CHAPTER 4: RESULTS AND DISCUSSION

4.1 Optimization of the Parameter of Extraction

4.1.1 Effect of Extraction Time

In order to examine the time for attaining extraction equilibrium, we measured the percentage extraction of Cu(II) and Fe(III) at various mixing time. Typical results for extraction of Cu(II) and Fe(III) from the aqueous to the $C_4mimNTf_2$ are shown in Figure 4.1.

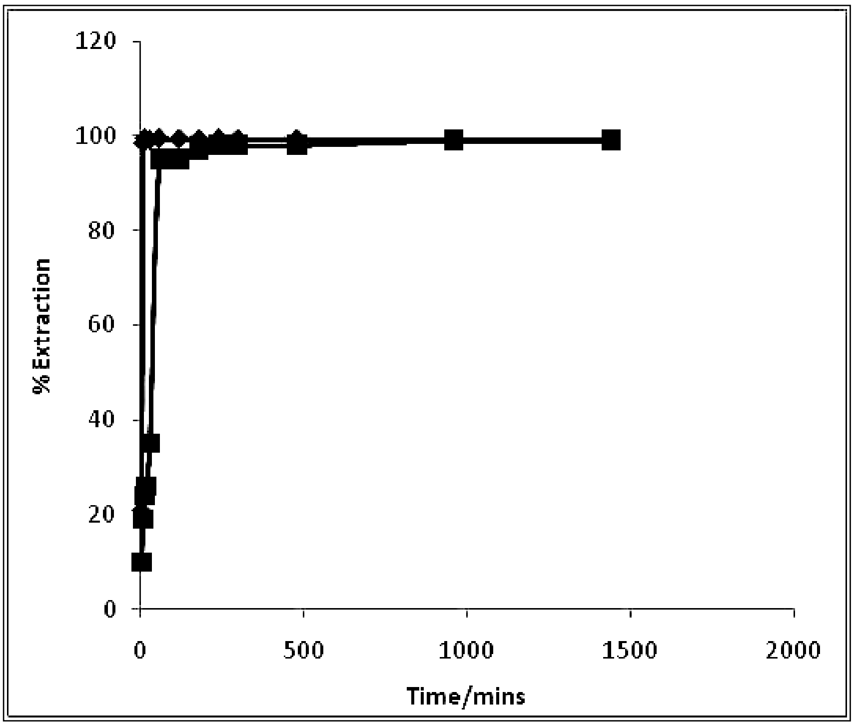

Figure 4.1: Effect of extraction time on metal extraction ♦) Cu(II), ■) Fe(III) in $C_4mimNTf_2$ with [Cu(II)=0.0003 M], [Fe(III)= 0.0003 M], [phen]=0.05M, ratio of ionic liquid to aqueous phase 0.5:10, [HCl]=0.01M.

From Figure 4.1, the extraction equilibrium is reached at around 60 min. Thus, all extraction experiments in the present study were carried out at the mixing time of 60 min.

4.1.2 Effect of Phase Volume Ratio

Table 4.1 shows the effect of phase volume ratios on the of extraction of Cu(II) and Fe(III) solutions contacting with $C_4mimNTf_2$. It can be seen that values of percentage extraction decrease significantly with increasing phase volume ratios. This is because higher volume ratio can be attributed to progressive loss of IL, because it is partially soluble in water. The optimal phase ratio was selected as 20.

Table 4.1: Percentage extraction of Cu(II) and Fe(III) in $C_4mimNTf_2$ at different phase volume ratio

Metals	**Ratio volume aqueous to ILs**				
	20	50	100	150	200
Cu(II) (% Extraction)	100.0	100.0	6.5	0.4	0.3
Fe(III) (% Extraction)	85.3	21.8	1.5	0.6	0.5

[Cu(II)]=0.0003M, [Fe(III)]=0.0003M, [phen]=0.05M, [HCl]=0.01M.

4.1.3 Effect of phen Concentration

In order to study the role of the extractant, the blank test for extraction was performed using phen –free ILs and with presence of phen at several aqueous phase pH conditions. From Figure 4.2, it was found that the metals were not extracted in the absence of phen in ILs systems. The obtained extraction percentage was <1% in all experiments condition. From this result, it was found that cation and anion of ILs do not act as strong extractant in this system. Hence, the optimization concentration of phen used was determined. Phen is added to the reaction solution to bind metal, accelerate reaction, prevent the disproportion and slow down the oxidation reaction. It is also important to optimize pH of extraction to increase the extraction performance. The pH dependencies of percentage extraction of Fe(III) in the ILs/aqueous systems also illustrated in Figure 4.2. The percentage extraction of Fe(III) is increased and appeared to be constant at high pH ranges. The pH of the aqueous phase affects the degree of ionization of a metal molecule.

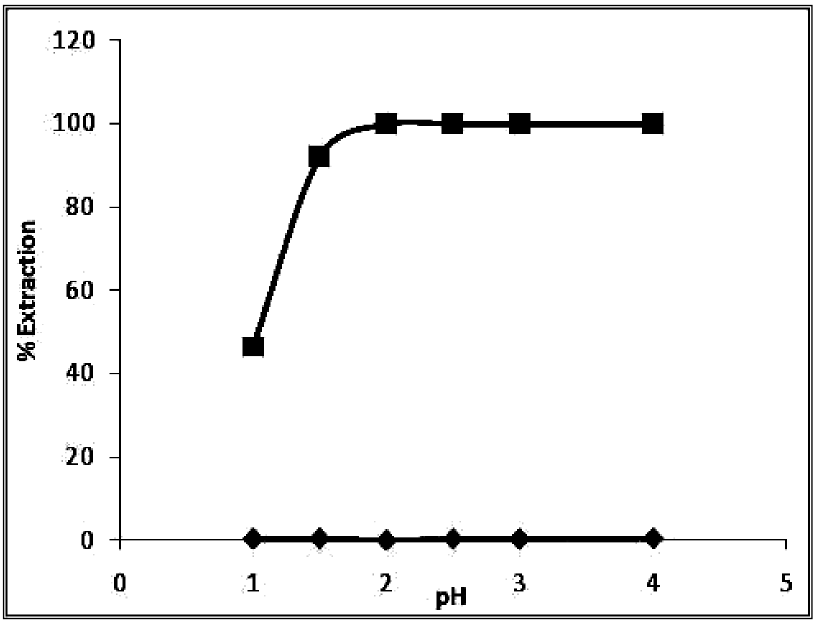

Figure 4.2: Effect of pH on the metal extraction ■) with phen, ♦) without phen [Fe(III)=0.003 M], ratio of ionic liquid to aqueous phase 0.5:10.

Table 4.2 shows that increasing the phen concentration increases the percentage extraction of metals. Phen with concentration of 0.05M was chosen for further experiment.

Table 4.2: Percentage extraction of Cu(II) and Fe(III) using $C_4mimNTf_2$ with different concentration of phen.

