Solvent Extraction and Liquid Membrane Containing Ionic Liquids and Deep Eutectic Solvents for Metal Separation

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CHAPTER 1

GENERAL INTRODUCTION

1

GENERAL INTRODUCTION

In the hydrometallurgical process of valuable metals extraction, the ores or scraps is leached with concentrated hydrochloric acid and the metals in the leachate are extracted using several methods including precipitation [1], reverse osmosis [2], adsorption [3], ion exchange [4], solvent extraction [5] and membrane permeation [6].

Amongst others, solvent extraction is the most widely used method due to the more convenient to adjust the parameters controling the extraction such as the organic phase, pH, extractants, allow to be implemented in the continuous mode and suitable for the processing of high metal feed concentrations [7]. The efficiency and selectivity which are the most important parameters determining the successfulness of the extraction process are absolutely influenced by the extractant used. Organic solvents are the most commonly used extractant for separation of metal ions. Not only are the volatility and flammability of the organic solvents as issue which is not environmental friendly, but the use of the very large amount of these organic solvents is also not economically profitable [8].

The use of greener solvents such as ionic liquids (ILs) and deep eutectic solvents (DESs) are considered as the better choice to overcome the flammability and volatility of organic solvents. While the use of the large amounts of organic solvents can be avoided by applying the liquid membrane permeation technique instead of solvent extraction technique. In this thesis ILs and DESs were used as extractant both in solvent extraction technique and as carrier in liquid membrane permeation for separation of metal ions.

Separation of metal ions is a hot topic and is important of economically and environmentally. Metals are obtained from ores or scraps by metallurgical process and then are processed into final products which are used by humans, directly or indirectly. All of the processes from raw materials to the final products produce the waste containing metal ions. The products are utilized and later on are also discarded as waste which will contaminate the environment. Because of the food chain, the contaminated materials from environment enter to the human body through food, water and air. Although some metals are essential for the human body, their presence in high concentrations will disturb the human metabolic system. The extraction of metal ions is an effort to recover the metal ions both from ores and from waste containing metal ions due to their limited availability in nature. On the other hand, the extraction of metal ions from metal–contained waste can reduce the level of environmental pollution. Therefore, an effective, efficient, economic and environmental friendly method for recovery of metal ions both from ores and from waste is absolutely needed.

In the following, the two extraction techniques employed i.e solvent extraction and liquid membrane permeation as well two kinds of green solvents i.e IL and DES will be briefly explained.

Extraction techniques

For separation of metal ions from aqueos solution, several techniques can be employed. However, with the reasons previously mentioned, solvent extraction and liquid membrane permeation were selected for extraction of metals.

(a) Solvent extraction

Amongst others, solvent extraction is one of the favored separation techniques because of its simplicity, speed, and wide scope [9]. It basically consists of three main steps. In the extraction step, the metal-bearing aqueous feed solution (effluent) is contacted with an organic (or solvent) phase that contains a diluted or undiluted extractant. The metal ions react with the extractant to form the hydrophobic complex with extractant and it is transferred from the aqueous phase to the organic phase driven by the difference of the complexes' affinity towards the aqueous phase and organic phase as well by the relative solubility of the complexes in both phases. The liquid phases are then separated and the aqueous one is submitted for the recovery of other metals, to be recycled or even discharged, while the organic phase goes on to the next step. If selectivity in the extraction step is low, the loaded organic phase goes to the scrubbing step to remove other metals or impurities co-extracted using a suitable aqueous solution that may be recycled to a stage up stream of the circuit. Finally, the metal in the loaded solvent is stripped out from the organic phase to some suitable aqueous solution resulting in a fairly concentrated solution on the metal of interest (as a metal salt form), which goes to further processing for pure metal or metal oxide production (electrolysis, evaporation, crystallization, etc.) [10].

Solvent extraction has the advantages that it can be implemented in a continuous mode and it is suitable for the processing of high metal feed concentrations [7]. Due to the easier to adjust the parameters controling the extraction but has a high efficiency and selectivity, solvent extraction based on ILs has been widely applied in extraction of metals [11, 12]. However, to the best of our knowledege, the use of solvent extraction technique based on ILs for separation of manganese both from ores and from scraps has not been investigated eventhough Mn is currently being used in many industries such as ferroalloy or steel industry, dry cel batteries, chemicals, fertilizers, glass, ceramics, paint and for numerous medicinal and chemical purposes [13]. Therefore, the application of solvent extraction technique for extraction of Mn(II) using IL and DES as extractant will be discussed in detail in the Chapter 2 and Chapter 3 respectively. In Chapter 2, Fe(III) was also included in this work because Fe is the second largest component in the manganese ores [14, 15]. Co (II) were also included in Chapter 3 because manganese is co-extracted with cobalt in the process to recover cobalt from laterite leach solution using Cyanex 272 as extractant [16]. As the last step of three main steps of solvent extraction technique, stripping of the interested metals will also reported in both chapters (Chapter 2 and chapter 3).

(b) Liquid membrane permeation

A liquid membrane system involves a liquid that is immiscible with the source (feed) and receiving (product) solutions and serves as a semipermeable and

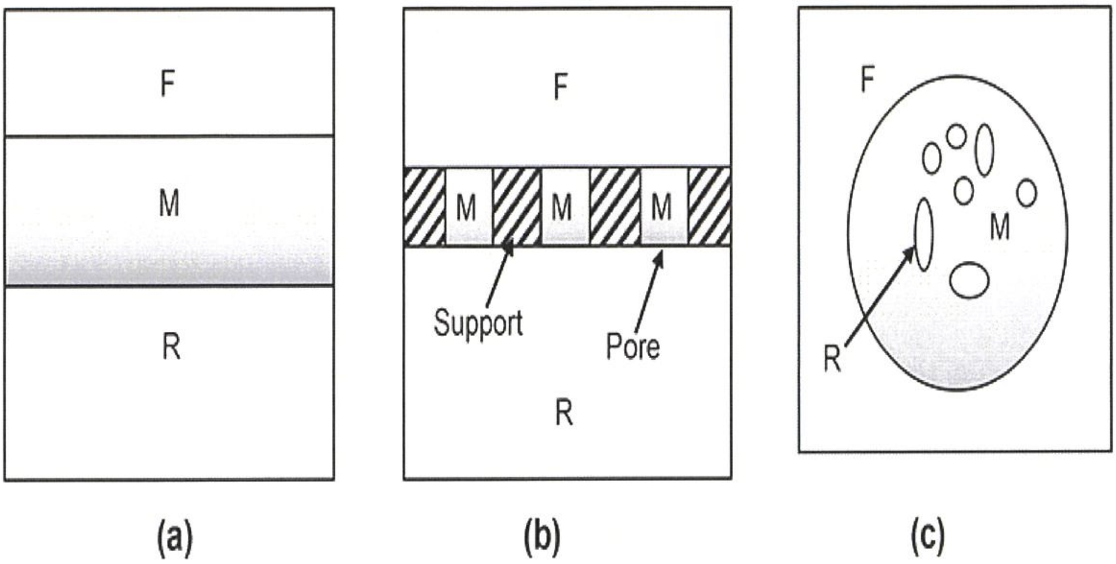


Figure 1. Liquid membranes: (a) bulk, (b) supported and (c) emulsion. (F: feed, M: membrane, R: receiving)

barrier between two liquid and gas phases [17]. Liquid membrane separation combines the solvent extraction and stripping (back extraction) in a single step. According to the configuration definition, liquid membrane can be categorized in three groups such shown in the Figure 1: bulk (BLM), supported or immobilized (SLM or ILM) and emulsion (ELM) liquid membrane transport [17].

Among these types, supported liquid membrane (SLM) process is being applied for the extraction/separation/removal of valuable metal ions from various resources [18]. Because of the specificity, the minimal amount of solvent needed and the fact that extraction and stripping steps are combined into a single step [19] SLM is considered as a cheaper and environmental friendlier separation method. The high separation efficiency can be obtained by this method because SLM acts on non-equilibrium mass-transfer characteristics where the separation is not limited by the conditions of equilibrium [18]. The limitations usually faced in solvent extraction technique such as aqueous/organic phase ratio, emulsification, flooding and loading limits, phase disengagement, large solvent inventory, and so forth can be avoided in SLM [4].

Although SLM has the advantages as mentioned, there are concerns regarding their stability and long-term performance in the supported liquid membrane processes employing the volatile organic solvents as carrier [20]. Therefore, substitution of the extractant with negligible vapor presure and more hydrophobic extractant such as ILs and DES for the conventional organic solvents increases the stability of membrane [21]. Hence, separation of the interested metal ions using liquid membrane with ILs and DES as carrier will be discussed in Chapter 4. In this thesis polymer inclusion membrane (PIM) which has similar configuration of supported ionic liquid membranes was used due to its higher stability than SILMs [22].

Green extractants: ILs and DESs

Use of green solvents as extractans for separation of metals is a way to bring the green chemistry in the reality. ILs and DESs categorized as green solvents were used as extractant in the solvent extraction and supported liquid membrane for separation of metal ions. These two kinds of green solvents will be briefly described in this section.

(a) Ionic liquid

Ionic liquids are commonly defined as systems which are composed entirely of ions and are liquid below 100 °C. They can easily be differentiated from molten salts, as ionic liquids tend to contain organic cation such as imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium instead of inorganic cation and counter ions can be either an inorganic (e.g. tetrafluoroborate, hexafluorophosphate, chloride, bromide) or an organic (e.g. trifluoromethylsulphonate, bis[(trifluoromethyl) sulphonyl]imide) anions [12].

ILs are kind of green solvents owing to their superior properties compared to organic solvents such as negligible vapor pressure, high thermal stability, high viscosity, good solvation ability, wide electrochemical windows, wide liquid range, and tunable polarity [20]. ILs can be applied as extractant of metal ions due to in solution metal salts predominantly form charged species, and therefore have a greater solubility in ILs. Even though there being a great number of combination possibility between cations and anions to form ILs, the using of more hydrophobic ILs will avoid their solubility in aqueous phase which in turn avoids the solubility of ILs in aqueous phase of solvent extraction technique and increases the stability of membrane in membrane permetaion. Aliquat-336, Cyphos IL-101 and Cyphos IL-102 were selected to be applied both in solvent extraction technique and in SLMs as described in Chapter 2 and Chapter 4, respectively.

(c) Deep eutectic solvent

Even though, usefull in fine chemical industry, application of ILs is still limited due to its very high cost generated by the very complex purification process. The analogious of ILs named deep eutectic solvents (DESs) can be used to overcome the limitations of ILs.

In a DES, two or three cheap and safe compounds acting as hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), respectively, can be connected one another with hydrogen bonding to form a eutectic mixture with melting point far below the individual components due to contain large and non-symmetric ions with low lattice energy [23, 24]. The formation of DES from two components A and B is schemed in phase diagram indicated in Figure 2. This mixture has the lowest melting point (E) due to the strength of interaction between the two components. Deep eutectic solvents can be described by the general formula:

$Cat^{+}X^{-}zY$,

where Cat^{+} is in principle any ammonium, phosphonium, or sulfonium cation, and X is a Lewis base, generally a halide anion. The complex anionic species are formed between X^{-} and either a Lewis or Brønsted acid Y (z refers to the number of Y molecules that interact with the anion) [25]. The major advantages of DESs

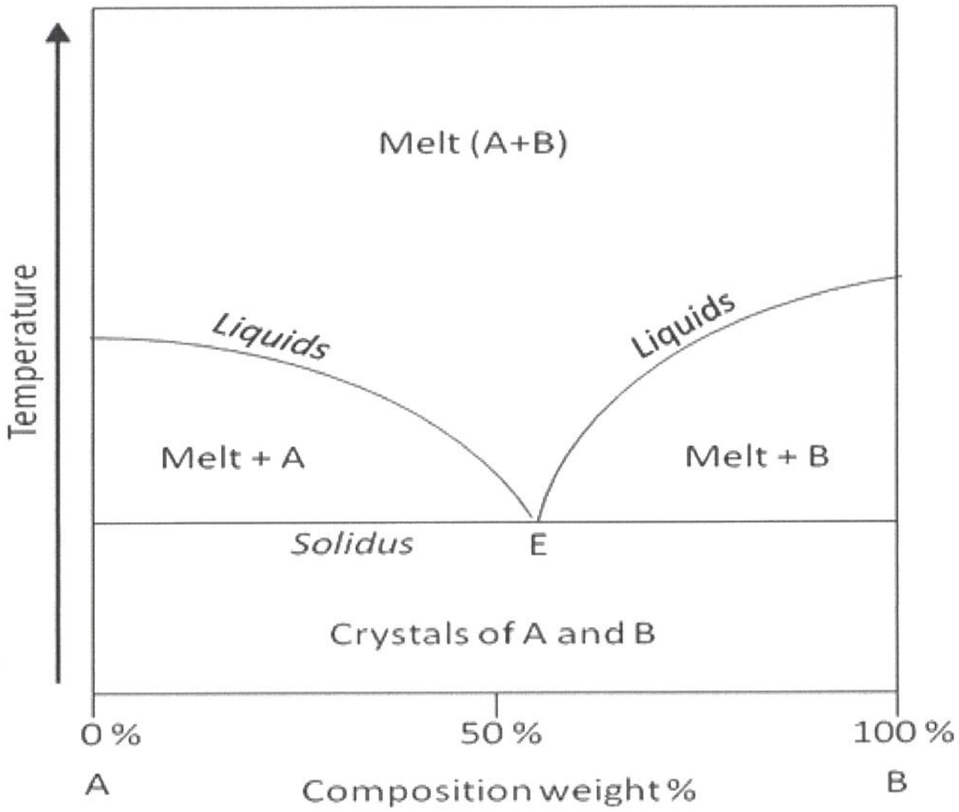


Figure 2. Schematic solid-liquid phase diagram for a binary mixture of a DES with A and B as constituent components

over ILs are their lower prices due to the very cheap of the constituent constituents at moderate temperatures resulting in a liquid DES, without the need for a solvent or complex purification step [25].

