CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Crude oils contain trace amount of metal that need to be removed. The process of removing metal is called demetallization. Farhat Ali (2006) says that the amounts of metals in crude oil are varying and more than 1000 ppm. The metals found are sodium, potassium, lithium, calcium, strontium, copper, silver, vanadium, manganese, tin, lead, cobalt, titanium, gold, chromium and nickel. The metals are undesirable as they not only contaminate the products, the metal chelates also cause poisoning and fouling of catalyst and corrode equipments. When oil is burned, metal in fuels oil produce ash that deposits in engines result in abrasion of the moving parts of the engines, and the ash is injurious to the walls of the equipments (US Patent, 2005). There are several physical and chemical methods already existed of demetallization (Ali and Abbas, 2006). Physical method such as distillation concentrates the metallic compounds in the residue. In chemical method, the metal is removed from the organic moiety with minimal conversion of the remaining petroleum by using acid. The reversible reaction occurs as following equation:

$$PM + HX \rightleftarrows PH + MX \tag{1.1}$$

According to M.F. Ali (2006),

> *In the treatment of petroleum residues with sulfuric acid, some of the acid is almost always reduced to sulfur dioxide. This sulfur dioxide may also react with some of the unsaturated hydrocarbons; forming various addition products and thus complicating still further the nature of the basic reactions. The basic reactions of sulfuric acid with olefins and substituted aromatics have been discussed extensively and it is a general knowledge that the reaction products may be of the type of sulfones, polysulfones, aromatic sulfonic acids and/or heteropolymeric gums. The fact that sulfuric acid reacts with and promotes reactions of hydrocarbons is a drawback to its use as an agent for removing metals, sulfur and nitrogen from oil. The hydrocarbon reactions increase the quantity of acid required and decrease the yield of fuel products.*

1.2 PROBLEM STATEMENT

Removal of metal from crude oil has been stated very crucial. However, the chemical method that uses acid to remove metal that applied in industry gives disadvantage that is corrosive, J.R. Maxwell, (1971). It is a crucial to find other solvent to replace acid that corrosive to equipments. As ionic liquid has been reported as green solvent in demetallization, it has attracted researchers to explore the unique of the ionic liquids. Many works has been done in extracting different type of metal such as alkali earth metal, alkali metal and also heavy metal from aqueous and non aqueous solvent. However, the research on extracting calcium from organic solvent that is fuel is still in the low stage and not adequate.

1.3 SIGNIFICANCE OF THE PROJECT

This project will not only provide solution of removing metal, but also providing solid proves of the ability of ionic liquid as green solvent in demetallization. Since the metal removals done by many researchers are concentrated on nickel, vanadium, and strontium, this project will extract calcium as it is also important in industry nowadays.

1.4 OBJECTIVE AND SCOPE OF WORK

The objective of this project is to determine the potential of three ionic liquids in order to extract calcium in dodecane with varying temperature and kinetic effect on demetallization.

The scope of work:
For this project, the scope of work will be focused on:

1. Concentrate on liquid-liquid extraction by using commercial ionic liquid
2. Screening on commercial three ionic liquid that effectively remove metal in room temperature, 50 ^{0}C and 60 ^{0}C.
3. Study of kinetic effect on demetallization

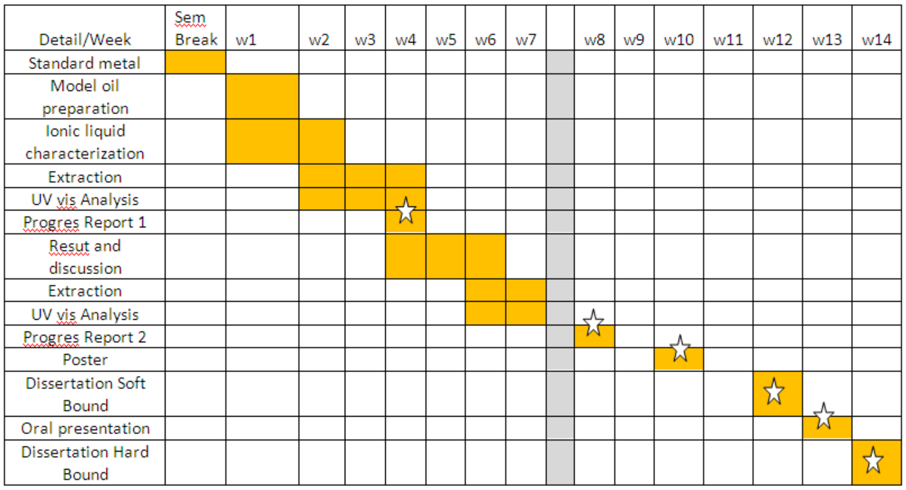
1.5 RELEVANCY OF THE PROJECT

This project is relevant to Chemical Engineering academic syllabus of Universiti Teknologi Petronas (UTP). It incorporates knowledge in organic chemistry and separation process. Research is a learning process that builds up student ability in findings knowledge. In addition, it also enhances project management and communication skills.

1.6 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

For this project, the first semester will cover formulation of methodology of liquid extraction by literature review. At final first semester and early second semester will be concentrated in experiment of the extraction. Based on the draft methodology, the project's objectives are achievable within the time frame.

Table 1.1: Milestone for FYP 2



Detail/Week	Sem Break	w1	w2	w3	w4	w5	w6	w7		w8	w9	w10	w11	w12	w13	w14
Standard metal	🟨															
Model oil preparation		🟨														
Ionic liquid characterization		🟨	🟨													
Extraction			🟨	🟨	🟨											
UV vis Analysis			🟨	🟨	🟨											
Progres Report 1					🟨 ☆											
Resut and discussion					🟨	🟨	🟨									
Extraction							🟨	🟨								
UV vis Analysis							🟨	🟨								
Progres Report 2										🟨 ☆						
Poster												🟨 ☆				
Dissertation Soft Bound														🟨 ☆		
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Dissertation Hard Bound																🟨 ☆

CHAPTER 2
LITERATURE REVIEW

2.1 IONIC LIQUIDS

2.1.1 Introduction

In the late 1990s, ILs became one of the most promising chemicals as solvents. Due to their unique properties, Ionic liquid (ILs) are proved to be increasingly interesting fluids for several application include electrolyte in batteries, lubricants, plasticizers, solvents and catalysis in synthesis, matrices for mass spectroscopy, solvents to manufacture nano-materials, extraction, gas absorption agents.