Metals	**Concentration Phen/M**				
	0.005	0.01	0.05	0.1	0.5
Cu(II) **% Extraction**	55.7	79.4	99.9	100.0	100.0
Fe(III) **% Extraction**	52.1	53.7	83.6	99.4	100.0

[Cu(II)]=0.0003M, [Fe(III)]=0.0003M, ratio of ionic liquid to aqueous phase 0.5:10, [HCl]=0.01M.

4.2 Solubility Measurements of ILs via Ultraviolet Spectroscopy

It was important to determine the aqueous solubility of hydrophobic imidazolium-based ILs to see the potential of ILs toward the extraction. Water solubility is not only undesirable because of costs associated with the loss of material but also because of the potential effects of these ILs on the environment. Data have been published for several ILs formed by 1-butyl-3-methylimidazolium salts with different anions and for bis(trifluoromethylsulfonyl)imide, NTf_2^-, salts with different cations (Carda-Broch *et al.*, 2003). Both anions and cations affect the hydrophobicity as summarized below (Ngo *et al.*, 2000):

$Br^-, Cl^- < BF_4^- < PF_6^- < NTf_2^- < BETI^-$

The aqueous solubilities of the liquid-phase imidazolium-based ILs were measured and shown in Figure 4.3. For a cation of the same alkyl chain length, the NTf_2^- IL had a lower solubility than the PF_6^- IL. Solubility decreases as the length of alkyl chain on the cation increases because of the increased hydrophobic nature of the IL. These results are agreement with studies done by Huddleston (Huddleston *et al.*, 2001), who demonstrated that for a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length from butyl to octyl increases the hydrophobicity of the ionic liquids. The result showed that both anion and cation of ILs contributed to the solubility of ILs. Hence, we can summarize that the order of hydrophobicity of ILs is $[C_4mimPF_6] > [C_6mimPF_6] > [C_4mimNTf_2] \approx [C_6mimNTf_2]$.

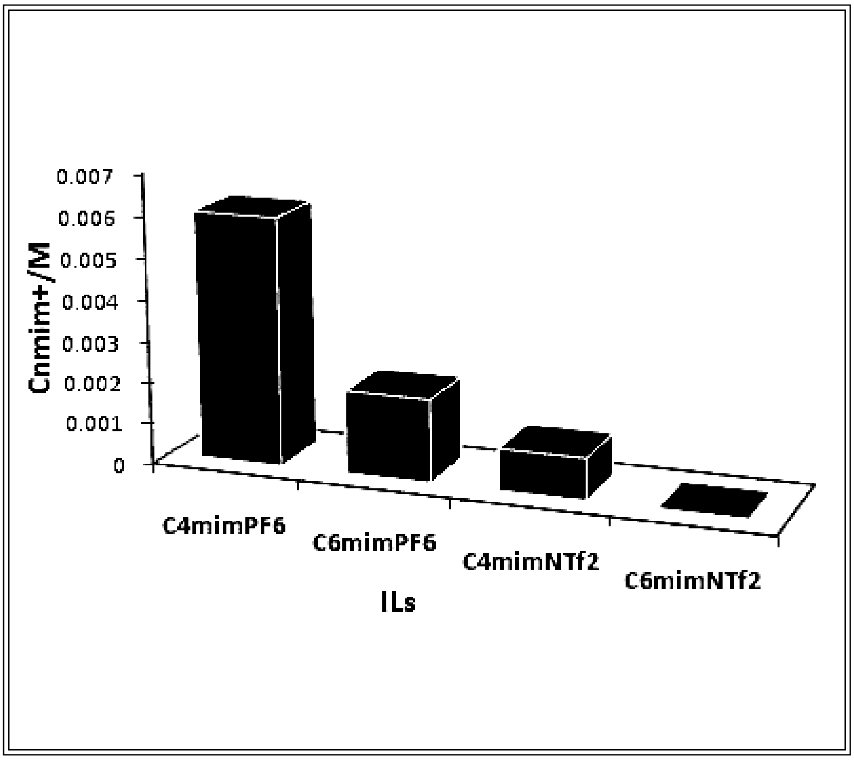

Figure 4.3: Concentration of C_nmim^+ in aqueous phase determined from UV-Vis absorption spectra at 270 nm wavelength.

4.3 Cu(II) Extraction

4.3.1 The selectivity of ILs toward the extraction

From Table 4.3, the distribution ratio of Cu(II) in ILs follows the order: [C_6mimNTf$_2$] < [C_6mimPF$_6$] < [C_4mimNTf$_2$] < [C_4mimPF$_6$]. It shows that the trend of Cu(II) partitioning into four ILs has increased with the decreasing hydrophobicity of ILs. As mentioned by other researchers, the hydrophobicity of ILs is dependent on the type of anion: PF_6<NTf_2<BETI (Welton, 1999). Cu(II) preferred distribution into [C_4mimPF$_6$] since the hydrophilic's nature of IL is compatible with Cu(II) in term of its hydrophilic properties. Based on 'like dissolve like' rule, it was easier for hydrophilic Cu(II) to be extracted into hydrophilic IL rather being extracted into more hydrophobic IL.

Table 4.3: Distribution ratio of Cu(II) in ILs phase after extraction

ILs	D Cu(II)
[C_4mimNTf$_2$]	**160.16**
[C_6mimNTf$_2$]	**113.40**
[C_4mimPF$_6$]	**1157.08**
[C_6mimPF$_6$]	**140.88**

[Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M, [HCl]=0.01M.

As shown in Table 4.3, the distribution ratio values for Cu(II) in [$C_n$mimNTf$_2$] systems were similar to each other ([C_4mimNTf$_2$]≈[C_6mimNTf$_2$]) while different to each other in [$C_n$mimPF$_6$] systems ([C_4mimPF$_6$]>[C_6mimPF$_6$]) . This result was exactly the same with the solubility test of ILs in aqueous phase as discussed previously in section 4.2. The distribution ratio of Cu(II) in NTf$_2$-type IL was not affected by IL's cation ($C_n$mim$^+$) because the hydrophobicity of NTf$_2^-$ suppressed the effect of IL's cation. As mentioned earlier, PF$_6^-$ is more soluble in water compared to NTf$_2^-$ therefore the alkyl chain of IL's cation affect the hydrophobicity of ILs and hence affect the distribution ratio of Cu(II) in PF$_6$ types IL.

4.3.2 The stoichiometry of Cu(II)-phen complexes

The slopes analyses were carried out to examine the stoichiometry of metal complexes. The number of ligands incorporated in the extractable metal complexes can be found from the slope of plot log D against log concentration of the free ligand at equilibrium in ILs as shown in Figure 4.4(a-d).