DES composed of decanoic acid and lidocaine (2-(diethylamino)-N-(2,6-dimethylphenyl) acetamide) used as extractant in solvent extraction will be discussed in Chapter 3 while as carrier for permeation of metal ions, the DES was prepared from decanoic acid and tetrabutylammonium bromide as reported in Chapter 4.

OUTLINE OF THIS THESIS

Separation and extraction of Fe (III), Mn (II) and Co (II) using solvent extraction technique and SLMs with ILs and DES as extractant were studied in this thesis. In order to obtain an understanding of the extraction mechnaism of interested metals using these technique, aqueous model solution of metal salts was used. As previously mentioned, metal ions are extracted by ionic liquids as metalchloro complex anion. Therefore, the concentration of hydrochloric acid used to dissolve metal salts absolutely affected the extractability of metal ions both in solvent extraction and in SLM permeation explained in Chapter 2 and Chapter 4 respectively. Unlike ILs, DES composed of decanoic acid and lidocaine employed in solvent extraction technique are a proton donors and proton acceptor respectively. As a result the extraction mechanism of metal ions highly influenced by the initial pH of metal ions solution such as discussed in Chapter 3. Another parameter highly determining the extraction percentage of metal ions is concentration of extractant. Hence, the effect of ILs and DES concentration was also reported in Chapter 2 and Chapter 3 respectively. In addition, stripping of metal ions from metals-loaded organic phase was also described in these two chapters. In chapter 4, separation of Fe (III) from Mn (II) was presented using polymer inclusion membrane. In general, using of ILs and DES as extractant in each technique presented in this thesis succesfully extract Fe (III), Mn (II) and Co (II) from aqueous solution.

References

[1] Fu, F., L. Xie, B. Tang, Q. Wang and S. Jiang. Application of a novel strategy-advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing waste water. Chem. Eng. J. (2012) 189–190, 283–287.

[2] Lee K. P., T. C. Arnot and D. Mattia. A review of reverse osmosis membrane materials for desalination: Development to date and future potential. J. Membr. Sci. (2011) 370, 1–22.

[3] Lakherwar, D. Adsorption of heavy metals: A review. Int. J. Environ. Res. Develop. (2014) 4, 41–48.

[4] Nikoloski, A. N. and K. Ang. Review of the application of ion exchange resins for the recovery of platinum - group metals from hydrochloric acid solutions. Mineral Process. Extr. Metal. Rev. (2014) 35, 369–389.

[5] Xie F., T. A. Zhang, D. Dresinger and F. Doyle. A critical review on solvent extraction of rare earths from aqueous solutions. Minerals Eng. (2014) 56, 10–28.

[6] Ola, P. D. and M. Matsumoto. Supported Ionic Liquid Membranes for Metal Separation. in: S. Handy (Ed.). Progress and Developments in Ionic Liquids. InTech (2017) pp.:539-555.

[7] Hoogerstraete, T. V., S. Wellens, K. Verachtert and K. Binnemans. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. Green Chem. (2013) 15, 919–927.

[8] Nee, K. and M. Nilsson. Experimental and theoretical studies of actinide and

lanthanide ion transport across supported liquid membranes. Solvent Extraction and Ion Exchange (2015) 33, 554–575. DOI: 10.1080/07366299.2015.1073973

[9] Kislik V., Solvent extraction, classical and novel approaches. Elsevier, Amsterdam (2011).

[10]Mansur, M. B. Solvent extraction for metal and water recovery from industrial wastes and effluents. REM: R. Esc. Minas, Ouro Preto (2011) 64(1), 051-055.

[11]Baba, Y., F. Kubota, N. Kamiya and M. Goto. Recent advances in extraction and separation of rare earth metals using ionic liquids. Journal of Chemical Engineering of Japan (2011) 44(10), 679-685.

[12]de los Ríos, P., F. J. Hernández-Fernández, L. J. Lozano, S. Sánchez, J. I. Moreno, and C. Godínez. Removal of metal ions from aqueous solutions by extraction with ionic liquids. *Journal of Chemical & Engineering Data* (2010) *55* (2), 605-608.

[13]Filiz, M. Extraction of Mn (II) from aqueous hydrochloric acid solutions into Alamine 336–m-xylene system. Hydrometallurgy (2007) 87 58–62.

[14]Sorensen, B., S. Gaal, M. Tangstad, E. Ringdalen, R. Kononov; and O. Ostrovski. Properties of manganese ores and their change in the process of calcination. The Twelfth International Ferroalloys Congress Sustainable Future; June 6 – 9, 2010 Helsinki, Finland.

[15]Krivenko, V. V., A. N. Ovcharuk, A. Yu, Taran, A. S. Filev, T. A. Oleynik and V. N. Kharitonov. Investigation of chemical and mineralogical composition of manganese ores from Central Asia deposits. Metallurgical

and Mining Industry (2010) 2(1), 7-12.

[16]Zhu, Z., P. Yoko and C. Y. Cheng. Recovery of cobalt and manganese from nickel laterite leach solutions containing chloride by solvent extraction using Cyphos IL 101. Hydrometallurgy (2017) 169, 213–218.

[17]Kislik, V.S. Introduction, General description, definitions, and classification. overview. in: V.S. Kislik (ed.). Liquid membranes. 1st ed. Elsevier Amsterdam (2009). p. 1–15.

[18]Parhi, P. K. Supported liquid membrane principle and its practices: a short review. Journal of Chemistry Volume 2013, Article ID 618236, 11 pages http://dx.doi.org/10.1155/2013/618236.

[19]Lozano, L. J., C. Godínez and F. J. Alguacil. Facilitated transport of vanadium (V) by supported liquid membranes. Hydrometallurgy (2005) 80, 196–202.

[20]Matsumoto, M. Ionic liquid-based supported liquid membranes. in: K. Mohanty and M. K. Purkait (eds.). Membrane Technology and Applications. CRC Press, Boca Raton, U.S.A. (2012) pp. 305–316,.

[21]Lozano, L. J., C. Godínez, A.P. de los Ríos, F. J. Hernández-Fernández, Sánchez-Segado and F. J. Alguacil. Recent advances in supported ionic liquid membrane technology. Journal of Membrane Science (2011) 376, 1 – 14.

[22]Matsumoto, M., Y. Murakami, Y. Minamidate and K. Kondo. Separation of lactic acid through polymer inclusion membranes containing ionic liquids. Sep. Sci. Technol. (2012) 47, 354–359.

[23]Zhao, B.-Y., P. Xu, F.-X. Yang, H. Wu, M.-H. Zong and W.-Y. Lou. Biocompatible deep eutectic solvents based on choline chloride: characterization and application to the extraction of rutin from sophora japonica. ACS Sustainable Chem. Eng. (2015) 3, 2746−2755.

[24]Zhang, Q., K. D. O. Vigier, S. Royer and F. Jérôme, Deep eutectic solvents: syntheses, properties and applications. Chem. Soc. Rev. (2012) 41, 7108–7146

[25]Smith, E. L., A. P. Abbott and K. S. Ryder. Deep eutectic solvents (DESs) and their applications. Chem. Rev. (2014) 114, 11060−11082.

CHAPTER 2

Solvent Extraction and Stripping of Fe(III) and Mn(II) with Ionic Liquids as Extractant

2

Solvent Extraction and Stripping of Fe (III) and Mn (II) with Ionic Liquids as extractant

Abstract: Use of ionic liquids as extractant instead of organic solvents in solvent extraction technique which is a widely used method for separation of metal ions is able to minimize the drawbacks derived by the using of flammable and or toxic of organic solvents. This chapter presents the use of ionic liquids as extractant for extraction of Fe(III) and Mn(II) as well the stripping of these metals from metals-loaded organic phase. In the solvent extraction, the metal anion chlorocomplexes, $FeCl_4^-$ and $MnCl_3^-$ formed in the presence of excess hydrochloric acid were extracted with all ionic liquids via anion exchange reaction. The largest extractability for recovery of Fe(III) and Mn(II) was shown by Cyphos IL 101 among the ionic liquids experimented. Sodium thiosulfate was the only one stripping agent, which gave the quantitative recovery of Fe(III) from Aliquat 336 solution. Mn(II) was effectively stripped by water from Aliquat 336 solution. The stripping percentages in metal-Cyphos IL 101 system were lower than those of metal-Aliquat 336 system. Aliquat 336 is found to be better extractant than Cyphos IL 101 because of its high stripping performance.

Introduction

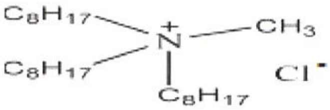
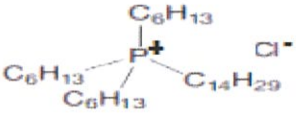
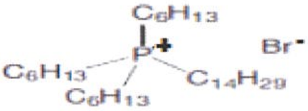
In general, concentrated hydrochloric acid is usually used to leach the ores or scraps in order to extract the metals including iron (Fe) and manganese (Mn) in hydrometallurgical process which is the most suitable technique compared to all other techniques including biometallurgical and pyrometallurgical [1]. The Fe and Mn in the resultant chloride rich solution can be extracted using several methods such as precipitation and solvent extraction. Because the solubility values of the metal ions are very close, the co-precipitation of the other metals can be occured which in turn decrease the extractability of the targeted metal(s). Solvent extraction is an economical and widely used process in hydrometallurgy for the recovery of valuable ions from aqueous solutions after the leaching process [2]. In this technique, a metal ion in the aqueous phase forms a hydrophobic complex with the extracting agent (extractant) and then migrates to the organic phase [3]. This means that the extent of the extractability in the term of efficiency and selectivity of a metal is absolutely influenced by the extractant used.

Conventionally, Fe and Mn can be extracted using many types of extractant such as di(2-ethylhexylphosphoric) acid (D2EHPA) [4, 5], bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [4, 6], 2-ethylexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) [7], *N,N*-dioctyl-1-octanamine (Alamine 336) [8], octylphenyl acid phosphate (OPAP) [5], bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) [9], tri-n-butyl phosphate (TBP) [10] and others. However, those conventional liquid−liquid extraction systems use the organic diluents and extractants, which are often harmful and/or flammable [11].

One of the reagents proposed to overcome the drawbacks of those extractants was ionic liquids (ILs). ILs have been considered as environmental benign solvents as compared to volatile organic one because their near-zero vapour pressure, their good chemical and thermal stability and their physicochemical properties can be varied by altering the subtitutive groups on the cation or the combined anion [12]. Solvent extraction with ILs of Fe(III) have been conducted using several ILs such as triethylpentylphosphonium (P_{2225}) bis(trifluoromethyl-sulfonyl)amide (TFSA) [13], Aliquat 336, [14, 15], 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][NTf_2]) [16], trihexyl(tetradecyl) phosphonium chloride (Cyphos IL 101) [17], trihexyl(tetradecyl) phosphoniumbis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) [18]. However, there are few studies of Mn(II) extraction with ILs. Mn is currently being used in many industries such as ferroalloy or steel industry, dry cell batteries, chemicals, fertilizers, glass, ceramics, paint and for numerous medicinal and chemical purposes [19].

In this thesis, ionic liquids aliquat-336, cyphos IL-101 and cyphos IL-102 were employed as extractant for separation of Fe(III) and Mn(II). Because the stripping of the metal from the metal-loaded organic phase is sometimes difficult especially when the concentration of loaded metal is high, it is important to spesifically study how to

Table 1. Molecular structure of ILs used

Product name	**Chemical name**	**Molecular structure**
Aliquat 336	*N*-Methyl-*N,N,N*-trioctylammonium chloride	
Cyphos IL 101	Trihexyl(tetradecyl)phosphonium chloride	
Cyphos IL 102	Trihexyl(tetradecyl)phosphonium bromide	

strip the metal from metal-loaded organic solution [20]. Liu *et al.* [20] reported that using of reductive or oxidative agent can decrease the the activity of metal ion in the aqueous phase which in turn can improve the stripping of metal ions. In this work, the author examined a number of stripping agents including both reductive and oxidative agents to strip Fe(III) and Mn(II) from the metal-loaded organic solution.

Experimental Section

Chemicals

Aliquat-336 (*N*-Methyl-*N,N,N*-trioctylammonium chloride), Cyphos IL 101 (Trihexyl(tetradecyl)phosphonium chloride) and Cyphos IL 102 (Trihexyl(tetradecyl)phosphonium bromide) used as ionic liquid extractants were purchased from Strem Chemicals Inc. and Cytec Industry Inc., respectively, and their molecular structures are shown in Table 1. Ferric chloride, manganese chloride, sodium sulphate, nitric acid, sulphuric acid and sodium nitrate were purchased from NacalaiTesque, Inc., Kyoto, Japan. Other reagents of G. R. grade were purchased from Wako Pure Chemical, Industries, Ltd, Osaka, Japan. All chemicals were used without further purification.

