Extraction of Ca^{2+} from dodecane using 1-butyl-3-methylimidazolium octylsulfate

by

MOHD HAFIZ BIN MOHD AMADZUN (10753)

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JAN 2012

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Malaysia

CERTIFICATION OF APPROVAL

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Approved by,

(Mr Mohd Faisal B. Taha)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JAN 2012

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 acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD HAFIZ BIN MOHD AMADZUN

ABSRACT

The used of volatile organic solvent in extraction of metal ion industry gives a detrimental impact to our environment and human health. This is due to the loss of organic diluents to environment via volatilization. Ionic liquids are currently being studied by many researchers as alternative solvent or alternative extracting agent for metal ions to replace the traditional volatile organic solvent. This is due to the uniqueness of the physical and chemical properties of ionic liquids such as a wide liquidus range, nonflammable and nonvolatile compound. In this study, an attempt was made to investigate the potential of 1-butyl-3methylimidazolium octylsulfate [BMIM][OCS] as extracting agent for Ca^{2+} from model oil, i.e. dodecane. Two factors affecting extraction of Ca^{2+} from dodecane using [BMIM][OCS] were studied: contact time of the mixture (between [BMIM][OCS] and dodecane containing Ca^{2+}) and loading od ionic liquids (different mass ratio of [BMIM][OCS] and dodecane containing Ca^{2+}). Mass ratio of 1:10 between [BMIM][OCS] and dodecane containing Ca^{2+} showed the highest efficiency of extraction which is 99.35% with 5 minutes of extraction process. These results indicate that use of ionic liquids as alternative to traditional extraction agents in liquid/liquid extraction of heavy metal ions is very promising.

ACKNOWLEDGEMENT

First and foremost, I would like to express the utmost gratitude towards Allah S.W.T for His blessing upon finishing this Final Year Project. During a time to complete this project, there were many people involved, who had contributed invaluable guidance, advice and assistance. I would like to express greatest thanks to my supervisor, Mr. Mohd Faisal B. Taha for his knowledge, ideas, guidance and outstanding support throughout the project.

I am also would like to take this opportunity to express very sincere thanks to Dr Lukman B. Ismail, coordinator of Final Year Project. Without his management and coordination, the flow of this project might not be as expected.

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Finally, I would like to express deepest appreciation to those involved directly and indirectly in the completion of this research project. With the full cooperation from these people, I have successfully achieved the objective of this project.

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ABRREVIATIONS

ppm – part per million

[Cl] - chloride

$[AlCl_3]$ – aluminiuim trichloride

$[AlCl_4^-]$ – aluminium tetrachloroaluminate ion

$[BCl_3]$ – boron trichloride

[CuCl] – copper chloride

$[BF_4^-]$ – tetrafluoroborate ion

$[PF_6^-]$ – hexafluorophosphate ion

$[HSO_4^-]$ – hydrogen sulfate ion

$[C_4mim][OH]$ – 1-butyl-3-methylimidazloium hydroxide

$[C_2mim][Cl]$ – 1-ethyl-3-methylimidazolium chloride

$[C_2mim][NO_2]$ - 1-ethyl-3-methylimidazolium nitrite

$[C_2mim][NO_3]$ - 1-ethyl-3-methylimidazolium nitrate

$[C_2mim][AlCl_4]$ - 1-ethyl-3-methylimidazolium aluminium chloride

$[C_2mim][BF_4]$ - 1-ethyl-3-methylimidazolium tetrafluoroborate

$[C_2mim][CF_3SO_3]$ - 1-ethyl-3-methylimidazolium triflate

$[C_2mim][CF_3CO_2]$ - 1-eutyl-3-methylimidazolium trifluoroacetate

CHAPTER 1

INTRODUCTION

1.1 Background of Study

For over past decades, the rapid increase in the use of heavy metal has inevitably involved an increased flux of metallic substances into natural water bodies and soils. The presence of heavy metals in the environment is particularly dangerous as there are toxic and persistent (Rios et al. 2010). Heavy metal that has been produced by industry through the production of wastewater is huge in amount. This wastewater contained heavy metal elements and need to be treated. This is because the presence of heavy metal in the environment is particularly dangerous since they have high level of toxicity. Besides, the presence of heavy metals in wastewater can destroy the effectiveness of normal wastewater treatment operations.

Several technologies such as precipitation, solvent extraction and ion exchange can be used to remove toxic metal from liquid effluents. Solvent extraction technology is widely used in the recovery and separation of metals from aqueous solution. For example, the extraction agent [di(2-ethylhexyl)phosphoric acid, tris(2-ethylhexyl)amine, liquid phosphine oxides, etc.] is dissolved in an organic solvent such as kerosene, toluene, etc which is used as the diluents (R[illegible] 2007). One of disadvantages this technology is the loss of organic diluents via volatilization which has bad impact on the environment and human health (Rios et al. 2010).

The used of ionic liquids could overcome this disadvantage. This is because ionic liquids are organic salts that are liquids over a wide temperature range. The most common ion liquid that being used are imidazolium, pyridinum and ammonium ions and anions such as halide, [BF_4^-], [Pf_6^-], or [NTf_2^-]. Nowadays, ionic liquid has been revealed as interesting clean alternatives to classical organic solvents in a wide range of chemical and biochemical processes ([illegible] 2008). Furthermore, ionic liquid also has been successfully applied in extraction processes, such as isolation of metal species and organic compound (i.e., esters, alcohols, and organic acids) ([illegible] 2010).

1.2 Problem Statement

1.2.1 Problem Identification

The presence of traces of heavy metals in the environment is particularly dangerous since most of them are toxic and persistent. This has increased the flux of metallic substances into natural water bodies and soils. Most of the industries are using solvent extraction process to overcome the problems. Solvents or organic diluents such as benzene and toluene that have been used in industry as solvent extraction process are having many problems. Volatilization of organic diluents to atmosphere gives a very bad impact to environment and human health. Thus, ionic liquids have been replaced organic solvents to overcome this problem or disadvantageous of organic solvents.

1.2.2 Significant of the project

Through this project, the potential of using [BMIM][OCS] as extracting agent for Ca^{2+} from dodecane can be studied and evaluated. By using ionic liquid as replacement of organic diluents, the volatization of organic dilents can be avoided. Thus, this could prevent the loss of organic solvents through volatilization.

1.3 Objectives

- To study the potential of [BMIM][OCS] to extract Ca^{2+} from dodecane at room temperature
- To perform the kinetic study in extracting Ca^{2+} with the usage of [BMIM][OCS]
    - Effect of contact time betweem [BMIM][OCS] and dodecane containing Ca^{2+}
    - Effect of loading of ionic liquid, i.e. mass ratio of [BMIM][OCS] and dodecane containing Ca^{2+}

1.4 Scope of Study

The first stage of study consists of industry case studies to understand the metal ion extraction process. Many references related to this study can be found. The understanding of the extraction process is important before moving to the second stage of study.

The second stage involved experiment work. A few parameters such as mixing time and mass ratio of [BMIM][OCS] and dodecane containing Ca^{2+} have been studied as these factors affect the extraction of metal ion process.

Then, analysis was performed based on the data collected from the experiment.

1.5 The relevancy of the project

The used of organic diluents in extraction process causing volatilization of organic diluents which is dangerous to our environment and human health. The used of ionic liquid could overcome this problem.

1.6 Feasibility of the project

This study is fully experimental based. The objectives can be achieved if procedures are closely followed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In general, compound that consists entirely of ions are called ionic liquid which are an organic cation and inorganic anion. Ionic liquid exist in liquid phase at room temperature. In other word, 'ionic liquid' refers to the salts that with a melting point below 100°C. Molten salt refer to high temperature melts. Any salts with a high melting point, basically above 100°C known as a molten salt ([illegible]). In comparison in these two salts, ionic liquid have relatively low viscosity whereas1molten salts are often highly corrosive and highly viscous.

