CHAPTER 1: INTRODUCTION

1.1 Background of Study

The art of separation (Horvath *et al.*, 1973) is a process that has had humans contending the second law of thermodynamics for centuries, commonly recognized as the distillation of alcohol for intoxicating effects. Metallurgy, extraction and purification of natural drugs, and the isolation of dyes are all separation processes that date back to ancient times. The industrial and scientific revolutions brought the need of substantial separation development. As the twentieth century has come to an end with advances far beyond our ancestors wildest dreams, we face new challenges. Our progress has led to environmental hazards that require new separation technology for removal of contaminants from biosphere.

Liquid-liquid extraction is one of the most versatile analytical techniques, because it has an extremely wide range of applications. It invokes most of the physical chemical principle used generally in analytical chemistry. The technique can be used for the purpose of preparation, purification, enrichment, separation and analysis. The popularity of liquid-liquid extraction has persisted due to its elegance and simplicity, while maintaining speed and applicability on all working scales, from microanalysis to production processes (Chalmers *et al.*, 1970). Liquid-liquid extraction is a mass transfer process based on the principle that a solute can distribute itself between two immiscible solvents.

Due to the impact of solvent toward the process, both feasibility and economics make the selection of solvent important (Cusack, 1996). A desirable extraction solvent should have the following features. A high distribution coefficient is essential. The miscibility of two phases should be low. The toxicity of the solvent must be minimal, especially in water treatment. Chemical stability is required for equipment design and wear, for considering the cost. Vapor pressure of the organic solvent should be minimal, to prevent volume changes.

Generally, liquid-liquid extraction process involves the removal of metals from water. One of the most important solvent selection feature listed previously is the low miscibility of the two phases. Typically, organic solvents are selected due to their low solubility in water. However, organic solvents commonly are toxic, flammable, and volatile. Another solvent selection feature, the high distribution coefficient, or the ability of the solvent to extract the solute further adds to the problem. Specific compounds, extractant, are added to the organic solvents for them to function efficiently in the process.

Wouldn't it be nice if there were stable solvent that is immiscible with water and causes no harm to the environment? A solvent that does not evaporate which will eliminate the containment costs. A solvent that could be regenerated and reused which will eliminate disposal costs.

The alternative green solvent such as ionic liquids (ILs) may just be the ideal solvent that we are looking for. Unique properties of ionic liquids such as negligible volatility, thermal stability and non-flammability make them acceptable as new green solvents. Because of this environmental friendly perception, they have been increasingly investigated worldwide for separation process (Ajioka *et al.*, 2008; Luo *et al.*, 2004; Shimojo and Goto, 2004; Visser *et al.*, 2001; Visser *et al.*, 2000; Wei *et al.*, 2003).

The development of ILs as solvents for extraction has gone on for nearly one decade since Huddleston and friends first applied [C_4mimPF_6] as the solvent for the extraction of organic benzene derivatives (Huddleston *et al.*, 1998). Since this initial report, numerous studies have appeared describing the application of ILs as solvents in the extraction of various simple metal ions (Chun *et al.*, 2001; Dai *et al.*, 1999; Giridhar *et al.*, 2004; Luo *et al.*, 2004; Nakashima *et al.*, 2003; Wei *et al.*, 2003). Actually, there are large differences between the chemical equilibria observed in ILs and traditional organic solvents (Dai *et al.*, 1999; Dietz and Dzielawa, 2001).

In comparison with traditional organic solvents, ILs exhibit enhanced distribution ratio when used with complexing ligands, such as extractants for metal ions from aqueous solution. Such enhancements were initially attributed to two major fundamental factors; ion recognition capabilities of the complexing ligands and unique ionic solvation environments provided by ILs for ionic species. Recent studies of the partitioning mechanism of Sr^{2+}-crown ether (Cocalia *et al.*, 2006; Jensen *et al.*, 2002) and UO^{2+}-carbamoylmethylenephosphine oxide complexes (Wei *et al.*, 2003) has shown that substituting a water immiscible 1-alkyl-3-methylimidazolium-based ionic liquid for traditional organic solvents in biphasic aqueous-organic solvent systems alters the stoichiometry, charge, and structure of the metal ion complexes in the organic phase.

The presence of two charged species from the ionic solvent itself, in an IL/aqueous biphasic system, makes the extraction a much more complex process than in traditional organic solvents. It is recognized that the ionic nature of these solvents can result in a variety of extraction mechanisms including solvent ion pair extraction, ion-exchange and simultaneous combinations of both. In the field of liquid-liquid extraction using ILs, many researchers have investigated the separation of metal ions and have identified ion exchange as the common mechanism involved in metal separation.

