rotating evaporator. The concentrated organic layer was partitioned with 40 mL of ultrapure water and 40 mL of hexane, and aqueous layer was collected. In the aqueous solution, 10.0 g of potassium chloride was added, dissolved, and the product was extracted with dichloromethane (3 × 30 mL). Solvent was evaporated with rotating evaporator and any remaining solid was vacuum filtered. A yellow, viscous oil was vacuum dried and collected (11.5 g, 60.3%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 1.10 (t, *J*=7.03 Hz, 3 H) 3.15 - 3.21 (m, 3 H) 3.39 - 3.46 (m, 2 H) 3.46 - 3.52 (m, 4 H) 3.52 - 3.59 (m, 4 H) 3.66 - 3.70 (m, 2 H) 4.29 - 4.33 (m, 2 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 15.58 (s, 1 C) 37.29 (s, 1 C) 66.01 (s, 1 C) 68.74 (s, 1 C) 69.67 (s, 1 C) 70.12 - 70.23 (m, 3 C) 70.24 - 70.36 (m, 1 C).

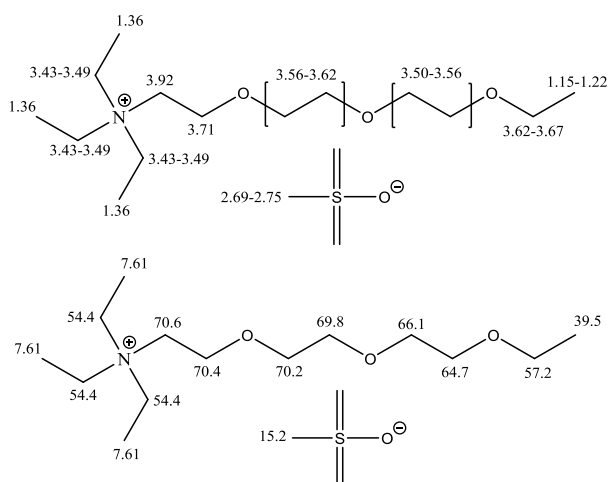
Method #2

The synthetic procedure follows the same as above. The amount and equivalence of the chemicals used in this method are as follows: tri(ethylene glycol) monoethyl ether (20.9 g, 117 mmol, 1.00 eqv), triethylamine (13.6 g, 135 mmol, 1.15 eqv), and methanesulfonyl chloride (14.1 g, 123 mmol, 1.05 eqv). After the reaction was complete, white solid in the mixture was vacuum filtered. To the collected yellow oil, 0.5 g of activated carbon was added to the mixture and mixed for 5 min at room temperature. Then activated carbon and remaining white solid was vacuum filtered and the collected liquid was filtered with approximately 3 cm of silica column (ultrapure, 60-200 μm , 60 $\text{\AA}$) in the vacuum filter dichloromethane. Solvent was evaporated by rotational evaporator at 50 $^{\circ}\text{C}$ and the final product of yellow liquid was collected with the yield of (14.4 g, 47.9%).

^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ ppm 1.10 (t, $J=7.03$ Hz, 3 H) 3.14 - 3.22 (m, 3 H) 3.43 (q, $J=7.03$ Hz, 2 H) 3.46 - 3.53 (m, 4 H) 3.53 - 3.59 (m, 4 H) 3.66 - 3.70 (m, 2 H) 4.27 - 4.36 (m, 2 H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$): δ ppm 15.59 (s, 1 C) 37.29 (s, 1 C) 66.01 (s, 1 C) 68.76 (s, 1 C) 69.67 (s, 1 C) 70.12 - 70.28 (m, 3 C) 70.30 (s, 1 C).

**2.3.4.12. 2-(2-(2-ethoxyethoxy)ethoxy)triethylethanammonium
methanesulfonate, [N₂₂₂EG₃C₂][MeSO₃]**



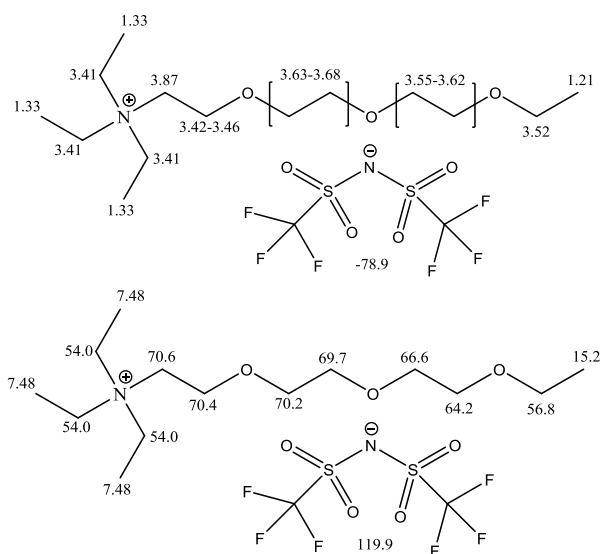
In a 250 mL double-neck flask equipped with a condenser, methane sulfonyl tri(ethylene glycol) monoethyl ether (15.8 g, 256 mmol, 1.1 eqv) and 10 mL of acetonitrile were added under inert atmosphere by argon while stirring. Corresponding amount of triethylamine (5.7 g, 56 mmol, 1.00 eqv) was added dropwise by a syringe at room temperature and the reaction temperature was increased to 50 °C. After 72 hours, the solvent was dried by rotating evaporator, dissolved in dichloromethane, and the final product was extracted by ultrapure water (3 × 10 mL). Water was evaporated and light yellow, transparent oil was collected (11.8 g 58.7%).

¹H NMR (400 MHz, CHLOROFORM-*d*): δ ppm 1.15 - 1.22 (m, 3 H) 1.36 (br t, *J*=6.59 Hz, 9 H) 2.69 - 2.75 (m, 3 H) 3.43 - 3.49 (m, 6 H) 3.50 - 3.56 (m, 4 H) 3.56 - 3.62 (m, 4 H) 3.62 - 3.67 (m, 2 H) 3.71 (br s, 2 H) 3.92 (br s, 2 H).

¹³C NMR (101 MHz, CHLOROFORM-*d*): δ ppm 7.92 (s, 3 C) 15.21 (s, 1 C) 39.52 (s, 1 C) 54.06 (s, 3 C) 57.18 (s, 1 C) 64.67 (s, 1 C) 66.61 (s, 1 C) 69.79 (s, 1 C) 70.23 (s, 1 C) 70.37 (s, 1 C) 70.56 (s, 1 C).

2.3.4.13. 2-Tri(ethylene glycol)ethyltriethylammonium

bis(trifluoromethylsulfonyl)amide, [N₂₂₂EG₃C₂][NTf₂]



[N₂₂₂EG₃C₂][CH₃O₃S] (7.48 g, 20.9 mmol, 1.00 eqv) was dissolved in ultrapure water in a 100 ml round bottom flask until the mixture became apparently less viscous. A corresponding amount of Li[NTf₂] (7.21 g, 25.1 mmol, 1.20 eqv) was dissolved in a minimum amount of ultrapure water and was added to the aqueous solution of [N₂₂₂EG₃C₂][CH₃O₃S] dropwise while stirring by magnet stirrer at room temperature. After 17 hours, the lower organic layer was separated, dissolved in dichloromethane, and washed with ultrapure water five times. Solvent was evaporated by rotating evaporator and the product was vacuum dried at 70 °C overnight. An yellow transparent, viscous oil was collected (8.79 g, 77.5%).

¹H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.21 (t, J=7.03 Hz, 3 H) 1.33 (t, J=7.22 Hz, 9 H) 3.39 (q, J=7.19 Hz, 6 H) 3.42 - 3.46 (m, 2 H) 3.52 (q, J=7.03 Hz, 2 H) 3.55 - 3.62 (m, 4 H) 3.63 - 3.68 (m, 4 H) 3.87 (br d, J=4.14 Hz, 2 H).

¹³C NMR (101 MHz, CHLOROFORM-*d*): δ ppm 7.48 (s, 3 C) 15.15 (s, 1 C) 53.96 (s, 3 C) 56.75 (br s, 1 C) 64.22 (s, 1 C) 66.56 (s, 1 C) 69.74 (s, 1 C) 70.23 (s, 1 C) 70.44 (s, 1 C) 70.57 (s, 1 C) 119.88 (d, *J*=321.31 Hz, 1 C).

¹⁹F NMR (377 MHz, CHLOROFORM-*d*): δ ppm -78.86 (s, 6 F)

ESI-MS (+ve) [C₁₄H₃₂N₁O₃]⁺: calculated 262.2377, found 262.2383

ESI-MS (+ve) [C₂F₆N₁O₄S₂]⁺: calculated 279.9178, found 279.9179

CHN Analysis: calculated C, 35.45; H, 5.95; N, 5.17, found: C, 35.27; H, 5.92; N, 5.52.

2.3.4.14. Triethyl-2-(methylthio)ethan ammonium chloride, [N₂₂₂EtS₁Me]Cl

In a 250 mL triple-neck flask equipped with a condenser and bleach system, 2-chloroethyl methyl sulfide (5.00 g, 45.2 mmol, 1.40 eqv) and of acetonitrile (10 mL) were added under inert atmosphere by argon while stirring. Corresponding amount of triethylamine (3.27g, 32.3 mmol, 1.00 eqv) was added dropwise by a syringe at room temperature and the reaction temperature was increased to 85 °C. After 72 hours, temperature was brought down to the room temperature and diethyl ether was added until the formation of crystals was observed. Viscos, brown liquid was also observed as crystals precipitated. The mixture was placed in freezer for overnight. The crystals were washed with a cold mixture of acetone and diethyl ether (3:1, 2 × 10 mL) and vacuum filtered. The crystals were dissolved in a minimum amount of acetonitrile, recrystallized by slowly adding diethyl ether dropwise while stirring with a magnetic stirring bar, and placed in freezer for overnight. The crystalline was vacuum-filtered and washed with diethyl ether (2 × 10 mL). White solids were collected with the yield of (1.14 g, 15.9%).

¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 1.18 (t, *J*=7.15 Hz, 9 H) 2.17 (s, 3 H)
2.76 - 2.87 (m, 2 H) 3.28 (q, *J*=7.19 Hz, 6 H) 3.33 - 3.40 (m, 2 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ ppm 7.70 (s, 3 C) 15.17 (s, 1 C) 24.93 -
25.00 (m, 1 C) 52.49 (s, 3 C) 55.73 (s, 1 C).

3. Metal Extraction by ILs

3.1. Introduction and Hypothesis

Based on the structure of the ILs designed and previous studies that extracted transition heavy metals by ILs,⁵⁴ ILs with shorter chain of the cationic functional groups were expected to undergo cationic exchange. The hydrophobic component of [NTf₂]⁻ group was expected to remain in the IL phase and the smaller, less hydrophobic cations were expected to favour the aqueous phase over the IL phase. Thus, the extraction mechanism would consist of cationic exchange where the charged metal ions in the aqueous phase would merging into the ILs phase as cationic component would leave the IL phase; maintaining the overall electrochemical neutrality.

Another possible extraction mechanism was developed. The PEGylated ILs were thought to have metal extraction ability where the oxygen atoms in the cation would interact with the metal ions in the aqueous phase. This hypothesis was driven from the studies of metal extraction using crown ether ligands where “hard” transition metals are efficiently extracted.⁶¹ With this logic, ILs with longer chain of ethylene glycol would act as a ligand and have a better extractability. In this mechanism, an ionic exchange would not occur, thus leaching of ILs would be prevented or minimized as opposed to the former hypothesis.

3.2. Results and Discussion

3.2.1. Synthesis of ILs

The percent product yields of ILs under similar synthetic methods are reported in **Table 3.1**. Quaternarization of triethylamine by alkyl chain was

simple and only required 10 to 20 mL of solvent to carry out the reaction. Recrystallization process was also simple and required acetonitrile and diethyl ether or ethyl acetate to obtain pure solid ILs with halide anion. To obtain a pure product, recrystallization was repeated one to three times. However, synthesis of PEGylated ammonium ILs presented some challenges. The major difficulty in the synthesis is the alkylation reaction to triethylamine in which the product yields were lower in the reactions of PEGylated ILs. Specifically, the product yield of [N₂₂₂C₂EG₂]
Br was significantly lower than that of the analogous [N₂₂₂₈]
Br. The lower product yields in PEGylated ILs may be due to the increase in the polarity of ILs that made more difficult to purify the final product from the alkylation step.

Table 3.1: Summary of percent product yields. Reaction I refers to the alkylation reaction and Reaction II refers to the metathesis step.

Ionic Liquid	Product Yield (%)	
	Reaction I	Reaction II
[N ₂₂₂₄][NTf ₂]	91.8	78.5
[N ₂₂₂₈][NTf ₂]	88.2	75.7
[N ₂₂₂₍₁₂₎][NTf ₂]	77.4	72.8
[N ₂₂₂ EG ₁ C ₁][NTf ₂]	88.9	88.7
[N ₂₂₂ EG ₂ C ₂][NTf ₂]	46.8	66.5
[N ₂₂₂ EG ₃ C ₂][NTf ₂]	58.7	77.5
[N ₂₂₂ EtS ₁ Me][NTf ₂]	15.9	----

Also after alkylation, coloured liquid byproducts were collected, which made the purification process challenging. The byproduct may be due to polymerization of amine group, although the exact cause of side reaction is unknown. Additionally, the colouring of ILs is due to the solvent used in the

reaction and the presence of a low concentration of impurities that is produced by the unwanted side reaction.⁶² Even though the colouring of the ILs were apparent, ¹H NMR and ¹³C NMR did not detect, or showed a very small amount of, the impurities. Although the presence of a small amount of impurity is unlikely to affect the synergic separation process by ILs, obtaining a pure IL may be challenging when considering the cost, labour, and time of the synthetic process at a larger scale. In such a challenging purification procedure, investigation in a simpler way of synthesizing pure ILs is desired.

Although the product yield of alkylation step differed between alkane-functionalized and PEG-functionalized ILs, the product yields of following metathesis step were within a close range, with the largest difference of approximately 30% between [N₂₂₂EG₁C₁][NTf₂] and [N₂₂₂EG₃C₂][NTf₂]. The purification process of [NTf₂] ILs after metathesis includes washing with ultrapure water five times and more, some of the product could be lost during the process of purification. Especially, as the viscosity of IL increased with the increasing alkyl chain length, washing process became more difficult. In such cases, water-insoluble solvents such as dichloromethane was used to reduce the viscosity. Thus, the purification process of ILs must be optimized to avoid the use of additional solvent while avoiding the loss of the final product.

For the sulfonation of alcohol chain, a large amount of white solid byproduct was produced, which was expected to be triethylammonium chloride based on the reaction (**Figure 2.2**). Because the byproduct is slightly insoluble in dichloromethane, separating the byproduct and the final product was challenging. To purify the final product, a short vacuum filtration chromatography with silica column was applied, which may have caused the

loss of the final product in the silica column phase (Method #2) as the product yield from the synthesis of $[\text{N}_{222}\text{EG}_3\text{C}_2][\text{MeSO}_3]$ is not particularly high. Although using a sulfonated chain is halide-free, thus considered as an environmentally friendly procedure, use of dichloromethane and lack in simplicity in the synthetic method counterbalance the benefit of halide-free alkylation. For these factors, synthetic method of $[\text{N}_{222}\text{EG}_3\text{C}_2][\text{NTf}_2]$ is desired to be improved in the future work in order to apply tri(ethylene glycol)-containing ILs in a larger scale.

In the reaction of the sulphur-containing IL, alkylation and purification process consisted of two major challenges. The first challenge is the low reactivity of 2-chloroethyl methyl sulfide and triethylamine. Thus, the ratio of 2-chloroethyl methyl sulfide to triethylamine was increased to 1.4:1.0, which resulted in a higher product yield, though, the final product yield was very low. The second challenge was the purification process where the impurity, which consisted of viscos, brown liquid, crushed out with the final product as diethyl ether was added to the reaction mixture of acetonitrile. Because of the close solubility of the both impurity and the final product in the antisolvent, the crystallization condition was carefully adjusted. Although crystals of pure final product was obtained, synthesis of $[\text{N}_{222}\text{EtS}_1\text{Me}][\text{NTf}_2]$ was no longer investigated due to the low final product yield.

3.2.2. Density and Viscosity Measurements

The results of the density measurements are reported in **Table 3.2**. The viscosities of ILs follow the trend seen in the literature wherein the viscosity of ILs increases with increasing alkyl chain; the electrostatic force within the ILs increases with increasing amount of hydrogen bonds.³⁶ The same trend was

seen in the PEGylated IL system, though, the difference in the viscosity within the PEGylated IL system was not as great as the alkyl chains.⁶³ In comparison, [N₂₂₂EG₁C₁][NTf₂] was less viscous than its analogous [N₂₂₂₄][NTf₂] whose the viscosities were 91.87 and 212.77 mPa.s, respectively. This comparison shows that incorporating an oxygen atom, a more electronegative atom than carbon, onto the alkyl chain dramatically reduces the viscosities of ILs. The difference in viscosity was greater in the longer chains. From this observation, a change in the chemical environment by changing the functional group, even only by one atom per molecule, has a large impact on the physical property of ILs. Such an ability to tune ILs allows specific applications to be optimized and accomplished, depending on the objective of the application. In the application of biphasic extraction, reduction in viscosity while maintaining the hydrophobicity of ILs is advantageous because such properties eases the handling of IL during the treatment and increases the physical dispersion of ILs in the aqueous phase, which allows the IL phase to interact with the molecules in the aqueous phase more effectively.