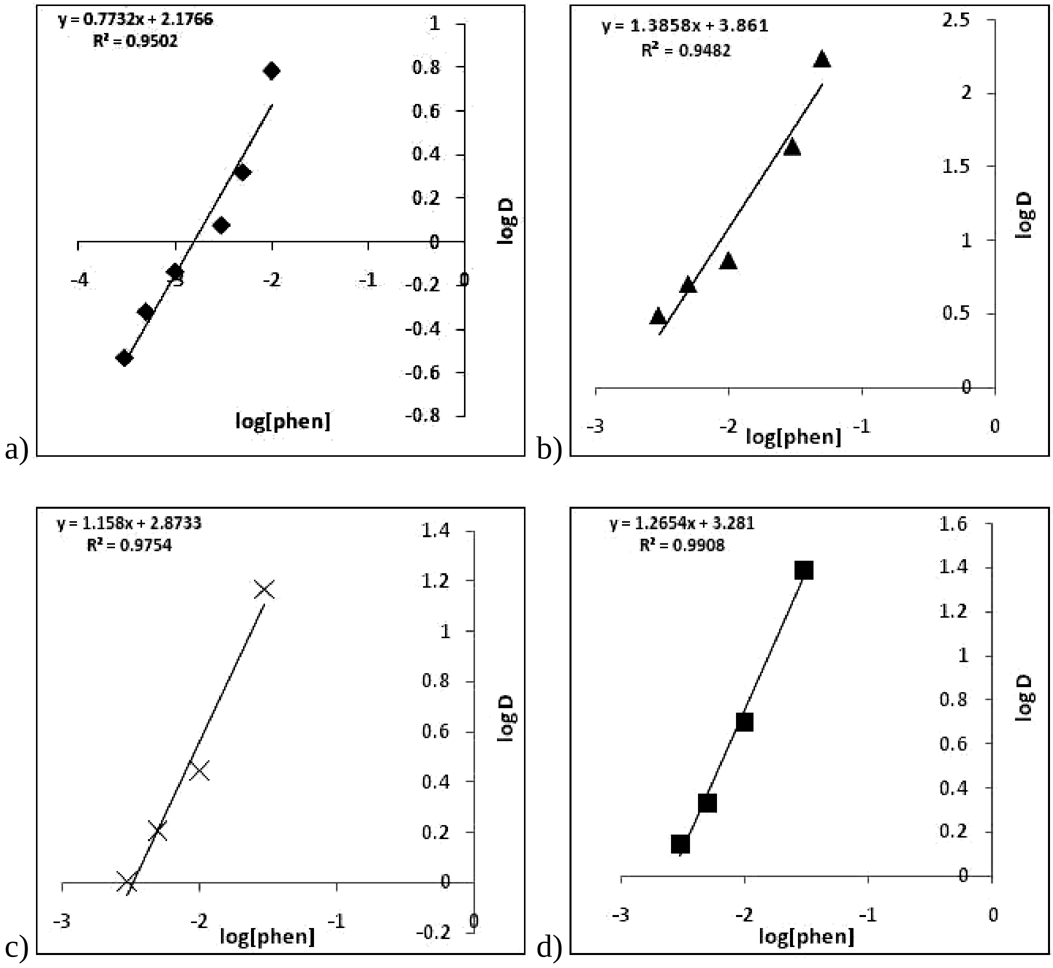

Figure 4.4: Plot of log D as a function of log concentration of free ligand in ILs (a)= [C_4mimPF_6] (b)= [$C_4mimNTf_2$] (c)= [C_6mimPF_6] (d)= [$C_6mimNTf_2$], [Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [HCl]=0.01M.

The slopes for the extraction of Cu(II) with C_4mimPF_6, $C_4mimNTf_2$, C_6mimPF_6, and $C_6mimNTf_2$ are 0.773, 1.385, 1.158, and 1.265 respectively, which indicate that the stoichiometric composition of the complex is 1:1 of Cu:phen, thus 1 mol of phen is required for 1 mol of Cu(II). The results of stoichiometry have demonstrated that the formation of Cu-phen complexes does not depend on the type of ILs. It also means that the hydrophobicity of ILs does not affect the metal complexes formation.

4.3.3 Mechanism of extraction

Generally, metal extraction using molecular organic solvents proceed via ion pair mechanism (Lo *et al.*, 1983; Rydberg *et al.*, 1992) meanwhile previous findings stated that metal extraction using ILs involves ion exchange mechanism (Jensen *et al.*, 2002; Jensen *et al.*, 2003; Visser *et al.*, 2003; Visser *et al.*, 2001). Ion pair can be illustrated in Eq.1 while ion exchange can be anionic or cationic as in Eq.2 and Eq.3, respectively.

$$M^{n+}_{(aq)} + xL_{(org)} + mCl^{-}_{(aq)} \leftrightarrow (ML_x(Cl)_m)_{(org)} \tag{1}$$

$$M^{n+}_{(aq)} + x(L)_{(IL)} + mCl^{-}_{(aq)} + pRmim^{+}_{(IL)} \leftrightarrow (ML_x(Cl)_m)^{n+}_{(IL)} + pRmim^{+}_{(aq)} \tag{2}$$

$$M^{n+}_{(aq)} + x(L)_{(IL)} + mCl^{-}_{(aq)} + pNTf_2{}^{-}_{(IL)} \leftrightarrow (ML_x(Cl)_m)^{n-}_{(IL)} + pNTf_2{}^{-}_{(aq)} \tag{3}$$

In order to investigate the mechanism of extraction, the experiments of extraction were done by mixing the aqueous solution in the presence of several salts with [C_4mimPF_6] and phen as extractant. [C_4mimPF_6] was chosen as the medium of solvent since Cu(II) is well distributed into this IL. Figure 4.5(a) clearly shows that the increase in the concentration of KPF_6 in aqueous phase gives the same value of extraction efficiency. This results indicate that K^+ and PF_6^- have no influence on the extraction of Cu(II). Therefore, it can be suggested that anion exchange mechanism does not occur in the extraction.