Hence it is important to establish the prevalence of cation or anion exchange as the mechanism of metal ion partitioning into ILs since ILs composes both cation and anion. However, the loss of ILs to the aqueous phase due to the ion exchange mechanism is the main limitation for utilizing ILs in separation application, thereby it is not possible to regard it as a totally green process (Dietz and Dzielawa, 2001).

Recently, several investigators have found that ion exchange is not the sole mode of cation or anion transfer into an ionic liquid (Cocalia *et al.*, 2006; Hirayama *et al.*, 2005; Kozonoi and Ikeda, 2007), thus offering renewed hope that practical, environmentally benign metal ion separation systems employing these solvents can be developed. The right combination of IL and ligand to obtain similar behavior as in traditional organic solvents (Cocalia *et al.*, 2006) or to control the aqueous composition (Dietz and Stepinski, 2008) is needed to achieve the green separation process. This information concerning the extraction mechanism and extractability of ILs in liquid-liquid extraction system has greatly inspired the researchers. Hence, we investigated the extraction behavior of Cu(II) and Fe(III) ions in aqueous solution into a series of hydrophobic ILs using 1,10-phenantroline (phen) as the extractant in order to examine the extraction mechanism. The structure of phen is showed in Figure 1.1.

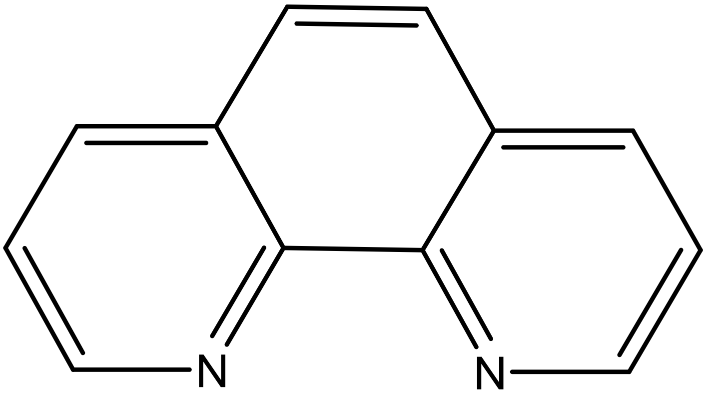


Figure 1.1: 1,10-phenanthroline

This research highlights the factors that control the extraction degree of Cu(II) and Fe(III) from aqueous phase, in order to improve the extraction efficiency of both metals by ILs. For this purpose, the effect of kinetic, ratio of aqueous phase to ILs phase and role of extractant were investigated. The stoichiometry of metal complexes was examined in view of ratio of metal to extractant (phen). The selectivity of ILs was studied to achieve excellent extraction. The important part to be investigated was the mechanism of extraction of Cu(II) and Fe(III) by the addition of numerous types of salt.

1.2 Research Objective

1) To investigate the parameters that control the extraction of Cu(II) and Fe(III).

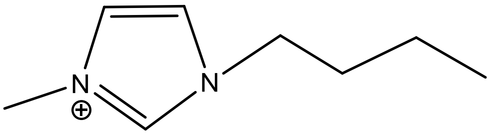
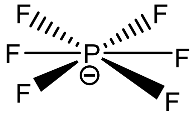
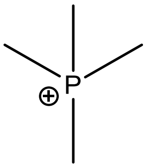
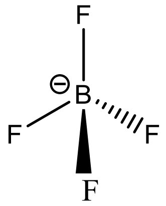
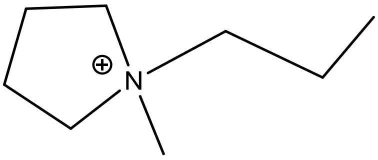
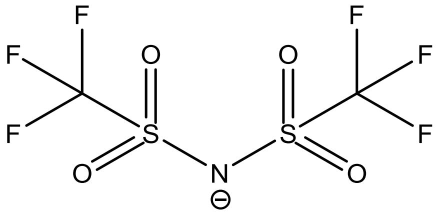
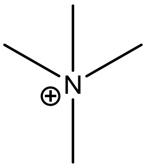
2) To determine the extraction behavior and stoichiometry of metal phenanthroline complexes of Cu(II) and Fe(III) using same series of ILs.