Table 3.2: *The measurement of viscosity and density of ILs are presented. The viscosity was measured at 20 °C and the density was measured at room temperature (23 – 24 °C).*

Ionic Liquid	Viscosity (mPa.s)	Density (g/mL)
[N ₂₂₂₄][NTf ₂]	212.77	1.304
[N ₂₂₂₈][NTf ₂]	329.00	1.233
[N ₂₂₂₍₁₂₎][NTf ₂]	522.05	1.219
[N ₂₂₂ EG ₁ C ₁][NTf ₂]	91.87	1.410
[N ₂₂₂ EG ₂ C ₂][NTf ₂]	98.59	1.342
[N ₂₂₂ EG ₃ C ₂][NTf ₂]	117.04	1.341

3.2.3. ICP-OES Results

After the metal extraction experiments were performed, the concentration of the metal in the posttreatment aqueous phase was analysed by ICP-OES. From the results of ICP-OES analysis, the metal extraction efficiencies of ILs were calculated by using **Equation 10**. The final results of metal extraction are summarized in **Figure 3.1**. For the actual values of the metal concentration after the extraction treatment, the extraction efficiencies, and the distribution coefficient, see Appendix.

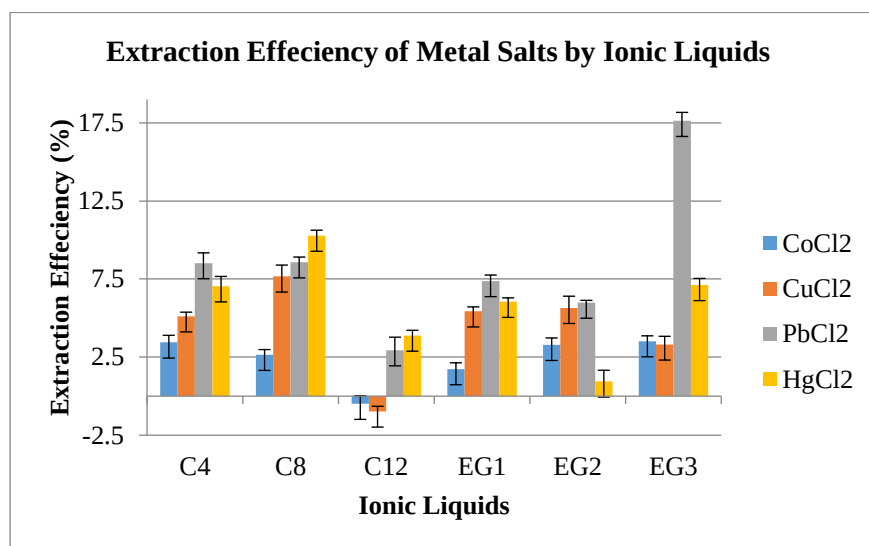


Figure 3.1: The efficiencies of metal extraction is summarized and reported ($P < 0.05$). Note that the efficiency is converted from the concentration of aqueous phase according to Equation 10.

Extraction of CoCl_2 showed a trend with increasing chain of the cationic component. The efficiency of CoCl_2 extraction decreased with the increasing length of the alkyl chain of ILs, where $[\text{N}_{222(12)}][\text{NTf}_2]$ showed no ability to extract CoCl_2 . This observation is likely due to the high non-polarity of the IL component, which consequently resulted in reduction of solubility of CoCl_2 in the IL. In contrast, when the chain length is increased in the

PEGylated IL system, there is an increase in polarity due to the oxygen groups present in the chain, which consequently increased the solubility of CoCl_2 .

Extraction of CuCl_2 showed a slightly different trend as compared to extraction of CoCl_2 . The inefficiency in extraction using $[\text{N}_{222(12)}][\text{NTf}_2]$ remained consistent for both metal salts. However, extraction by $[\text{N}_{2228}][\text{NTf}_2]$ exceeded the extraction efficiency by $[\text{N}_{2224}][\text{NTf}_2]$ where the average extraction efficiencies for $[\text{N}_{2228}][\text{NTf}_2]$ and $[\text{N}_{2224}][\text{NTf}_2]$ are 7.70 % and 5.11 %, respectively. Although there is no clear explanation to this trend, the data suggest that increase in the length of alkyl chain, does not always contribute in decrease of the extraction efficiency. This observation suggests that the polarities of ILs are not the only factors influencing the solubility of metal salts in ILs. The trend in the CuCl_2 extraction efficiency is also inconsistent with the trend of the viscosities of ILs. The result showed that there are unexpected compatibilities of ILs and metal salt, which must be taken consideration when optimizing the extraction parameter.

The trend of the extraction of PbCl_2 by alkyl ILs followed the same trend as when extracting CuCl_2 . Again, this result supports that there may be a preferred length of cationic chain of IL where there is a good balance of polarity and viscosity of ILs in order to optimize the solubility of respective metal salt. One inconsistency was observed for $[\text{N}_{222}\text{C}_2\text{EG}_2]$ and showed a significantly higher extraction ability than any other experiments. This interesting outcome triggers a further investigation of lead extraction by PEGylated ILs.

The extraction of HgCl_2 by alkyl ILs follows the similar trends as those with CoCl_2 extraction where the extraction efficiency for both treatment in the alkyl ILs followed the order of $[\text{N}_{222(12)}][\text{NTf}_2] > [\text{N}_{2224}][\text{NTf}_2] > [\text{N}_{2228}][\text{NTf}_2]$. The order of the extraction efficiency in the PEGylated ILs was $[\text{N}_{222}\text{C}_2\text{EG}_3] > [\text{N}_{222}\text{C}_1\text{EG}_1] > [\text{N}_{222}\text{C}_2\text{EG}_2]$, which is the same as PbCl_2 treatments. However, the extraction efficiency of $[\text{N}_{222}\text{C}_2\text{EG}_2]$ in HgCl_2 experiment was less than 1%, which suggest that oxygen atoms negatively impacted the extraction because analogous $[\text{N}_{2228}][\text{NTf}_2]$ has the highest efficiency with 10.3%.

The overall result showed that, except for the result from extraction of PbCl_2 by $[\text{N}_{222}\text{C}_2\text{EG}_2]$, the ILs used in this study demonstrated no to a very small metal extraction ability.

3.2.4. UV-vis Spectroscopy Results

The UV-vis spectra of ILs and the spectra of IL phases after the metal extraction experiments were measured in acetonitrile. The spectra of ILs presented in **Figure 3.2** showed some similarities based on the length of the alkyl and PEGylated chains of the cation. The pair of $[\text{N}_{2224}][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_1\text{EG}_1]$ showed a clear band at 275 nm. The analogous pair of $[\text{N}_{2228}][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_2\text{EG}_2]$ also showed a similar spectral appearance with a difference in the peaks at 218 nm and 227 nm, respectively. For the comparison of $[\text{N}_{222(12)}][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$, the peak at 282 nm is only seen in the $[\text{N}_{222(12)}][\text{NTf}_2]$. The absorbance peak of the ILs are attributed to the cationic component of the ILs because $[\text{NTf}_2]$ is not UV-active and does not appear in the UV-vis spectrum.⁶⁴ From these observations, it may be concluded that the cations with the same chain lengths, hence the similar size

of ILs, may attribute to similar UV-vis spectral appearances, thus comparable electronic transition of the cationic component of ILs. In this section, only the appearance of the spectra are discussed as the investigation in the activities of ILs under UV-vis spectral regions would require more detailed experiments.

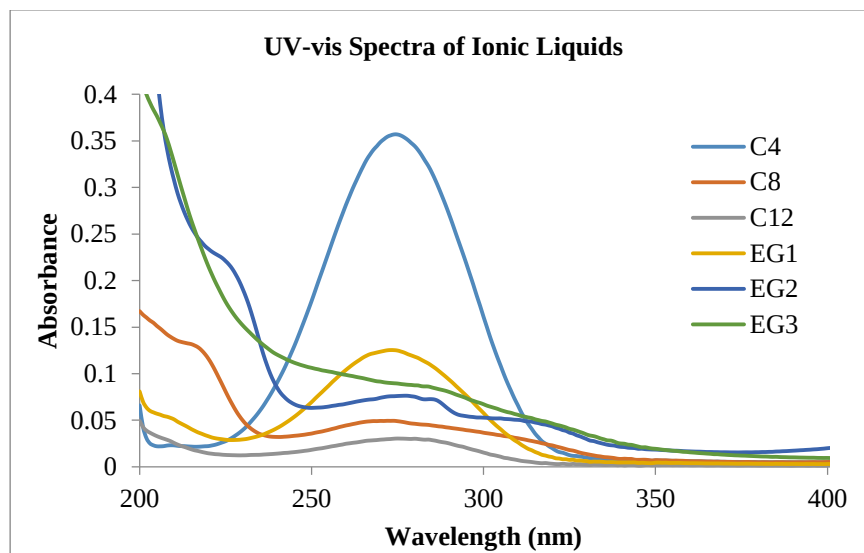


Figure 3.2: UV-vis spectra of ILs were measured with acetonitrile. Samples were vacuum dried prior to the measurement and the spectra were normalized to the concentration of IL in acetonitrile (mg/mL).

An example of the UV-vis spectra of the $[N_{2224}][NTf_2]$ phase before and after metal extraction are presented in **Figure 3.3**. The spectra suggest that after the metal extraction process, the UV-vis activities of the IL are altered. The spectral difference could be due to the interaction of ILs with water and/or the respective metal salt. Some ILs after metal extraction did not show any absorption activities and some resulted in altered absorption peaks compared to the spectra of the ILs. For the rest of the spectra of IL phase after metal extraction, see Appendix.

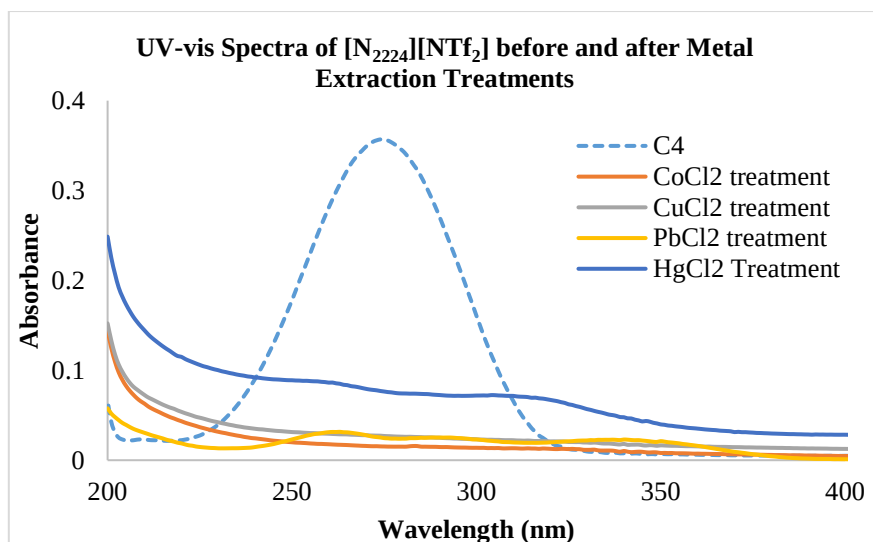


Figure 3.3: The UV-vis spectra of $[N_{2224}][NTf_2]$ were recorded by dissolving in acetonitrile. The dotted spectrum is the $[N_{2224}][NTf_2]$ before the treatment and the rest are the IL phases after metal extraction.

3.2.5. Ion Chromatography Analysis

The results from ion chromatography analysis (see Appendix) of the aqueous phase after a treatment without metal salt in the aqueous phase showed traces of IL components present. The detection of ILs in the aqueous phase is most likely due to leaching effect of ILs into water, even though $[NTf_2]^-$ is considered to be one of the most hydrophobic IL anions. Leaching of IL component into the aqueous phase must be considered in the application of ILs because of their toxicities.

3.3. Conclusion

The experiments of extracting metal ions and/or metals chloride salts by ILs were performed. Contrary to the initial hypotheses, ILs did not show effective extraction abilities, with the maximum extraction performance of $[N_{222}C_2EG_3][NTf_2]$ on $PbCl_2$ extraction (17.6%). In the series of alkyl chain, the longest alkyl chain, $[N_{222(12)}][NTf_2]$ consistently showed the lowest

extraction efficiency for all experiments. Generally speaking, the highest extraction efficiency was obtained by [N₂₂₂₈][NTf₂] and [N₂₂₂₄][NTf₂] wherein the extraction by their analogous PEGylated ILs did not increase significantly. However, extraction by [N₂₂₂C₂EG₃][NTf₂] as compared to [N₂₂₂₍₁₂₎][NTf₂] increased for all four metal chloride extractions, which may be due to decrease in viscosity of the IL that resulted in a better interaction of the IL and metal salts within the chosen extraction time.

To conclude, the set of ammonium ILs, both alkyl- and PEGylated, did not demonstrate a great capacity of metal extraction. However, extraction of metal salts can be controlled by tuning the cationic component of hydrophobic ILs, which ultimately helps to selectively extract metal ions.

4. Metal Extraction by ILs and Htta

4.1. Introduction of 2-Thenoyltrifluoroacetone and Hypothesis

In the application of chelating ligands to extract metal ions, hydrophobic solvents are used as a medium to establish biphasic systems with an aqueous phase. In such applications, the use of ILs is advantageous as compared traditional solvents because ILs have negligible vapour pressure that prevents the release of hazardous compounds into the atmosphere.

Use of ligands in wastewater treatment is known as “chelation technology”. It is considered to be a green water purification process because of their simple processes. Chelates possess atom-donating sites where a metal ion binds to form a metal-ligand complex whose ability to form the complex depends on the thermodynamic relationship of the complexation process:⁵⁵

$$\Delta G^\circ = -RT\ln(K) = \Delta H^\circ - T(\Delta S^\circ) \quad [11]$$

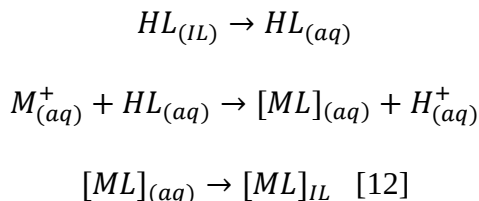
Where ΔH , enthalpy, relates to the ligand property of repulsion, distortion and crystal field stabilization, and ΔS , entropy, is related to the probability factors that govern the stability of the complex. The initial stage of metal-ligand complexation takes place in the aqueous phase. The water molecules bounded to the metal ion is replaced by the donating site of the chelating ligands. In the studies of biphasic metal extractions by chelating ligands, the effect of pH has been widely investigated due to the properties of ionization of ligands wherein the rate of deprotonation increases at a higher pH level.^{42, 57, 65}

4.1.1. Extraction by Ionizable Ligands

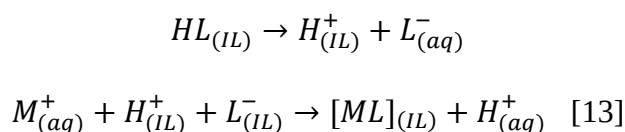
Ionizable ligands have been investigated widely in separation of metals with the use of ILs. The previous studies have shown the mechanism of metal

extractions wherein neutral extraction and ion exchange using the ionizable ligands are the dominant mechanisms:⁴⁹

Neutral Extraction by Ionizable Ligands:



Ion Exchange by Ionizable Ligands:



Where HL represents an IL phase that contains an ionizable component, either as an external ligand that is added to the IL phase or a ligand component within the IL structure. In this case, the sites of protonation and deprotonation are facilitated by the chelating ligands. Because the metal extraction mechanisms in the use of chelating ligands includes the interaction with water, the hydrophobicity of the IL components may play an important role. By using a hydrophobic cation that contains a long alkyl chain, cationic extraction mechanism is suppressed and using hydrophobic anion such as $[NTf_2]^-$ suppresses the anionic exchange.⁵⁷

4.1.2. 2-Thenoyltrifluoroacetone

To increase the extractability of the metals, an ionisable ligand, 2-thenoyltrifluoroacetone (Htta), was chosen to extract the heavy metal ions from the aqueous phase. The previous studies using Htta have demonstrated its extractability of lanthanides from aqueous phase.^{66, 67} Also, some researchers have also extracted divalent heavy metals with Htta by using imidazolium-

based ILs.^{57, 67} The Htta ligand is considered to be hydrophobic, therefore metal extraction by Htta and hydrophobic solvent system provides promising outcomes. The Htta molecules that failed to react with the metal ions remain in the organic solvent phase.

In the applications of Htta with an aqueous phase, the structure of Htta plays an important role (**Figure 4.1**). Htta contains two ketone sites, thus it is categorized as a diketo ligand. At this site, the double-bond closer to the CF₃ group is hydrated to become the enol form of Htta in the presence of water. With a further hydration, the Htta molecule tautomerizes to the keto-hydrate form where the molecule contains two hydroxyl groups. It has been understood that binding of metal occurs when the Htta molecule is in the enol form where the site of monoketone and enol creates a conjugated system that allows a metal ion to be bounded, though the rate of the transformation differs depending on the external conditions such as the pH of the environment and the concentration of the water molecules.⁶⁸

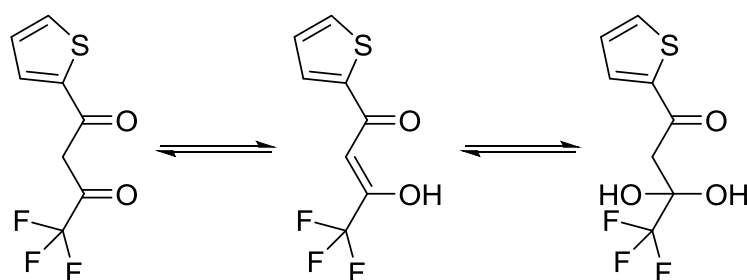


Figure 4.1: Tautomerization of 2-thenoyltrifluoroacetone is affected by the presence and water molecules and its concentration with in the environment. From left to right: Htta in dry environment, Htta in enol form after the first hydration, Htta in keto-hydrate form after the second hydration.

