

## **CERTIFICATION OF APPROVAL**

### **Metal Extraction and Analysis on The Effect of Alkyl Chain Length on Thiosalicylate Based Ionic Liquids**

by

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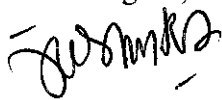
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## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references, and that the original work contained herein have not been undertaken or done by unspecified persons.

The undersigned,



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Julian Rizky Adha (12299)

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## ABSTRACT

The process of removing metal is one of the important parts in industrial wastewater treatment. Many technologies have been developed to do so, such as dissolving an organic solvent (kerosene, toluene, etc.), or using extraction agent. However, none of them is regarded as *green technology* because they cause detrimental effect to the environment and human body. The use of Ionic Liquids (ILs) is believed to be the answer to overcome the problem.

Ionic Liquids are generally defined as molten salts that are consisting entirely of anions and organic cations. This project is designed as further study for Thiosalicylate anion-based ILs on metal extraction process, and efficiency of incorporating different type of chain length. There are 3 (three) types of alkyl chain length tested, hexyl-, octyl-, and dodecyl- chloride. Simulated industrial wastewater is used for the experiment by inducing heavy metal ( $\text{Cr}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.) into the deionized water. At last, the whole project is expected to proof that metal extraction by using Ionic Liquids is promising, as well as to find the most optimum Thiosalicylate anion-based ILs to be utilized by considering several parameters.

# CHAPTER 1

## INTRODUCTION

### 1.1 Project Background

For the last few decades, the industrial use of heavy metals has been immensely increasing. Unfortunately, it relates to some chain effect, which is bad to natural substances like water and soils. The occurrence of heavy metals in the environment, even though only in trace amount, could be particularly dangerous since most of them are toxic and persistent. The recent European Union Water Framework Directive (WFD) sets high Environmental Quality Standards (EQS) for priority substances in surface water regulating the annual averages and maximum allowable concentrations in surface water. The list of priority substances includes 33 organic and inorganic compounds, which have become serious problem in the aquatic environment. Most of the heavy metals and their compounds belong to the list of priority substances due to their level of toxicity, bioaccumulation, and other constraints (Fischer et al, 2011).

Heavy metals are general collective form applying to the group of metals with an atomic density greater than  $6 \text{ g/cm}^3$  (Rajendran et al., 2011). It is widely recognized and usually applied to the elements such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), magnesium (Mg), nickel (Ni), and zinc (Zn), which are commonly, associated with pollution and toxicity problems. Some of the elements in this group are required by most living organism in small amount, thus excess concentration causes toxicity. For instance, chromium is a carcinogenic, tasteless and odourless chemical that is associated with industrial waste from metal plating operations and other manufacturing concerns. Chromium has been linked to concern and other serious health problems through inhalation, ingestion, and other contact. Aerosol from chromium regining planets affects a number of people causing cancer and chromates act as irritants to eyes. Chromium exposure causes damage to liver and kidney. It also causes chromosome abnormalities (Kilivelu and Yatimah, 2008).



Further, Nordberg (1992) specifically mentioned about cadmium as one of the metal with most toxicity level, it finds its way to water bodies through wastewater from metal-plating industries, nickel, cadmium batteries, phosphate fertilizers, mining, pigments, stabilizers, ceramics, and metallurgical and photographic products. The presence of cadmium ions in many industrial aqueous waste solutions is a complex example of pollution because its toxicity, which affects aquatic life and even human life. Therefore industrial wastewater treatment, including metal extraction process is of great importance in the environmental field of waste and pollution reduction.

Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc. Among these technologies, solvent extraction is widely used in the recovery and separation of metals from aqueous solutions. However, it can cause loss of organic diluent via volatilization, which has harmful effect to the environment (De Los Rios et al., 2010). Therefore, heavy metal extraction process by using ILs is proposed as a *greener* technology that is expected to fill in those hitches from prior practices.

### **1.1.1 Ionic Liquids**

Ionic Liquids are salts that exist in liquid form at temperatures below 100°C, their molecules are composed of a large asymmetric cation, e.g., 1-alkyl-3-methylimidazolium, N-alkylpyridinium, and an organic or inorganic anion (Swalowski, 2002). They show extraordinary properties such as an extremely low vapour pressure, high thermal stability and their physico-chemical properties can be tuned by modifying their chemical structure (Marsh et al., 2004; Zhao et al., 2005; Pandey, 2006; Han and Armstrong, 2007). Rajendran (2010) later explained, the uniqueness of ILs is able to give them the capability to expand traditional laws of chemistry. As example, if the ILs are highly polar, yet non coordinating, they can be miscible with water and/or a number of organic solvents with flexible number of reaction and separation schemes, and they are non-volatile even at elevated temperature. Their physical and chemical properties can be tuned by varying the structure of the component ions to obtain desired solvent properties.

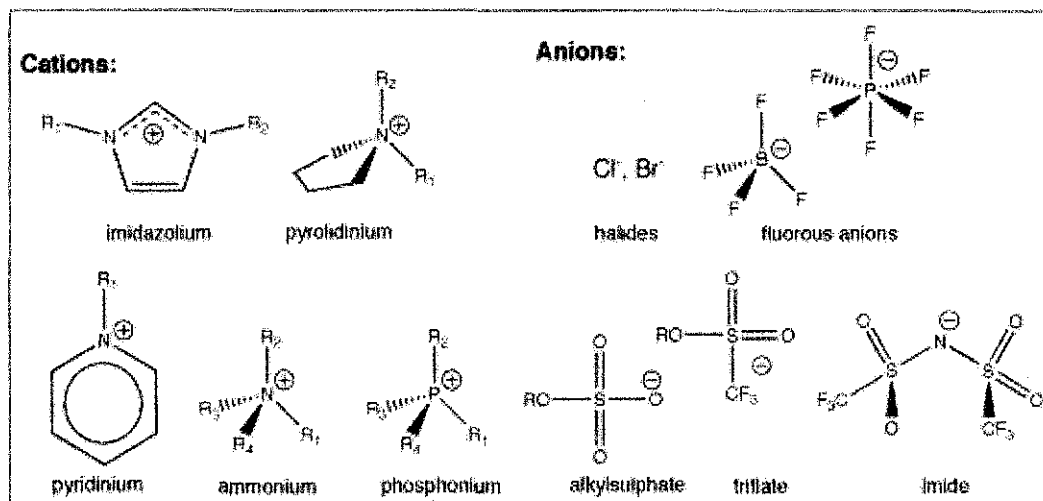


Figure 1.1: Cations and Anions Structure of ILs

(Courtesy of <http://www.huntresearchgroup.org.uk>)

The figure above has shown the most common classes of cations and anions. In the 1970s and 1980s there was interest in ILs based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, initially developed for electrolytes in battery applications. An important property of the imidazolium halogenoaluminate salts was that their viscosity, melting point, and acidity could be adjusted by changing alkyl substituent and the cation and anion ratios (Wasserscheid and Welton, 2002). Since early 1990s, the development of ILs has been rapidly growing. There are several fields of ILs application that are categorized as follow:

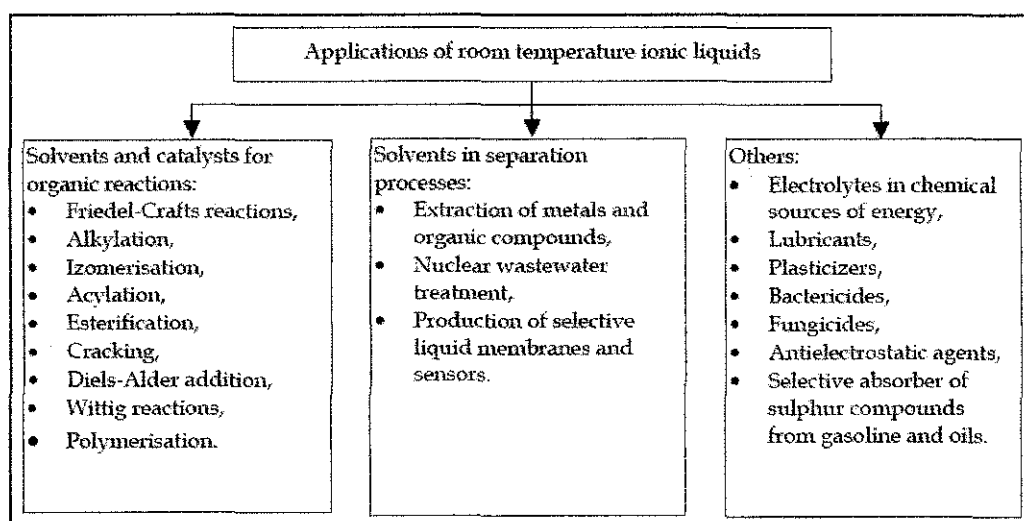


Figure 1.2: Scheme of ILs Applications

(Regel-Rosocka and Wisniewski, 2011)

## 1.2 Problem Statement

As previously described in the project background, the industries nowadays are in desperate need of green technology for wastewater treatment. There are already several methods to do so, however, every single one of them has their own disadvantages as follows:

Methods	Disadvantages
Phytoremediation	Limited surface area, need long term commitment
Chemical Precipitation	Might effect pH of water, need a lot of operator
Ion Exchange	Problem of disposing large quantity of resins
Reverse Osmosis	Need lot of water, have low-back pressure

Table 1.1: Methods of Metal Extraction

Therefore, this project is meant to contribute the development of ILs for metal extraction, specifically on industrial wastewater, because although it has been regarded as one of the promising way for metal extraction process, there has not been much comprehensive study of the process. Specifically in this project, the uses of different alkyl chain length are also observed in order to find the most efficient IL for metal extraction process. Moreover, most of the earlier studies on metal extraction by Ionic Liquids were only using TOMATS (Trioctylmethylammonium thiosalicylate). Thus, it is also one of the problems that is going to be solved by producing various Ionic Liquids with Thiosalicylic based anion.

## 1.3 Objectives

In summary, the objectives of this project are:

- To synthesis different alkyl chain length for Thiosalicylate anion-based ILs
- To study the kinetic of the Ionic Liquids with several analyzing methods
- To apply the synthesized ILs for metal extraction process
- To find the most efficient Ionic Liquid for metal extraction

## **1.4 Scopes of Work**

Based on the mentioned objectives, there are several things come up as scopes of work that need to be overlooked in order to achieve the completion of the project. In this project there are 3 (three) different Alkyl chain length (hexyl-, octyl-, dodecyl-) that are going to be engaged with Pyridine as their cation via quaternization and Thiosalicylate as their anion via metathesis process.

Subsequently, the kinetic of Thiosalicylate anion-based ILs will be observed through some analysis such as TGA (Thermogravimetric Analysis), NMR (Nuclear Magnetic Resonance), Ion Chromatography (Halide content testing), DSC (Deferential Scanning Calorimetry), and analytical test to measure Water content.

## **1.5 Relevancy of Project**

This project can be considered appropriately relevant considering the lack of comprehensive studies on Ionic Liquids, especially those comprising removal or extraction of metal from the wastewater. Moreover, prior studies were using similar type of Ionic Liquids, for example is TOMATS, which has been used for umpteenth times for the journal and paper about ILs. Hence, this project can be a breakthrough.