3) To compare the mechanism of extraction between Cu(II) and Fe(III) using [C_4mimPF_6] and [$C_6mimNTf_2$], respectively.

CHAPTER 2: LITERATURE REVIEW

ILs is salts that are liquid at ambient temperature. ILs consists of cation and anion. Typically, the cation of ILs consists of large organic ion while anion of ILs can be smaller organic or inorganic ion. Intuitively, salts are expected to be solid at room temperature and to melt only at very high temperatures. The ions forming ILs do not pack well, which explains why they can remain liquid at low temperature (Larsen *et al.*, 2000). The most common cations and anions of ionic liquids are showed in Table 2.1

Table 2.1 : Typical types of IL.

Cation	Anion
 1-butyl-3-methylimidazole	 Hexafluorophosphate
 Phosphonium	 Tetrafluoroborate
 1-methyl-1-propyl pyrrolidinium	 Bis(trifluoromethanesulfonyl)imide
 Ammonium	

The important physio-chemical properties of ILs when applied in separation science include their electrical conductivity which is important as ILs are used as an electrolyte in Capillary Electrophoresis, their viscosity and surface tension that are related to their coating properties in Gas Chromatography, their solubility in non-aqueous solvent, solvating properties and ability to dissolve compounds which is important in liquid extraction and headspace preconcentration (Andre *et al.*, 2005).

The main advantage of ILs is that they are a new class of solvents due to their non-molecular nature. The ILs environment is very different from that of all molecular polar or non-polar organic solvents (Fitzwater *et al.*, 2005). Like any other salts, ILs has negligible vapor pressure. They cannot be evaporated and the only limitation on their use at high temperatures is their thermal stability. The degradation of the ILs will occur at lower temperatures if they are heated for a long period. As the ILs can be heated to high temperatures than traditional organic solvents, so they can be used in a wide range of temperature. The extremely low volatility of ILs renders them only slightly flammable so they could be the candidate to replace organic pollutant solvents.

In order to address the ILs as the solvents, the understanding of their structure in the presence of other solute/solvent fluid is a key feature to predict the reactivity and selectivity of the system involving this compound. The strong cation-anion electrostatic interaction is believed to be the major source of interaction in ILs, although the fact that the contribution of that arises from polarization also needs to be considered. Beside that, hydrogen bonding between ions are also present in imidazolium-based ILs.

Actually, the combinations of cations and anions possess widely tunable properties with regard to solubility, polarity, viscosity and density of ILs. Solubility of ILs depends strongly on the structure of the associated anion. Almost all ILs are hygroscopic, even the ones insoluble in water. Since some ILs are insoluble in water, they can replace traditional organic solvents in liquid-liquid extraction.

As mentioned earlier, cations and anions can be used to control the water miscibility of the resulting ILs and the choice of anion has been used to the greatest effect on controlling hydrophobicity. 1-alkyl-3-methylimidazolium salts of PF_6^- are water immiscible, BF_4^- salts are water miscible depending on alkyl chain length, and tetrahaloaluminate salts are moisture sensitive. Fluorinated anions such as $N(SO_2CF_3)_2^-$ impart even greater hydrophobicity despite increased expense (Bonhote *et al.*, 1996).

ILs are expected to be very polar since they are salt. Thus they are capable of dissolving the charged solutes. They can be very viscous because of their saline structure. The viscosity of these ionic liquids is regulated by van der waals interactions and hydrogen bonding. Other than size and basicity of anion, the symmetry of anion also affects the viscosity. Therefore, ILs can be alternative solvent in liquid-liquid extraction for their unique properties.

Recent work by a number of investigators has been directed at the application of ILs in various separation processes, among them the liquid-liquid extraction of metal ions. Although certain IL-extractant combinations have been shown to yield metal ion extraction efficiencies far greater than those obtained with traditional organic solvents, other works suggests that the utility of ILs may be limited by solubilization losses and difficulty in recovering the extracted metal ions. In this review, recent efforts to overcome these limitations and improved understanding on the fundamental aspects of metal ion transfer into ILs are described.

In 2000, Visser and friends (Visser *et al.*, 2000) investigated the extraction of Na^+, Cs^+ and Sr^+ by crown ethers (18-crown-6, dicychlohexano-18-crown-6 and 4,4-(5)-di-(tert-butylcyclohexano)-18-crown-6) into ILs ($[C_nmimPF_6]$,n=4,6,8) from aqueous phase containing various mineral acids or metal salts.

