การสกัดไอออนโลหะด้วย 2-อะมิโนไทโอฟีนอลในของเหลวไอออนิก 1-บิวทิล-3-เมทิลอิมิดาโซเลียมเฮกซะฟลูออโรฟอสเฟต

นางสาว รัฐยา เลิศลาภวศิน

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IONIC LIQUID EXTRACTION OF METAL IONS BY 2-AMINOTHIOPHENOL IN 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE

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รัฐยา เลิศลาภวศิน : การสกัดไอออนโลหะด้วย 2-อะมิโนไทโอฟีนอลในของเหลวไอออนิก 1-บิวทิล-3-เมทิลอิมิดาโซเลียมเฮกซะฟลูออโรฟอสเฟต. (IONIC LIQUID EXTRACTION OF METAL IONS BY 2-AMINOTHIOPHENOL IN 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE) อ. ที่ปรึกษา: ผศ.ดร อภิชาติ อิ่มยิ้ม, อ.ที่ปรึกษาร่วม: ผศ.ดร. เสาวรักษ์ เฟื่องสวัสดิ์, 123 หน้า.

สังเคราะห์ของเหลวไอออนิก 1-บิวทิล-3-เมทิลอิมิดาโซเลียมเฮกซะฟลูออโรฟอสเฟต ($[BMIM]PF_6$) หาลักษณะเฉพาะด้วยเทคนิคอินฟราเรดและเทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี ศึกษาภาวะที่เหมาะสมในการสกัดไอออนของนิกเกิล (II) ทองแดง (II) และตะกั่ว (II) ในน้ำ ด้วยวิธีการสกัดของเหลวโดยของเหลว โดยใช้ของเหลวไอออนิกที่สังเคราะห์ได้ร่วมกับลิแกนด์ 2-อะมิโนไทโอฟีนอล พบว่า พีเอชของสารละลายที่เหมาะสมต่อการสกัดไอออนนิกเกิลและตะกั่วคือ 4-6 และ 5 ตามลำดับ พีเอชของสารละลายไม่มีผลต่อการสกัดไอออนทองแดง โดยมีประสิทธิภาพการสกัดไอออนนิกเกิลและทองแดงใกล้เคียง 100 เปอร์เซนต์ และประสิทธิภาพการสกัดไอออนตะกั่วเท่ากับ 80 เปอร์เซนต์เมื่อใช้สารละลายโลหะเข้มข้น 5 มิลลิกรัมต่อลิตร และ 57 76 และ 20 เปอร์เซนต์เมื่อใช้สารละลายโลหะเข้มข้น 1.0 มิลลิโมลาร์ ตามลำดับ การสกัดไอออนนิกเกิล ทองแดง และตะกั่วเข้าสู่สมดุลตั้งแต่เวลา 120 นาที 30 นาที และ 30 นาที และพบว่าการมีไอออนโซเดียม แคลเซียม แมกนีเซียม ซัลเฟตและคลอไรด์ร่วมในสารละลายไม่ส่งผลต่อประสิทธิภาพการสกัดไอออนโลหะทั้งสามชนิด โดยปริมาณสารสัมพันธ์ของการเกิดสารประกอบเชิงซ้อนระหว่างไอออนนิกเกิล ทองแดง และตะกั่วกับลิแกนด์เป็น 1:3 1:2 และ 1:2 ตามลำดับ สำหรับตัวชะที่เหมาะสมในการชะไอออนนิกเกิลคือ 3 % ไฮโดรเจนเปอร์ออกไซด์ในกรดไนตริกเข้มข้น 0.5 โมลต่อลิตร ที่เวลาตั้งแต่ 20 นาทีเป็นต้นไป ตัวชะที่เหมาะสมในการชะไอออนทองแดงและตะกั่วคือ กรดไนตริกเข้มข้น 1 โมลต่อลิตร โดยใช้เวลาในการชะ 20 นาที และ 10 นาที ตามลำดับ โดยมีประสิทธิภาพการชะไอออนทั้งสามชนิดมากกว่า 95 เปอร์เซนต์ นอกจากนี้พบว่าการสกัดไอออนโลหะทั้งสามชนิดด้วยลิแกนด์ 2-อะมิโนไทโอฟีนอลในของเหลวไอออนิกให้ประสิทธิภาพสูงกว่าการสกัดเมื่อใช้คลอโรฟอร์มเป็นตัวทำละลายที่ภาวะเดียวกัน และมีค่าคงที่การเกิดสารประกอบเชิงซ้อนของไอออนนิกเกิลและตะกั่วในของเหลวไอออนิกเป็น 5.47×10^7 และ 51.1 ตามลำดับ

ภาควิชา ....เคมี........... ลายมือชื่อนิสิต....รัฐยา.....เลิศลาภวศิน....................
สาขาวิชา ....เคมี........... ลายมือชื่ออาจารย์ที่ปรึกษา....................................
ปีการศึกษา ....2550......... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.............................

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KEY WORD: IONIC LIQUID / 2-AMINOTHIOPHENOL / ASSOCIATION CONSTANT / LIQUID-LIQUID EXTRACTION

RATTHAYA LERTLAPWASIN: IONIC LIQUID EXTRACTION OF METAL IONS BY 2-AMINOTHIOPHENOL IN 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE. THESIS ADVISOR: ASST.PROF. APICHAT IMYIM, Ph.D., THESIS COADVISOR: ASST.PROF. SAOWARUX FUANGSWASDI, Ph.D., 123 pp.

The ionic liquid namely 1-butyl-3-methylimidazolium hexafluorophosphate was synthesized and characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The optimum conditions for the extraction of Ni^{2+}, Cu^{2+} and Pb^{2+} in water by liquid-liquid extraction method was investigated using the synthetic ionic liquid combined with 2-aminothiophenol ligand. The results showed that the optimum pH for the extraction of Ni^{2+} and Pb^{2+} were 4-6 and 5, respectively. The percentage extractions of Ni^{2+}, Cu^{2+} and Pb^{2+} were about 100, 100, and 80% when using 5 mg L^{-1} of metal solution and 56, 76, and 20%, when using 1.0 mM of metal solution, respectively. The extraction of Cu^{2+} is independent of the pH of solution. The extraction equilibria of Ni^{2+}, Cu^{2+} and Pb^{2+} were reached within 120, 30 and 30 min. The existence of sodium, calcium, magnesium, sulphate and chloride ions did not significantly affect the extraction efficiency of all metal ions. The stoichiometries of complexes between Ni^{2+}, Cu^{2+} and Pb^{2+} and the ligand are 1:3, 1:2 and 1:2, respectively. The extracted Ni^{2+} in ionic liquid phase could be back-transferred into 3% H_2O_2 in 0.5 M HNO_3 at 20 min of contact time and the extracted Cu^{2+} and Pb^{2+} could be stripped with 1 M HNO_3 at the contact time of 20 min and 10 min, respectively, with the percentage stripping higher than 95 %. The extraction efficiency of all metal ions with the ligand in the ionic liquid was higher than that obtained in chloroform at the same conditions. The association constants of complexes between Ni^{2+} and Pb^{2+} and the ligand in ionic liquid are 5.47×10^7 and 51.1, respectively.

Department : ....Chemistry............ Student's signature : Ratthaya Lertlapwasin
Field of study : ....Chemistry............ Advisor's signature : ....
Academic year : ....2007..................... Co-advisor's signature : ....

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

IL	Ionic liquid
RTIL	Room temperature ionic liquid
LLE	Liquid-liquid extraction
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-AES	Inductive couple plasma atomic emission spectrometry
ICP-MS	Inductive couple plasma mass spectrometry
FTIR	Fourier transform infrared spectrometry
NMR	Nuclear magnetic resonance spectrometry
XRD	Single crystal X-Ray diffractometry
ESR	Electron spinning resonance spectrometry
AT	2-Aminothiophenol
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
$[BMIM]PF_6$	1-butyl-3-methylimidazolium hexafluorophosphate
IC	Ion chromatography
UV-Vis	Ultra-violet spectrophotometry
%E	Percentage extraction
D	Distribution ratio
K_D	Distribution coefficient
K_{ass}	Association constant
K_{ex}	Extraction constant
K_a	Acid-ionization constant
K_f	Formation constant
D_{HL}	Ligand distribution ratio
D_{ML}	Metal complex distribution ratio

CHAPTER I

INTRODUCTION

1.1 State of the Problem

In the present days, the environmental damage is the global problem and many organizations are alert to solve it. Some of the several environmental issues are green house effect, water-air pollution and hazardous waste generation. Wastewater from industries is one of the main causes of these problems. A lot of wastewater was disposed to the environment because of the increasing of manufactory, therefore the wastewater treatment is necessary especially treatment of heavy metals. Heavy metals such as lead (Pb), nickel (Ni), copper (Cu), arsenic (As) and mercury (Hg) are usually applied in various fields such as in manufactory of pesticide, batteries, steels, alloys, electroplated metal parts and paints etc. Heavy metals pollute the environment via accumulation in soil and contamination in water and air. Their toxicity can release to soil, water and air and enter the human body through food, water, air or absorption through skin. Copper (II), nickel (II) and lead (II) ions are known to be toxic to human health. They can accumulate in biological organism and affect the metabolism ability.

A liquid-liquid extraction (LLE) is one of the efficient techniques for the separation and concentration of metal ions on industrial scale. This technique is based on the principle of like dissolve like that the solute is extracted from one phase to the other immiscible phase. The traditional liquid-liquid extraction involves the use of organic solvent with extractants to extract metal ions from wastewater. The disadvantages of organic solvents such as their toxicity, flammability and volatility have led to the usage of new green solvents, namely ionic liquids.

Ionic liquids (ILs) are molten salts whose melting point is below 100 ^{0}C. More specifically, if the melting point is below room temperature, it is known as room temperature ionic liquids (RTIL). ILs consist of bulky asymmetry organic cation and organic or inorganic anion. Ionic liquids are increasingly investigated worldwide as alternative reaction media to replace traditional organic solvents in organic synthesis, catalytic reaction, electrochemical application, separation, biochemistry and material engineering because of the perception of a friendly environment. Their unique properties such as negligible volatility, thermal stability and non-flammability have been accepted as a new green solvent. The replacement of traditional organic solvent with ionic liquid would reduce the use of hazardous and polluting organic solvents, avoiding the environmental and safety problems generated from the toxicity and volatilization especially in the case of liquid-liquid extraction.

In this research, a synthetic room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (Figure 1.1) combined with 2-aminothiophenol ligand (Figure 1.2) was used for the extraction of Ni(II), Cu(II) and Pb(II) in water. The optimum condition of metal extraction and stripping was studied and the association constant between the ligand and each metal ion in ionic liquid was calculated.

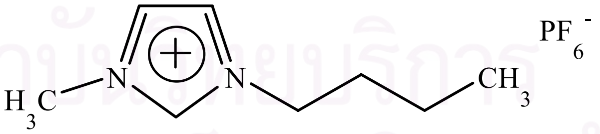


Figure 1.1 Structure of 1-butyl-3-methylimidazolium hexafluorophosphate.

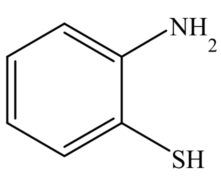


Figure 1.2 Structure of 2-aminothiophenol.

1.2 Objectives

The aims of this research are 1) to study the possibility of replacing an organic solvent with a room temperature ionic liquid in liquid-liquid extraction (LLE) technique for extraction of Ni(II), Cu(II) and Pb(II) in aqueous solution by 2-aminothiophenol ligand and 2) to calculate the association constants between the metal ions and the ligand.

1.3 Scope of the Research

Initially, the ionic liquid was synthesized by anion metathesis reaction. Then, the optimum condition for extraction of Ni(II), Cu(II) and Pb(II) in aqueous solution using 2-aminothiophenol ligand in ionic liquid by liquid-liquid extraction technique was investigated. The concentration of metal ions in aqueous solution was determined by flame atomic absorption spectrometry (FAAS).

Various parameters impacting on the ionic liquid extraction such as pH of solution, extraction time, type and concentration of stripping agent, stripping time, interference ions (SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}), were studied. And the association constants of metal-ligand were calculated.

1.4 The Benefits of this Research

In this research, ionic liquid can replace an organic solvent which is benign to the environment and improves the metal extraction efficiency. The knowledge of extraction properties of 2-aminothiophenol in ionic liquid towards the metal ions can be applied for other applications such as the removal of metal ions in wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Heavy Metals in the Environment [1]

2.1.1 Recent Regulations

Environmental contamination and exposure of heavy metals are a serious growing problem throughout the world. Heavy metals are described as metallic chemical elements with a specific gravity (density) more than 5 g cm^{-1}. Interestingly, in the right concentration, many metals such as copper, nickel, chromium, silver, zinc, manganese and iron are nutritionally essential trace elements for healthy life, but their excess amount even though at low concentration are poisonous interference to enzyme systems and the metabolism of the body. Heavy metals are taken into the body via inhalation, ingestion, and skin absorption. The human activities are main source of exposure of heavy metals to the environment. The major activities are mining and ore processing, coal and fuel combustion, agriculture, domestic, transportation and industrial processing.

In general, heavy metal toxicity is produced by forming complexes with organic compounds containing oxygen, sulfur and nitrogen. These modified biological molecules lose their ability to active enzyme system or to affect protein structure, resulting in death of the affected cells and tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical's concentration in the environment.

According to the widespread applications of heavy metals in various fields of our life especially in industrial applications, heavy metals have been inherently emitted into the environment around us, thus the waste treatment before disposal is necessary. The recent regulation, Notification of the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992) has regulated the industrial effluent standard values of heavy metal as shown in Table 2.1.

Table 2.1 The industrial effluent standard values [2]

Heavy Metals	Standard value
Copper	not more than 2.0 mg/l
Lead	not more than 0.2 mg/l
Nickel	not more than 1.0 mg/l
Chromium (trivalent)	not more than 0.75 mg/l
Chromium (hexavalent)	not more than 0.25 mg/l
Mercury	not more than 0.005 mg/l
Manganese	not more than 5.0 mg/l
Arsenic	not more than 0.25 mg/l
Cadmium	not more than 0.03 mg/l
Zinc	not more than 5.0 mg/l

2.1.2 Background Information of Metals [1]

2.1.2.1 Copper

Copper is a reddish, malleable, ductile metal with very good heat and electricity conductivity. There are two oxidation states: Cu^+ and Cu^{2+}.

Copper is a trace element that is essential to maintain the metabolism of human body. It is necessarily used in the modified redox reaction of enzyme and in some oxygen-carrying systems. Although humans can handle proportionally large concentrations of copper, excess amount of copper can still cause eminent health problems. In high doses, copper can cause anemia, liver and kidney damage and stomach and intestinal irritation. It causes headache, stomachache, dizziness, vomiting and diarrhea with long-term exposure.

The application of copper is mostly for electrical equipment, construction such as roofing and plumbing, industrial machinery such as heat exchangers and alloys. Some other applications are feed additives, fungicide, growth promoter, bactericide and fertilizers.

2.1.2.2 Lead

Lead is a soft, malleable, ductile metal with a poor electricity conductor and very resistant to corrosion. The occurred oxidation states of lead are Pb^{2+} (in most inorganic compounds) and Pb^{4+}.

Lead has been used for more than 5000 years. Due to it suitable physical and chemical properties, lead is applied in the manufacturing, construction and chemical industry such as rechargeable batteries, petroleum additives, rolled and extruded products, alloys, pigments, cable sheathing, shot and ammunition. Moreover, lead is also used as radiation sheeting and as a heating stabilizer in PVC.

In the environment, lead is known to be toxic to plants, animals and microorganisms. Many countries have banned the Pb-containing pesticides. In humans, lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing fetus and infant being more sensitive to lead than adult. High levels of exposure may result in toxic biochemical effects, which in turn cause problems in the synthesis of hemoglobin, a rise in blood pressure, effects on the kidneys, declined fertility of men through sperm damage, gastrointestinal tract, joints and reproductive system and acute or chronic damage to the nervous system.

2.1.2.3 Nickel

Nickel is a silvery-white, hard, malleable, ductile and ferromagnetic metal. It normally occurs in oxidation states Ni^0 and Ni^{2+} whereas under certain conditions Ni^+ and Ni^{3+} can exist but are not stable in aqueous solution.

Nickel is a metal that is easy to work and can be drawn into wire. The most common applications of nickel are used as an additive of steel and other metal products. It is used in the preparation of strength, ductility, and corrosion and heat resistance alloys or super alloys, one composition to make stainless steel, rechargeable batteries, catalysts and other chemicals, coinage, foundry products, and plating.

Small amount of nickel are necessary for human life to produce red blood cells, but uptake of large quantity of nickel can become toxic. Long-term exposure can cause body weight loss, heart and liver damage, skin irritation, higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer, respiratory failure and birth defects.

2.1.3 Determination of Metals [1, 3]

The selection of suitable technique for metal determination depends on the concentration level of metal in sample that is related to the detection limit of the chosen determination technique. Equipment, ease of operation, number of analyses and personal skill are also influential factors. The spectroscopic methods, the most common methods for metal determination, include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) or electro thermal vaporization atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF).

FAAS is very specific technique for a routine determination of a single element for most elements. This technique is known as a technique with few problems related to interference effects. However, detection limits of FAAS are relatively high for some elements. GFAAS, another technique with higher sensitivity, is thus more powerful and suitable for trace analysis. Nevertheless, matrix effects from components in the sample other than the analyte are more sensitive. Therefore, matrix component removal and preconcentration of the analytes are often necessary.

ICP-AES is a routine analytical method especially used when the large number of elements has to be determined in many samples. The sequential and simultaneous mode allows rapid analysis, therefore dramatically improving throughput. The detection limits of ICP-AES for most elements are much lower than that of FAAS.

ICP-MS is a multi-element technique that is suitable for trace analysis. Its most effective and very fast response time offer a long linear range and low background for most elements. Moreover, due to the high sensitivity and resolution, the detection limit obtained is much lower than that of ICP-AES but this costly and skill-required instrument may be prohibitive to many laboratories.

2.1.4 Separation Technology for the Recycling and Reuse of Liquid Waste Streams [4-6]

The industries also introduce pollutants into the air, water, and land. The potential for an increasing environmental impact will inevitably result in society's setting even at lower allowable levels for pollutants. Companies are increasingly being focused on both the regulatory and cost pressures to reduce the amount and environmental sensitivity of the liquid waste produced. Minimization of waste production and the practice of recycling and reuse can improve the economy and can minimize the potential environmental impact. The economic advantages, coupled with reduced environmental impact and consideration of full cycle benefits, could provide a sound incentive for recycle and reuse.

Recycling and resource recovery technologies include those that recover materials from waste streams before disposal or recycling of waste streams for reuse in other processes. An important step of waste minimization is recycling and reuse of valuable materials from potential waste streams. A combination of physico-chemical processes such as flocculation, precipitation, filtration and biological processes such as activated sludge is a traditionally wastewater stream treatment. Such treatments are usually effective in reducing organic pollutants to a suitable disposal level. Nevertheless, they often fail to reduce the concentration of heavy metals below permissible limits.

The removal of toxic heavy metal ions from wastewater is of great concern in the environmental field of waste and pollution reduction. Separation process leading to recovery, recycling or reuse of metal also prevents discharge to the environment. The wastewater stream is fractionated into two or more liquid phases that are either recyclable, saleable or discarded as waste. Solvent extraction, membrane technology, ion exchange and adsorption process [4, 7] are separation technologies that facilitate the recycling.

2.2 Liquid-Liquid Extraction [8-11]

2.2.1 LLE Principle

Liquid – liquid extraction (LLE) or solvent extraction is a useful technique for separating both organic and inorganic compounds from interferences based on the partitioning between two immiscible liquid phases. This technique can separate substances in the concentration range of trace to macro level. One phase in LLE is usually aqueous and the other phase is an organic solvent. More hydrophilic compounds prefer the polar aqueous phase, whereas more hydrophobic compounds prefer the organic solvent.

The extraction is carried out by adding the extractive solvent to the aqueous sample solution in the vessel and shaking vigorously to create a temporary emulsion. The emulsion is the very small spherical droplets of the extractive liquid that suspend in the aqueous phase. The increasing of contact area promotes the rapid mass transfer of the desired solute from one phase to the other. Sometime, to attain the true equilibrium of the solutes between the two phases, the continuous shaking is necessary.

2.2.2 Distribution Coefficient and Distribution Ratio

Nernst Distribution Law is the fundamental law of quantitative basis governing of a solute between two immiscible solvents. This can be stated that at equilibrium, constant temperature and pressure, any solute will distribute between two essential immiscible solvents with the constant ratio of the concentration of solute in the two phases. For a solute X distributing between aqueous and organic solvent, the distribution coefficient, K_D is defined as follows:

$$X_{aq} \rightleftharpoons X_{org}$$

$$K_D = \frac{[X]_{org}}{[X]_{aq}} \qquad \text{at equilibrium}$$

where $[X]_{org}$ is the concentration of solute in organic solvent

$[X]_{aq}$ is the concentration of solute in aqueous solution

It is important to realize that the distribution coefficient refers to only one specific species. The distribution coefficient is roughly a measure of the relative solubility of the particular species, and is not a total actual concentration in each phase. When more than one species are involved in the distribution, each species will distribute independently of all other, the distribution ratio, D is evaluated.

The distribution ratio is defined as the ratio of the concentration of all the species of the solute in each phase. The distribution of a solute X with numerous forms in solution between aqueous and organic solvent is

$$D = \frac{\left|[X]_{org}\right|}{\left|[X]_{aq}\right|} \qquad \text{at equilibrium}$$

where $\left|[X]_{org}\right|$ is total concentration of solute in organic solvent

$\left|[X]_{aq}\right|$ is total concentration of solute in aqueous solution

For example, in an extraction of organic acid (HA) from water into organic solvent where HA is monoacid and dissociates into H^+ and A^- in water and only HA is extracted into the organic solvent, K_D and D are defined as follows:

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \text{ and } D = \frac{[HA]_{org}}{[HA]_{aq} + [A^-]_{aq}}$$

Although the distribution ratio is not constant and can vary with experimental conditions that might affect the chemical equilibrium, e.g. pH, it is important to remember that the value of the equilibrium constant for each individual equilibrium remains constant.

2.2.3 Percentage Extraction (%E)

The distribution ratio is a constant independent of the volume ratio. However, the fraction of the solute extracted will depend on the volume ration of the two solvents. The fraction of analyte extracted (%E) into the organic phase is given by

$$E(\%) = \frac{\text{amount of extracted substrance}}{\text{total amount of substance present in both phases}} \times 100$$

Or can be defined as follows:

$$E(\%) = \frac{w_0 - w_i}{w_0} \times 100$$

where w_0 is substance contained at the beginning

w_i is substance left in the aqueous phase

2.2.4 Extraction of Metal Ions

The most important application of solvent extraction is the metal extraction from water into an organic solvent. Metal ions do not tend to dissolve in the organic layer by the principle of "like dissolve like". To extract metal ions from water into an organic solvent, their charge must be neutralized and something must be added to make them "organic like". There are two principal ways to perform, i.e. ion association system and chelating system.

2.2.4.1 Ion Association System

In ion association system, the metal ion is incorporated into a bulky molecule and associates with an opposite charged ion to form neutral species, an ion-pair or the metal ion associates with another ion of great size (organic-like). The attraction force of ion pair formation is physical as contrast to the chemical force in the formation of coordination complex. Hence, for two ions A^+ and B^- which associate to form (A^+, B^-) according to the equation

$$A^{+} + B^{-} \rightleftharpoons \left(A^{+}, B^{-}\right)$$

The equilibrium expression is

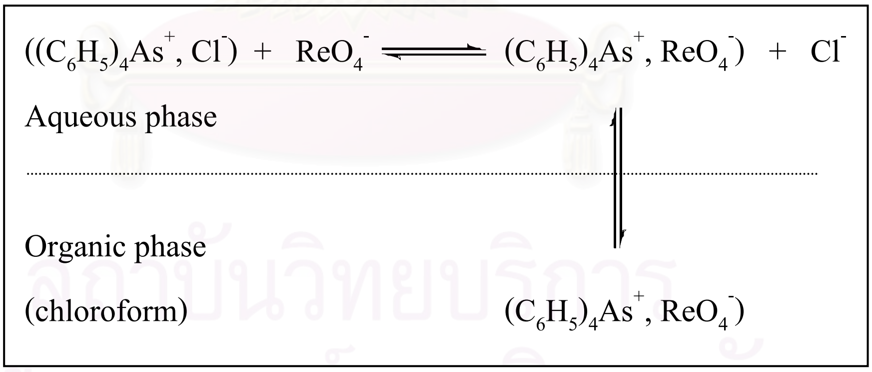
$$K = \frac{\left[\left(A^{+}, B^{-}\right)\right]}{\left[A^{+}\right]\left[B^{-}\right]}$$

The ion association system can be classified into three categories that are (a) ion association alone, (b) chelation and ion association with either cationic or anionic metal chelates and (c) simple coordination and ion association-liquid ion exchangers and the "onium" systems.

2.2.4.1.1 Simple Ion Association

This system involves large and bulky cation and anion whose size and structure do not have a primary hydration shell. Addition of large ion containing bulky organic group to incorporate with metal ion will form an ion of large size that disrupts the hydrogen-bonding water structure. Examples of the reagent cation and anion being used include the tetraphenylarsonium $(C_6H_5)_4\ As^+$ and tetrabutylammonium $(n\text{-}Bu_4N^+)$ ions for ReO_4^-, MnO_4^-, $FeCl_4^-$ and $HgCl_4^{2-}$ and $(C_6H_5)_4\ B^-$ for Cs^+.