## **1.6 Feasibility of Project within Time Frame**

If everything is running smoothly, this project should be finished within the given time frame. Throughout the last 8 weeks of FYP II, all 3 (three) ionic liquids have been synthesized and several characterizations have been preceded. With remaining 2-3 weeks time frame, the whole project should be able to be finished, hopefully earlier. Therefore, project feasibility supposedly not an issue.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Metal Extraction

Extraction of metal, also known as *metal remediation*, has been publicly introduced since early 19<sup>th</sup> century. It basically defines as the separation of metals contaminant in a pure or relatively pure state from liquid or solid medium. Many technologies have been developed in order to fulfill the industrial need of the process, mostly due to environmental issues. Besides *ionic liquid*, there are some other techniques on metal extraction, as follows:

##### 2.1.1 In Situ Remediation

###### 2.1.1.1 Phytoremediation

Phytoremediation is a process of removing contaminants such as metals, fuels, VOCs (Volatile Organic Compounds) and SVOCs (Semi-Volatile Organic Compounds) through the use of vegetation. It starts with a process called *phytoextraction*, where plants and trees are used to take up contaminants. Then, the respective plants are to be destroyed to eliminate contamination.

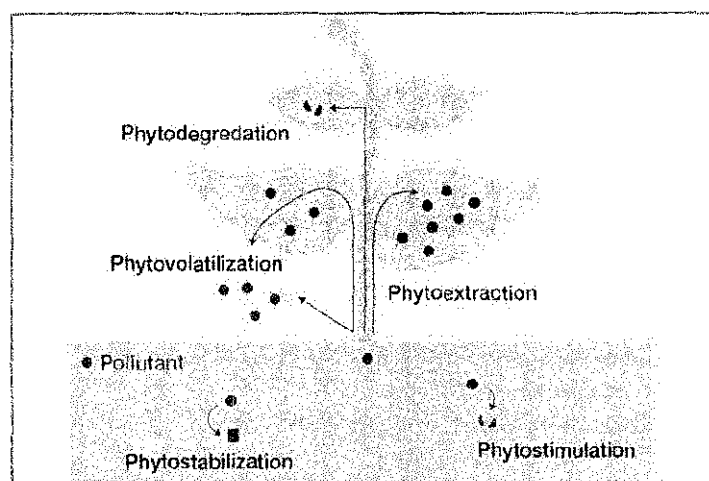


Figure 2.1: Phytoremediation Process  
(Retrieved from <http://systemsbiology.usm.edu>)

Next process called *phytodegradation*, where plants' enzymes break down the organic contaminants. Lastly, *phytovolatilization* follows when a contaminant is passed through the plant and evaporated into the atmosphere.

## 2.1.2 Ex Situ Remediation

### 2.1.2.1 Pump and Treat

This process is used to extract metal from ground water. It remediates sites with various contaminants including dissolved minerals, fuels, and metals. To maximize the process efficiency, series of extraction wells are proposed based on site features. The water is pumped from the extraction wells into holding tanks. Once removed, treatment is done before the groundwater is discharged.

### 2.1.2.2 Chemical Precipitation

Precipitation is the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid, the solid formed is called the *precipitate*, or when compacted by a centrifuge, a pellet. The liquid remaining above the solid is in either case called the *supernate* or *supernatant*. Powders derived from precipitation have also historically been known as flowers (Wikipedia, 2012).

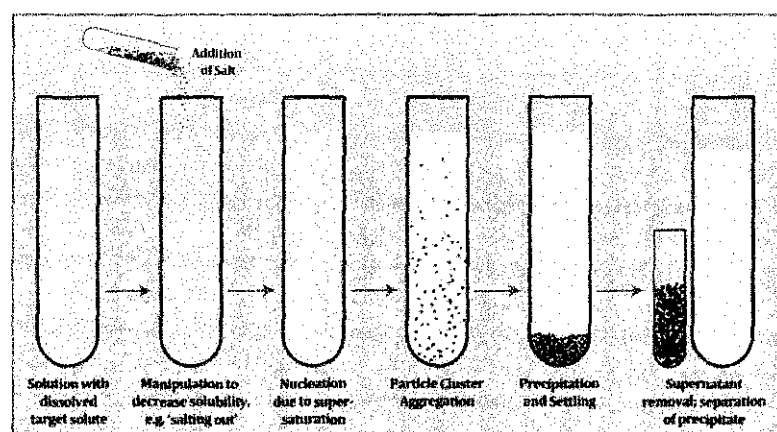


Figure 2.2: Precipitation method  
(Retrieved from <http://en.citizendium.org>)

One of the most common method in precipitation is gravimetric precipitation. This method is based on the formation of an insoluble compound following the addition of a precipitating reagent, or precipitant, to a solution of the analyte. Typically, any reaction generating a precipitate can potentially serve as a gravimetric method.

#### 2.1.2.3 Reverse Osmosis

The process is applicable for separation, concentration and fractionation of organic or inorganic substances in aqueous or non-aqueous solutions. It uses a membrane that is semipermeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. RO membranes deemed to be able to produce high quality water, and to reclaim wastewater effluents. Removal of heavy metals (such as  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) is done in low-pressure conditions, usually with the help of EDTA or *ethylenediaminetetraacetic acid* (Ujang and Anderson, 1996).

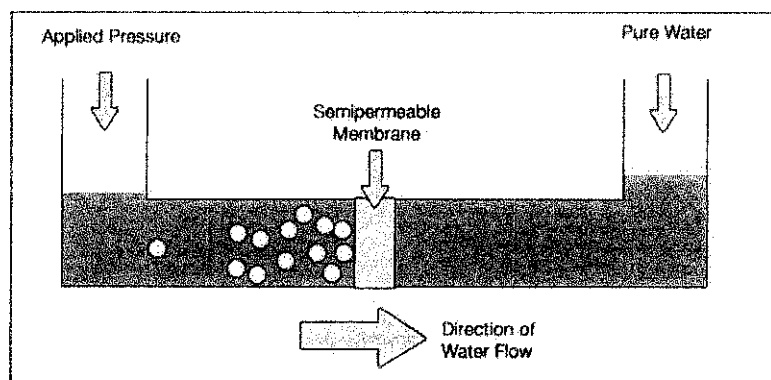


Figure 2.3: Reverse Osmosis

#### 2.1.2.4 Ion Exchange

Ion exchange uses ions from an ion exchange resin to exchange with contaminant ions in an aqueous solution containing the contaminant. Fernandez et al. (2005) mentioned variety of different types of exchange materials, which may be mineral in nature (aluminas, carbons, silicates and aluminosilicates) or synthetic (synthetic zeolites, resins).

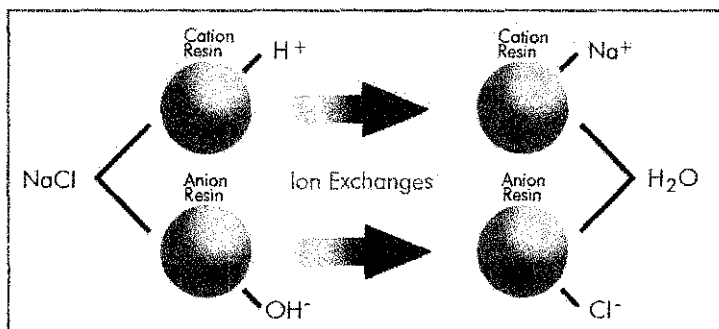


Figure 2.4: Ion Exchange

Zeolites can act as highly efficient porous media in ion exchange or adsorption processes made of *hydrated aluminosilicates*, whereby resins are formed by a matrix, made from a polymeric material, to which functional ion groups of an acid, basic or chelate-forming nature, are fixed. Resins are distinguished on the basis of this functionality: cationic exchange resins (with  $SO_3H$  and  $COOH$  active groups), anionic exchange resins (with  $N^+-(CH_3)_3$ ;  $N-R_2$ ;  $N-RH$  active groups), or chelating resins (with active iminodiacetate, carboxylate, aminophosphonate groups). Some drawbacks to this technology are the cost and disposal problems that are associated with the resin. Additionally, the removal efficiency also decreases when multiple metals are present.

## 2.2 Ionic Liquids on Metal Extraction

The task specific ionic liquid, which is used for selective liquid/liquid extraction of heavy metals, firstly published at 2001 by Robin D. Rogers and friends. Integrating imidazolium cations with thioether-, urea- or thiourea-derivatized side chains act as metal ligating moieties, whereas the  $PF_6^-$  anion provides the desired water immiscibility. Nernst distribution ratios were reported for  $Cd^{2+}$  and  $Hg^{2+}$  to be  $< 380$ . Yet, the hexafluorophosphate anion is known to be quite unstable to hydrolysis, producing toxic and corrosive. The toxicity of the imidazolium cation is hard to estimate while toxicological study would be expensive. Furthermore, the synthesis on a larger scale is problematical (Kalb and Kotschan, 2006).



2.2.1 Trioctylmethylammonium Thiosalicylate (TOMATS)

Development of ionic liquid on metal extraction has been growing from time to time since early 2001. The birth of TOMATS or *Trioctylmethylammonium thiosalicylate* has marked the major progress on it. It is a noble, task specific ionic liquid that contains no fluorine and stable for hydrolysis process. As to fill in the downside of from the prior invention, TOMATS is also built as a noncorrosive ionic liquid, that does not release HF or fluorides and certainly disposable (Kalb and Kotschan, 2006).

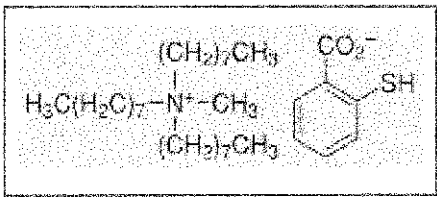


Figure 2.5: Chemical structure of Trioctylmethylammonium thiosalicylate (TOMATS)  
(Retrieved from <http://www.sigmaaldrich.com>)

The low toxicity of the cation is known from related compounds like Trioctylammonium chloride and thiosalicylic acid or its salts are typically classified as irritants. The distribution coefficients of heavy metals typically show values higher than 50,000, which may be rationalized by the chelating effect of the ortho-positioned carboxylate group relative to the thiol functionality.

Besides, the synthesis is simple and can be done at industrial scales. The characteristics of Trioctylammonium thiosalicylate are shown in Table 2.1 and 2.2.

Temperature (°C)	Density (g/cm <sup>3</sup> )	Viscosity (mPa.s)
20	0.9556	1500
40	0.9445	352
60	0.9325	119
80	0.9213	50

Table 2.1: Density and Viscosity of TOMATS 100%  
(Retrieved from <http://www.sigmaaldrich.com>)

Parameters	Remarks
Appearance	Olive green, viscous liquid
Relative Molecular Mass	521.89 g/mol
Empirical Formula	C <sub>32</sub> H <sub>59</sub> NO <sub>2</sub> S
Solubility	<i>Soluble</i> in alcohols, ethyl acetate, THF, acetonitrile, acetone, dichloromethane, DMSO; <i>Insoluble</i> in water, hexane
Nerst Distribution Coefficient	Cd <sup>2+</sup> >50,000; Pb <sup>2+</sup> >100,000 Cu <sup>2+</sup> >50,000; Hg <sup>2+</sup> >100,000
Melting Point	<30°C
Refractive Index	n <sub>D</sub> <sup>20</sup> = 1.5185
Leaching into aqueous phase	<100 ppm

Table 2.2: Characteristics of Trioctylammonium thiosalicylate (TOMATS)  
(Retrieved from <http://www.sigmacaldrich.com>)

As recorded in Aldrich ChemFiles (2006), TOMATS had been experimentally tested to the extraction of copper from a blue colored aqueous Cu<sup>2+</sup>-tetramine phase at temperature of 20°C. The experiment was having a drawback since TOMATS is having a very high level of viscosity at the respective temperature, which is 1500 mPa.s. However, it could have actually been overcome by adding a water-immiscible organic solvent like ethyl acetate, or by gentle heating of the mixture. By doing those opted resolution, the phase separation can work much faster.