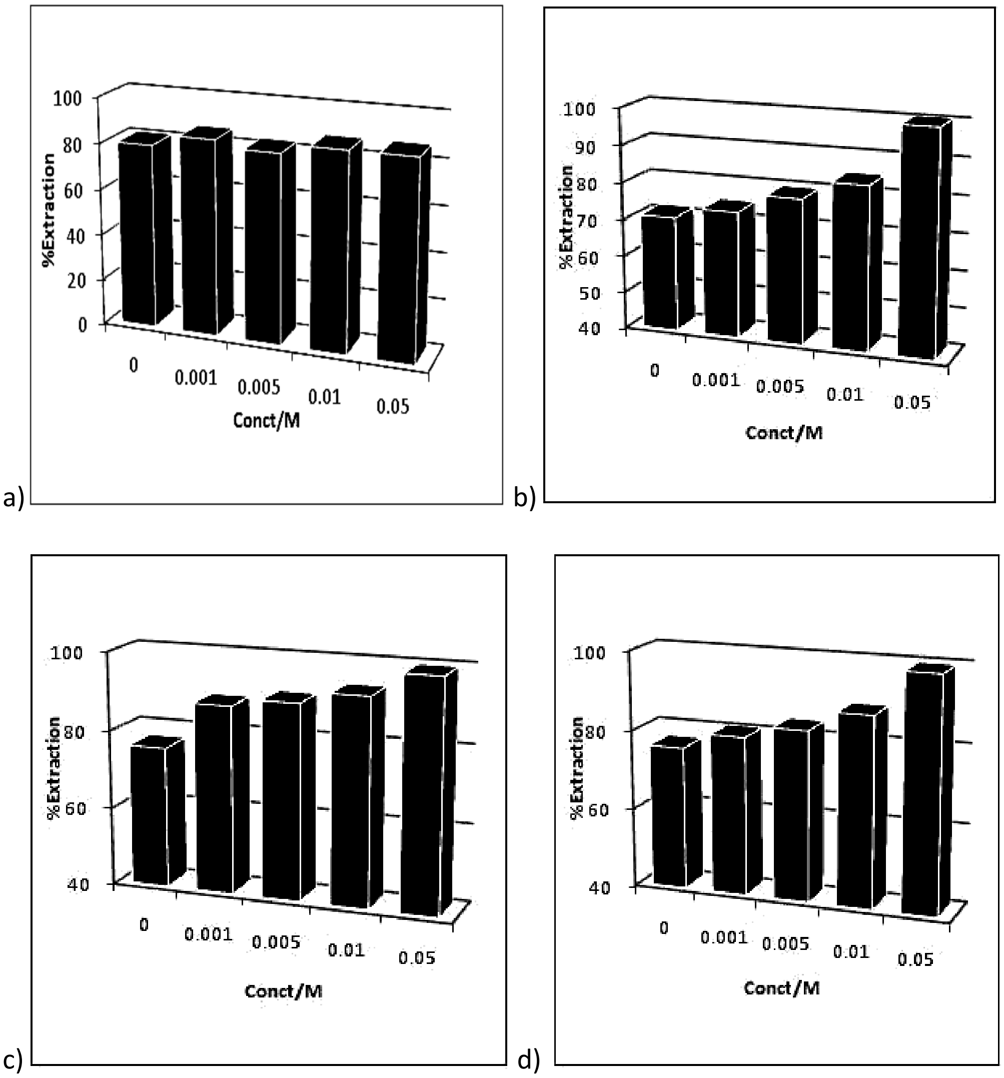

Figure 4.5: Impact of the initial concentrations of a) KPF_6 b) C_4mimBr c) KBr d) KCl on the extraction of Cu(II) by C_4mimPF_6.[Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M, [HCl]=0.01M.

As shown in Eq.2, the increasing concentration of $Rmim^+$ in aqueous phase should decrease the partition of Cu(II) to the IL phase. However as shown in Figure 4.5(b), the addition of C_4mimBr increased the extraction efficiency. This evidence implies that the mechanism of extraction was not through cation exchange since it does not follow Eq.2. This result suggests that Br^- might play a role as a counter ion to enhance the extraction. This argument is further supported by the addition of KBr into aqueous as shown in Figure 4.5(c) which gave positive impact on the extraction of Cu(II). It is reasonable to say that ion pair mechanism occurs in the Cu(II) extraction since counter ion has contributed to the extraction (Shimojo and Goto, 2004; Svetlana *et al.*, 2004).

In order to confirm whether the proposed mechanism is reasonable, the impact of KCl onto the extraction was examined as illustrated in Figure 4.5(d). Eq.1 states that increasing Cl^- in aqueous phase will enhance the Cu(II) extraction according to Le Chatelier's principle. If counter ions are necessary for the extraction, an increase in its concentration in the aqueous phase will lead to an increase in the extraction efficiency of Cu(II) ion. As shown in Figure 4.5(d), the addition of Cl^- showed great impact on the extraction of Cu(II). This result proves again that the extraction of Cu(II) ion agrees with the mechanism of ion pair.

The ion pair can also be proven by comparing the extraction efficiency in the presence of different counter ion because ion-pair complex formation depends on the type of counter ion (Shimojo and Goto, 2004; Svetlana *et al.*, 2004). As a further step, the distribution of Cu(II) ion was studied in more detail with different type of acids employed as counter ion.

As shown in Figure 4.6, the distribution of Cu(II) ion in [C_4mimPF_6] phase increased with the addition of Cl^- ion and the extraction was reduced when SO_4^{2-} and NO_3^- were used as the anion. The results indicates that the anionic species greatly affects the distribution of Cu(II) ion.

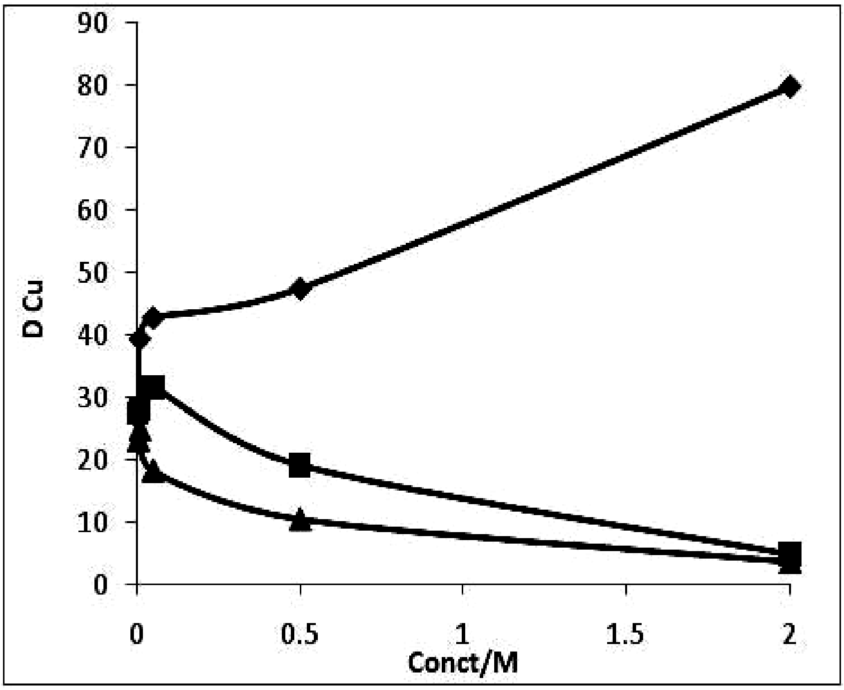

Figure 4.6: Distribution ratios for Cu(II) with phen in [C_4mimPF_6] with various acid: (♦) HCl, (■) HNO_3, (▲) H_2SO_4.[Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M.

Schilt and friends (Schilt *et al.*, 1973) revealed that in molecular organic solvent, the transfer of Zn^{2+} with 1,10-phenantroline proceed through ion pair extraction. In order to confirm whether the extraction mechanism in [C_4mimPF_6] and molecular organic solvent system are similar, we investigated the distribution of Cu(II) ion with different type of acids in chlorobenzene system.