Ionic liquid is a molten salt, are made of positively and negatively charged ions which remain liquid at lower temperatures (<100 ^{0}C) and is liquid at room temperature (R. Renner, 2001). Compared to other salt, ionic liquid consist solely of ions without any additional solvent. Furthermore, it also not disassociate to ions as other salt do.

2.1.2 Physical Properties

Seda Keskin (2007) says that ionic liquid has common advantages that are non-volatility and nonflammability, which has the possibility of tuning the chemical and physical properties of ILs by changing anion–cation combination to obtain task-specific ILs for a multitude of specific applications.

The IL solvents have the low melting point that is below 100 ^{0}C. This property leads to the practical replacement of conventional volatile organic compound (VOC). ILs have negligible vapor pressure, not explosive and may be feasible to recycle and repeatedly reuse them. The non-evaporating properties of ILs eliminate the hazardous exposure and air pollution problems. This new chemical group can reduce the use of hazardous and polluting organic solvents and are called green solvent due to this property.

The other physical properties of ionic liquid are as below:

- ✓ ILs are highly polar.
- ✓ ILs consist of loosely coordinating bulky ions.
- ✓ Most of ILs have a liquid window of up to 200 ◦C which enables wide kinetic control.
- ✓ ILs have high thermal conductivity and a large electrochemical window.
- ✓ ILs are nonaqueous polar alternatives for phase transfer processes.
- ✓ The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations.

The physical properties are summarized as follows:

PROPERTIES	**REMARKS**
Low melting points	IL can react as solvent where reaction can be performed
Negligible vapor pressure	• No volatile, easy separation • The non-evaporating eliminate the hazardous exposure and air pollution problem
Non-flammability	Low combustible
Made of ion	Give distinctive selectivity and reactivity
ILs is immiscible with many organic solvents.	Suitable for separation

Feasible to recycle and repeatedly reuse them	Lower cost
Thermally stable, approximately up to 300 ◦C.	Reaction may be carried stably and easily separated from the reaction product
ILs has the ability to dissolve many different organic, inorganic and organometallic materials.	A good solvent

Table 2.1: Physical properties of ionic liquid

2.1.3 Structure

Structure of organic cation and anion gives influence to the physical properties of ILs. According to Q Yang (2004):

> *Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point.*

Besides, the physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. Extraction efficiency will increase with alkyl chain length decrease (Urszula and Rekawek, 2009). This is because density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion.

Organic Cation

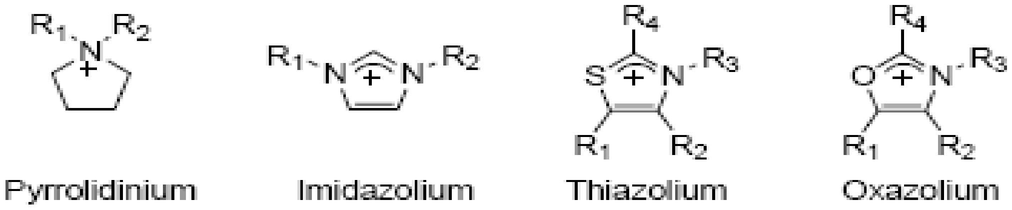


Figure 2.1: Several types of cation

Organic/Inorganic Anion

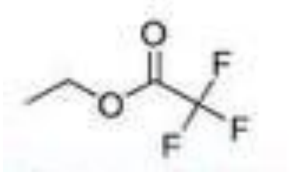


Figure 2.2: Trifluoroacetate

2.2 CALCIUM METAL IN CRUDE OIL

A number of important crude feedstocks contain levels of calcium which render them difficult to process using conventional refining techniques. The calcium which causes particular problems is present in these feedstocks as organically-bound compounds, which are not easily dissociated or removed by conventional water washing or desalting processes. These calcium compounds quickly decompose during typical catalytic operations, such as during hydroprocessing or during fluid catalytic cracking, causing rapid fouling or deactivation of the catalysts in the catalytic operation. It is desirable to remove these compounds before additional processing.

Calcium were observed at the 0.5 -7 ppm level in crude oil (Bukhori, 1983) a few, but increasingly important. The calcium contaminants causing particular problems are non-porphyrin, organometallically-bound compounds. These species have been only recently discovered in crude oils, very heavy crude oils in particular, and are apparently relatively rare. One class of these calcium-containing contaminant compounds identified, in particular, is the calcium naphthenates and their homologous series. Examples of feedstocks demonstrating objectionably high levels of calcium compounds are those from the San Joaquin Valley in California.

There are many work has been done to remove calcium from crude oil, however by using acid. In U.S.Pat. Nos. 4,778,589; 4,778,590; 4,778,591; 4,778,592; 4,789,463; 4,853,109; 5,593,573 and 4,988,433, commonly assigned to the assignee of the present invention, various agents including mineral acids, aminocarboxylic acids, hydroxo-carboxylic acids, dibasic carboxylic acids, monobasic carboxylic acids and carbonic acid, and their salts, are generally taught for removing organically-bound calcium from hydro carbonaceous feedstocks. As reported by Ali (2006), acid has several disadvantages as it reduces to other product and cause the yield of desired product decrease. It is also corrosive and its volatility is not suitable as solvent in liquid-liquid extraction.

Therefore, further researches need to be done to replace the acid and other agents as extracting solvent that are volatile and corrosive. Ionic liquid as a new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses.

2.3 THE CONCEPT OF LIQUID-LIQUID EXTRACTION

Following to J. M. Coulson and J. F. Richardson (2005), extraction should be considered as an alternative to distillation in the following situations:

a. Where the components in the feed have close boiling points. Extraction in a suitable solvent may be more economic if the relative volatility is below 1.2.

b. If the feed components form an azeotrope.

c. If the solute is heat sensitive, and can be extracted in to a lower boiling solvent, to reduce the heat history during recovery.