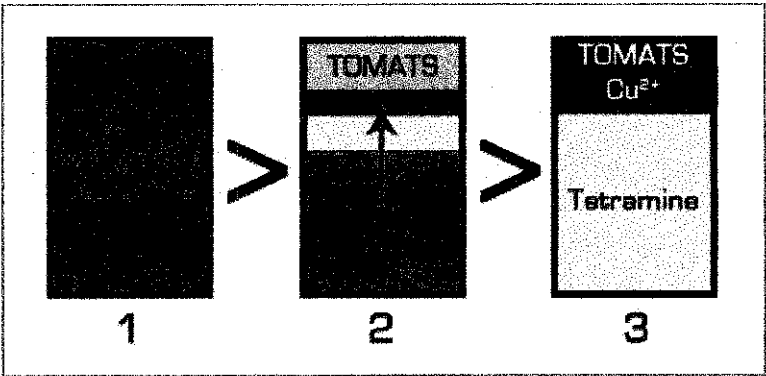


Figure 2.6: Schematic flow of Copper Extraction Experiment

Shown on *Figure 2.6*, there are 3 (three) containers with different layering. The first one is filled with blue colored aqueous  $\text{Cu}^{2+}$ -tetramine phase before addition of TOMATS. After addition of the novel ionic liquid (in olive green), colorless diffusion zone is revealed and some amount of  $\text{Cu}^{2+}$  is upraised (in black). The last container indicated the post-shaking condition where  $\text{Cu}^{2+}$  is almost, if not all, extracted from the aqueous solution and mixed with the ionic liquid. As stated earlier, the above experiment had a timing issue during phase separation.

### 2.2.2 Alkyl Chain Length

Alkyl, generally abbreviated with the symbol R, is a functional group or side-chain that, like an alkane, consists solely of single-bonded carbon and hydrogen atoms, for example a methyl or ethyl group. The modification of the alkyl chain length could make massive differences in the melting points, as well as the affinity of the ionic liquids to form glasses rather than crystalline solids on cooling due to the change in ion packing efficiency (Tariq et al., 2009).

Besides, the manipulation of the chain length will also affect the viscosity and solubility level (Ziyada et al., 2011). The physical property such as density is also very indispensable for the equipment design, and the longer alkyl chain length could correspondingly cause the lower density of ionic liquids.



Name	Structure	Mol. Weight	Density	Boiling Point
1-Chlorohexane	C <sub>6</sub> H <sub>13</sub> Cl	120.62 g/mol	0.879 g/ml	133.5°C
1-Chlorooctane	C <sub>8</sub> H <sub>17</sub> Cl	148.67 g/mol	0.875 g/ml	183°C
Pyridine	C <sub>5</sub> H <sub>5</sub> N	79.09 g/mol	0.978 g/ml	115°C
Sodium hydroxide	NaOH	39.99 g/mol	2.13 g/ml	1390°C
Thiosalicylic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> S	154.19 g/mol	1.489 g/cm <sup>3</sup>	163.5°C

Table 3.1: Properties of Reactants

3.1.1.1 Amount of Reactants

All of the reactions are equimolar with pyridine as limiting reactant. Therefore, chlorohexane and chlorooctane are set to be excessed in order to make sure the reactions to finish completely. Acetonitrile is used as intermediate solvent.

Reactants to produce 1-hexyl pyridinium bromide [HPY]Cl:

C <sub>6</sub> H <sub>13</sub> Cl	C <sub>5</sub> H <sub>5</sub> N
17.02 ml + 3 ml	10 ml
14.96 g + 2.64 g	9.78 g
0.124 mol + 0.022 mol	0.124 mol

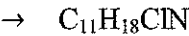


Table 3.2: Amount of Reactants for [HPY]Cl

Reactants to produce 1-octyl pyridinium bromide [OPY]Cl:

C <sub>8</sub> H <sub>17</sub> Br	C <sub>5</sub> H <sub>5</sub> N
21.07 ml + 4 ml	10 ml
18.44 g + 3.5 g	9.78 g
0.124 mol + 0.024 mol	0.124 mol

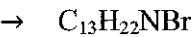


Table 3.3: Amount of Reactants [OPY]Cl

### 3.1.1.2 Quarternization Procedures

Three-neck round bottom flasks were prepared. The system must be flushed with nitrogen gas before reactants addition to ensure the reaction is not under ambient air.



Figure 3.2: Three-Neck Round Bottom Flask

Specified amount of pyridine, alkyl chloride, and acetonitrile were set up as pictured.



Figure 3.3: Reactants

All reactants were put into the three-neck round bottom flask. Set all of the laboratory equipment such as thermocouple, stirrer, heater, and others as shown later in Figure 3.3. The stirrer was set into 300-400 rpm, and temperature was 80°C. Since pyridine was involved, the reactions took not less than 200 hours.

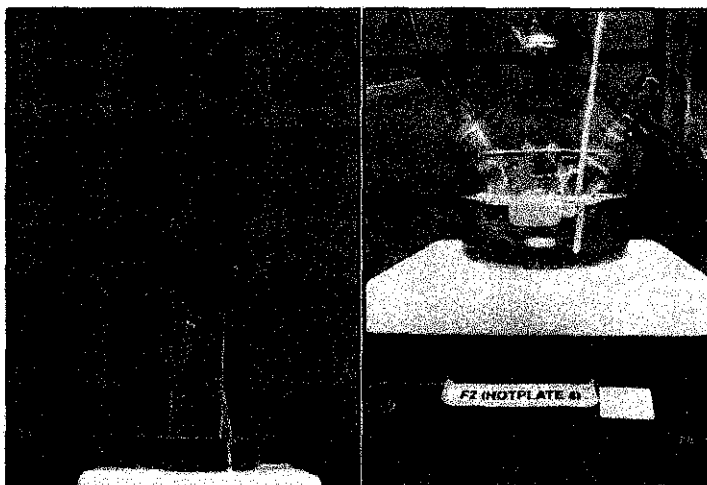


Figure 3.4: Experiment Setup

After few days, the mixture has changed its color into brownish yellow, similar to cooking oil, shown on *Figure 3.5*. Not only the color, but also the viscosity changes could visibly noticed at both liquids.

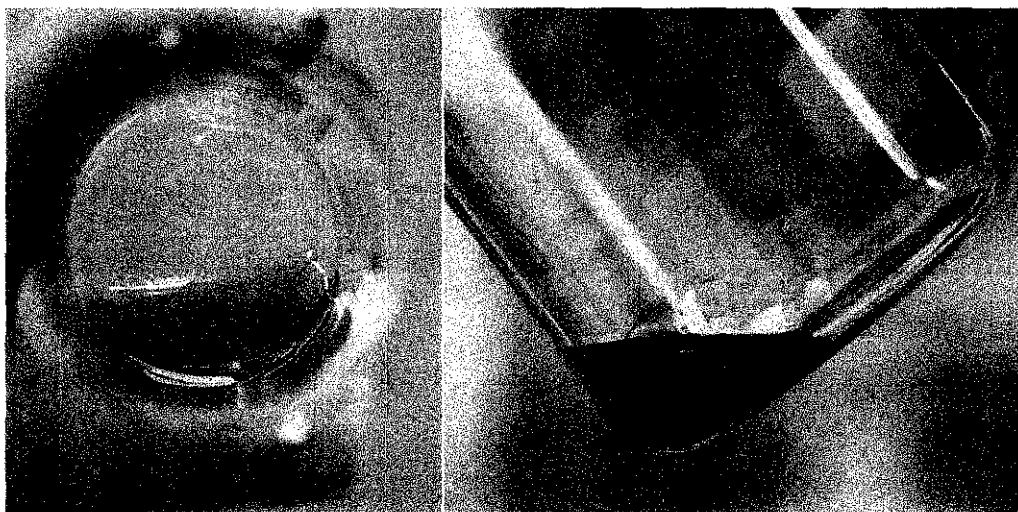


Figure 3.5: Bright-Yellow colored mixture

#### 3.1.1.3 Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC) analysis is aimed to monitor the reaction yield before going to the next stage. It is done by getting small amounts (about 1 droplet) of pyridine as the original reactant and the synthesized mixture, which was diluted in sample bottle by acetonitrile. Do clean pipettes before each use.

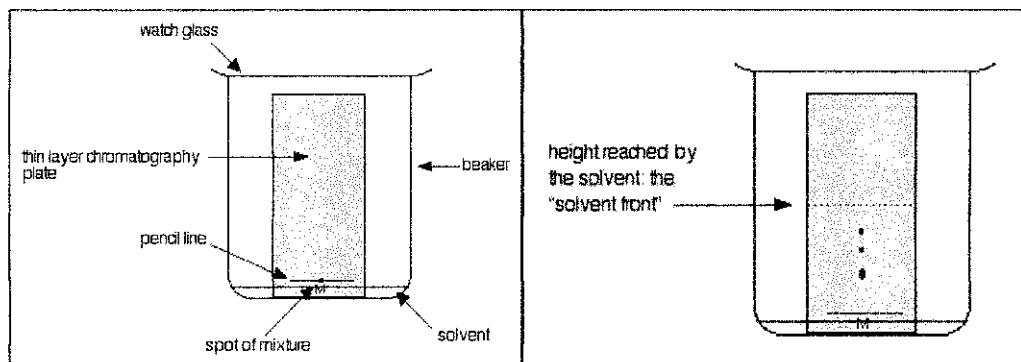


Figure 3.6: Thin Layer Chromatography

After dropping the samples to TLC paper, move the paper into the glass box with 5-6 ml of acetonitrile. Wait until everything is dried out, then measure the distance of molecules movement from the starting material and the mixture. In case if the dots are not visible enough, few drops of methanol can be added to the acetonitrile inside the glass box. The product 'dot' must not reach the same line with the reactant, more importantly pyridine as the limiting reactant. Failure to get such result means longer quarternization time might be needed.

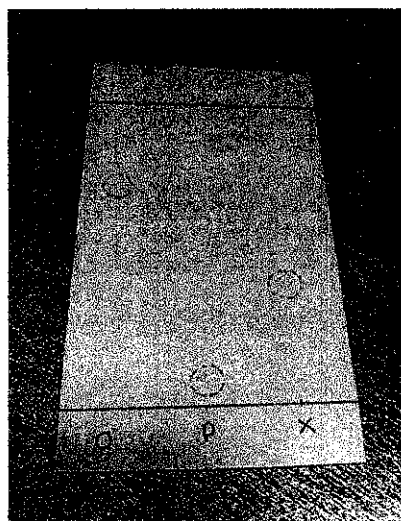


Figure 3.7: TLC for [OPY]Cl

At the figure above, chlorooctane is noted as O, pyridine as P, and X is the product. The result has shown that the product has been completely reacted and it is nowhere located in the same line with its reactants, both pyridine and chlorooctane.



### 3.1.2 Purification and Drying

Purification is the process of removing residues from ionic liquids. It is done by washing the ionic liquids with ethyl acetate in the separation funnel. Acetonitrile as the intermediate solvent has to be removed as well by using rotary evaporator with temperature of 80°C, wait until about 1 hour.