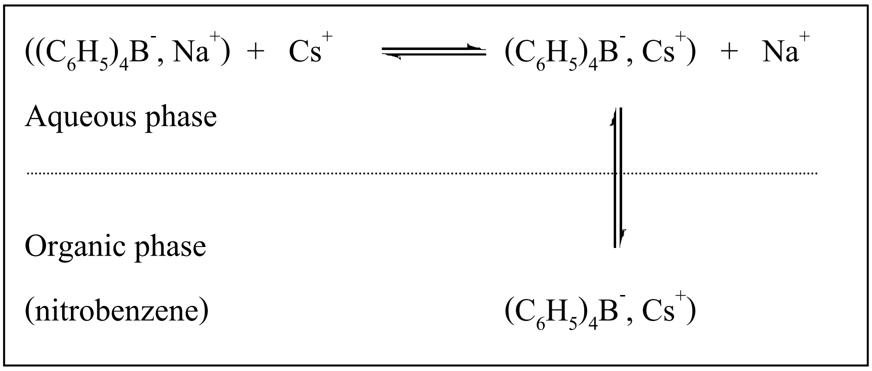
Example of a bulky cation being used:



$$((C_6H_5)_4As^+, Cl^-) + ReO_4^- \rightleftharpoons (C_6H_5)_4As^+, ReO_4^-) + Cl^-$$

$$(C_6H_5)_4As^+, ReO_4^-)$$

Example of a bulky anion being similarly used:

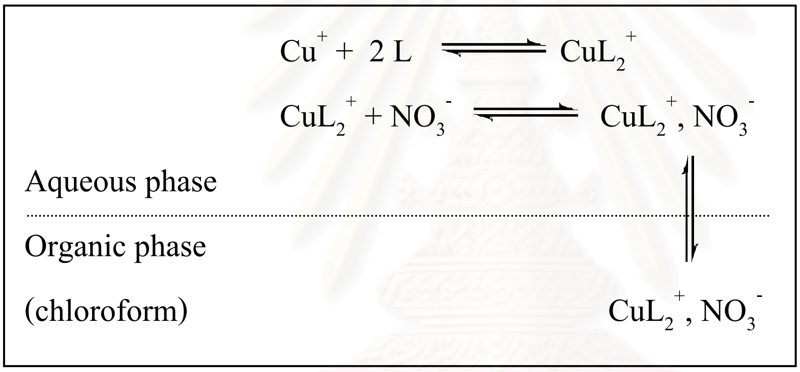


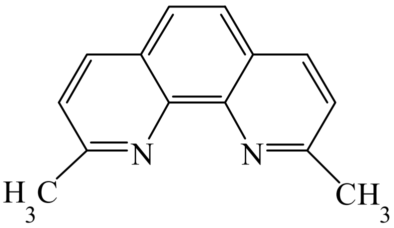
$$((C_6H_5)_4B^-, Na^+) + Cs^+ \rightleftharpoons (C_6H_5)_4B^-, Cs^+) + Na^+$$

$$(C_6H_5)_4B^-, Cs^+)$$

2.2.4.1.2 Chelation and Ion Association

The polyvalent cation can be extracted by incorporation with chelate reagents that having uncharged coordinating atoms such as 1,10-phenanthroline and neocuproine or associates with another great size ion which forms cationic complex chelating with metal ions such as iron (II), iron (III), cobalt (II) and copper (II). The metal cation is transformed into large positively charged chelate complex and associates with a nitrate or perchlorate anion to form an extractable compound into organic solvent.





L = Neocuproine

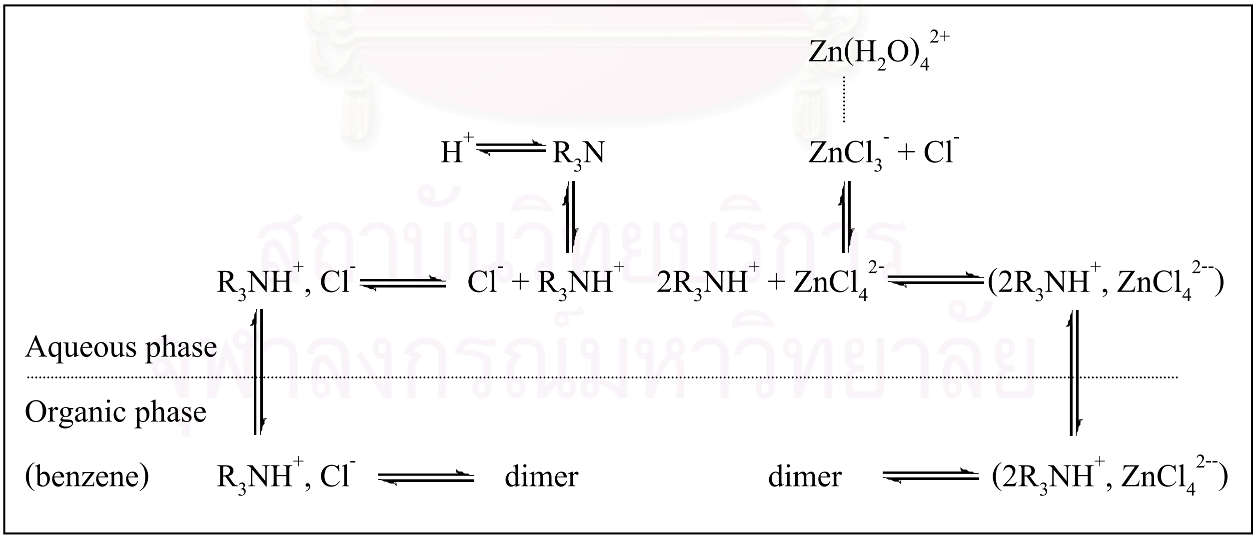
2.2.4.1.3 Liquid Ion Exchange

Liquid ion exchangers are solutions of ionogenic groups which are attached to a high molecular weigh (250-500) organic molecule dissolved in a water immiscible organic solvent. The partitioning of an ionic carrier between water and an organic phase is desirable. Since most of the water immiscible organic solvents have a low dielectric constant, the charged solute should contain organic residues of sufficient size to constrain the molecule completely to the organic medium. The properties of liquid ion exchanger in extraction are similar to weak base and weak acid ion exchange resins. Typical ion exchangers with a high solubility in the organic phase are generally amines or alkyl phosphoric acids.

The acidic liquid phosphate ester such as butyl dihydrogen phosphate ($C_4H_9OPO_3H_2$), dibutyl hydrogen phosphate ($(C_4H_9)_2OPO_2H$) and di(2-ethylhexyl) phosphate are water immiscible or can be dissolved in inert diluents immiscible in water. For cation extraction, the phosphate esters can exchange protons with the cation in aqueous phase, chelating and solvating the cations. These systems are known as liquid cation exchange.

In the same way, the protonated of tri(2-ethylhexy)amine, methyldioctylamine and tribenzylamine are large cations that can form extractable ion pairs with various anions. Under acidic condition, the amine is converted to its stable positive species that is practically dissociated in the amine diluent solution. The anion attached to the ammonium cation may be exchanged for other anion species. These systems are known as liquid anion exchange.

As an illustration of the complex metal acid removal, the extraction of zinc as $ZnCl_4^{2-}$ from a HCl solution using a benzene solution of tribenzylamine R_3N is consided below.



“Onium” Systems Solvent molecules may participate in ionic reaction as in onium-salt formation. The highly oxidation metal ions are extracted from acidic media into oxygen containing organic solvent (oxonium extraction system) such as isobutyl methyl ketone, butyl acetate, amyl alcohol and ethyl ether. Metal ions are converted to anionic complex by the reaction with the anion of acid and the cation must be stabilized by hydrogen bonding to the solvent. Protons from the acid are then solvated by the solvent to form the oxonium ion. The species of metal anion complex that forms ion-pair with the oxonium ion is extractable. The excellent example of an onium extraction system is the extraction of Fe(III) from HCl solution into ketone.

2.2.4.2 Chelating System

The chelating system is the most widely applied metal ion extraction. The formation of metal ion and chelating molecule (an organic chelating agent) is a neutral chelate complex. Metal chelates represent a type of coordination compound in which a metal ion combines with a polyfunctional base chelating molecule. The chelating molecules occupy two or more positions of the coordination sphere of the metal ion, so that no water is coordinated. The neutral complex should be free of polar group not involved in coordination, so they are often insoluble in water but usually soluble in organic solvents such as chloroform, carbon tetrachloride and dichloromethane.

2.2.4.2.1 Chelating Agent

The functional groups of the organic base must be situated in the molecule so that they permit the formation of a stable ring, normally found are nitrogen, sulfur and oxygen in the molecule. Chelating agents possessing acidic groups function as base by ionization in water and the ionizable protons are replaced by the metal ion when the chelate is formed and the charge on the organic compound neutralizes the charge on the metal ion, anionic form of molecule is the actually reacting species. A number of typical basic groups are tabulated in Table 2.2.

Table 2.2 Representative basic groups

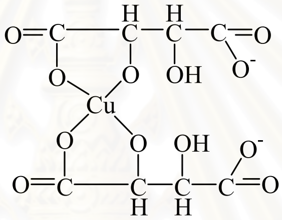
Uncharged	Anionic
Aliphatic amines	Carboxylate
$C_2H_5NH_2$	Acetate
$(C_2H_5)_2NH$	Salicylate
$(C_2H_5)_3N$	Oxalate
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$	Phenolates
Aromatic amines	Phenolate
Aniline	Enolate
p-Nitroaniline	Acetylacetonate
p-Toluidine	Mercaptide
Heterocyclic amines	Thiophenolate
Pyridine	Oximate
Quinoline	Dimethylglyoximate
Piperidine	
o-Phenantholine	
Miscellaneous	
Carbonyl group	
Ether oxygen	
Hydroxyl group	
Nitroso group	

Chelating agent can be conveniently classified according to the charge type of the basic groups present. When both basic groups of the reagent are uncharged or one group is anionic, the positively charged metal chelates and the neutral chalates are formed, respectively. The presence of multiple negative charges on the chelating agent may result in the negatively charged chelates. Some of the important types of chelating agents are summarized as follows,

1. Bidentate reagent

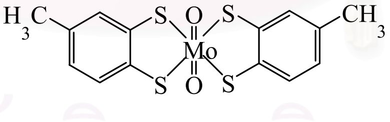
    1.1 Two anionic basic groups

    a. Hydroxycarboxylic acids, e.g. tartaric and citric acid



Copper tartrate

b. Dimercapto compounds, e.g. toluenedithiol and 1,2-dimercaptoethane (BAL)

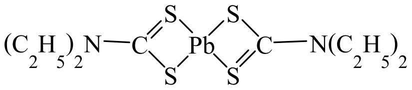


Molybbenum- toluenedithiol complex

1.2 One anionic and one uncharged basic groups

1.2.1 Four-membered ring formers

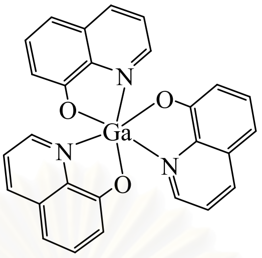
a. Dithiocarboxylic acids, e.g. xanthates and dithiocarbamates



Lead dithiocarbamate

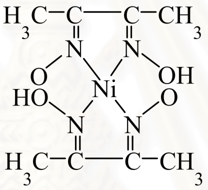
1.2.2 Five-membered ring formers

a. Compounds having the reactive grouping N-C-C-O$^-$, e.g. α -amino acids, 8-quinolinol, α- benzoinoxime



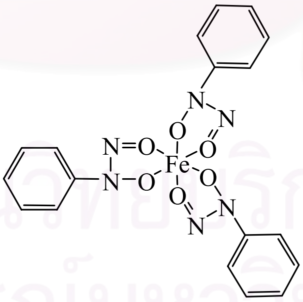
Gallium 8-quinolinate

b. Compounds having the reactive grouping N=C-C=N$^-$, e.g. dimethylglyoxime



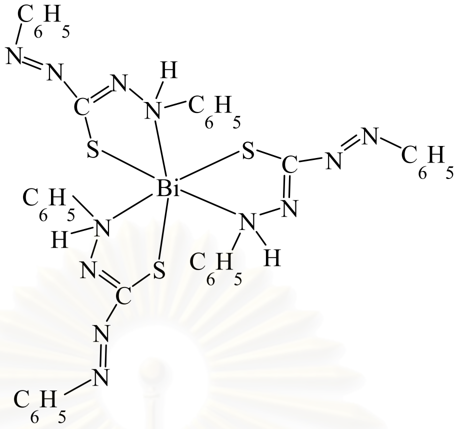
Nickel dimethylglyoximate

c. Compounds having the reactive grouping O=N-N-O$^-$, e.g. cupferron



Iron (III) cupferrate

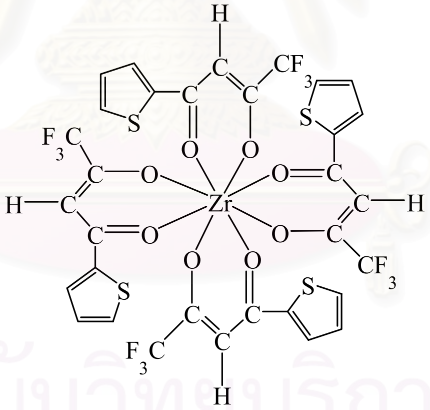
d. Compounds having the reactive grouping N-N=C-S$^-$, e.g. dithizone, dithiooxmide



Bismuth dithizonate

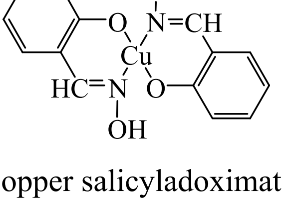
1.2.3 Six-membered ring formers

a. Compounds having the reactive grouping O=C-C=C-O$^-$, e.g. β-diketones, salicyladehyde, hydroxyanthraquinone



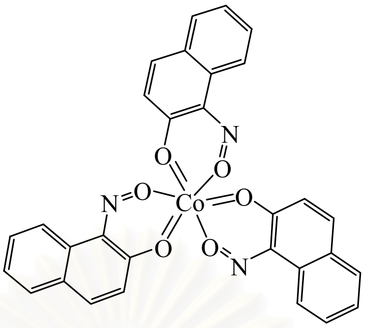
Zirconium thenoyltrifluoroacetonate

b. Compounds having the reactive grouping N=C-C=C-O$^-$, e.g. salicyladoxime



Copper salicyladoximate

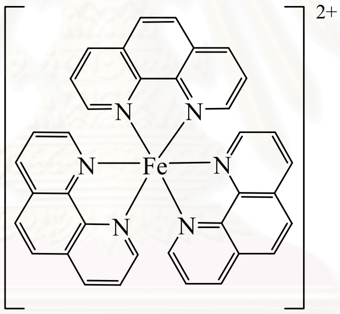
c. Compounds having the reactive grouping O=N-C=C-O$^-$, e.g. 1-mitroso-2-naphtol



Cobalt (III) complex

1.3 Two uncharged basic groups

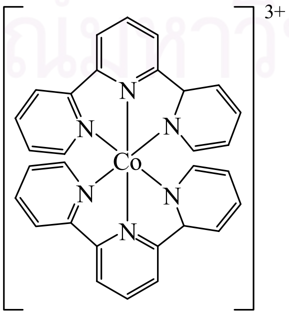
a. Compounds having the reactive grouping N-C-C-N, e.g. ethylenediamine, dipyridyl,phenanthroline



Tris-(phenanthroline)-iron (II)

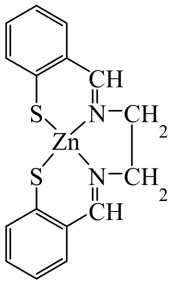
2. Polydentate reagent

2.1 Tridentate, e.g. terpyridyl



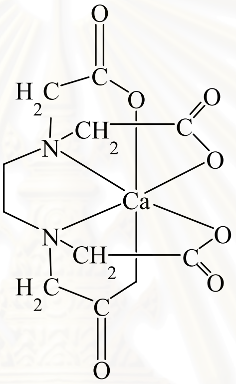
Bis(terpyridyl)-cobalt (III)

2.2 Tetradentate, e.g. thiosalicylideneethylenediimine



Thiosalicylideneethylenediimine-zinc

2.3 Hexadentate, e.g. ethylenediamintetraacetic acid (EDTA)



Calcium-EDTA complex

Normally, in complexation between metal ion and chelating agent, the functional group of chelating agent acts as an electron pair donor (Lewis base) which is capable of bonding to an electron pair acceptor, metal ion (Lewis acid). According to the hard soft acid base (HSAB) principle the hard (Lewis) acids prefer to bind hard (Lewis) bases and the soft (Lewis) acids prefer to bind soft (Lewis) bases. The classified Lewis acids - bases are tabulated in Table 2.3 and Table 2.4.

Table 2.3 Classification of Lewis acids [12]

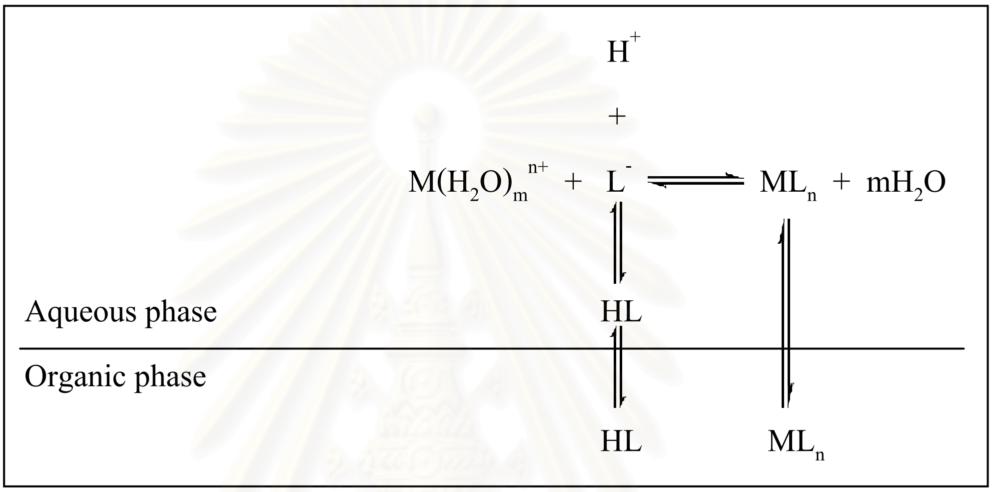
Hard Acids	**Borderline Acids**	**Soft Acids**
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},	Cu^+, Pd^{2+}, Ag^+, Cd^{2+} Pt^{2+}, Pt^{4+},
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	Zn^{2+}, Ru^{2+}, Rh^{3+}, Os^{2+},	Au^+
Sc^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+},	Ir^{3+}	Hg^+, Hg_2^{2+}, CH_3Hg^+
Mo^{3+}, In^{3+}, Ce^{3+}	Sn^{2+}, Pb^{2+}, Bi^{3+}	Tl^+, Tl^{3+}
Al^{3+}, AlH_3, $AlCl_3$, $Al(CH_3)_3$		Br_2, Br^+, I_2, I^+
BF_3, BCl_3, BOR	$B(CH_3)_3$, SO_2, CR_3^+,	BH_3, $R\text{-}O^+$, $R\text{-}Se^+$,
NO_2^+, SO_3, CO_2	$C_6H_5^+$	
Ions with oxidation states of 4 or higher e.g. Sn^{4+}, Ti^{4+}, Zr^{4+}		Metals with zero oxidation state π acceptors e.g. trinitrobenzene

Table 2.4 Classification of Lewis bases [12]

Hard Bases	**Borderline Bases**	**Soft Bases**
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		CN^-, SCN^-, R-NC, CO
ClO_4^-, NO_3^-	N_3^-, NO_2^-	H^-, R^-
CO_3^{2-}, PO_4^{3-}, SO_4^{2-}	SO_3^{2-}	$S_2O_3^{2-}$
ROH, R_2O, RO^-, CH_3COO^-		H_2S, HS^-, S^{2-}, R_2S, R-SH, $R\text{-}S^-$
RNH_2, $H_2N\text{-}NH_2$	$C_6H_5NH_2$, C_5H_5N, N_2	C_2H_4, C_6H_6, R_3P, $(RO)_3P$

2.2.4.2.2 Extraction Equilibrium

The usual chelating system practice is addition of the chelating agent to the organic phase. The extraction process in a metal chelate extraction system involves four steps, each with an equilibrium constant in the following manners:



First, the chelating agent HL, usually a weak, polyfunctional organic acid, distributes between the aqueous and the organic phases:

$$(HL)_{\mathbf{org}} \rightleftharpoons (HL)_{aq}\,; \qquad K_{D_{HL}} = \frac{[HL]_{org}}{[HL]_{aq}}$$

Second, the reagent in the aqueous phase ionizes:

$$HL \rightleftharpoons H^+ + L^-,\ K_a = \frac{[H^+][L^-]}{[HL]}$$

Third, the metal ion chelates with the free chelating agent in the aqueous to form an extractable chelate, ML_n:

$$M^{n+} + nL \rightleftharpoons ML_n \; ; \; K_f = \frac{[ML_n]}{[M^{n+}][L]^n}$$

Finally, the chelate distributes between the organic and aqueous phases:

$$(ML_n)_{aq} \rightleftharpoons (ML_n)_{org} \; ; \; K_{D_{ML}} = \frac{[ML_n]_{org}}{[ML_n]_{aq}}$$

$K_{D_{HL}}$ and $K_{D_{ML}}$ are the distribution coefficients of the reagent and the chelate, respectively; K_a is the ionization constant of the chelating agent; and K_f is the formation constant of the chelate complex.

Assuming that the chelated portion of the metal distributes largely into the organic phase, the metal ion does not hydrolyze in the aqueous phase, and the chelate is essentially undissociated in the nonpolar organic solvent, the distribution ratio is given by

$$D \approx \frac{[ML_n]_{org}}{[M^{n+}]_{aq}}$$

All of four equilibrium constants are included and the following equation can be derived:

$$D = \frac{K_{D_{ML_n}} K_f K_a^n}{K_{D_{HL}}^n} \frac{[HL]_{org}^n}{[H^+]_{aq}^n} = K^* \frac{[HL]_{org}^n}{[H^+]_{aq}^n}$$

where K^* is the extraction constant according to the equilibrium:

$$\left(M^{n+}\right)_{aq} + n(HL)_{org} \rightleftharpoons \left(ML_n\right)_{org} + n\left(H^+\right)_{aq}$$

$$K_{ex} = \frac{\left[ML_n\right]_{org}\left[H^+\right]_{aq}^{n}}{\left[M^{n+}\right]_{aq}\left[HL\right]_{org}^{n}}$$

Thus, this equation can be obtained:

$$\log D = \log K^{*} + n\log[HL]_{org} + n\,pH$$

In general, the extraction of a simple metal chelate can be described by a plot of log D and pH at constant reagent concentration $[HL]_{org}$ in the organic phase. The slope n is equal to the number of hydrogen ions released per metal ion in the overall extraction reaction. This method is called slope analysis method.

The extraction systems are highly pH dependent because of the release of H^+ on complex formation, therefore extraction is suppressed at low pH. However, extraction is also often suppressed at high pH. This is because the anionic form of the chelating agent has to compete with hydroxide ions that will preferentially react with the metal ion to form non-extractable hydroxide complex.

2.2.5 Job's Method for Determination of Stoichiometry [13]

Job's method is the continuous variation method that is simple and effective to identify the chemical stoichiometry of the predominant complex when the complex is formed by two reacting species, according to the equilibrium:

$$aM + bL \rightleftharpoons M_aL_b$$

The method is based on the preparation of a series of solutions which contain the fixing total mole number of reactant (a + b) whereas the mole fraction is systematically varied. The amount of product was measured and plot versus the mole fraction of M or L. The mole fraction of M and L is calculated from the equation 2.1, a and b being mole number of M and L, respectively.

$$\text{Mole fraction of M, } X_M = \frac{a}{a+b} \qquad 2.1$$

$$\text{Mole fraction of L, } X_L = \frac{b}{b+a} \qquad 2.2$$

The mole fraction of L where the maximum amount of product is found leads to stoichiometry of the predominant product as depicted in Figure 2.1.

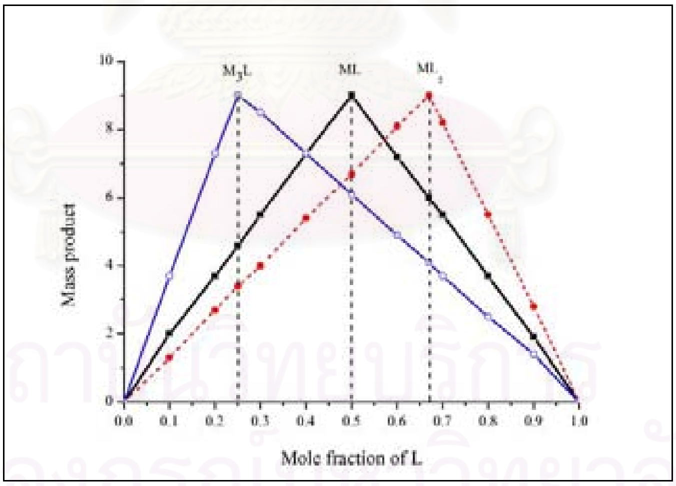


Figure 2.1 Ideal behaviors of Job's plots for formation of the complexes M_3L, ML and ML_2.

2.3 2-Aminothiophenol Ligand

2-Aminothiophenol (alternative names are 2-Aminobenzenethiol, 2-Mercaptoaniline, 2-Aminophenyl Mercaptan) is a bidentate ligand that consists of nitrogen-sulfur as active sites (donor atoms) which are effective for coordination of metal ions. The structure of this ligand is shown in Figure 1.2.

Although the nature of 2-aminothiophenol are toxic and air-sensitive but the abilities of the good color-forming reagent and the dual acting as monoanionic and dianionic by deprotonation of thio- and the amino- group make this ligand attractive for metal complexation [14-19]. 2-Aminothiophenol is able to react with several different metal ions. Several researches showed successful syntheses of the 2-aminothiophenol complexes of metal ions such as Cu^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, Ag^{+}, Mo^{6+} and Hg^{2+}. Moreover, the color changing and solubility of chelating complexes were also investigated. For example, the complexation of 2-aminothiophenol and Mo^{6+} in chloroform formed a green complex with a maximum absorbance at 700 nm and is stable for 2 hours [17]. Furthermore, since this ligand forms complex with many metal ions with different solubility in various solvents, its complexes can be easily separated for further study.

Moreover, 2-aminothiophenol can form complex by ligand-to-metal electron transfer (π-bonding change) of the sulfur and nitrogen bound complex [14-23]. This electron transfer while coordinated to metal is due to the existence of four oxidation states from deprotonation process (N and S in deprotonated form (2-aminothiophenolate), Figure 2.2 [21]. 2-Aminothiophenol complexes of Cu^{2+}, Mo^{6+}, ReO_4^{-}, Co^{3+} and Ni^{2+} by charge transfer reaction have been observed [15, 21, 22].

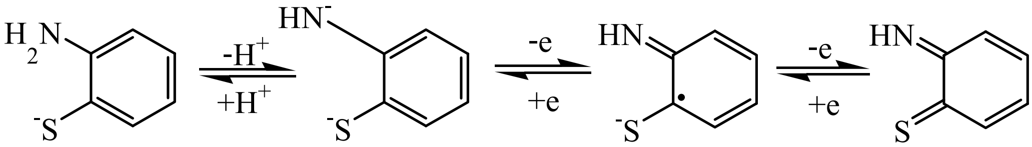


Figure 2.2 Redox activity of 2-aminothiophenolate.

According to the advantages of being good complexant, 2-aminothiophenol is also a good coloring agent, able to doubly deprotonate and form charge transfer complex and soluble in organic solvents. Thus, 2-aminothiophenol in ionic liquid is appropriate as a ligand for extracting metal ions with liquid-liquid extraction method.