2.3.1 Solvent Selection

The following factors need to be considered when selecting a suitable solvent for a given extraction.

a. Affinity for solute: the selectivity, which is a measure of the distribution of the solute between the two solvents (concentration of solute in feed-solvent divided by the concentration in extraction-solvent). Selectivity is analogous to relative volatility in distillation. The greater the difference in solubility of the solute between the two solvents, the easier it will be to extract.

b. Partition ratio: this is the weight fraction of the solute in the extract divided by the weight fraction in the raffinate. This determines the quantity of solvent needed. The less solvent needed the lower will be the solvent and solvent recovery costs.

c. Density: the greater the density difference between the feed and extraction solvents the easier it will be to separate the solvents.

d. Miscibility: ideally the two solvents should be immiscible. The greater the solubility of the exaction solvent in the feed solvent the more difficult it will be to recover the solvent from the raffinate, and the higher the cost.

e. Safety: if possible and all other factors considered, a solvent should be chosen that is not toxic or dangerously inflammable.

f. Cost: the purchase cost of the solvent is important but should not be considered in isolation from the total process costs. It may be worth considering a more expensive solvent if it is more effective and easier to recover.

2.4 IONIC LIQUID IN DEMETALLIZATION

2.4.1 Ionic Liquid as Extracting Solvent

Ionic liquid is a good extractability for various organic compounds and metal ions. As a class of liquids, they are fundamentally different from molecular solvents and from salt solutions. Compare to conventional molecular solvents, ILs exhibit enhanced distribution coefficients (*D*M*)* for a number of complexing ligands in the extraction of metal ions from aqueous solutions. (Raimondo et. al, 2007)

Following to Urszula and Rekawek (2009), hydrophobic character in ILs allows them to extract hydrophobic compounds in biphasic separations. Metal ions tend to stay in the aqueous phase because they are hydrated. Therefore, in order to remove metal ions from the aqueous phase into hydrophobic ILs, extractants are normally needed to form complexes thereby increasing the metal's hydrophobicity. Although certain IL-extractant combinations have been shown to yield metal ion extraction efficiencies far greater than those obtained with molecular organic solvents, other work suggests that the utility of ILs may be limited by solubilization losses and the difficulty in recovering the extracted metal ions.

The salvation of ionic species, such as crown-ether complexes, NO_3 and SO_2, in the IL, should be much more favored thermodynamically than those of conventional solvent extractions and this is one of the key advantages of using ILs in separations involving ionic species (Urszula and Rekawek , 2009).

The mechanism and the selectivity of extraction is dependent on the nature of the ionic liquid, its alkyl chain and the kind of lipophylic derivatives such as crown ethers, calixarenes, and Task Specific Ionic Liquid (TSIL) (Lee, 2006). It was also shows that anions of ILs play a key role in solvent extraction.

In order to extract metal ion, Task-specific ionic liquids (TSIL) concept is introduced in order to synthesize ILs with desired properties. A special class of ionic that is TSIL has functional groups that permit the extraction of metal ions from aqueous solution. These ionic liquids can act as both solvents and extractants. The first investigations of metal ion extraction in IL/aqueous systems showed extremely high metal ion partitioning to the IL phase. It was the success of these initial studies that led to conjecture that ILs could also be used for the removal of hazardous metal ion.

Visser et. al. (2002) designed and synthesized several ILs to remove cadmium and mercury from contaminated water. The hydrophobic ILs come into contact with contaminated water and they snatch the metal ions out of water. Visser et al produced TSIL cations by appending different functional groups (namely thiother, urea and thiourea) to imidazolium cations. The results of the study gave significant distribution ratios for mercury and cadmium in liquid–liquid separations and minimized the reliance on traditional organic solvents for this process.

2.4.2 Type of Metal Extracted

Different types of metal ions have been the subject of extractions, among them alkali metals, alkaline earths metals, heavy- and radioactive metals. Ionic liquids were also applied for the extraction of lanthanide ions (Binnemans et. al, 2007). An overview of the metals that have been extracted and the ionic liquids that have been used for extractions has been published by Zhao et.al (2005).

2.4.3 Ionic Liquid Alkyl Chain Effect in Extraction

Alkyl chain lengthy gives the different effect to extraction efficiency. Urszula and Rekawek (2009) reported that an increase in the alkyl chain length from ethyl- to hexyl- decreases the extraction process resulting extraction efficiency for [EEIM][NTf2] is 99.3%, while for [HEIM][NTf2] it is 98.9%.

The different is due to the lower solubility of the metal-dithizone complex in the organic phase. When longer alkyl chains are substituted at the imidazole ring, it can be noticed that lengthening of the aliphatic chain on the cation results in the same effects on complex formation with metal ion. For example, 1-Alkyl-3-ethylimidazolium-based ionic liquids versus 1-alkyl-3-methylimidazolium-based ionic liquids show slightly worst extraction efficiency, but can be easier used in practice because the density of the ethyl substituent IL is lower than that of the methyl substituent IL.

2.4.4 Temperature Effect in Extraction

To further investigate the partitioning behaviour of Ca^{2+} ions in ionic liquids, the temperature will be varied in the range 25–70 ^{0}C. Raimondo et al (2007) reported the extraction of mercury with the temperature effect in [C_8MIM][PF6] as follows:

> *Independently of the working temperature, a complete Hg(II) ion transfer in RTIL was achieved and the higher temperature was used, the faster metal ion transfer in ionic liquid carried on. The high viscosity of most 1, 3- dialkylimidazolium ionic liquids can significantly reduce the rates of mass transfer between the two phases in a liquid/liquid extraction process. Viscosity markedly decreased as the temperature is increased in the range 25–100^{0}C and such behavior could then provide a rationale for our results.*

2.4.4 Solvent Volume Ratio

The influence of different volumes of the extraction solvents on the extraction efficiency of the metal ion was also investigated by Urszula and Rekawek, (2009). In their experiment, extraction decreases for the lower volume of chloroform and increases for the lower volume of ionic liquid

2.4.5 Ionic Liquid Recycle

Urszula and Rekawek, (2009) also discuss wether that ILs can be recycled for reuse in liquid–liquid extraction of metal ion. The general function of the re-extraction process can be tailored by changing the pH of the system (decreasing pH results in an increase of re-extraction).