Solvent extraction experiment

The aqueous solution was prepared by dissolving 10 mM of metal solution in various concentrations of hydrochloric acid. The organic solution was prepared by dissolving IL in *n*-heptane. Variations in the concentration of the IL were also conducted in order to evaluate the effect of the IL concentration on the extractability of the metals. Equal volume of the aqueous and organic solutions were mixed and shaken (120 rpm) in a thermostat water bath at 303 K. After shaking for 3 h to attain equilibrium, the concentration of metal in the aqueous phase was measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ICPS-8000, Shimadzu, Kyoto, Japan). The percentage of extraction and the distribution ratio, *D*, were calculated using equation (1) and (2).

$$\%E = \frac{[M]_{org.eq}}{[M]_{aq.int}} x100 = \frac{[M]_{aq.int} - [M]_{aq.eq}}{[M]_{aq.int}} x100 \qquad (1)$$

$$D = \frac{[M]_{aq.int} - [M]_{aq.eq}}{[M]_{aq.eq}} \qquad (2)$$

where $[M]_{org.eq}$ and $[M]_{aq.eq}$ are the equilibrium concentration of metal in the organic and aqueous phase, respectively, and $[M]_{aq.int}$ is the initial metal concentration in the aqueous phase.

Stripping experiment

The metal-loaded organic solution was prepared by mixing of 50 mL of aqueous solution containing 10 mM of metals in 5 mol/L of hydrochloric acid with 50 mL of organic solution containing 2 M of Aliquat 336 or 1 M of Cyphos IL 101 in heptane. After mixing, the concentration of the metals in the aqueous phase was firstly measured to determine the initial concentration of metals in the organic phase which was the initial metal concentration in the organic phase ($[M]_{org.int.}$). The equal volume of metal-loaded organic solution and aqueous phase containing stripping agent was mixed. After shaking for 10 min, the mixture was then placed in the thermostat water bath at 303 K for 3 h to allow the complete separation between organic phase and aqueous phase. The concentration of the metals in the aqueous phase was then measured using ICP-AES (ICPS-8000) and the percentage of metal stripping was calculated using equation (3).

$$\%\text{Stripping} = \frac{[M]_{aq.eq.}}{[M]_{org.int.}} x100 \qquad (3)$$

Where $[M]_{org.int}$ is the difference between $[M]_{aq}$ before and after mixing with the organic phase.

Results and Discussion

Solvent extraction experiment

A key point for the effective application of the solvent extraction for selective recovery of valuable metals is to find an appropriate extractant and to design suitable separation procedures [21]. There are two parameters which absolutely affect the separation of metals using ionic liquid as extractant that is concentration of ligand which is form anion complex with metal and concentration of ionic liquid. This experiment was conducted in order to evaluate the influence of hydrochloric acid concentration and ionic liquid concentration on the recovery of Fe(III) and Mn(II).

As reported by Wei et al. [21], the transport of metals from aqueous solution to organic solution containing ionic liquid is due to anion exchange reaction between anion of ionic liquid and anionic form of metal which is produced by the reaction of metal cation with chloride anion as illustrated in equation 4 and 5.

$$M^{n+} + (n+1)HCl \leftrightarrow MCl_{n+1}^{-} + (n+1)H^{+} \qquad (4)$$

$$MCl_{n+1}^{-} + Q^{+} \leftrightarrow Q^{+}MCl_{n+1}^{-} \qquad (5)$$

where M^{n+} is the metal ion with ion valence n and Q^{+} is the cation of the ionic liquid. As seen in the Equation 4, Fe(III) and Mn(II) in the excess presence of hydrochloric acid form the anionic chlorocomplexes, $FeCl_4^-$ [3, 15, 17, 18] and $MnCl_3^-$ [22]. Figure 1 shows effect of HCl concentration on the extractability with the three ionic liquids. As shown in Figure 1(a), Fe(III) was completely extracted with three ionic liquid when the concentration of HCl and ionic liquid were 1.0 M. Ability of anion exchange of the ionic liquids toward $FeCl_4^-$ is as follows; Aliquat 336 ≈ Cyphos IL 102 < Cyphos IL 101. The extractability of Mn(II) was lower than that of Fe(III) as shown in Figure 1 (a) and (b). The highest extractability of Mn(II), 91 %, was reach when the concentration of HCl was 6.0 M using 1.0 M of Cyphos IL 101. This indicates that the amount of HCl needed to form a stable anion complex with Mn(II) is larger than that with Fe(III). This is due to the smaller stability constant of Mn(II) to form $MnCl_3^-$ [22]. It is also seen in the Fig. 1(b), ability of anion exchange of the ionic liquids toward $MnCl_3^-$ is as follows; Aliquat 336 < Cyphos IL 102 < Cyphos IL 101. The highest extractability of Mn(II) using conventional quaternary ammonium salt, Aliquat336, was only about 37 %. This suggests that phosphonium-based ionic liquids have the larger anion exchange ability than ammonium-based ionic liquids and are preferable to the extraction of metal anion species.

The similar trend was found when the concentrations of ILs were varied in the presence of 4.0 M of hydrochloric acid concentration as shown in Figure 2.

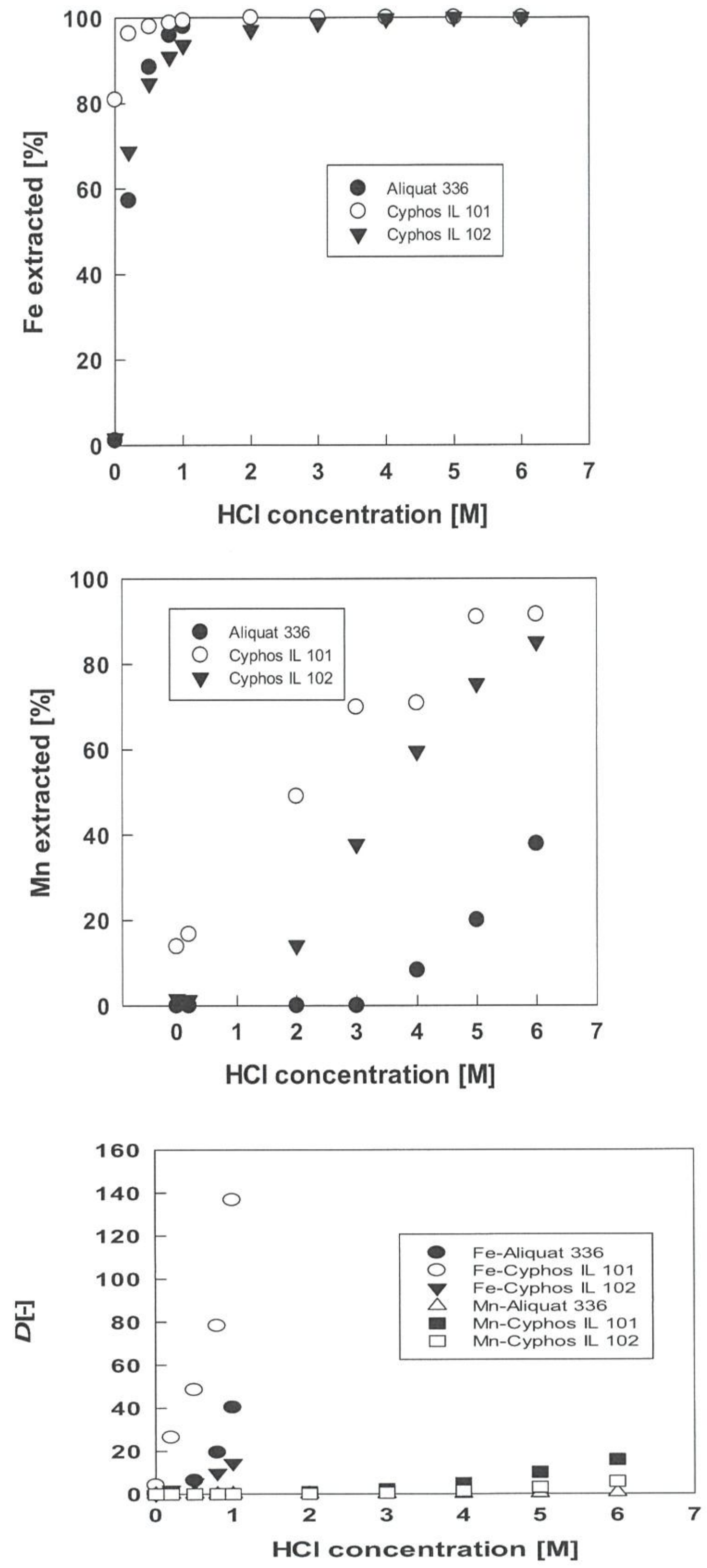


Figure 1. Influence of HCl concentration on the extractability of Fe(III) (a) and Mn(II) (b) and distribution ratio of Fe(III) and Mn(II) (c). Concentration of ionic liquid is 1.0 M

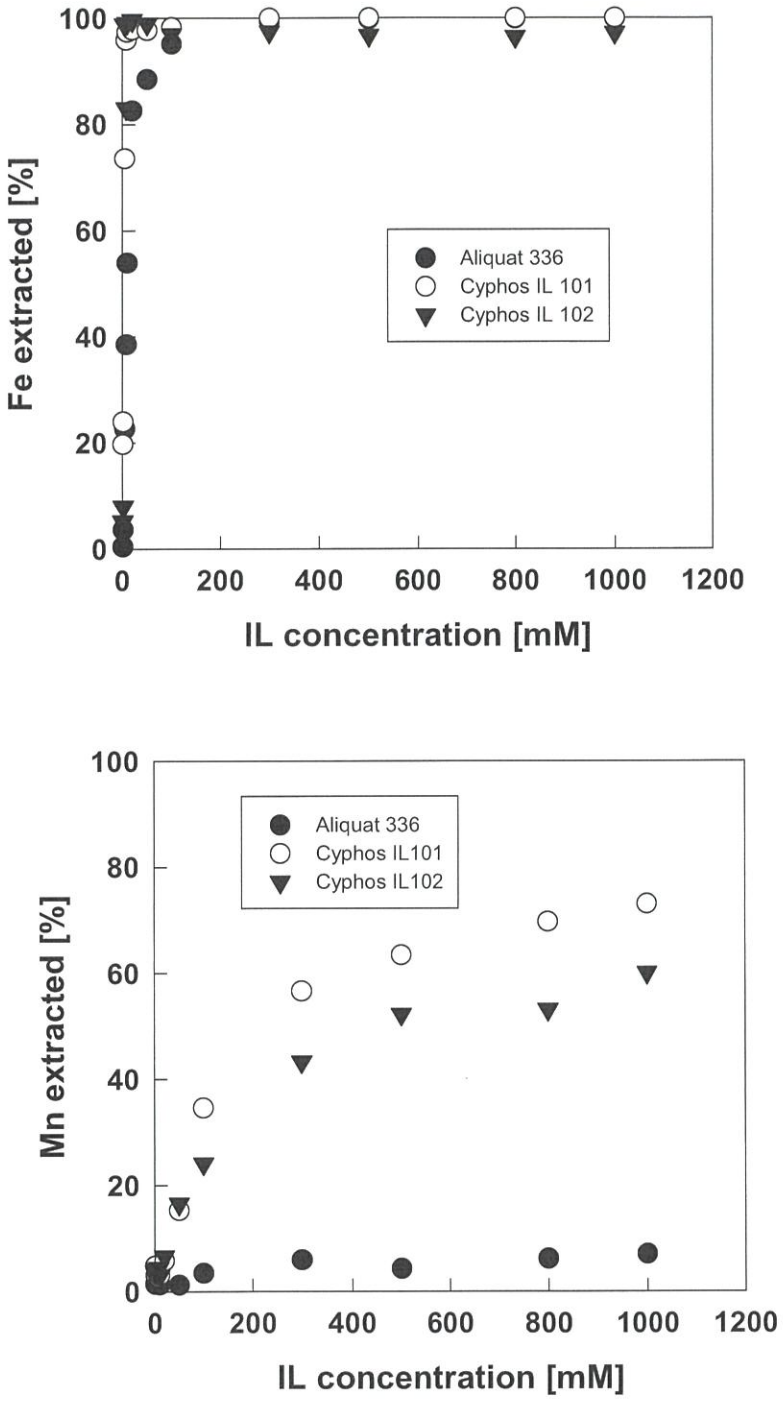


Figure 2. Influence of ionic liquid concentration on the extractability of Fe(III) (a) and Mn(II) (b). Hydrochloric acid concentration is 4.0 M.

Stripping of metal ions

In this thesis the stripping of Fe(III) and Mn(II) from the Fe(III)- and Mn(II)-loaded organic solutions were investigated. The solvent extraction experiment showed that Cyphos IL 101 was the best extractant for extraction of Fe(III) and Mn(II) among the three kinds of ILs applied while Aliquat 336 was the most commonly used extractant in the metals separation. Hence, these two ionic liquids were selected as extractant in the experiment of metals stripping. In previous studies on the stripping of Fe(III) from organic solutions containing Aliquat 336 and Cyphos IL 101, water for Aliquat 336 [15] and 0.5 mol/L HCl and H_2SO_4 for Cyphos 101 [17, 18] were used for stripping agent. However there are no studies on the stripping of Mn(II) with Aliquat 336 and Cyphos IL 101.