The results obtained showed important differences between the effectiveness of crown ethers for metal ion separations in traditional solvent extraction versus IL-based liquid-liquid systems. For a series of crown ethers derivatives, the highest Cs^+ and Sr^+ distribution ratios were observed with the most hydrophobic crown ether, 4,4-(5)-di-(tert-butylcyclohexano)-18-crown-6. When the aqueous phase contained hydrated anions such as Cl^- or NO_3^-, the highest distribution ratio values for Sr^+ and Cs^+ were obtained with the lowest acid concentrations.

As a conclusion, Visser and his co-workers stated that ILs may indeed replace certain volatile organic solvents in some solvent extraction processes; however extreme caution is needed in the interpretation of the results. The complexity of ionic versus molecular solvents dictates review of possible ion exchange as well as partitioning mechanism.

Another research by Nakashima and group (Nakashima *et al.*, 2005) on the feasibility of ILs as alternative separation media for industrial solvent extraction processes. His group investigated the extraction of rare earth metals ($Ce^{3+,}$ Eu^{3+} and Y^{3+}) into ILs ([$C_n$mimPF_6] and [$C_n$mimNTf_2] using octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) as the extractant. The extraction efficiency and selectivity of CMPO for the metal ions was compared when *n*-dodecane was used as the extracting phase. The extraction mechanism was studied by slope analysis and extraction tests. Furthermore, they were accomplish the studied by stripping of metals from ILs into an aqueous phase by complexing agents and recycling the extracting ILs phase.

They found that CMPO dissolved in an IL, [C_4mimPF_6] showed extremely high extraction ability and selectivity of metal ions compared to ordinary diluent, *n*-dodecane. Partitioning of the metal cations into the IL with CMPO appears to proceed via cation exchange mechanism. They observed that the employment of a water-soluble complexing agent was valid for the stripping of metal cations and that the addition of C_4mim^+ cation into the aqueous phase promotes the stripping.

In 2007, Kozonoi and partner (Kozonoi and Ikeda, 2007) investigated the extraction mechanism of metal ions (Li^+, Na^+, Cs^+, Ca^{2+}, Sr^{2+} and La^{3+}) from aqueous solution to the hydrophobic ILs, 1-butyl-3-methylimidazolium Nonafluorobutanesulfonate [C_4mimN*f*O]. Furthermore, they investigated the extraction behavior of La^{3+} species using 1-pentyl and 1-hexyl-3-methylimidazolium nonafluorobutansulfonate ([C_5mimN*f*O], [C_6mimN*f*O], which are more hydrophobic than [C_4mimN*f*O].

They found that Li^+, Na^+, Cs^+, Ca^{2+}, Sr^{2+} and La^{3+} were extracted into [C_4mimN*f*O] without using an extractant. Metal cations with large hydrated radii were more effectively extracted into the ILs. The percent extraction of La^{3+} decreases with the increase of HNO_3 in aqueous solution, and also decrease with the increase in hydrophobicities of ILs, i.e., [C_4mimN*f*O]> [C_5mimN*f*O]> [C_6mimN*f*O]. The amount of La^{3+} transferred into [C_4mimN*f*O] increases linearly with an increase in concentration of [C_4mim^+] transferred into aqueous phase. They proposed that the extraction of metal ionic species from the aqueous to the [C_4mimN*f*O], [C_5mimN*f*O], and [C_6mimN*f*O] proceeds mainly through cation exchange.

A research done by Kidani and friends (Kidani *et al.*, 2008) was based on the extraction behavior of divalent metal cations (M^{2+} = Cu, Mn, Co, Ni, Zn and Cd) in IL chelate extraction systems using 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides [$C_nmimNTf_2$] and thenoyltrifluoroacetone, (Htta) as the extractant. The behavior was compared with that using less hydrophobic 1-alkyl-3-methylimidazolium hexafluorophosphates [C_nmimPF_6].

They found that M^{2+} was not extracted in the absence of (Htta) in all [$C_n$mimNTf$_2$] systems, and concluded that neither $C_n$mim$^+$ cations nor NTf_2^- anions act as extractants in these systems. They found that the extracted species in the [$C_n$mimNTf$_2$] systems were neutral M(tta)$_2$ for M = Cu and anionic M(tta)$_3^-$ for M = Mn, Co, Ni, Zn and Cd. The value of log K_{ex} for Cu^{2+} into [$C_n$mimNTf$_2$] was similar to one another but the order of log K_{ex} values was [C_4mimPF$_6$]>[C_6mimPF$_6$]>[C_8mimPF$_6$] in PF_6 systems. These results suggested that the alkyl chain length of $C_n$mim$^+$ hardly affects the extractability of Cu^{2+} into [$C_n$mimNTf$_2$] systems compared with the effect in [$C_n$mimPF$_6$] systems.