In 1990s, the term "ionic liquid" has been introduced to distinguish the low-temperature molten salts, also known as room temperature molten salts from high-temperature melts molten salts. This is because low temperature molten salts are operated at high temperatures.

Many organic salts have low melting points, but the most investigated salts consists of organic 1-alkyl-3-methylimidazolium $[C_n\text{mim}]^+$, where n is the number of carbon atoms in a linear alkyl chain and tetraalkylammonium cations, etc. These cations are combined with either organic or inorganic anions such as hexaflurophospate tetrafluoroborate, trifluoromethylsulfonate, nitrate halide, etc. The potential number of ionic liquids is immense as a lot of possibility combination of anion-cation ([illegible]).

For decades, the research has been done on the properties of ionic liquid which concentrated on developing and understanding the relationship between cation, anion and physical properties. Besides having a low melting point, ionic liquids also compounds which are having negligible vapor pressure, wide liquidus range, high electrochemical stability, high thermal stability and low flammability. Most of the ionic liquid will meet all these criteria except for some ionic liquids which are explosive, electrochemical and thermally unstable (Ben Thijis, 2010).

Ionic liquid have a negligible vapor pressure thus, it has a potential of being 'green solvent'. The ionic liquid is non-volatile due to low melting point and higher boiling point. One of the examples is, $[C_4mim][OH]$ ionic liquid which has been used as green solvent for a Koevenagel reaction. RANU et al. is using this method in order to avoid using harmful organic solvent that will negatively effect on environment (Kenneth et al., 2000; Ranu et al. 2006). Figure 1 shows the examples of ionic liquids that have low volatility compared to other solutions.

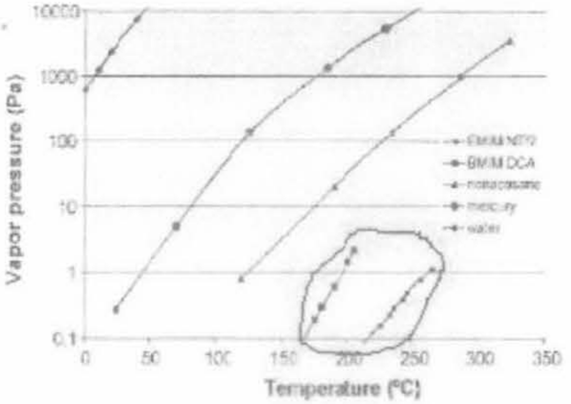


Figure 1: Vapor pressure of molecular liquids as compared to ionic liquids

Another property that is important to know is melting point of ionic liquid. The melting point of ionic liquids is influence by both cation and anion, and basically it is closed to or below 100 ^{0}C. Charge distribution on the ions, H-bonding ability, the symmetry of the ions and van der Waals interaction are the factors that influence the melting point (Wasserscheid et al., 2003; Earle et al., 2000).

In ionic liquid, cation has a low degree of symmetry which reduces the lattice energy of the crystalline form of the salt, thus lowering the melting point. Moreover, the relatively large size of anion contributes in lowering the melting point too. Basically, the size of the ions in ionic liquid is inversely proportional to the melting point of the ionic liquid.

Table 1: Influence of anion size on melting point

Imidazolium Salt	**Melting Point (^{0}C)**
[C_2mim][Cl]	87
[C_2mim][NO_2]	55
[C_2mim][NO_3]	38
[C_2mim][$AlCl_4$]	7
[C_2mim][BF_4]	6
[C_2mim][CF_3SO_3]	-9
[C_2mim][CF_3CO_2]	-14

The choice of anion and cation greatly influence the viscosity of ionic liquid. The longer alkyl chain will contribute to higher viscosity and on the other hand, modest size of alkyl chain will result in lower viscosity. As mention earlier, van der Waals forces between the cations, increases the energy required for molecular motion (Ben Phiis 2010). This is because, ionic liquid with higher molecular size and higher molar mass, it will have higher viscosity. Cation that is more asymmetrical will contribute to low viscosity. For example, Imidazolium-based ionic liquid decreases when compact and branched alkyl chains are used (Ben Phiis 2010; [illegible] 2006).

The thermal stability of the ionic liquid is affected by the anion. By having more nucleophilic and coordinating anions, it will result in lower thermal stability (Ben Phiis 2010). Imidazolium-based ionic liquid has been used in most study to prove the statement above (Ngo et al., 2000).

Anion will determine the hydrophobicity of ionic liquid. Ionic liquid with more hydrophobic character can be generated by fluorinated anions. Besides, the chain length on the cation also influences the hydrophobicity. For example, it was demonstrated by using imidazolium-based tetrafluoroborate ionic liquid ([illegible] 1999).

2.2 Application of Ionic Liquid

Over a past decade, many applications of ionic liquid have been reported. As stated earlier, the uniqueness of ionic liquid properties mainly contributes to their application in industry. Several features of ionic liquid are as below ([illegible] 2007).

- Many have negligible vapor pressure
- Many have tunable solubility
- Many have good thermal stability
- Many have electric conductivity
- Many have wide electrochemical window
- Many are liquid in a wide range of temperature
- They are easy to be synthesized

With these features, ionic liquid has been used in many applications such as:

- Solvents
    - Organic reaction and catalyst
    - Biphasis reactions
    - Polymerization
    - Protein crystallization
- Separation
    - Gas absorption
    - Extraction
    - Membranes
- Electrolytes

  - Batteries
  - Fuel cells
  - Sensors
  - Coating
- Engineering Fluids
  - Lubricants
  - Thermodynamics fluids
- Catalysts

2.3 Ionic Liquid as Potential Metal Extraction Agent

Ionic liquid can be used as replacement of organic solvents in a wide range of application in industry due to their uniqueness of chemical and physical properties. Organic solvent are being used in synthesis, catalysis, electrochemisty, liquid-liquid extraction etc. Properties such negligible vapor pressure, good thermal stability and tunable miscibility of ionic liquid are important for separation processes. For separation applications, the ability to dissolve a variety number of solute is an important characteristic. Thus, ionic liquid with these kinds of properties may be very useful for the extraction of metal ions (Lee, 2006).

Ionic liquid also can be used in the extraction of metal ions from aqueous phase of biphasic water-ionic liquid system. This is due to the hydrophobic character of ionic liquid. There is a need of extractant that form stable complexes with metal ions that are hydrated in aqueous phase and this extractant is dissolved in the hydrophobic ionic liquid. According to Lee, Visser *et al.* and Cocalia *et al.* the problem that have been encountered is to find the extractant compound that remain exclusively in the ionic liquid under all process conditions. The right combination of ionic liquid and ligand need to be obtained. A lot of metals have been subjected to extractions such as alkali metals, alkaline earths metals, heavy- and radioactive metals. . Crown ethers, calixarenes etc, are the metal complexing agents that contained in metals that has been extracted by ionic liquid. This has been reviewed by Zhao *et al.* Also, there are few reports stated about a combination of a chelating agent and an ionic liquid are used to extract metals from aqueous.

Lee reviewed the new method for metal ion extraction which is by using task-specific ionic liquid. This task-specific ionic liquid can acts as both solvents and extractants. This ionic liquid contain specific chelating group that incorporated with one of the ionic liquid components, commonly cation. The objective of this new approach is to prevent the loss of chelating agent to the aqueous media. Also, to increase the affinity of the target metal ion to the ionic liquid. Many report show that metal ions removal from aqueous solution using task-specific ionic liquid incorporating disulfide-, thioether-, urea-, and hydroxybenzylamine as extracting agents (Lee, 2006). Most of the task-specific ionic liquids described in the literature are based on imidazolium-, piperidinium-, pyrrolidinium- and pyridinium cations and fluorine containing anions.