In this investigation, performances of a number of stripping agent including reductive or oxidative agents was experimented and the results of stripping percentage of Fe(III) and Mn(II) from metal-Aliquat 336 complexes were summarized in Table 2. From Table 2, it is found that the stripping percentages of metal ions from the metal-loaded organic phase were greatly affected by the nature of the stripping agents and generally the stripping of Fe(III) was difficult compared with that of Mn(II). In the extraction experiment of Fe(III) and Mn(II) using Aliquat 336 and Cyphos IL101 as extractants, it was found that the extraction percentage of Fe(III) was higher than that of Mn (II) due to the higher stability constant of $FeCl_4^-$ compared to $MnCl_3^-$ as shown in equation (4) and (5). Therefore, it can be expected that stripping of Fe (III) from Aliquat 336 solution will be more difficult than Mn(II) because the stripping is reverse reaction of the extraction.

The stripping percentages of Fe(III) listed in Table 2, except sodium thiosulfate, were below 45 % with most of them lower than 15 %. The stripping reaction was considered to be the anion exchange between the $Q^+FeCl_4^-$ of organic phase with anion of stripping agent. This was confirmed by the fact that there was no stripping of Fe(III) by using non-ionic agent such as D-sorbitol ($C_6H_{14}O_6$). Unlike in the previous report (Mishra *et al.*, 2011) on the stripping of Fe(III) from Fe-Aliquat 336 complex, water was good stripping agent not for Fe(III) but for Mn(II).

Sodium thiosulfate was the only stripping agent, which gave the high recovery of Fe(III) (99.4 %), among the agents investigated for Fe(III). The ability of sodium thiosulfate to reduce the oxidation number of Fe(III) to the lower oxidation state was the reason why it was most compatible stripping agent for stripping of Fe(III) from the Fe(III)-Aliquat 336 complex. Because the Fe(III) was already in the highest oxidation state, the reaction of the oxidative stripping agents (NH_4NO_3 and HNO_3) with Fe(III) was not occured.

Figure 3. shows the effect of thiosulfate concentration on the stripping percentage. In the figure, "zero" concentration means the use of water as a stripping agent. In Fe-Aliquat 336 complex system, Fe(III) is quantitatively stripped by 1 M the sodium thiosulfate solution. For stripping of Mn(II) in Table 2, the stripping percentages of Mn(II) in all stripping agents excepting Na_2SO_3 were higher than 70 %. Mn (II) with the oxidation state +2 can be either oxidised to the higher oxidation state or reduced to the lower oxidation state. Therefore, both oxidator (NH_4NO_3 and HNO_3) and reductor (Na_2SO_3 and $Na_2S_2O_3$) can be employed as stripping agents to improve the recovery of Mn(II) from Aliquat 336 solution. The lower stripping percentage of Mn(II) using sodium sulfite as stripping agent compared to sodium thiosulfate probably is due to its lower potential reduction. Moreover, not only inorganic reductive agent but also organic reductive agent such as sodium ascorbate ($C_6H_7NaO_6$) can be used as agent for stripping of Mn(II) from Aliquat 336 solution. However, as shown in Table 2 and Figure 3, unlike stripping of Fe(III), Mn(II) was effectively stripped by water and neutral salt (Na_2SO_4) solution from the complex of $Q^+MnCl_3^-$ in the organic phase to aqueous phase compared with the oxidative and reductive stripping agents. From these facts, the following stripping reaction in water is considered to proceed because of small stability constant of $MnCl_3^-$(Morris and Short, 1961).

$$Q^+MnCl^-_{3,org} \rightleftharpoons Q^+Cl^-_{org} + Mn^{2+}_{aq} + 2Cl^-_{aq} \qquad (6)$$

In metal-Cyphos IL 101 system shown in Figure 3, it was found that the maximum stripping percentages of Mn(II) and Fe(III) were 83.6 and 58.2 % at the concentration of sodium thiosulfate of 0.1 M and 0.5 M, respectively. The stripping percentages in metal-Cyphos IL 101 system were lower than those of metal-Aliquat 336 system. This is because extractabilities of Fe(III) and Mn(II) with Cyphos IL 101 were larger than those of Aliquat 336.

Considering both extraction and stripping processes of Fe(III) and Mn(II), Aliquat 336 is better extractant than Cyphos IL 101. This is because the metal ions

Table 2. Stripping percentage of Fe(III) and Mn(II) from metal-Aliquat 336 complex

Stripping agent	Water	Na_2SO_3	Na_2SO_4	NH_4NO_3	$Na_2S_2O_3$	Sodium ascorbate	HNO_3	H_2SO_4
Fe(III)	0.50	0.0	0.0	0.0	99.4	43.8	10.7	21.0
Mn(II)	92.6	22.5	96.1	83.6	78.4	72.6	80.4	85.7

*Concentrations of stripping agents were 1.0 M except for water and Na_2SO_4 (0.3 M).

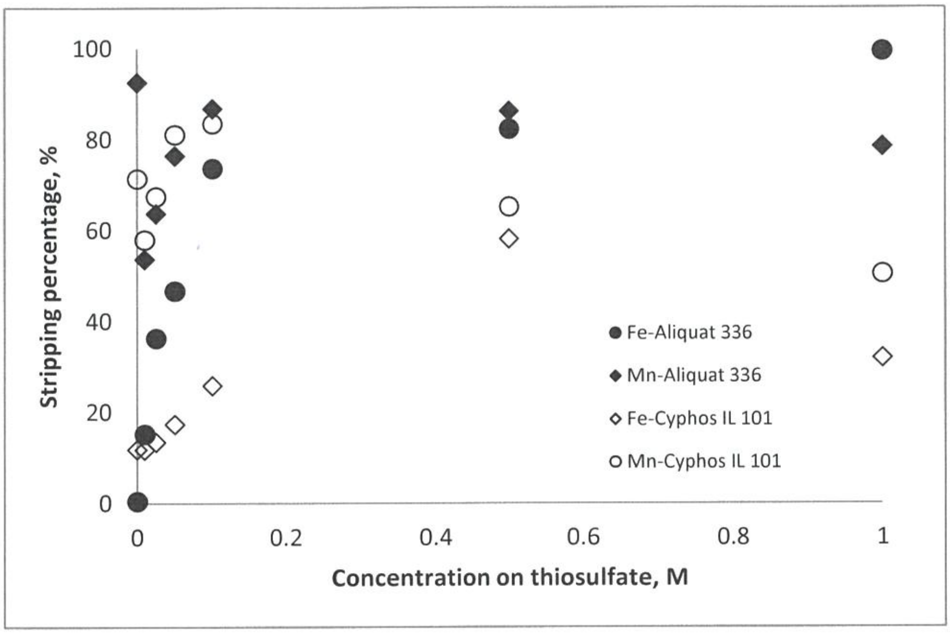


Figure 3. Effect of thiosulfate concentration on stripping of Fe(III) and Mn(II).

were quantitatively stripped from metal-Aliquat 336 complexes by one batch experiment, although the extractability with Aliquat 336 was slightly lower than that of Cyphos IL 101. Moreover, water, which is an economical and more environmental-friendly stripping agent, can be used in the stripping from Mn(II)-Aliquat 336 complex.

Conclusion

In this study, ILs such as Aliquat-336, Cyphos IL 101 and Cyphos IL102 were used as complexing reagents to recover Fe(III) and Mn(II) in the processes of the solvent extraction. In the solvent extraction, the anionic chlorocomplexes, $FeCl_4^-$ and $MnCl_3^-$ formed in the presence of excess hydrochloric acid were extracted with all ionic liquids via anion exchange reaction. Cyphos IL 101 among the ionic liquids investigated was the largest extractability for recovery of Fe(III) and Mn(II). A number of stripping agents were tested for recovery of Fe(III) and Mn(II). The recovery of Fe(III) can be achieved by using reductive stripping agent. Sodium thiosulfate was the only one stripping agent, which gave the quantitative recovery of Fe(III) from Aliquat 336 solution. Mn(II) was effectively stripped by water and neutral salt (Na_2SO_4) solution from Aliquat 336 solution. Stripping for Fe(III) is derived by anion exchange reaction between anion of metal chlorocomplex ($FeCl_4^-$) of metal-loaded organic solution with anion of stripping agents of aqueous solution. This mechanism was probably occured when Mn(II) was stripped with neutral salt. On the other hand, the stripping with water is caused by decomposition of metal chlorocomplex ($MnCl_3^-$). The stripping percentages in metal-Cyphos IL 101 system were lower than those of metal-Aliquat 336 system because extractabilities of Fe(III) and Mn(II) with Cyphos IL 101 were larger than those of Aliquat 336. Considering both extraction and stripping processes of Fe(III) and Mn(II), Aliquat 336 is better extractant than Cyphos IL 101 because of its high stripping performance.

References

[1] Baba, A. A., I. Lateef, F. A. Adekola, R. B. Bale, M. K. Ghosh, A. R. Sheik, S. R. Pradhan, O. S. Ayanda and I. O. Folorunsho. Hydrometallurgical processing of manganese ores: A review. J. Minerals Mat. Charac. Eng., (2014) 2, 230-247.

[2] Quijada-Maldonado, E., J. Romero and I. Osorio. Selective removal of iron (III) from synthetic copper (II) pregnant leach solutions using [Bmim][Tf_2N] as diluent and TFA as extracting agent. Hydrometaliurgy (2016) 159, 54-59.

[3] Hoogerstraete, T. V., S. Wellens, K. Verachtert and K. Binn. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. Green Chem. (2013) 15, 919–927.

[4] Pérez-Garibay, R., J. Martínez-Jiménez, A. Uribe-Salas and A. Martínez-Luévanos. Comparative study between D2EHPA and Cyanex 272 as extractants of Mn (II) from a leached liquor produced by reductive leaching of a pyrolusite Ore with SO_2. Engineering (2012) 4, 526-531.

[5] Principe, F. and G. P. Demopoulos. Comparative study of iron(III) separation from zinc sulphate-sulphuric acid solutions using the organophosphorus extractants, OPAP and D2EHPA, Part I: Extraction. Hydrometallurgy (2004) 74, 93-102.

[6] Biswas, R. K. and M. S. Rahman. Solvent extraction of manganese from sulphate-acetato medium with cyanex 272. Indian J. Chem.Technol. (2011) 18, 372-380.

[7] Ahn, J. G., K. H. Park and J. S. Sohn., Solvent extraction separation of Co, Mn and Zn from Ni rich-leaching solution by Na-PC88A. Mat. Trans. (2002) 43, 20169-20172.

[8] Lee, M. S. and M. Filiz. Solvent extraction of Mn(II) from hydrochloric acid solutions by alamine336. Materials Transactions (2008) 49(11), 2642-2647.

[9] Alia, M. R., R. K. Biswas, S. M. A. Salam, A. Akhter, A. K. Karmakar and M. H. Ullaha. Cyanex 302: An extractant for Fe^{3+} from chloride medium. Bangladesh, J. Sci. Ind. Res. (2011) 46, 407-414.

[10]Patnaik, P., A. A. Baba, K. C. Nathsarma, K. Sarangi and T. Subbaiah. Separation of iron and zinc from manganese nodule leach liquor using TBP as extractant. Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C) (2013) 122, 179-185

[11]Parmentier, D., T. V. Hoogerstraete, S.J. Metz, K. Binnemans and M.C. Kroon. Selective extraction of metals from chloride solutions with the tetraoctylphosphonium oleate ionic liquid. Ind. Eng. Chem. Res., (2015) 5, 5149−5158.

[12]Matsumoto, M. Ionic liquid-based supported liquid membranes, in: Mohanty, K. and M. K. Purkait (eds.). Membrane Technology and Applications. CRC Press, Boca Raton, U.S.A. (2012) pp. 305–316.

[13]Matsumiya, M., T. Yamada, Y. Kikuchi and S. Kawakami. Removal of iron and boron by solvent extraction with ionic iquids and recovery of neodymium metal by direct electrodeposition. Solv. Extr. Ion Exch. (2016) 34, 522–534.

[14]de los Ríos, A. P., F. J. Hernández-Fernández, S. Sánchez-Segado, L. J. Lozano, J. I. Moreno and C. Goínez. Selective separation of Zn(II) over Fe(III) from acidic media using ionic liquids as sole extraction agents. Chemical Engineering Transactions (2010) 21, 625-630.

[15]Mishra, R. K., P. C. Rout, K. Sarangi and K. C. Nathsarma. Solvent extraction of Fe(III) from the chloride rich liquor of low grade iron ore tailings using Aliquat 336. Hydrometallurgy (2011) 108, 93-99.

[16]Hussin, N. H., I. Yusoff, Y. Alias, S. Mohamad, N. Y. Rahim and M. A. Ashraf. Ionic liquid as a medium to remove iron and other metal ions: a case study of the North Kelantan Aquifer. Malaysia, Environ. Earth Sci. (2014) 71, 2105–2113.

[17]Kogelnig, D., A. Stojanovic, F. Jirsa, W. Korner, R. Krachler and B. K. Keppler. Transport and separation of iron(III) from nickel(II) with ionic liquid trihexyl(tetradecyl)phosponium chloride. Separ. Purif. Technol. (2010) 72: 56-60.

[18]Regel-Rosocka, M., L. Nowak and M. Wisniewski. Removal of zinc(II) and iron ions from chloride solutions with phosponium ionic liquids. Separ. Purif. Technol., (2012) 97: 158-163.

[19]Filiz, M. Extraction of Mn(II) from aqueous hydrochloric acid solutions into Alamine 336–m-xylene system. Hydrometallurgy (2007) 87, 58–62.