4.1.3. Hypothesis

As described previously, Htta is known to extract some lanthanides, as well as divalent metal ions at the monoketone-enol site. The chelating site of

Htta contains two oxygen atoms that are considered to be “hard” electron donors, which favours to interact with hard metals such as copper and cobalt. However, Htta can bound to larger metal ion as in the case of lanthanide extractions, the extraction of softer heavy metals such as lead and mercury were expected. The presence thiophene ring was also expected to increase the affinity to the softer heavy metals.

4.2. Experimental

The procedure of the metal extraction experiment and analytical methods were the same as the ones described in Section 3. Into the IL phase, 2.33 mg of Htta per 1.00 mL of IL was dissolved. Solid Htta (99% purity) was obtained from Acros Organics and used without any further purification. 2.33 mg of Htta was completely dissolved in 1 mL of IL. The rest of the extraction procedure was the same as the ones described Section 2.2.

4.3. Results and Discussion

4.3.1. ICP-OES Results

After the metal extraction experiments, the metal concentration in the aqueous phase was determined by ICP-OES and the extraction efficiencies were calculated. The results are presented in **Figure 4.2**. The results from the CoCl_2 extraction experiments showed a distinct trend. The increase in the length of alkyl chain showed a decreasing trend in the efficiency of CoCl_2 extraction. This trend also is seen in the PEGylated ILs, where the increase in the length of PEGylated chain also decreased the extraction efficiency. The trend in the PEGylated system was surprisingly reverse as compared to the extraction experiment without Htta. This phenomenon may be due to the fact that the solubility of Co-tta complex into ILs may differ depending on the

physical properties of the ILs. This logic can be explained by comparing the results from the viscosity measurement and the extraction efficiency. Although the Htta molecules and complexes are hydrophobic, the increase in hydrophobicity with the increase in viscosity reduced the extraction efficiency. Thus, the solubility of the metal-ligand complex and the physical property of ILs can affect the overall extraction efficiency.

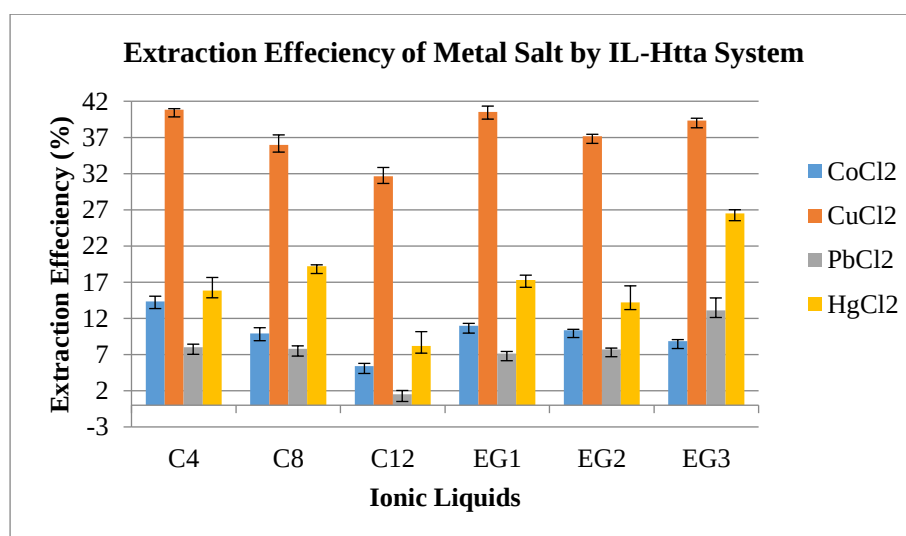


Figure 4.2: Result from metal extraction experiments are summarized ($P < 0.05$). The concentration of the metal in the aqueous phase was measured by ICP-OES with two recommended wavelengths. For further information, see Appendix.

The extraction of CuCl_2 by IL-Htta systems showed the highest efficiencies of all treatments tested in this study. These outcomes may be due to a higher stability of the Cu-tta complex as compared its analogous Co-tta complex. Although both divalent metals are arbitrarily classified as “hard” or “borderline” Lewis acids in the general concept of HSAB theory, the slightly different properties of the metals may have a large impact on formation of metal-ligand complex, which ultimately affected the extraction efficiency of metal by use of chelating ligand. The property of ILs also contributed to the

trend of extraction efficiency. As seen in the extraction of CoCl_2 by Htta-IL system, the increase in alkyl chain decreased the extraction efficiency. Again, this may be mainly due to the increase in the viscosity of the IL where the probability of the collision of the metal atoms and ligands during the treatment may have been decreased. Finally, even though there was not a large difference in the result of the extraction within the PEGylated system, comparing the extraction efficiencies by $[\text{N}_{222(12)}][\text{NTf}_2]$ - and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ -Htta system supports that decrease in viscosity of IL may contribute to the increase in the extraction efficiency.

The trend of the extraction efficiency of PbCl_2 by alkyl ILs followed the same trend as the result from the CuCl_2 extraction experiments. Again, these results support the logic that there may be a preferred length of cationic chain of IL - tuning the properties of ILs such as viscosity - in order to optimize the solubility of the metal salt into the IL phase. However, unlike the other metal salt extraction treatments, the treatment of PbCl_2 showed a general trend where the presence of Htta molecules in the IL phase decreased the efficiency as compared to the experiments with ILs alone. This was unexpected because even if the PbCl_2 and Htta molecules appeared to be incompatible to form a metal-ligand complex whilst the thiopene ring was expected to attract softer metal ions based on HSAB theory. Therein the results may suggest that the presence of one type of ligand molecules, a monoketone ligand in this study, can decrease the extractability of metal ions by ILs. Although such a phenomenon may seem to be disadvantageous in metal extraction, utilization of ligands may enhance the selectivity in metal extraction treatments from a solution containing different types of metal ions.

The result of HgCl_2 extraction showed a surprising outcome. Even though the chelating site of Htta consists of a diketone group, which is considered as hard Lewis base, Htta showed the ability to extract mercury ions. Moreover, extraction efficiency of HgCl_2 were higher than it is of CoCl_2 . Based on the HSAB theory, Htta was thought to extract hard metals like cobalt more efficiently than soft metals like mercury. Based on these results, the thiophene ring of Htta may have a significant impact on interacting with mercury, because mercury is known to favourably interact with sulphur. Likewise, the presence of the sulphur atom may have interfered with cobalt atoms based on the HSAB theory.

Furthermore, the extraction of HgCl_2 by alkyl ILs followed the same trend as the one seen in extraction of CuCl_2 , where the extraction efficiency for both treatment followed the order of $[\text{N}_{222(12)}][\text{NTf}_2] > [\text{N}_{2224}][\text{NTf}_2] > [\text{N}_{2228}][\text{NTf}_2]$. The order of the extraction efficiency in the PEGylated ILs appeared to be $[\text{N}_{222}\text{C}_2\text{EG}_2] > [\text{N}_{222}\text{C}_1\text{EG}_1] > [\text{N}_{222}\text{C}_2\text{EG}_3]$, which is the same trend as the PbCl_2 treatments. Lastly, the efficiency of HgCl_2 extraction in both with and without Htta showed the same trend. This comparison shows that the physical properties of ILs contribute to the extraction ability of the ligand.

To understand the effect of the concentration of Htta in the ILs phase, $[\text{N}_{2224}][\text{NTf}_2]$ and CuCl_2 were selected to perform the extraction experiments whilst differing the Htta concentration, as the pair demonstrated one the highest extraction efficiency. Also $[\text{N}_{2224}][\text{NTf}_2]$ is the simplest form of the ILs studied in this project. Following the same procedure described in the Section 4.2, varying amounts of Htta were dissolved in the ILs: 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 mmol of Htta. The result is presented in **Figure 4.3**. The increase

of the concentration of Htta in the IL phase increased the extraction efficiency up to 71.08 %. This is a very promising result in terms of optimizing the extraction efficiency. The extraction efficiency can be also optimized by changing other extraction parameters such as contact time and temperature, which ultimately increase the rate of collision and helps the ligand and metal ions to form a complex.^{38, 39}

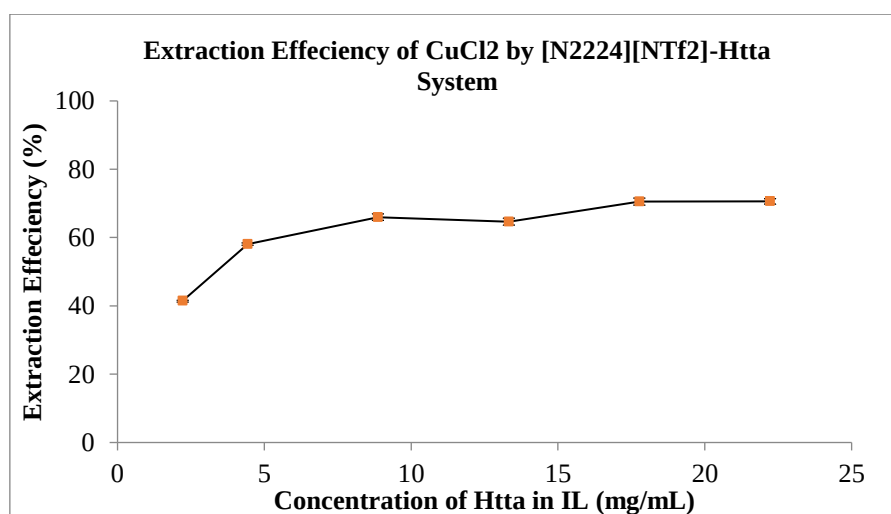


Figure 4.3: The results from CuCl_2 extraction with varying concentration of Htta are presented ($P < 0.05$). For further information, see Appendix.

To compare the extraction ability with the traditional solvent, CuCl_2 extraction experiments were performed with some hydrophobic solvents, with and without Htta. Dichloromethane, chloroform, toluene, and ethyl acetate, were chosen based on literature.⁶⁹ The results are presented in **Table 4.1**. The experiment with ethyl acetate formed monophasic system with the aqueous phase at the end of the treatment. In the resulting monophasic solution of water and ethyl acetate, green solids were obtained (**Figure 4.4**).

The results from the extraction using traditional solvents without Htta suggest that each solvent possesses different levels of the ability to extract the

metal chloride salts. Both treatments with and without Htta agree with the results from the IL treatments where the addition of Htta dramatically increased the extraction efficiency. As compared to chloroform and DCM, toluene showed the best compatibility with Htta to extract CuCl_2 . The high extraction efficiency by toluene-Htta system may be due to the structural nature of toluene where the π -bond interaction of the conjugated ring favours the interaction with the conjugated system of CuCl_2 -Htta.⁴⁴ Based on the results of using the traditional solvents, the mechanism of the extraction process of CuCl_2 by ILs is determined to be neutral extraction whereby Htta molecules and copper ions form an uncharged complex, which is extracted into the solvent phase. The possibility of the ion exchange mechanism is eliminated because the solvents used were electrically neutral.

Table 4.1: Results from CuCl_2 extraction by conventional solvent are reported with the value of standard deviation ($P < 0.05$)

Solvent	Extraction Efficiency (%)	
	Without Htta	With Htta
Dichloromethane	12.11 ± 0.61	45.61 ± 0.63
Chloroform	5.54 ± 0.18	37.39 ± 2.13
Toluene	2.45 ± 0.66	49.06 ± 4.47

As mentioned previously, due to the miscibility of ethyl acetate with water in a proportionally large amount of water, the solutions formed monophasic system, thus the result was not obtained. Instead, at the end of the two-hour treatment, green solids were found floating on the surface of the solution. From this observation, a hypothesis was developed that by using a water-soluble solvent, metal-Htta crystals can be synthesized. Further experiments and discussions are detailed in Section 4.4.



Figure 4.4: Green solids found after the trial of CuCl_2 extraction by ethyl acetate and Htta. The solids were found floating in on the surface of the solution after two hours of treatment

4.3.2. UV-vis Spectroscopy

In order to understand the interaction between ILs and Htta, UV-vis spectroscopy of Htta in different environments of ILs were taken. **Figure 4.5** shows the spectra of $[\text{N}_{2224}][\text{NTf}_2]$ -Htta system in a dry and water-saturated environment. The wet $[\text{N}_{2224}][\text{NTf}_2]$ -Htta system is prepared by dissolving 1.05×10^{-2} mol of Htta into 1 mL of IL and equilibrated with 1 mL of ultrapure water by stirring overnight. The dry system was prepared by mixing the same amount of Htta in dry IL. It is well studied that Htta undergoes enol-keto tautomerization in the presence of water.⁷⁰ The peaks at 268 nm and 295 nm indicate the keto-hydrate form of Htta in the wet IL. The spectrum of $[\text{N}_{2224}][\text{NTf}_2]$ -Htta in the dry environment shows a peak at 324 nm and shoulder bands at 355 nm and 271 nm. These peaks indicate the enol form of Htta. Also, it is known that the rate of tautomerization of Htta is depended on the solvation kinetics; the amount of water molecule present within the

system.⁷⁰ In the use of Htta as the metal extractant and IL as the solvent medium, it is important to note that the extraction efficiency may be impacted on the presence of water in the IL phase as the enol form of Htta bounds to a metal ion. Thus it is important to note that different ILs possess different levels of water content depending on their functional groups.

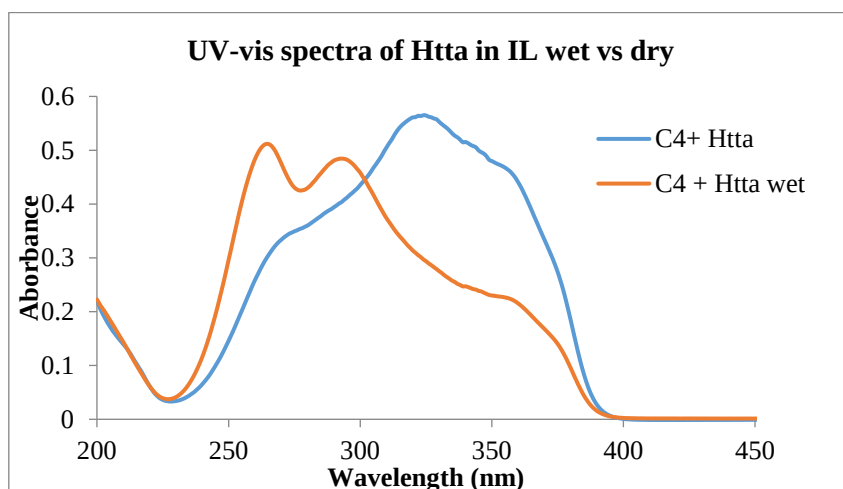


Figure 4.5: UV-vis spectra of Htta in $[N_{2224}][NTf_2]$ in dry and wet environment. The samples were prepared in dry acetonitrile solution.

The **Figure 4.6** shows the UV-vis spectra of IL phase after each metal chloride treatment by $[N_{2224}][NTf_2]$ /Htta system. Although the spectra are of the same IL, some spectra confirmed the presence the metal-ligand complex formed after the process. The spectra of the IL phases after the $HgCl_2$ and $CoCl_2$ treatment show very similar trends with the peaks at 264 nm and 292 nm. The broader bands around 333 nm to 336 nm may indicate a low concentration of the metal-ligand complexes formed in the IL phase after the treatment, which corresponds to the lower extraction efficiencies as compared to $CuCl_2$ extraction treatment. The spectrum of the IL phase after $PbCl_2$ treatment did not show a notable peak as seen in the other spectra. The broad

peak at 264 nm may indicate the presence of the keto-hydrate form of Htta, and there is a broad peak seen at 336 nm, which may confirm the formation of the metal-ligand complex. Nevertheless, the peak near 264 nm that is seen in the other spectra is not notable in the spectrum. To further understand the IL phase and the behaviour of Htta after the metal extraction treatments, UV-vis spectra of all post-treatment IL phases were taken.

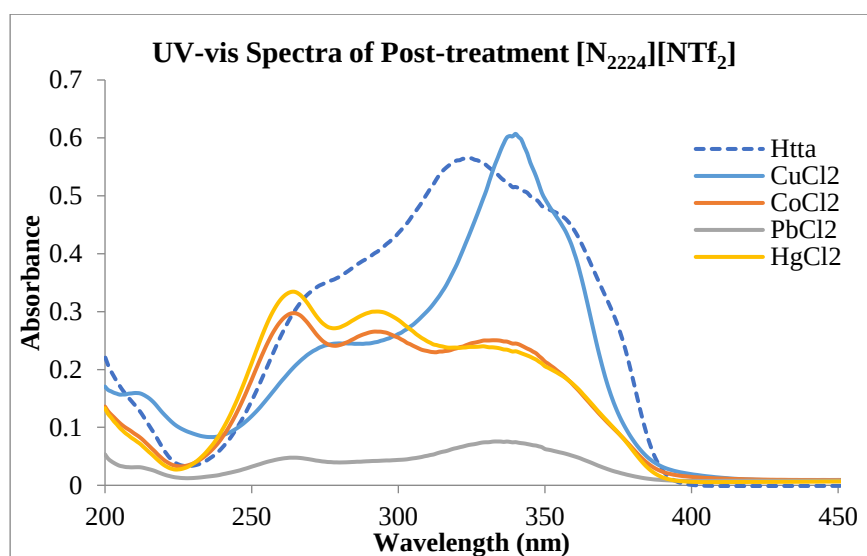


Figure 4.6: Comparative UV-vis spectra of $[N_{2224}][NTf_2]$ after each metal extraction. The dotted spectrum is Htta in enol form. Note the shift in peak after the $CuCl_2$ extraction treatment.

The spectra from $CoCl_2$ treatment with Htta (**Figure 4.7**) showed a trend in the alkane-functionalized ILs. Relatively speaking, the difference in the intensity of peak at 331 nm compared to the peak at 265 nm in ratio appeared to be smaller in the alkyl ILs than that of the PEGylated ILs, . Furthermore, the broad peak at 331 nm is absent in the spectrum of $[N_{222}C_2EG_3][NTf_2]$ -Htta phase. The spectra of Htta in the alkyl ILs may be assigned to a mixture of the enol form of Htta and the formation of a cobalt-Htta complex, because the peak of the enol form of Htta appears at 324 nm.