The concept of task-specific ionic liquids to extract heavy metal ions was introduced by Davis and Rogers. They designed metal ion-ligating groups such as thioether (Figure 2a), thiourea (Figure 2b) and urea (Figure 2c) were incorporated into the imidazolium cation to extract mercury (II) and cadmium (II) from aqueous solution (Lee, 2006).

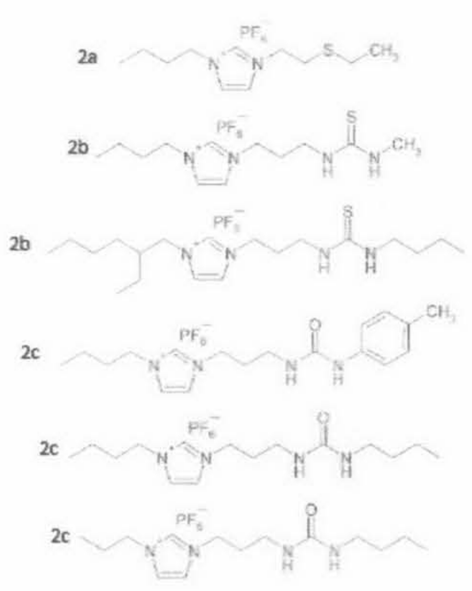


Figure 2: Structure of the task-specific ionic liquids with thioether, thiourea and urea derivatised-based cations

2.4 Preparation of Ionic Liquid

In general, the steps for preparation of ionic liquid are simple. A reaction scheme for the basis synthesis of ionic liquid is shown in Figure 2 using imidazolium cation. The common cations used are shown in Figure 1 (Kenneth et al., 2000).

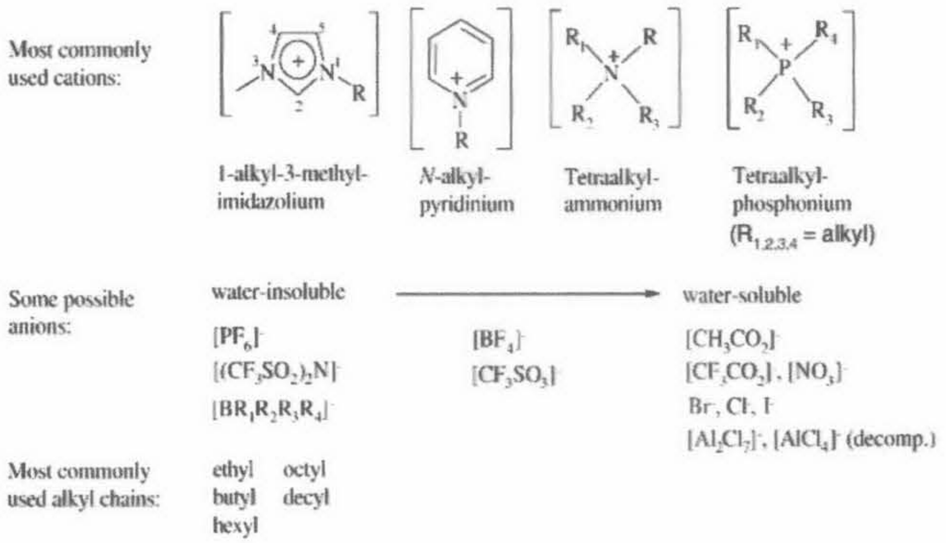


Figure 3: Common types of cation in ionic liquid

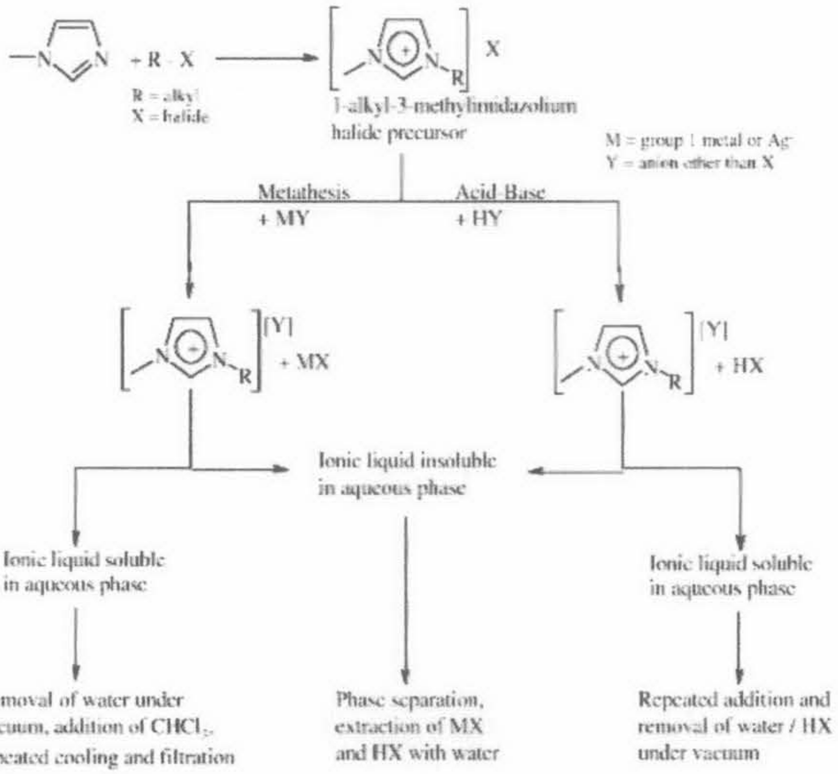


Figure 4: Synthesis path for the preparation of ionic liquid exemplified for an imidazolium-based ionic liquid.

The imidazolium-based liquids used are derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide, in general known as chloride or other alkylating agent. The precursor is prepared by alkylation of 1-methylimidazole, as depicted in Figure 2. The halide salts with different anions can be prepared depending on the alkylating reagent. The halide salts then is converted to the desired ionic liquid by reacting them with salts or acids containing the desired anion (Wasserscheid et al., 2003). Table 1 below shown the example of ionic liquids that can be obtained using different alkylating agents through quaternisation reactions.

Table 2: Examples of ionic liquid that can be formed through direct quarternisation[14]

Ionic Liquid	**Alkylation Agent**	**Melting point (^{0}C)**
[EMIM][CF_3SO_3][a]	Methyl triflate	-9
[BMIM][CF_3SO_3][b]	Methyl triflate	16
[PH_3PO_c][OT_s][c]	OcOTs	10-71
[Bu_3NMe][OTs]	MeOTs	62
[BMIM][Cl]	Chlorobutane	65-69

[a] EMIM = 1-ethyl-3-methylimidazolium; CF_3SO_3 = triflate anion
[b] BMIM = 1-n-butyl-3-methylimidazolium
[c] Oc = octyl; Ts = $H_3CC_6H_4$-SO_2 (tosyl)

Another two methods that can be used to obtain the desired anion are:

i) The first route which called acid-based neutralization reactions, is by reacting the halide salt with a Lewis acid HY containing the desired anion (Kenneth et al., 2000; Wasswrscheid et al., 2000).
ii) The second route which called metathesis is by exchanging the halide ion X^- for the desired ion. Metal salt MY is added over an ion exchanger.