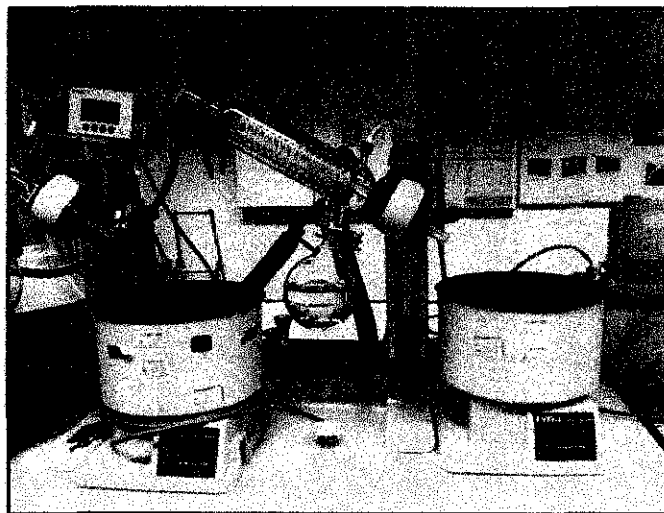


Figure 3.8: Rotary Evaporator

There is no need to wait for too long because the quarternization process was supposed to preliminarily removed acetonitrile from the mixture since it was also set at 80°C (boiling point of acetonitrile is 82°C at 1 atm). After washing, drying process follows; the ionic liquids were put into the oven at 70°C and vacuum pressure for approximately 48 hours before undergoing *metathesis* process.

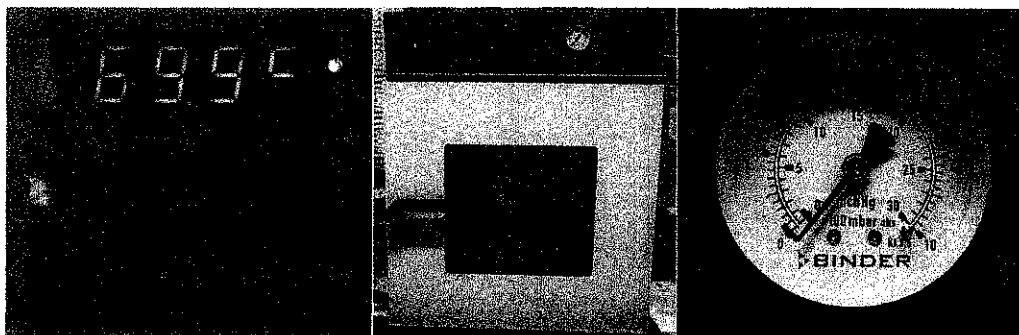


Figure 3.9: Oven Setup

Quarternization is duplicated since there are 2 (two) alkyl chlorides.

### 3.1.3 Metathesis

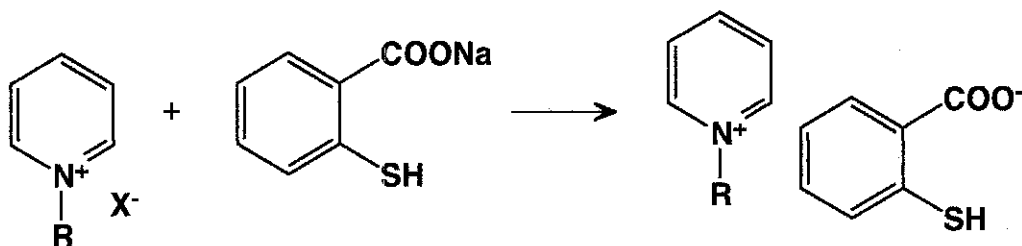


Figure 3.10: Metathesis Process

Metathesis is the continuation process of *quarternization*. During the metathesis process, halide is being removed and the anion is being engaged to the cation. Before metathesis, simple neutralization reaction was made in order to prepare sodium thiosalicylate. It was done by dilluting equimolar amount of thiosalicylate acid and sodium hydroxide in distilled water at room temperature and ambient pressure for about 30 minutes until the solution has become transparent.

After the neutralization reaction, tare the weight of the intermediate ionic liquids (from quarternization) and calculate the amount of mole. Subsequently, prepare equimolar amount of sodium thiosalicylate and mix it with the intermediate ionic liquid. The process required no heating, only stirring. Put the solution into closed vessel and stir at 500-600 rpm. The reaction took 48 hours for [HPY]TS, 72 hours for [OPY]TS, and roughly 100 hours for [DDPY]TS.

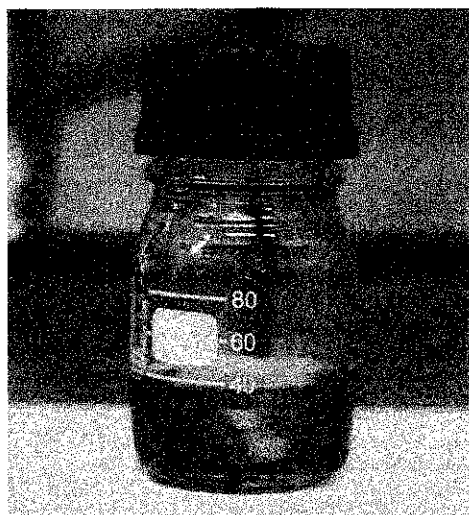


Figure 3.11: Metathesis of [HPY]TS

### 3.1.4 Metal Extraction

Metal extraction is one of the major parts in the whole project. After all ionic liquids have been synthesized, several sample of metal ion solutions are prepared. The samples are simulated deionized/distilled water that has been induced with 3 (three) heavy metals from transition metal group ( $\text{Ni}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$ ) and a light metal from alkaline group ( $\text{Ca}^{2+}$ ). Since there are 3 (three) ionic liquids, there would be 12 samples in total. Before metal extraction, 0.5 g from every ionic liquid was diluted in 2 ml of water. Each of the samples was added with 0.3 ml of the solution and mixed on a Vortex for 3 minutes at 2200 rpm. After that, those samples were put inside a Centrifuge for 60 minutes at 4000 rpm, and leave it for few hours until the metal completely extracted to the bottom of the tubes.

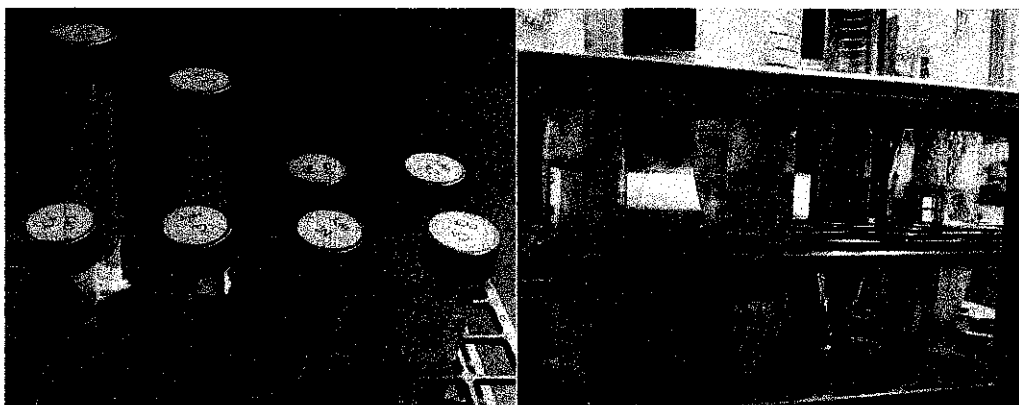


Figure 3.12: Metal Extraction

Take 5 ml from the topside of each sample to prevent sedimentation and AAS (Atomic Absorption Spectroscopy) was conducted in order to detect the remaining metal concentration in the distilled water. Detailed result will be further discussed in the Result and Discussion (Chapter 4).

3.2 Gantt Chart

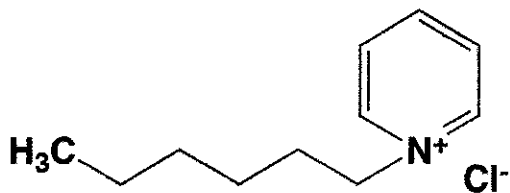
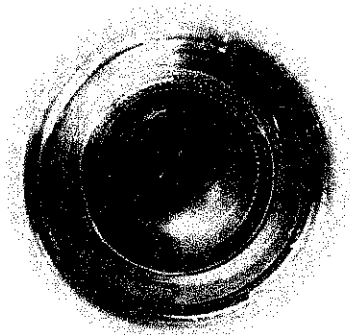
Planned activity for CBB4614 Final Year Project II:

	Remarks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project work continues							MID SEMESTER								
2	Progress report submission															
3	Project work continues															
4	Pre-EDX															
5	Draft report submission															
6	Dissertation (soft bound)															
7	Technical paper submission															
8	Oral presentation															
9	Dissertation (hard bound)															

CHAPTER 4  
RESULT & DISCUSSION

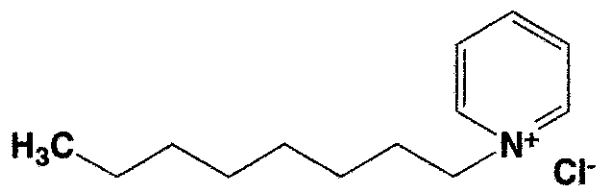
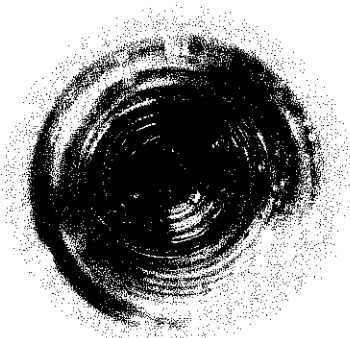
4.1 Ionic Liquids

4.1.1 Hexyl Pyridinium Chloride [HPY]Cl



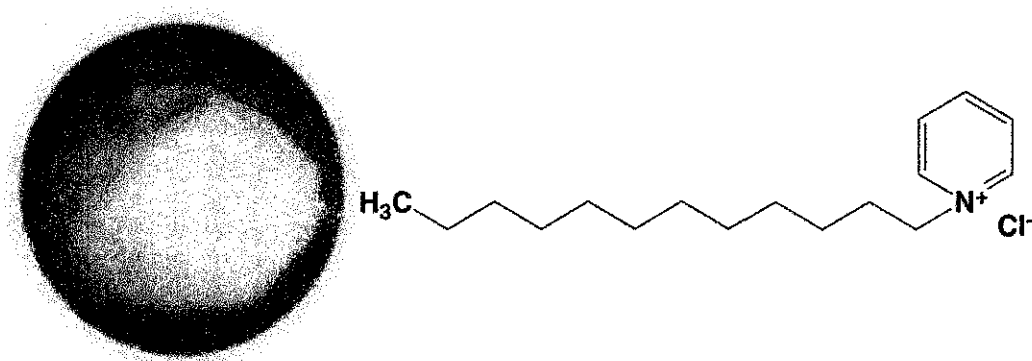
Properties	Remarks
Color	Bright yellow
Molecular structure	C <sub>11</sub> H <sub>18</sub> ClN
Molecular weight	199.5 g/mol
Synthesis condition	80°C, 1 atm, 320 rpm stirring

4.1.2 Octyl Pyridinium Chloride [OPY]Cl



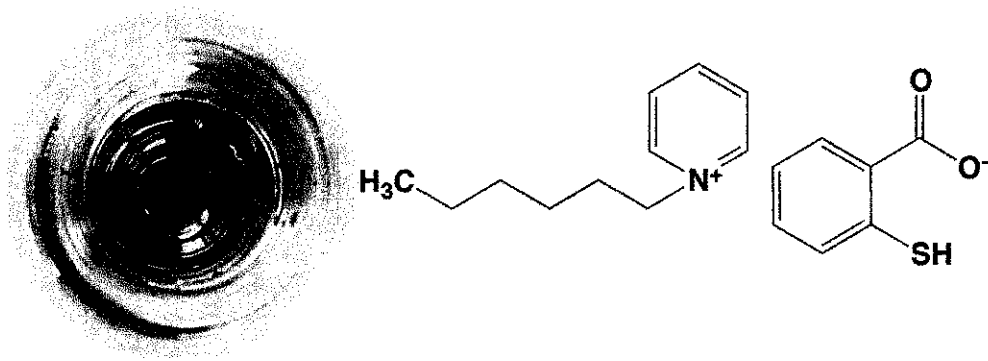
Properties	Remarks
Color	Brownish yellow
Molecular structure	C <sub>13</sub> H <sub>22</sub> ClN
Molecular weight	227.5 g/mol
Synthesis condition	80°C, 1 atm, 400 rpm stirring