The merging of the two peaks is especially notable in the spectrum of [N₂₂₈][NTf₂] system where the peak at 324 nm is more apparent but the shoulder band the enol form of Htta around 355 nm is absent in the spectrum. Nevertheless, all the spectra of the posttreatment IL-Htta system showed the presence of the keto-hydrate form of Htta that failed to form a metal-ligand complex with CoCl₂.

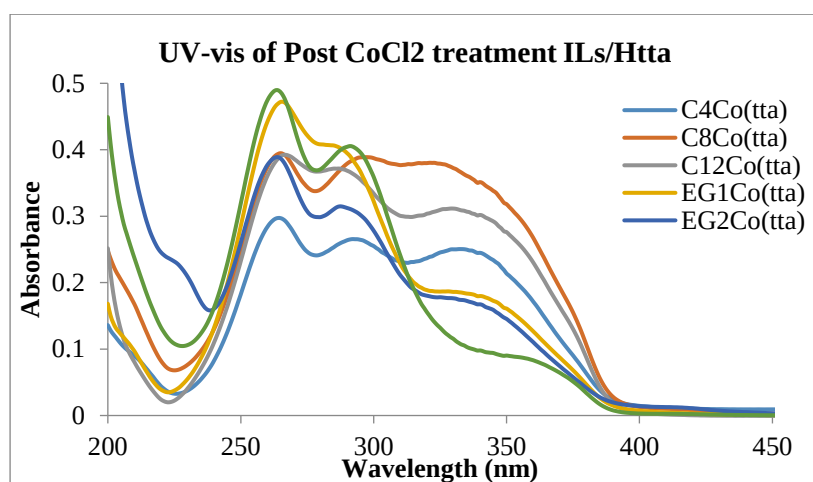


Figure 4.7: UV-vis Spectra of ILs containing Htta after CoCl₂ extraction treatment. A relatively large amount of Htta molecule in keto-hydrate form is present in all ILs.

Unlike the UV-vis spectra of the ILs after CoCl₂ extraction treatment with Htta (**Figure 4.7**), the spectra of the treatment of CuCl₂ (**Figure 4.8**) showed the formation of complex of copper and Htta. The new peak appears at 341 nm for all IL-Htta phase, as explained previously. The spectra are consistent with the result from ICP-OES, however, it is important to note the peak of the keto-hydrate form of Htta in the [N₂₂₂C₂EG₃][NTf₂] phase, which is more intense than the peak assigned to the copper-Htta complex. This comparison may indicate that not all Htta molecules in ILs reacted with the metal ions.

In comparison to the other IL-Htta system, the intensity of the peak at 266 nm is relatively higher than the newly formed peak of copper-Htta complex at 341 nm in the spectra of $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$. This relatively more intense peak at 266 nm indicates the presence of a high concentration of keto-hydrate form of Htta, which is not seen in the other IL-Htta system. This may be due to the high water absorption capacity of $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$, which ultimately creates the chemical environment of which the Htta molecules favour the keto-hydrate form. A similar effect is observed in the $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$ -Htta phase, however, the peak at 341 nm is still more intense than the peak at 266 nm, as seen in the spectra of other IL-Htta phases.

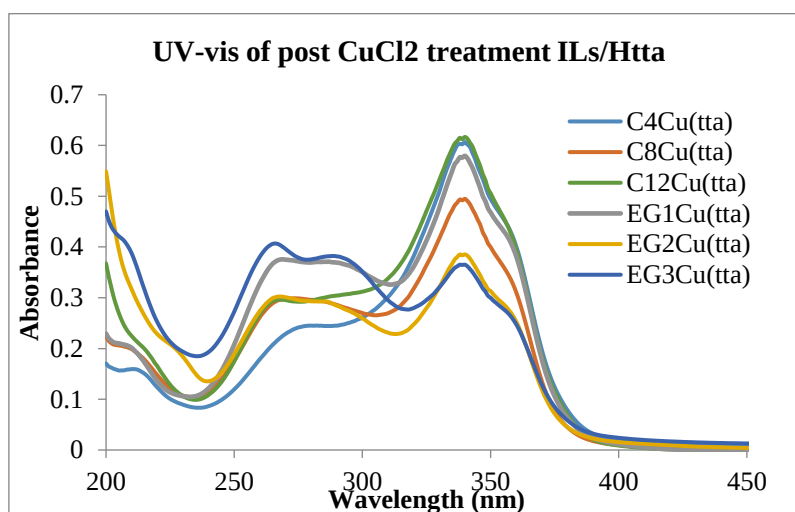


Figure 4.8: UV-vis Spectra of ILs containing Htta after CuCl_2 extraction treatment. New peak at 341 nm is assigned to a new copper-Htta complex.

The UV-vis spectral measurements of IL phases after PbCl_2 treatments (**Figure 4.9**) showed some different results as compared to other posttreatment of metal extraction. The spectrum of posttreatment by $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ showed bands at 313 nm and 414 nm, which were also seen in the spectrum of $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ after PbCl_2 extraction without Htta. Although whether if

the peak shift is due to the interaction of the IL, ligand, and/or PbCl_2 is unclear, these peaks could come from impurities in the IL as $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ is particularly difficult to purify.⁷¹

Similarly, the spectra of $[\text{N}_{2228}][\text{NTf}_2]$ and $[\text{N}_{222(12)}][\text{NTf}_2]$ showed peaks at 318 nm and 337 nm, respectively. Both peaks are as intense as, or more intense than the peak of keto-hydrate Htta at 264 nm, which indicates that the concentration of what is causing these broad peaks is higher than that of the unreacted Htta in the IL phase. Based on the posttreatment spectrum of $[\text{N}_{2228}][\text{NTf}_2]$ without Htta (see Appendix), the possibility of IL alone causing the appearance of new peak after PbCl_2 treatment can be eliminated, because the new peak appeared around 325 nm. The same reasoning can be applied to the spectra of $[\text{N}_{222(12)}][\text{NTf}_2]$. Therefore, the new peaks may indicate a new activity of Htta, lead, and/or ILs under the UV-vis range. Nevertheless, all spectra from IL-Htta system after PbCl_2 treatment showed a peak of keto-hydrate form of Htta at 264 nm, which indicates presence high concentration of unreacted Htta molecules.

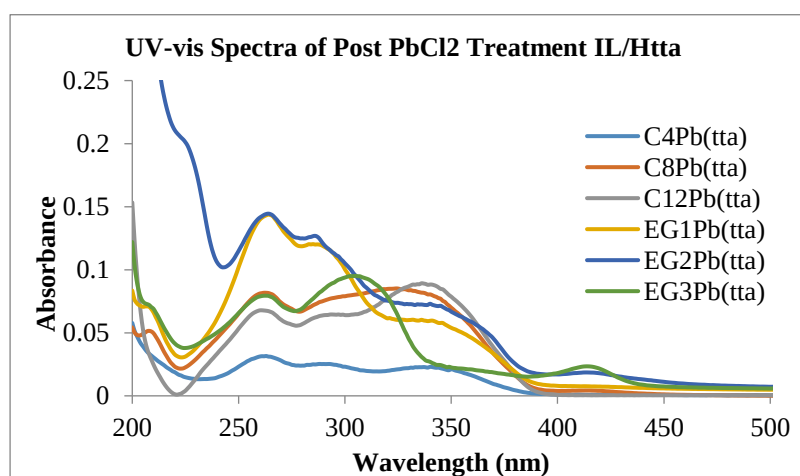


Figure 4.9: UV-vis Spectra of ILs containing Htta after PbCl_2 extraction treatment. The peak for keto-hydrate form of Htta at 267 nm is consistently observed.

The extraction of HgCl_2 by IL-Htta system showed some interesting spectral appearances. First, after the treatment without Htta, the spectra of $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ and $[\text{N}_{2228}][\text{NTf}_2]$ the bands at 312 and 314 nm, respectively, which is consistent with the PbCl_2 treatments. Therefore, these bands most likely come from ILs themselves, rather than because of the interaction between the ILs and metal chlorides.

Secondly, the spectra of $[\text{N}_{2228}][\text{NTf}_2]$ and $[\text{N}_{222(12)}][\text{NTf}_2]$ with Htta showed a formation of broader bands around 327 to 330 nm, which may indicate the formation of mercury-Htta complex, or tautomerization effect of Htta where Htta remained in its enol form, because these two ILs are especially hydrophobic as compared to other ILs studied in this study. The spectra of PEGylated ILs after HgCl_2 treatment with Htta resulted in higher extraction efficiency, yet, did not show the new peak of mercury-Htta complex as intense as $[\text{N}_{2228}][\text{NTf}_2]$ and $[\text{N}_{222(12)}][\text{NTf}_2]$. Although the appearances of these peaks are very similar to the ones observed in the spectra of post CoCl_2 treatment by Htta-IL system (**Figure 4.8**), the high concentration of unreacted Htta is most likely caused the appearance of the spectra.

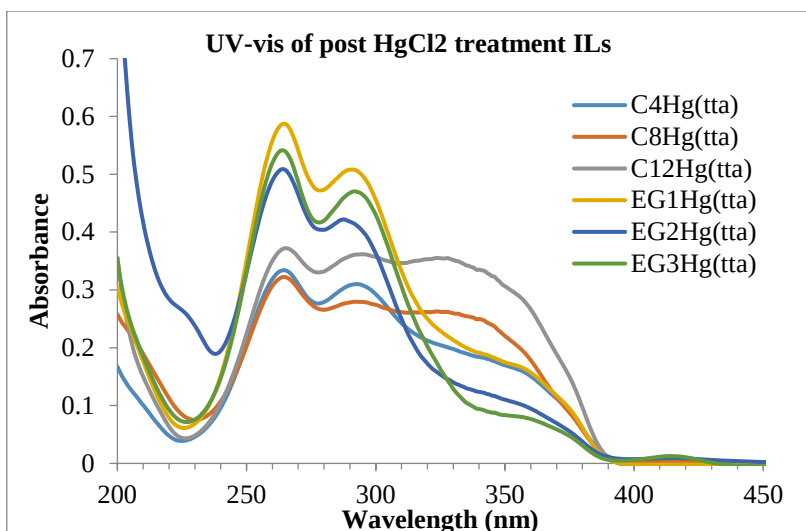


Figure 4.10 : UV-vis Spectra of ILs containing *Htta* after HgCl_2 extraction treatment. The spectra show a similar trend the one seen in the result from CoCl_2 in Figure 4.7.

The recycling of IL after CuCl_2 extraction treatment was performed with aqueous acetic acid solution (0.5 M) according to literature.⁴³ The spectrum of the post-recycling $[\text{N}_{2224}][\text{NTf}_2]$ phase shows the absence of Cu-tta complex in the $[\text{N}_{2224}][\text{NTf}_2]$ phase (**Figure 4.11**). The IL is washed with water after being treated with acid and the spectrum of post-recycling shows the keto-hydrate form of *Htta* due to the presence of high concentration of water molecules. The spectrum also confirms that upon recycling of IL, the ligand molecules stay in the IL phase, and that only the copper ions are separated from the IL phase. The process of recycling consists of protonation of the ligand by acidic aqueous solution, which releases the hydrophilic metal chloride salts into the acid phase from the IL phase.⁴³ This is advantageous because the ligands can be recycled with ILs in one process. The recycling process was also successful in by using hydrochloric acid and nitric acid. The samples from recycling of $[\text{N}_{222(12)}][\text{NTf}_2]$ using HCl are presented in **Figure 4.12**, as the colours of $[\text{N}_{222(12)}][\text{NTf}_2]$ and HCl effectively showed the

difference in the appearance of the phases after each step from extraction to recycling.

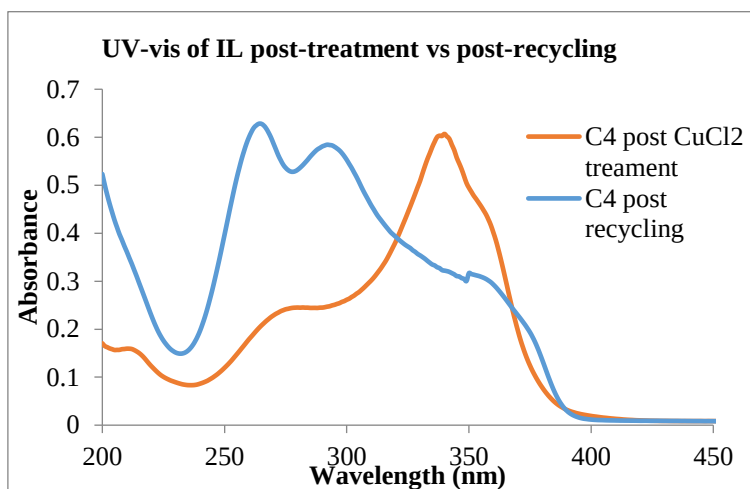


Figure 4.11: Comparative spectra of $[N_{2224}][NTf_2]$ after $CuCl_2$ extraction and post-recycling are presented. The bump in the spectrum of post-recycling IL at 350 nm is due to the UV-vis spectrometer changing the lamp during the measurement.

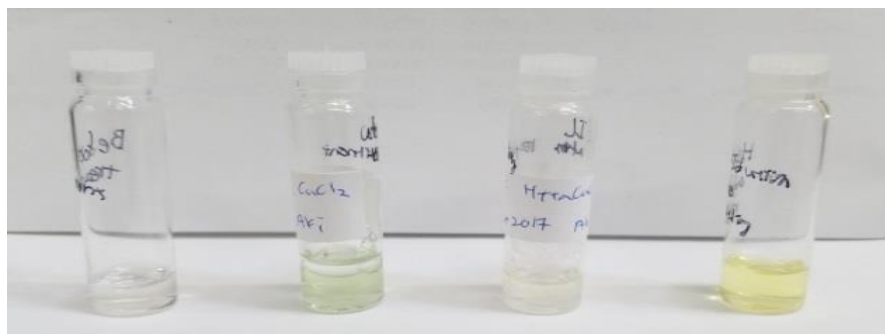


Figure 4.12: $[N_{222(12)}][NTf_2]$ is presented in the figure as it was the most transparent, colourless IL. From left to right: IL before metal extraction process, IL after extraction process, IL after recycling by HCl, and the aqueous HCl phase separated from the IL phase after recycling.

4.4. Synthesis of Metal-Htta Complexes and Characterization

As previously stated, after the $CuCl_2$ extraction treatment by ethyl acetate-Htta system that resulted in collection of the green solids, a hypothesis

was developed that the crystals obtained were what is present in the ILs phase. Thus, synthesis and characterization of the Cu(tta) complex and Co(tta) complex were attempted. Synthesis method of metal(tta) complex is illustrated as follows:

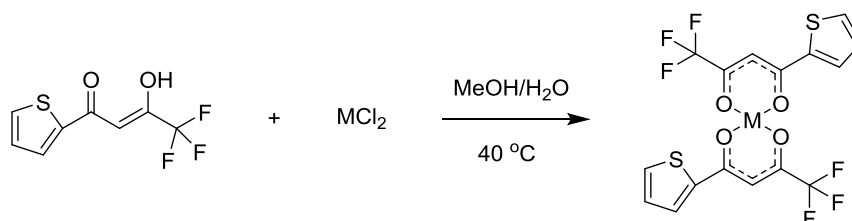


Figure 4.13: General synthesis of metal(II)-Htta complex. Moderate heat was apply in order to catalyse the complex formation

Synthesis of Pb(tta) and Hg(tta) complexes were avoided due to their high toxicity. Characterization of the complexes was done by CHN analysis, UV-vis spectroscopy, thermogravimetric analysis, and differential scanning calorimeter. NMR spectral analysis were not successful due to the paramagnetic nature of the complexes. The UV-vis spectra of the complexes were compared to the spectra from the ILs after the metal extraction experiment.

4.4.1. Instrumentation

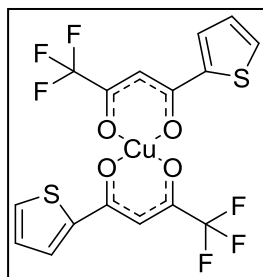
4.4.1.1. Thermogravimetric Analysis

Discovery TGA (TA Instruments) fitted to Discovery common cabinet was used. Platinum HT pan (100 μ L) were used for all analysis. The instrument was equilibrated at 40.00 $^{\circ}$ C. The ramp was set to be 20.00 $^{\circ}$ C/min throughout analysis and isothermal was set for 3 min after 100.00 $^{\circ}$ C. The results were reported in the weight of the sample (%) respect to temperature.

4.4.1.2. Differential Scanning Calorimeter

Discovery DSC (TA Instruments) fitted Discovery common cabinet was used. The samples were prepared in Tzero pan and lid using Tzero sample press kit. The ramp was set to be 5.00 °C/min to 150.00 °C, isothermal for 5 minutes, and 5.00 °C/min to -80 °C. The cycle was repeated three times. The results were reported as normalized heat flow respect to temperature.

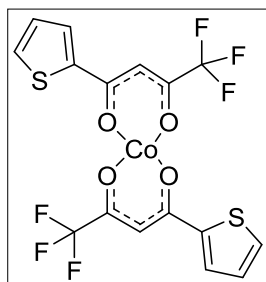
4.4.2. Synthesis of copper-di(2-trifluoroacetone) complex, Cu(tta)



In a 100 mL single-neck round-bottom flask, 2-thenoyltrifluoroacetone (3.34 g, 17.28 mmol, 2.0 eqv) was dissolved in 10 mL of methanol. While stirring with a magnetic stirrer, CuCl₂ (1.16 g, 8.64 mmol, 1.0 eqv) dissolved in minimal amount of ultrapure water was added into the mixture drop wise. The temperature was brought up to 40 °C and the reaction was left for 2 hours. After 2 hours, green crystals were vacuum filtered and washed with cold ultrapure water and cold methanol. The green crystals were air-dried overnight and collected (3.04 g, 60.8%).