Examples of ionic liquids that can be prepared by both reactions mention above are shown in Table 2 and 3 (Zhang et al., 2007)

Table 3: Examples of ionic liquids that can be prepared by the reaction of a halide with Lewis acid

Ionic Liquid[a]	**Established anion**
[cation][Cl/$AlCl_3$]	Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$
[cation][Cl/$AlEtCl_2$]	$AlEtCl_3^-$, $Al_2Et_2Cl_5^-$
[cation][Cl/BCl_3]	Cl^-, BCl_4^-
[cation][CuCl]	$CuCl_2^-$, $Cu_2Cl_3^-$
[cation][Cl/$SnCl_2$]	$SbCl_3^-$, $Sn_2Cl_5^-$

[a] cation = pyridium, imidazolium ion

Table 4: Examples of ionic liquids that can be prepared by anion exchange

Ionic liquid[a]
[cation][BF_4]
[cation][PF_6]
[cation][SbF_6]
[cation][NO_3]
[cation][CH_3CO_2]
[cation][HSO_4]
[cation][B(Et_3Hex)]

[a] = pyridium, imidazolium, ammonium ion

CHAPTER 3

METHODOLOGY

3.1: Methodology Process

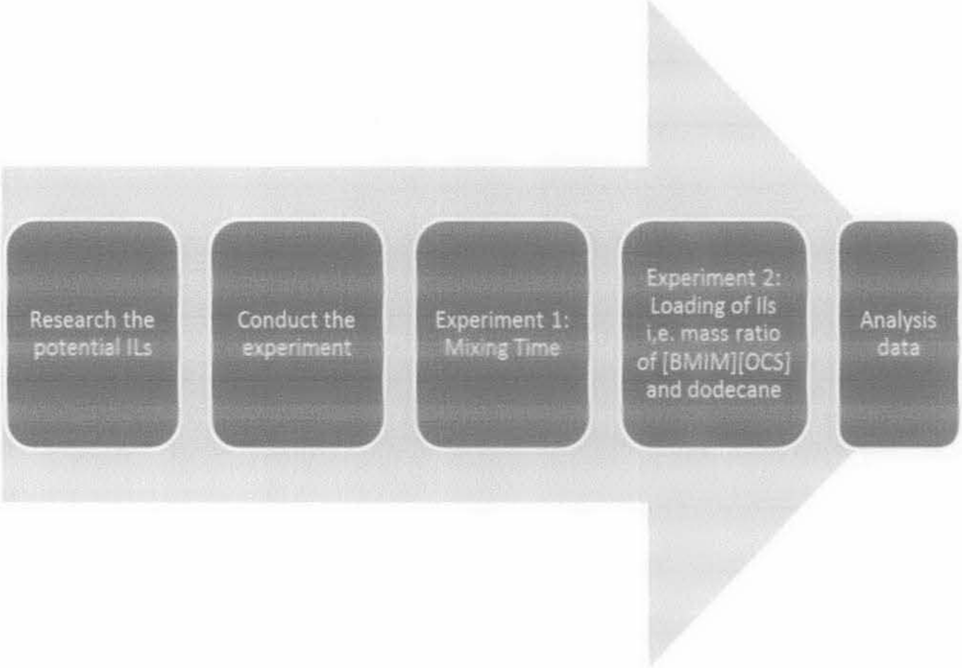


Figure 5: Methodology Chart

3.2 Characterization of [BMIM][OCS]

3.2.1 Measurement of Water Content

1) [BMIM][OCS] is place in the oven at 70°C for 5 days for the purpose of drying.

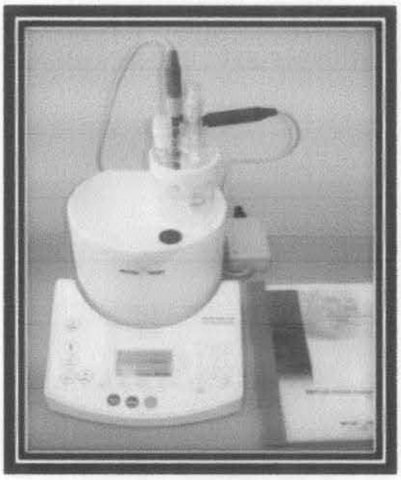
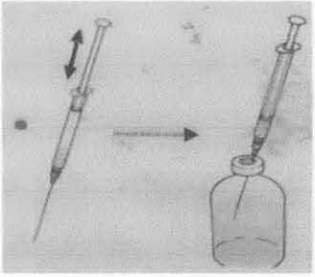
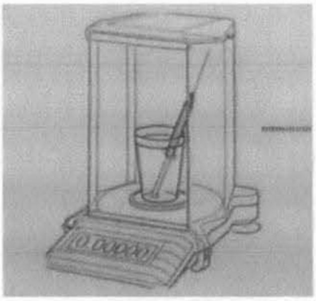


Figure 6: Karl-Fisher Coulometer DL39

2) Karl-Fisher is switched on (Method 1).
3) OK button is pressed and pretitration will take place. Standby mode will appear right after pretitration is finished. Drift must be less than 20 in order to continue.
4) The syringe is emptied into the waste bottle and is repeated 2 or 3 times.

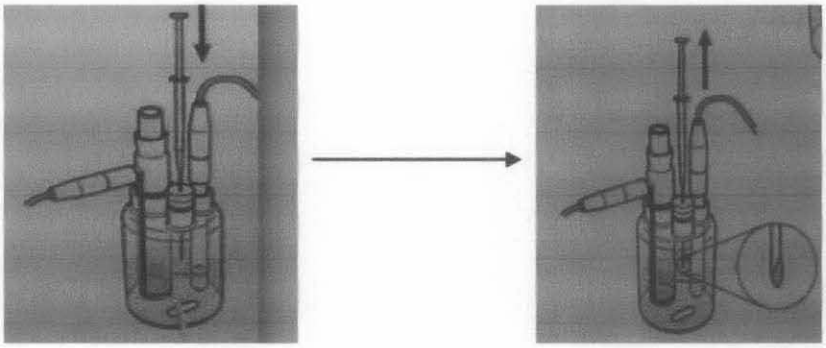


5) The syringe is placed in the beaker on the balance pan and is tare to "0".

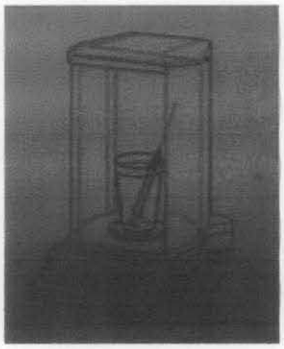


6) Sample is added and the maximum of the weight is 5 g.

7) Sample is injected into the titration cell and OK button is pressed.



8) Sample button is pressed and the value of weight is entered.
9) After a few minutes, the value of moisture content will appear.