2.4 Ionic Liquids

2.4.1 Background Information [24-26]

The observed "red oil" in a Friedel-Crafts reaction in the middle of the nineteenth century led to the discovery of an ionic liquid. The first room temperature ionic liquid, ethylammonium nitrate ($[C_2H_5NH_3]$ NO_3) was reported by Walden in 1914. The ionic liquid was synthesized by the reaction of ethylamine with concentrated nitric acid and had a melting point of 12 ^{0}C. In 1951, Hurley and Wier developed a low temperature molten salt, $AlCl_3$- based ionic liquid for electroplating aluminum by mixing and warming 1-ethylpyridinium chloride with aluminium chloride. During the 1970s and 1980s these ionic liquids were studied mainly for electrochemical applications. Hunssey et al. wrote the first review of room temperature ionic liquid based on $AlCl_3$. In the mid 1980s the ionic liquid started to be used as solvent for organic synthesis, the Friedel-Crafts alkylation was the first organic reaction that was carried out in an acidic tetrachloroaluminate ionic liquid. Because $AlCl_3$- based ionic liquids are very hygroscopic and air-sensitive so that they are difficult to handle, the air and moisture stable ionic liquids were considered to solve this problem. In 1992 the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cation with anions such as halides, tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$) and triflate ($[CF_3CO_2]^-$) were discovered by Wilkes and Zaworotko.

Compared to organic solvents, ionic liquids do not contain any molecule but they are made of ions. Ionic liquids consist of organic cation and large organic or inorganic anion. The common cations are bulky and asymmetric cations containing nitrogen or phosphorus atoms such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, N- methyl-N-alkylpyrrodinium and ammonium ion (Figure 2.3). Anions include inorganic anion, e.g. halides, tetrachloroaluminate, bis(trifluoromethylsulfony)limide, hexafluorophosphate, and tetrafluoroborate; and organic anions, e.g. alkylsulfate, alkylsulfonate, p-toluenesulfonate (tosylate) and trifluoroacetate (Figure 2.4). The structure and short name of the most widely used ionic liquids are depicted in Table 2.5.

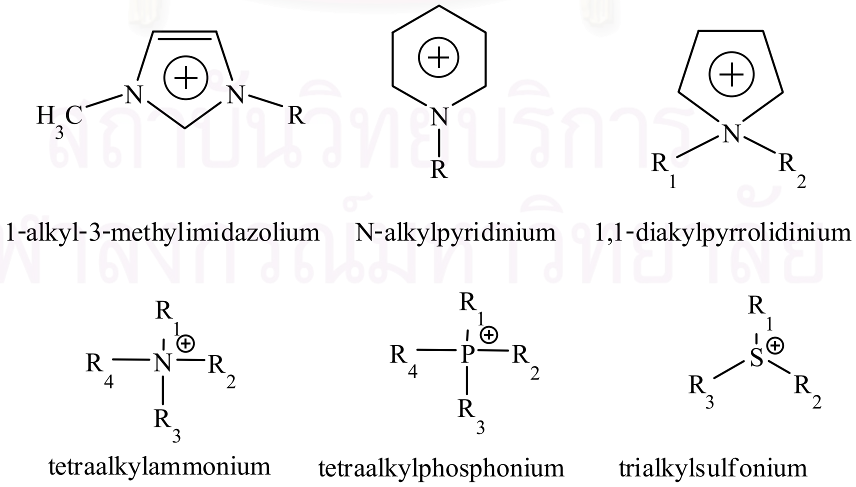


Figure 2.3 Commonly used cations in ionic liquids.

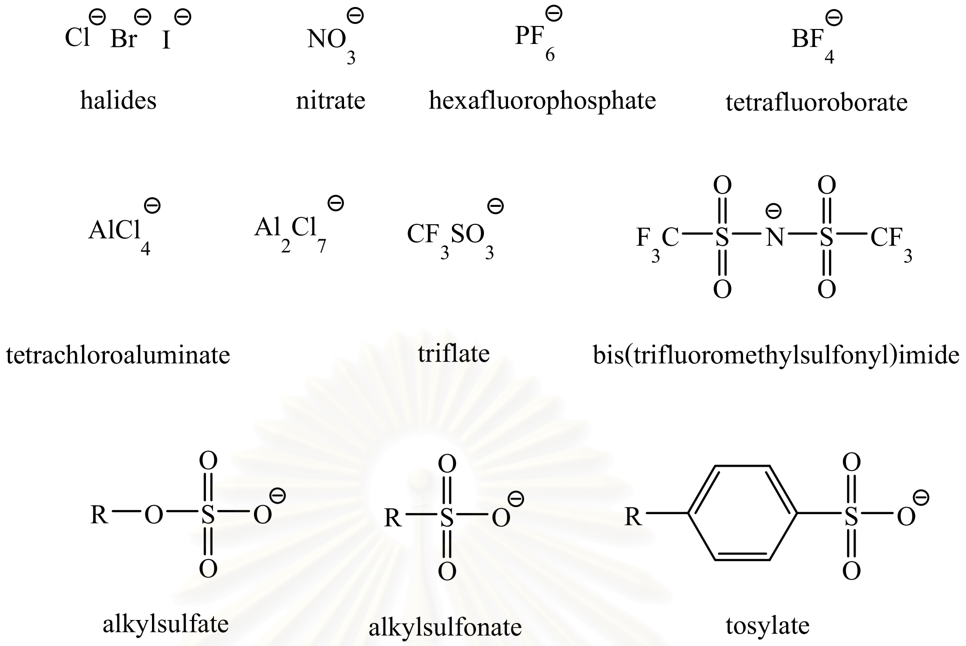


Figure 2.4 Commonly used anions in ionic liquids.

Table 2.5 Structures and short names of most widely used ionic liquids [26]

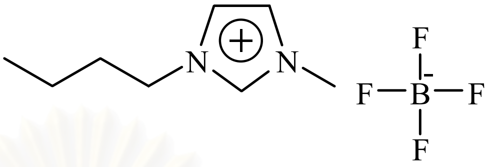
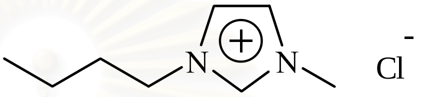
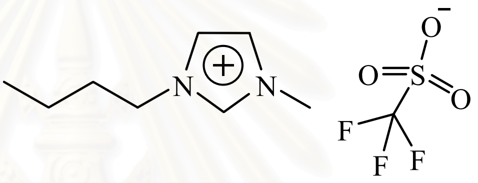
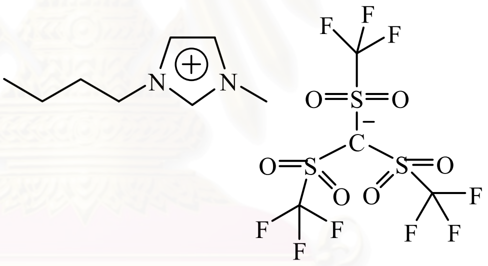
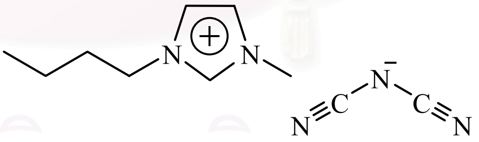
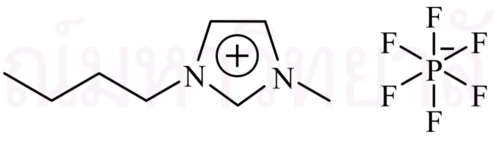
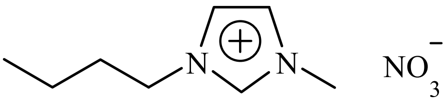
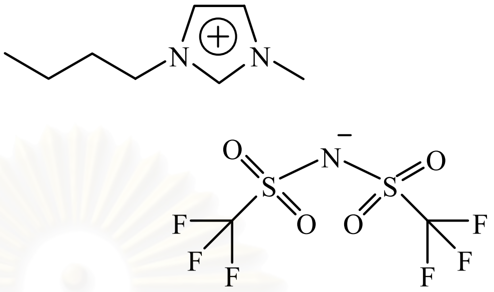
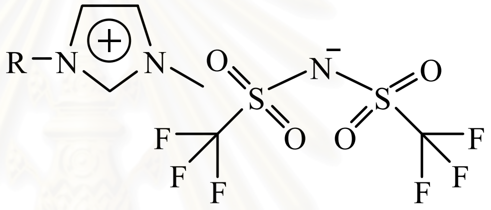
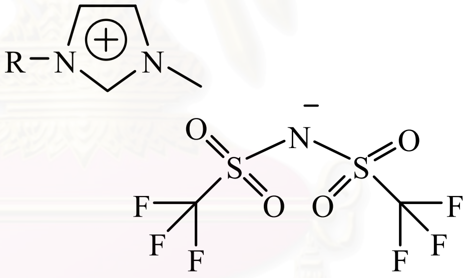
Ionic liquid	Structure	Short name
1-butyl-3-methylimidazolium tetrafluoroborate		[BMIM]BF_4
1-butyl-3-methylimidazolium chloride		[BMIM]Cl
1-butyl-3-methylimidazolium trifluoromethansulfonate (triflate)		[BMIM]TfO
1-butyl-3-methylimidazolium methide		[BMIM] methide
1-butyl-3-methylimidazolium dicyanamide		[BMIM]DCA
1-butyl-3-methylimidazolium hexafluorophosphate		[BMIM]PF_6
1-butyl-3-methylimidazolium nitrate		[BMIM]NO_3

Table 2.5 Structures and short names of most widely used ionic liquids (cont.)

Ionic liquid	Structure	Short name
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide		[BMIM]Tf_2N
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, R= C_6H_{17}		[HMIM]Tf_2N
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, R= C_6H_{17}		[OMIM]Tf_2N

2.4.2 Properties of Ionic Liquids [25-32]

The ionic liquids are generally defined as salts which have a melting point lower than 100 ^{0}C. Because the unique feature of ionic liquids are that they can be tuned their chemical and physical properties by selecting cation and anion composition, they are often denoted as “designed solvent”. Seddon has estimated that over 10^{18} ionic liquids could be prepared from varying ion combination.

2.4.2.1 Melting Point

The low melting point is the important reason of ionic liquids to be a preferable medium in organic reactions and other chemical processes. Both cations and anions can affect the melting point of ionic liquids. The charge distribution on the ion, hydrogen bonding ability, the symmetry of the ions and van der Waals interaction are the main factors that influent the melting point. The large and asymmetric cations result in a decrease of the melting point whereas branching of alkyl groups results in an increase of melting point in comparison to the linear analogs. The increasing in anion size of the same charge leads to a decrease of the melting point. For example, the melting point of 1-ethyl-3-methtlimidazolium salt ionic liquid decreases from 55 ^{0}C to 38 ^{0}C when anion changes from NO_2^- to NO_3^-.

2.4.2.2 Water Solubility

The miscibility of ionic liquid with water varies with changing of cation and anion structure of ionic liquid. The influences of cation structure on the miscibility are the similarity of the polarity between ionic liquid and water and the free space between molecules caused by large side chains. The longer chain of cation, thus less polarity and hydrophobic, the lesser miscibility in water or polar solvent. On the other hand, the anion in ionic liquid usually shows an influence on the miscibility property. Normally, ionic liquid consisted of anion such as all halides, ethanolate, nitrate, trifluoroacetate and chloroaluminate-based ionic liquid are fully water-soluble while those containing anion hexafluorophosphate, bis(trifluoromethylsulfonyl)imide and tetraalkylborate form biphasic mixture with water. However, for the ionic liquid based on tetrafluoroborate and trifluoromethanesulfinate, the water solubility mostly depends on the properties of the cation.

2.4.2.3 Stability

The thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon or heteroatom-hydrogen bonds and the stability of the ion species formed. In general, ionic liquids have a high thermal stability up to 400 ^{0}C with minimal vapor pressure below their decomposition temperature. Thermogravimetric analysis (TGA) and differential thermal analysis are used to determine the degradation temperature of ionic liquids. In terms of thermal degradation, the phosphonium cation is more stable than imidazolium cation and ammonium cation. Anions have stronger effect on the temperature degradation. Ionic liquids containing weakly coordinating anions possess high thermal stability. The presence of impurities especially water and halide will affect physical properties such as density, viscosity, melting point and degradation temperature. Halide anions dramatically reduce the thermal stability of ionic liquid with the decomposition occurring at least at 100 ^{0}C.

2.4.2.4 Polarity

The high polarity is one of special properties for ionic liquids. The polarity and polarizability are the critical indexes of solvent strength. Solvatochromic dyes such as Reichardt’s dyes and Nile Red have been widely used to determine the solvent strength of ionic liquids based on the shift of the charge-transfer absorption band of a solvatochromic probe. Fluorescent probe is commonly used to determine the solvent strength of organic solvents and have been recently used for ionic liquids. Normally, the polarity of imidazolium-based ionic liquids is close to the low molecular weight alcohols and formamide. The decrease in length of alkyl-substituting on imidazolium cation and anion size leads to an increase in polarity.

2.4.3 Preparation of Ionic Liquid [25, 26, 33, 34]

Ionic liquids can be synthesized from amines, phosphenes, or sulfonates. There are three basic methods to synthesize ionic liquid, e.g. quaternization reaction, anion metathesis and Lewis acid-base neutralization as shown in Figure 2.5.

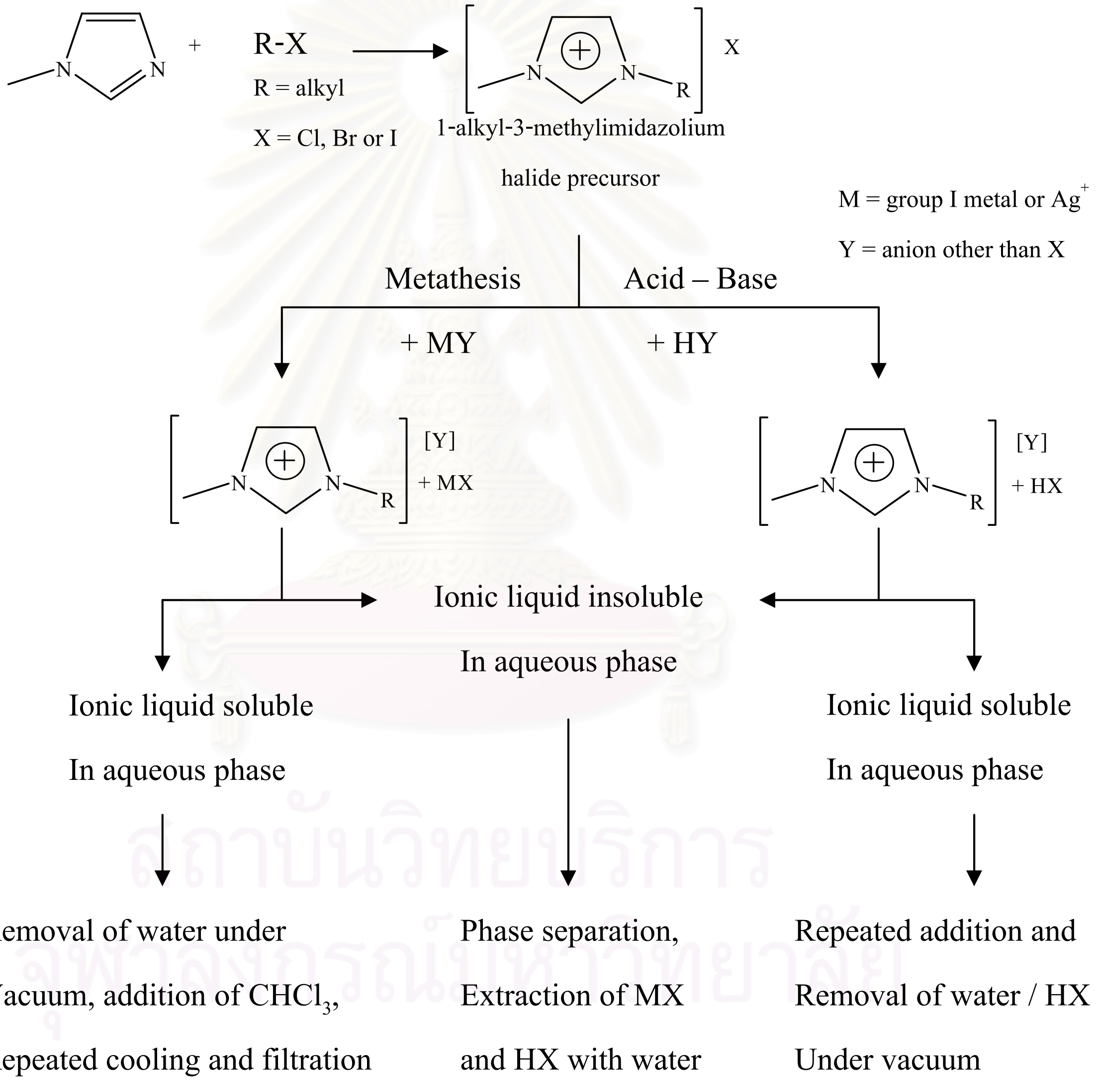


Figure 2.5 Synthetic pathways for preparation of ionic liquids.

Most ionic liquids are synthesized using a two step process. Generally, the first step is the quaternization reaction of nitrogen-containing hetrerocycles, where an amine is alkylated with an alkylation reagent, alkyl halide or alkyl sulfate being widely used, resulting in the corresponding ionic liquid. The nucleophilic substitution reaction involves the mixing of amine and desired alkyl halide and then reflux for 2-3 days in an inert atmosphere. The reaction temperature and reaction time affect the reactivity of the alkyl halide in a way that increasing of the alkyl chain length reduces the reactivity. In this step, the synthetic ionic liquids are called alkylated halide precursor.

Ionic liquids based on halides are easily converted into desired ionic liquids by anion exchange upon Lewis acid-base neutralization or anion metathesis reaction. Lewis acid-base ionic liquids are prepared by mixing appropriate amounts of a precursor and a Lewis acid MX_y without solvent. $AlCl_3$ is the mostly used Lewis acid in the preparation of ionic liquid but other Lewis acids such as $EtAlCl_2$, BCl_3, $CuCl_2$, $SnCl_2$, $GeCl_2$ and $InCl_3$ can also be used. To prevent the heat of reaction, which decomposes and discolors the ionic liquid, the reaction is cooled down with an ice bath and slowly added a Lewis acid. However, using Lewis acid has a drawback in the way that the anion generated from Lewis acid can be water-sensitive, making the obtained ionic liquid also water-sensitive. To synthesize air- and water- stable ionic liquid, lithium, sodium and potassium salts have been used in anion metathesis reaction. The reaction can be performed in the organic solvent such as dichloromethane or acetone. In addition to metal salts, Bronsted acids have also been used in metathesis reactions. Like Lewis acid-base neutralization, the reaction is exothermic, therefore the reaction vessel has to be cooled with an ice bath.

Being conventional reaction, quaternization preparation is time consuming and usually requires a large molar excess of alkyl halide to achieve good yield thus the clean and efficient technology are focused. Microwave assisted preparation of ionic liquid has gained interests especially in the industrial scale reaction. The solvent-free condition and the shorten reaction time are the advantages of microwave assistance over the conventional preparation. Imidazolium, pyrazolium and thiazolium ionic liquids can be prepared in a domestic microwave oven but the reactions are not reproducible and the products lack a scientific value. Luckily, the microwave reactor are recently developed to enable better reaction control and more accurate results are gained [35-37].

Another method to prepare ionic liquids is the ultrasound-assisted method that increases yields, reduces the reaction time and improves the quality of the products resulting from solvent-free reaction [38].

2.4.4 Characterization of Ionic Liquid [3, 39]

The purity of an ionic liquid is very important since the impurities have a strong influence on their chemical and physical properties and stability. Ionic liquid should be carefully characterized with several methods such as nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), Fourier-transform infrared spectrometry (FTIR), elemental analysis (EA) and single crystal X-ray diffractometry (XRD) to confirm its structure. Thermogravimetric analysis (TGA) is used to determine the thermal stability in order to know its upper temperature limit whereas differential scanning calorimetry (DSC) is used to measure the melting point.

2.4.4.1 Nuclear Magnetic Resonance Spectroscopy [40, 41]

The nuclei information of nuclear magnetic resonance spectroscopy is the importance application to determine the molecular structures in a wide varied of chemical systems. This technique provides reproducible results and high sensitivity to small variations in chemical structures. NMR spectroscopy has a high potential for investigating the liquid phase structure of ionic liquids. Moreover it can be applied to investigate the ion-pair formation, proton conductance and the structural consequences of halide and water trace.

2.4.4.2 Infrared Spectroscopy [39, 42-44]

Infrared spectrometry is one of the most commonly used in spectroscopic techniques for routine identity and purity examination in both organic and inorganic analytes. The infrared spectrometry is based on the molecular infrared absorption of radiation frequency to excite from one vibrational or rotational level to another. The vibrational frequencies depend on the shape of molecules, the mass of the atoms and the associated vibronic coupling in chemical bond which provide the specific frequency. Due to the fact that the absorbance frequencies of IR radiation for each functional group has its individual characteristic thus the sample molecular structure and chemical nature can be interpreted by the presence of chemical function groups in the matrix of IR spectra.

The characteristic frequencies of functional groups in organic molecules can be summarized in Figure 2.6.

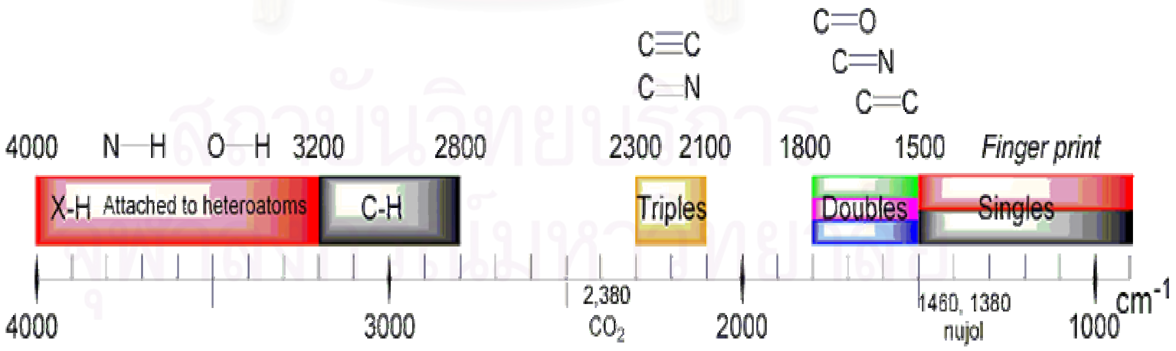


Figure 2.6 Summary of bond absorptions in organic molecules [45].

Infrared spectroscopy is the most powerful method to probe the molecular state of water present in ionic liquids. The stretching modes of water have been used to indicate the type of bonding between water molecules in the liquid, solid and vapor phases, as well as interactions between water and many chemical substances whereas the vibrational modes of water that result in bands in the IR spectrum are very sensitive to the environment and intermolecular interactions.

2.4.4.3 Mass Spectrometry [46, 47]

Mass spectrometry is a useful analytical tool for measuring quantitation of atoms or molecules and for determining chemical and structural information about molecules. The neutral species are ionized and the mass of those ions are determined based on the mass to charge ratio. Molecules have distinctive fragmentation patterns that provide structural information to identify structural components. Mass spectrometer may be used to determine the isotopic distribution of an element, the elemental and molecular composition of a sample, or the structure of a compound or its molecular mass. This method is highly specific, sensitive and reliable and has a very low detection limit.

Anion and cation of ionic liquids can be analyzed by electrospray ionization mass spectrometry with both positive and negative modes. Electrospray ionization (ESI) is the atmospheric pressure ionisation (API) technique and is well suited to the analysis of polar molecules. Likewise, laser desorption/ionization (LDI), matrix-assisted laser desorption/ionization (MALDI) and fast atomic bombardment (FAB) mass spectrometry are methods which allow the investigation and characterization of the structure of ionic liquids.

2.4.4.4 UV-Visible Spectroscopy [48, 49]

UV-Visible spectrometry is a powerful method to probe the electronic structures of materials, which provides information about the molecular structure and functional groups present. All of the imidazolium-based ionic liquids have the significant absorption in the entire UV region and a long tail that extends to the visible region. The absorption characteristics are attributed to the imidazolium moiety and its various associate structures.

2.4.5 Ionic liquids as Solvents for Metal Extraction

A hydrophobic and high ionic character is a distinct property of ionic liquids. Their property is useful as a unique separation media for ionic liquid/aqueous solvent extraction. Robins Rogers and collaborators [50] were the first to propose utilization of ionic liquid for liquid-liquid extraction processing as reported in the study of substituted-benzene derivatives partitioning between water and [BMIM]PF_6. The research was reported that ionic liquid might be suitable for replacement of organic solvent. Subsequently, utilization of dye thymol blue indicator in the reversible pH-dependent liquid-liquid partitioning of ionic liquid containing system was investigated [51].

Differences in solvent behavior of ionic liquids and conventional organic solvents, especially hydrophobic ionic liquids, have been manifested. Large distribution coefficients for the extraction of metal ions from aqueous solution to ionic liquid containing complexing extractants have been observed.

Dai et al. [52] firstly reported a very highly efficient procedure for extraction of a fission product, $Sr(NO_3)_2$, from aqueous phase into disubstituted imidazolium-based hexafluorophosphates and bis(trifluoromethyl)sulfonylamides ionic liquids by using crown ether, dicyclohexano-18-crown-6 (DC18C6), as extractant.

Visser et al. studied the extraction of alkaline and alkaline earth metal ions e.g., Na^+, Cs^+ and Sr^{2+} from aqueous solution using crown ethers such as 18-crown-6 (18C6), 4,4'-(5')-di-(tertbutylcyclohexano)-18-crown-6 (Dtb18C6) and dicyclohexano-18-crown-6 (DCH18C6) in room temperature ionic liquid 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM]PF_6$, n=4, 6, 8) [53]. The extraction of heavy metals; Cd^{2+}, Co^{2+}, Ni^{2+} and Fe^{2+}; to $[C_nMIM]PF_6$ (n=4, 6) using both organic and inorganic anion extractant was studied [54].

Subsequently, Visser et al. designed and synthesized several ionic liquids in the concept of task specific ionic liquid (TSIL) to coordinate cadmium and mercury and extract them from contaminated waste. These novel classes of task-specific ionic liquid cations were produced by substitution of alkyl group into the imidazolium parent compound with different functional groups (urea, thiourea, and thioether). Synthesized TSIL cations were combined with PF_6^- anion and used alone or in a mixture with $[BMIM]PF_6$. The result showed that using cation containing thiourea and urea yielded the highest distribution ratio for the two metals (Cd^{2+} and Hg^{2+}) [55].

Chun et al. [56] investigated the influence structure of $[C_nMIM]PF_6$ (n=4-9)] on the selectivity and the efficiency of competitive alkali metal chloride extraction using a crown ether, dicyclohexano-18-crown-6 (DC18C6), as an extractant. The extraction efficiency generally diminished as the length of the 1-alkyl group increased.