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 REAGENTS AND APPARATUS

3.1.1 Dodecane

Before we proceed to use crude oil, we use dodecane as model oil containing calcium. It is fundamental study before we proceed to the real crude oil. Dodecane is a liquid alkane hydrocarbon. It is also known as dihexyl, bihexyl, adakane 12 or duodecane with the chemical formula $CH_3(CH_2)_{10}CH_{3.}$

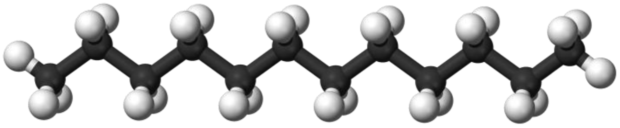


Figure 3.1: A straight chain of hydrocarbon

It is easier to remove metal in a straight chain dodecane compared to octane that is in more complex chain and octane also has many isomer that will constraint the metal extraction process.

3.1.2 Calcium Organic

The calcium used in this experiment is calcium organic supplied by CONOSTAN, as the solvent that is dodecane is also organic. It is to make sure that the metal dissolves thoroughly in the dodecane as model oil. Some stirring and heating are needed to fully dissolve the metal.

3.1.3 Ionic Liquids

Solvent used to extract metal in this experiment are three ionic liquid supplied by MERCK namely [EMIM] DEP, [EMIM] FAP and [EMIM] HSO_4. The three ionic liquid will be screened and be examined the extraction efficiency of each ionic liquid in different temperature and kinetic effect. As discussed above, the shorter the alkyl chain gives the best extraction efficiency. Ethyl will be better extracting solvent compared to butyl and hexyls. In this project, EMIM is chosen and anion varies from others.

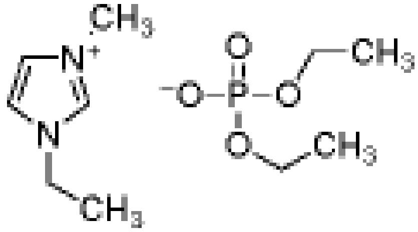


Figure 3.2: 1-ethyl-3-methylimidazolium diethyl phosphate, [EMIM] DEP

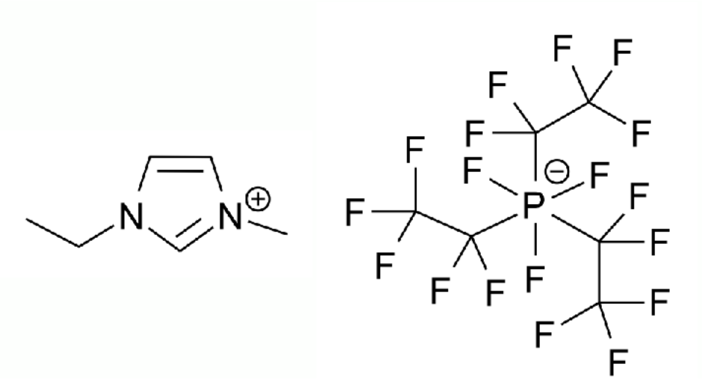


Figure 3.3: 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [EMIM] FAP

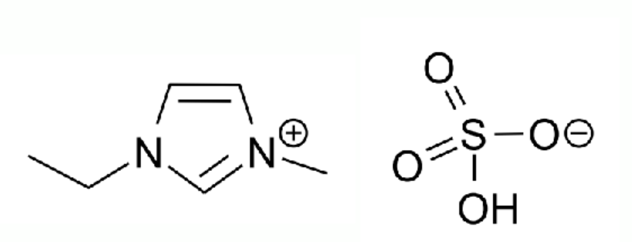


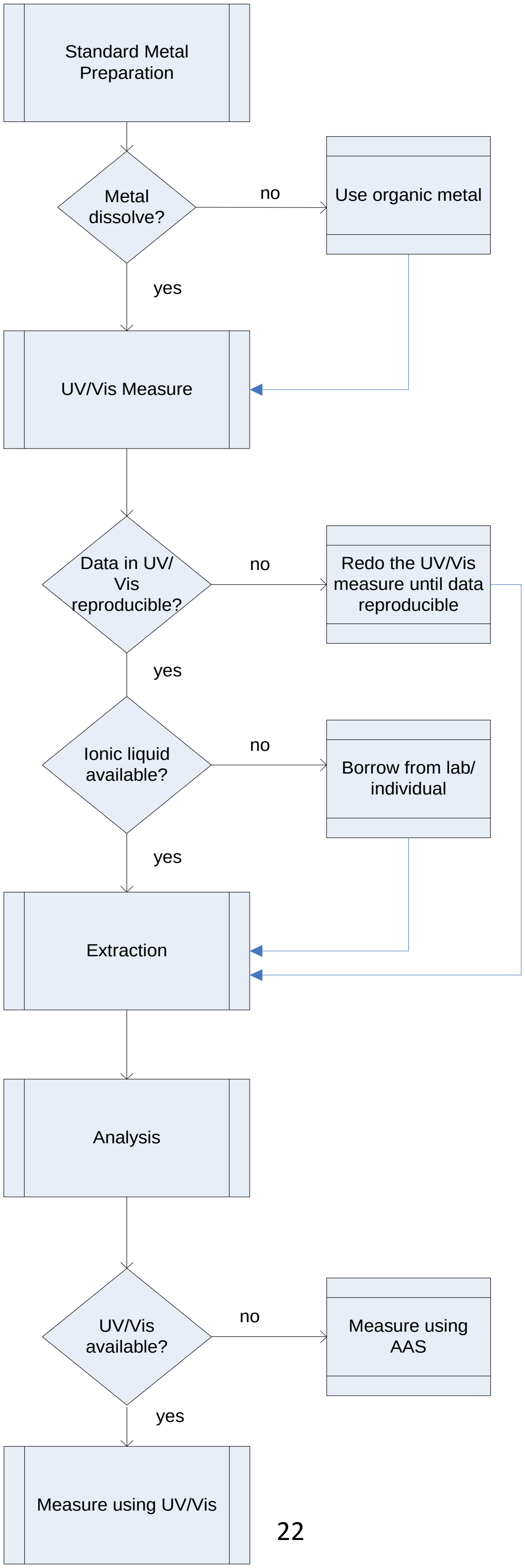
Figure 3.4: 1-ethyl-3-methylimidazolium hydrogen sulfate [EMIM] HSO_4

3.1.4 Apparatus

Below is the equipment required to run the experiment.