3.2.2 Measurement of Density

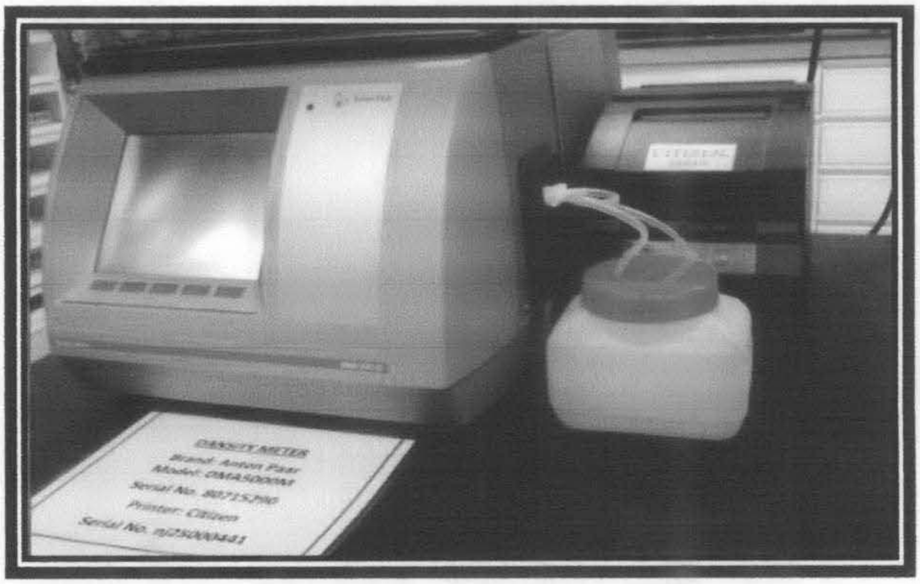


Figure 7: Densitometer DMA 5000M

1) The DMA 5000M is switched on.
2) The syringe is filled in with [BMIM][OCS] up to 4ml.

3) The sample is injected at the sample inlet until some of the sample flow out at the waste tube.
4) The oscillating tube is observed by pressing the EYE IKON tab. Bubble must not present in the oscillating tube.
5) "X" button is pressed to go back to main page.
6) START button is pressed. The DMA will start to equilibrate to the starting temperature and measurement will take place.
7) USB is connected to the equipment. MAIN SCREEN > MENU > DATA MEMORY > MEASURED DATA > EXPORT DATA > PDF. This steps is followed in order to get the data.

3.3 Extraction Study

1) Calcium solutions (CONOSTAN) with the 1000 ppm concentration were diluted into 25 ml volumetric flask. 4 sets of stock solution which are 20 ppm, 30 ppm, 40 ppm and 50 ppm were prepared.
2) All 4 samples were tested using UV-VIS spectrophotometer for a qualitative and quantitative determination of calcium in model oil and ionic liquid.
3) The experiment was started with 30 ppm dodecane containing Ca^{2+}. Seven samples of 30 ppm dodecane containing Ca^{2+} with mass ratio of 1:5 were prepared. A 0.5 gram of [BMIM][OCS] was mixed with 2.5 gram dodecane containing Ca^{2+} (30 ppm).

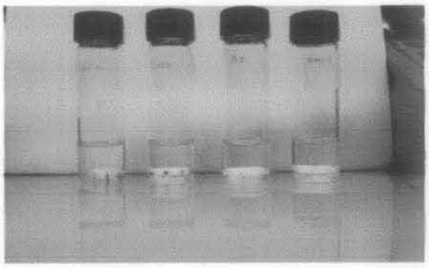


Figure 8: Mass ratio 1:5 of [BMIM][OCS] and dodecane containing Ca^{2+}

4) Sample was mixed and stirred at 600 ppm at 25^{0}C using a stem block heater for 5 minutes. This step was repeated for different interval time: 10, 15, 20, 25 minutes.

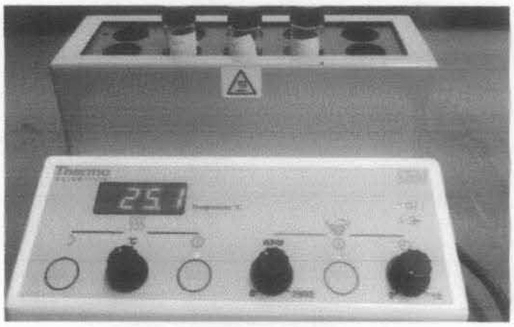
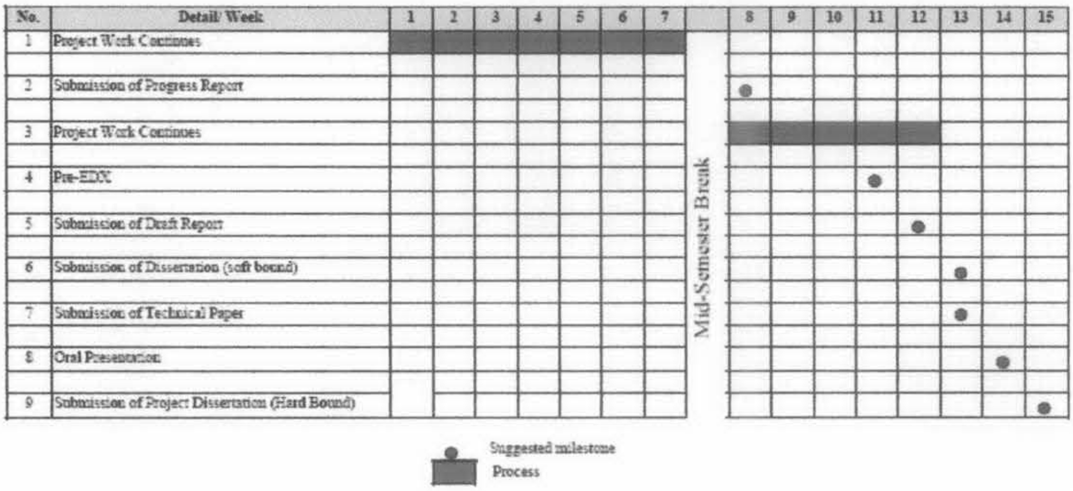


Figure 9: Stem Block

5) Sample was left for 10 minutes for settling process.
6) Sample of dodecane containing Ca^{2+} was separated from [BMIM][OCS] and the sample was analysed again using UV spectrophotometer.
7) Experiment was repeated from method 3 – 6 using different mass ratio approach.

3.4: Gantt Chart and Key Milestone



No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	▨	▨	▨	▨	▨	▨	▨	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									▨	▨	▨	▨	▨			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone
▨ Process

Figure 10: Gantt Chart and Key Milestone table

3.5 Tools, Equipments and materials

There are several tools that required using for this project. The tools are:

1. Karl Fischer Coulometer DL39
2. Densitometer DMA 5000M
3. Shimadzu UV-VIS spectrophotometer
4. Magnetic stirrer
5. Stem block
6. Centrifuge tube

The chemicals needed for this project is:

1. Calcium solution (CONOSTAN) 1000 ppm
2. Dodecane
3. Bmim Octylsulfate

CHAPTER 4

RESULTS AND DISCCUSIONS

4.1 Characterization of [BMIM][OCS]

4.1.1 Moisture content

After the [BMIM][OCS] was placed in the oven at 70°C for 5 days, the moisture content was determined using Karl-Fisher.

Table 5: Moisture Content of [BMIM][OCS]

No	Weight Sample (g)	Moisture Content (%)	Moisture Content (ppm)
1	0.0505	1.82	18167.33
2	0.0262	3.94	39379.58
3	0.0197	2.75	27474.96

As the moisture content was higher than 1%, further drying was conducted. The [BMIM][OCS] was placed in the oven for another 2 days. Again, the moisture content was determined.

Table 6: Moisture Content of [BMIM][OCS]

No	Weight (g)	Moisture Content (%)	Moisture Content (ppm)
1	0.00600	0.81	8115.000
2	0.00109	0.65	6538.991

4.1.2 Density Measurement

By using densitometer, the density of the [BMIM][OCS] can be determined. The density is different at different temperature. The density of the [BMIM][OCS] was determined from 25 ^{0}C until 50 ^{0}C. Table below shows the results.