[20]Liu, Y., S-H. Nam and M. Lee. Stripping of Fe(III) from the loaded mixture of D_2EHPA and TBP with sulfuric acid containing reducing agents. Bull. Korean Chem. Soc. (2014) 35, 2109-2113.

[21]Wei, W., C.-W. Cho, S. Kim, M.-H. Song, J. K. Bediako and Y.-S. Yun. Selective recovery of Au(III), Pt(IV), and Pd(II) from aqueous solutions by liquid–liquid

extraction using ionic liquid Aliquat-336. J. Mol. Liq., (2016) 216, 18–24.
[22]Morris, D. F. C. and E. L. Short. Manganese(II) chloride complexes. Part I. Stability constants, J. Chem. Soc. (1961) 5148–5153.

CHAPTER 3

Solvent Extraction and Stripping of Fe(III), Mn(II) and Co(II) with Deep Eutectic Solvent as Extractant

3

Solvent Extraction and Stripping of Fe(III), Mn(II) and Co(II) with Deep Eutectic Solvent as Extractant

Abstract. Use of an appropriate extractant categorized as green solvent in the solvent extraction technique is a manner to bring the green chemistry into reality. This Chapter discusses the use of deep eutectic solvent (DES) composed of decanoic acid and lidocaine which has characteristic as green solvent for separation of Fe(III), Mn(II) and Co(II). It was found that the pH of the initial metal solution strongly influenced the extraction mechanism. Fe(III) can be extracted at pH 1.0 to 2.0 due to the ion pair reaction between Fe(III) and decanoic anion, while at the higher pH the extraction mechanism cannot be evaluated due to the formation of precipitation at the aqueous phase. In the case of Mn(II) andCo (II) the ion pair reaction was occurred at the pH of lower than 2.5 and higher than 3.5 for Mn(II) while for Co(II) this mechanism was observed at the pH of lower than 1.5 and higher than 2.5. Between these two ranges of pH, the most possible mechanism was the cation exchange reaction between metal cation with lidocaine cation. The DES concentration needed to reach the complete separation of Fe(III) was about 25 g/L while Mn(II) and Co(II) were completely extracted using about 300 g/L of DES. The metals in the metals-loaded DES solution were successfully stripped using hydrochloric acid as stripping agent through cation exchange mecahnism.

Introduction

Use of an appropriate extractant categorized as green solvent in the solvent extraction technique is a manner to bring the green chemistry into reality. Ionic liquids (ILs) can be classified as a class of green solvents and have attracted the considerable attention of the researchers because of their physical and chemical properties such as near-zero vapor pressure, good chemical and thermal stability as well as the tunability of the physicochemical properties by altering the substitutive groups on the cation or the combined anion [1]. However, it has been reported that ILs have the limitations such as toxicity [2, 3], poor biodegradability [4], and high cost especially in the purification process [5]. Therefore, deep eutectic solvents (DESs) have been developed to overcome the limitations of ILs.

In a DES, two or three cheap and safe compounds acting as hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) respectively can be connected one another with hydrogen bonding to form a eutectic mixture with melting point far below the individual components due to contain large and non-symmetric ions with low lattice energy [6, 7]. The major advantages of DESs over ILs are their lower prices and easy preparation due to simply mixing the two solid constituents at moderate temperatures resulting in a liquid DES, without the need for a solvent or complex purification step [7]. Furthermore, in a DES the excellent advantages of ILs can be maintained and also the disadvantages of ILs can be avoided at the same time [8].

With a unique combination of physical and chemical properties, DES can be employed in several areas of application such as metal processing, organic synthesis, biodiesel purification, and catalysis applications [6, 7]. One of the applications of the DESs in metal processing largely investigated nowadays is the use of DESs as extractant for recovery of metal ions employing solvent extraction technique.

Solvent extraction is a widely economical used process in hydrometallurgy for recovery of valuable ions [9]. It is because solvent extraction can be operated in continuous mode using relatively simple equipment but has a high efficiency and selectivity. The efficiency and selectivity of this technique is highly influenced by the extractant applied. Use of DES as extractant for separation of metals has been conducted by several research groups [10-12]. The investigation for removal of alkali and transition metal ions including Fe(II), Mn II) and Co(II) using DES composed of decanoic acid and lidocaine concluded that extraction process involved the cation exchange reaction between metal ions and lidocaine cation [12]. However the effect of the pH of the initial metal solution was not investigated even though the structure of DES consisting of HBD and HBA was strongly influenced by the solution pH.

Therefore in this chapter the DES was used to recover Fe(III), Mn(II) and Co(II) from aqueous solution with emphasis on the pH effect in order to elucidate the extraction mechanism. Because the stripping of the metal from the metal-loaded organic phase is sometimes difficult especially when the concentration of loaded

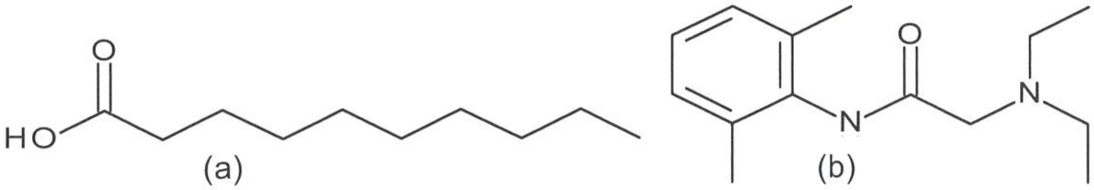


Figure 1. Molecule structures of decanoic acid (a) and lidocaine (2-(diethylamino)-N-(2,6-dimethylphenyl) acetamide), (b)

metal is high [13], this work also investigate the stripping of metals from metal-loaded organic phase.

Experimental Section

Chemicals

Decanoic acid, lidocaine and sodium acetate trihydrate were purchased from Wako and the molecular structures of decanoic acid (a) and lidocaine (b) are shown in Figure 1. Ferric chloride, manganese chloride, Cobalt chloride, nitric acid and acetic acid were purchased from NacalaiTesque, Inc., Kyoto, Japan. All chemicals were used without further purification.

Preparation of DES

DES was prepared by mixing of HBD and HBA by the following procedure: decanoic acid and lidocaine in the molar ratio of 2 :1 were weighed in a beaker and the beaker was closed with para film to avoid the contamination with water. The mixture was stirred at room temperature until a clear liquid appeared. The inside of the beaker was rinsed with the DESs to ensure that all solids are in the liquid phase, and then the DESs were stirred again until a clear homogenous mixture was formed. Before use, the DESs were left overnight at room temperature to investigate if recrystallization occurred.

Solvent extraction of Fe(III), Mn(II) and Co(II)

The organic phase was prepared by dissolving of DES in n-heptane and the aqueous phase was 10 mM of aqueous metal solution. The pHs of metal solution were adjusted using nitric acid, acetic acid and sodium acetate. Equal volume of organic solution and metal solution were mixed. The mixture was shook using Test Tube mixture (SHIBATA TTM-1) for 3 minutes and centrifuged (himac CT 4D) at 1500 rpm for 15 minutes. The concentration of metal and lidocaine in the aqueous phases were measured using ICP-AES (ICPS-8000) and UV-VIS spectrophotometer (UV-2500PC) respectively. The distribution ratio, *D,* and the extractability of metals were calculated using equation (1) and (2) rspectively.

$$D = \frac{[M]_{aq,int} - [M]_{aq,eq}}{[M]_{aq,eq}} \qquad (1)$$

$$\%\text{Extractability} = \frac{[M]_{org,eq}}{[M]_{aq,int}} \text{ x } 100$$

$$= \frac{[M]_{aq,int} - [M]_{aq,eq}}{[M]_{aq,int}} \text{ x } 100 \qquad (2)$$

where $[M]_{org.eq}$ is the equilibrium concentration of metal in the organic phase and $[M]_{aq.int}$ is the initial concentration of metal in the aqueous phase.

Stripping experiment

The metal-loaded organic solution was prepared by mixing of 10 mL of aqueous solution containing 10 mmol/L pH 2.0 for Fe(III) and pH 5.0 for Mn(II) and Co(II) with 10 mL of DES solution in heptane with concentration 25 g/L contacted with Fe(III) and 300 g/L contacted with Mn(II) and Co(II). After mixing for 3 minutes using Test Tube mixture (SHIBATA TTM-1), the concentration of the metals in the aqueous phase was firstly measured to determine the initial concentration of metals in the organic phase which was the initial metal concentration in the organic phase ($[M]_{org.int.}$). The equal volume of metal-loaded organic solution and hydrochloric acid as stripping agent were mixed using Test Tube mixture (SHIBATA TTM-1) for 3 minutes and was followed by centrifugation for 15 minutes at 1500 rpm. The concentration of the metals in the aqueous phase was then measured using ICP-AES (ICPS-8000) and the percentage of metal stripping was calculated using equation (3).

$$\%\text{Stripping} = \frac{[M]_{aq.eq.}}{[M]_{org.int.}} \times 100 \qquad (3)$$

where $[M]_{org.int}$ is the difference between $[M]_{aq}$ before and after mixing with the organic phase.

Result and Discussion

Effect of pH on the extractability of metals

Hypothetically, DES employed in this experiment will be strongly influenced by the pH of the initial metal solution. It is because structurally both lidocaine and decanoic acid as the constituents of this DES can accept and donate the protons. Therefore we experimented the effect of the Fe(III) solution pH on the extractability and distribution ratio as shown in Figure 2(a). The extractability and distribution ratio at

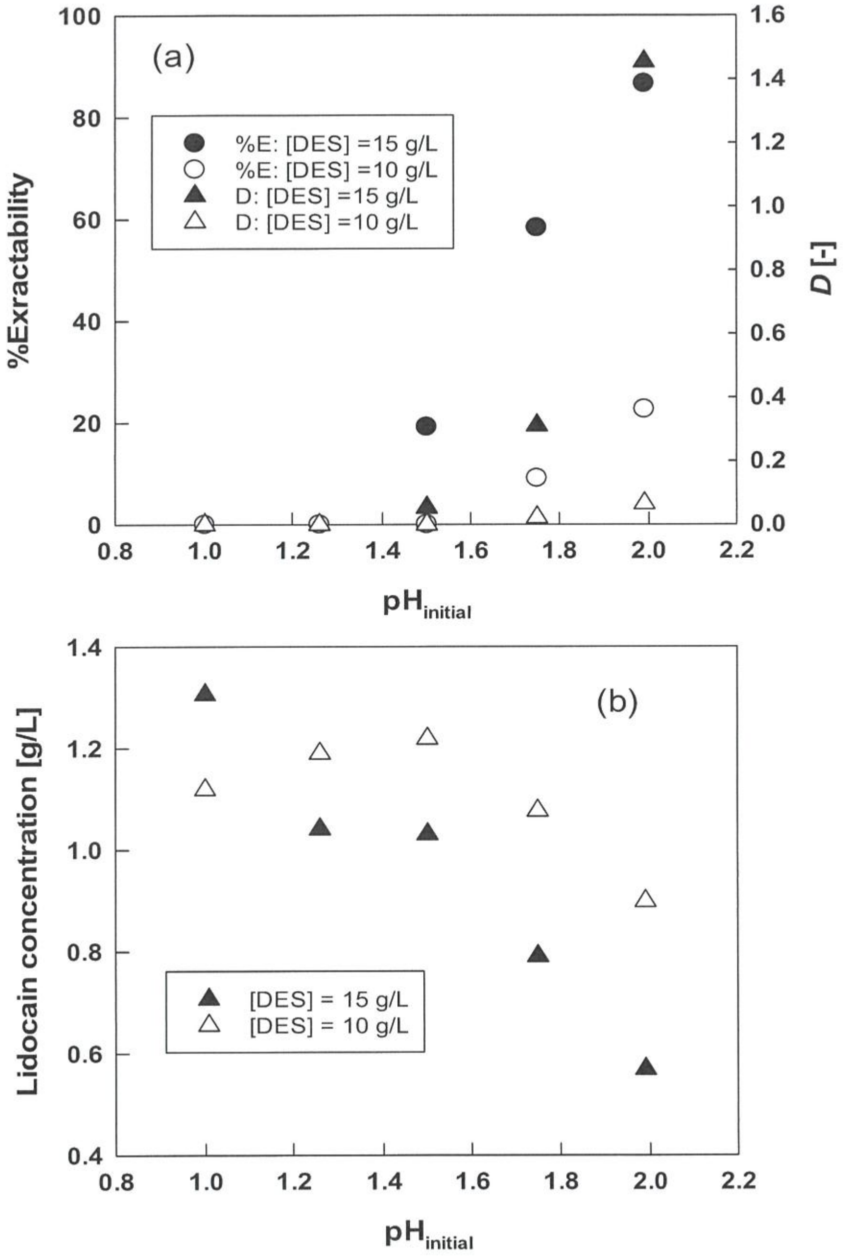


Figure 2. Effect of the initial solution's pH on extractability and distribution ratio of Fe(III) (a) and concentration of lidocaine in aqueous phase (b)

the higher pH of the Fe(III) solution cannot be evaluated because of the formation of precipitation at the bottom phase. It was reported that cation exchange between lidocaine cation which was formed from the protonation of lidocaine with metal ions dominated the reaction of alkali and transition metal ions separation using DES composed of decanoic acid and lidocaine [12].