1. SHIMADZU UV-Vis Spectrophotometer 3150 to measure metal absorbance
2. IKA Vortex Genius 3 to vortex sample
3. Polyscience Waterbath to vary temperature of sample
4. Centrifuge KUBOTA 5200 to centrifuge sample

3.2 METHODOLOGY



3.2.1 Experimental

The ionic liquid used in this work is 1-ethyl-3-methylimidazolium diethylphosphate [EMIM] DEP, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [EMIM] FAP, 1-ethyl-3-methylimidazolium hydrogen sulfates [EMIM] HSO_4. The ILs was purchased from Merck and was used without further purification. The water content was measured by a Karl-Fischer titration (Metrohm 831 KF). The viscosity measured by Anton Paar. Standard metal and model oil are prepared by mixing n-dodecane from Haltermann (99%) with spiked calcium organic purchased from Sigma Aldrich. Some heating and stirring needed to make sure metal fully dissolve. The metal concentration in the standard and model oils was measured by SHIMADZU UV-Vis Spectrophotometer 3150. The calcium standard curve is done and wavelength is selected at 240 nm. The extraction experiments were conducted using an IL-to model oil ratio (related to volume) of one, with 3.5 mL of both oil and IL in the first extraction step. Extraction time was 5 min by vortex the sample in IKA Vortex Genius 3. It was assured that the extraction equilibrium was always reached by centrifuging the sample in Centrifuge KUBOTA 5200 for 5 minutes with 2 x 100 rpm. The samples are remained in Polyscience Waterbath with 50^0C and 60^0C for 15 minutes to differ them with RT. The vortex time is also varied from 30 sec, 2 minute, and 5 minutes. The extraction efficiency is measured by comparing the metal calcium concentration before extraction and the remaining in the model oil after extraction. Mass balances are done to measure the mass transfer of metal calcium to ILs. The corresponding extraction efficiency is defined by

$$E\,(\%) = \frac{(C_i) - (C_f)}{(C_i)} \times 100 \qquad [3.1]$$

Figure 3.5: Before extraction with EMIM FAP

Figure 3.6: Vortex for 5 minutes

Figure 3.7 After extraction
with EMIM FAP

Figure 3.8: Centrifuge for 2 min

CHAPTER 4

RESULT AND DISCUSSION

4.1 RESULT

4.1.1 Standard Metal

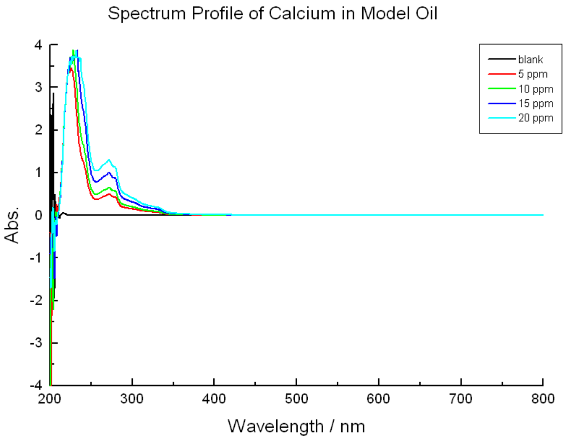


Figure 4.1: Spectrum Profile of Calcium in Model Oil (200-800 nm wavelengths)

The figure above shows spectrum profile of calcium, absorbance vs wavelength. It shows that at certain wavelength, absorbance for all concentration increase.

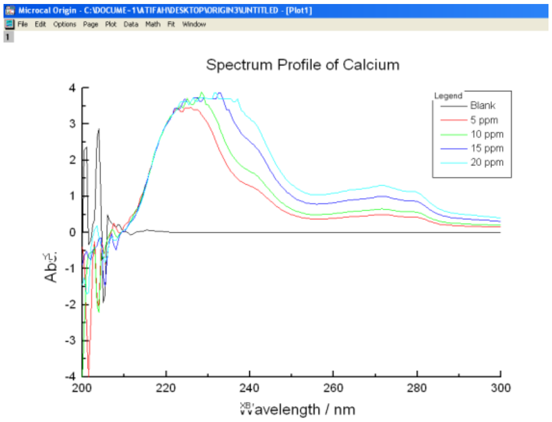


Figure 4.2: Spectrum Profile of Calcium (200-300nm wavelength)

The figure shows peak in the range of 220 nm to 240nm. There peak also shown in the range of 250nm to 270nm. By considering on literature review, regression value and data reproducible, wavelength of 240nm is chosen. By using this peak, standard curve is plotted as below.