Table 7: Density of [BMIM][OCS] at different temperature

Temperature (^{0}C)	**Density (g/cm^3)**
20	1.0650
25	1.0616
30	1.0584
35	1.0551
40	1.0519
45	1.0487
50	1.0455

Density is inversely proportional to temperature. As the temperature increases, the density of [BMIM][OCS] decreases. Graph below was plotted in order to study the relationship between density and temperature. (See Figure 11)

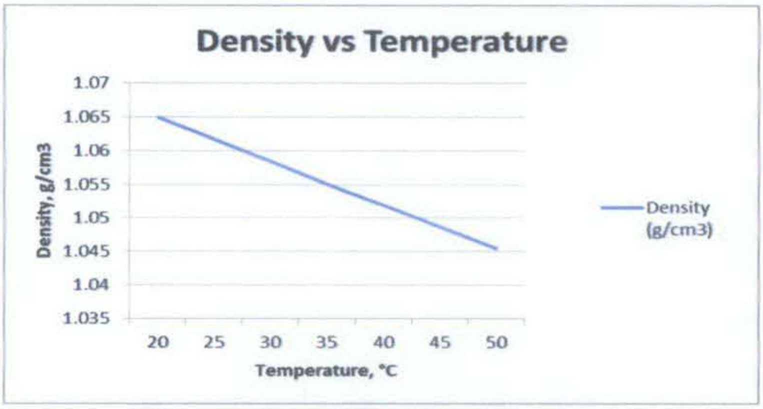


Figure 11: Graph of Density vs Temperature

4.1.3 CHNS

By using CHNS model 932, carbon, hydrogen, nitrogen and sulfur content were determined.

Table 8: Composition of [BMIM][OCS]

Sample/Composition	Carbon	Hydrogen	Nitrogen	Sulfur
1	53.04	9.214	8.231	9.771
2	50.36	8.434	7.041	8.256
3	50.56	8.137	7.887	7.800
Average	**51.32**	**8.595**	**7.720**	**8.609**

4.2 Extraction Study

4.2.1 Calibration Data

Table 9: Absorbance height at 271 μM for respective concentration

Wavelength(μm)	Absorbance, Å			
	20ppm	**30ppm**	**40ppm**	**50ppm**
271	0.941	1.573	1.984	2.167

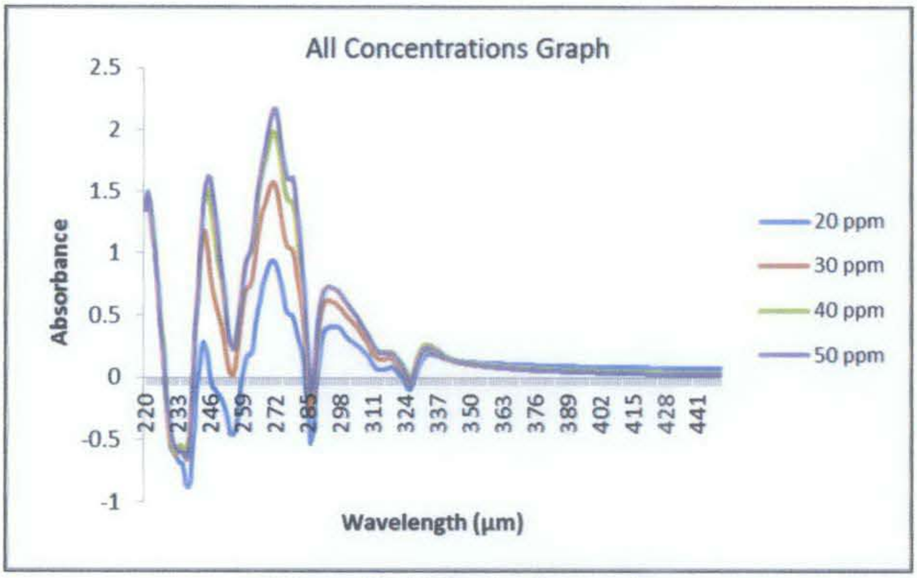


Figure 12: Calibration data graph

The graph below (Figure 13) was obtained from the UV-VIS spectrophotometer data for dodecane containing Ca^{2+} (30 ppm) **before being extracted** by [BMIM][OCS]. From the graph, calcium ion can be found approximately at 271 μm wavelength. In this study, the wavelength 271 μm was used as a reference in order to determine the concentration of Ca^{2+}.

4.2.2 Calibration Curve

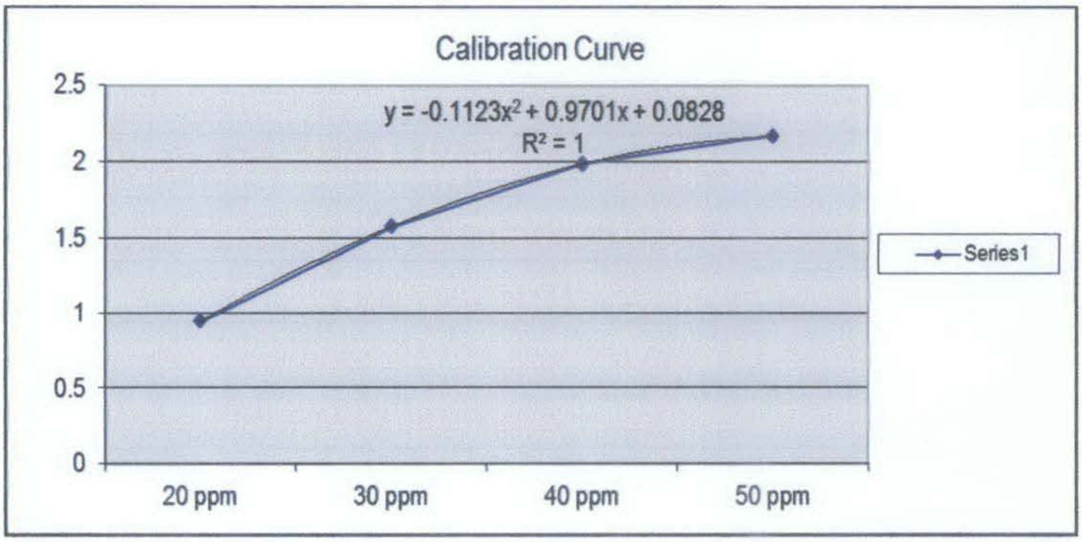


Figure 13: Calibration curve

From the calibration data gain from UV-VIS spectrophotometer, calibration curve was plotted. The black polynomial line represents the best fit line for the data as the value of R^2 is equal to 1.

4.2.3 Prescreening of extraction study

Pre-screening of extraction study was done to see the effects of mass ratio. Mass ratio of **1:5, 1:10, and 1:15** of [BMIM][OCS] and dodecane in Ca^{2+} respectively were tested until **15 min of mixing time with interval time of 5 min**.