Figure 4.7 shows that the extraction behavior of Cu(II) ion in chlorobenzene also dependent on the type of counter ion. Extraction was most efficient from aqueous solutions containing Cl^- ions compared to SO_4^{2-} and NO_3^- ions. These results suggest that the extraction of Cu(II) ion in [C_4mimPF_6] proceeds via similar mechanism with that of molecular organic solvent.

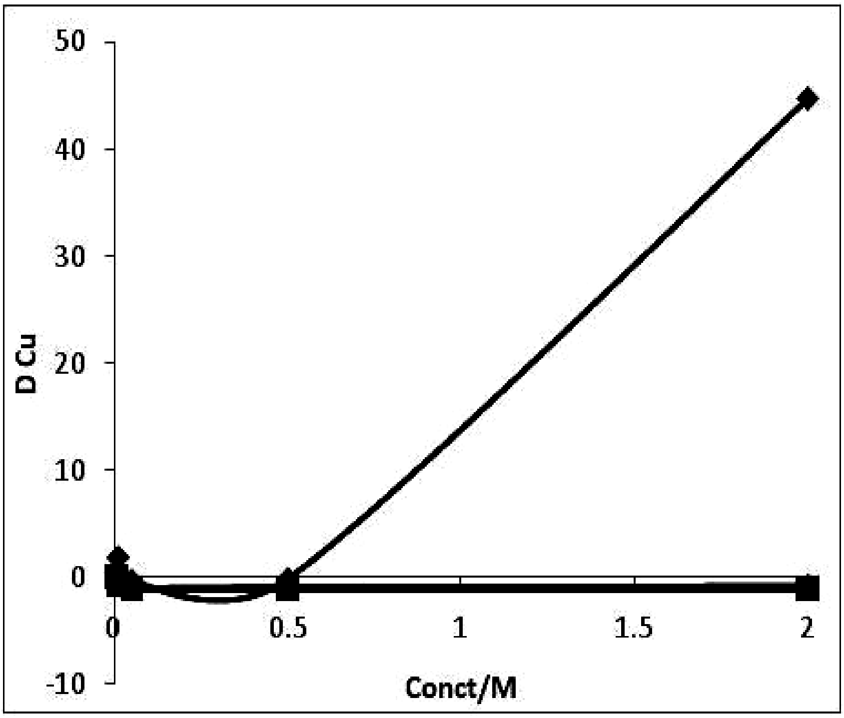

Figure 4.7: Distribution ratios for Cu(II) with phen in chlorobenzene with various acid: (♦) HCl, (■) HNO_3, (▲) H_2SO_4.[Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M.

The other investigation supporting the ion pair mechanism is the need for counter ion, Cl^- for the formation of copper-phen-chloride complex in the IL phase. Hence, we examined the distribution of Cl^- in [C_4mimPF_6] phase after extraction. Figure 4.8 shows the Cl^- values in IL increases with the addition of KCl in aqueous phase. This observation is agreed well with the study of various concentrations of HCl as shown in Figure 4.6. This proved that Cu(II) was extracted into the IL phase as copper-phen-chloride complex. From the ion chromatography results, we found that two chloride ions are co-extracted with $Cu(phen)^{2+}$ complex. The equilibrium of the Cu(II) extraction in IL phase can be written as:

$$Cu^{2+} + phen_{(IL)} + 2\,Cl^- \leftrightarrow (Cuphen)^{2+}(Cl^-)_{2(IL)} \qquad (4)$$

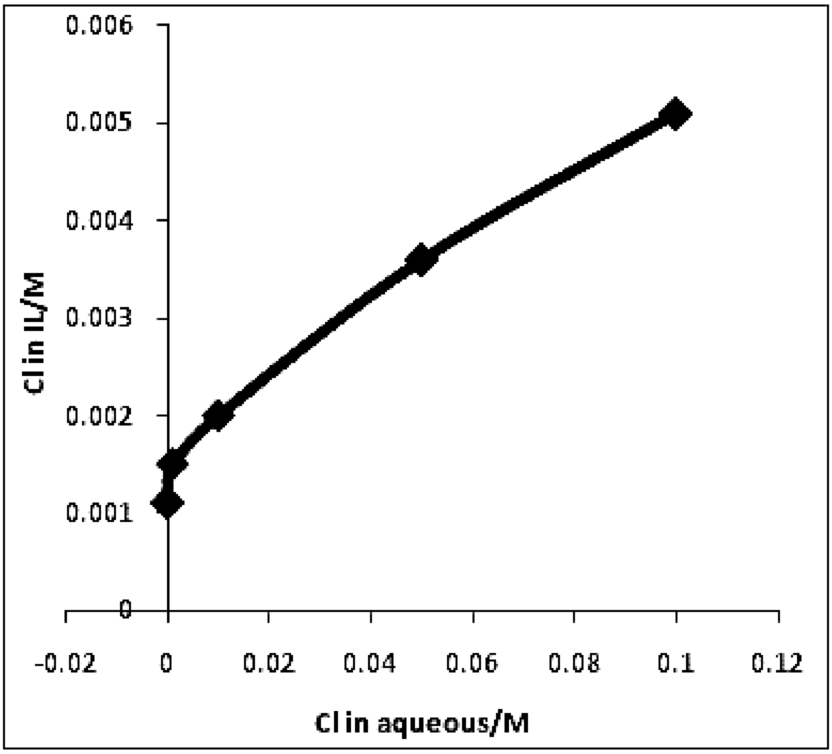

Figure 4.8: Concentration of Cl^- ion in C_4mimPF_6 phase after addition of KCl in aqueous phase. [Cu(II)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [Phen]=0.05M, [HCl]=0.01M.

The extracted ion pair easily dissociates into free cations and anions in the high dielectric medium of ILs. The dielectric constant of ILs effect the ion pair complexing extraction based on the Coulomb interaction which is distributed readily to the ferroelectric IL phase (Nakashima *et al.*, 2003).

4.4 Fe(III) Extraction

4.4.1 The selectivity of ILs toward the extraction

From Table 4.4, the distribution ratio of Fe(III) in ILs follows the order: [C_4mimPF_6] < [C_4mimNTf_2] < [C_6mimPF_6] < [C_6mimNTf_2]. The trend illustrates that partitioning of Fe(III) is increased with increasing hydrophobicity of ILs. The hydrophobic property is related to the solubility of ILs in water. Usually, the hydrophobic character of ILs is due to the type of anion. As mentioned earlier, NTf_2-type IL is more hydrophobic than PF_6-type IL. Despite that, increasing alkyl chain of IL’s cation will enhance the hydrophobicity of ILs.

Table 4.4: Distribution ratio of Fe(III) in ILs phase after extraction

ILs	D Fe(III)
[C_4mim][NTf_2]	**756.62**
[C_6mim][NTf_2]	**1227.30**
[C_4mim][PF_6]	**129.87**
[C_6mim][PF_6]	**810.90**

[Fe(III)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M, [HCl]=0.01M.