4.1.3 Dodecyl Pyridinium Chloride [DDPY]Cl



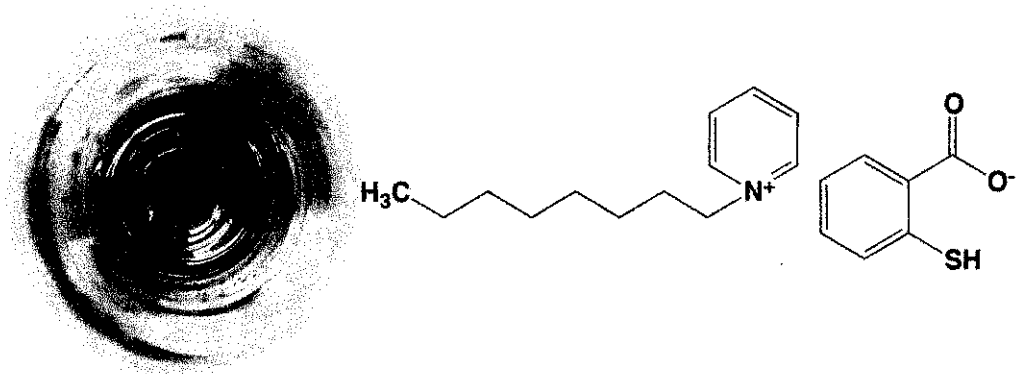
Properties	Remarks
Color	White (solid)
Molecular structure	C <sub>17</sub> H <sub>30</sub> ClN
Molecular weight	283.5 g/mol
Synthesis condition	-

4.1.4 Hexyl Pyridinium Thiosalicylate [HPY]TS



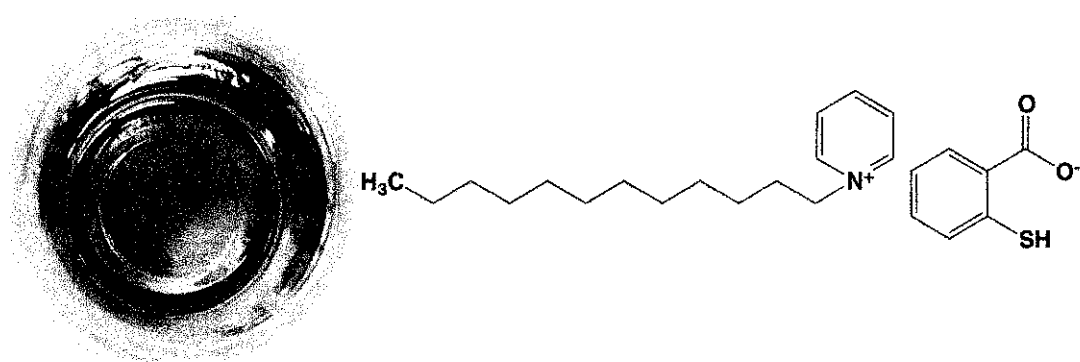
Properties	Remarks
Color	Dark red
Molecular structure	C <sub>18</sub> H <sub>23</sub> O <sub>2</sub> NS
Molecular weight	317.07 g/mol
Synthesis condition	25°C, 1 atm, 600 rpm stirring

4.1.5 Octyl Pyridinium Thiosalicylate [OPY]TS



Properties	Remarks
Color	Dark brown
Molecular structure	C <sub>20</sub> H <sub>27</sub> O <sub>2</sub> NS
Molecular weight	345.07 g/mol
Synthesis condition	25°C, 1 atm, 500 rpm stirring

4.1.6 Dodecyl Pyridinium Thiosalicylate [DDPY]TS



Properties	Remarks
Color	Yellow
Molecular structure	C <sub>24</sub> H <sub>35</sub> O <sub>2</sub> NS
Molecular weight	401.07 g/mol
Synthesis condition	25°C, 1 atm, 500 rpm stirring

4.2 Atomic Absorption Spectroscopy

As the main objective of the thesis, metal extraction is surely the one to wait. All product ionic liquids (not including intermediate) have been tested at 4 (four) different types of metals. There was a little twitch in the procedure where there were not just heavy metals used in the experiment as mentioned previously. The results of the metal extraction are measured with Atomic Absorption Spectroscopy (AAS) and fragmented down into specific metal as listed below:

4.2.1 Nickel ( $Ni^{2+}$ )

Nickel is a hazardous metal. It is carcinogenic; meaning that inhaling this substance is hazardous to your lungs and nasal canal. Since nickel can be found in the work place, and is therefore an occupational hazard. The levels of exposure to carcinogens/nickel are very minute, and all necessary precautions should be taken to reduce your risk to nickel exposure. According to OSHA, the legal airborne limit to nickel exposure is 1 milligram per every eight hours. Larger doses of nickel, such as accidental ingestion, have been shown to have more adverse health effects ranging from stomachaches to heart failure.

The following graph shown the effectiveness of thiosalicylate based ILs on Nickel removal from water. The initial samples were all set at 10 ppm (high concentration).

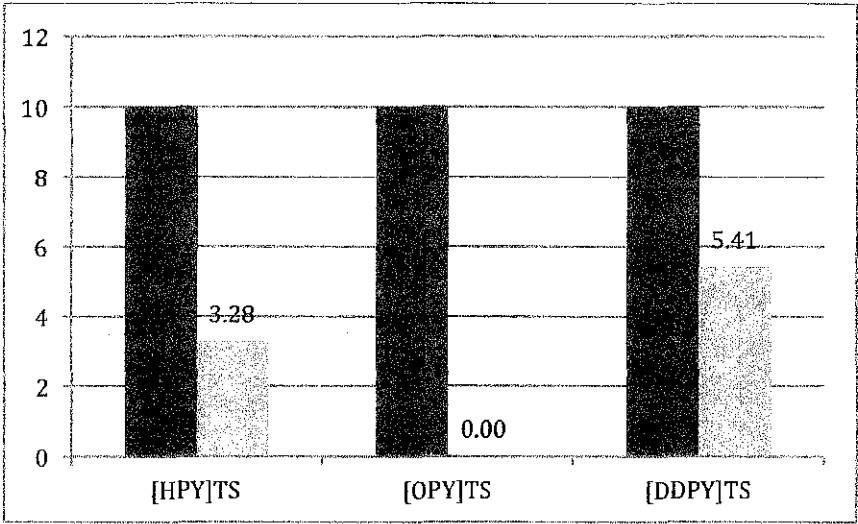


Figure 4.1: Atomic Absorption Spectroscopy Result ( $Ni^{2+}$ )



Ionic Liquid	Initial Metal Concentration	Final Metal Concentration	Efficiency (%)
[HPY]TS	10 ppm	3.28 ppm	67.2%
[OPY]TS	10 ppm	0.00 ppm	100%
[DDPY]TS	10 ppm	5.41 ppm	45.9%

Table 4.1: Atomic Absorption Spectroscopy Result (Ni<sup>2+</sup>)

The table above is the result gathered from AAS (Atomic Absorption Spectroscopy). Noticable differences can be seen, where [OPY]TS aced the other ionic liquids and have 100% percentage of removal. Meanwhile, [DDPY]TS has the least percentage removal of all with only 45.9%, which means, not even half of the Nickel content was extracted from water.

4.2.2 Copper (Cu<sup>2+</sup>)

Cu<sup>2+</sup> levels in the environment have increased in recent years due to anthropogenic activities, such as industrial discharges, and use of the metal in the manufacture of kitchen tools, paintings, plumbing materials, and water pipes. All together this could lead to water contamination and poor water quality.

The following graph shown the effectiveness of thiosalicylate based ILs on Nickel removal from water. The initial samples were all set at 10 ppm (high concentration).

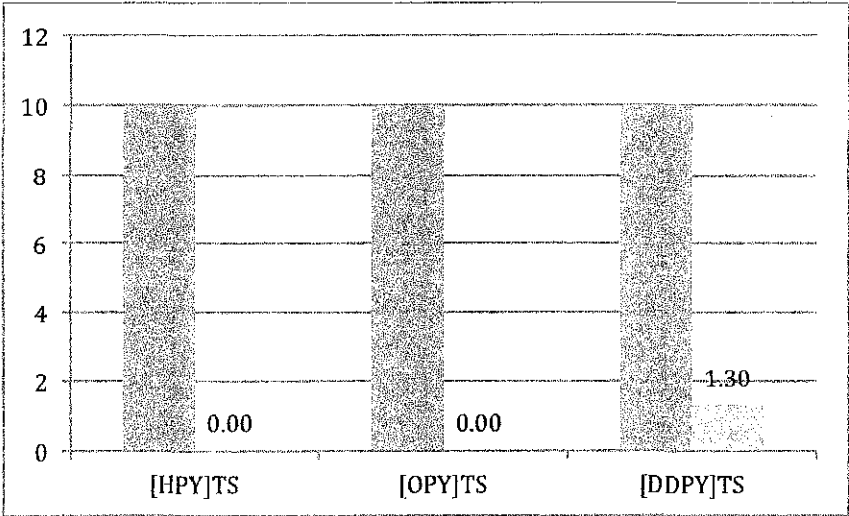


Figure 4.2: Atomic Absorption Spectroscopy Result (Cu<sup>2+</sup>)

Ionic Liquid	Initial Metal Concentration	Final Metal Concentration	Efficiency (%)
[HPY]TS	10 ppm	0.00 ppm	100%
[OPY]TS	10 ppm	0.00 ppm	100%
[DDPY]TS	10 ppm	1.30 ppm	87%

Table 4.2: Atomic Absorption Spectroscopy Result (Cu<sup>2+</sup>)

Remarkably, all ionic liquids paraded satisfying percentage of Copper removal. Both [HPY]TS and [OPY]TS are having 100% efficiency, whereby [DDPY]TS, as the least performer still have a considerably good result with 87%.

4.2.3 Chromium (Cr<sup>2+</sup>)

Chromium is a heavy metal, which can be easily found in air, soil, and water after release from the manufacture, use, and disposal of chromium-based products, and during the manufacturing process. It does not usually remain in the atmosphere, but is deposited into the soil and water. Similar to other heavy metals, it can cause severe health issues. Breathing high levels of chromium can cause irritation to the lining of the nose, nose ulcers, runny nose, and breathing problems, such as asthma, cough, shortness of breath, or wheezing. Sperm damage and damage to the male reproductive system has also been seen in laboratory animals exposed to chromium.