4.2.3.1 Extraction of 30 ppm dodecane containing Ca^{2+} (mass ratio of 1:5)

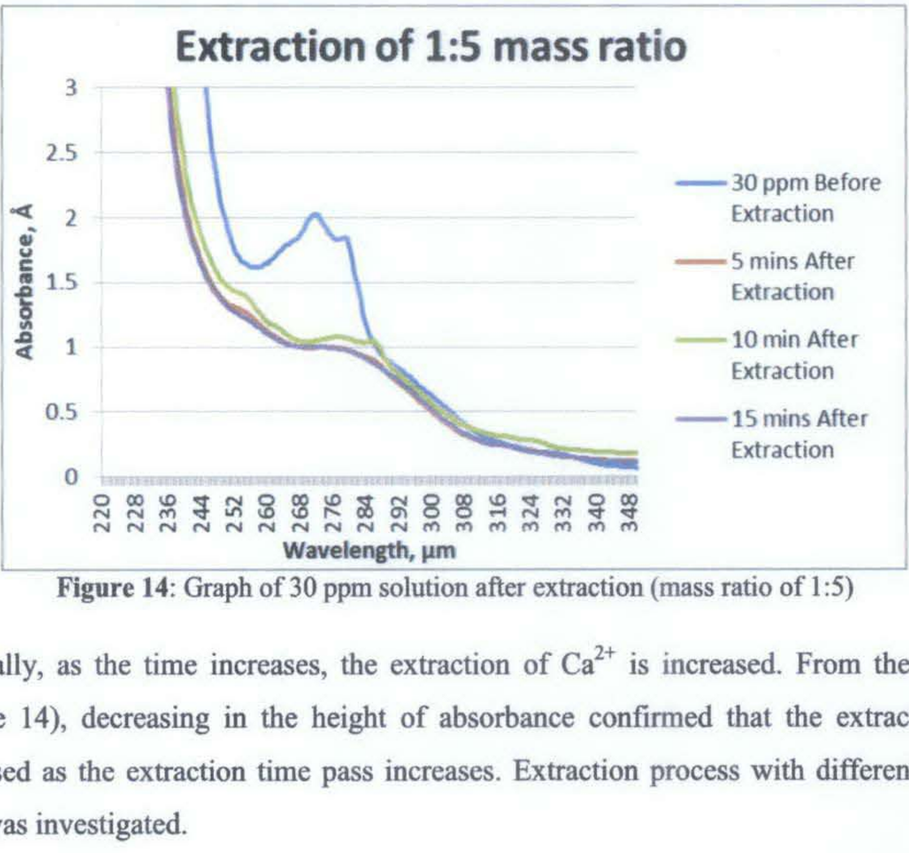


Figure 14: Graph of 30 ppm solution after extraction (mass ratio of 1:5)

Generally, as the time increases, the extraction of Ca^{2+} is increased. From the graph (Figure 14), decreasing in the height of absorbance confirmed that the extraction is increased as the extraction time pass increases. Extraction process with different mass ratio was investigated.

4.2.3.2 Extraction of 30 ppm dodecane containing Ca^{2+} **(mass ratio of 1:10)**

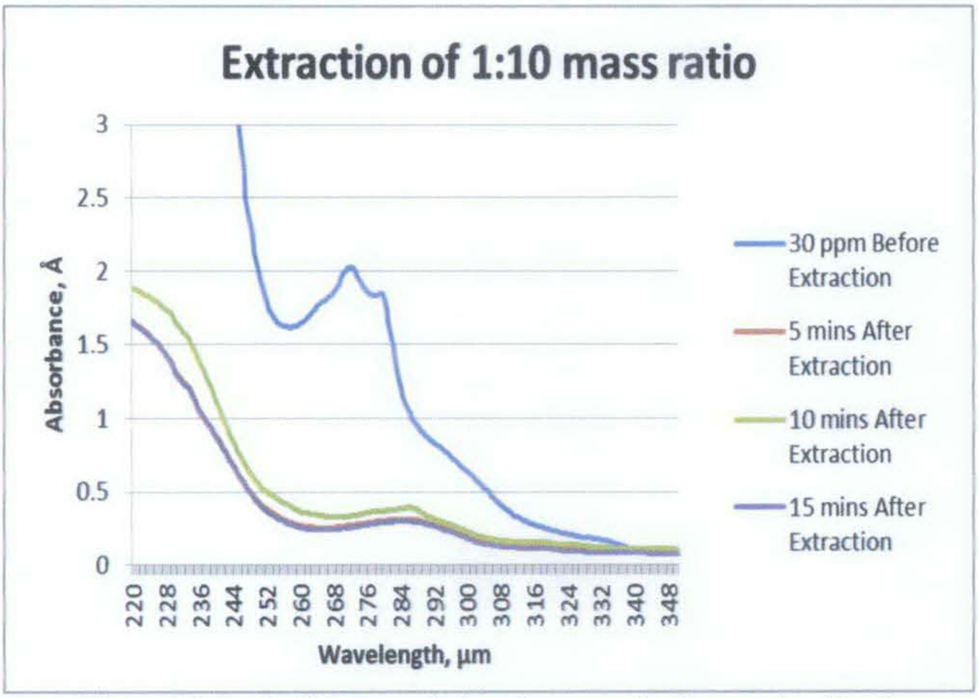


Figure 15: Graph of 30 ppm solution after extraction (mass ratio of 1:10)

4.2.3.3 Extraction of 30 ppm dodecane containing Ca^{2+} **(mass ratio of 1:15)**

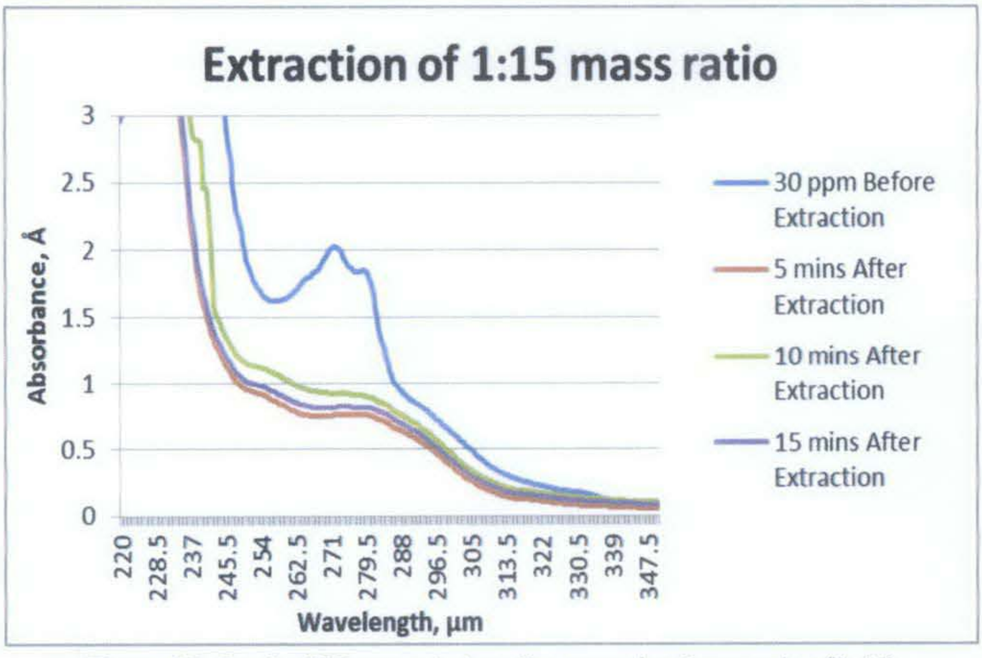


Figure 16: Graph of 30 ppm solution after extraction (mass ratio of 1:15)

All of the extraction studies showed the same trend of results. It was found that optimum time for the extraction was around after 5 minutes of mixing.

Extraction studies for mass ratio 1:25, 1:35 and 1:45 of [BMIM][OCS] and dodecane containing Ca^{2+} respectively, with 5 min of mixing time was conducted.