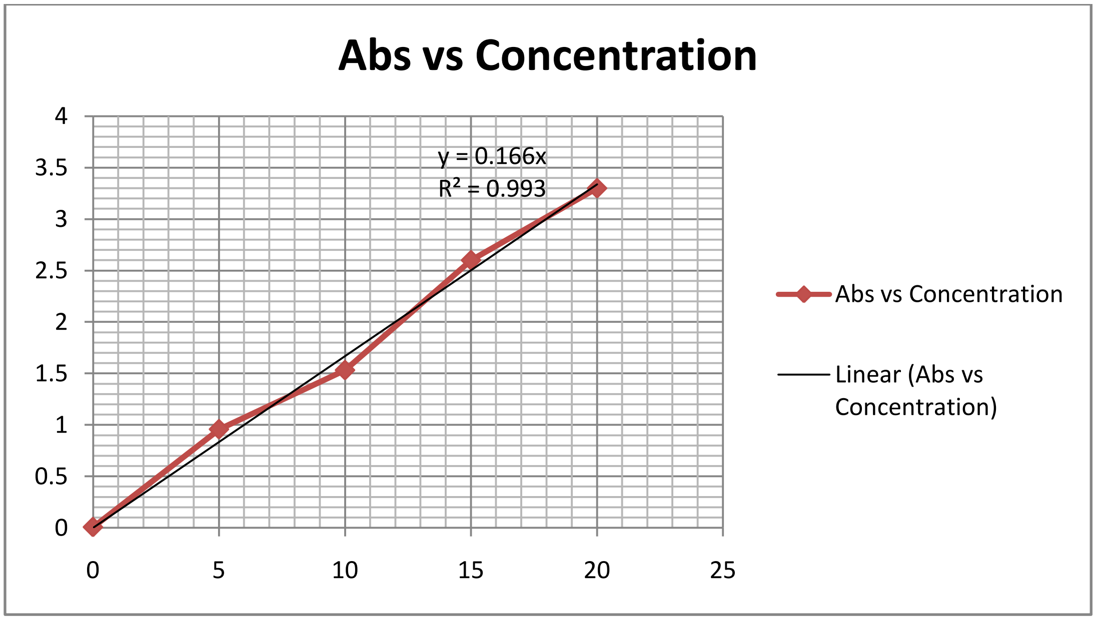


Figure 4.3: Standard Curve of Calcium (240 nm wavelength)

4.1.2. Extraction of Calcium by EMIM [DEP], EMIM [FAP] and EMIM [$HS0_4$]

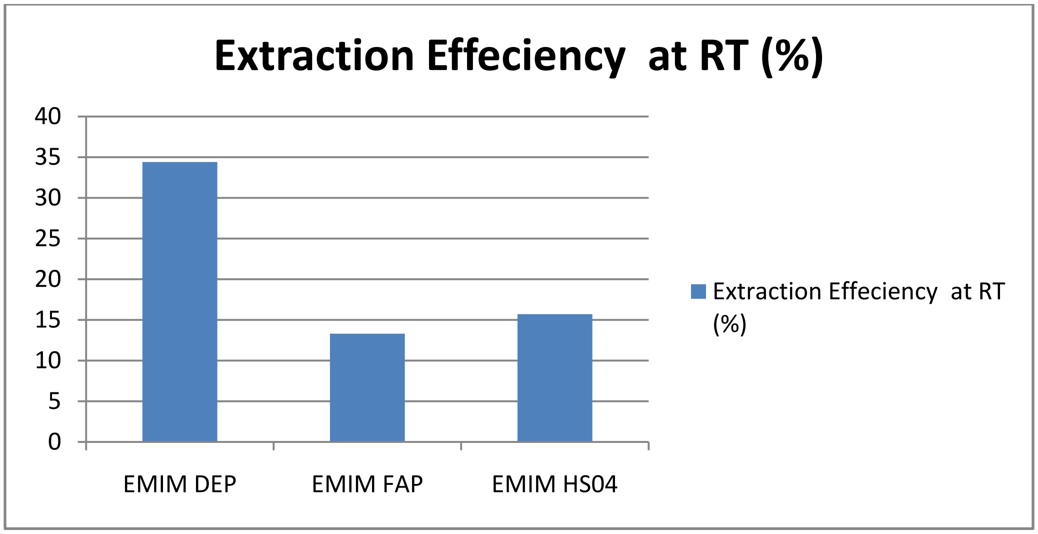


Figure 4.4: Extraction efficiency at RT for different ILs

From the figure, it can be seen that calcium extraction followed in order EMIM [DEP]> EMIM [FAP] > EMIM [$HS0_4$].

4.1.3 Influence of Temperature Variation to Extraction

Table 4.1: Extraction of EMIM [DEP] at different temperature

INITIAL	TEMP	FINAL	% EFF
3.34	25	2.192	34.4
	50	0.321	90.4
	55	0.346	89.6
	60	0.376	88.7

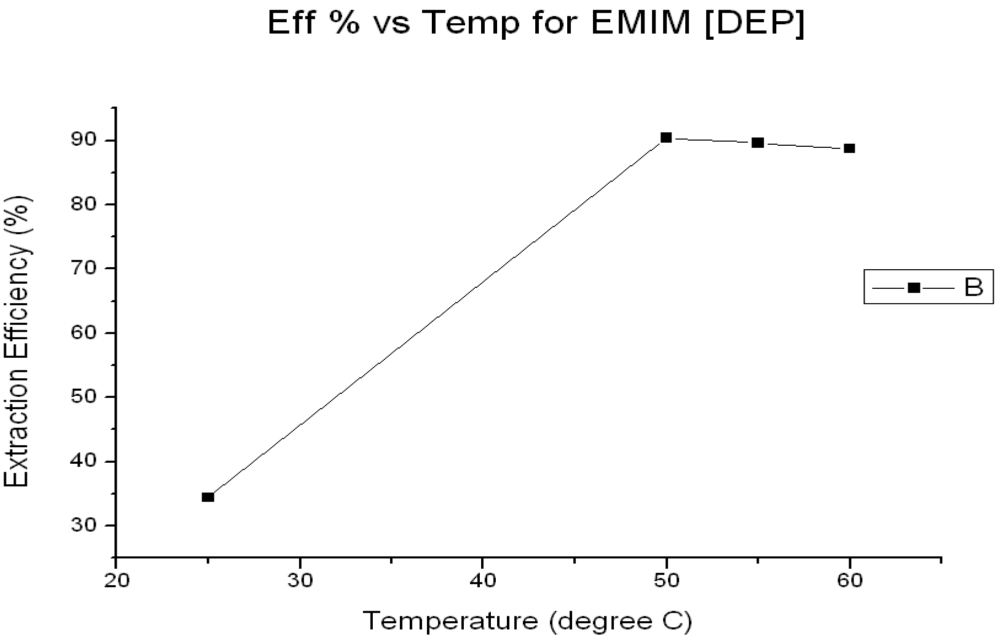


Figure 4.5: Extraction of EMIM [DEP] at different temperature

The extraction efficiency by EMIM [DEP] has been seen increase as temperature increase. The optimum temperature is at 50^{0}C with 90.4% calcium extraction. At 55 ^{0}C and 60 ^{0}C, the efficiency seems start to decrease. This is due to the temperature that may influence the extraction process due to the temperature effect on vapor pressure which also influences the solubility