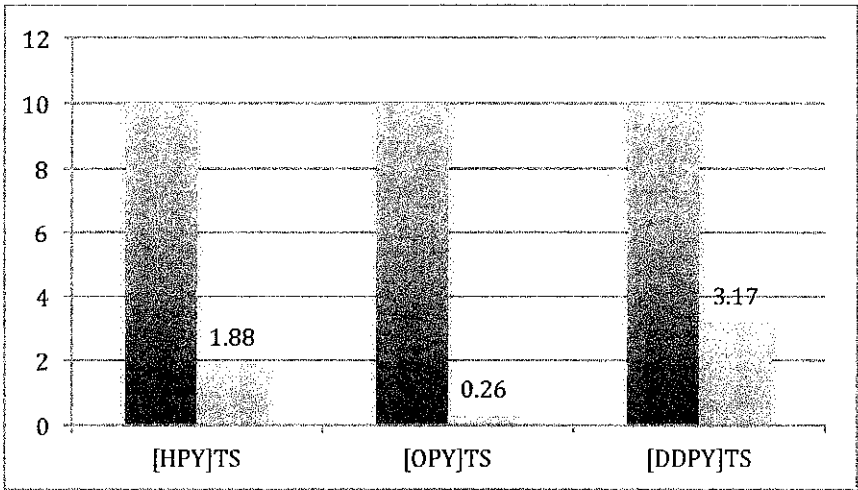


Figure 4.3: Atomic Absorption Spectroscopy Result (Cr<sup>2+</sup>)

Ionic Liquid	Initial Metal Concentration	Final Metal Concentration	Efficiency (%)
[HPY]TS	10 ppm	1.88 ppm	81.2%
[OPY]TS	10 ppm	0.26 ppm	97.4%
[DDPY]TS	10 ppm	3.17 ppm	68.3%

Table 4.3: Atomic Absorption Spectroscopy Result ( $\text{Cr}^{2+}$ )

Comparable to the other results, the trend is static, [OPY]TS is the best all-round performer in metal extraction and [HPY]TS is a considerable alternative. However, [DDPY]TS unexpectedly turned out to be the bottom line although it has the longest alkyl chain length among the other two.

Based on its visible structure, [DDPY]TS is significantly different. It forms foam when it is mixed with water, due to possible existence of Sodium lauryl sulfate, which makes it hard to solute in the aqueous metal. Moreover, the longer chain length theoretically would have the best metal extraction performance but also to be remembered that ionic liquids with long alkyl chain tend to be hydrophobic. Therefore, [DDPY]TS or Dodecyl Pyridinium Thiosalicylate could be more suitable to be used in metal extraction on petroleum product.

4.2.4 Calcium ( $\text{Ca}^{2+}$ )

As known, Calcium is a member of alkaline metal. It is presented in order to crisscross the side effect of the ionic liquid to the environment. Calcium is a metal that is essential for living organisms, particularly in cell physiology. As major material used in mineralization of bones and shells, calcium is the most abundant metal by mass in many animals. Hence, unlike the other tested metals, specifically for Calcium, all ionic liquids are longed to have least removal percentage.

The results from AAS (Atomic Absorption Spectroscopy) are deliberately outstanding for all tested ionic liquids. The reading showed there was very small, if not 0%, changes in  $\text{Ca}^{2+}$  concentration in the samples. Since Calcium has similarity to Sodium (Na, which is a stronger alkali metal), it means if the ILs are being set off to the sea, most probably it will not affect the Sodium level of the water.

### 4.3 Characterization

There are several parameters to be tested in order to understand the detailed structure and behavior of the ionic liquids. Analysis techniques are used to amplify the specimen, to visualize internal structure, and to gain knowledge as to the distribution of elements within the specimen and their interactions. Physical properties such as density, viscosity and decomposition temperature are measured at certain temperature and pressure. According to Ziyada et al. (2011), various characterizing and properties measurement methods are as follows:

#### 4.3.1 Thermogravimetry Analysis

Thermogravimetric Analysis (TGA) is proposed to observe decomposition temperature for all synthesized pure ionic liquids by heating the sample at a rate of  $10^{\circ}\text{C}$  from  $50^{\circ}\text{C}$  to  $400^{\circ}\text{C}$  on aluminium pans under nitrogen atmosphere. From the results below, it can be concluded that the longer alkyl chain length leads to higher decomposition temperature. The details are shown as follows:

- Hexyl Pyridinium Chloride [HPY]Cl

Decomposition temperature:  $221.23^{\circ}\text{C}$

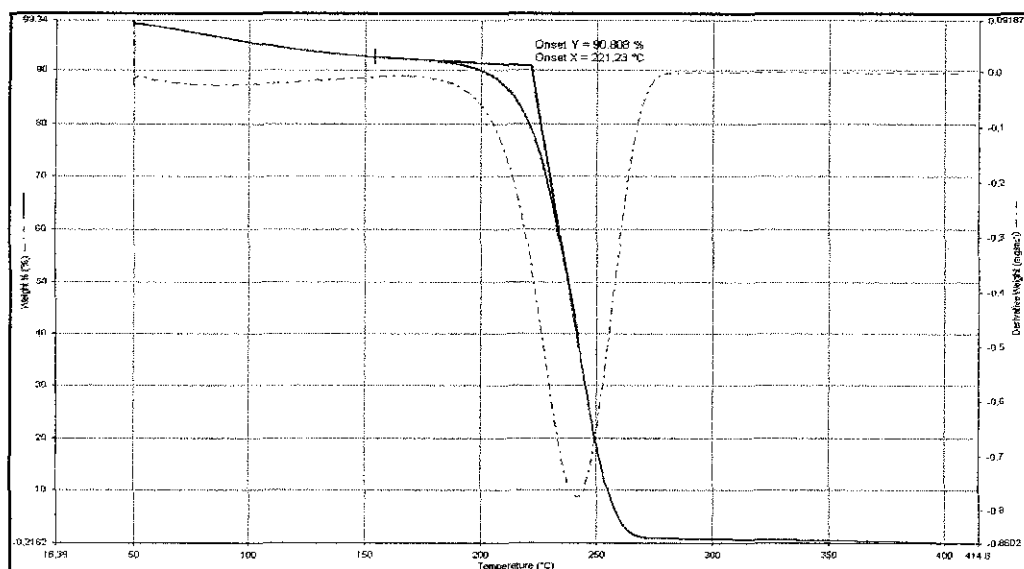


Figure 4.4: Thermogravimetry Analysis for [HPY]Cl

- Octyl Pyridinium Chloride [OPY]Cl

Decomposition temperature: 222.95°C

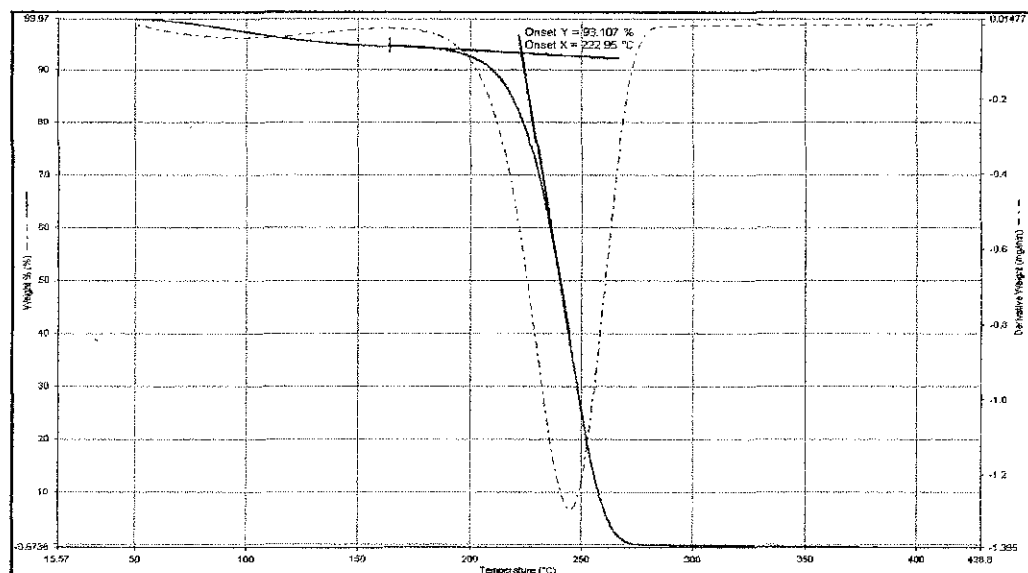


Figure 4.5: Thermogravimetry Analysis for [OPY]Cl

- Hexyl Pyridinium Thiosalicylate [HPY]TS

Decomposition temperature: 244.19°C

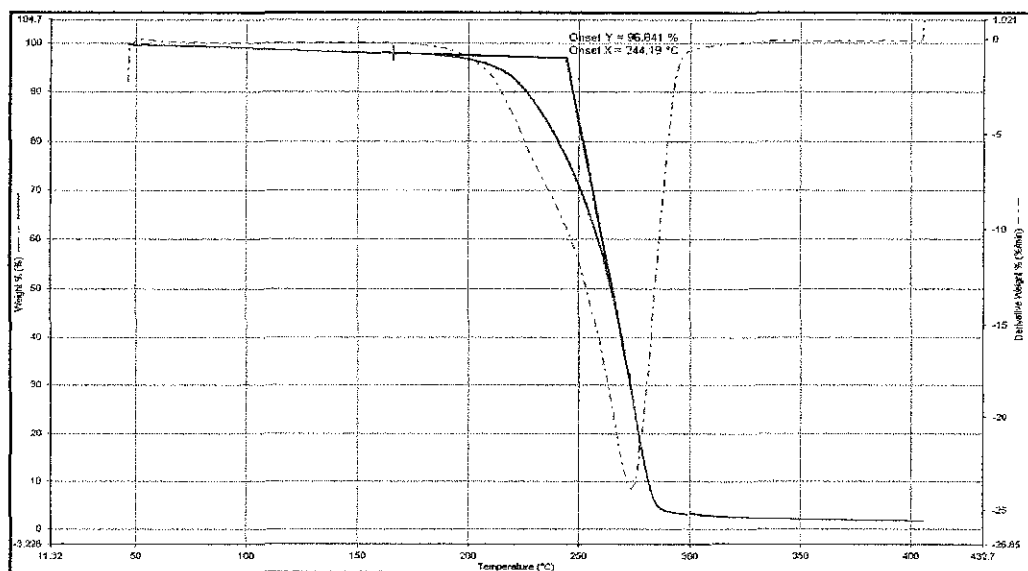


Figure 4.6: Thermogravimetry Analysis for [HPY]TS

- Octyl Pyridinium Thiosalicylate [OPY]TS

Decomposition temperature: 253.22°C

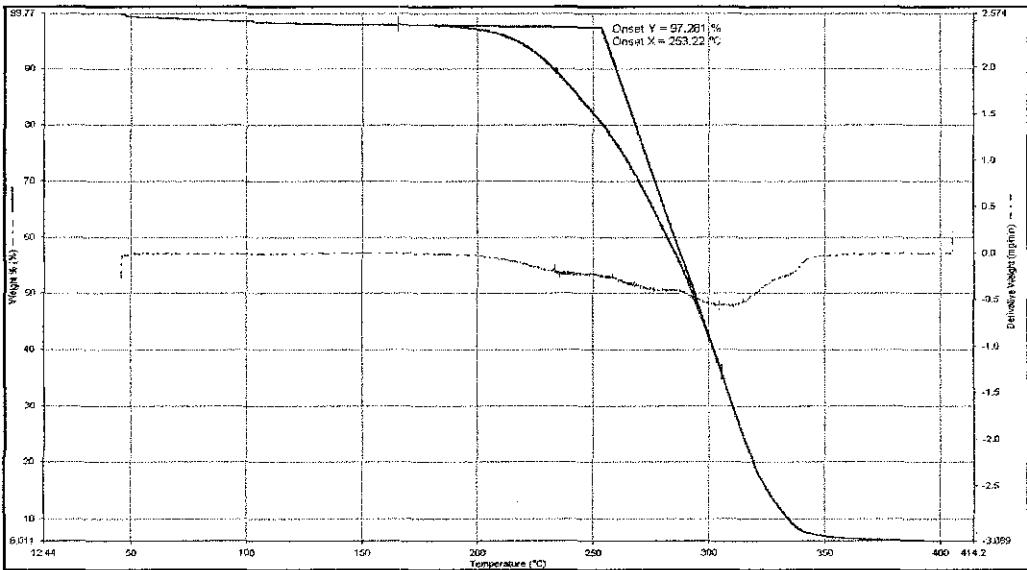


Figure 4.7: Thermogravimetry Analysis for [OPY]TS

- Dodecyl Pyridinium Thiosalicylate [DDPY]TS

Decomposition temperature: 253.36°C

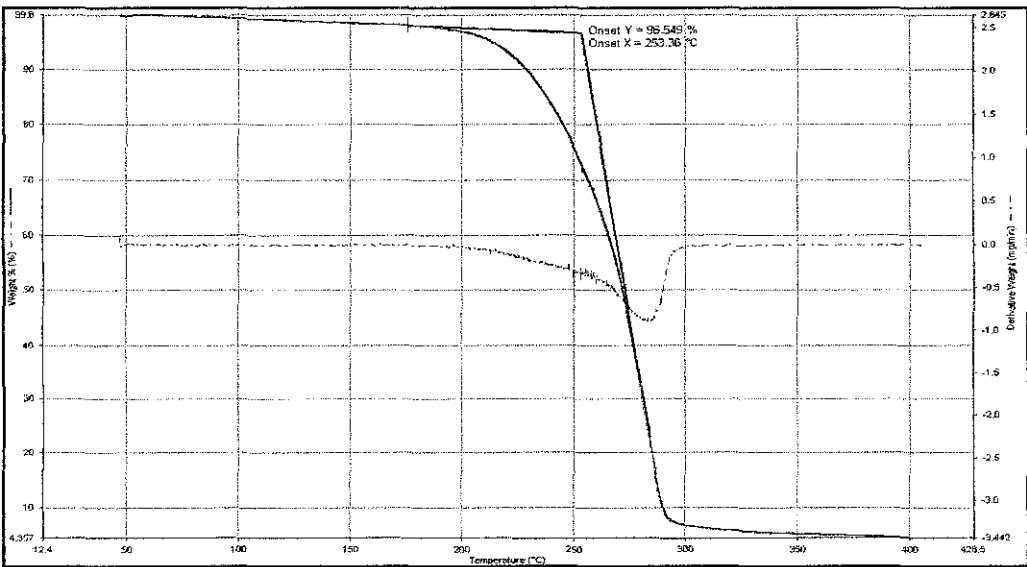


Figure 4.8: Thermogravimetry Analysis for [DDPY]TS

#### 4.3.2 Water Content Measurement

In order to measure the water content, Karl-Fisher titrator, together with its reagent is used. The measurement for each ionic liquid will be made triplicate and average value will be recorded. Water content is very important in ionic liquids because it might affect the density and viscosity analysis. The analysis was done twice for 3 (three) product ionic liquids, not including intermediate, at before and after drying, to also see the effectiveness of vacuum oven.

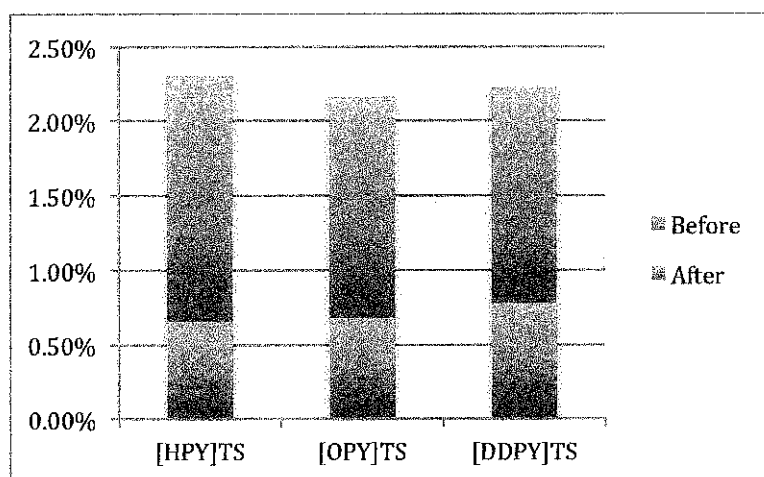


Figure 4.9: Water Content Before-After Drying

Although the effect of the drying is visibly significant, the period should also be taken account. All ionic liquids have been through 96 hours of drying in order to reduce the water content to be less than 1%. The use of vacuum line could be considered as future upgrade of the experiment, because it is claimed to be able to reduce water content from 3% to 0.5% in less than 24 hours.

#### 4.3.3 Nuclear Magnetic Resonance

NMR or *Nuclear Magnetic Resonance* is aimed to analyze the purity of ionic liquids by locating the hydrogen atoms position in the spectrum and number of these atoms by integration. Key feature of NMR is that the resonance frequency of a particular substance is directly proportional to the strength of the applied magnetic field. It is this feature that is exploited in imaging techniques; if a sample is placed in a non-uniform magnetic field then the resonance frequencies of the sample's nuclei depend on where in the field they are located.