4.2.3.4 Extraction of 30 ppm dodecane containing Ca^{2+} after 5 min of mixing and stirring **(mass ratio of 1:25, 1:35 and 1:45)**

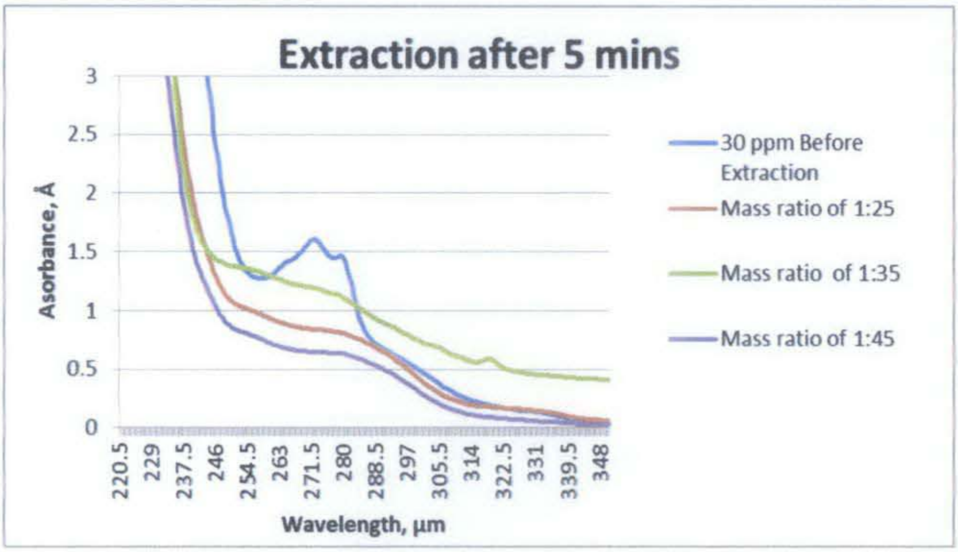


Figure 17: Extraction after 5 min for mass ratio of 1:25, 1:35, and 1:45

4.2.4 Efficiency of Extraction

The percentage of extraction after 5 min of mixing and stirring was calculated for different mass ratio between [BMIM][OCS] and dodecane containing Ca^{2+}. The efficiency is presented in Table 10.

Table 10: Efficiency of extraction process

Mass Ratio (IL/Dodecane)	Efficiency (%)
1:5	96.43
1:10	99.35
1:15	98.10
1:25	97.35
1:35	96.99
1:45	96.55

The formula used to calculate the percentage of extraction is shown below;

$$\%E = \frac{(\text{absorbance before extraction} - \text{absorbance after extraction})}{\text{absorbance before extraction}} \text{x}100\%$$

From the results obtained, it was found that the mass ratio 1:10 which is 0.5 g and 5 g of [BMIM][OCS] and dodecane containing Ca^{2+} respectively, showed the highest extraction efficiency which is 99.35%. Hence, mass ratio of 1:10 was selected to perform the kinetic study. The effect of mixing time was studied as well.

Table 11: Percentage of Extraction (mass ratio of 1:10)

Time (min)	Percentage of Extraction (%)
0	0
5	99.35
10	99.12
15	99.40
20	99.44
25	99.29
30	99.05
35	99.33

The results above were plotted in graph as shown below;

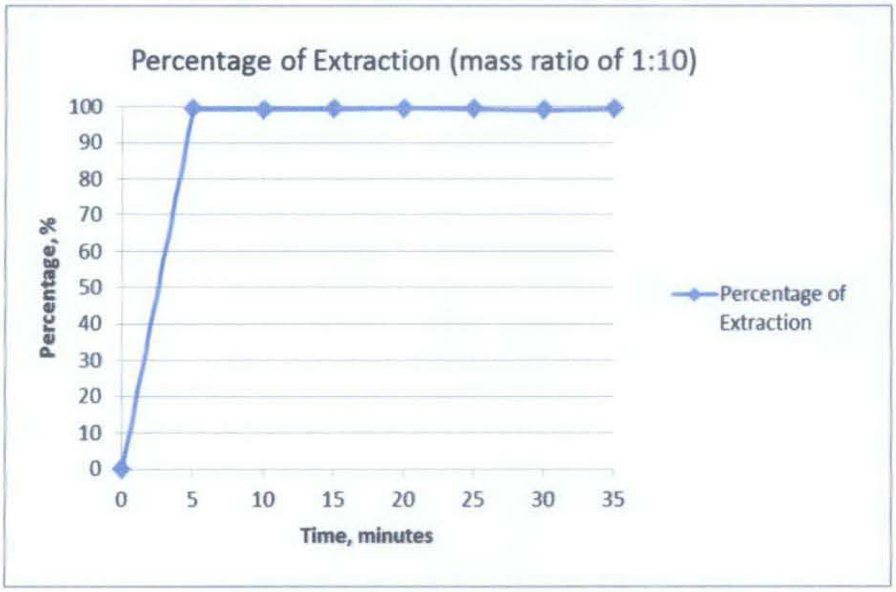


Figure 18: Percentage of Extraction

For mass ratio of 1:10, [BMIM][OCS] was found to extract Ca^{2+} from dodecane efficiently even after 5 min of mixing Ca^{2+} from 5 min to 35 min. The percentage of extraction for 5 min of interval time was about 99%. Based on the data obtained, the optimum time for extraction was 5 minutes as the equilibrium reached after 5 minutes of mixing.

Percentage of extraction for mass ratio 1:5 and 1:15 can be found in appendixes.

CHAPTER 5

CONCLUSIONS & RECOMMENDATION

5.1 Conclusions

The extraction of metal ion with dodecane in a biphasic system consisting ionic liquid and organic solvent was demonstrated. Ionic liquids can be employed for extraction of metal ions. Also, ionic liquids are environmentally benign because of their unique properties such as nonvolatile and nonflammable.

[BMIM][OCS] showed a good potential as extraction agent for Ca^{2+} from model oil, dodecane. Parameters such as mixing time and loading of [BMIM][OCS] affect the extraction process. Hence, ionic liquid have a potential to replace traditional volatile organic solvent in liquid/liquid extraction of metal ions.

5.2 Recommendation

From this study, several recommendations have been identified in order to improve the usage of ionic liquids in liquid/liquid extraction of metal ions;

1) To study the effects of mixing temperature.

2) To study more ionic liquid's characteristic to obtain the best extracting agent for organic solvent.

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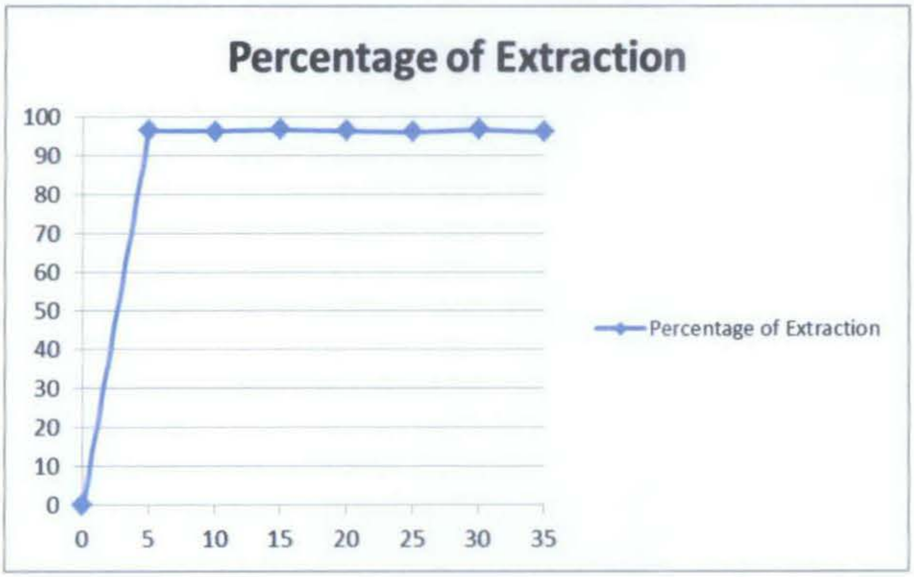
APPENDIXES

Appendix A: Mass ratio of 1:5 between [BMIM][OCS] and dodecane containing Ca^{2+}



Appendix B: Mass ratio of 1:15 between [BMIM][OCS] and dodecane containing Ca^{2+}