Ionic liquid $[BMIM]PF_6$ in concerted with dithaizone as metal chelator successfully extracted heavy metals; Ag^+, Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}; in aqueous by forming neutral metal-dithaizone complex. It was found that the extraction efficiency of ionic liquid was higher than in chloroform at low pH. When the pH of extraction system was manipulated, heavy metals could be extracted, separated and preconcentrated with the biphasic system of $[BMIM]PF_6$ and aqueous as well as $[BMIM]PF_6$ could be recycled [57].

Recently studied, the ionic liquids ($[C_nMIM](CF_3SO_2)_2N$, n=2-8) containing eight kinds of monoaza-substituted crown ethers (n-alkyl aza-18-crown-6 series) were used as recyclable extractant for separating Sr^{2+} and Cs^+ from aqueous solution [58]. The pH-sensitive complexation capability of these ligands allowed for a facile stripping process, so both macrocyclic ligands and ionic liquids can be reused.

Moreover, the same authors also synthesized calixarene crown ether (Calix[4]arene-bis(tert-octylbenzo-crown-6), BOBCalixC6) as an extractant in hydrophobic ionic liquid to extract Cs^+ from aqueous solution and using sodium tetraphenylborate as a sacrificial cation exchanger to control the loss of imidazolium cation to aqueous phase by ion exchange [59].

Shimojo and Goto [60] found that a calix[4]arene-bearing pyridine (pyridinocalix[4]arene) which dissolved in 1-alkyl-3-methylimidazolium hexafluorophosphate showed a high extraction ability and selectivity for Ag^+ and it was easy to strip extracted Ag^+ from ionic liquid by controlling the pH of aqueous phase.

A novel study of metal extraction is the using of anionic chelating agent, 8-sulfonamidoquinoline, in ionic liquid $[BMIM]PF_6$ to extract several divalent metal cations. It was found that the extractability in $[BMIM]PF_6$ system was superior to that in chloroform system. Only Cd^{2+} was extracted as anionic complex accompanied with anion exchange process using the derivative having trifluoromethyl group [61].

Generally, for extraction of metal ions using ionic liquid, the side chain of cation and the structure of ionic liquid have effect on the extraction efficiency. The side chain of the cation influences the hydrophobic character of the ionic liquid and thus the partition coefficient of the metal ions is affected.

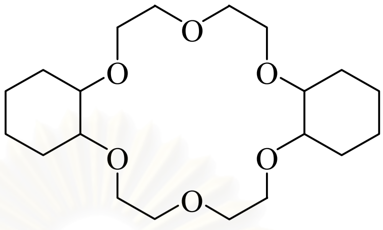
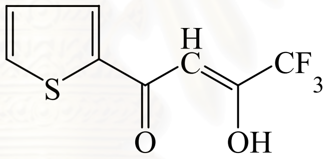
2.4.6 Mechanism of Metal Ion Transfer into Ionic Liquid [61-64]

Many researches studied the extraction mechanism of ionic liquid as a solvent extraction. The differences in solvent behavior of ionic liquids and conventional organic solvents, especially hydrophobic ionic liquids, have been manifested in enhanced distribution of metal extraction complex in biphasic systems. The presence of two charge species from the ionic solvent itself, in an ionic liquid/aqueous biphasic system, makes metal ion separation a much more complexed process than in traditional solvents.

The high distributions in ionic liquid/aqueous system are due to a change in extraction equilibria in comparison to the organic solvent. For example, Sr^{2+} is extracted as a strontium nitrato-crown ether complex in octanol [62] (Table 2.6 Eq.(1)) whereas in ionic liquid, the species $Sr(CE)(H_2O)_2^{2+}$ where CE is dicyclohexano-18-crown-6-ether is transferred into ionic liquid phase by substituting two axial bound nitrates with two water molecules bound to the metal ion [65]. The two imidazolium cations migrated to the aqueous phase to maintain the neutrality of the system (Table 2.6 Eq.(2)). Further study showed the same extraction mechanism as in octanol when using more liphophilic ionic liquid $[C_{10}MIM]Tf_2N$ (Table 2.6 Eq.(3)). However, the coordination environment of metal ion was different from that observed in octanol/aqueous biphasic system with nitrate ions lying outside of the metal ion’s inner coordination sphere.

Not only the nature of the ionic liquid but also the ligand types are important factors to determine the metal extraction pathway. For example, the extraction of La^{3+} using Htta in an ionic liquid/aqueous system showed the anion exchange mechanism (Table 2.6 Eq.(4)) in contrast to the cation exchange observed in molecular solvent (Table 2.6 Eqs.(5) and (6)). Here, changing of the lipophilicity of the ionic liquid did not change the partitioning mechanism [63].

Table 2.6 Extraction mechanisms in ionic liquid or organic/aqueous biphasic system

	 L= Dicyclohexyl-18-crown-6
(1)	$Sr^{2+}_{aq} + L_{org} + 2NO^{-}_{3\,aq} \rightleftharpoons \left[Sr(NO_3)_2\,L\right]_{org}$
(2)	$Sr^{2+}_{aq} + L_{IL} + 2\left[C_5mim\right]^{+}_{IL} + 2H_2O \rightleftharpoons \left[(SrL)(H_2O)_2\right]^{2+}_{IL} + 2\left[C_5mim\right]^{+}_{aq}$
(3)	$Sr^{2+}_{aq} + 2NO_{3\,aq} + L_{IL} \rightleftharpoons [SrL].(NO_3)_{2\,IL}$
	 L = Htta
(4)	$Ln^{3+}_{aq} + 4HL_{IL} + \left[C_4mim\right]\left[Tf_2N\right] \rightleftharpoons \left[C_4mim\right]^{+}\left[LnL_4\right]^{-}_{IL} + 4H^{+}_{aq} + \left[Tf_2N\right]^{-}_{aq}$
(5)	$Ln(H_2O)^{3+}_{n\ aq} + 3HL_{org} \rightleftharpoons \left[LnL_3(H_2O)_{n-6}\right] + 3H^{+}_{aq} + 6H_2O_{aq}$
(6)	$Ln(H_2O)^{3+}_{n\ aq} + 4HL_{org} \rightleftharpoons LnL_3.\,HL_{org} + 3H^{+}_{aq} + nH_2O_{aq}$

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Apparatus

3.1.1 Flame Atomic Absorption Spectrometer

A flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin-Elmer) was used for the determination of metal concentration. The instrument parameters are listed in Table 3.1.

Table 3.1 FAAS conditions for determination of metal concentration in solutions

Operating conditions	**Ni**	**Cu**	**Pb**
Wavelength (nm)	232.0	324.8	283.3
Slit width	0.20	0.70	0.70
Lamp type	HCL[a]	HCL[a]	HCL[a]
Lamp current (mA)	25	15	10
C_2H_2 flow-rate (min^{-1})	3	3	3
Air flow rate (min^{-1})	10	10	10

[a] Hallow Cathode Lamp

3.1.2 UV-Vis Spectrophotometer

A UV-Vis spectrophotometer model HP 8453 was used for the determination of ionic liquid (1-butyl-3-methylimidazolium hexaflurophosphate, [BMIM]PF_6) concentration.

3.1.3 Nuclear Magnetic Resonance Spectrometer

A nuclear magnetic resonance spectrometer (NMR) model Varian Mercury + 400 was used for the characterization of ionic liquid (1-butyl-3-methylimidazolium hexaflurophosphate, [BMIM]PF_6). NMR spectra were recorded in $CDCl_3$.

3.1.4 Fourier Transform Infrared Spectrometer

A fourier transform infrared spectrometer (FTIR) model Nicolet Impact 410 was used for the characterization of ionic liquid (1-butyl-3-methylimidazolium hexaflurophosphate, [BMIM]PF_6). Infrared spectra were recorded from 400 to 4000 cm^{-1} in transmittance mode by neat film in NaCl plate technique.

3.1.5 Mechanical Shaker

A Yamato Shaker model SA-31 was used to shake solutions for metal extraction.

3.1.6 pH Meter

A pH meter model pH 211 (Hanna instruments) was used for pH measurement.

3.1.7 Centrifuge

A centrifuge model SUNYO CENTAUR 2 was used for the separation of two phases (aqueous and ionic liquid).

3.1.8 Electron Spin Resonance Spectrometer

An electron spin resonance spectrometer of JEOL, model JES-RE2X was used for the determination of the species of Cu complex.

3.1.9 Ion Chromatograph

An ion chromatograph (IC) model Metrohm 813 was used for the determination of nitrate (NO_3^-) concentration in aqueous phase. The instrument parameters are listed in Table 3.2.

Table 3.2 IC conditions for determination of nitrate concentration in solutions

Operating Conditions	
Separating column	METROSEP A SUPP 4 (6.1006.430)
Column size	4 mm ID x 50 mm.
Suppressor	Metrohm Suppressor Module (50 mmol/L H_2SO_4)
Injection volume	20 µL
Eluent	1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$
Flowrate	1.0 mL/min
Temperarure	Ambient (ca. 25 °C)
Detector	Conductivity with Suppress CD

3.2 Chemicals

All Chemicals were ACS grade listed in Table 3.3.

Table 3.3 Chemical list

Chemicals	Supplier
2-Aminothiophenol	MERCK
1-butyl-3-methylimidazolium chloride	Fluka
1-butyl-3-methylimidazolium hexafluorophosphate	Fluka
Hexafluorophosphate acid 65%	Fluka
Chloroform	Fisher Science

Table 3.3 Chemical list (Cont.)

Chemicals	Supplier
Nickel (II) nitrate	MERCK
Copper (II) nitrate	MERCK
Lead (II) nitrate	May & Baker
Nitric acid 65 %	MERCK
Hydrochloric acid 37%	MERCK
Sulfuric acid 98%	LAB-SCAN
Potassium hydroxide	MERCK
Sodium nitrate	Fluka
Sodium sulphate	MERCK
Sodium chloride	Carlo-Erba
Calcium nitrate tetrahydrate	Riedel de Haen
Magnesium nitrate	MERCK
Hydrogen peroxide 30%	Fisher Science
Sodium hydrogen carbonate	MERCK
Sodium carbonate	Fluka
Sodium hydroxide	Carlo-Erba
Ethylene diamine tetraacetic acid (EDTA)	BDH
Chloroform-d1	MERCK

3.3 Methodology

3.3.1 Preparation of Chemicals

All solutions for extraction were prepared using deionized water.

a) Stock Standard Solutions

Stock solutions of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ (1.00 M) were prepared by dissolution of an exactly weighed amount of metal salt.

b) Working Standard Solutions

Stock standard solutions of Ni(II), Cu(II) and Pb(II) were used to prepare working standard solutions by stepwise dilution to the desired concentrations.

c) Water Rich Ionic Liquid ([BMIM]PF_6)-Saturated Deionized Water

Deionized water was contacted with ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate for 180 minutes and it was used to dilute $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solutions.

Water rich ionic liquid was also used for the determination of the metal ions and proton distribution constants.

d) Standard Calibration Solutions

Solutions A: for the determination of initial concentration of metal ions, six concentrations of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solution (0.02, 0.04, 0.06, 0.08, 0.10 and 0.12 mM) were prepared by dilution of the stock solution of each metal ion with deionized water.

Solutions B: for the determination of metal ion concentration in a solution after extraction, six concentrations of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solution (0.02, 0.04, 0.06, 0.08, 0.10 and 0.12 mM) were prepared by dilution of the stock solution of each metal ion with deionized water saturated with ionic liquid ($[BMIM]PF_6$).

e) Interference Ion Solutions

Solutions A: for the study of competitive anion affecting $Ni(NO_3)_2$, $Pb(NO_3)_2$ and $Cu(NO_3)_2$ extraction, solutions were prepared by mixing individual anion (sodium salt of NO_3^-, SO_4^{2-} and Cl^-) with the stock solutions of $Ni(NO_3)_2$ and $Cu(NO_3)_2$ and mixing only sodium salt of NO_3^- with the stock solution of $Pb(NO_3)_2$. The concentrations of anion in aqueous solution were 1 mM, 10 mM, 100 mM and 1 M.

Solutions B: for the study of the effect of competitive cations on $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ extraction, the solutions were prepared by mixing individual cation (nitrate salt of Na^+, Ca^{2+}, Mg^{2+}) with the stock solutions of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$. The concentrations of cations in aqueous solution were 1 mM, 10 mM, 100 mM and 1 M.

Solutions C: for the study of cation exchange mechanism, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solutions were prepared by mixing [BMIM]Cl to the stock solutions of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$. The concentrations of [BMIM]Cl were 1 mM, 10 mM, 100 mM and 1 M.

f) Job's Plot Solutions

The solutions for the study of Job's plot at varied molar fraction, (X_m=0.10-0.50) were prepared with the total mole of metal ions and 2-aminothiophenol ligand in ionic liquid of 15.00 as shown in Table 3.4. The volume of metal ions and ligand for the extraction is 5.0 mL and 1.0 mL, respectively.

Table 3.4 Preparation of Job's plot solutions

solution	X_m	[M] mM	$[AT]_{\text{ionic liquid}}$ mM
1	0.10	0.30	13.50
2	0.20	0.60	12.00
3	0.25	0.75	11.25
4	0.33	0.99	10.05
5	0.40	1.20	9.00
6	0.50	1.50	7.50

where X_m is a mole fraction of metal ion

[M] is a concentration of metal ion

$[AT]_{\text{ionic liquid}}$ is a concentration of 2-aminothiophenol in ionic liquid

Considering the equilibrium:

$$aM + bL \rightleftharpoons M_aL_b$$

$$\text{Mole fraction of metal, } X_m = \frac{\text{mole of metal ion}}{\text{total mole of metal ion and ligand}} = \frac{a}{a+b}$$

$$X_m = \frac{a}{15}$$

$$\text{Concentration of metal ion (mM), } [M] = \frac{\text{mole of metal ion}}{\text{volume of aqueous solution}}$$

$$\text{Concentration of ligand (mM), } [AT] = \frac{\text{mole of ligand}}{\text{volume of ionic liquid}}$$

g) Potassium Hydroxide Solutions

KOH solutions (1% and 5% w/v) were prepared by dissolving the appropriate amount of KOH in deionized water.

h) Nitric Acid Solutions

Nitric acid solutions were prepared by direct dilution from the concentrated solution.

i) Hydrochloric Acid Solutions

Hydrochloric acid solutions were prepared by direct dilution from the concentrated solution.

j) Hydrogen Peroxide Solutions

3% v/v hydrogen peroxide solutions were prepared daily by direct dilution from the concentrated solution with 0.5 M and 1 M of HNO_3 and 0.1 M of NaOH.

k) EDTA Solutions

0.1 M, 0.5 M and 1.0 M EDTA solutions were prepared by dissolution of a weighed amount of EDTA salt in deionized water.

l) Reagents for Ion Chromatography Determination

All solutions for a determination of nitrate ion with IC were prepared in Milli Q water filtrated with a 0.45 μm membrane.

Solution A: an eluent, 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 was prepared by dissolution of a weighed amount of $NaHCO_3$ and Na_2CO_3. The solution was filtrated with a 0.45 μm membrane.

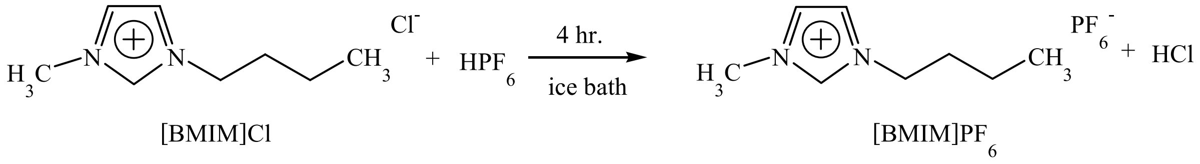
Solution B: a suppressor reagent solution (50 mM H_2SO_4) was prepared by direct dilution from the concentrated solution. The solution was filtrated with a 0.45 μm membrane.

Solution C: a nitrate stock solution (1.00 M), $NaNO_3$ was dried at 105 °C for 24 hours, dissolved in Milli Q water, and diluted to 100 mL in a class A volumetric flask.

Solutions D: five standard calibration solutions of $NaNO_3$ solution (0.40×10^{-3}, 0.80×10^{-3}, 0.01, 0.10 and 0.20 mM) for the determination of nitrate concentration were prepared by dilution of the stock standard solution of $NaNO_3$ solution with Milli Q water.

3.3.2 Preparation of Ionic Liquid; 1-Butyl-3-Methyl Imidazolium Hexafluorophosphate, [BMIM]PF_6

1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was transferred into a plastic bottle placed in an ice bath and then 400 mL of deionized water was added. Hexafluorophosphoric acid (65% w/v HPF_6) was slowly added with 1:1.3 mole equivalents. After stirring the mixture for 4 hours at room temperature, [BMIM]PF_6 was formed in the bottom phase and the upper acidic aqueous solution was then decanted. The product was washed several times with water and heated to 70 °C under vacuum to remove remaining water. The reaction was depicted in Scheme 3.1.



Scheme 3.1 Synthetic methodology of ionic liquid.

3.4 Characterization

The synthetic ionic liquid was characterized by ^{1}H- NMR ($CDCl_3$) and Fourier transform infrared spectroscopy (neat film on NaCl plate).

3.5 Liquid-liquid Extraction (LLE) Procedure

1.0 mL of ionic liquid consisted of 10.0 mM of 2-aminothiophenol and 5.0 mL of 1.0 mM of metal ion solution were placed in a LLE tube. The biphase was shaken for 180 minutes for $Ni(NO_3)_2$ solution and 30 minutes for $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solutions, and then centrifuged for 5 minutes to completely separate the two phases. The upper aqueous phase was taken out to measure the concentration of metal ion by FAAS.

For studying the effect of interfering ions in the aqueous phase, Job's plot method and slope analysis, the extraction were performed in the same manner.

In order to study the back-transfer efficiency, 5.0 mL of stripping solution was added to the extracted ionic liquid phase. After that the mixture was shaken for 60 minutes and then centrifuged, the upper stripping phase was collected to determine the metal concentration.

3.6 Parameters Studied on Liquid-Liquid Extraction

3.6.1 Extraction Efficiency by Ionic Liquid (Blank Test)

5.0 mL of 1.0 mM $Ni(NO_3)_2$ was added to 1.0 mL of ionic liquid in a LLE tube. The biphase was shaken for 180 minutes. The blank test of $Cu(NO_3)_2$ and $Pb(NO_3)_2$ were performed in the same manner but the shaking was 30 minutes.

3.6.2 pH Effect on Extraction Efficiency

5.0 mL of 5 mg L^{-1} and 1.0 mM $Ni(NO_3)_2$ and $Cu(NO_3)_2$ at different pH ranging from 2-6 (pH adjusted by HNO_3 and KOH solutions) were extracted by 10.0 mM of 2-aminothiophenol ligand in ionic liquid. The extraction times were 180 minutes and 30 minutes, respectively. The pH range in the case of $Pb(NO_3)_2$ was 2-5 with extraction time of 30 minutes. The upper solution was kept to determine the remaining metal ions.

3.6.3 Extraction Time

5.0 mL of 1.0 mM $Ni(NO_3)_2$ was contacted with 10.0 mM 2-aminothiophenol in ionic liquid (1.0 mL) at different extraction times of 10, 20, 30, 60, 90, 120, 180 and 240 minutes. The upper phase was kept to determine the remaining Ni(II) in solution.

The study of $Cu(NO_3)_2$ and $Pb(NO_3)_2$ were performed in the same manner with the contact time of 10, 30, 60 and 120 minutes.

3.6.4 Effect of Competitive Anions and Cations

5.0 mL of 1.0 mM $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solutions consisted of 1 mM, 10 mM, 100 mM and 1 M of competitive anions and cations were extracted in the same extractant with the optimum contact time experiment. The remaining amount of metal ion in solution was determined by FAAS. The effect of [BMIM]Cl was studied using the same procedure.

3.6.5 Job's Method

A set of metal ion solutions and ionic liquid at concentrations following Table 3.4 was shaken at the optimum pH and extraction time. The metal ions remaining in aqueous phase was determined by FAAS.

3.6.6 Slope Analysis

5.0 mL of 1.0 mM of $Ni(NO_3)_2$, $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solutions were extracted with 2-aminothiophenol in ionic liquid at various concentrations ranging from 5.0 mM to 30.0 mM at the optimum pH and extraction time. The concentration of metal in aqueous phase was determined by FAAS.

3.6.7 Metal Distribution Constant

5.0 mL of 1.0 mM $Ni(NO_3)_2$ was added to 1.0 mL of water rich ionic liquid in a LLE tube. The biphase was shaken for 180 minutes. The studies of $Cu(NO_3)_2$ and $Pb(NO_3)_2$ were performed in the same manner but the shaking time was 30 minutes.

3.6.8 Proton Distribution Constant

5.0 mL of DI water saturated with ionic liquid at pH 2 (pH adjusted by HNO_3) was added to 1.0 mL of water rich ionic liquid. The biphase was shaken for 30 minutes. The pH value of the extracted solution was measured.

3.6.9 Effect of Stripping Solution

The back-extraction of metal ions from the ionic liquid phase was investigated using 5.0 mL of stripping agent. Nitric acid (0.1- 5 M), hydrochloric acid (0.1-2 M), EDTA solutions (0.1-1.0 M) and 3% H_2O_2 diluted in 0.5, 1 M HNO_3, water and 0.1 M NaOH) were used as eluents for Ni(II). The amount of Ni(II) in the stripping solution was determined by FAAS.

The stripping of Cu(II) and Pb(II) were performed in the same manner. Nitric acid and hydrochloric acid (0.1-2M) were used as stripping agents for Cu(II) and only nitric acid (0.1-2 M) for Pb(II).

3.6.10 Effect of Stripping Time

The effect of stripping time on the back-extraction efficiency was studied by adding 5.0 mL of the suitable stripping agent to each metal extracting ionic liquid phase. All of metals were back-extracted at different time of 10, 20, 30 and 60 minutes.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Ionic Liquid

The ionic liquid, 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]PF_6), was synthesized via the anion metathesis reaction between 1-butyl-3-methyl imidazolium chloride, [BMIM]Cl, and hexafluorophosphoric acid, HPF_6. The viscous yellow product was washed with water until the washing was no longer acidic. The synthetic ionic liquid was characterize by FITR and ^{1}H NMR compared with commercial ionic liquid [BMIM]PF_6 and [BMIM]Cl from Fluka. The structure of the ionic liquid was shown in Figure 4.1

4.1.1 ^{1}H NMR

The ^{1}H NMR spectra of the synthetic and commercial ionic liquid [BMIM]PF_6 were depicted in Figure 4.2. The ^{1}H NMR spectra showed the existence of imidazolium ring and the chemical shifts were obtained as follows: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1H), 7.32 (t, 1H, *J*=1.8), 7.22 (t, 1H, *J*=1.8), 4.05 (t, 2H, *J*=4.0), 3.86 (s, 3H), 1.81 (pen, 2H, *J*=7.6), 1.21 (sept, 2H, *J*=7.5) and 0.86 (t, 3H, *J*=7.2).

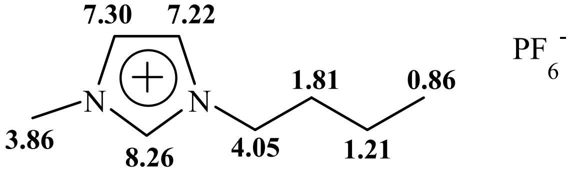


Figure 4.1 Structure and chemical shifts of ionic liquid [BMIM]PF_6.

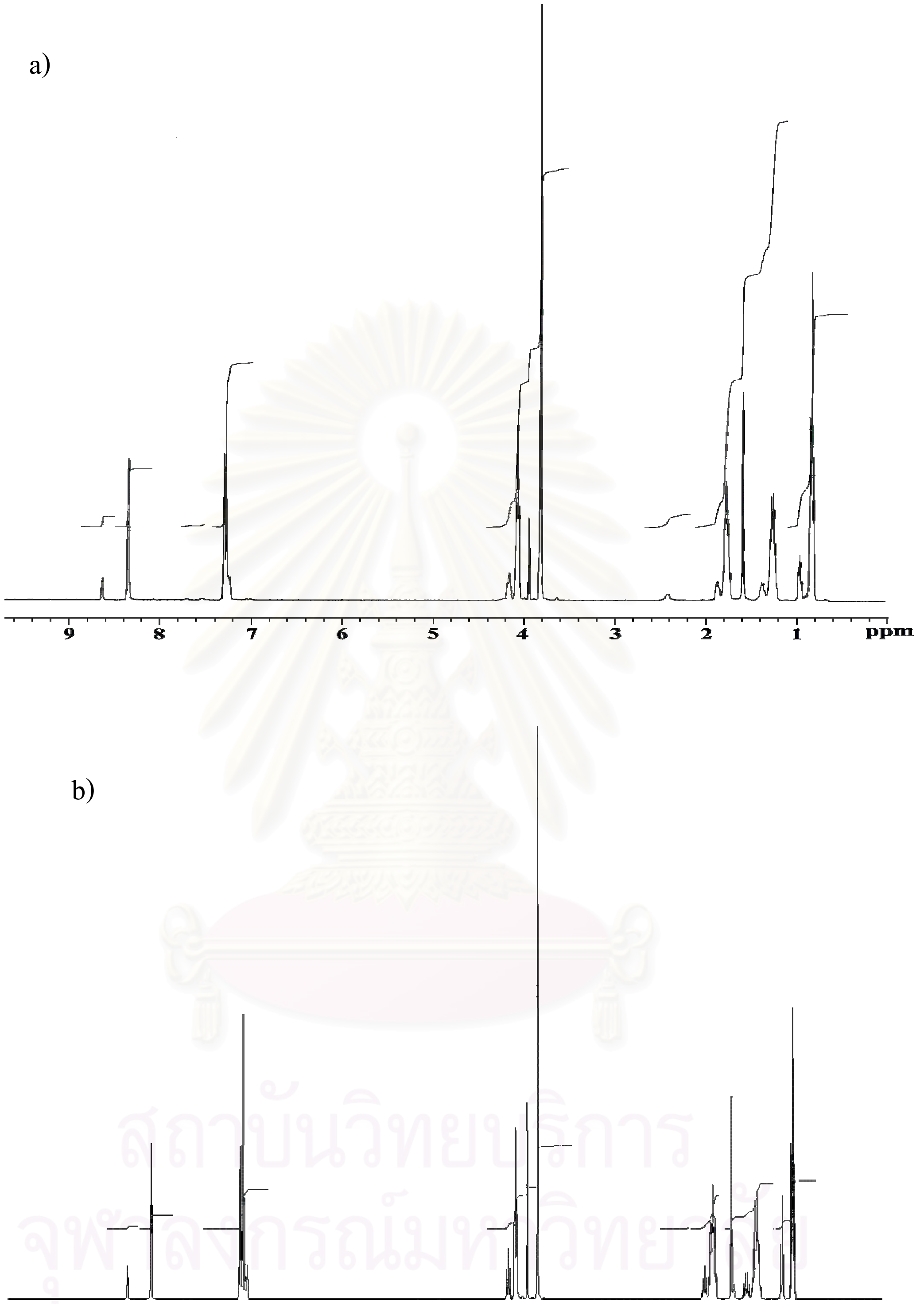


Figure 4.2 ^{1}H NMR spectra of a) synthetic ionic liquid [BMIM]PF_6 and b) commercial ionic liquid [BMIM]PF_6.