CHN Analysis: calculated for C₁₆H₆CuF₆O₄S₂: C, 37.99; H, 1.59; found: C, 38.44; H, 1.24.

4.4.3. Synthesis of copper-di(2-trifluoroacetone) complex, Co(tta)



In a 50 mL single-neck round-bottom flask. 2-thenoyltrifluoroacetone (4.34 g, 19.53 mmol, 2 eqv) was dissolved in 10 mL of methanol. While stirring with a magnetic stirrer, CoCl_2 (2.32 g, 9.76 mmol, 2 eqv)

dissolved in minimal amount of ultrapure water was added in to the mixture dropwise. The temperature was brought up to 40 °C and the reaction was left for 2 hours. After 2 hours, milky orange solids were vacuum filtered. The collected solids were dried and dissolved in diethyl ether, then crushed out with hexane. Orange powdery solids were dried in vacuum at 70 °C and collected (0.51 g, 10.2 %).

CHN Analysis: calculated for $\text{C}_{16}\text{H}_6\text{CoF}_6\text{O}_4\text{S}_2$: C, 38.34; H, 1.61; found: C, 37.75; H, 1.34

4.5. Results and Discussion

Metal-ligand complexes of Co(tta) and Cu(tta) were synthesized. While Cu(tta) consisted of fine green crystals, Co(tta) consisted of orange powder, which were more difficult to purify in comparison. The UV-vis spectra (**Figure 4.14** and **Figure 4.15**) of the complexes and the $[\text{N}_{2224}][\text{NTf}_2]$ phases after the corresponding metal extractions showed matching peaks that indicate that the complexes formed in the ILs phase are the same as the complexes synthesized. This confirmation allows further studies on the metal extraction mechanisms and properties of the complexes. The structure of the complex helps to understand the chelation process where the release of protons of Htta molecules into the aqueous phase may occur. It is also supported by the study

of recycling process where the Htta molecules in the complex is re-protonated and metal ions are released into the aqueous acid phase.

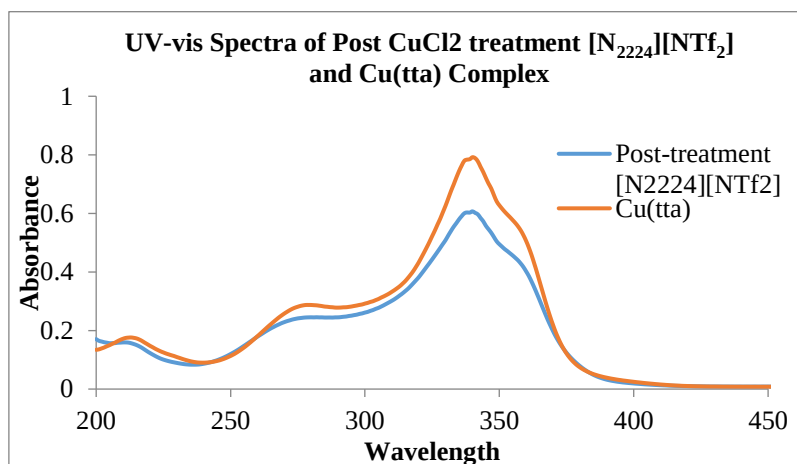


Figure 4.14: The UV-vis spectrum of $[N_{222}][NTf_2]$ after $CuCl_2$ treatment is compared with synthesized $Cu(tta)$ complex. The absorbance peaks at 342 nm are consistent in both spectra.

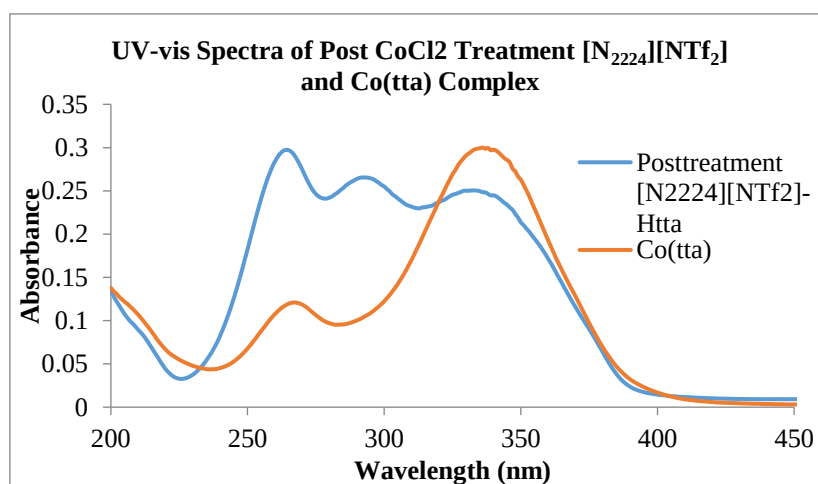


Figure 4.15: The UV-vis spectrum of $[N_{2224}][NTf_2]$ phase after $CoCl_2$ extraction is compared with synthesized $Co(tta)$ complex. The spectrum of $Co(tta)$ complex shows a peak at 339 nm. The IL phase shows apparent peak of Htta, but lacks the broad shoulder band of its enol form at 357 nm.

The results from TGA analysis of $Co(tta)$, $Cu(tta)$, and Htta show different decomposition temperatures of the complexes (**Figure 4.16**). While

Co(tta) begins to decompose at 222.6 °C and completely decomposes at 268.4 °C, Cu(tta) begins to decompose at 240.0 °C and completely decomposes at 297.6 °C. These differences in the decomposition temperature indicate that the Cu(tta) complex is more stable than the Co(tta) complex. These results from TGA analysis are consistent with the study by Jaffe, *et. al.* where the kinetic formation constant of monothienoyltrifluoroacetone complex of copper was much higher than the analogous cobalt complex.⁷² The result from DSC analysis are presented in Appendix.

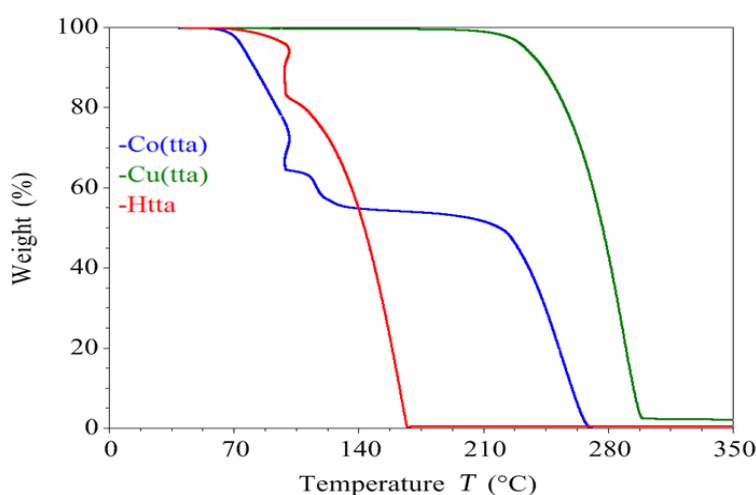


Figure 4.16: The result from TGA analysis of Htta (red), Co(tta), and Cu(tta) are presented. The first decomposition peak of Co(tta) is attributed to unreacted Htta complex within the structure.

4.6. Conclusion

The extraction of the metal chlorides by IL-Htta system were performed. The extraction of CuCl₂ improved drastically where the extraction of CoCl₂ and HgCl₂ were not as efficient, and the extraction efficiency from some of the PbCl₂ extraction experiments even decreased as compared to the extraction by ILs alone. The UV-vis spectra of ILs after the extraction process

showed corresponding appearance of Htta and/or metal(tta) complexes. It was also repeatedly observed that Htta is in the keto-hydrate form after being saturated by water especially in the PEGylated IL systems.

The solid complexes of Co(tta) and Cu(tta) were synthesized and characterised. Based on the results from CHN analysis, UV-vis spectroscopy, and TGA analysis, the extraction mechanism of CuCl₂ and CoCl₂ were determined to be neutral extraction where two ligands bound to one metal ion. The Cu(tta) complex was determined to be more stable than the Co(tta) complex. The stability of the complexes correspond to the extraction efficiencies as CuCl₂ were extracted more than CoCl₂. This correlation suggest that the combination of metal and ligand, as well as the stability of the corresponding complex primarily govern the extraction efficiency of the system.

5. Interaction of ILs, Htta, and Water

The results from the metal extraction experiments demonstrated that the extraction efficiency depends on the combination of ILs, metal ions being extracted, and the ligand, as well as their properties. Furthermore, the environment and condition of which the extraction process takes place must be also considered. The results from UV-vis spectroscopy analysis the IL phases after the metal extraction treatment with Htta suggested that water molecules play an important role in extraction using Htta and ILs. Thus, relationship between water, Htta, and ILs were investigated.

5.1. Experimentation

5.1.1. Moisture Measurement of ILs

Prior to the experiment, 0.6 mL of ionic liquids were dried at 5×10^{-5} atm at 70 °C in 3.5 mL vial (SAMLO) equipped with a larger test tube, connected to the shlenkline. After drying, the vial containing ILs were quickly capped. Two to three drops of IL was injected into the Karl-Fischer by using 1 mL syringe and needle. After the initial measurement, the remaining ILs were exposed to the atmosphere for 6 hours and the same measurement procedure was repeated. Water-saturated ILs were prepared by mixing 0.75 mL of IL and 15 mL of water were mixed for 2 hours in a 20 mL test tube. The water content of ionic liquids were measured by the same procedure as described previously.

5.1.2. Study of the Effect of Water in ILs

The structural effect of water on ILs were investigated by ATR-FTIR spectroscopy. Single measurements were obtained by measuring the background before the measurement and placing 1 to 2 drops of samples on the

surface of diamond. The tests on the effect of water in IL were done by placing 2 to 3 drops dry IL on the diamond surface of ATR-FTIR and a drop of ultrapure water next to the IL, barely in contact with the IL. Continuous measurement was taken until saturation of water was confirmed.

5.1.3. Htta Tautomerization Measurement

The stock solutions of Htta solution was prepared by making 1 mg/mL of Htta in acetonitrile in a 10 mL volumetric flask. The standard solutions of Htta-acetonitrile with varying concentrations of water were prepared by mixing 1 to 10 consecutive drops of water by syringe and needle with 200 μ L of the stock solution in the 10 mL volumetric flasks. The flasks were filled with acetonitrile to the line. The concentration of water in each standard solution was measured by Karl-Fischer moisturemeter. The UV-vis spectra of the standard solutions were taken by UV-vis spectrometer and the spectra are normalized by integrating the area under the curve using MatLab 2017a.

5.2. Instrumentation

5.2.1. Karl-Fischer Moisture Meter

CA-200 Moisturmeter (MITSUBISHI CHEMICAL ANALYTECH) was used to determine the moisture content of ILs. The instrument was titrated prior to measurement. The water content was reported in concentration in ppm and in mass per amount of sample injected in μ g.

5.2.2. ATR-FTIR

VERTEX 70 ATR-FT-IR (Bruker) was used for infrared spectroscopy measurements. The spectra of ILs were measured by locating IL on the diamond surface using a syringe and needle. All measurements were taken

with the resolution of 4 cm^{-1} , sample scan time of 32 scans, and background of 128 scans. The range of measurement was 6000 to 30 cm^{-1} . Repeated measurements were set up to maximum of 240 scans with 1 second delay between each measurement.

5.3. Results and Discussion

5.3.1. Moisture Content in ILs

The moisture measurements using Karl-Fischer moisture meter were performed to understand the structural effect of the ILs and their varying hygroscopicity. The results are presented in **Table 5.1**. The water contents of the ILs containing hydroxyl chain, $[\text{N}_{222}\text{C}_1\text{EG}_1][\text{NTf}_2]$, $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$, and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$, showed a greater water absorption capacity than the ILs with alkyl chain, except for $[\text{N}_{2224}][\text{NTf}_2]$, after being exposed to the atmosphere for 6 hours. The increase in hygroscopicity respect to the increase of the length of PEG chain is due to increased polarity of the side chain that enhances the interaction between the IL and water molecule.⁷³ Similarly, hygroscopicity decreases as the alkyl chain length increases because the non-polar, hydrophobic region of the ILs increases with the increasing alkyl chain length; repulsing the interaction of ILs and water molecules.⁷³ This effect can be also explained by the three dimensional structure of ILs whereby the charged and polar region of ILs are hidden by the swelling of nonpolar chain in a given dimension, physically blocking the more polar region of ILs to interact with water molecules on the surface of the IL.³⁵

Table 5.1: *The measurement of water content in ILs 1) soon after drying, 2) after six hours of exposure in atmosphere after drying, and 3) after saturated by water for 2 hours.*

Ionic Liquid	Water Content (ppm)		
	Dry	6 hrs	Water-saturated
[N ₂₂₂₄][NTf ₂]	17	2454.64	9664.1
[N ₂₂₂₈][NTf ₂]	19.9	1208.33	7195.2
[N ₂₂₂₍₁₂₎][NTf ₂]	20.14	547.06	5210.4
[N ₂₂₂ EG ₁ C ₁][NTf ₂]	479.85	19401.41	14720.8
[N ₂₂₂ EG ₂ C ₂][NTf ₂]	547.79	25040.98	26846.4
[N ₂₂₂ EG ₃ C ₂][NTf ₂]	564.2	25580.15	50063.5

The water absorption capacities of ILs are more distinctly seen in the measurement from the experiment of saturating ILs with water. From these results, it can be concluded that although [NTf₂]⁻-based ILs are considered to be hydrophobic, the concentration of water molecules present in ILs dramatically differ by changing the functional group, even within the same cationic core. This factor may play a crucial role in separation chemistry using ILs because presence of water in the IL phase could interfere with applications, as seen in the extraction experiments using Htta.

5.3.2. Structural Effect of Water in ILs

In order to understand the structural behavior of the ILs with water, ATR-FTIR spectra of each dry ILs were first assigned and studied. The spectra are presented from 1500 cm⁻¹ to 130 cm⁻¹ (see Appendix) and from 3050 cm⁻¹ to 2750 cm⁻¹ (**Figure 5.1** and **Figure 5.2**). The rest of the spectra is omitted as peaks related to the IL structures were not observed. The peaks of the spectra are assigned according to the literatures.⁷⁴⁻⁷⁷ The spectra between 3050 cm⁻¹ and 2750 cm⁻¹ correspond to the C-H stretching in cation, which differ

depending on the functional group due to the presence of the oxygen atom altering the electric environment of the cationic core as in the interaction of N-C-CH₂-O and N-C-CH₂-CH₂, which is also seen in the ¹H NMR analysis (Section 2.3.4).

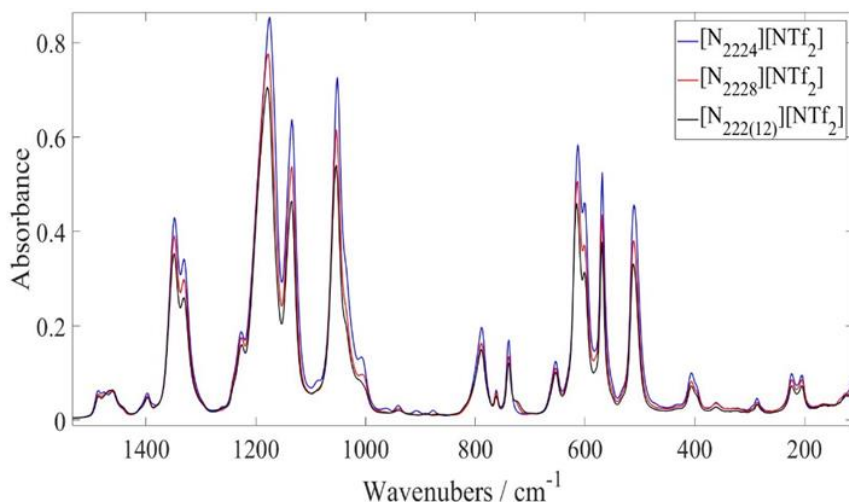


Figure 5.1: The ATR-IR spectra of alkyl ILs in the region of 1500 cm⁻¹ to 130 cm⁻¹ are overlaid. ILs were dried prior to the measurement and the measurement was taken at the room temperature.

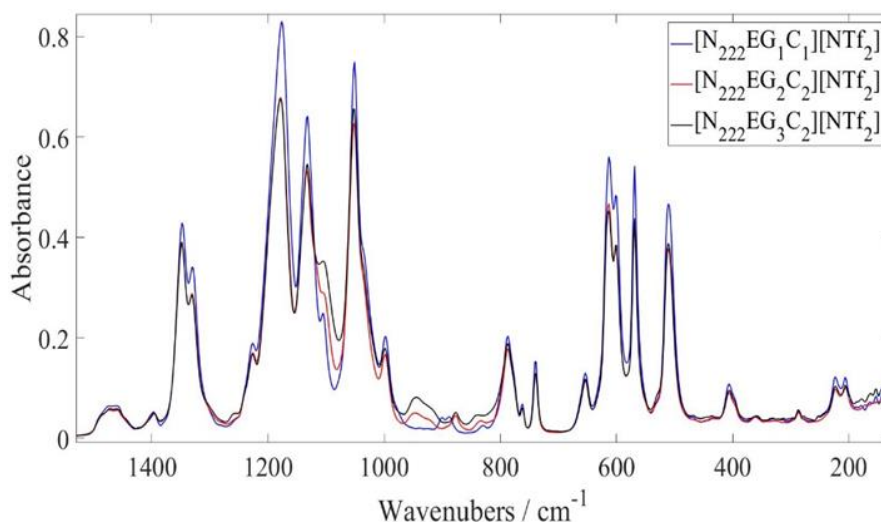


Figure 5.2: The ATR-FTIR spectra of PEGylated ILs in the region of 1500 cm⁻¹ to 130 cm⁻¹ are overlaid. The measurement parameter followed the same as the one for the measurement of alkyl ILs..