Table 4.2: Extraction of EMIM [$HS0_4$] at different temperature

INITIAL	TEMP	FINAL	% EFF
3.34	25	2.812	15.8
	50	2.954	11.6
	60	2.914	12.8

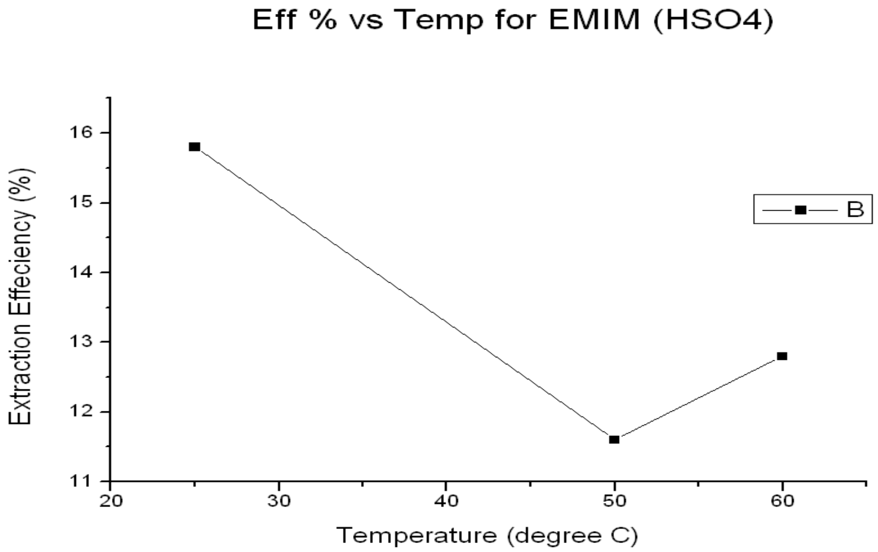


Figure 4.6: Extraction of EMIM [$HS0_4$] at different temperature

The extraction efficiency has been seen decrease as temperature increase. The optimum temperature is at 25^0C with only 15.8 % calcium extraction.

Table 4.3: Extraction of EMIM [FAP] at different temperature

INITIAL	TEMP	FINAL	% EFF
3.34	25	2.89	13.5
	50	3.118	6.6
	60	3.201	4.2

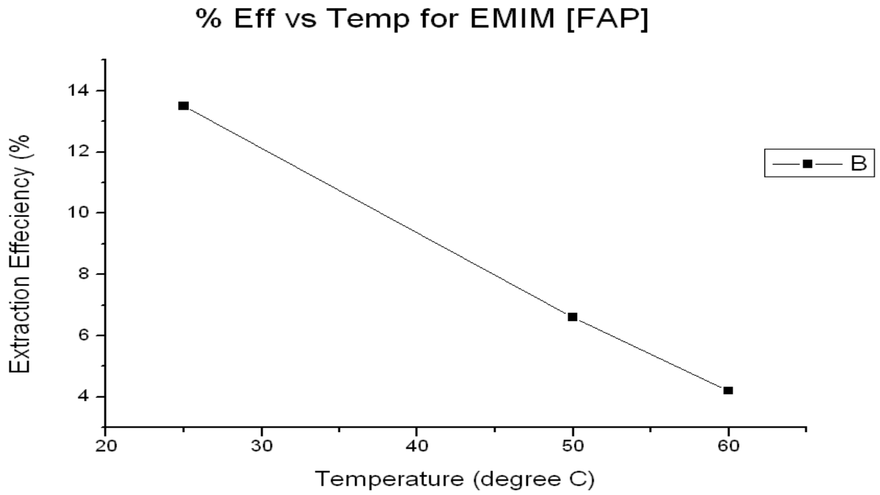


Figure 4.7: Extraction of EMIM [FAP] at different temperature

The extraction efficiency has been seen decrease as temperature increase. The optimum temperature is at 25^0C with only 13.5 % calcium extraction.

4.1.4 Influence of Shaking Time as Kinetic Effect

Table 4.4: Kinetic Effect on Extraction Efficiency of EMIM [DEP] at RT

INITIAL	TIME(s)	FINAL	% EFF
3.34	30	1.3	61.1
	120	0.551	83.5
	300	0.4	88.0

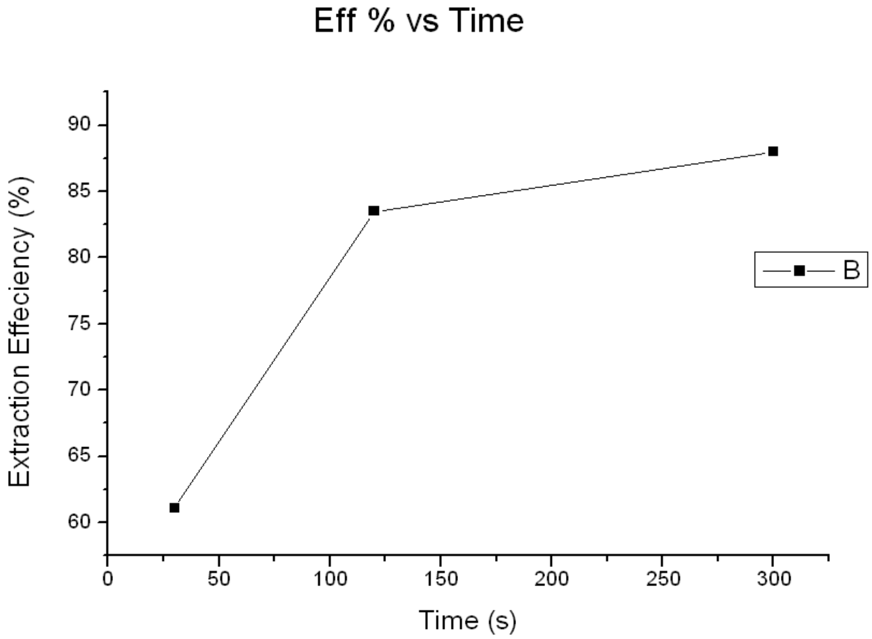


Figure 4.8: Extraction of EMIM [DEP] at different vortex time

The extraction efficiency has been seen increase vortex time increase. The optimum vortex time is at 5 minutes or 300 seconds with only 88.0 % calcium extraction. However, between 2 to 5 minutes, the extraction efficiency does not vary much. Many works in literature review also done at 2 minutes.