4.1.2 Infrared Spectrometry

The synthetic ionic liquid was characterized by FTIR with neat film/NaCl plate. The IR spectra were depicted in Figure 4.3.

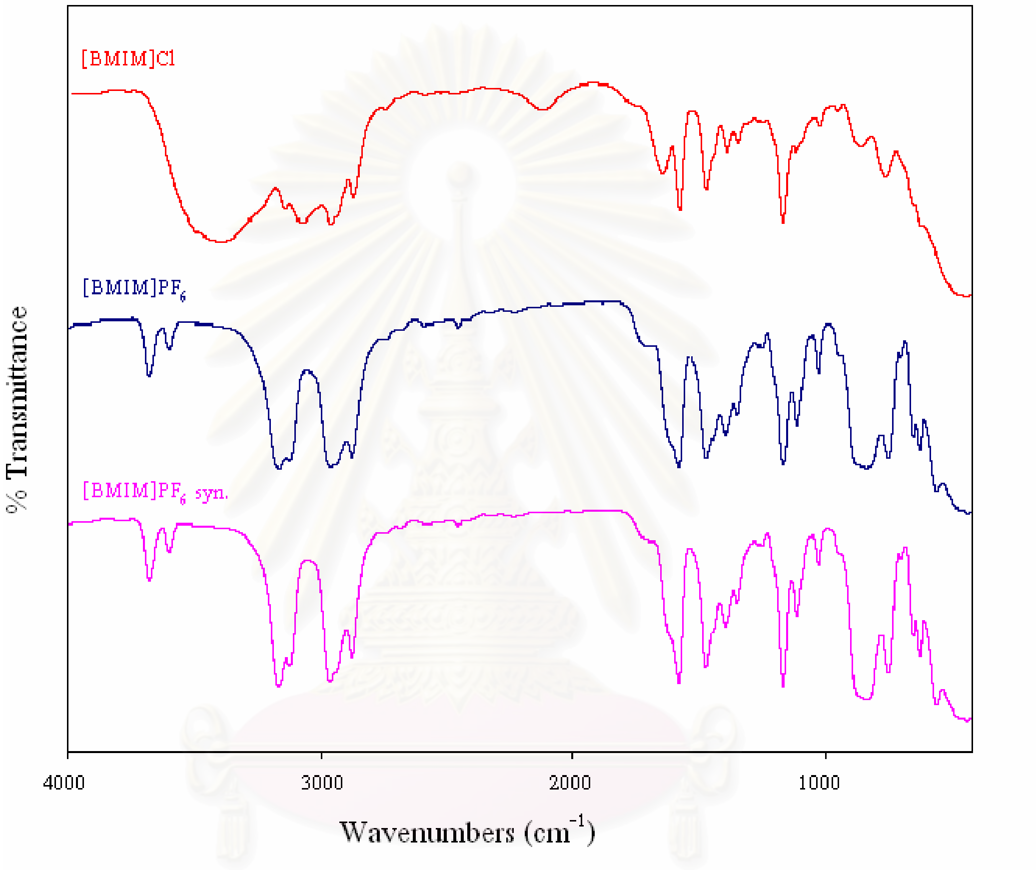


Figure 4.3 FT-IR spectra of [BMIM]Cl (top spectrum), commercial [BMIM]PF_6 (middle spectrum) and synthetic [BMIM]PF_6 (bottom spectrum).

FT-IR spectrum of [BMIM]Cl showed the absorption band of aliphatic C-H stretching appearing between 2966-2878 cm^{-1} and imidazole C-H stretching peak between 3169-3125 cm^{-1}. The C=C aromatic stretching absorption band appeared around 1573, 1468 cm^{-1} and the absorption band of (N)CH_3 stretching appeared around

1336 cm^{-1}. The hydrogen bonding of C(2)H…Cl appeared around 3050-3080 cm^{-1}. And the O-H stretching of water appeared around 3412 cm^{-1}.

FT-IR spectra of the synthetic ionic liquid and the commercial one shown in Figure 4.1 are similar. They also resemble the spectrum of imidazolium-based [BMIM]Cl. However, important characteristics which are significantly different from the spectrum of [BMIM]Cl can be seen. There are an appearance of the PF stretching absorption band at 841 cm^{-1} and the two peaks of O-H stretching of water around 3671 and 3587 cm^{-1} but the absorption band of hydrogen bonding disappears.

The lack of hydrogen bonding band in the 3000-3100 cm^{-1} region in ionic liquid [BMIM]PF_6, in contrast to that observed in [BMIM]Cl, is due to that fact that hexafluorophosphate (PF_6^-) is a weakly coordinating anion which is not expected to participate in strong hydrogen bonding. The difference of water absorption bands, O-H stretching, in [BMIM]PF_6 and [BMIM]Cl are influenced by anion types which affect the water solubility of ionic liquid. The broad band observed in water soluble [BMIM]Cl represents the anti-symmetric stretching mode of water hydrogen bond with an anion which is the result of several water molecules aggregating or interaction of water with Cl^- anions. Whereas in ionic liquid [BMIM]PF_6, the molecules of water dissolved in ionic liquid bound with PF_6^- via hydrogen bonds, as shown in Figure 4.4. The complex of water and PF_6^- is symmetric and IR inactive, thus the IR spectrum does not exhibit O-H stretching band [39, 43].

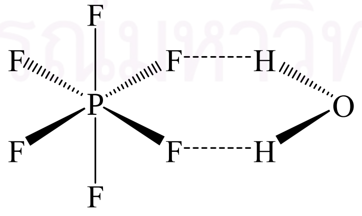


Figure 4.4 Water-PF_6^- complex.

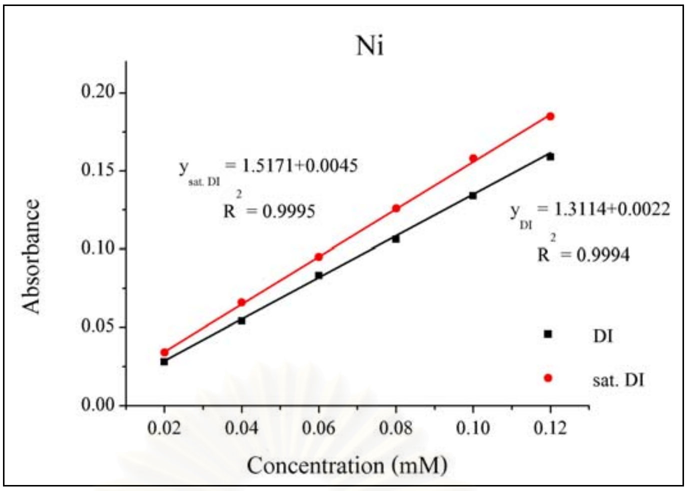
4.2 Influence of Ionic Liquid on Metal Calibration Curve

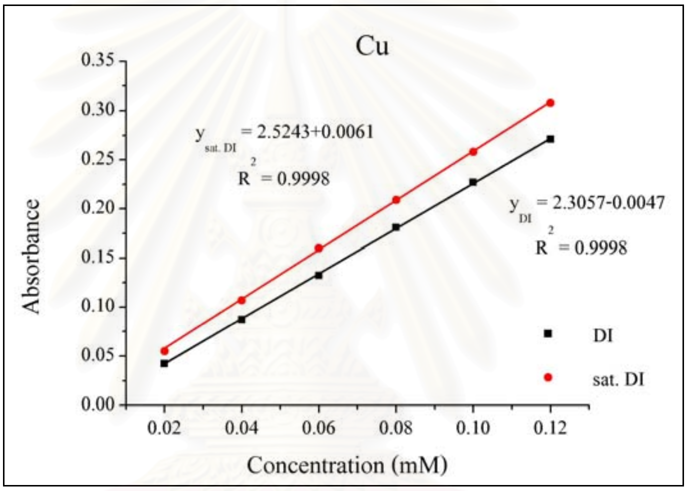
Flame atomic absorption spectrometry (FAAS) is a technique widely used to determine single metal concentration because of high specificity, ease and low cost. The concentration of metal ion was estimated by comparing the signal of unknown to a calibration curve (standard curve). Therefore the satisfaction of calibration curve is important for the accuracy of the analytical results.

The FAAS technique is also known that the matrix in sample affects the response of analyte and standard so the investigation of matrix effect is necessary. Because the slope of the calibration equation shows the sensitivity of the metal determination that relates to the matrix effect, the significant test of slope of calibration curves in two matrices: DI water and saturated DI water with ionic liquid, was studied using pair-t test at 95 % confidence limit to demonstrate the effect of ionic liquid on the metal determination.

The calibration curve of all metal in DI water and saturated DI, as shown in Figure 4.5, illustrated the comparison of matrix effect. In saturated DI, the sensitivity of the determination of all metal ions was higher than in DI water. Considering the result of significant test shown in Table 4.1 where the $\left|t_{stat}\right|$ value of all metal is higher than $t_{critical}$, the determination of metal ions in both matrices is significantly different. The supporting of ionic liquid on the response of determination is due to the decrease of water surface tension and the increase of water viscosity by the organic cation and the high viscosity of ionic liquid which increases the mist of sample into the nebulizer in the atomization process that improves the free metal atom for determination [66].

This result showed that the dissolved ionic liquid in DI water affects the response of FAAS. For certain metal ion determination, the concentration of metal before and after extraction was determined by using the calibration equation from standard curve preparing in DI water and saturated DI water, respectively.





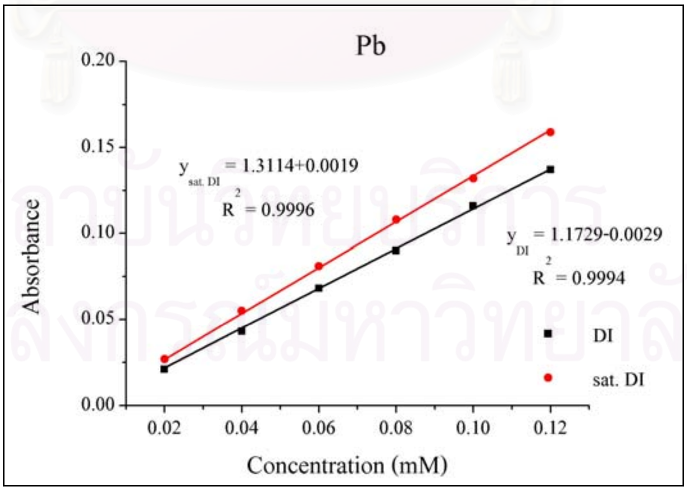


Figure 4.5 Calibration curves of Ni, Cu and Pb preparing in ■ DI water and ● saturated DI water.

Table 4.1 Pair t-test between the determination of metal ion in DI and saturated DI water matrix

Metal	$\left\|t_{stat}\right\|$	$t_{critical}$ (n-1=14)
Ni	9.23	2.14
Cu	13.99	2.14
Pb	13.88	2.14

4.3 Determination of Extraction Mechanism

The extraction efficiency of metal was represented in term of percentage extraction (%E) that was calculated from the ratio of concentration of extracted metal (a difference between starting and final metal concentration in aqueous phase) and starting metal concentration according to Equation 4.1. The distribution coefficient (D) for extraction is defined in Equation 4.2 as

$$\%E = \frac{(C_i)_{aq} - (C_f)_{aq}}{(C_i)_{aq}} \times 100 \tag{4.1}$$

$$D = \frac{(C_i - C_f)_{aq}}{(C_f)_{aq}} \times \frac{\text{volume of aqueous phase}}{\text{volume of IL phase}} \tag{4.2}$$

where $(C_i)_{aq}$ is the initial concentration of metal ions in aqueous phase before extraction (mM)

$(C_f)_{aq}$ is the concentration of metal ions in aqueous phase after extraction (mM)

4.3.1 Extraction Efficiency by Ionic Liquid (Blank Test)

Solvent extraction studies of Ni(II), Cu(II) and Pb(II) with ionic liquid [BMIM]PF_6 without 2-aminothiophenol extractant were performed using 1.0 mM of metal solution. The data listed in Table 4.2 show no significant extraction of metal ion into [BMIM]PF_6 phase (%E less than 1.8 for all metal ions, three replicate extractions). The results reveal that the ionic liquid alone has no extractive capacity towards the metal ions.

Table 4.2 Extraction of each metal with ionic liquid [BMIM]PF_6 (n=3)

No	Concentration of Ni^{2+} in aqueous phase (mM)		% E	Mean±SD
	initial	After extraction		
1	1.002	0.984	1.79	1.79 ± 0.01
2		0.984	1.79	
3		0.984	1.79	

No	Concentration of Cu^{2+} in aqueous phase (mM)		% E	Mean±SD
	initial	After extraction		
1	1.004	0.986	1.76	1.76 ± 0.01
2		0.986	1.76	
3		0.986	1.76	

Table 4.2 Extraction of each metal with ionic liquid [BMIM]PF_6 (n=3) (conts.)

No	Concentration of Pb^{2+} in aqueous phase (mM)		% E	Mean±SD
	initial	After extraction		
1	0.975	0.958	1.79	1.79 ±0.01
2		0.958	1.79	
3		0.958	1.79	

4.3.2 pH Effect on Extraction Efficiency

As early stated in chapter II, the complexation of metal ion with 2-aminothiophenol occurs via 2 paths that are the deprotonation of active site (-SH and $-NH_2$) and the electron charge transfer reaction. In the case of the complexation with the deprotonated form of ligand, pH of solution is an important parameter that can affect the extraction efficiency of metal ions. In the acidic medium, the competitive equilibria between the protonation of ligand and the coordination of metal ions are present. In contrast, at higher pH the ligand is deprotonated and ready to complex with metal ion but the precipitation of metal hydroxide can occur. There are the competitive equilibria between the coordination of ligand and the formation of metal hydroxide in the basic medium.

In the beginning of this study, a solution containing 5 mg L^{-1} of metal ion at various pHs was used. The results in Figure 4.6 showed that the percentage extractions of Ni^{2+} and Cu^{2+} attained around 100% when the solution pHs were above 4 and 3, respectively, while the percentage extraction of Pb^{2+} increased gradually until 80% when increasing pH from 3 to 6.

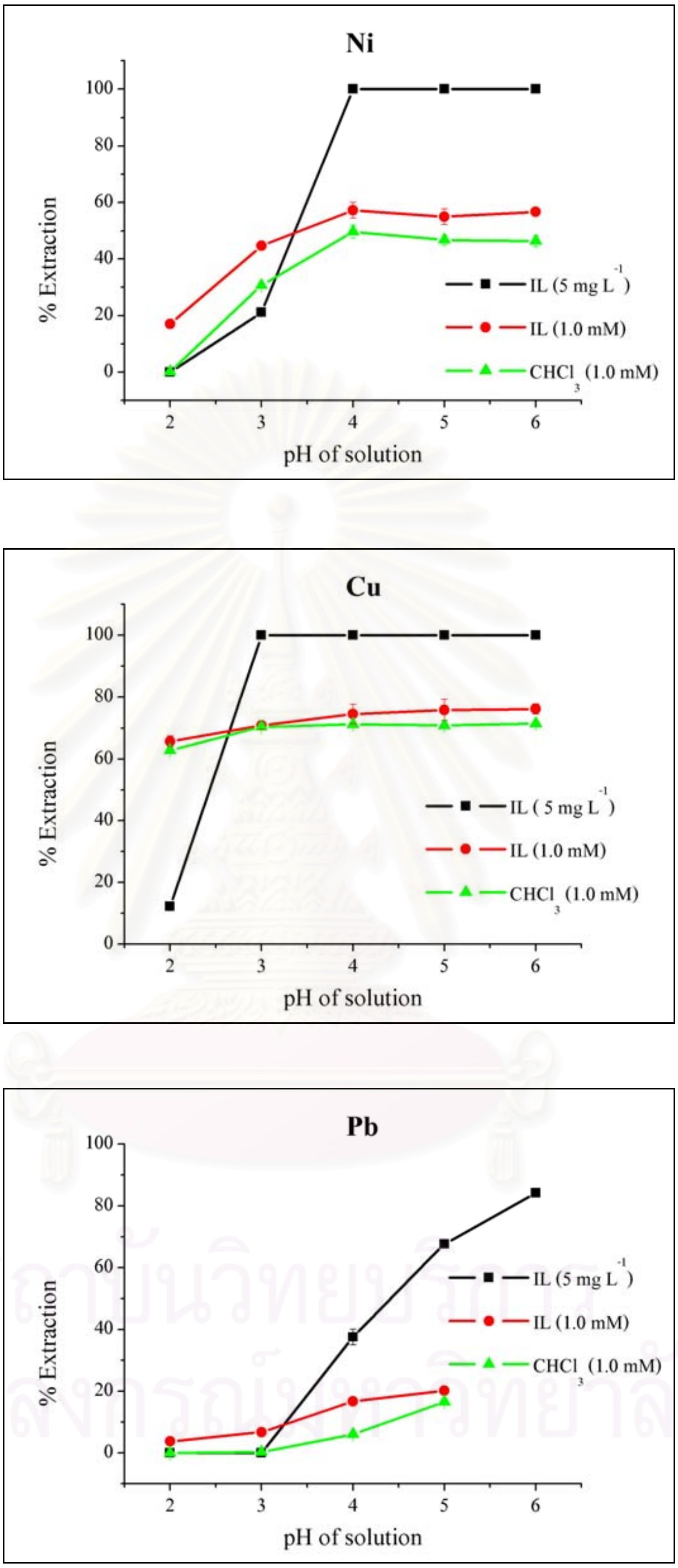


Figure 4.6 Comparison of pH effect on Ni^{2+}, Cu^{2+} and Pb^{2+} extraction with different solvents:■ionic liquid (5 mg L^{-1}),● ionic liquid (1.0 mM) and▲$CHCl_3$ (1.0 mM), (n=3).

Due to the total extraction in case of Ni^{2+} and Cu^{2+} and too high percentage extraction for Pb^{2+}, the distribution ratio which is one of important factor for further study cannot be estimated, thus the concentration of metal ions in solution was changed to 1.0 mM, corresponding to 58.7, 63.5, and, 207.2 mg L^{-1} of Ni^{2+}, Cu^{2+} and Pb^{2+}, respectively.

In order to study the pH effect on the extraction efficiency of metal ions at 1.0 mM metal concentration, the solution pH values were varied from 2-6 for Ni^{2+} and Cu^{2+}. Because of the precipitation of $Pb(OH)_2$ at pH >5, only pH of solution at 2-5 was studied for Pb^{2+}. The influence of pH value on the extraction of 2-aminothiophenol complex of Ni^{2+}, Cu^{2+} and Pb^{2+} in chloroform and ionic liquid are compared and shown in Figure 4.6.

Both biphasic systems of all metal extraction showed similar behavior that is the extraction of Ni^{2+} and Pb^{2+} depends on the pH value of solution while the extraction of Cu^{2+} is independent of the pH value. The optimum pHs for the extraction are at pH $\geq$ 4 for Ni^{2+} and Cu^{2+} and at pH 5 for Pb^{2+} with the percentage extractions of 57, 76 and 20, respectively. Since the optimum pH value of each metal solution is approximately 5. The solutions would be used in further studied without adjusting pH.

The result of pH effect on metal extraction is in agreement with many researches that the 2-aminothiophenol complexation with Ni^{2+} and Pb^{2+} occurred via the deprotonation of active site [14, 67] of which the deprotonation of thiol group (-SH) is preferred. For Cu^{2+}, the dark blue complex in ionic liquid phase was observed. Larkworthy et al. reported that Cu^{2+} oxidized 2-aminothiophenol and formed complex by electron transfer reaction [14]. To elucidate this hypothesis, electron spinning resonance spectroscopy (ESR) was used to identify the species of Cu-2-aminothiophenol complex. The ESR results are illustrated in Appendix A. No peak was found in the ESR spectrum. The inactive ESR indicated that copper in Cu complex was Cu^{+} which had no unpaired electron ($[Ar]3d^{10}$).

To confirm the hydrogen ion dependency on complexation of metal, the pH values of aqueous solution after extraction at constant ligand concentration were determined and plotted as a function of distribution ratio according the extraction equilibrium, Equation 4.3. The slope y is equal to the number of hydrogen ions released in the overall extraction reaction.

$$aM^{n+}_{aq} + bH_2L_{IL} \rightleftharpoons \left(M_aL_bH_{2b-y}\right)^{(an+y-2b)}_{IL} + yH^{+}_{aq}$$

The extraction equilibrium constant K_{ex} is (complex's charge omitted)

$$K_{ex} = \frac{\left[M_aL_bH_{2b-y}\right]_{IL}\left[H^+\right]^y_{aq}}{\left[M^{n+}\right]^a_{aq}\left[H_2L\right]^b_{IL}}$$

And the distribution ratio D is given by

$$D = \frac{K_{ex}\left[H_2L\right]^b_{IL}}{\left[H^+\right]^y_{aq}}$$

Thus, the following equation can be obtained

$$\log D = \log K_{ex} + b \log [H_2L]_{IL} - y \log [H^+]_{aq} \qquad (4.3)$$

On the account of many researches, the decomposition of PF_6^- to HF and PO_4^{3-} in the presence of water or nitric acid in ionic liquid [27, 53] as shown in Equation 4.4 in which nitric acid acts as a catalyst was proposed. The pH values of blank extraction (DI water) with ionic liquid were determined and shown in Table 4.3.

$$H^+ + PF_6^- + 6H_2O + 3HNO_3 \longrightarrow H_3PO_4 + 6HF + 3HNO_3 + 2H_2O \qquad (4.4)$$

Table 4.3 pH values of blank solution (DI water) before and after extraction

No.	Solution pH values		Mean±SD
	Before extraction	After extraction	
1	5.107	3.568	3.575±0.009
2		3.586	
3		3.572	

Consequently, the plot of log D versus different pH values (ΔpH) between extracted metal solution and blank extraction of each pH in Figure 4.7 leads to the straight line and the slope of the graph is the number of dissociation protons shown in Table 4.4. The number of proton dissociating from 2-aminothiophenol is 2 for Ni^{2+} and Pb^{2+} complex whereas insignificant dissociation of proton from Cu^{2+} complex was observed.

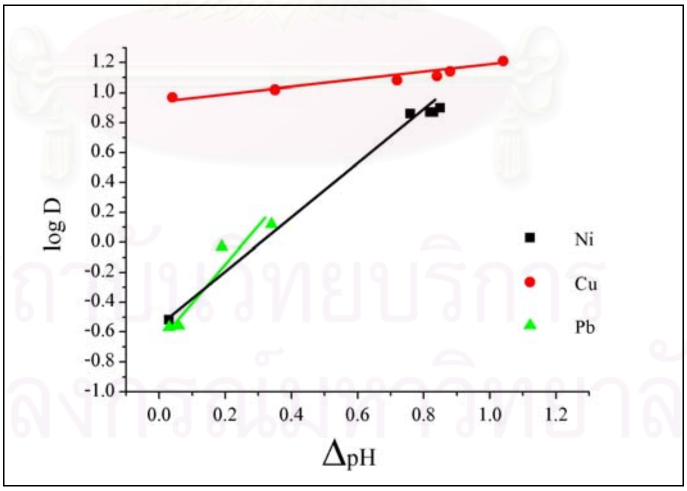


Figure 4.7 Plots of log D *vs* ΔpH of solution after extraction of Ni^{2+}, Cu^{2+} and Pb^{2+} with 2-aminothiophenol in ionic liquid.

Table 4.4 Summary the equation data from the plot of log D *vs* pH

Metal	Equation	R^2	No. of H^+ dissociated
Ni	y = 1.7686x - 0.5668	0.9920	2
Cu	y = 0.2136x + 0.9507	0.9203	-
Pb	y = 2.3728x - 0.6342	0.9202	2

Moreover, Figure 4.6 reveals that the extraction efficiency in ionic liquid is higher than that in chloroform. It is on the account of either higher formation constant of 2-aminothiophenol-metal complex or some of 2-aminothiophenol might introduce to the aqueous phase due to partially water solubility of [BMIM]PF_6. This argument is supported by the absorbance of DI water saturated with ionic liquid combined with 2-aminothiophenol being higher than that of DI water saturated with only ionic liquid as shown in Table 4.5.

Table 4.5 Absorbance of saturated DI water with ionic liquid and ionic liquid containing 2-amionothiophenol at wavelength 243 nm

Sample	Absorbance (AU)	Mean±SD
Saturated DI water with [BMIM]PF_6	0.342 0.350 0.331	0.344±0.005
Saturated DI water with 2-aminothiophenol in [BMIM]PF_6	0.514 0.464 0.455	0.478±0.006

Because the absorption spectrum of 2-aminothiophenol in ethanol is similar to that of the ionic liquid as shown in Figure 4.8, the increase of absorbance of saturated DI water with ionic liquid containing 2-aminothiophenol suggests that some of 2-aminothiophenol are together distributed into aqueous phase.

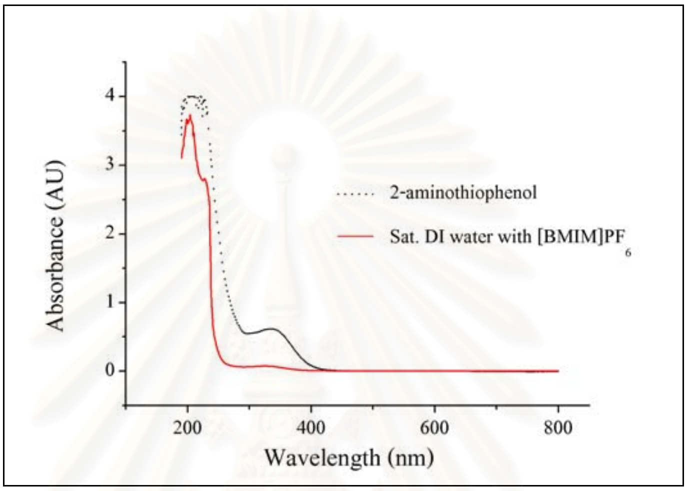


Figure 4.8 UV spectra of 1.0 mM 2-aminothiophenol in ethanol and saturated DI water with [BMIM]PF_6.

4.3.3 Effect of Extraction Time

The extraction equilibrium time is an important factor for the metal extraction and accurate calculation of the association constant. The extraction efficiency depends on the extraction time in case of slow extraction equilibrium. Using extraction time less than that required to reach equilibrium reduces the extraction efficiency.

To study the influence of extraction time on metal extraction, each of metal solution was extracted with various times. The results of each metal extraction as a function of time are presented in Figure 4.9.