The region of 1500 to 130 cm^{-1} consists of both anionic and cationic bonding of the ILs with some differences in the spectra that can be assigned to the different cationic chain. First off, all ILs used in this study showed almost the same $[\text{NTf}_2]^-$ spectral appearances between 1473 and 997 cm^{-1} , and between 789 and 204 cm^{-1} with minor differences. The peaks between 1473 to 1460 cm^{-1} in PEGylated ILs and 1487 to 1460 cm^{-1} in alkyl-ILs are attributed to bending of C-H bonds in cation.⁷⁵ The spectra of PEGylated ILs in the region appeared to be consistent with very similar appearance of the peaks and their locations. In contrast, alkyl-ILs showed varying spectral appearances in the respective region. Based on these observations of the different C-H bending activities between the alkyl and PEGylated IL systems, the solvation and physical properties of ILs can be related. The increasing chain length of the ILs affects the structural behavior of H-C bonds in the alkyl ILs, but not as significant in the PEGylated systems. This observation can be related to the viscosity studies of dry ILs where the lowest viscosity in the alkyl ILs was 212.77 mPa.s for $[\text{N}_{2224}][\text{NTf}_2]$ and the highest was 522.05 mPa.s for $[\text{N}_{222(12)}][\text{NTf}_2]$, while the lowest viscosity in the PEGylated IL system was 91.87 mPa.s and the highest was 117.04 mPa.s for $[\text{N}_{222} \text{C}_{1}\text{EG}_1][\text{NTf}_2]$ $[\text{N}_{222} \text{C}_2\text{EG}_3][\text{NTf}_2]$, respectively (**Table 3.2**).

Besides the different appearance in C-H bending peaks, there are three minor notable differences between the PEGylated ILs and alkyl-ILs. The first difference is the peaks at 1105 cm^{-1} in the PEGylated ILs, which most likely indicate the C-O stretching of the ethylene glycol chain. Although the peaks come from the cationic chain, the presence of oxygen atoms in cation may have an affect on the structural behavior of the anion as the peak at 1134 cm^{-1}

in alkyl ILs, which attributes to O-S-O stretching in $[\text{NTf}_2]^-$,⁷⁷ has shifted to 1132 cm^{-1} in the PEGylated ILs.

Secondly, the peaks at 788 cm^{-1} in the alkyl ILs, which is attributed to C-S stretching of $[\text{NTf}_2]^-$,⁷⁶ have shifted to 786 cm^{-1} in the PEGylated ILs. Again, this is most likely due to the presence of the oxygen atoms in ILs as the same spectral effects have been observed for O-S-O stretching peak at 1132 cm^{-1} .

Thirdly, the peaks at 204 cm^{-1} , which resulted from rocking of CF_3 and twisting of SO_2 atoms,^{77, 78} have shifted to 206 cm^{-1} . This shift of the peaks is towards the higher wavenumber, which indicated a stronger vibrations of corresponding atoms. It is evident that the ethylene glycol chain is causing a structural difference and the responding behavior to $[\text{NTf}_2]^-$ molecules as compared to the alkyl IL system. Further, based on all of the peak shifts described above, a prediction can be developed that the oxygen atoms of the cation interfere with the sulfur atoms of the $[\text{NTf}_2]^-$ component. These intermolecular interactions of ILs alters the physical properties of the ILs that ultimately enhances or suppresses the efficiency of extraction processes.

In the region of 970 to 840 cm^{-1} , the peaks are assigned to be C-N interactions of the cations.⁷⁵ One notable spectral appearance in this region is the spectra of $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$. The spectra of these two followed the same appearance with peaks at 945 and 877 cm^{-1} , however, the spectrum of $[\text{N}_{222}\text{C}_1\text{EG}_1][\text{NTf}_2]$ consisted of peaks at 900 and 887 cm^{-1} in the same region. This difference may indicate that increasing the ethylene glycol chain in the IL system does not play a significant role on changing the

property of the ILs after the second ethylene glycol group. This observation may be related to the densities of $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ whose densities were measured to be 1.342 g/mL, as the difference in the densities of the ILs were negligible. Nevertheless, in order to confirm this, a more precise investigation of $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$ and $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ is required. If the two ILs possesses almost identical properties, use of $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$ is preferred over $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2]$ in order to improve the atom economy of the system, and because of simplicity in synthesis of $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$.

Because the amount of water present in IL affects the nature of ILs and the structural behavior of Htta as discussed previously, continuous ATR-FT-IR spectra of ILs respect to saturation by water were monitored and obtained.

Figure 5.3 shows the representative spectra of $[\text{N}_{2228}][\text{NTf}_2]$ where saturation of water is observed in the region between 3750 cm^{-1} to 3060 cm^{-1} and 1720 cm^{-1} to 1570 cm^{-1} , which are assigned to be O-H stretch and O-H bend of the water molecule, respectively. The region between 500 cm^{-1} and 220 cm^{-1} also changed the intensity of the absorbance peaks as the concentration of the water increased (**Figure 5.4**). As discussed previously, this region of ILs are attributed to anionic component; specifically to the sulphur atoms of $[\text{NTf}_2]^-$. This change in the spectra indicates that, although $[\text{NTf}_2]^-$ is considered to be a hydrophobic anion, water molecule interacts with $[\text{NTf}_2]^-$ more than they interact with the cationic component of the ILs. The same effect was observed in the analogous IL, $[\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2]$, where the same change in the spectra was obtained (see Appendix).

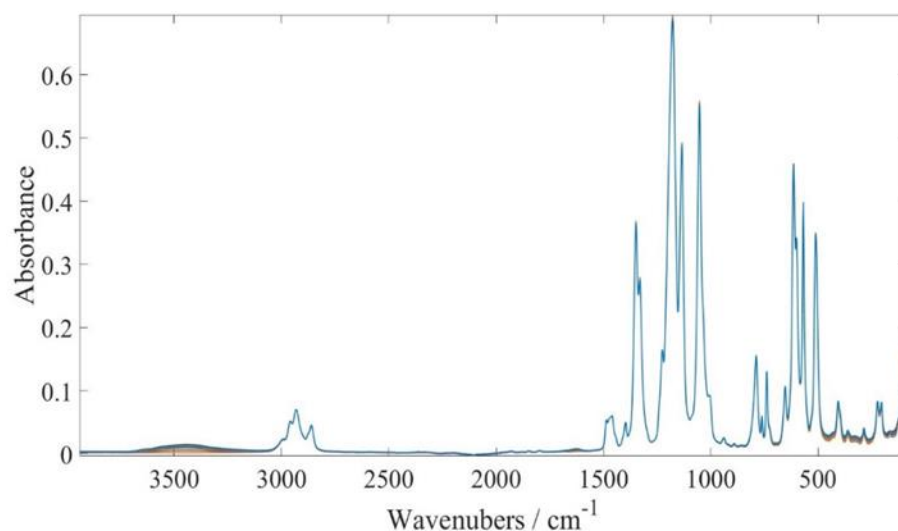


Figure 5.3: The continuous ATR-FTIR spectra of $[N_{2228}][NTf_2]$ by water over time. The changes in absorbance are recorded around 3400 cm^{-1} (O-H stretch), 1600 cm^{-1} (O-H bend), and 500 to 200 cm^{-1} .

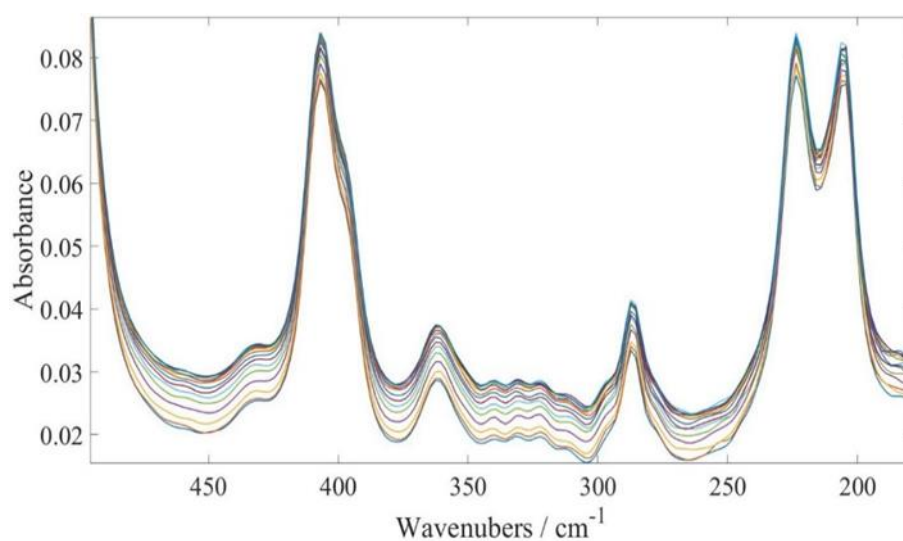


Figure 5.4: The focused Spectra of ATR-FTIR Spectra of $[N_{2228}][NTf_2]$ (Figure 5.3) between 500 to 200 cm^{-1} . Saturation of water in the IL is observed overtime.

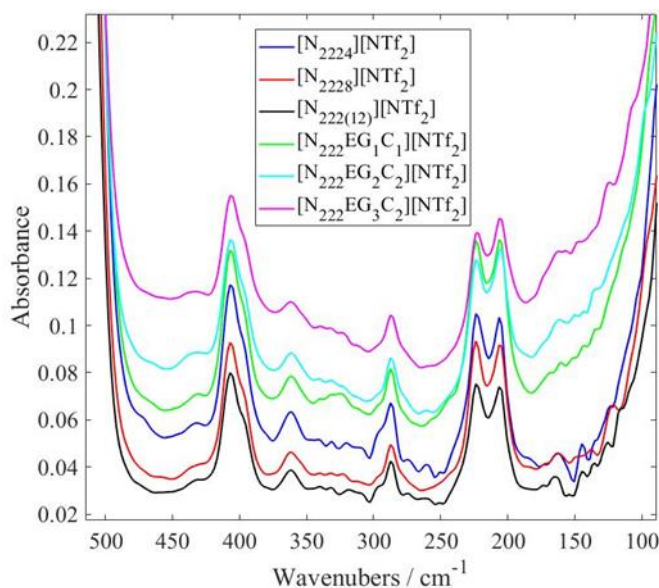


Figure 5.5: The focused view of ATR-FTIR spectra of all ILs saturated by water overnight.

The hydrophobicity of ILs, which is tuned by changing the cationic component, can also be observed in the spectra of the same region of 500 to 200 cm^{-1} (**Figure 5.5**). Each IL was saturated by water overnight prior to the measurement. In the anionic region where the effect of water saturation is observed, the order of water saturation level in the ILs is recorded as $[\text{N}_{222}\text{C}_2\text{EG}_3][\text{NTf}_2] < [\text{N}_{222}\text{C}_2\text{EG}_2][\text{NTf}_2] < [\text{N}_{222}\text{C}_1\text{EG}_1][\text{NTf}_2] < [\text{N}_{2224}][\text{NTf}_2] < [\text{N}_{2228}][\text{NTf}_2] < [\text{N}_{222(12)}][\text{NTf}_2]$. This order is in agreement with the result from the Karl-Fischer measurement where the water content in ILs decreased with increasing alkane chain length and the effect was reverse in the PEGylated IL system. These observations of cationic effect validate that O-S-O component of $[\text{NTf}_2]^{-1}$ is responsible for interacting with the water molecules, whose hydrophobicity is depended on the overall polarity of the cation. It is important to note such effects and behaviour of the ILs if the water contents in ILs alter the outcome of IL applications.

5.3.3. Htta Tautomerization

To understand the behaviour of Htta respect to presence of water, UV-vis spectra of Htta tautomerization were recorded with increasing concentration of water in the solution of acetonitrile and Htta (**Figure 5.6**). The collected data were normalized to the area under the curve to obtain the spectra respect to the molar concentration of Htta molecule in the solution. From the spectra obtained, the isosbestic point of tautomerization of Htta at 305 nm was determined, which is in agreement with previous literatures.^{70, 79} Although there are two other isosbestic points at 208 and 227 nm that were not discussed in the previous studies, these isosbestic points may indicate other conformational change of Htta within the enol and keto-hydrate form,⁶⁸ whose stability may also be affected by the presence of water.

Additionally, with the spectra of tautomerization, more specific assignment of the peaks is possible. According to the literature, the peak at 267 nm is attributed to the electric transition of thiopene ring, 296 nm is for the keto-hydrate carbonyl group and its tautomeric transition, and 327 nm is for the electric transition of the delocalization of the ligand.⁸⁰ With the spectra of Htta tautomerization, the activities of Htta molecules with the targeted metal ions can be monitored to the amount of water present in ILs.

Also, based on the spectra obtained, the majority of tautomerization of Htta from enol to keto-hydrate form is complete somewhere between 4032 ppm to 5760 ppm of water is present in the solution. The experiment of the moisture content in ILs showed that only [N₂₂₂(12)][NTf₂] was able to maintain that level of water content after saturation. These results indicate that for the purpose of maintaining the enol form of Htta - the form that allows the ligand

to react with metal ions to form a complex - $[N_{222(12)}][NTf_2]$ has the best capacity, despite the lower extraction efficiency due to its high viscosity. Although it is difficult to control the exact amount of water present in IL during the extraction treatment by Htta-IL system, the water absorption capacity of ILs must be considered in order to optimise the extraction efficiency.

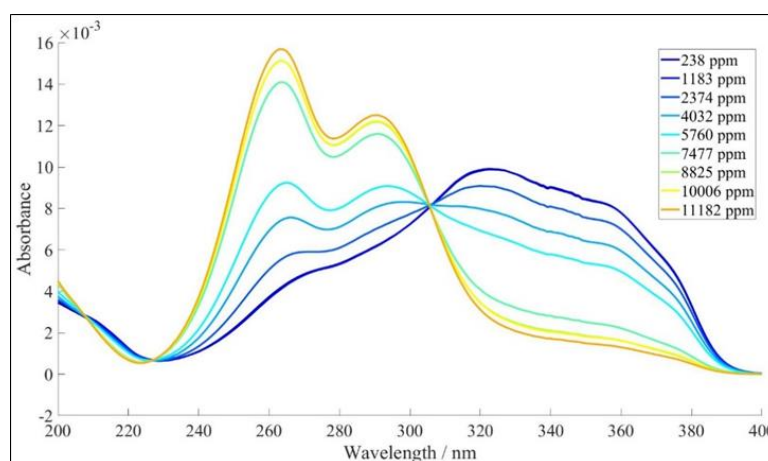


Figure 5.6: The tautomerization curve of Htta was obtained by increasing the water content in the solution of acetonitrile and Htta. Its Isosbetic point is at 305 nm.

5.3.4. Conclusion

The relationships between the structure of the ILs and Htta respect to the presence of water were investigated. The ATR-FTIR study revealed that the oxygen atoms of the PEGylated ILs effect the structural behaviour of $[NTf_2]^-$ molecules, specifically at its sulphur atoms. The experiments of saturating ILs with water further demonstrated that the water molecules interfere with the O-S-O region of $[NTf_2]^-$. The interference by water increases with longer ethylene glycol chain and decreases with longer alkyl chain, which was also demonstrated in the moisture meter experiment.

The study of tautomerization of Htta provided its detailed structural behaviour respect to the concentration of water in its surround environment. The structural behaviour of Htta is affected by the water content of ILs, which was also seen in the UV-vis spectra of IL phase after the extraction processes. These combined results suggest that in the application of ionisable ligands with ILs, hydrophobicity of ILs must be considered on top of other physical and chemical properties of ILs such as viscosity.

6. Conclusion and Future Work

6.1. Overall Conclusion

In this project, alkyl- and PEGylated triethylammonium ILs on extraction of copper, cobalt, lead, and mercury were investigated. The extraction efficiency by ILs mainly depend on the physical property of ILs such as viscosity, which are altered by the functional group within the same cation core and anion pair. However, despite the initial hypotheses based on HSAB theory, PEGylated ILs did not show effective extraction property of copper and cobalt. Extraction of the selected heavy metals by ILs showed small extraction abilities. Therefore, the direction of the project changed to biphasic extraction using a chelating ligand, Htta.

In the treatment of the heavy metals by Htta, it was demonstrated that Htta is most suitable to extract copper of all the selected heavy metal chlorides. The high extraction efficiency is due to the stability of the metal-ligand complex, which was supported by synthesizing the complexes and measuring their thermodynamic stability. However, extraction of lead showed that combination of the ligand and metal can also suppress the extraction efficiency as compared to extraction only by ILs. Such a difference in extraction efficiency would allow selective extraction from a solution containing multiple metal ions. It was also demonstrated that ILs and Htta molecules can be recycled after the metal extraction treatment with aqueous acids.

To further understand the behaviour of Htta and ILs within the extraction systems, the structural effects of ILs and Htta respect to the presence of water were investigated. Because Htta undergoes tautomerization with the

presence of water whereby only the enol form of the ligand is able to react with metal ions, Htta takes different structural conformation in different ILs. This effect is directly affected by the physical properties of the IL wherein the ethylene glycol chain enhances the interaction of water and ILs, increasing the water content within the IL phase; favouring the keto-hydrate form of Htta. Also, the studies by ATR-FTIR demonstrated that within the triethylammonium-based $[\text{NTf}_2]^-$ ILs, the sulphur atoms of the $[\text{NTf}_2]^-$ molecules are mostly responsible for the hygroscopic property of the ILs, which is increased or decreased by the cationic functional group. It is important to note that while $[\text{NTf}]^-$ is considered to be one of the most hydrophobic ILs, $[\text{NTf}_2]^-$ itself interact with water and affect the behaviour of the solutes in the system.