The selection of ILs to extract Fe(III) depends on the properties of Fe-phen complexes well suited with ILs with regards to the hydrophobicity of ILs and complexes. Table 4.4 shows that Fe-phen species favor extraction into the hydrophobic IL, [C_6mimNTf_2]. These results provide us important information to suggest that Fe-phen complex is an anionic species. Hirayama and friends (Hirayama *et al.*, 2005) have pointed out that the anionic complex species favors the hydrophobic nature. Generally, anionic metal complex is formed depending on charges of metal, extractant used and counter ion effect. Therefore, the counter ion's role toward Fe(III) extraction was investigated in part 4.4.3.

To compare the extraction of Fe(III) and Cu(II) in the selectivity of ILs, $C_6mimNTf_2$ has the best extraction ability for Fe(III) while C_4mimPF_6 was found to be the best IL used for Cu(II). This is because each metal have the ability to form different type of complexes with the extractant (phen) and counter ions that determines appropriate ILs for extraction. From the comparative study toward the selectivity of ILs, we suggest that Fe(III)-phen complexes extracted into IL in the form of hydrophobic anionic species meanwhile Cu(II)-phen complexes partitioned into IL in the form of ion pair species.

4.4.2 The stoichiometry of Fe(III)-phen complexes

The slope analysis was carried out to examine the stoichiometry of metal complexes. The number of ligands incorporated in the extractable metal complexes (Fe(III)) can be calculated from the slope of plot log D against log concentration of the free ligand at equilibrium in ILs as shown in Figure 4.9(a-d). The slope for extraction of Fe(III) with C_4mimPF_6, $C_4mimNTf_{2,}$ C_6mimPF_6, and $C_6mimNTf_2$ were 1.177, 0.800, 0.565, and 0.879 respectively. The plot produced straight lines with a slope of 1 for all ILs used. These results indicate that phen also forms a 1:1 complex with Fe(III) similar to Cu(II)-phen complex stoichiometry and that the formation of Fe-phen complexes was also not dependent on the IL types.

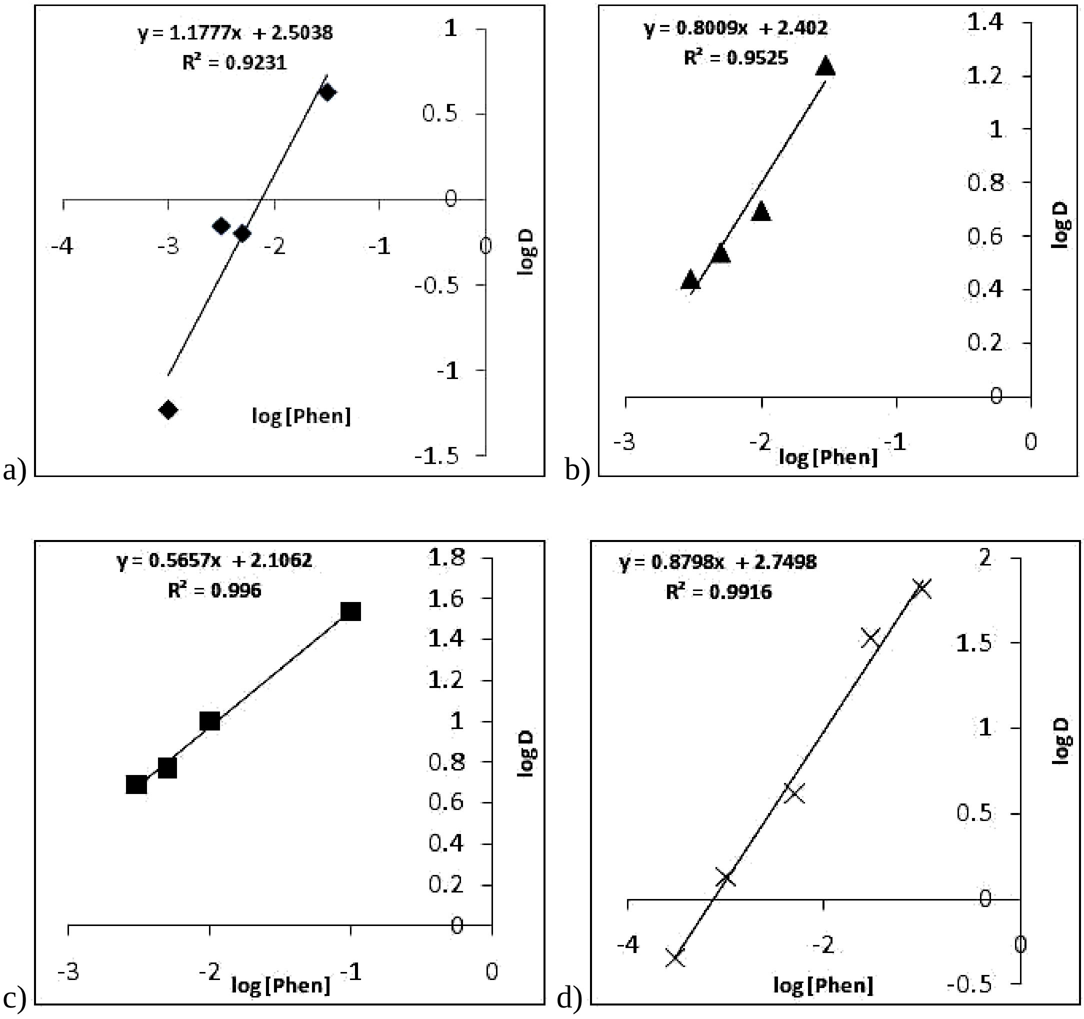

Figure 4.9: Plot of log D as a function of log concentration of free ligand in ILs (a)= [C_4mimPF_6] (b)= [C_4mimNTf_2] (c)= [C_6mimPF_6] (d)= [C_6mimNTf_2], [Fe(III)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [HCl]=0.01M.

4.4.3 Mechanism of extraction

In order to investigate the mechanism of extraction, we carried out experiments of extraction by mixing the aqueous solution in the presence of several salts with [C_6mimNTf$_2$] and phen as extractant. [C_6mimNTf$_2$] was chosen as the solvent medium for Fe(III) extraction since the distribution ratio of Fe-phen complexes was highest in those IL studied in part 4.4.1.

Figure 4.10(a) and 4.10(b) clearly shows that the cation (C_6mim^+) and anion (NTf_2^-) of IL gave negative impacts to the extraction of Fe(III). Eq. 2 and 3 demonstrated that increasing the concentration of C_6mim^+ or NTf_2^- in aqueous phase reduces the metal ion partitioning into IL phase according to Le Chatelier's principle. Based on the result and the equation, we suggested that either anion or cation exchange mechanism is involved in the Fe(III) extraction. However, as stated in part 4.4.1, the extracted species of Fe(III) is anionic species. Therefore, the mechanism extraction of Fe(III) might proceed via anion exchange. In order to support this hypothesis, we continued the experimental work by looking into the effect of counter ions towards the extraction. Usually, the effect of counter ions should be noticeable since they contribute towards the mechanisms.