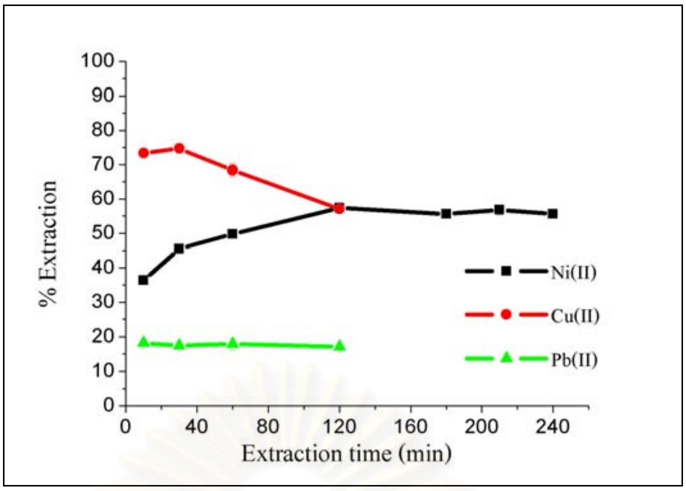


Figure 4.9 Effect of extraction time on metal ion extraction (n=3).

The results showed that the extraction of Pb^{2+} reached the equilibrium in a short time, within 10 minutes. On the contrary, the extraction equilibrium of Ni^{2+} required longer time. The extraction efficiency increased by increasing the extraction time but extraction time of more than 120 minutes is insignificant to the extraction efficiency. For Cu^{2+}, the extraction efficiency is maximum at the extraction time less than 30 minutes and then reduced when the extraction time increased. The decrease of Cu^{2+} extraction might be due to the dissolution of some complexes into aqueous phase or due to the fact that 2-aminothiophenol might be oxidized by Cu^{2+} to disulfide (RSSR) as reported earlier [14].

In conclusion, the optimum extraction times of Ni^{2+}, Cu^{2+} and Pb^{2+} are 180, 30 and 30 minutes, respectively. The equilibrium extraction time of each metal extraction was fixed for further experiments.

4.3.4 Effect of Competitive Anions and Cations

Type and concentration of anions and cations are ones of the factors that affect the metal ion extraction especially in case of real samples. Cations might provide the competitive extraction with desized metal ions while the anion can form complex with the metal ions or generate unextractable metal species.

Moreover, the impact of competitive ions on metal extraction can illustrate the extraction mechanism. The extraction of metal ion from aqueous into another phase must convert them to an extractable complex which is either neutral chelate complexes or ion-association complexes (ion-pair). In order to extract the neutral chelate complex, metal ions must react with the coordination site of the chelating agent to form a neutral complex. For ion-pair complex, metal ions associate with an oppositely charged ion to form a neutral species (ion-pair) which is extractable into the extraction phase. Normally metal ions incorporate with either a large, bulky organic ion or a suitable counter ion. Because ion-pair complex depends on the type of counter ion, changing of ion in solution affects the extraction efficiency [11, 60].

The studies of competitive cations and anion such as Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- which are normally found in natural water at various concentrations were carried out. The results are displayed in Table 4.6. The results indicated that in case of Ni^{2+} extraction, the change of extraction efficiency in the absence and presence of interfering ions at different concentrations was not significant. The changing of counter ions did not affect the extraction. For Cu^{2+} extraction, the results showed that only high concentration of Cl^- affected the extraction because of the formation of $CuCl^+$ in the solution whose the stability constant is 0.40 [68]. Due to the precipitation of $PbSO_4$ and $PbCl_2$, the effect of competitive ion on the Pb^{2+} extraction was studied only in the presence of nitrate salt such as Na^+, Ca^{2+} and Mg^{2+}. The results showed that Na^+, Ca^{2+} and Mg^{2+} has no effect on the extraction except at high concentration (1 M).

The decrease of extraction efficiency might be the result of the increase of ionic strength.

Table 4.6 Effect of the interfering ions on the Ni^{2+}, Cu^{2+} and Pb^{2+} extraction

Element	Interfering ions	% Extraction*				
	concentration (mM)	0	1	10	100	1000
Ni	Na^+	58±1	59±1	59±1	59±1	58±1
	Ca^{2+}	58±1	61±2	60±2	59±1	58±1
	Mg^{2+}	55±1	57±1	58±1	57±2	54±1
	SO_4^{2-}	58±1	59±2	59±2	58±2	60±1
	Cl^-	55±1	57±1	57±2	56±2	54±2
Cu	Na^+	76±1	76±1	75±2	77±2	74±3
	Ca^{2+}	79±2	78±1	80±1	79±1	80±1
	Mg^{2+}	79±2	77±2	78±3	80±1	83±1
	SO_4^{2-}	76±1	76±2	77±2	77±1	80±1
	Cl^-	76±1	75±1	73±1	66±2	46±2
Pb	Na^+	20±1	21±1	20±1	18±1	9±1
	Ca^{2+}	20±1	23±1	21±1	18±1	8±1
	Mg^{2+}	20±1	20±1	21±1	15±1	11±1

*Mean value±SD, n=3

As mentioned previously that the extraction efficiency is independent of the type of counter ion therefore the extraction mechanism should not be an ion-association extraction. The way to confirm the ion-association extraction system is the determination of the concentration of NO_3^- in the extracted aqueous solution. In this extraction system, if ever applied, metal ion must generate the extractable ion-pair species via association with the NO_3^- in solution before being extracted into ionic liquid phase therefore the number of NO_3^- in aqueous phase after extraction should decrease. Table 4.7 showed the remaining NO_3^- in aqueous solution investigated using ion chromatography (IC) technique (conditions described in section 3.1.5). The result showed that the loss of NO_3^- to the ionic liquid phase was negligible suggesting that the extraction of metal ion is not the ion-association extraction system.

Table 4.7 Loss of NO_3^- after the Ni^{2+}, Cu^{2+} and Pb^{2+} extraction

Metal	Concentration of NO_3^- (mM)		% loss*
(%E)	Before extraction	After extraction	
Ni (53)	2.099	2.003	4.8±0.4
		2.005	
		1.988	
Cu (74)	2.163	2.024	3.4±1.7
		2.112	
		2.109	
Pb (16)	2.088	2.069	0.8±0.4
		2.062	
		2.079	

*Mean value±SD, n=3

Because of water solubility of ionic liquid, ion exchange is one possible mechanism for metal extraction. There are many researches reported that ionic liquid can act as both solvent like conventional organic solvent and cation exchanger which depends on the extraction condition [61, 62, 64]. Using [BMIM]PF_6 ionic liquid, $[BMIM]^+$ can act as a cation being able to exchange with metal cation.

To examine the ion exchange mechanism, the extraction of metal ion with various concentrations of [BMIM]Cl in aqueous phase was studied. Increasing of [BMIM]Cl in the solution means the concentration of $[BMIM]^+$ in the solution increases and the extraction equilibrium is driven to the left hand as in the following Equation 4.5. The exchange of metal ion for $[BMIM]^+$ issued from ionic liquid phase becomes difficult when the concentration of $[BMIM]^+$ in the aqueous phase is high therefore the extraction efficiency of metal ion will decrease according to the Le Châtelier's principle. In contrast, the transfer of Ni^{2+}, Cu^{2+} and Pb^{2+} into chloroform should be independent of the concentration of [BMIM]Cl in aqueous phase.

$$\left(M^{n+}\right)_{aq} + (L)_{IL} + \left([BMIM]^{+}\right)_{IL} \rightleftharpoons (ML)^{n+}_{IL} + \left([BMIM]^{+}\right)_{aq} \qquad (4.5)$$

The results of the effect of [BMIM]Cl at various concentrations on the metal extraction in biphasic phase using ionic liquid and chloroform are depicted in Figure 4.10. Both biphasic systems showed similar extraction behavior that $[BMIM]^+$ has no effect on each metal extraction. The decreasing of Cu^{2+} extraction at 100 mM [BMIM]Cl is probably due to the formation of $CuCl^+$ which decreases the concentration of Cu^{2+} before extraction. At 1 M of [BMIM]Cl, the concentration of Cu^{2+} increased presumably due to the generation of new extractable species as the color of solution changed from colorless to green. The new species might be the interaction of Cu(II) chloride with [BMIM]Cl as previously reported that the interaction of Cu(II) chloride with [EMIM]Cl, 1-ethyl-3-methylimidazolium chloride, in ethanol yielded a yellow solution [69]. For Pb^{2+} extraction, the extraction efficiency decreased due to the changing from extractable species to the precipitate $PbCl_2$ which suspended in the solution.

Table 4.8 Initial concentration of Ni^{2+}, Cu^{2+} and Pb^{2+} in various concentrations of [BMIM]Cl in aqueous phase

Metal	Initial concentration of metal in [BMIM]Cl (mM)			
	1	10	100	1000
Ni^{2+}	0.947	0.937	0.956	0.975
Cu^{2+}	0.918	0.912	0.662	0.941
Pb^{2+}	0.916	0.906	0.990	0.971

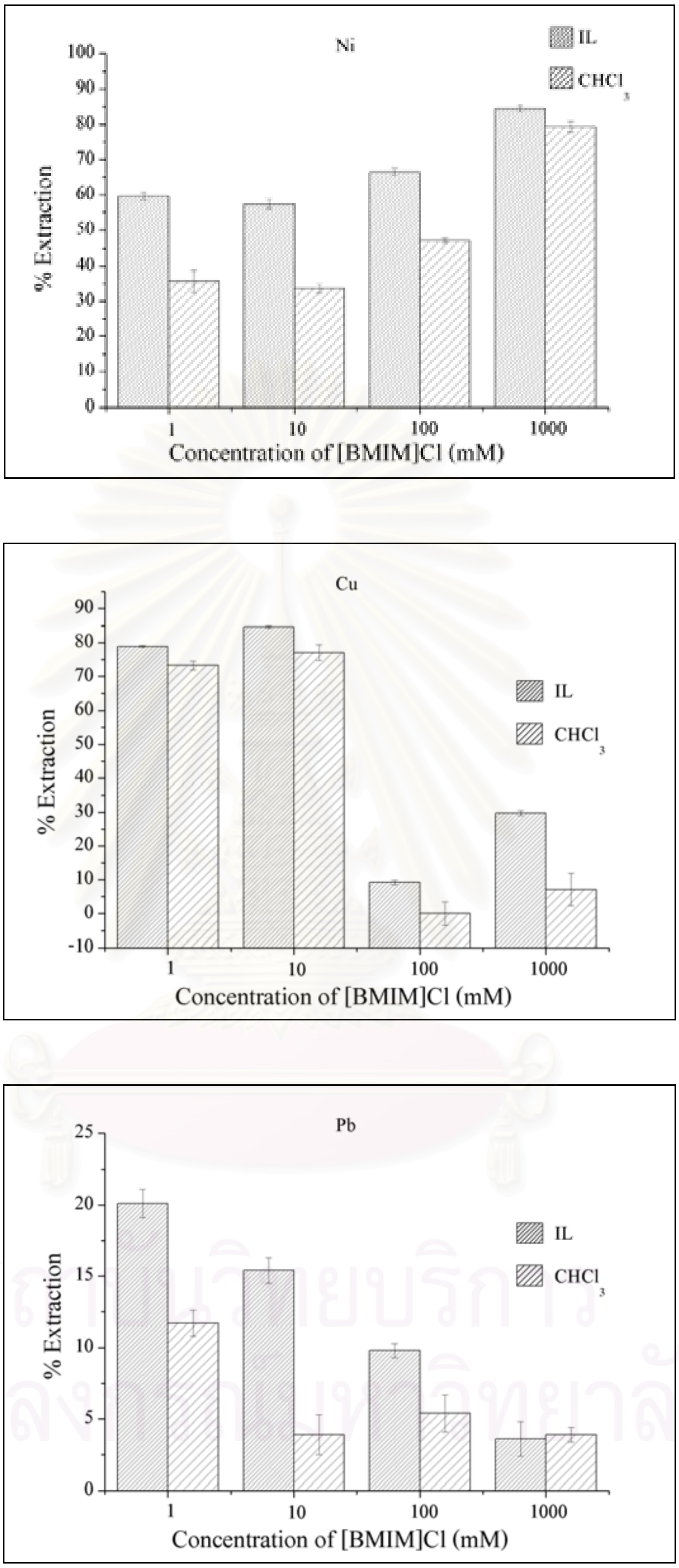


Figure 4.10 Effect of [BMIM]Cl on Ni^{2+}, Cu^{2+} and Pb^{2+} extraction.

4.3.5 Stoichiometry of Extraction Equilibrium

4.3.5.1 Job's Plot

Job's plot is a continuous variation method to determine the stoichiometry of complex. The mass product was plot as a function of mole fraction of metal or ligand (X_M or X_L), the position of mole fraction having a maximum mass product is the stoichiometry of the complex.

To investigate the stoichiometry, the total mole number of metal and ligand were fixed at 15 and the concentrations of metal and ligand solutions were prepared following Table 3.4. The results are illustrated in Figure 4.11. The concentration of Ni^{2+}, Cu^{2+} and Pb^{2+} in ionic liquid phase reached a maximum value at the mole fraction of the metal, X_M of 0.25, 0.33 and 0.33, respectively.

According to the mole fraction of metal which is the ratio of mole of metal and total mole number, the stoichiometry of ligand and each metal can be calculated following Equation 2.1. For example, Ni^{2+} extraction: $X_M = 0.25$, mole $Ni^{2+} + H_2L = 15$

$$X_M = \frac{\text{mole Ni}^{2+}}{\text{mole Ni}^{2+} + \text{mole H}_2\text{L}}\text{; } 0.25 = \frac{\text{mole Ni}^{2+}}{15}$$

$$\text{mole Ni}^{2+} = 0.25 \times 15 = 3.75 \text{ and mole H}_2\text{L} = 15 - 3.75 = 11.25$$

$$\text{mole Ni}^{2+} : \text{mole H}_2\text{L} = 3.75 : 11.25 = 1 : 3$$

The stoichiometry of Cu^{2+} and Pb^{2+} are calculated by the same procedure. The result concluded that the extraction of one mole of Ni^{2+}, Cu^{2+} and Pb^{2+} required 3, 2 and 2 moles of 2-aminothiophenol, the mole ratio between metal and ligand is1:3, 1:2 and 1:2, respectively.

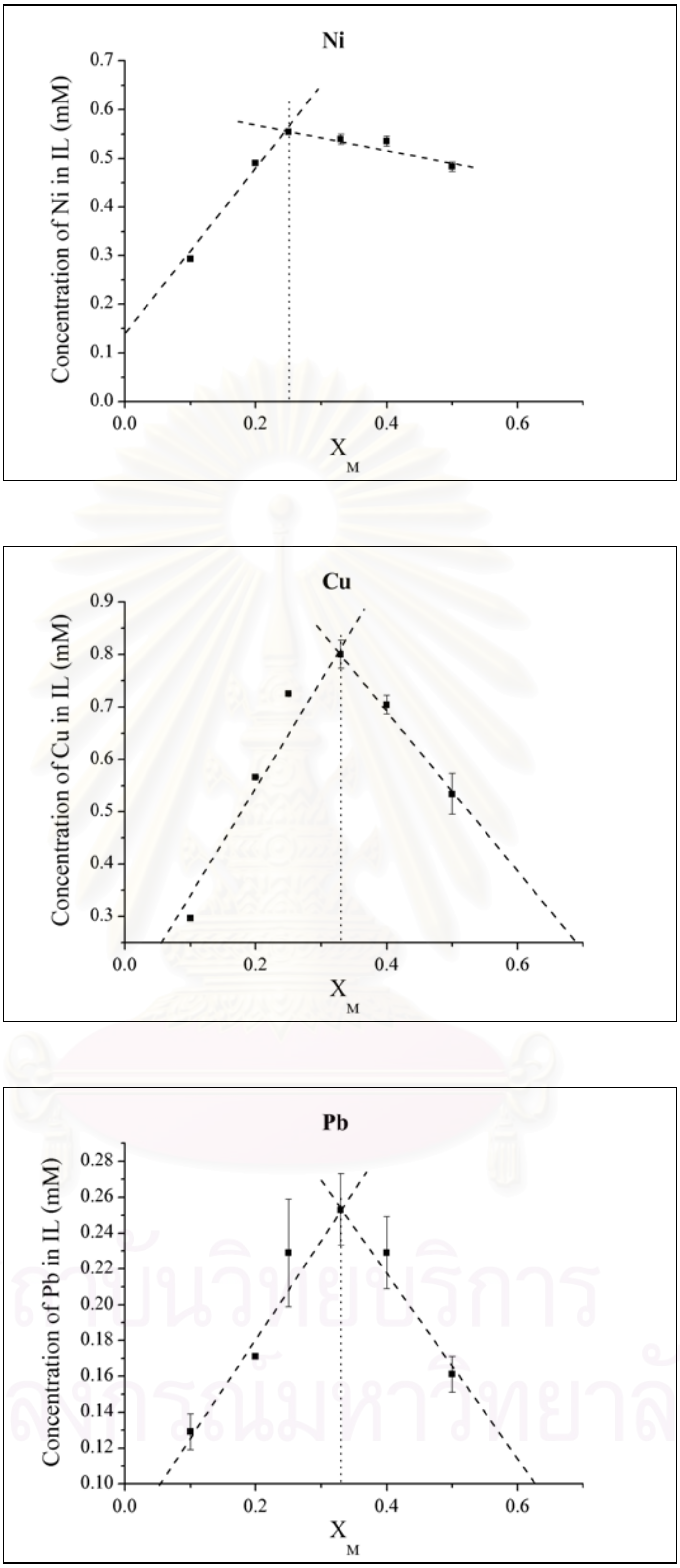


Figure 4.11 Job's plots of the complexation between metal ions and 2-aminothiophenol in ionic liquid, [BMIM]PF_6.

As the results of pH effect study, competitive ion effect study and Job's plots, the proposed complexation of Ni^{2+}, Cu^{2+} and Pb^{2+} with 2-aminothiophenol are shown in Figure 4.12. In case of Cu^{2+}, the radical form of deprotonated 2-aminothiophenol in the complex with Cu^{+} was proposed according to the previous study reported by Kapre [21] and the elucidation of copper speciation by ESR technique (Appendix A).

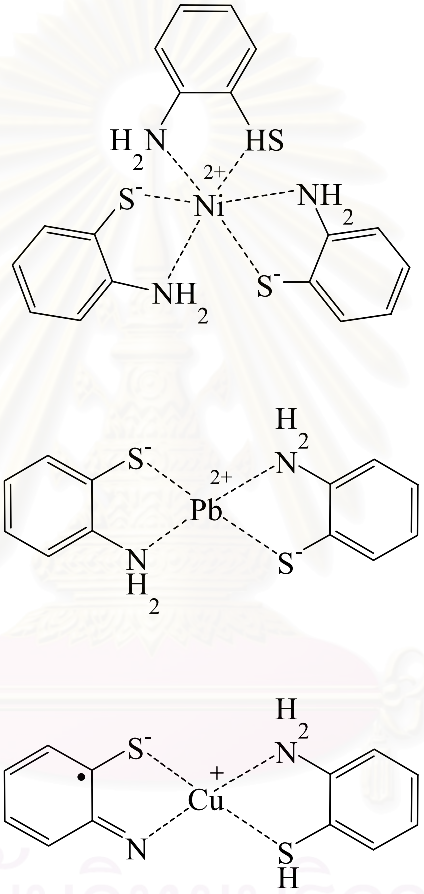


Figure 4.12 The proposed structures of metal chelated with 2-aminothiophenol.

4.3.5.2 Slope Analysis

The slope analysis as described in section 2.4.4.2.2 was examined to confirm the stoichiometry of metal complex and determine the extraction constant K_{ex}. Various concentrations of 2-aminothiophenol were used to extract the metal ions studied. The number of ligands incorporated in the metal extractable complex is the slope of the plot between log D against log concentration of free ligand in ionic liquid.

According to the result in section 4.3.2 which showed that the complexation of metal ion with 2-aminothiophenol occurred via the deprotonation of active site and the electron charge transfer reaction. The 2-aminothiophenol complexation of Ni^{2+} and Pb^{2+} are proposed to occur by the deprotonation of active sites since the extraction depends on pH of solution and number of releasing hydrogen ions from the ligand. In contrast, the Cu^{2+} complexation is a result of redox reaction that is independent of the solution pH value.

Moreover, the result in section 4.3.4 showed that the extraction mechanism of all metal ions is the neutral chelating extraction and the ionic liquid acts only as the medium for extraction, which rules out the mechanism of cation exchange between $[BMIM]^+$ of ionic liquid and metal ions. Thus, the mechanism of neutral chelate extraction of each metal ion is considered. The extraction equilibria using the stoichiometry obtained from Job's plot results are proposed as following:

Extraction equilibrium 1 is defined as the ligand extracts Ni^{2+} (1:3 ratio) and releases 2 hydrogen ions:

$$\left(\mathrm{Ni}^{2+}\right)_{aq} + 3\left(\mathrm{H_2L}\right)_{IL} \rightleftharpoons \left(\mathrm{Ni(HL)_2(H_2L)}\right)_{IL} + 2\left(\mathrm{H}^{+}\right)_{aq}$$

where H_2L is 2-aminothiophenol ligand and the subscription aq and IL refer to aqueous phase and ionic liquid phase, respectively.

The extraction equilibrium constant $K_{ex,Ni}$ is

$$K_{ex,Ni} = \frac{\left[Ni(HL)_2(H_2L)\right]_{IL}\left[H^+\right]_{aq}^2}{\left[Ni^{2+}\right]_{aq}\left[H_2L\right]_{IL}^3}$$

And the distribution ratio D is given by

$$D = \frac{\left[Ni(HL)_2(H_2L)\right]_{IL}}{\left[Ni^{2+}\right]_{aq}} = \frac{K_{ex,Ni}\left[H_2L\right]_{IL}^3}{\left[H^+\right]_{aq}^2}$$

Thus, the following equation can be obtained:

$$\log D = \log K_{ex,Ni} + 3\log\left[H_2L\right]_{IL} + 2pH$$

Extraction equilibrium 2 is defined as the ligand extracts Pb^{2+} (1:2 ratio) and releases 2 hydrogen ions:

$$\left(Pb^{2+}\right)_{aq} + 2\left(H_2L\right)_{IL} \rightleftharpoons \left(Pb(HL)_2\right)_{IL} + 2\left(H^+\right)_{aq}$$

The extraction equilibrium constant $K_{ex,Pb}$ is

$$K_{ex,Pb} = \frac{\left[Pb(HL)_2\right]_{IL}\left[H^+\right]_{aq}^2}{\left[Pb^{2+}\right]_{aq}\left[H_2L\right]_{IL}^2}$$

And the distribution ratio D is given by

$$D = \frac{\left[Pb(HL)_2\right]_{IL}}{\left[Pb^{2+}\right]_{aq}} = \frac{K_{ex,Pb}\left[H_2L\right]_{IL}^2}{\left[H^+\right]_{aq}^2}$$

Thus, the following equation can be obtained:

$$\log D = \log K_{ex,Pb} + 2\log\left[H_2L\right]_{IL} + 2\,pH$$

Extraction equilibrium 3 is defined as the ligand extracts Cu^{2+} hydration species (1:2 ratio):

$$\left(Cu(OH)_2\right)_{aq} + 2\left(H_2L\right)_{IL} \rightleftharpoons \left(CuL\left(H_2L\right)\right)_{IL} + 2\,H_2O$$

The extraction equilibrium constant $K_{ex,Cu}$ is

$$K_{ex,Cu} = \frac{\left[CuL\left(H_2L\right)\right]_{IL}}{\left[Cu(OH)_2\right]_{aq}\left[H_2L\right]_{IL}^2}$$

And the distribution ratio D is given by

$$D = \frac{\left[CuL\left(H_2L\right)\right]_{IL}}{\left[Cu(OH)_2\right]_{aq}} = K_{ex,Cu}\left[H_2L\right]_{IL}^2$$

Thus, the following equation can be obtained:

$$\log D = \log K_{ex,Cu} + 2\log\left[H_2L\right]_{IL}$$

Consequently, plots of log D as a function of log $\left[H_2L\right]_{IL}$ at constant pH value should lead to a straight line whose slope is close to 3, 2 and 2 for Ni^{2+}, Cu^{2+} and Pb^{2+} extraction, respectively. The K_{ex} of Cu^{2+} extraction can be calculated from the intercept of the graph. For Ni^{2+} and Pb^{2+} extraction, K_{ex} values were calculated from the minus of intercept and changing pH values after extraction of blank extraction (without ligand) for Ni^{2+} and Pb^{2+} that are 0.054 and 0.160, respectively.

The plot of log D versus log $\left[H_2L\right]_{IL}$ of Ni^{2+}, Cu^{2+} and Pb^{2+} extraction are shown in Figure 4.13. The result indicated that the distribution ratios increase along the concentration of 2-aminothiophenol. The slopes of linear plot between log D versus log $\left[H_2L\right]_{IL}$ are given in Table 4.9. The number of ligand in extracted complexes found by this slope analysis is close to that found using Job's plot, i.e. 3 and 2 for the complexes of Ni^{2+} and Cu^{2+}, respectively, except for Pb^{2+}.

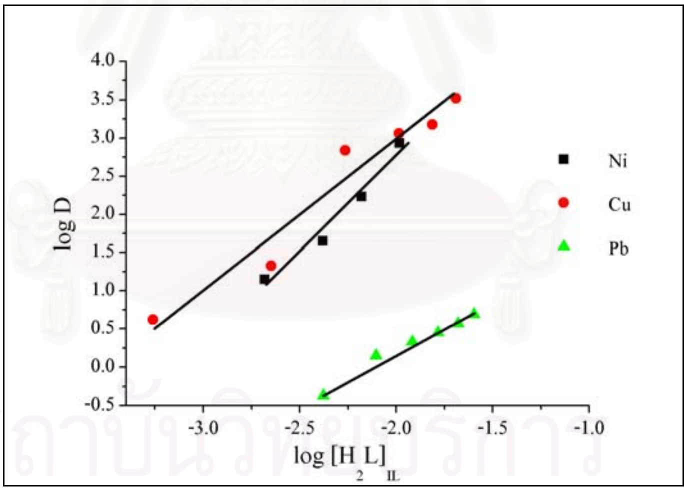


Figure 4.13 Extraction of metal ions by 2-aminothiophenol in ionic liquid at 25 °C.

where $[H_2L]_{IL}$ is a concentration of free ligand in ionic liquid

$= [H_2L]_{int} - 3[Ni^{2+}]_{IL}$ for Ni^{2+} extraction

$= [H_2L]_{int} - 2[Cu^{2+}]_{IL}$ for Cu^{2+} extraction

$= [H_2L]_{int} - 2[Pb^{2+}]_{IL}$ for Pb^{2+} extraction

Table 4.9 Summary of the equation data from the plots of log D *vs* $\left[H_2L\right]_{IL}$

Metal	Equation	R^2
Ni	y = 3.1540x + 8.5822	0.9858
Cu	y = 1.9212x + 6.7992	0.9511
Pb	y = 1.2888x + 2.7637	0.9751

The result shows that the experimental slopes are close to the slope of the proposed mechanism which supports the proposed equilibrium. The extraction constant for each metal is summarized in Table 4.10.