In order to confirm the extraction mechanism of Fe(III), the concentration of lidocaine in the aqueous phase at various pH of Fe(III) solution was also measured as shown in Figure 2(b). As seen in the Figure 2, the extractability of Fe(III) inversely proportional to lidocaine concentration in the aqueous phase. This result explicitly illustrates that the cation exchange between lidocaine cation and Fe^{3+} perhaps was not occurred in this extraction process. If the cation exchange reaction takes place in this system, the increase in Fe(III) extractability should be followed by increasing the lidocaine concentration in the aqueous phase as a consequence of the higher solubility of lidocaine cation in the aqueous phase than that of lidocaine itself. However, lidocaine concentration in the aqueous solution for 15 g/L DES is lower than that of 10 g/L DES. This is suggesting that lidocaine solvates the complex in the organic phase.

Another way to prove that cation exchange reaction was not occured in this process was to examine the effect of the metal solution pH on the extractability of metals using decanoic acid or lidocaine solution as extractant as shown in Table 1. The results shown in the Table 1 indicated that the change of pH was more drastical for metal solution contacted with lidocaine solution than that of cantacted with decanoic acid. This result confirmed that the protonation of lidocaine was really happened. At the lower pH of metal solution the concentration of lidocaine cation should be higher than that of at the higher pH. If the cation exchange mechanism really occured, the extractability of the both metals should not be zero at the lower pH. Therefore, this result also confirmed that the cation exchange reaction was not the mechanism generating the extractability of metals. The extractability resulted at the higher pH probably derived from the deprotonation of both lidocaine and decanoic acid resulting the anion of lidocaine and decanoic which then reacted with metal ions.

Table 1. Effect of pH on the extractability of Fe(III) and Mn(II) using lidocaine (lid.) and decanoic acid (DA) solution as extractant

	pH$_{int}$	**Lid. 10 g/L**		**DA 100g/L**	
		pH$_{eq}$	**%E**	**pH$_{eq}$**	**%E**
Fe (III)	1.1	2.3	0.0	1.9	0.0
	1.5	3.0	0.0	1.9	0.0
	2.0	3.8	0.0	2.3	0.0
	2.5	4.1	15.4	2.5	19.3
	3.0	4.2	37.1	2.8	39.3
	3.5	4.3	43.4	3.3	46.3
	4.0	4.3	22.4	Formation of precipitation at the bottom phase	
	4.5	4.7	33.4		
	5.0	6.2	99.4		
		Lid. 50 g/L		**DA 100g/L**	
	pH$_{int}$	**pH$_{eq}$**	**%E**	**pH$_{eq}$**	**%E**
Mn (II)	1.0	6.3	0.0	1.8	0.0
	1.5	6.6	0.0	1.8	0.1
	2.0	6.9	0.0	2.2	0.0
	2.5	7.0	0.0	2.5	0.0
	3.0	6.6	0.0	3.0	0.1
	3.5	6.5	0.0	3.5	0.0
	4.0	6.8	0.0	3.9	0.0
	4.5	7.0	0.0	4.1	0.0
	7.4	8.0	8.3	5.5	19.4

The most likely mechanism was the ion pair reaction between Fe^{3+} and the decanoic anion. Griffin et al., (2014) reported that the DES composed of decanoic acid and lidocaine in the molar ratio of 2 : 1 contained 25 % of decanoic anion [14]. Hence, the increase in the Fe(III) extractability by increasing of the initial pH of Fe(III) solution was probably derived by the competition between the lidocaine cation and Fe(III) to react with decanoic anion. Increasing of pH decreased the concentration of lidocaine cation which in turn increased the extractability of Fe(III). The extraction mechanism of Fe(III) using DES can be schemed as follows:

pH < 2.0:

$$Fe^{3+}_{aq} + 3RCOO^{-}_{org} + nLid_{org} \rightleftharpoons Fe(RCOO)_3(Lid)_{n,org} \qquad (4)$$

pH > 2.0: The extractability cannot be evaluated due to the formation of precipitation at the aqueous phase.

where R is the nonyl group.

Unlike Fe(III), effect of pH on the extractability Mn(II) and Co(II) can be evaluated at the broader range of pH because the precipitation was only observed at the boundary phase for the system applying solution with higher pH. The effect of the initial Mn(II) and Co(II) solution's pH on the extractability is shown in Figure 3. Because most of the distribution ratio values were infinite, these values are not shown in this graph. The result shown in Figure 3 can be split into three ranges of pH. The similar trend to the extractability of Fe(III) observed at the pH 1.0–2.5 for Mn(II) and 1.0-1.5 for Co(II) indicated the ion pair reaction between metals cation with decanoic anion already contained in the DES. The top of the extractability reached at pH 2.5 and 1.5 for Mn(II) and Co(II) respectively probably denoted that the decanoic anion completely reacted with metal cations at this point.

The opposite trend observed from pH 2.5-3.5 for Mn(II) and 1.5-2.5 for Co(II) was doubtless derived from the different mechanism. As at this pH range, the 25 % decanoic anion naturally contained in the DES has completely reacted with metal cation, while the pH of solution was not high enough to allow the formation of the decanoic anion through the deprotonation of decanoic acid, the ion pair reaction should not be happened in this pH range. The most possible reaction occurred in this pH range was the cation exchange between metal cation and lidocaine cation. The decrease in the extractability was caused by decreasing of the lidocaine cation concentration as a consequence of the increase in the solution pH.

The formation of the decanoic anion through deprotonation of decanoic acid was just started at the solution's pH of higher than 3.5 and 2.5 for Mn(II) and Co(II) respectively increased the metals extractability at this pH range. The deprotonation of decanoic acid at this pH range can also be clarified from the data in Table 1 and pKa of decanoic acid (= 4.95). Therefore, the influence of pH on the extractability of Mn (II) can be represented in the equation (5) and (6).

pH < 2.5, pH > 3.5 for Mn (II) or pH < 1.5, pH > 2.5 for Co (II)

$$M^{2+}{}_{aq} + 2RCOO^{-}{}_{org} + mLid_{\ org} \leftrightarrow M(RCOO)_2(Lid)_{m,\ org} \qquad (5)$$

2.5 > pH > 3.5 for Mn (II) or 1.5 > pH > 2.5 for Co (II)

$$M^{2+}_{aq} + 2Lid^{+}{}_{org} \leftrightarrow M^{2+}_{org} + 2Lid^{+}{}_{aq} \qquad (6)$$

Effect of DES concentration on the extractability of metals

The concentration of the DES is another parameter extremely influencing the extractability of metal ions. In general, the extractability of metals is directly proportional to DES concentration. However, use of excess DES concentration will be not economically profitable. Therefore it will be better to apply the lowest DES concentration resulting the highest extractability.

The dependence of the extractability on the DES concentration is shown in Figure 4. Generally, Figure 4 shows that the concentration of DES needed to reach the complete separation for Fe(III) was lower than that of for Mn(II) and Co(II). It is probably due to the reaction constant of the equation (4) is larger than that of equation (5) and (6) as a consequence of the higher oxidation number of Fe(III). In the case of Fe(III), it is seems that the better condition of separation was at pH of 2.0 because the Fe(III) was completely extracted at the DES concentration about 15 g/L. However, at this initial pH, the mixture was not clear at the DES concentration of 10 g/L and higher. On the contrary, at pH of lower than 1.5, the extractability was still very low for each DES concentration. Therefore the pH of 1.5 was recomended as optimum pH for recovery of Fe(III). For Mn (II) and Co(II), it seems that the pH of initial metal solution did not significantly affect the extractability. However, application of the lower pH is better due to the tendency of the metal ions to precipitate at the higher pH.

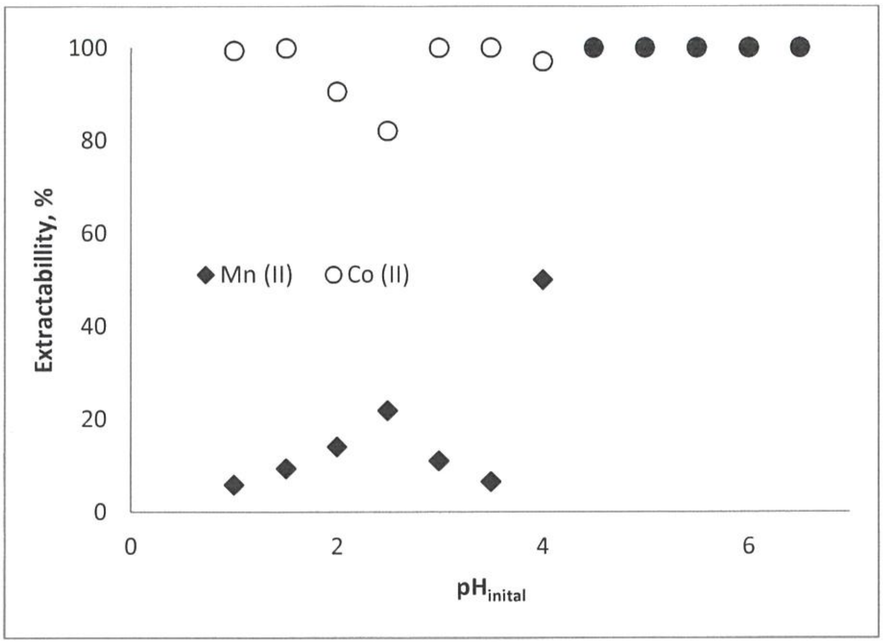


Figure 3. Effect of the pH on extractability of Mn(II) and Co(II). DES concentration was 100 g/L

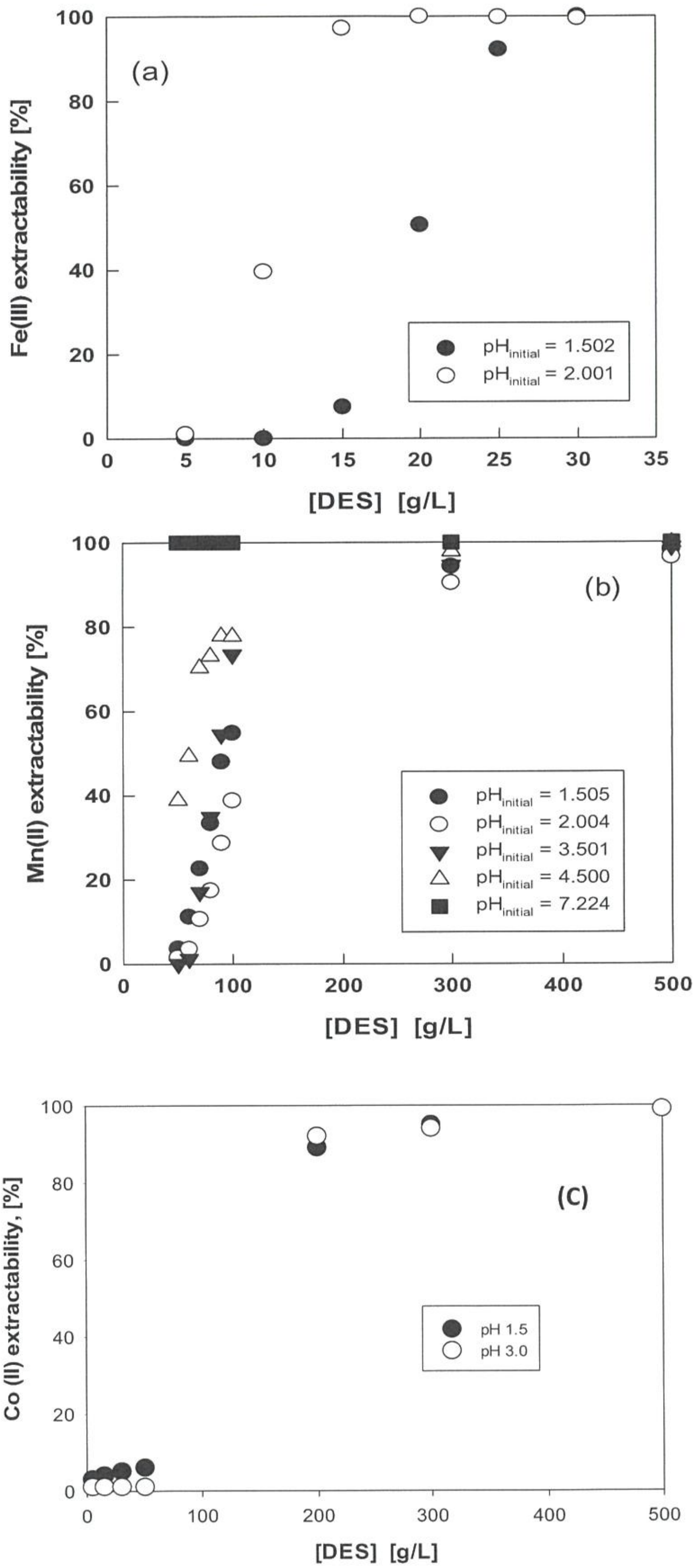


Figure 4. Effect of the DES concentration on the extractability of (a) Fe(III), (b) Mn(II) and (c) Co(II)

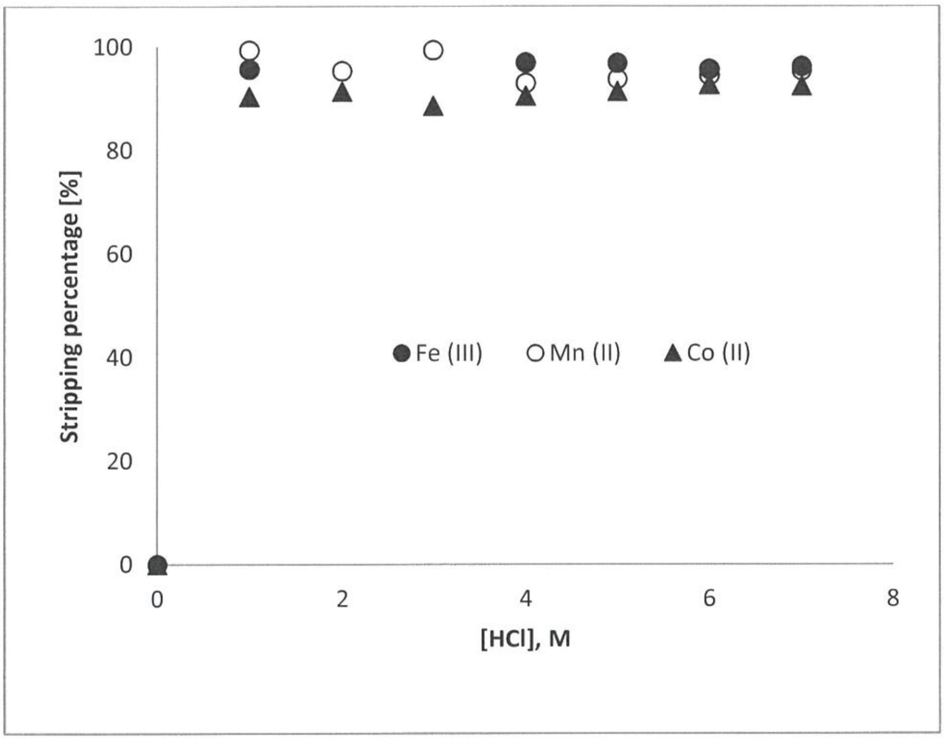


Figure 5. Effect of hydrochloric acid concentration on the stripping percentage of metals.