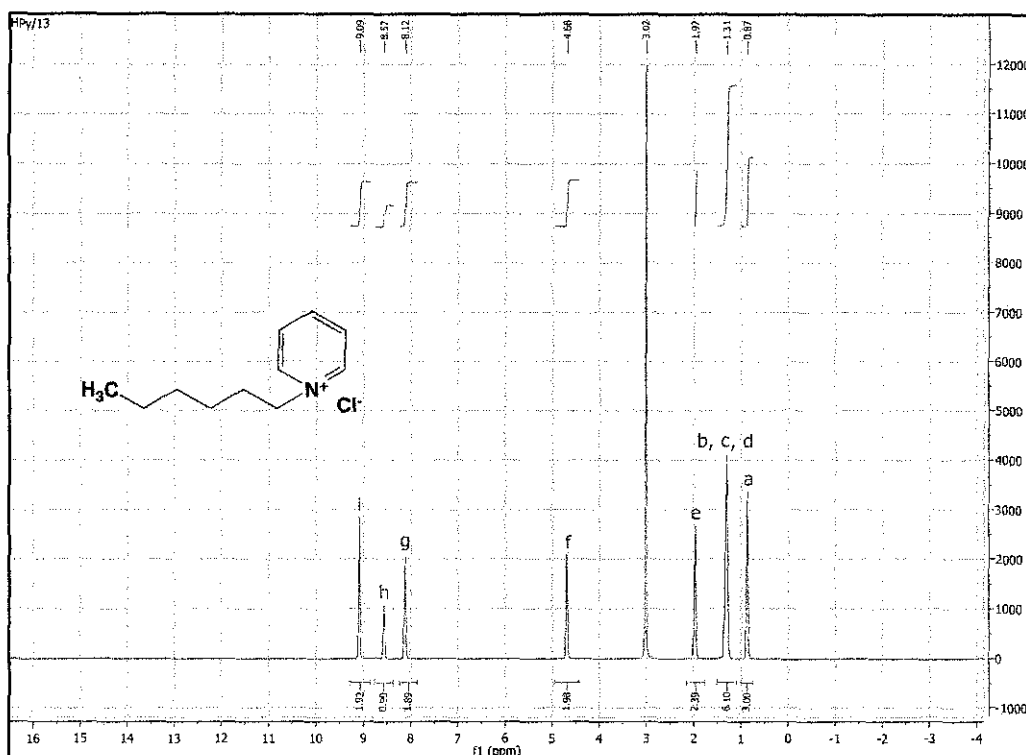


Figure 4.10: <sup>1</sup>H NMR for [HPY]Cl

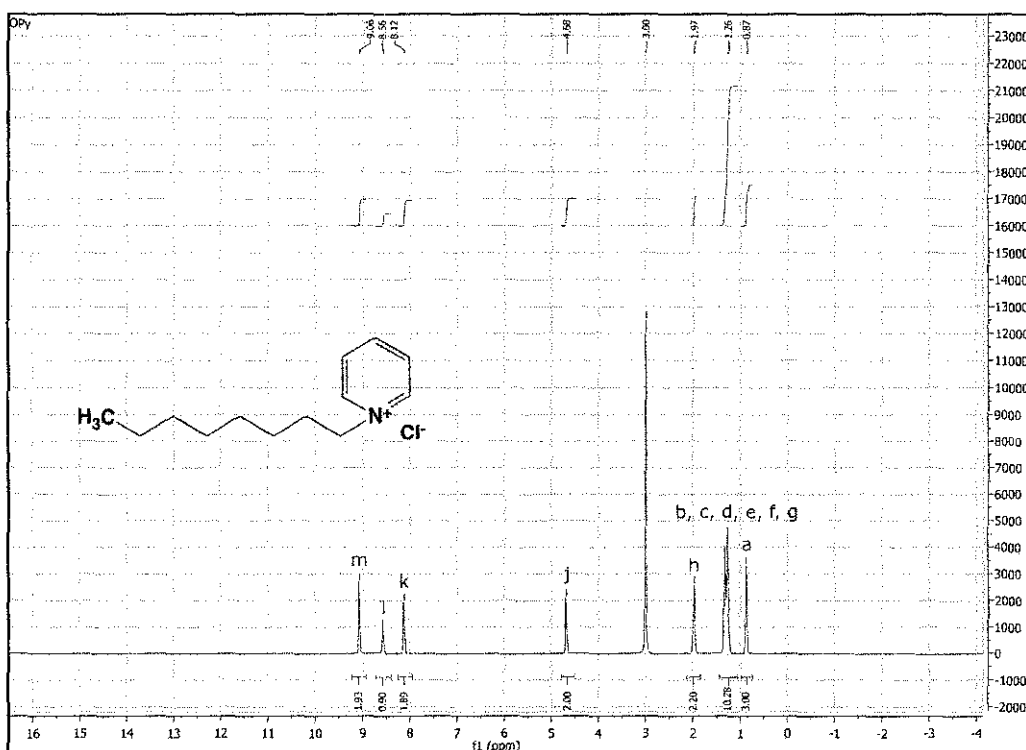


Figure 4.11: <sup>1</sup>H NMR for [OPY]Cl



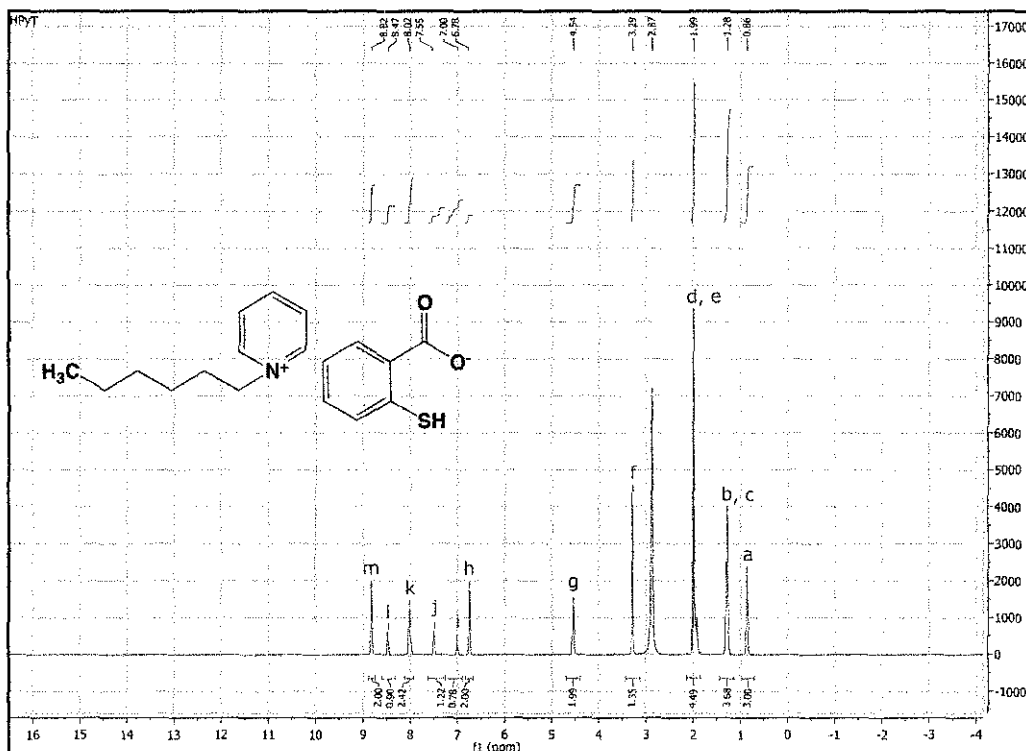


Figure 4.12:  $^1\text{H}$  NMR for [HPY]TS

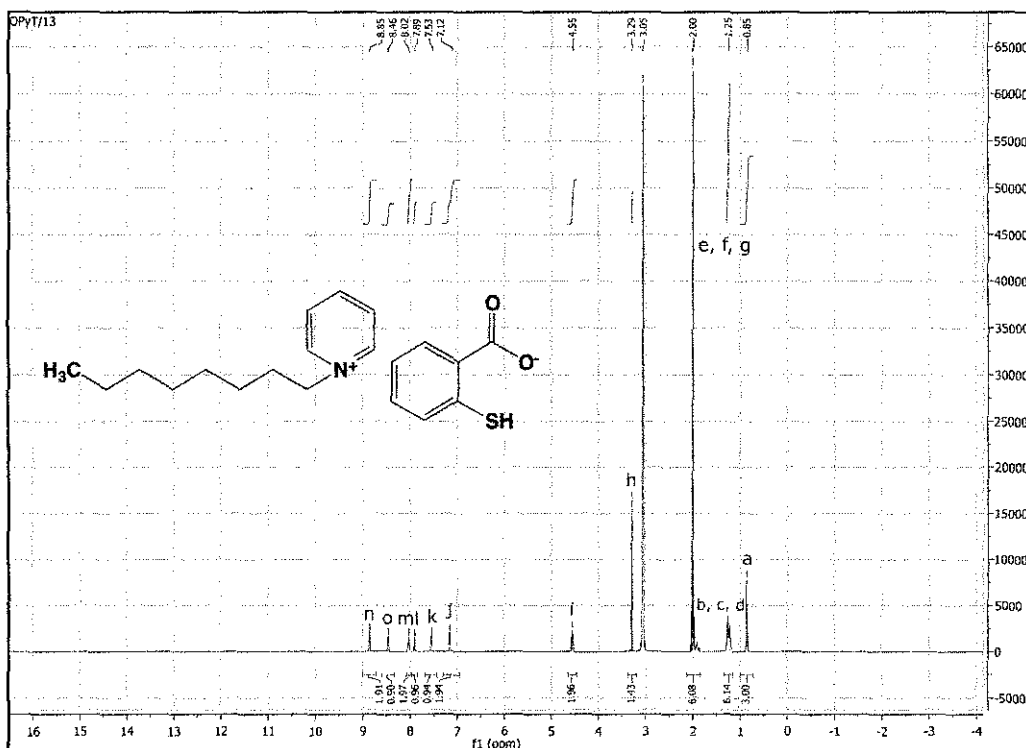


Figure 4.13:  $^1\text{H}$  NMR for [OPY]TS

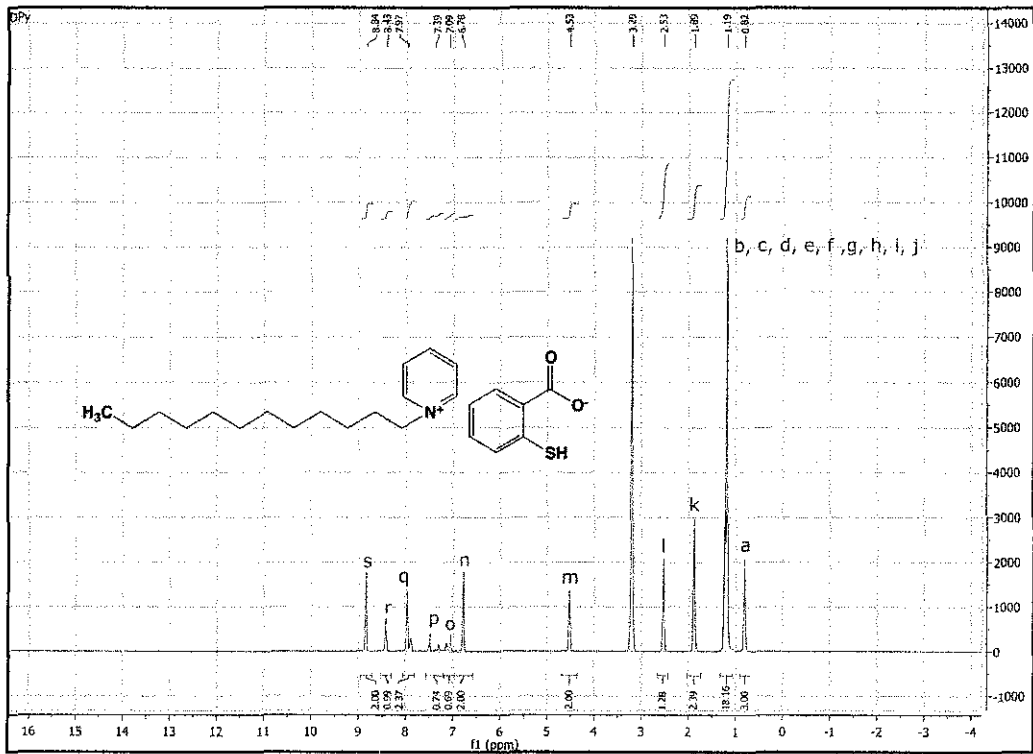


Figure 4.14: <sup>1</sup>H NMR for [DDPY]TS

$\alpha$	T	[HPY]Cl	T	[OPY]Cl	T	[HPY]TS	T	[OPY]TS	T	[DDPY]TS
a	3	3.00	3	3.00	3	3.00	3	3.00	3	3.00
b	2	6.10	2	10.28	2	3.68	2	6.14	2	18.16
c	2		2		2		2		2	
d	2		2		2		2		2	
e	2	2.39	2		2	4.49	2	6.08	2	
f	2	1.98	2		1	1.35	2		2	
g	2	1.89	2	2.20	2	1.99	2		2	
h	1	0.90	2	2.00	2	2.00	1	1.43	2	
i	2	1.92	2	1.89	1	0.78	2	1.96	2	
j			1	0.90	1	1.22	2	1.94	2	
k			2	1.93	2	2.42	1	0.94	2	2.39
l					1	0.90	1	0.96	1	1.28
m					2	2.00	2	1.97	2	2.00
n							1	0.90	2	2.00
o							2	1.91	1	0.69
p									1	0.74
q									2	2.37
r									1	0.99
s									2	2.00

Table 4.4: NMR Actual vs. Theoretical Reading

Parameters	[HPY]TS	[OPY]TS	[DDPY]TS
Density	1.279 g/cm <sup>3</sup>	1.188 g/cm <sup>3</sup>	1.096 g/cm <sup>3</sup>
Viscosity	3258 cP	5899 cP	8698 cP
Salt content	0.71%	0.43%	>1%
Water content	0.65%	0.67%	0.76%

Table 4.5: Ionic Liquids Properties

#### 4.3.4 Ion Chromatography

Ion chromatography is basically the experiment setup, which aims to detect the halide content of the ionic liquids. The process allows the separation of ions and polar molecules based on their charge. The solution to be injected is usually called a *sample*, and the individually separated components are called *analytes*. It is often used in protein purification, water analysis, and quality control. The table above showed both [HPY]TS and [OPY]TS have salt content less than 1%, whereby [DDPY]TS have it a lot more. It might be caused by the existence of Sodium in Sodium lauryl sulfate that is trapped inside the ionic liquid structure and hard to be separated with normal method. Dialysis and/or membrane separation could be considered to remove the sodium from [DDPY]TS.

#### 4.3.5 Density and Viscosity Measurements

Both density and viscosity of the ionic liquids is recorded under standard temperature and pressure (25°C, 1 atm). The viscosity is measured by using viscometer. Moreover, dynamic viscosity is also necessary to be recorded, as it is a measure of the resistance to the liquid flow. The results show that the longer alkyl chain length has higher viscosity, which due to lesser kinetic energy within the molecules. The density, however, is the opposite because the shorter hydrocarbon chain makes the molecule tends to be heavier compare to the longer one.

#### 4.3.6 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a test to examine the heat capacity or the enthalphy of the pure ionic liquids. However, the reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

4.3.7 Microwave Synthesis (Additional)

As a spin-off of the project, there was a trial on microwave synthesis. This method is deemed to score shorter synthesis time compare to reflux method, and no nitrogen is needed throughout the whole procedure. For this test, again, [HPY]Cl and [OPY]Cl were re-quarternized simultaneously within 27 hours and no solvent was used.

Reactants to produce 1-hexyl pyridinium bromide [HPY]Cl:

C <sub>6</sub> H <sub>13</sub> Cl	C <sub>5</sub> H <sub>5</sub> N	→ C <sub>11</sub> H <sub>18</sub> CIN
17.290 ml + 3.431 ml	10.225 ml	
15.198 g + 3.016 g	10 g	
0.126 mol + 0.025 mol	0.126 mol	

Table 4.6: Amount of Reactants for [HPY]Cl (Microwave)

Reactants to produce 1-octyl pyridinium bromide [OPY]Cl:

C <sub>8</sub> H <sub>17</sub> Br	C <sub>5</sub> H <sub>5</sub> N	→ C <sub>13</sub> H <sub>22</sub> NBr
21.408 ml + 4.248 ml	10.225 ml	
18.732 g + 3.717 g	10 g	
0.126 mol + 0.025 mol	0.126 mol	

Table 4.7: Amount of Reactants [OPY]Cl (Microwave)

The result showed some amount of product after the stated reaction time, as follows:

Parameters	[HPY]Cl	[OPY]Cl
Volume	2.817 ml	2.428 ml
Mass	3.603 g	2.884 g
Mole	0.0114 mol	0.00836 mol
Yield (%)	9.048%	6.635%

Table 4.8: Result of Microwave Synthesis

Summarizing from the table above, synthesis method by using microwave does not seem to be significantly better compared to reflux in Pyridinium based ILs. The product yield for both ILs is considerably small and not really applicable.

## CHAPTER 5

### CONCLUSION

All objectives of the project have been successfully fulfilled. All 3 (three) ionic liquids with different alkyl chain length, accomodating Thiosalicylate anion have been synthesized. Several analyzing methods such as Thermogravimetry analysis, Karl-Fisher water content analysis,  $H^1$  Nuclear Magnetic Resonance, and Ion Chromatography have been done. TGA showed theoretical result, where the longer alkyl chain tends to have higher decomposition temperature. Karl-Fischer test has also shown substantially good result with every ionic liquids having less than 0.8% water content. The chain length also has major role in affecting the viscosity and density, whereby the longer chain results in higher density but lower density.

The most important part, the metal extraction objective is also pretty much achieved by attaining **99.133%** average efficiency rate of [OPY]TS in removing all 3 (three) heavy metals. Another success story comes from the **zero** removal rate of Calcium from the alkaline metal group. By getting such outcome, those ionic liquids are expected to be a totally environment friendly because of its ability in removing only heavy metal and keep the stability and sustainability of all other useful metals.

Nevertheless, although [DDPY]TS turns out to be the worst performer throughout the project, but it has to be taken account that the experiment was done by using water as medium. It is recommended for future FYP project to proceed on metal extraction from crude oil or petroleum product that utilizes longer alkyl chain ILs.

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