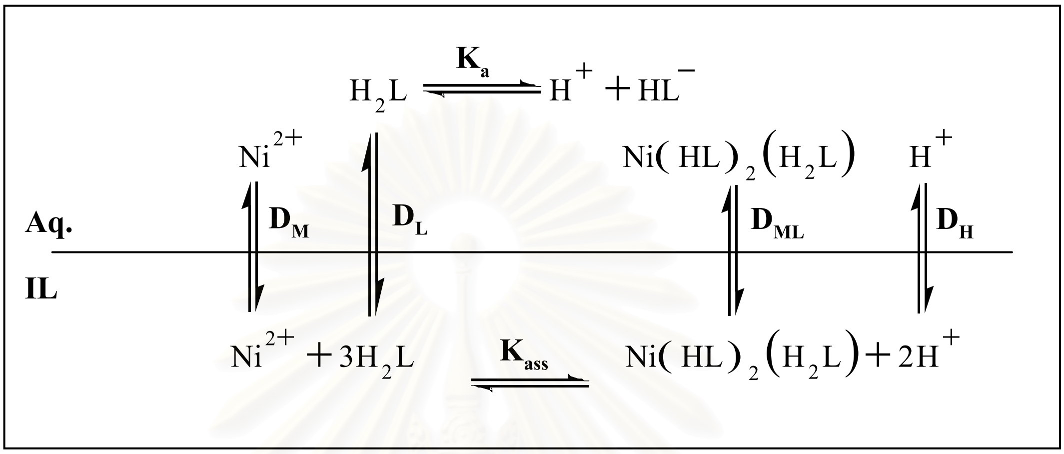
Table 4.10 Extraction constant, K_{ex} of Ni^{2+}, Cu^{2+} and Pb^{2+}

Metal	log K_{ex}	K_{ex}
Ni	8.47	2.95×10^8
Cu	6.80	6.31×10^6
Pb	2.44	2.75×10^2

As the results of extraction study in section 4.3.2 to 4.3.5 and the early discussion of the classical solvent extraction system in section 2.2.4, the possible assumption of extraction mechanism of Ni^{2+}, Cu^{2+} and Pb^{2+} with 2-aminothiophenol in ionic liquid, $[BMIM]PF_6$ could be proposed as follows:

A. Monoprotonated form of 2-Aminothiophenol for Ni^{2+} and Pb^{2+} Extraction

(a) The extraction scheme of Ni^{2+} is illustrated in Scheme 4.1.:



Scheme 4.1 Diagram of chelate extraction system of Ni^{2+} with 2-aminothiophenol (H_2L).

The equilibrium constants are defined as:

Distribution of H_2L, $$D_L = \frac{[H_2L]_{IL}}{[H_2L]_{aq}}$$

Acid-dissociation of H_2L, $$K_a = \frac{[H^+]_{aq}[HL^-]_{aq}}{[H_2L]_{aq}}$$

Formation constant of Ni^{2+} complex, $$K_f = \frac{[Ni(HL)_2(H_2L)]_{aq}[H^+]^2}{[Ni^{2+}]_{aq}[H_2L]^3_{aq}}$$

Distribution of Ni complex, $\mathrm{D_{ML}} = \dfrac{\left[\mathrm{Ni(HL)^{2}(H_2L)}\right]_{\mathrm{IL}}}{\left[\mathrm{Ni(HL)^{2}(H_2L)}\right]_{\mathrm{aq}}}$

Extraction constant, $\mathrm{K_{ex,Ni}} = \dfrac{\left[\mathrm{Ni(HL)_2(H_2L)}\right]_{\mathrm{IL}}\left[\mathrm{H^+}\right]^2_{\mathrm{aq}}}{\left[\mathrm{Ni^{2+}}\right]_{\mathrm{aq}}\left[\mathrm{H_2L}\right]^3_{\mathrm{IL}}}$

$$= \frac{\mathrm{K_f} \cdot \mathrm{D_{ML}}}{\mathrm{D^3_L}}$$

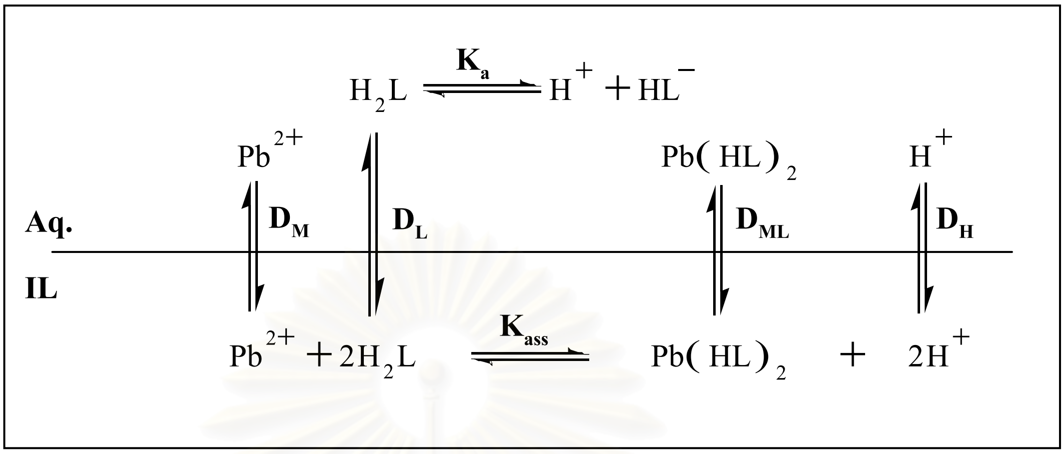
Distribution of H⁺, $\mathrm{D_H} = \dfrac{\left[\mathrm{H^+}\right]_{\mathrm{IL}}}{\left[\mathrm{H^+}\right]_{\mathrm{aq}}}$

Distribution of Ni²⁺, $\mathrm{D_M} = \dfrac{\left[\mathrm{Ni^{2+}}\right]_{\mathrm{IL}}}{\left[\mathrm{Ni^{2+}}\right]_{\mathrm{aq}}}$

Association constant, $\mathrm{K_{ass}} = \dfrac{\left[\mathrm{Ni(HL)_2(H_2L)}\right]_{\mathrm{IL}} \cdot \left[\mathrm{H^+}\right]^2_{\mathrm{IL}}}{\left[\mathrm{Ni^{2+}}\right]_{\mathrm{IL}}\left[\mathrm{H_2L}\right]^3_{\mathrm{IL}}}$

$$= \frac{\mathrm{K_{ex,Ni}} \cdot \mathrm{D^2_H}}{\mathrm{D_M}} \qquad (4.6)$$

(b) The extraction scheme of Pb^{2+} is illustrated in Scheme 4.2.:



Scheme 4.2 Diagram of chelate extraction system of Pb^{2+} with 2-aminothiophenol (H_2L).

The equilibrium constants are defined as:

Distribution of H_2L, $$D_L = \frac{[H_2L]_{IL}}{[H_2L]_{aq}}$$

Acid-dissociation of H_2L, $$K_a = \frac{[H^+]_{aq}[HL^-]_{aq}}{[H_2L]_{aq}}$$

Formation constant of Pb^{2+}, $$K_f = \frac{[Pb(HL)_2]_{aq}[H^+]_{aq}^2}{[Pb^{2+}]_{aq}[H_2L]_{aq}^2}$$

Distribution of Pb complex, $$D_{ML} = \frac{[Pb(HL)^2]_{IL}}{[Pb(HL)^2]_{aq}}$$

Extraction constant, $$K_{ex,Pb} = \frac{\left[Pb(HL)_2\right]_{IL}\left[H^+\right]_{aq}^2}{\left[Pb^{2+}\right]_{aq}\left[H_2L\right]_{IL}^2}$$

$$= \frac{K_f \cdot D_{ML}}{D_L^2}$$

Distribution of Pb^{2+}, $$D_M = \frac{\left[Pb^{2+}\right]_{IL}}{\left[Pb^{2+}\right]_{aq}}$$

Distribution of H$^+$, $$D_H = \frac{\left[H^+\right]_{IL}}{\left[H^+\right]_{aq}}$$

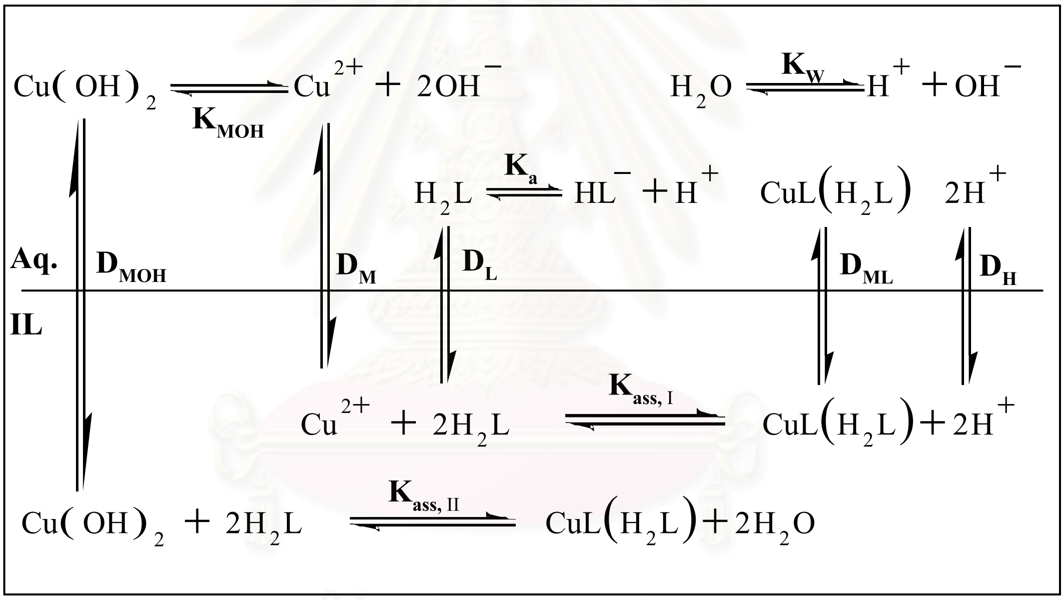
Association constant, $$K_{ass} = \frac{\left[Pb(HL)_2\right]_{IL} \cdot \left[H^+\right]_{IL}^2}{\left[Pb^{2+}\right]_{IL}\left[H_2L\right]_{IL}^2}$$

$$= \frac{K_{ex,Pb} \cdot D_H^2}{D_M} \qquad (4.7)$$

B. Coordinated π Radical form of 2-Aminothiophenol for Cu^{2+} Extraction

As seen in the previous result of the effect of pH on Cu^{2+} extraction, the percentage extraction of Cu^{2+} is independent of the pH values. The extraction mechanism presumably involves redox reaction. Cu^{2+} could be reduced to Cu^{+} by 2-aminothiophenol. This result was confirmed by ESR result (section 4.3.2). Thus the extraction mechanism was proposed as follows.

The extraction scheme of Cu^{2+} is illustrated in Scheme 4.3.:



Scheme 4.3 Diagram of chelate extraction system of Cu^{2+} with 2-aminothiophenol (H_2L).

The equilibrium constants are defined as:

Distribution of H_2L, $$D_L = \frac{[H_2L]_{IL}}{[H_2L]_{aq}}$$

Acid-dissociation of H_2L, $$K_a = \frac{[H^+]_{aq}^2[L^{2-}]_{aq}}{[H_2L]_{aq}}$$

Formation constant of Cu^{2+}, $$K_f = \frac{[CuL(H_2L)]_{aq}[H^+]_{aq}^2}{[Cu^{2+}]_{aq}[H_2L]_{IL}^2}$$

Distribution of Cu complex, $$D_{ML} = \frac{[CuL(H_2L)]_{IL}}{[CuL(H_2L)]_{aq}}$$

Metal hydration constant, $$K_{MOH} = \frac{[Cu(OH)_2]_{aq}}{[Cu^{2+}]_{aq}[OH^-]^2} = 6.31\times 10^{12}$$ [68]

Ion-product constant, $$K_w = [H^+][OH^-] = 1.0\times 10^{-14}$$

Extraction constant, $$K_{ex,Cu} = \frac{[CuL(H_2L)]_{IL}}{[Cu(OH)_2]_{aq}[H_2L]_{IL}^2}$$

$$= \frac{K_f \cdot D_{ML}}{K_{MOH} \cdot K_w^2 \cdot D_L^2}$$

Distribution of Cu^{2+}, $$D_M = \frac{[Cu^{2+}]_{IL}}{[Cu^{2+}]_{aq}}$$

Distribution of H^+, $$D_H = \frac{[H^+]_{IL}}{[H^+]_{aq}}$$

Distribution of H_2O, $D_{H_2O} = \dfrac{[H_2O]_{IL}}{[H_2O]_{aq}}$

As supposed that the copper extracted species involved the extraction of Cu^{2+} might be either $Cu(OH)_2$ or Cu^{2+}, the association constant of Cu^{2+} extraction can derive in 2 cases as follow.

<u>Case I:</u> the extracted species is Cu^{2+}

Association constant, $K_{ass,I} = \dfrac{[CuL(H_2L)]_{IL} \cdot [H^+]^2_{IL}}{[Cu^{2+}]_{IL}[H_2L]^2_{IL}}$

$$= \frac{K_{ex,Cu} \cdot D^2_H \cdot K_{MOH} \cdot K^2_W}{D_M} \qquad (4.8)$$

<u>Case II:</u> the extracted species is $Cu(OH)_2$

Association constant, $K_{ass,II} = \dfrac{[CuL(H_2L)]_{IL} \cdot [H_2O]^2_{IL}}{[Cu(OH)_2]_{IL}[H_2L]^2_{IL}}$

$$= \frac{K_{ex,Cu} \cdot D^2_{H_2O}}{D_{MOH}} \qquad (4.9)$$

Normally, the separation efficiency of metal ions in solvent extraction is reported in term of distribution ratio or percentage extraction. The distribution ratio or percentage extraction values can be predicted from a set of equilibrium constants. Association constant is one parameter that can forecast the metal extraction efficiency. The association constant is calculated from the relation between extraction constant and other equilibrium constants that are the distribution constant of each metal ion and the distribution constant of proton as shown in Equation 4.6 to 4.8. The metal distribution constant is estimated from the blank extraction of each metal ion with water rich ionic liquid (ionic liquid saturated with DI water). The experimental values are showed in Table 4.11.

Table 4.11 Value of metal distribution constant, D_M

Metal	D_M	Mean±SD*
Ni	9.11×10^{-2}	$9.11 \times 10^{-2} \pm 0.01$
	9.11×10^{-2}	
	9.11×10^{-2}	
Cu	8.94×10^{-2}	$8.94 \times 10^{-2} \pm 0.01$
	8.94×10^{-2}	
	8.94×10^{-2}	
Pb	9.09×10^{-2}	$9.09 \times 10^{-2} \pm 0.01$
	9.09×10^{-2}	
	9.09×10^{-2}	

Since PF_6^- in ionic liquid can decompose and be hydrolyzed to an acid which affects the determination of proton distribution constant, thus the study was performed by adjustment the pH value of saturated DI water to 2 and let it contact with water-rich ionic liquid. The pH values of aqueous solution before and after extraction were measured. The result showed that after extraction the pH value of aqueous solution is changed from 2.019 to 2.031 and the calculated proton distribution constant is 0.13±0.02 (n=10). The calculated association of Ni^{2+}, Cu^{2+} and Pb^{2+} extraction are displayed in Table 4.12.

Table 4.12 Summary of values of equilibrium constant and association constant of Ni^{2+}, Cu^{2+} and Pb^{2+} extraction

Metal	K_{ex}	D_H	D_M	D_{MOH}	K_w	K_{ass}	K_{ass} (value)
Ni	2.95×10^8	0.13	0.0911	-	10^{-14}	$\frac{K_{ex} \cdot D_H^2}{D_M}$	5.47×10^7
Cu	6.31×10^6	0.13	0.0894	6.31×10^{12}	10^{-14}	$\frac{K_{ex} \cdot D_H^2 \cdot K_{MOH} \cdot K_W^2}{D_M}$	7.53×10^{-10}
Pb	2.75×10^2	0.13	0.0909	-	10^{-14}	$\frac{K_{ex} \cdot D_H^2}{D_M}$	51.1

As mentioned in Equation 4.9, the association constant of $Cu(OH)_2$ correlated to the distribution of water. Since the distribution of water cannot be determined so the association constant of $Cu(OH)_2$ extraction; $K_{ass,II}$, cannot be calculated. For Cu^{2+}, the calculated association constant in Table 4.12 shows a low association constant that conflict with the previously observed high percentage extraction (up to 75%). This result indicates that Cu^{2+} is not a main extracting species by 2-aminothiophenol.

4.4 Stripping Study

4.4.1 Type and Concentration of Stripping Reagents

Stripping is a recovery of extracted metal ions from the extractant phase to the stripping phase. Types and concentration of stripping agent have to be compatible with the determination technique if an analytical application is desired. The selection of stripping agent depends on the extraction mechanism and the strong interaction between metal and ligand. The results were plotted between the percentage stripping (% Stripping) versus the concentration of stripping agent.

Because the absolute separation of the aqueous phase from the ionic liquid phase is impossible, the stripping study was performed by removing 4.5 mL of extracted aqueous metal ion solution, following by addition of 5.0 mL of the stripping agent solution to the remaining mixture (0.5 mL aqueous + 1.0 mL ionic liquid). The results of stripping efficiency are shown in term of percentage stripping (% Stripping) calculated from Equation 4.10.

$$\%\text{Stripping} = \frac{\left(C_s \times 5.5\right)_{aq} - \left(C_f \times 0.5\right)_{aq}}{\left(C_i - C_f\right)_{aq}} \times 100 \qquad (4.10)$$

where $\left(C_i\right)_{aq}$ is the initial concentration of metal ions in aqueous phase before extraction (mM)

$\left(C_f\right)_{aq}$ is the concentration of metal ions in aqueous phase after extraction (mM)

$\left(C_s\right)_{aq}$ is the concentration of metal ions in aqueous phase after stripping (mM)

Since the previous results showed that the extraction of metal ions depends on the pH of solution, acid solution was attractive as stripping solution. In addition, for the determination of metal ion using FAAS, the technique-compatible nitric acid solution was firstly selected as a stripping agent. Moreover, nitric acid can react with the complex of Cu that occurred via electron transfer reaction by acting as oxidizing agent to remover Cu^{+} to Cu^{2+}. The stripping efficiency of Ni^{2+}, Cu^{2+} and Pb^{2+} with nitric acid at various concentrations (0.5-2 M) is illustrated in Figure 4.14. The results showed that using 0.5 M or higher concentration of nitric acid, more than 90% stripping of Cu^{2+} and Pb^{2+} was obtained. For Ni^{2+} stripping, the result suggested that the stripping efficiency increased gradually with increasing of the concentration of the acid. The study found that the concentration of nitric acid at 3 to 5 M was sufficient to strip Ni^{2+} with more than 90% stripping.

However, using of high acidic solution for stripping Ni^{2+} led to decomposition reaction of PF_6^- producing HF and PO_4^{3-} [27]. An alternative way is to use a chelating agent that form stronger complex with Ni^{2+} than 2-aminothiophenol, one of the choices is EDTA which is known for high formation constants with many metal ions. However, the results obtained in Table 4.13 showed that the amounts of Ni^{2+} after stripping with EDTA were under instrumental limit of detection, which means remaining Ni^{2+} after extraction was also drawn into ionic liquid phase in the stripping step. This is probably explained by the dissolution of Ni-EDTA complex in ionic liquid phase.

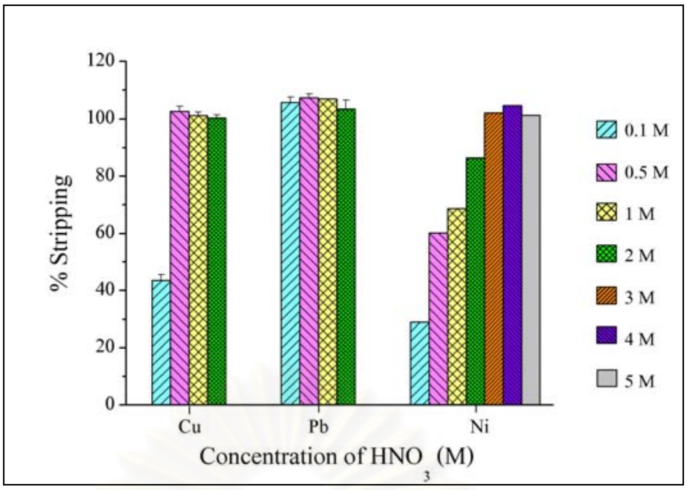


Figure 4.14 Effect of HNO_3 concentration on the stripping efficiency of each metal.

Table 4.13 Effect of EDTA and H_2O_2 on the Ni^{2+} stripping

Stripping agent	Concentration	% Stripping*
EDTA (M)		
	0.1	ND
	0.5	ND
	1.0	ND
H_2O_2 (%)		
in 0.5 M HNO_3	3	98±1
in 1.0 M HNO_3	3	102±3
in DI water	3	65±1
in 0.1 M NaOH	3	ND

*Mean value±SD, n=3

ND = Not Detectable, LOD = 3.31 x 10^{-7} mM

On the account that 2-aminothiophenol has an electron charge transfer property, the alternative way for stripping Ni^{2+} is by using a oxidizing agent. H_2O_2 is an attractive stripping agent due to their dual properties of oxidizing and reducing agent in acid and basic medium following Equation 4.11.

$$\text{Acidic medium:} \quad H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad (4.11)$$

$$\text{Basic medium:} \quad H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

The stripping ability of H_2O_2 in acidic and basic medium was shown in Table 4.13. The result showed that more than 95 % of Ni^{2+} was stripped using H_2O_2 in 0.5 M and 1 M HNO_3. In contrast, using H_2O_2 in 0.1 M NaOH is unable to strip Ni^{2+}. The different stripping efficiency of H_2O_2 in each medium can be explained by the redox property of H_2O_2. In the acidic medium, H_2O_2 acts as oxidizing agent that probably might oxidize the coordinated 2-aminothiophenol as shown in the oxidation in Equation 4.12 [70]. The reduced ligand species probably forms less stable complex with Ni^{2+} leading to higher stripping efficiency.

$$2RSH \longrightarrow RSSH + 2H^+ + 2e^- \qquad (4.12)$$

$$2RSH \longrightarrow 2RS + 2H^+ + 2e^-$$

The result concluded that the suitable stripping agent was HNO_3 at concentration higher than 0.5 M for Cu^{2+} and Pb^{2+}. The HNO_3 at least 3 M and 3% H_2O_2 in acid solution were suitable for Ni^{2+} stripping.

4.4.2 Stripping Time

The kinetics of stripping was studied by determination of % stripping as a function of time. The result in Figure 4.15 showed that more than 95% stripping of Pb^{2+} and Cu^{2+} by 1 M HNO_3 occurred rapidly within 10 minutes and 20 minutes, respectively. For Ni^{2+}, the kinetic studies of three types of stripping agents, 3 M HNO_3, 3% H_2O_2 in 0.5 M and 1 M HNO_3 were compared in Figure 4.16. The stripping kinetics of H_2O_2 occurred in a shorter time than HNO_3. More than 95 % stripping of Ni^{2+} by 3 M HNO_3, 3% H_2O_2 in 0.5 M and 1M HNO_3 occurred at 30, 20 and 10 minutes, respectively.

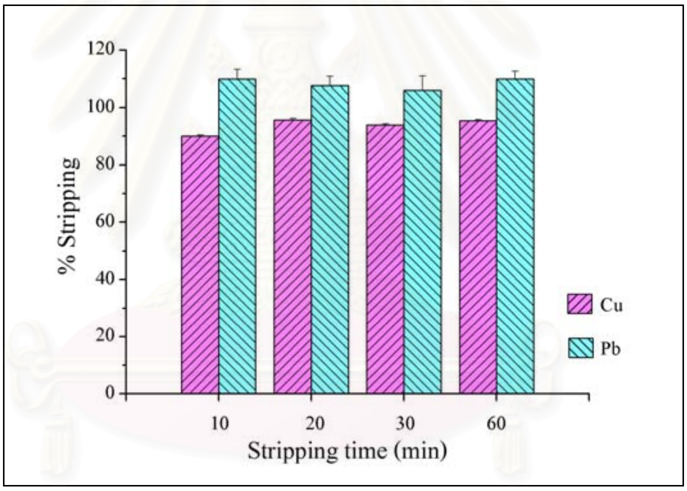


Figure 4.15 Effect of stripping time for Cu^{2+} and Pb^{2+} by 1 M HNO_3.

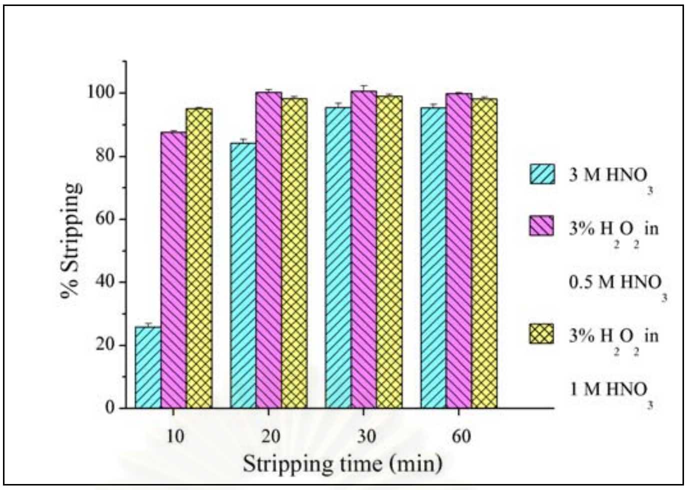


Figure 4.16 Effect of stripping time for Ni^{2+} by 3 M HNO_3, 3% H_2O_2 in 0.5 M and 1 M HNO_3.

CHAPTER V

CONCLUSION

A room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), was synthesized via the reaction of anion metathesis between 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and hexafluorophosphoric acid (HPF_6). The characterization of viscous yellow liquid product with FTIR and ^{1}H-NMR showed that the synthesis of ionic liquid was successful. The comparison of FTIR spectra between the synthetic product and the commercial ionic liquid displayed the similar spectra of ν(P-F) at wavenumber 841 cm^{-1} and the disappearance of the hydrogen bonding of CH…Cl around 3000-3100 cm^{-1}. The similarity between ^{1}H NMR spectra of synthetic and commercial ionic liquid [BMIM]PF_6 showed the existence of an imidazolium ring.