They considered that the extracted Cu(tta)$_2$ in an IL phase seems to be hydrated, Cu(tta)$_2$(H_2O) since log K_{ex} value is highest in [C_8mimPF$_6$], the less hydrophobic IL. Since the solubility of water in [$C_n$mimNTf$_2$] is sufficiently smaller than in [$C_n$mimPF$_6$], they suggested that stabilization of the hydrated Cu(tta)$_2$ in [$C_n$mimNTf$_2$] is relatively suppressed and that the log K_{ex} values for Cu^{2+} in [$C_n$mimNTf$_2$] systems are similar to each other. They also concluded that, in the IL chelate extraction system, the selection of IL is an important factor to control extraction selectivity and to create a novel separation system.

At the same time with Kidani, Yong Zuo and friends (Zuo *et al.*, 2008) studied the extraction behavior of Ce(IV) from HNO_3 solutions containing Thorium(IV) and Lanthanides(III) using pure [C_8mimPF$_6$] as the extracting phase. The initial intent of their work is to study the separation behavior of Ce(IV), Th(IV), and lanthanides(III) from nitric acid medium by di(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP) and [C_8mimPF$_6$] combination as the extracting phase because of the satisfactory behavior of DEHEHP in *n*-heptane.

In their study, [C_8mimPF_6] was demonstrated to have high selectivity on the extraction of Ce(IV), Th(IV), and Ln(III) from nitric acid medium. The unique extraction behavior of Ce(IV) by [C_8mimPF_6) is mainly due to the formation of $Ce(NO_3)_6^{2-}$ in nitric acid solutions, which is likely to form new IL with C_8mim^+ cation. Although the anion exchange mechanism may result in IL loss during the extraction process, the recycle test of IL demonstrated that the loss of IL could be controlled via addition of [C_8mim^+] to the initial $Ce(NO_3)_4$ solutions and/or using KPF_6 as the strippant. Their preliminary conclusion stated that it is quite possible that [C_8mimPF_6] alone may act as the extracting phase or anion exchanger for the recovery of Ce(IV) from nitric acid medium containing Th(IV) and Ln(III).

Recently, Lertlapwasin and friends (Lertlapwasin *et al.*, 2010) studied ionic liquid extraction of heavy metal ions (Ni^{2+}, Cu^{2+}, Pb^{2+}) by 2-aminothiophenol in [C_4mimPF_6]. Lertlapwasin and co-workers confirmed that IL was a medium with higher metal extraction efficiency compared to chloroform. The competitive ions such as Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- did not significantly affect the extraction efficiency of the metal ions studied. Ni^{2+} and Pb^{2+} were extracted via proton transfer mechanism while Cu^{2+} was extracted through redox mechanism. The stripping of Pb^{2+} and Cu^{2+} could be done by HNO_3 while Ni^{2+} could be stripped by H_2O_2 in HNO_3.

With interest from all over the world on ILs, many researchers found that the ion-exchange process in ILs have become more difficult because of the unique physicochemical properties of ILs. However, ion-exchange is not an universal mechanism for metal extraction. There are other pathways for metal ion partitioning into ILs beside that of ion-exchange such as ion pairing and the combination of both mechanisms. A lot of things should be considered when applying ILs in separation processes to get a clear view toward the extraction.

Numerous studies describing the application of ILs as solvents in the extraction of various metal ions concentrates on the types of ILs, effect of neutral or anionic extractant used and impact of counter ion. Besides the good performance of ILs in separation process, researchers were also concerned on the effect of ILs toward the environment and the reusability of ILs.

ILs were quickly considered as green solvents even when full toxicity studies were not completed. It seems that many ionic liquids have significant ecotoxicity (Zhao *et al.*, 2007). For example, the slow hydrolysis of the hexafluorophosphate anions released in water produced free toxic fluoride anions (Swatloski *et al.*, 2003). Hence, the green chemistry standpoint based on chemical and physical properties of ILs warrants further study and exploration. Thus, the number of new and exciting examples of IL implementation in separations schemes is limited to time and imagination.