Stripping of metals

Stripping of metals from the metals-loaded organic phase is the last step of three steps of solvent extraction technique [15]. It was found that the three metal ions experimented were successfully stripped using hydrochloric acid as stripping agent such shown in the Figure 5. Figure 5 also shows that water that is the zero concentration of hydrochloric acid in this figure was not compatible for stripping of metal ion from metals-loaded DES phase. Because metals-loaded DES phase was obtained by mixing of organic phase containing DES with metal solution at the pH where ion pair reaction between metal ion with decanoic anion generating the metals extractability, the stripping mechanism can be shown in equation (7).

$$\mathrm{M(RCOO)_{n\ org} + nHCl_{\ aq} \leftrightarrow MCl_{n,\ aq} + nRCOOH_{\ org}} \qquad (7)$$

Conclusion

The pH of initial metal solution strongly affected the separation of Fe(III), Mn(II) and Co(II) from aqueous solution using DES composed of decanoic acid and lidocaine as extractant. In the case of Fe(III), extraction mechanism involved the ion pair reaction between Fe^{3+} and decanoic anion at the pH of lower than 2.0, while at the larger pH the precipitation was formed at the aqueous phase causing the effect of pH cannot be evaluated. In the case of Mn(II) this mechanism was observed at pH of lower than 2.5 and higher than 3.5 and at the pH of lower than 1.5 and higher than 2.5 for Co(II). Between these two ranges of pH, the most possible mechanism was the cation exchange reaction between metal cations with lidocaine cation. Fe(III) needed the lower concentration of DES (25 g/L) to reach the complete extraction than Mn(II) and Co(II) (300 g/L). The metals in the metals-loaded organic phase were successfully stripped using hydrochloric acid solution through the cation exchange mechanism.

References

[1] Matsumoto, M. Ionic liquid-based supported liquid membranes. in: Mohanty, K., and M.K. Purkait (Eds.). Membrane technology and applications. CRC Press, Boca Raton, USA. (2012) pp. 305–316.

[2] Pham, T. P. T., C. Chul-Woong and Y. Yeoung-Sang. Environmental fate and toxicity of ionic liquids: A review. Water research (2010) 44, 352–372.

[3] Biczak, R., B. Pawłowska, P. Bałczewski and P. Rychter. The role of the anion in the toxicity of imidazolium ionic liquids. Journal of Hazardous Materials. (2014) 274,181-190.

[4] Stolte, S., S. Steudte, A. Igartua and P. Stepnowski. The Biodegradation of ionic liquids - the view from a chemical structure perspective. Current Organic Chemistry (2011) 15 (12), 1-28.

[5] Kareem, M. A., F. S. Mjalli, M. A. Hashim and I. M. AlNashef. Phosphonium-based ionic liquids analogues and their physical properties. J. Chem. Eng. Data (2010) 55, 4632–4637

[6] Zhao, B.-Y., P. Xu, F.-X Yang, H. Wu, M.-H. Zong and W.-Y. Lou. Biocompatible deep eutectic solvents based on choline chloride: Characterization and application to the extraction of rutin from sophora japonica. ACS Sustainable Chem. Eng. (2015) 3, 2746−2755

[7] Zhang, Q., K. D. O. Vigier, S. Royer and F. Jérôme. Deep eutectic solvents: syntheses, properties and applications. Chem. Soc. Rev. (2012)41, 7108–7146

[8] Smith, E. L., A. P. Abbott and K. S. Ryder. Deep eutectic solvents (DESs) and their applications. Chem. Rev. (2014) 114, 11060−11082.

[9] Katsuta, S., Y. Watanabe,; Y. Araki and Y. Kudo. Extraction of gold(III) from hydrochloric acid into various ionic liquids: Relationship between extraction efficiency and aqueous solubility of ionic liquids. ACS Sust. Chem. Eng. (2016) 4, 564−571

[10]Foreman, M. R. StJ. Progress towards a process for the recycling of nickel metal hydride electric cells using a deep eutectic solvent. Cog. Chem. (2016) 2, 1139289.

[11]Tereshatov, E. E., M. Y. Boltoeva and C. M. Folden III. First evidence of metal transfer into hydrophobic deep eutectic and low-transition-temperature mixtures:

indium extraction from hydrochloric and oxalic acid. Green Chem. (2016) 8, 4616–4622

[12]van Osch, D. J. G. P., D. Parmentier,; C. H. J. Dietz, A. van den Bruinhorst, R. Tuinier and M. C. Kroon. Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents. Chem. Commun. (2016) 52, 11987–11990

[13]Liu, Y., S-H. Nam and M. Lee. Stripping of Fe (III) from the loaded mixture of D2EHPA and TBP with sulfuric acid containingreducing agents. Bull. Korean Chem. Soc., (2014) 35, 2109-2113.

[14]Grffin, P. J., T. Cosby, A. P. Holt, R. S. Benson and J. R. Sangoro. Charge transport and structural dynamics in carboxylic-acid-based deep eutectic mixtures. J. Phys. Chem. B (2014)118, 9378–9385.

[15]Mansur, M. B. Solvent extraction for metal and water recovery from industrial wastes and effluents. REM: R. Esc. Minas, Ouro Preto (2011) 64(1), 051-055.

Chapter 4

Liquid Membrane Permeation of Fe(III) and Mn(II) with Ionic Liquid and DES as Carrier

4

Liquid Membrane Permeation of Fe(III) and Mn(II) with Ionic Liquid and DES as Carrier

Abstract: The main disadvantage of the solvent extraction technique for separation of metals is the large amount of extractants required in this process. This drawback can be resolved using liquid membrane permeation which significantly reduced the amount of extractant. This chapter discuss the use of supported ionic liquid membrane for separation of Fe(III) and Mn(II). It was found that the combination of Aliquat-336 as a carrier and 0.1 M Na_2SO_4 as a stripping phase gave a largest permeability of Fe(III) (approximately 80 %). In the case of Cyphos IL-101, the stripping rate was found to be considerably slow. The permeation rate of Mn(II) in membrane permeation using Aliquat 336 was smaller than that of Fe(III). This suggests that the kinetic separation of Fe(III) and Mn(II) is possible. Unlike ILs, DES composed of decanoic acid and tetrabutylammonium bromide cannot permeate Mn(II) at all.

Introduction

One of the main step determining the cost of metals production is separation and purification steps. It was reported that up to 30% of the energy required is employed in separation processes of metals [1]. Therefore, an effective, economic and environmental friendly method is highly needed in order to reduce the production cost without neglecting the environmetal impact derived by the process. Solvent extraction is a widely used method in metal extraction due to its simplicity, speed, and wide scope [2]. The main advantage of solvent extraction technique is that it is easier to control the paramaters controling extraction such as organic phase, pH or extractant can be changed, possible to operate in continuous mode and it is suitable for the processing of high metal feed concentrations [3]. However, the main downside of this method include the production of large amount of organic waste, possible formation of third phase, and involvement of aggressive chemicals that may degrade the organic solvent and extractants during prolonged contact [4]. In order to avoid these commonly occured problems during solvent extraction process, supported liquid membrane (SLM) have been developed [5].

The SLM technique which the porous solid structure impregnated with liquid is a combination of three simultaneously occurring processes: molecule extraction from the feed phase to the SLM, diffusion through SLM and re-extraction to the received phase [6]. SLM can be used to separate the two aqueous phases because organic liquid is immiscible with the aqueous feed and stripping solution [7]. By using the SLM, the amount of organic solvent can be reduced due to the smaller organic phase volume existing in the membrane pores. Degradation of the organic solvent and extractant, as well as the formation of emulsions, may be reduced by not directly mixing aqueous and organic phases as is the practice in solvent extraction [4]. Since the volume of organic components used in the membrane is small and because the extraction and re-extraction carried out in one technological step, it provides many advantages such as: expensive carriers may be used, higher separation factors are obtained due to the non-equilibrium mass-transfer characteristics occurred where the separation is not limited by the conditions of equilibrium [8], they are easy to scale-up, most importantly they have very low energy requirements, low capital and operating costs. Hence the use of liquid membrane technology for the separation of components is a promising technology for metals extraction [9]. However, the use of volatile organic solvents as carrier in SLM is still have problems associated with the membrane stability due to the lost of organic phase from the supporting membrane, either by evaporation or dissolution/dispersion into the adjacent phases, pressure difference, etc. [10]. Substitution of the non-volatile carrier such as Ionic liquid (ILs) and deep eutectic solvents (DES) for the conventional organic solvents can improve the stability of membrane.

ILs which are generally composed of organic cations such as imidazolium, pyridinium, pyrrolidinium, phosphonium and ammonium and counter ions can be either an inorganic (e.g. tetrafluoroborate, hexafluorophosphate, chloride, bromide) or an organic (e.g. trifluoromethylsulphonate, bis[(trifluoromethyl) sulphonyl]imide) anions [11] undoubtedly are a class of green solvent owing to their unique properties such as negligible vapor pressure, high thermal stability, high viscosity, good solvation ability, a wide liquid range, and tunable polarity [12]. Application of ILs in SLIM enables the increasing in the stability of the membrane because ILs cannot easily evaporate from the pores of the membrane. In addition, because of high viscosity, they cannot be easily replaced from the pores of the membrane. DES is the analogues of ILs but is more superior than that of ILs due to the lower price and very easy in preparation [13]. The constituents of DES components are very cheap and can be prepared by simply mixing the two solid constituents at moderate temperatures resulting in a liquid DES, without the need for a solvent or complex purification step [13].

In this thesis, the polymer inclusion membrane (PIM) with ILs or DES as carrier were employed for permeation of Fe (III) and Mn (II). PIM which has a similar configuration to supported ionic liquid membranes and were formed by casting a solution containing ionic liquid or DES and base polymer poly(vinyl chloride) (PVC) in the absence of plasticizer to form a thin, flexible, and stable film, became more stable than supported ionic liquid membrane [14].

Experimental section

Chemicals

Aliquat 336 and Cyphous IL101 (used as ILs) were purchased from Strem Chemicals Inc. and Cytec Industry Inc. respectively, and their molecular structures are shown in Figure 1. Decanoic acid and tetrabutylammonium bromide (as component of DES) were purchased from Wako and their molecular structures are shown in Figure 2. The base polymer used was PVC from Wako Pure Chemical Industries, Ltd, Osaka. (n = 1,100). Ferric chloride and manganese chloride of GR grade were purchased from Nacalai Tesque, Inc., Kyoto, Japan. Concentrated hydrochloric acid solutions (Wako Pure Chemical, Industries, Ltd., Osaka, Japan) were used in preparing the feed solution. All chemicals were used without further purification.

DES preparation

DES was prepared by mixing of HBD and HBA by the following procedure: decanoic acid and tetrabutylammonium bromide in the molar ratio of 2 :1 were weighed in a beaker and the beaker was closed with para film to avoid the contamination with water. The mixture was stirred at room temperature until a clear liquid appeared. The inside of the beaker was rinsed with the DESs to ensure that all solids are in the liquid phase, and then the DESs were stirred again until a clear homogenous mixture was formed. Before use, the DESs were left overnight at room temperature to investigate if recrystallization occurred.

PIMs preparation

The PIMs used to permeate the metals were prepared by means of the solution casting method described in previous papers [14, 15]. The polymer solution was prepared by dissolving 1.5 g of ionic liquid or DES and 0.6 g of PVC in 40 mL of tetrahydrofuran (THF). The solution mixture was stirred with homogenizer and poured into a Petri dish. It was then kept at room temperature for 24 hours to allow for the evaporation of THF. The membrane was then released from the dish. The polymer membranes have an effective area, A, of 12 cm^2 and were fixed in the apparatus shown in Figure 3.