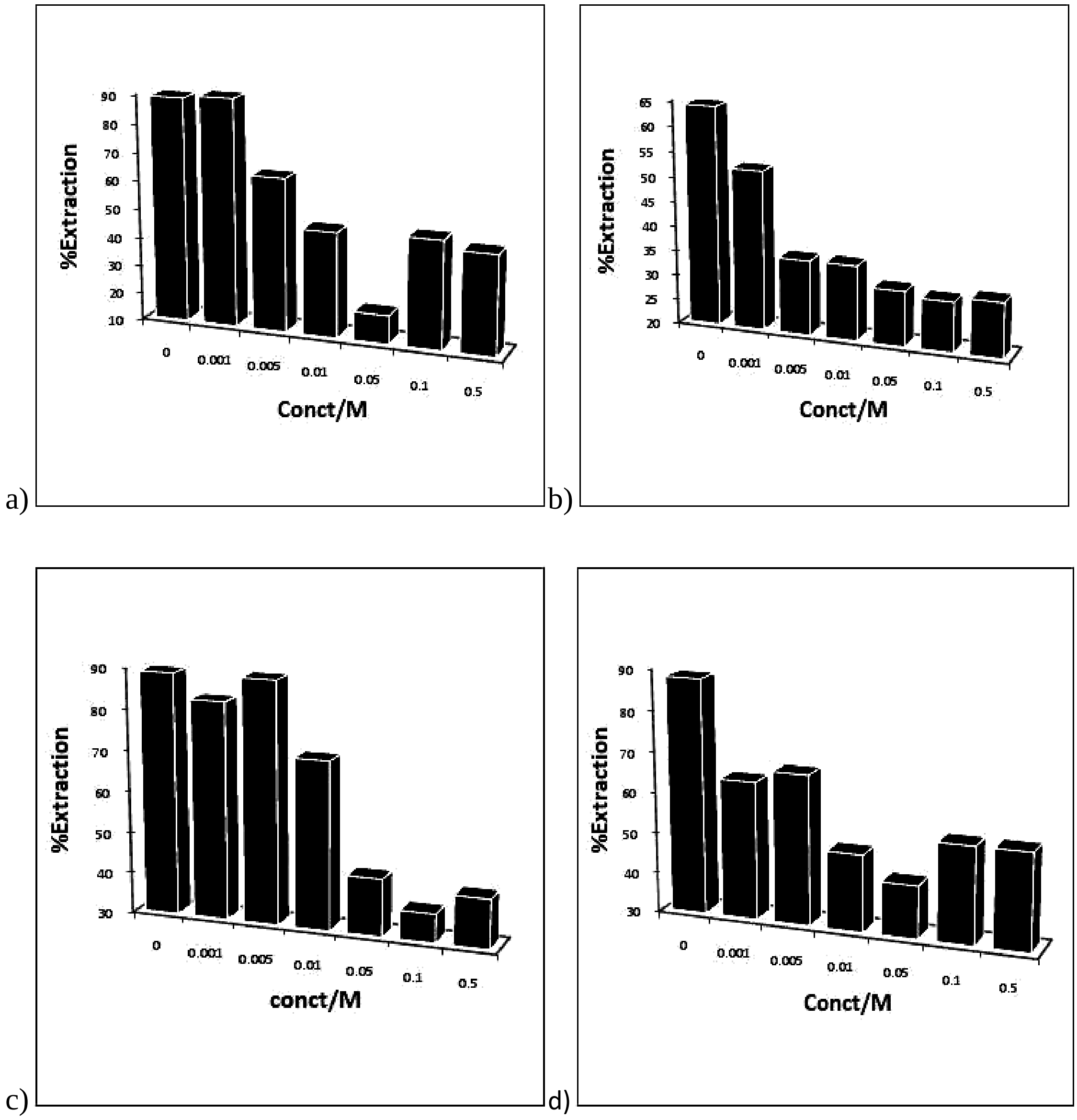

Figure 4.10: Impact of the initial concentrations of a) C_6mimCl b) $LiNTf_2$ c) LiBr d) KCl on the extraction of Fe(III) by $C_6mimNTf_2$.[Fe(III)]=0.001M, ratio of ionic liquid to aqueous phase 0.5:10, [phen]=0.05M, [HCl]=0.01M.

As shown in Figure 4.10(c) and (d), the addition of LiBr and KCl, respectively decreased the extraction efficiency of Fe(III). Referring to Eq.1, it states that increased concentration of counter ion such as Br^- or Cl^- in the aqueous phase would increase the extraction efficiency of metal complexes. However, the results shown in Figure 4.10(c) and (d) do not follow Eq.1. This finding suggests that ion pair is not the mechanism involved in Fe(III) extraction.

From the study in part 4.4.1 and 4.4.3, we decided that the anionic exchange is the mechanism of Fe(III) extraction. As confirmation, we examined the distribution of NTf_2^- and C_6mim^+ in aqueous phase which have been contacted with KCl. The partitioning of NTf_2^- increases in aqueous phase as the mechanism involved is anion exchange. Meanwhile the partitioning of C_6mim^+ increases in aqueous as the cation exchange is the mechanism of extraction.

From Figure 4.11, we reconfirmed that anion exchange was the mechanism involved in Fe(III) extraction as there is an increase of NTf_2^- in aqueous phase after extraction. NTf_2^- has been exchanged with anionic species of Fe(III) complex. Thus, cation exchange is no longer involved in the extraction. This has been proven by measuring the partitioning of C_nmim^+ in aqueous phase after extraction.

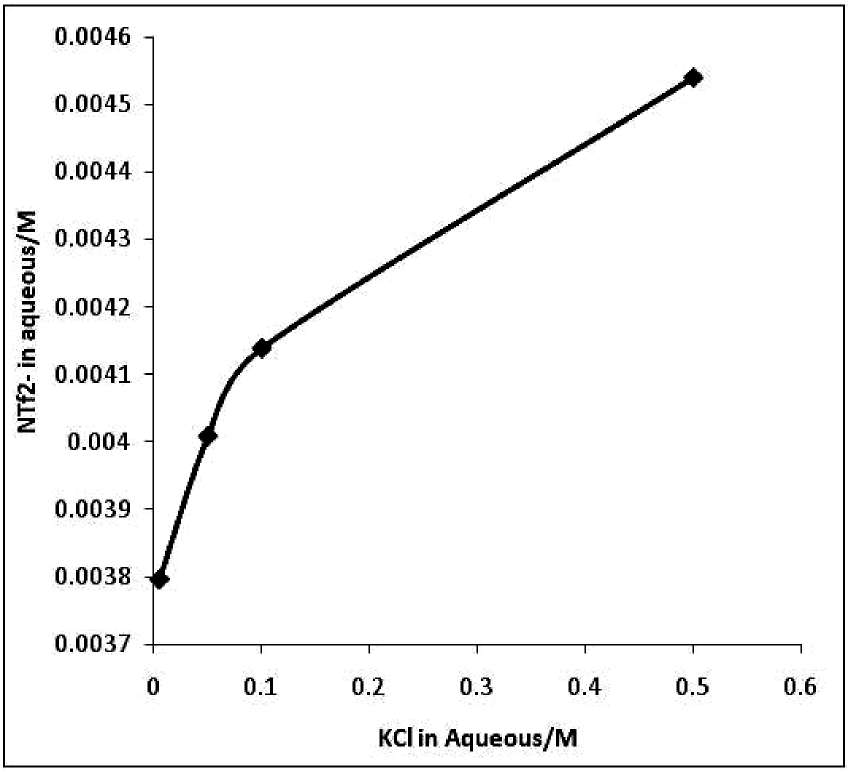

Figure 4.11: Concentration of NTf_2^- in aqueous phase with increasing concentrations of KCl in aqueous.

