

CHAPTER 3: METHODOLOGY

3.1 Materials

All chemicals and solvents were reagent grade and were used without purification. 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mimPF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mimPF_6]$), 1-butyl-3-methylimidazolium bistrifluoromethylsulfonyl imide ($[C_4mimNTf_2]$) and 1-hexyl-3-methylimidazolium bistrifluoromethylsulfonyl imide ($[C_6mimNTf_2]$) were ILs used in the extraction. These ILs, 1,10-phenanthroline (phen) and stock solution of Cu(II) and Fe(III) were supplied by Merck (Darmstadt, Germany). HPLC grade acetonitrile and acetone were also obtained from Merck. Hydrochloric acid was obtained from Fisher Scientific (United States) whereas sodium hydrogen carbonate and sodium carbonate of Analar grade for preparing Ion Chromatography (IC) eluents were supplied by BDH (UK). The aqueous solution was prepared using ultra pure water with specific resistance of 18.2 M Ω -cm. The concentrations of Cu(II) and Fe(III) in aqueous phase after extraction was determined by flame atomic absorption spectroscopy (FAAS) Perkin-Elmer AAnalyst 400 (Uerlingen, Germany). The pH value of the extraction system was measured by the Eutech Instruments Cyberscan pH meter (Singapore). The concentration of ILs anion was measured by 850 Professional Ion Chromatography (IC) Metrohm (Switzerland).

3.2 Experimental

3.2.1 General Extraction Procedure

Extraction was performed at room temperature ($24\pm 1^\circ\text{C}$). A known amount of Cu(II) and Fe(III) salt was dissolved in ultrapure water to prepare aqueous metal solutions with adjustment of pH by HCl. 10 mL of metal solution was mixed with 0.5 mL of ILs which had been added with 0.05 M 1,10-phenanthroline. The phase contacting experiments were carried out in vials. The system was vigorously shaken with TS 560-orbital shaker. After stirring for 60 minutes, the two phases were carefully separated using a Kubota centrifugal machine. The concentrations of a given metal in aqueous solution before and after extraction were determined by FAAS. Distribution ratios of the metals between a given ILs and aqueous solution was calculated by:

$$D = (C_o - C_f) / C_f \times V_{\text{aq}} / V_{\text{IL}}$$

The extraction percentage (E) also was calculated by:

$$E = (100 \times D) / (D + V_{\text{aq}} / V_{\text{IL}})$$

C_o and C_f refers to initial and final concentration of metals in the aqueous phase, respectively. Meanwhile, V_{aq} and V_{IL} refers to volume of aqueous solution and volume of IL used in the extraction, respectively.

3.2.2 Optimization of the Parameter of Extraction

(i) Effect of Extraction Time

Metal ions extractions were carried out in a series of vials at room temperature by adding of 10 ml of metal solution (concentration 0.0003 M) to 0.5 ml ILs added with 1,10-phenanthroline. Each vial was shaken at different time lengths starting from 5

minutes to 24 hours, and then centrifuged to completely separate the two phases. The optimum shaking time was selected based on the best extraction efficiency.

(ii) Effect of Phase Volume Ratio

The optimum extraction phase volume ratio was tested with a series of experiments. The experiment started with the ratio of aqueous to organic at 20. The next series of ratios of aqueous to organic were 50,100, 150 and 200. Extraction process was then performed at room temperature in a series of vials. The vials were placed in orbital shaker for 60 minutes. After centrifuging the samples, the phases were separated. The optimum phase volume ratio was selected based on the best extraction efficiency.

(iii) Effect of phen Concentration

Extraction was performed at room temperature. A known concentration of metal solution was added to ILs. Before that ILs was mixed with 1,10-phenanthroline at different concentration such as 0.005 M, 0.01 M, 0.05 M, 0.1 M and 0.5 M. The experiments were carried out in vials. The mixture was vigorously shaken with a shaker. After shaking for 60 minutes, the two phases were carefully separated using centrifugal machine. The optimum concentration of phen was selected based on the best extraction efficiency.

3.2.3 Examining the Stoichiometry of Metal Complexes

The stoichiometry of metal complexes was investigated by determining the number of ligand (phen) incorporated with the metals using hydrophobic ILs. The slope of plot log distribution ratio against log concentration phen demonstrated the number of phen attached to metal. In each vials, an aliquot (0.5 ml) of an IL containing 0.0003-0.03 M of phen and 10 ml of an aqueous phase containing 0.001M metals solution were shaken for 60 minutes. After the two phases were separated by centrifugation, the distribution

ratios of metals in ILs were determined. The experimental was carried out with ILs such as [C₄mimPF₆], [C₆mimPF₆], [C₄mimNTf₂] and [C₆mimNTf₂].

3.2.4 Investigation on the Mechanism of Extraction

The extracting phase ([C₄mimPF₆] and [C₆mimNTf₂]) was prepared by dissolving the extractant phen in ILs. The composition of the aqueous phase was different from the previously determined because the experiment of extraction was done by mixing the aqueous solution with several of salts. Table 3.1 showed various salts added into Cu(II) and Fe(III) solution. [C₄mimPF₆] and [C₆mimNTf₂] were chosen as the solvent for determination of Cu(II) and Fe(III) extraction, respectively since the metals distributed well into these ILs.

Table 3.1: IL used and types of salt that added into Cu(II) and Fe(III) aqueous to determine the mechanism of extraction.

Cu(II)			Fe(III)		
IL used	Salt added	Concentration salt (M)	IL used	Salt added	Concentration salt (M)
C ₄ mimPF ₆	KPF ₆	0-0.05	C ₆ mimNTf ₂	LiNTf ₂	0-0.05
	C ₄ mimBr	0-0.05		C ₆ mimCl	0-0.05
	KBr	0-0.05		LiBr	0-0.05
	KCl	0-0.05		KCl	0-0.05

3.2.5 PF₆⁻ and NTf₂⁻ Partitioning

The presence of PF₆⁻ and NTf₂⁻ in the aqueous phase was examined to define that anion exchange involved in the mechanism. The used ILs was diluted with 10% acetone and ultrapure water. The concentration of PF₆⁻ and NTf₂⁻ was determined by IC. In the anion analysis, the eluent was prepared by mixing 3.2 mM Na₂CO₃ and 1 mM NaHCO₃ with 25% acetonitrile (Stepnowski and Markowski, 2008).