4.2 DISCUSSION

Above is the result of standard metal preparation. In the Figure 4.1, for all metal concentration, the peak shows in range of 200 to 300 nm wavelength. Referring to literature review and regression value, wavelength of 240 nm is selected.

4.2.1 Extraction of Calcium by EMIM [DEP], EMIM [FAP] and EMIM [$HS0_4$]

As result above, it is seen that EMIM [DEP] is the best extractor compared to others. The extraction efficiency is always higher not only in room temperature, but also in higher temperature. This is due to the imidazolium-based alkylphosphate ionic liquid has been reported effective in sulfur removal, X. Jiang et al. (2008). In this experiment, it is proven that [EMIM] DEP is also effective in metal removal. The extractive ability of the alkylphosphate ILs was dominated by the structure of the cation and however anion effect is limited. The alkylphosphate ILs are insoluble in fuel. EMIM[DEP] is also reported might be used as a promising solvent for the extractive desulfurization of fuel, considering its higher sulfur extractive ability, lower solubility for fuel and thus negligible influence on the constituent of fuel. However, there is no report in literature for EMIM [FAP] and EMIM [$HS0_4$] in extraction.

Metal removal ability of phosphate ILs [EMIM][DEP], is satisfactory in comparison with most ILs as it can be seen by the KN values. Therefore, the demetallization process using phosphate ILs can at least be used as a complementary technology for the traditional solvent. In addition to the high extractive demetallization ability, phosphate ILs [EMIM][DEP], also has feature good stability, fluidity, non-toxicity, and nonsensitivity to moisture and air, which make them superior to other ILs like [EMIM][HSO_4] and [EMIM][FAP]. The mechanism for the extraction of metal with imidazolium-based IL is likely relevant to the formation of liquid clathrate due to the p–p interaction between unsaturated bonds of aromatic metal-compound and the imidazole ring of ILs. And as the conjugated ring of the metal components or the alkyl-substitutes in imidazole ring becomes larger, the induced polarity and dispersive energy of the pelectron rings become higher, leading to a stronger p–p interaction between aromatic metal-compound and the imidazole ring of ILs.

For the ILs with common cation, the anion size has a marginal effect on the metal partition coefficients at least from the limited information available at the present time. The solubility of fuel oils in phosphate ILs is likely originated from the dispersive interaction between oil, a mixture of non-polar or weak polar molecules, and the alkyl substitutes involved in the IL. As a result, the oil solubility in ILs always increases with the size of the IL increase.

As a promising extractant, it is better to have both high KN value for metal compounds and low solubility for the fuel oils. Following to X. Jiang et al. (2008) in his paper in comparing the phosphate ILs, in this regard, [MMIM][DMP], [BEIM][DBP] and [BMIM][DBP] are not recommendable either for its very low KN value or for their very high solubility for fuel oils compared [EMIM][DEP]. However, [EEIM][DEP] seems more recommendable as a solvent for the extracting of fuel oils as a compromise between the two factors, viz. its KN value and solubility for fuel oils because [EEIM][DEP] has the highest KN value while its solubility for fuel oils is still in an acceptable range.

4.2.2 Influence of Temperature Variation to Extraction

The higher temperature used should faster metal ion transfer in ionic liquid carried on. The high viscosity of most ionic liquids can significantly reduce the rates of mass transfer between the two phases in a liquid/liquid extraction process. Viscosity markedly decreased as the temperature is increased in the range 25–100^0C. In the experiment, the optimum temperature for metal extraction using EMIM DEP is seen at 50 ^{0}C. However, these not occur for higher temperature for EMIM HSO_4 and EMIM FAP.

For EMIM DEP, by increasing the temperature of the system from 25^0C to 50^0C, the extraction efficiency increased. The highest extraction efficiency was obtained at 50^0C as shown in Figure 4.5. Following to El-Fatah (2002), by increasing the temperature at a certain value of pressure, vapor pressure of solutes increases. On the other hand, the density of the supercritical fluid will decrease gradually with temperature. Thus, there is a maximum value for the solubility and then extraction efficiency. At higher temperature that is 55^0C, the extraction efficiency starts to decrease. This is due to the temperature that may influence the extraction process due to the temperature effect on vapor pressure which also influences the solubility.

4.2.3 Influence of the Vortex Time as Kinetic Effect

The variation of kinetic will give effect on the extraction. The experiments were performed at three different speeds, 30s, 120s, and 300s. In the Figure 4.8, the results show that the longer the shaking time, the more metal will be extracted. This is supported in literature by Maria Pesavento, (1986), and Nezhadali et al (2010). The effect of the vortex time on the diffusion of species through organic extraction is an important factor in order to minimize the diffusion layer at the interfaces This is because; the ionic liquid is given enough time to extract the metal. However, if the effect does not vary much from time to time, it is better to fix at the average time in this experiment is 2 minutes. This is due to time and cost consideration. Longer the vortex time will higher more electricity that cause higher operation cost.

CHAPTER 6: CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The objective to prove that ionic liquid can be in calcium removal has been achieved. The best ionic liquid in metal extraction is EMIM [DEP]. The effect of temperature is also has been achieve. For EMIM [DEP], the efficiency of extraction is higher for higher temperature until certain temperature where the extractions decrease. The kinetic effect is also has been done where the higher vortex time will cause higher efficiency until a certain time. Further research in manipulating the cation and anion will give best efficiency in metal extraction. It can be concluded that the Ionic Liquid is capable as green solvent as researchers found.

6.2 Recommendation

In order to improve the project, the following are recommended. Shaking the mixture gives better result instead of vortex. Besides, the centrifuge rotation (rpm) should also be alternate to achieve better result. This is because; the different speed of rotation will give different extraction result.

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