These findings and relationships between the ILs, Htta, and water, revealed important factors respect to the outcome of the heavy metal extraction experiments. In the applications of utilizing ILs in metal extraction, these factors involving metal extractions must be considered in order to develop a greener and more efficient treatment process.

6.2. Future Work

To improve the overall project procedure and increase the amount of results, the scale of the experiment is desired to be reduced. As described in Section 2.2, 15 mL of sample aqueous per measurement was needed in order to produce 3 repeated measurement during the ICP-OES analysis. For 15 mL of aqueous sample, 0.75 mL of IL was used (5% by volume) where 3 trials per experiment were required to monitor the consistency of each experiment. Ultimately, this scale of the experiment limited a further investigation on other

metals as well as optimization of extraction process due to the large amount of ILs required overall. The improvement for this solution can be made by applying microextraction procedure proposed by Fischer, *et. al.*,³⁹ where they used 0.01 mL of IL per experiment. Such a smaller scale would allow a wider comparative studies with different ILs metal ions, ligands, and extraction parameters.

In terms of the designing of the IL, triethylammonium was suited cation core because of the simplicity in synthesis. One change that would improve the overall atom economy of the system is to change the alkyl chain of the cation to trimethyl group. Although this change in the structure may also alter the hydrophobicity of the ILs, by keeping the fourth alkyl chain long enough - perhaps as long as an octyl chain - the hydrophobicity of ILs can be maintained. Additionally, by decreasing the amount of hydrocarbons within the system, the overall electrostatic force will also decrease, hence the viscosity of the system would be decreased, as lowering the viscosity of ILs contributes to improve the extraction efficiency. Conclusively, butyl and octyl sidechain ILs performed the majority of the highest extraction, thus any longer lengths of the fourth alkyl chain can be eliminated in the future work.

For the application of PEGylated ILs, it would be interesting to investigate if the PEGylated ILs are capable to interact with smaller metals such as alkaline earth metals without using additional ligands. If the PEGylated ILs possess an affinity to smaller metals, which was not the case in the larger heavy metals extraction experiments, a selective extraction of alkaline earth metals from a solution containing multiple kinds of metal ions would be achievable.

Although the experiments using ILs with thio-based sidechain was not possible due to the low product yield, sulphur-containing ILs are still attractive in the application of soft heavy metal extraction. An alternative way of synthesizing $[N_{222}EtS_1Me][NTf_2]$ would be to change the reagent to thio-containing amine group and alkylate the cationic core with ethyl iodide, which should result in a higher product yield as iodide molecules are more reactive as compared to chloride and bromide molecules.

As seen in the Section 4, the thermodynamic properties of synthesized metal-ligand complexes can be used to predict the extraction efficiency of the metals. For this reason, the metal-ligand complexes can be synthesized and characterized *prior* to the extraction experiment in order to select the correct pairs of the metal and ligands. This strategy would help to target the metals in the future study. For example, Jaffe, *et. al.* determined the equilibrium constant of formation of Fe^{3+} and monothienyltrifluoroacetone to be 1.0×10^3 , which is much higher than the value of its analogous Co^{2+} complex, 3.2×10^{-1} .⁷² Based on these values, extraction efficiency of Fe^{3+} ions by Htta must be greater than the result from $CoCl_2$ extraction. However, to develop a parallel condition as the extraction method, external factors such as pH, temperature, and buffers in the synthesis must be the same, or at least very similar to, the parameter of extraction.

To complete the cycle of metal extraction process, recycling methods must be improved. Although recycling of ILs was achieved by the use of aqueous acid, the use of acids are desired to be avoided at a larger scale of treatment due to their hazard and toxicity. Instead, recycling of ILs by metal deposition by means of electrochemical treatment may be very beneficial.

During this project, electrochemical window of [N₂₂₂₄][NTf₂] and [N₂₂₂₈][NTf₂] (see Appendix) were obtained, however, due to the complication of establishing the experiment involving electrochemical factors such as selection of the electrodes and experimental parameters, the project in the electrochemical sector was no longer continued.

Finally, the leaching effect of ILs into the aqueous phase must be emphasized to apply the system in the industrial scale. If the purpose of the treatment is only to extract metal ions from an aqueous solution, leaching of IL may not be as concerning. But if the ultimate purpose of the treatment is to produce clean water at the end, the leaching effect of IL into the aqueous phase is seriously concerning, as the toxicity of ILs differ by different functional groups. It is, however, possible to distillate water from IL as ILs have extremely low vapour pressure, though such an extra step would defeat the idea of the simplicity of extraction treatment by ILs.

To conclude, there are numbers of factors that can improve the metal extraction efficiency, the effectiveness of the treatment, and the applicability of the established treatment methods to the industrial use. The factors elaborated based on the outcome of this project will help to improve the future application of ILs.

7. Acknowledgements

First and foremost, I would like to thank my supervisor, Prof. Peter Licence, for his guidance and advises throughout my research. He has taught me how to carry a research independently and provided with very useful tools and insights. Without his time and effort, my experience at the University of Nottingham would not have been the same. Thank you, Pete.

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8. References

1. M. Palaniappan, Gleick, P., Allen, L., Cohen, M., Christian-Smith, J., Smith, C., *Journal*, 2010.
2. E. Corcoran, Nellesmann, C., Baker, E., Bos, R., Osborn, D., Savelli, H., *Sick Water? The central role of wastewater management in sustainable development*, United Nations Environment Programme, Norway, 2010.
3. B. Yousaf, G. J. Liu, R. W. Wang, M. Imtiaz, M. Zia-ur-Rehman, M. A. M. Munir and Z. Y. Niu, *Environ. Sci. Pollut. Res.*, 2016, **23**, 22443-22453.
4. A. Khan, S. Khan, M. A. Khan, Z. Qamar and M. Waqas, *Environ. Sci. Pollut. Res.*, 2015, **22**, 13772-13799.
5. A. Kumar and M. Holuszko, *Resources-Basel*, 2016, **5**, 19.
6. D. G. Barceloux, *J. Toxicol.-Clin. Toxicol.*, 1999, **37**, 217-230.
7. V. Mishra, *Desalin. Water Treat.*, 2016, **57**, 12141-12155.
8. O. B. Akpor and M. Muchie, *Int. J. Phys. Sci.*, 2010, **5**, 1807-1817.
9. N. Gupta, A. K. Kushwaha and M. C. Chattopadhyaya, *J. Taiwan Inst. Chem. Eng.*, 2012, **43**, 125-131.
10. J. Kim, Gibb, H., Howe, P., *Cobalt and Inorganic Cobalt Compounds*, United Nations Environment Programme, the International Labour Organization, the World Health Organization, Stuttgart, Germany, 2006.
11. A. K. Dalai and B. H. Davis, *Applied Catalysis a-General*, 2008, **348**, 1-15.
12. F. Ghanbari and M. Moradi, *Chem. Eng. J.*, 2017, **310**, 41-62.
13. A. Akcil, F. Veglio, F. Ferella, M. D. Okudan and A. Tuncuk, *Waste Manage.*, 2015, **45**, 420-433.
14. S. H. Abdel-Halim, A. M. A. Shehata and M. F. El-Shahat, *Water Res.*, 2003, **37**, 1678-1683.
15. K. H. Nelke, M. Mulak, K. Luczak, W. Pawlak, J. Nienartowicz, D. Szumny, M. Kochman and H. Gerber, *Pol. J. Environ. Stud.*, 2015, **24**, 1491-1496.
16. M. Ekinici, E. Ceylan, H. H. Cagatay, S. Keles, H. Altinkaynak, B. Kartal, Y. Koban and N. Huseyinoglu, *Curr. Eye Res.*, 2014, **39**, 853-858.
17. J. Zheng, K. H. Chen, X. Yan, S. J. Chen, G. C. Hu, X. W. Peng, J. G. Yuan, B. X. Mai and Z. Y. Yang, *Ecotox. Environ. Safe.*, 2013, **96**, 205-212.
18. W. C. Tsai, M. D. G. de Luna, H. L. P. Bermillo-Arriesgado, C. M. Futralan, J. I. Colades and M. W. Wan, *International Journal of Polymer Science*, 2016, DOI: 10.1155/2016/1608939.
19. B. F. Trueman, E. Camara and G. A. Gagnon, *Environ. Sci. Technol.*, 2016, **50**, 7389-7396.
20. T. W. Clarkson and L. Magos, *Crit. Rev. Toxicol.*, 2006, **36**, 609-662.
21. L. Jarup, Department of Epidemiology and Public Health, Imperial College, London, UK, *British Medical Bulletin*, 2003, **68**, 167-182.
22. Y. A. Hu and H. F. Cheng, *Environ. Pollut.*, 2016, **218**, 1209-1221.

23. M. E. Finster, M. R. Raymond, M. A. Scofield and K. P. Smith, *J. Environ. Manage.*, 2015, **161**, 303-308.
24. C. H. Lee, S. R. Popuri, Y. H. Peng, S. S. Fang, K. L. Lin, K. S. Fan and T. C. Chang, *J. Mater. Cycles Waste Manag.*, 2015, **17**, 312-323.
25. World Health Organization, *Int. J. Environ. Sci. Technol.*, 1990.
26. C. J. Lin and S. O. Pehkonen, *Atmos. Environ.*, 1999, **33**, 2067-2079.
27. S. Yoshida, S. Matsumoto, T. Kanchika, T. Hagiwara and T. Minami, *Neurotoxicology*, 2016, **57**, 69-74.
28. V. N. Thekkudan, V. K. Vaidyanathan, S. K. Ponnusamy, C. Charles, S. Sundar, D. Vishnu, S. Anbalagan, V. K. Vaithyanathan and S. Subramanian, *IET Nanobiotechnol.*, 2017, **11**, 213-224.
29. F. L. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407-418.
30. A. Azimi, A. Azari, M. Rezakazemi and M. Ansarpour, *Chembioeng Reviews*, 2017, **4**, 37-59.
31. T. A. Kurniawan, G. Y. S. Chan, W. H. Lo and S. Babel, *Chem. Eng. J.*, 2006, **118**, 83-98.
32. J. Park, Y. Jung, P. Kusumah, J. Lee, K. Kwon and C. K. Lee, *Int. J. Mol. Sci.*, 2014, **15**, 15320-15343.
33. R. Rama, A. Rout, K. A. Venkatesan and M. P. Antony, *Separation and Purification Technology*, 2017, **172**, 7-15.
34. J. F. Brennecke and E. J. Maginn, *Aiche J.*, 2001, **47**, 2384-2389.
35. J. Lopes and A. A. H. Padua, *J. Phys. Chem. B*, 2006, **110**, 3330-3335.
36. M. H. Ghatee, M. Bahrami and N. Khanjari, *Journal of Chemical Thermodynamics*, 2013, **65**, 42-52.
37. R. Arvai, F. Toulgoat, B. R. Langlois, J. Y. Sanchez and M. Medebielle, *Tetrahedron*, 2009, **65**, 5361-5368.
38. T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659-1663.
39. L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601-4614.
40. M. J. Salar-Garcia, V. M. Ortiz-Martinez, F. J. Hernandez-Fernandez, A. P. de los Rios and J. Quesada-Medina, *J. Hazard. Mater.*, 2017, **321**, 484-499.
41. D. Kogelnig, A. Stojanovic, M. Galanski, M. Groessl, F. Iirsa, R. Krachler and B. K. Keppler, *Tetrahedron Letters*, 2008, **49**, 2782-2785.
42. V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, Torocheshnikova, II, S. V. Smirnova and I. V. Pletnev, *Talanta*, 2010, **80**, 1177-1182.
43. M. A. V. Vergara, I. V. Lijanova, N. V. Likhanova, O. O. Xometl, D. J. Viguera and A. J. M. Ramirez, *Separation and Purification Technology*, 2015, **155**, 110-117.
44. W. J. Lu, P. S. Barber, S. P. Kelley and R. D. Rogers, *Dalton Transactions*, 2013, **42**, 12908-12916.
45. A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis and R. D. Rogers, *Environ. Sci. Technol.*, 2002, **36**, 2523-2529.
46. N. Papaiconomou, J. M. Lee, J. Salminen, M. von Stosch and J. M. Prausnitz, *Industrial & Engineering Chemistry Research*, 2008, **47**, 5080-5086.

47. R. G. Pearson, *Coord. Chem. Rev.*, 1990, **100**, 403-425.
48. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533-&.
49. C. H. C. Janssen, N. A. Macias-Ruvalcaba, M. Aguilar-Martinez and M. N. Kobrak, *International Reviews in Physical Chemistry*, 2015, **34**, 591-622.
50. S. S. Swain, B. Nayak, N. Devi, S. Das and N. Swain, *Hydrometallurgy*, 2016, **162**, 63-70.
51. A. Rout and K. Binnemans, *Dalton Transactions*, 2015, **44**, 1379-1387.
52. R. Germani, M. V. Mancini, G. Savelli and N. Spreti, *Tetrahedron Letters*, 2007, **48**, 1767-1769.
53. M. Kobrak, *Solvent Extr. Ion Exch.*, 2008, **26**, 735-748.
54. C. H. C. Janssen, A. Sanchez, G. J. Witkamp and M. N. Kobrak, *ChemPhysChem*, 2013, **14**, 3806-3813.
55. G. Chauhan, K. K. Pant and K. D. P. Nigam, *Environmental Science-Processes & Impacts*, 2015, **17**, 12-40.
56. H. Luo, S. Dai, P. V. Bonnesen, T. J. Haverlock, B. A. Moyer and A. C. Buchanan, *Solvent Extr. Ion Exch.*, 2006, **24**, 19-31.
57. K. Kidani, N. Hirayama and H. Imura, *Anal. Sci.*, 2008, **24**, 1251-1254.
58. H. Shirota, H. Fukazawa, T. Fujisawa and J. F. Wishart, *J. Phys. Chem. B*, 2010, **114**, 9400-9412.
59. H. S. Schrekker, D. O. Silva, M. A. Gelesky, M. P. Stracke, C. M. L. Schrekker, R. S. Goncalves and J. Dupont, *Journal of the Brazilian Chemical Society*, 2008, **19**, 426-433.
60. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
61. M. Regel-Rosocka and M. Wisniewski, *Applications of Ionic Liquids in Science and Technology*, 2011, 375-398.
62. T. W. Peter Wasserscheid, 2002.
63. A. Baghban, M. N. Kardani and S. Habibzadeh, *Journal of Molecular Liquids*, 2017, **236**, 452-464.
64. S. O. Wang, J. Z. Liu, L. Y. Yuan, Z. P. Cui, J. Peng, J. Q. Li, M. L. Zhai and W. J. Liu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18729-18735.
65. Y. Baba, F. Kubota, N. Kamiya and M. Goto, *J. Chem. Eng. Jpn.*, 2011, **44**, 679-685.
66. V. K. Manchanda and C. A. Chang, *Analytical Chemistry*, 1986, **58**, 2269-2275.
67. M. P. Jensen, M. Borkowski, I. Laszak, J. V. Beitz, P. G. Rickert and M. L. Dietz, *Separation Science and Technology*, 2012, **47**, 233-243.
68. S. F. Tayyari, A. R. Nekoei, M. Vakili, M. Hassanpour and Y. A. Wang, *Journal of Theoretical & Computational Chemistry*, 2006, **5**, 647-664.
69. S. Jafari, M. R. Yafian and M. Parinejad, *Iranian Journal of Chemistry & Chemical Engineering-International English Edition*, 2011, **30**, 89-96.
70. I. Billard, S. Mekki, A. Ouadi, C. Gaillard, D. Trubert and G. Moutiers, *Comptes Rendus Chimie*, 2007, **10**, 1117-1121.
71. D. O. S. Henri S. Schrekker, Marcos A. Gelesky, Marcel P. Stracke, Clarissa M. L. Schrekker, Reinaldo S. Concalves, Jairton Dupont, *Journal of the Brazilian Chemical Society*, 2008, **19**, 426-433.

72. D. P. F. Marvin R. Jaffe, Michael Cefola, Norman Sutin, *J. Am. Chem. Soc.*, 1971, **93**, 2878-2886.
73. Y. Y. Cao, Y. Chen, X. F. Sun, Z. M. Zhang and T. C. Mu, *Phys. Chem. Chem. Phys.*, 2012, **14**, 12252-12262.
74. F. M. Vitucci, F. Trequattrini, O. Palumbo, J. B. Brubach, P. Roy and A. Paolone, *Vib. Spectrosc.*, 2014, **74**, 81-87.
75. K. Hanke, M. Kaufmann, G. Schwaab, M. Havenith, C. T. Wolke, O. Gorlova, M. A. Johnson, B. P. Kar, W. Sander and E. Sanchez-Garcia, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8518-8529.
76. M. Herstedt, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant and J. C. Lassegues, *Journal of Raman Spectroscopy*, 2005, **36**, 762-770.
77. I. Rey, P. Johansson, J. Lindgren, J. C. Lassegues, J. Grondin and L. Servant, *J. Phys. Chem. A*, 1998, **102**, 3249-3258.
78. H. Azizi-Toupkanloo, S. F. Tayyari and P. Nancarrow, *J. Iran Chem. Soc.*, 2017, **14**, 1281-1300.
79. K. Kidani and H. Imura, *Talanta*, 2010, **83**, 299-304.
80. Z. M. Chen, Y. Q. Wu, F. X. Huang, D. H. Gu and F. X. Gan, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 2007, **66**, 1024-1029.

9. Appendix

Appendix i: Average metal extraction efficiency (%) by ionic liquids.