The synthetic ionic liquid was used as a biphasic phase combined with 2-aminothiophenol ligand for the extraction of Ni^{2+}, Cu^{2+} and Pb^{2+} in water. Various parameters affecting the liquid-liquid extraction efficiency, i.e. solution pH, extraction time, interfering ions, types of stripping agent and stripping time were studied. The comparison of the extraction efficiency in two mediums; ionic liquid and chloroform showed that using of ionic liquid as a medium gave metal extraction efficiencies higher than using chloroform.

The study of optimum condition for Ni^{2+}, Cu^{2+} and Pb^{2+} extraction manifested that the extraction of Ni^{2+}, Pb^{2+} depended on the pH value of solution where the complex is formed via the deprotonation of thio- active site. The optimum pH values for Ni^{2+} and Pb^{2+} extraction are 4-6 and 5, respectively. The number of proton dissociated of both metal ions is 2. For Cu^{2+}, the extraction efficiency is independent of the pH of solution because the complex occurred via an electron transfer reaction. The percentage extractions of Ni^{2+}, Cu^{2+} and Pb^{2+} were about 100%, 100% and 80%, respectively when using their initial metal concentration of 5 mg L^{-1} and 57%, 76% and 20%, respectively, when using their initial metal concentration of 1.0 mM. The extraction reached equilibrium at more than 120 minutes for Ni^{2+} and 30 minutes for Cu^{2+} and Pb^{2+}. The competitive ions such as Na^{+}, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^{-} did not significantly affect the extraction efficiency of Ni^{2+}, Cu^{2+} and Pb^{2+}. The extraction of three metal ions is independent of the type of counter-ion and concentration of [BMIM]Cl in aqueous phase. This revealed that the extraction mechanism is not the cation exchange of $[BMIM]^{+}$. The percentage losses of NO_3^{-} during Ni^{2+}, Cu^{2+} and Pb^{2+} extraction are 4.8±0.4, 3.4±1.7 and 0.8±0.4, respectively. This represented that the extraction mechanism is not ion-pair extraction system.

The extracted Ni^{2+} in ionic liquid phase could be back-transferred with HNO_3 at concentration more than 3 M with contact time of 30 minutes and 3% H_2O_2 in 0.5 M and 1 M HNO_3 at 20 minutes of contact time with the percentage stripping higher than 95 %. Both Cu^{2+} and Pb^{2+} could be stripped with 1 M HNO_3 with the percentage stripping of more than 95 % at contact time of 20 and 10 minutes, respectively.

The extraction mechanisms of Ni^{2+}, Cu^{2+} and Pb^{2+} were determined by classical slope analysis method. The result of the slope analysis is similar to the Job's plot method. It indicated that the stoichiometries of metal : ligand are 1:3, 1:2 and 1:2 for Ni^{2+}, Cu^{2+} and Pb^{2+}, respectively. The values of association constant are 5.47×10^{7} and 51.1 for Ni^{2+} and Pb^{2+}, respectively.

Suggestions for Future Work

As the aforementioned results and discussion, the ionic liquid could be a suitable agent for organic solvent replacement. The knowledge of liquid-liquid extraction and properties of 2-aminothiophenol in ionic liquid toward Ni^{2+}, Cu^{2+} and Pb^{2+} could predict the extraction efficiency and be applied for real wastewater. Future works may focus on the application of the ligand in ionic liquid for extraction of metal ions from real wastewater. Moreover, the analytical application of the proposed extraction method for the enrichment of trace amount of the studied metal ions from aqueous samples prior to determination by FAAS is very interesting to investigate.

REFERENCES

[1] Bradl, H.B. Heavy metals in the environment. Interface Science and Technology 6 (2005).

[2] The Ministry of Science, Technology and Environment of Thailand. The notification the Ministry of Science, Technology and Environment, No. 3, [B.E.2539 (1996)] issued under the enhancement and conservation of the national environmental quality act B.E.2535 (1992), 1996.

[3] Gunzler, H.; and Williams, A. Handbook of analytical techniques. Weinheim, Germany: WILEY-VCH, 2001.

[4] Kentish, S.E.; and Stevens, G.W. Innovations in separations technology for the recycling and re-use of liquid waste streams. Chemical Engineering Journal 84 (2001): 149-159.

[5] Liquid Separation Technologies and Equipment, LLC [Online]. (n.d.). Available from: http://lst-equip.com/industry.htm[2008, March 1]

[6] Wernick, I.; and Themelis, N.J. Recycling metals for the environment. Annual Review of Energy and the Environment 23 (1998): 465-497.

[7] Frenzel, I.; Stamatialis, D.F.; and Wessling, M. Water recycling from mixed chromic acid waste effluents by membrane technology. Separation and Purification Technology 49(1) (2006): 76-83.

[8] Christian, G.D. Analytical chemistry. 5th ed., 1994.

[9] Dean, J.A. Chemical separation methods., New York: D. Van Nostrand Company, 1969.

[10] Synder, L.R.; Kirkland, J.J.; and Glajch, J.L. Practical HPLC method development. 2nd ed. USA: John Wiley & sons, 1997.

[11] Morrison, G.H.; and Freiser, H. Solvent extraction in analytical chemistry. 2nd ed. New York: John Wiely & sons, 1962.

[12] Mark, R.L. The hard soft [Lewis] acid base principle [online]. (n.d.). Available from: http://www.metasynthesis.com/webbook/43_hsab/HSAB.html[2005 August 10]

[13] Harris, D.C. Quantitative chemical analysis. 6th ed. New York: Michelle Russel Julet, 2002.

[14] Larkworthy, L.F.; Murphy, J.M.; and Phillips, D.J. Metal complexes of o-aminobenzenethiol. Inorganic Chemistry 7(7) (1968): 1436-1443.

[15] Gardner, J.K.; Pariyadath, N.; Corbin, J. L.; and Stiefel, E. I. Molybdenum and rhenium complexes of aromatic aminethiolate ligands. Inorganic Chemistry 17(4) (1978): 897-904.

[16] Affsprung, H.E.; and Mitchell, R.E. o-Aminobenzenethiol: an oxidimetric indicator for hydrogen ion and reagent for metals. Analytica Chimica Acta 32 (1965): 496-499.

[17] Chakrabarti, A.K.; and Bag, S.P. Solvent extraction and photometric determination of molybdenum (VI) with 2-aminobenzenethiol. Talanta 23(10) (1976): 736-738.

[18] Casassas, E.; and Visa, T. Synthesis and characterization of Bi(III) complexes of 2-aminobenzenethiol. Polyhedron 5(10) (1986): 1513-1518.

[19] Alonzo, G. Synthesis and characterization of some arsenic, antimony and bismuth complexes of 2-mercaptoaniline. Inorganica Chimica Acta 73 (1983): 141-144.

[20] Holm, R.H.; Balch, A.L.; Davison, A.; Maki, A.H.; and Berry, T.E. Electron-transfer complexes of the [M-N_2S_2] type. The existence of cation-stabilized free-radical complexes. Journal of the American Chemical Society 89(12) (1967): 2866-2874.

[21] Kapre, R.R. Experimental study on transition metal complexes containing N,S'-, S,S'- and O,O'- coordinated radicals in chemistry. Ruhr-Universitut Bochum: Mulheim an der Ruhr. (2005):1-33.

[22] Stiefel, E.I.; Waters, J.H.; Billig, E.; and Gray, H.B. The myth of Nickel(III) and Nickel(IV) in planar complexes. Journal of the American Chemical Society 87(13) (1965): 3016-3017.

[23] Balch, A.L.; Rohrscheid, F.; and Holm, R.H. New systems of complexes related by electron-transfer reactions. Journal of the American Chemical Society 87(10) (1965): 2301-2302.

[24] Bankmann, D.; and Giernoth, R. Magnetic resonance spectroscopy in ionic liquids. Progress in Nuclear Magnetic Resonance Spectroscopy 51 (2007): 63-90.

[25] Karkkainen, J. Preparation and characterization of some ionic liquids and their use in the dimerization reaction of 2-methylpropene. Acta Universitatis Ouluexsis. A Scientiae Rerum Naturalium 480, 2007.

[26] Senda, K.; Defne K.T.; Ugur, A.; and Oner, H. A review of ionic liquids towards supercritical fluid applications. The Journal of Supercritical Fluids 43(1) (2007): 150-180.

[27] Huddleston, J.G.; Visser, A.E.; Reichert, W.M.; Willauer, H.D.; Broker, G.A.; and Rogers, R.D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. Green Chemistry 3 (2001): 156-164.

[28] Zhao, H. Current studies on some physical properties of ionic liquids. Physics and Chemistry of Liquids 41(6) (2003): 545-557.

[29] Seddon, R.K.; Stark, A.; and Torres, M.J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. Pure and Applied Chemistry 72(12) (2000): 2275-2287.

[30] Dupont, J.; Souza, R.F.; and Suarez, P.A.Z. Ionic liquid (molten salt) phase organometallic catalysis. Chemical Reviews 102(10) (2002): 3667-3692.

[31] Yang, Z.; and Pan, W. Ionic liquids: Green solvents for non aqueous biocatalysis. Enzyme and Microbial Technology 37(1) (2005): 19-28.

[32] Marsh, K.N.; Boxall, J.A.; and Lichtenthaler, R. Room temperature ionic liquids and their mixtures--a review. Fluid Phase Equilibria 219(1) (2004): 93-98.

[33] Dupont, J.; Consorti, R.S.; Suarez, P.A.Z.; and Souza, R.F. Preparation of 1-butyl-3-methyl imidazolium-based room temperature ionic liquids. Organic Syntheses 10 (2004): 184.

[34] Villagran, C.; Deetlefs, M.; Pitner, W.R.; and Hardacre, C. Quantification of halide in ionic liquids using ion chromatography. Analytical Chemistry 76(7) (2004.): 2118-2123.

[35] Varma, R.S.; and Namboodiri, V.V. An expeditious solvent-free route to ionic liquids using microwaves Chemical Communications 7 (2001): 643 - 644.

[36] Deetlefs, M.; and Seddon, K.R. Improved preparations of ionic liquids using microwave irradiation. Green Chemistry 5 (2003): 181-186.

[37] Khadilkar, B.M.; and Rebeiro, G.L. Microwave-assisted synthesis of room-temperature ionic liquid precursor in closed vessel. Organic Process Research and Development 6(6) (2002): 826-828.

[38] Lévêque, J.M.; Luche, J.L.; Pétrier, C.; Roux R.; and Bonrath, W. An improved preparation of ionic liquids by ultrasound. Green Chemistry 4 (2002): 357-360.

[39] Koel, M. Physical and chemical properties of ionic liquids based on the dialkylimidazolium cation. Proceedings of the Estonian Academy of Sciences, Chemistry. 49 (2000): 145-155.

[40] Huang, J.F.; Chen, P.Y.; Sun, I.W.; and Wang, S.P. NMR evidence of hydrogen bonding in 1-ethyl-3-methylimidazolium-tetrafluoroborate room temperature ionic liquid. Inorganica Chimica Acta 320(1-2) (2001): 7-11.

[41] Lin, S.T.; Ding, M.F.; Chang, C.W.; and Lue, S.S. Nuclear magnetic resonance spectroscopic study on ionic liquids of 1-alkyl-3-methylimidazolium salts. Tetrahedron 60(42) (2004): 9441-9446.

[42] Tait, S.; and Osteryoung, R.A. Infrared study of ambient-temperature chloroaluminates as a function of melt acidity. Inorganic Chemistry 23(25) (1984): 4352-4360.

[43] Cammarata, L.; Kazarian, S. G.; Salter, P. A.; and Welton, T. Molecular states of water in room temperature ionic liquids. Physical Chemistry Chemical Physics 3 (2001): 5192-5200.

[44] Talaty, E.R.; Raja, S.; Storhaug, V.J.; Dolle, A.; and Carper, W.R. Raman and infrared spectra and ab initio calculations of C_{2-4}MIM imidazolium hexafluorophosphate Ionic Liquids. Journal of Physical Chemistry B 108(35) (2004):13177-13184.

[45] Infrared Spectroscopy [Online] Wikipedia, t.f.e. Available from: http://en.wikipedia.org/wiki/Infrared_spectroscopy[2008 January12]

[46] Endres, F.; and Abedin, S.Z.E. Air and water stable ionic liquids in physical chemistry. Physical Chemistry Chemical Physics 8 (2006): 2101-2116.

[47] Dupont, J. On the solid, liquid and solution structural organization of imidazolium ionic liquids. Journal of the Brazilian Chemical Society 15(3) (2004): 341-350.

[48] Paul, A.; Mandal, P.K.; and Samanta, A. How transparent are the imidazolium ionic liquids? A case study with 1-methyl-3-butylimidazolium hexafluorophosphate, [BMIM][PF_6]. Chemical Physics Letters 402(4-6) (2005): 375-379.

[49] Paul, A.; Mandal, P.K.; and Samanta, A. On the optical properties of the imidazolium ionic liquids. Journal of Physical Chemistry B 109(18) (2005): 9148-9153.

[50] Huddleston, J.G.; Willauer, H.D.; Swatloski, R.P.; Visser, A.E.; and Rogers, R.D. Room temperature ionic liquids as novel media for ‘clean’ liquid–liquid extraction. Chemical Communications 16 (1998): 1765-1766.

[51] Visser, A.E.; Swatloski, R.P.; and Rogers, R.D. pH-Dependent partitioning in room temperature ionic liquids provides a link to traditional solvent extraction behavior. Green Chemistry 1 (2000): 1-4.

[52] Dai, S.; Ju, Y.H.; and Barnes, C.E. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. Journal of the Chemical Society, Dalton Transactions 8 (1999): 1201-1202.

[53] Visser, A.E.; Swatloski, R.P.; Reichert, W.M.; Griffin, S.T.; and Rogers, R.D. Traditional extractants in nontraditional solvents: Groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. Industrial and Engineering Chemistry Research 39(10) (2000): 3596-3604.

[54] Visser, A.E.; Swatloski, R.P.; Griffin, S.T.; Hartman, D.H.; and Rogers, R.D. Liquid-liquid extraction of metal ions in room temperature ionic liquids. Separation Science and Technology 36(5-6) (2001): 785-804.

[55] Visser, A.E.; Swatloski, R.P.; Reichert, W.M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J.H.; and Rogers, R.D. Task-specific ionic liquids incorporating novel cations for the coordination and extraction of Hg^{2+} and Cd^{2+}: synthesis, characterization, and extraction studies. Environmental Science and Technology 36(11) (2002): 2523-2529.

[56] Chun, S.; Dzyuba, S.V.; and Bartsch, R.A. Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a Crown Ether. Analytical Chemistry 73(15) (2001): 3737-3741.

[57] Wei, G.T.; Yang, Z.; and Chen, C.J. Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions. Analytica Chimica Acta 488(2) (2003): 183-192.

[58] Luo, H.; Dai, S.; and Bonnesen, P.V. Solvent extraction of Sr^{2+} and Cs^{+} based on room-temperature ionic liquids containing Monoaza-Substituted Crown Ethers. Analytical Chemistry 76(10) (2004): 2773-2779.

[59] Luo, H.; Dai, S.; Bonnesen, P.V.; Buchanan, A.C.; Holbrey, J.D.; Bridges, N.J.; and Rogers, R.D. Extraction of cesium ions from aqueous solutions using Calix[4]arene-bis(*tert*-octylbenzo-crown-6) in ionic liquids. Analytical Chemistry 76(11) (2004): 3078-3083.

[60] Shimojo, K.; and Goto, M. Solvent extraction and stripping of silver ions in room-temperature ionic liquids containing calixarenes. Analytical Chemistry 76(17) (2004): 5039-5044.

[61] Ajioka, T.; Oshima, S.; and Hirayama, N. Use of 8-sulfonamidoquinoline derivatives as chelate extraction reagents in ionic liquid extraction system. Talanta 74(4) (2008): 903-908.

[62] Dietz, M.L.; and Dzielawa, J.A. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the 'greenness' of ionic liquids as diluents in liquid–liquid extraction. Chemical Communications 20 (2001): 2124-2125.

[63] Jensen, M.P.; Neuefeind, J.; Beitz, J.V.; Skanthakumar, S.; and Soderholm, L. Mechanisms of metal ion transfer into room-temperature ionic liquids: the role of anion exchange. Journal of the American Chemical Society 125(50) (2003): 15466-15473.

[64] Cocalia, V.A.; Holbrey, J.D.; Gutowski, K.E.; Bridges, N.J.; and Rogers, R.D. Separations of metal ions using ionic liquids: the challenges of multiple mechanisms. Tsinghua Science & Technology 11(2) (2006): 188-193.

[65] Jensen, M.P.; Dzielawa, J.A.; Rickert, P.; and Dietz, M.L. EXAFS investigations of the mechanism of facilitated ion transfer into a room-temperature ionic liquid. Journal of the American Chemical Society 124(36) (2002): 10664-10665.

[66] Skoog, D.A.; and West, D.M. Fundamentals of analytical chemistry. 2nd ed. Holt, Rinehart and Winston, 1969.

[67] Olszewski, E.J.; and Albinak, M.J. Synthesis and properties of some complexes of 2-aminobenzenethiol. Journal of Inorganic and Nuclear Chemistry 27(6) (1965): 1431-1433.

[68] Smith, R.M.; and Martell, A.E. Critical stability constant. 4 (1981).

[69] Holbrey, J.D.; Seddon, K.R.; and Wareing, R. A simple colorimetric method for the quality control of 1-alkyl-3-methylimidazolium ionic liquid precursors. Green Chemistry 3 (2001): 33-36.

[70] Parkash, R.; Kalia, R.K.; Singh, R.P.; and Kmnar, N. Polarographic studies on o-aminobenzenethiol Monatshefte fur Chemie 108 (1977): 589-598.

APPENDIX

Appendix A. ESR Results

Two ESR spectra were obtained from two ionic liquid solutions as follows.

Spectrum A.1: Cu^+ solution was prepared by dissolving CuCl in DI water. The Cu^+ solution was contacted with ionic liquid containing 2-aminothiophenol ligand. The ionic liquid became deep blue after the extraction with Cu^+. The deep blue ionic liquid phase was separated and characterized by ESR spectrometry at the Scientific and technology Research Equipment Center, Chulalongkorn University, using ESR Spectrometer of JEOL, model JES-RE2X. The ESR conditions are as follows:

1. Microwave unit : X band, frequency : 8.8-9.6 GHz
2. Cavity : cylindrical, operating in TE_{011} mode
3. Mn^{2+}/MgO is used for calibration. The g value of the fourth signal from the lowest magnetic field is known as 1.981 and the value of the third signal should be 2.034
4. g value = 0.071448 x microwave frequency (GHz)/ magnetic field (Tesla)

Spectrum A.2: the spectrum A.2 was obtained by the same procedure as described above, except that the Cu^{2+} solution prepared from $Cu(NO_3)_2$ was used. The similar deep blue color of ionic liquid phase was observed.

Both spectra display the same feather. No ESR active peak was found. This indicates that copper ion in two ionic liquid phases are Cu^+ which is ESR inactive due to its $[Ar]3d^{10}$ configuration, while Cu^{2+} is ESR active ion which has an unpaired electron in $[Ar]3d^9$ configuration.

Figure A.1 ESR spectrum of Cu^+ complexed with 2-aminothiophenol.

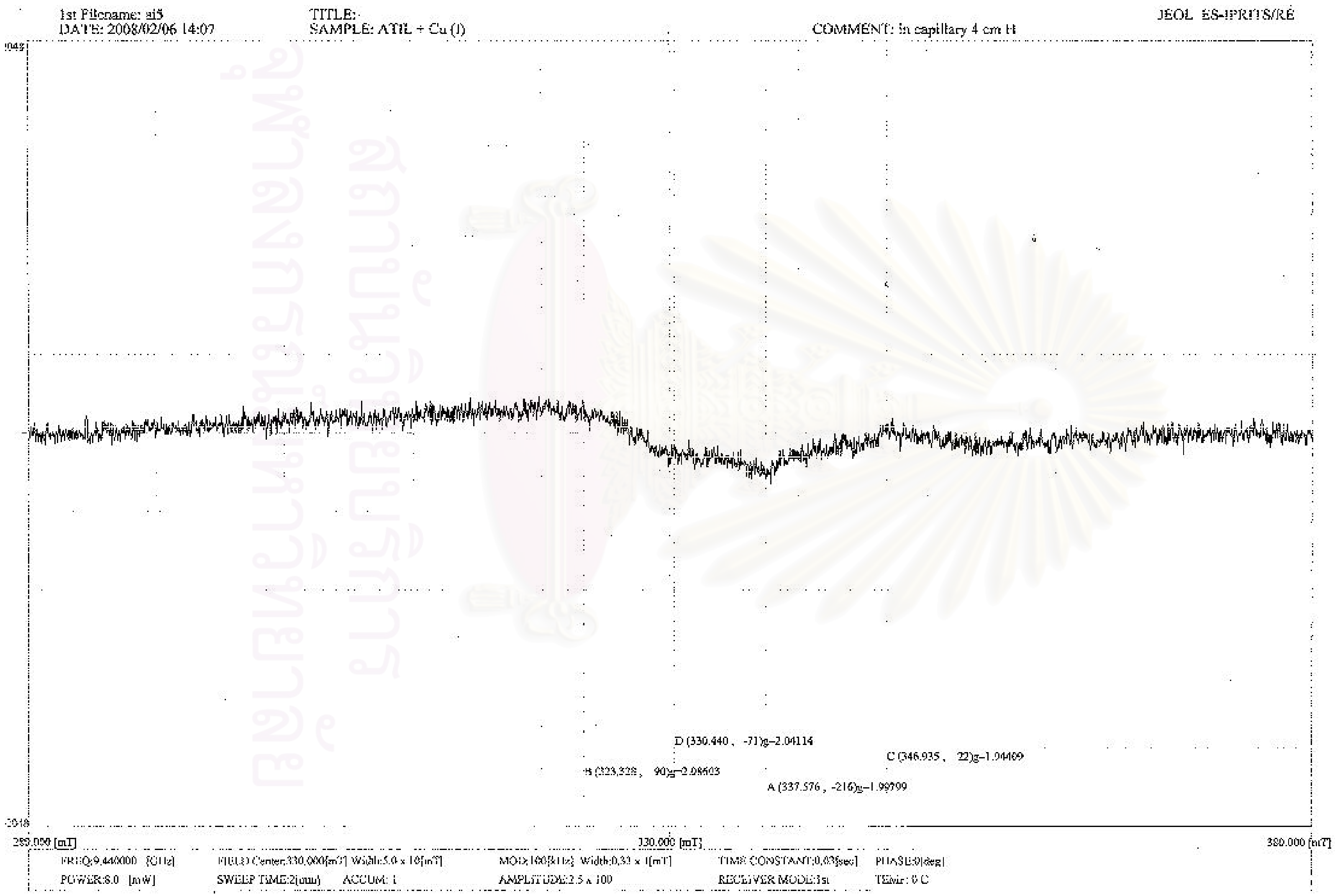
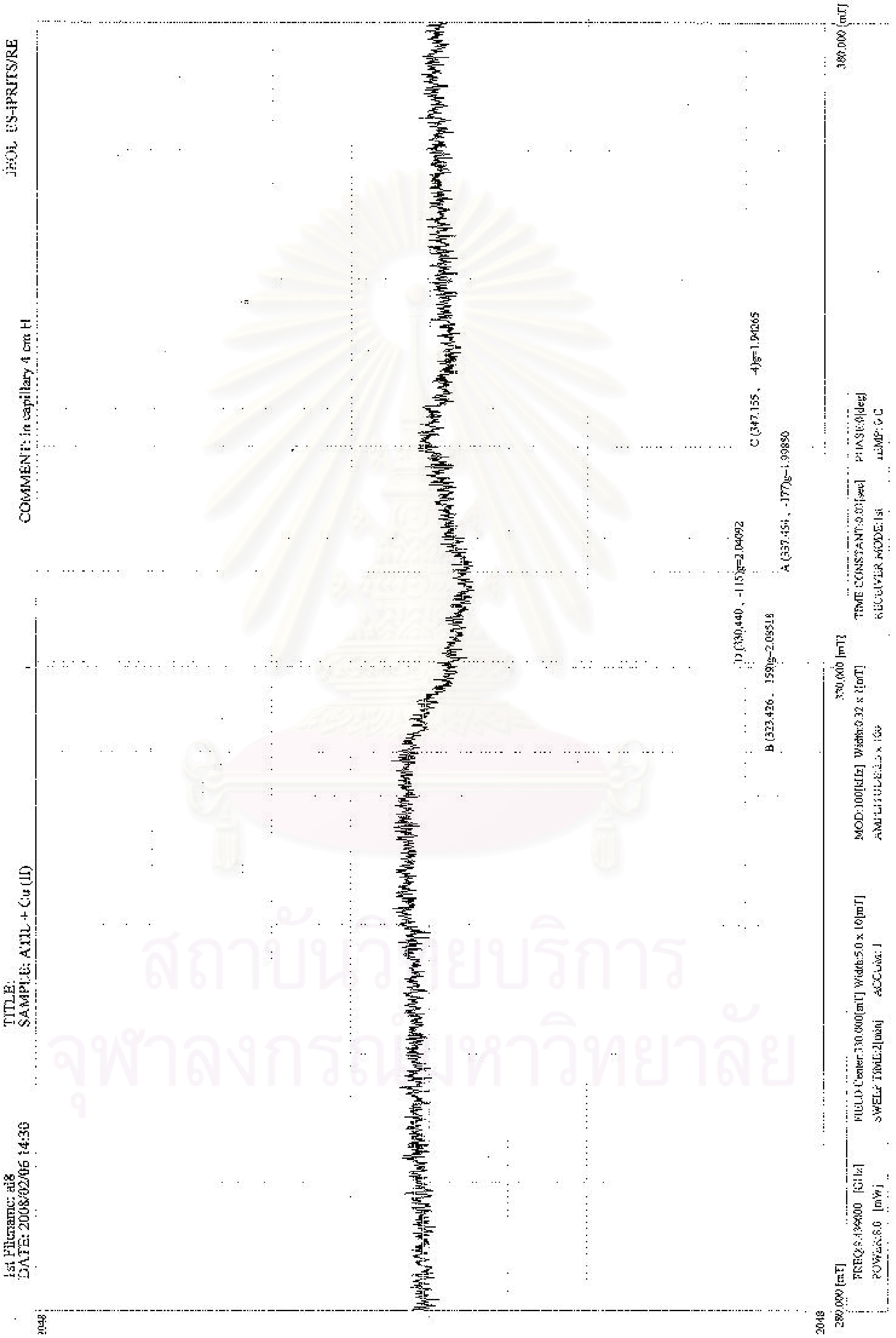


Figure A.2 ESR spectrum of Cu^{2+} complexed with 2-aminothiophenol.



VITA

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