Figure 4.12 show that the partitioning of C_nmim^+ in aqueous phase has no effect with different concentrations of KCl. This result clearly shows that the mechanism of extraction does not proceed via cation exchange.

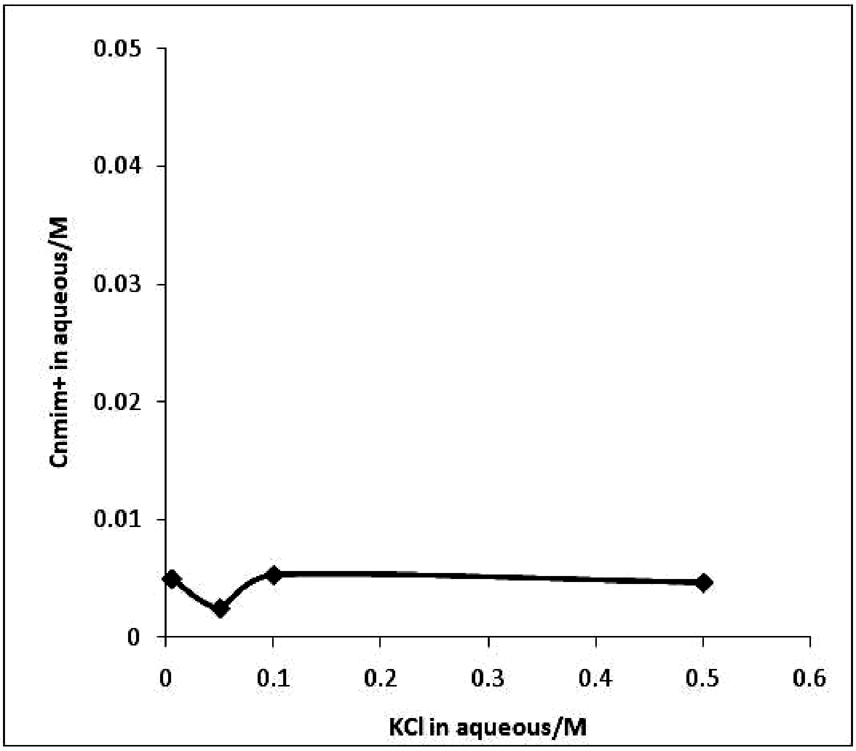

Figure 4.12: The concentration of C_nmim^+ in aqueous phase with addition of KCl in aqueous phase determined by UV-Vis spectra at 270 nm wavelengths.

As compared to Cu(II) extraction, the mechanism proceeded via ion pair as observed in part 4.3.3. Both Cu(II) and Fe(III) indicate different extraction mechanism because each metal has different properties due to their sizes and charge. Each metal was able to coordinate with extractant forming either neutral or charged metal complexes. Hence Cu(II) was preferred to form ion pair and Fe(III) form anionic complexes. Both of metal complexes species require different type of ILs which are compatible with them.

As we go through on the effect of cation and anion of ILs for the extraction of Cu(II) and Fe(III), we found that IL's cation do not influence Cu(II) and Fe(III) extraction as discussed in part 4.3.3 and 4.4.3, respectively. Therefore, cation exchange was not involved in both extractions. Anion of IL was unaffected in the Cu(II) extraction whereas they do give an impact to the Fe(III) extraction. Hence, we summarized that anion exchange is the mechanism extraction in Fe(III) extraction.

In view of counter ions participation, Cu(II) extraction proceeded with ion pair mechanism assisted by counter ion to neutralize the metal complexes charges. Meanwhile, counter ions accompanied the Fe-phen complexes forming hydrophobic anionic metal complexes species. This species made anion exchange as the mechanism of extraction of Fe(III).

CHAPTER 5: CONCLUSIONS

From the study, it is demonstrated that the distribution ratio of Cu(II) decreased with the increase of hydrophobicity of ILs. The stoichiometry of Cu-phen complexes in all ILs are 1:1 and illustrate that the formation of Cu-phen complexes is not dependent on the type of ILs used as far as it's hydrophobic properties are concerned. The effect of C_4mim^+ and PF_6^- ions on Cu(II) extraction was insignificant and showed that ion exchange will not occur in this extraction system. However, the great impact on the extraction efficiency of Cu(II) in the presence of counter ions in aqueous phase proved that the mechanism of extraction proceed via ion pair. The involvement of ion pair mechanism will help us to attain the green separation process since no loss of IL's cation and anion into aqueous phase. However, it is important to emphasize that considerable care should be taken when handling IL such as [C_4mimPF_6]. The contamination of HF into aqueous phase is not to be considered as green separation process. Our preliminary results show that the separation schemes in ILs can be same as in traditional organic solvents when appropriate metal ions/ligand/IL system is used.

As observed from result of distribution ratio of Fe(III) in ILs phase, it demonstrates that when using [$C_6mimNTf_2$] as solvent, it give the highest distribution ratio since the condition of Fe(III) complexes is favorable with most hydrophobic IL. The slope analysis of log D versus log concentration phenanthroline illustrate the extraction is independent of the ILs used. The presence of NTf_2^- anion in aqueous phase proved that the mechanism of extraction proceeding via anion exchange.

Comparing the extraction behavior between Cu(II) and Fe(III), we can conclude that the different metal contacted with same series of ILs will give different trend of extraction behavior. Hence, we have to consider the selectivity of ILs concerning the metal types to get excellent extraction efficiency. Although both metals have different extraction behavior, but the stoichiometries for both metals with extractant (phen) are not affected by the ILs. It has been demonstrated that the Cu(II) extraction using [C_4mimPF_6] have the same behavior as the extraction using traditional organic solvent. We can consider that the mechanism is environmental friendly since there is no loss of IL to the aqueous phase. Meanwhile, extraction of Fe(III) using [$C_6mimNTf_2$] proceeds via anion exchange. The loss of IL into the aqueous phase for the extraction of Fe(III) is a matter of concern. As mentioned above, we can control the extraction mechanism by selecting the metal with the extractant to reform the species which will be extracted into ILs.