IL	CoCl ₂	CuCl ₂	PbCl ₂	HgCl ₂
[N ₂₂₂₄][NTf ₂]	3.44 ± 0.79	5.11 ± 0.47	8.51 ± 1.14	7.03 ± 1.10
[N ₂₂₂₈][NTf ₂]	2.64 ± 0.58	7.66 ± 1.26	8.57 ± 0.58	10.27 ± 0.61
[N ₂₂₂₍₁₂₎][NTf ₂]	-0.48 ± 0.90	-0.97 ± 0.58	2.94 ± 1.44	3.87 ± 0.59
[N ₂₂₂ C ₁ EG ₁][NTf ₂]	1.73 ± 0.70	5.42 ± 0.49	7.37 ± 0.67	6.04 ± 0.43
[N ₂₂₂ C ₂ EG ₂][NTf ₂]	3.28 ± 0.76	5.65 ± 1.30	5.99 ± 0.25	0.94 ± 1.24
[N ₂₂₂ C ₂ EG ₃][NTf ₂]	3.51 ± 0.60	3.31 ± 0.90	17.63 ± 0.93	7.11 ± 0.73

Appendix ii: Average metal extraction efficiency (%) by ionic liquids and Htta.

IL/Htta	CoCl ₂	CuCl ₂	PbCl ₂	HgCl ₂
[N ₂₂₂₄][NTf ₂]	14.35 ± 1.23	40.83 ± 0.25	8.03 ± 0.70	15.84 ± 3.14
[N ₂₂₂₈][NTf ₂]	9.91 ± 1.37	35.97 ± 2.38	7.79 ± 0.70	19.20 ± 0.34
[N ₂₂₂₍₁₂₎][NTf ₂]	5.39 ± 0.68	31.64 ± 2.09	1.52 ± 0.91	8.19 ± 3.42
[N ₂₂₂ C ₁ EG ₁][NTf ₂]	10.97 ± 0.59	40.53 ± 1.39	7.15 ± 0.34	17.29 ± 1.18
[N ₂₂₂ C ₂ EG ₂][NTf ₂]	10.35 ± 0.23	37.18 ± 0.45	7.70 ± 0.34	14.21 ± 3.95
[N ₂₂₂ C ₂ EG ₃][NTf ₂]	8.83 ± 0.41	39.33 ± 0.56	13.12 ± 2.93	26.50 ± 0.90

Appendix iii: Distribution constant from metal extraction by ionic liquids.

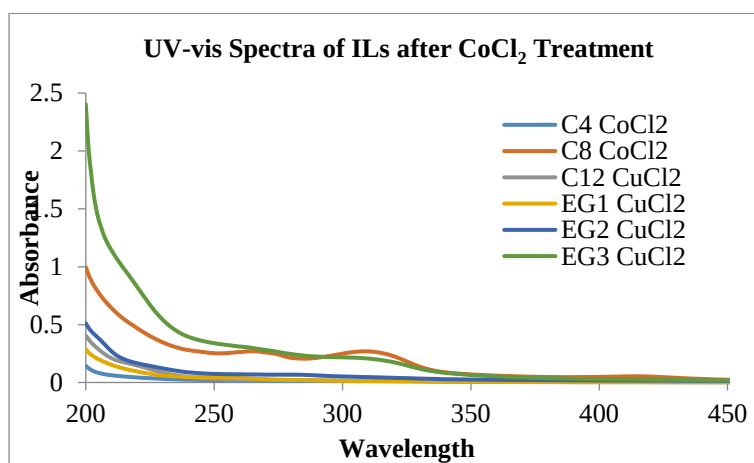
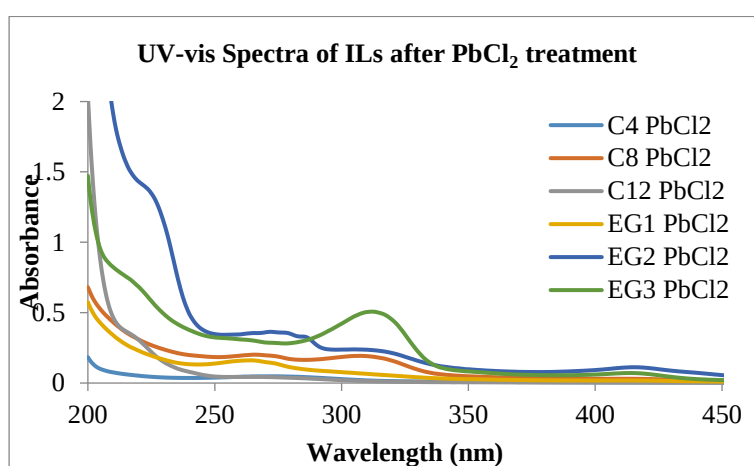
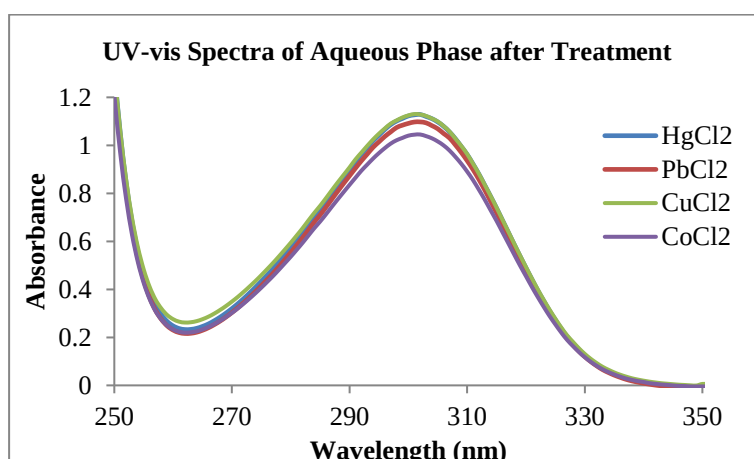
IL	CoCl ₂	CuCl ₂	PbCl ₂	HgCl ₂
[N ₂₂₂₄][NTf ₂]	0.69	1.02	1.70	1.41
[N ₂₂₂₈][NTf ₂]	0.53	1.53	1.71	2.06
[N ₂₂₂₍₁₂₎][NTf ₂]	-0.10	-0.20	0.59	0.78
[N ₂₂₂ C ₁ EG ₁][NTf ₂]	0.35	1.09	1.47	1.21
[N ₂₂₂ C ₂ EG ₂][NTf ₂]	0.66	1.13	1.20	0.19
[N ₂₂₂ C ₂ EG ₃][NTf ₂]	0.70	0.66	3.53	1.42

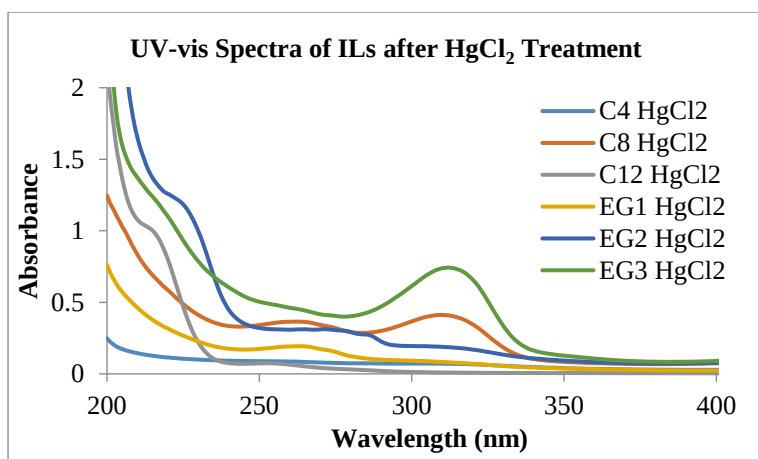
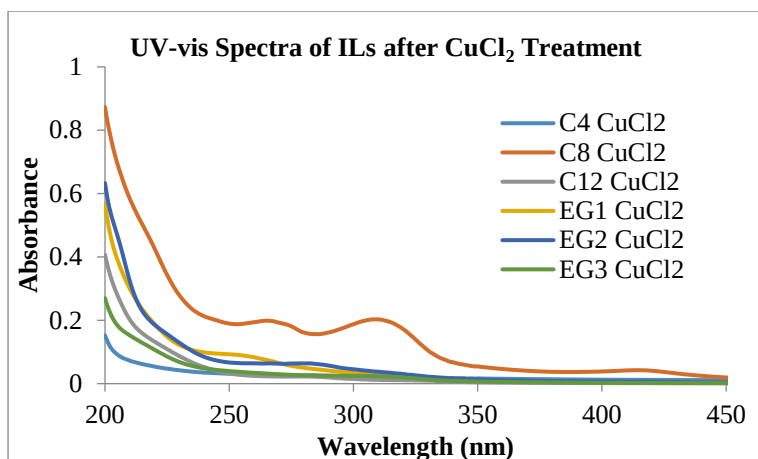
Appendix iv: Distribution constant from metal extraction by ionic liquids and Htta.

IL/Htta	CoCl ₂	CuCl ₂	PbCl ₂	HgCl ₂
[N ₂₂₂₄][NTf ₂]	2.87	8.17	1.61	3.17
[N ₂₂₂₈][NTf ₂]	1.98	7.19	1.56	3.84
[N ₂₂₂₍₁₂₎][NTf ₂]	1.08	6.33	0.30	1.64

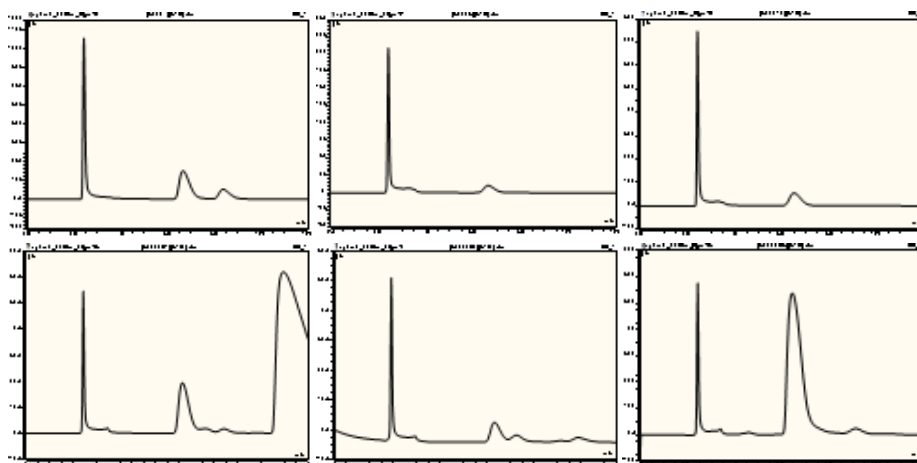
$[N_{222}C_1EG_1][NTf_2]$	2.19	8.11	1.43	3.46
$[N_{222}C_2EG_2][NTf_2]$	2.07	7.44	1.54	2.84
$[N_{222}C_2EG_3][NTf_2]$	1.77	7.87	2.62	5.30

Appendix v: UV-vis spectra of ILs and aqueous phase.

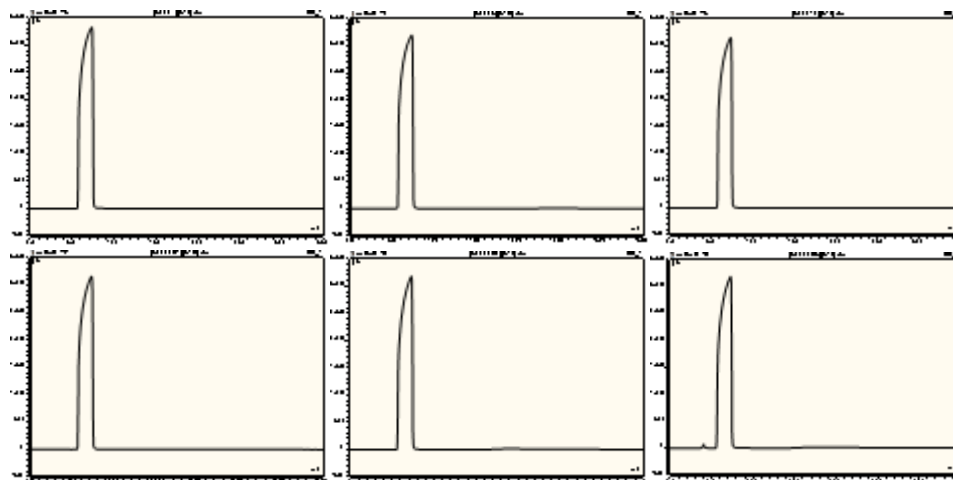




Appendix vi: *The results from cation IC analysis of aqueous phase after blank treatment*



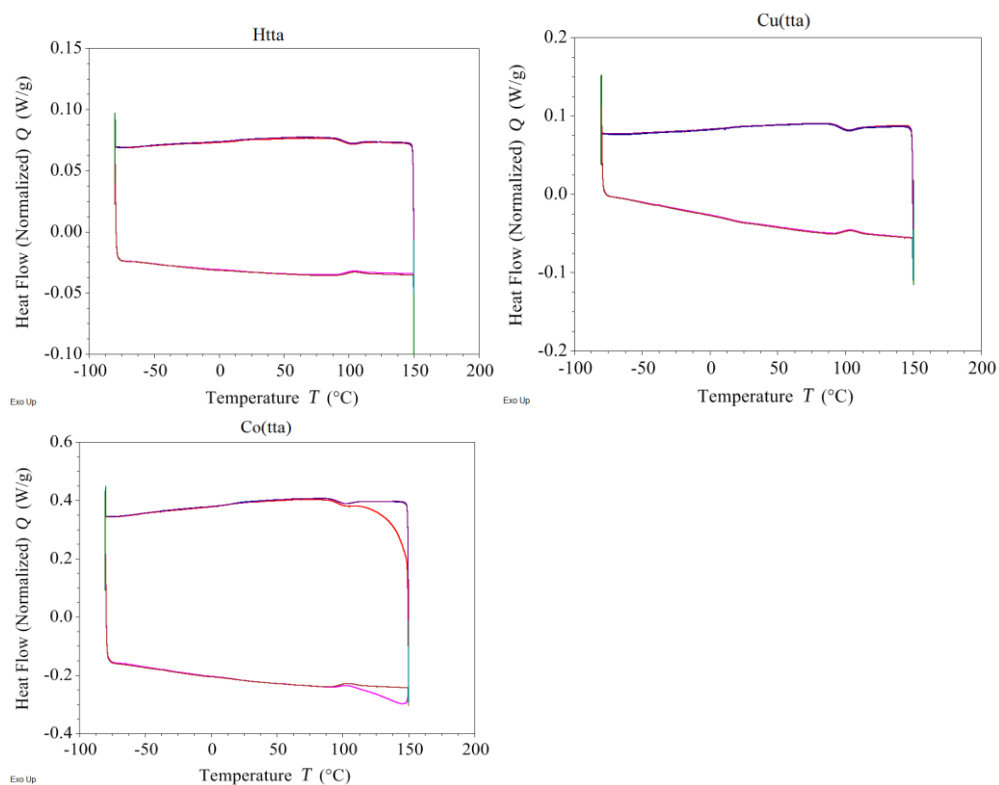
Appendix vii: The results from anion IC analysis of aqueous phase after blank treatment.



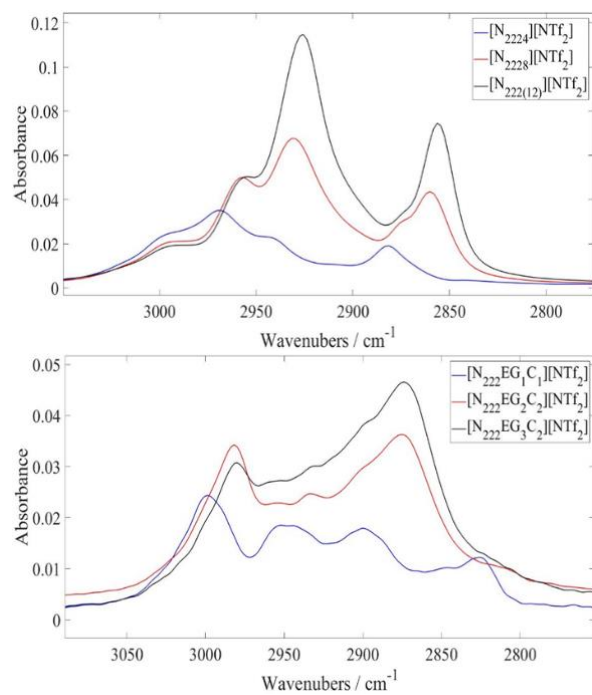
Appendix viii: The efficiency of $[N_{2224}][NTf_2]$ on $CuCl_2$ extraction in varying Htta concentrations.

Concentration of Htta (mmol)	Extraction Efficiency (%)
0.01	32.03 ± 0.14
0.02	58.49 ± 0.30
0.04	66.19 ± 0.95
0.06	64.74 ± 1.02
0.08	71.08 ± 1.02
0.1	70.64 ± 0.78

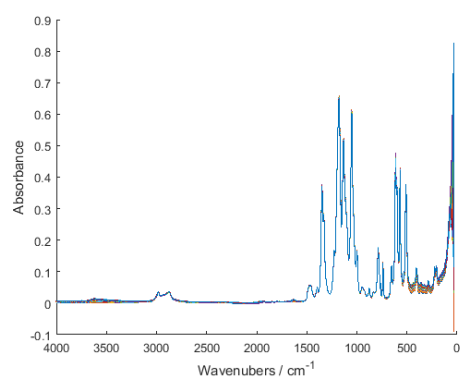
Appendix ix: DSC results of Htta, Co(tta), and Cu(tta).



Appendix x: ATR-FTIR Spectra of ILs between 3100 and 2750 cm^{-1} .



Appendix xi: A continuous ATR-FTIR spectra of $[N_{222}C_2EG_2][NTf_2]$



Appendix xii: Cyclic Voltammetry of $[N_{2224}][NTf_2]$ (top left), $[N_{2224}][NTf_2]$ with $CuCl_2$ (top right), and $[N_{2224}][NTf_2]$ with $Cu(tta)$ complex (bottom left).