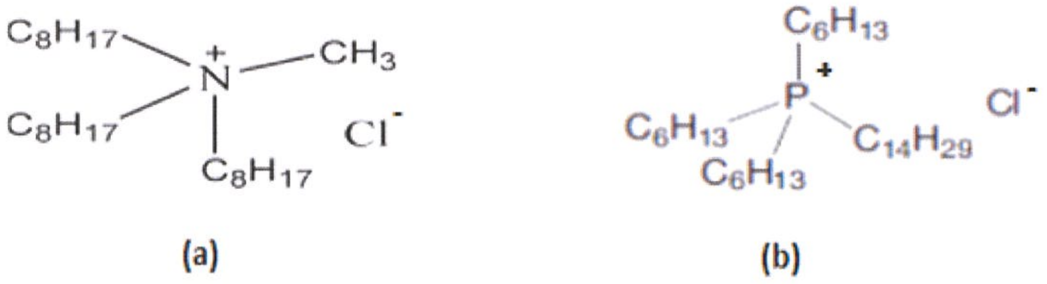


Figure 1. Molecule structures of ILs used: (a) Aliquat 336 (*N*-Methyl-*N,N,N*-trioctylammonium chloride) and (b) Cyphos IL-101 (Trihexyl(tetradecyl)phosphonium chloride)

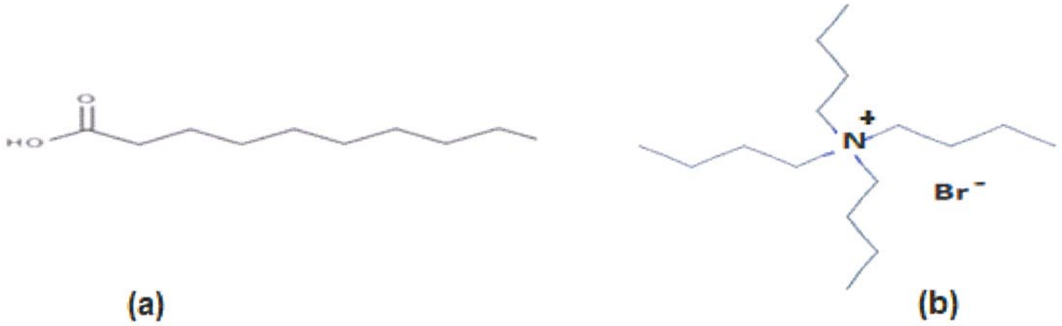


Figure 2. Molecule structures of (a) decanoic acid and (b) tetrabutylammonium bromide

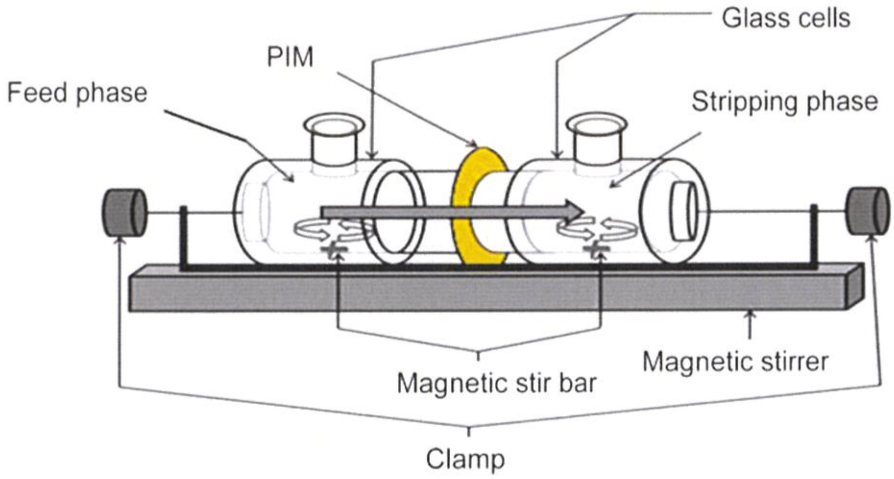


Figure 3. Schematic diagram of the experimental setup for the permeation experiment

PIMs permeation

The permeation experiment was conducted using the apparatus shown in Figure 3. The feed phase was metal salts dissolved in hydrochloric acid solution and the stripping phase was one of the following aqueous solutions; Na_2SO_4, $NaHSO_4$ and HCl etc. Each compartment was filled with 100 mL of the respective solution at room temperature under the initial conditions. The stirring speed of the magnetic bar in each cell was controlled at 200 rpm. Samples from both solutions were withdrawn at regular intervals, and the pH in both cells was measured with a pH meter (Horiba F-71). The concentrations of metals in both compartments were determined using ICP-AES. The permeation percentage was calculated using equation (1).

$$\text{Permeation}\ (\%) = \frac{[\mathrm{M}]_{\mathrm{s,t}}}{[\mathrm{M}]_{\mathrm{f,0}}} \times 100 \qquad (1)$$

where $[M]_{s,t}$ is the metal concentration in the stripping phase at a certain time and $[M]_{f,0}$ is the initial metal concentration in the feed phase.

Result and Discussion

Experiments regarding membrane permeation were conducted based on results concluded in the solvent extraction experiments. In the solvent extraction experiments, it was found that the three ILs used were great carriers for the

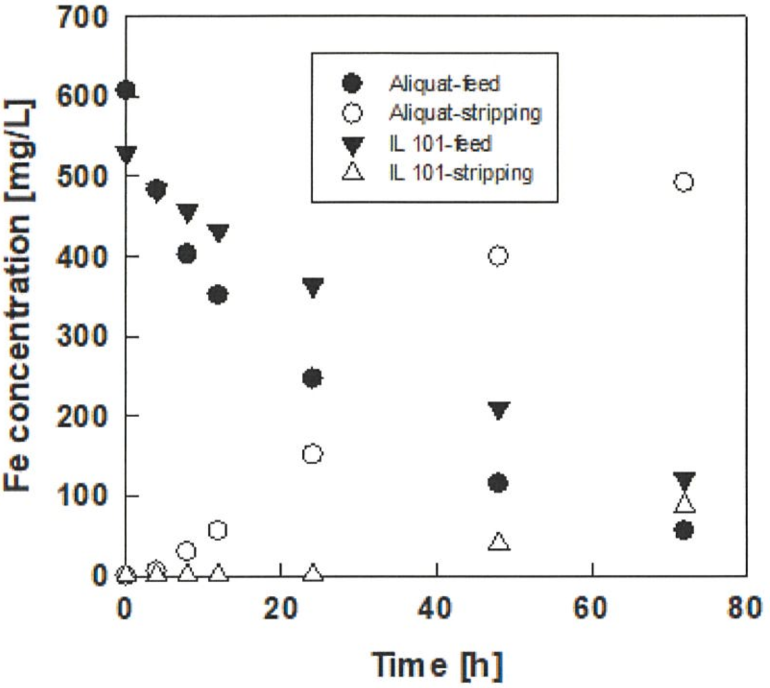


Figure 4. Permeation of Fe(III) using Aliquat-336 and Cyphos IL-101 as carrier

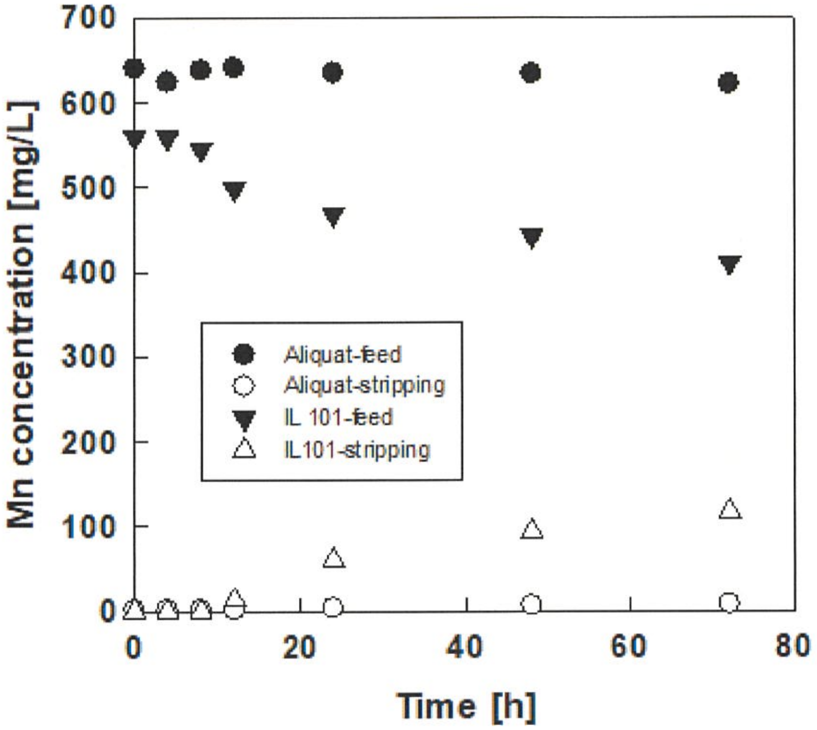


Figure 5. Permeation of Mn(II) using Aliquat-336 and Cyphos IL-101 as carrier

extraction of Fe(III). However, for Mn(II), Cyphos IL 101 was the best extractant. Hence, in the membrane permeation experiment the recovery of Fe(III) and Mn(II) were evaluated using Aliquat 336 and Cyphos IL 101 as a membrane carrier.

The results of the Fe(III) permeation using 0.1 M Na_2SO_4 as a stripping reagent were shown in Figure 4. Figure 4 shows that the recovery of Fe(III) in the combination of Aliquat 336 and Na_2SO_4 0.1 M as carrier and stripping phases respectively (80.94 %), resulted higher than that of Cyphos IL101 and Na_2SO_4 0.1 M (16.43 %). In the case of Aliquat 336, the decrease in concentration in the feed phase almost corresponded to the increase in concentration in the stripping phase. However, in the case of Cyphos IL 101, although Fe concentration decreased in the feed phase, Fe concentration did not increase correspondingly in the stripping phase, suggesting that Cyphos IL 101 and Fe(III) form a very stable complex. This was difficult to strip and remained in the membrane phase. Successful permeation of Fe (III) through PIM composed of Cyphos IL 101 as a carrier, cellulose triacetate as a base polymer and *o*-nitrophenyl octyl ether as a plasticizer was reported [15]. This difference in the permeation behavior of Fe(III) may have been caused by the interaction between the base polymer used and the metal complex.

The recoveries of Mn(II) from 4 M or 6 M hydrochloric acid solutions with PIM were carried out using Cyphos IL101 as a carrier. In the case of Aliquat 336, Mn(II) was not permeated at all. Figure 5 shows the permeation of Mn(II) from the 4 M HCl solution to the Na_2SO_4 solution. The sum of concentrations of Mn(II) in feed and stripping phases was similar to the initial concentration, suggesting that the permeation of Mn(II) was successful, but the permeation rate was slower than the Fe(III) permeation. Table 1 lists the effect of a stripping reagent on the permeation.

Table 1 shows that the recovery of Mn(II) with PIM in all of the stripping phases was still below 35 %. Recovery of Mn(II) using HCl as a stripping phase was inversely proportional to the concentration of HCl because the formation of $MnCl_3^-$ in the concentrated hydrochloric acid solution of the stripping phase resulted in a decrease in the concentration difference in $MnCl_3^-$. It seems that HCl as a stripping phase accelerated the permeation rate. Unfortunately, the membranes were damaged after 24 hours of permeation. Usage of Na_2SO_4 and $NaHSO_4$ as stripping phases demonstrated excellent stability of membranes up to 72 hours of permeation.

In the case of the use of DES as carrier, the result showed that the DES composed of decanoic acid and tetrabutylammonium bromide was not compatible for separation of Mn(II).

Conclusion

In the liquid membrane permeation with ILs as carrier, the combination of Aliquat-336 as a carrier and 0.1 M Na_2SO_4 as a stripping phase gave a largest permeability of Fe(III) (approximately 80 %). In the case of Cyphos IL-101, the stripping rate was found to be considerably slow. The permeation rate of Mn(II) in membrane permeation using Aliquat 336 was smaller than that of Fe(III). This suggests that the kinetic separation of Fe(III) and Mn(II) is possible. DES composed of decanoic acid and tetrabutylammonium bromide was not compatible for separation of Mn(II).

Table 1. Recovery of Mn(II) using liquid membrane permeation with Cyphos IL-101 as an extractant

Feed phase	**Stripping phase**	**Time course (h)**	**Recovery (%)**	**Membranes condition**
10 mM Mn(II) in 6 M of HCl	HCl 0.01 M	24	34.04	broken after 24 h of permeation
	HCl 0.1 M	24	12.18	
	HCl 1.0 M	72	3.90	still good until 72 h of permeation
10 mM Mn(II) in 4 M of HCl	Na_2SO_4 0.1 M	72	20.82	
	Na_2SO_4 0.5 M	72	32.11	
	$NaHSO_4$ 0.1 M	72	31.45	

References

[1] Kislik V., Solvent extraction, classical and novel approaches. Elsevier, Amsterdam, 2011.

[2] Hoogerstraete, T. V., S. Wellens, K. Verachtert and K. Binnemans. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. Green Chem. (2013) 15, 919.

[3] Nee, K. and M. Nilsson. Experimental and theoretical studies of actinide and lanthanide ion transport across supported liquid membranes. Solvent Extraction and Ion Exchange (2015) 33, 554–575.

[4] Rout, P. C. and K. Sarangi. Comparison of hollow fiber membrane and solvent extraction techniques for extraction of cerium and preparation of ceria by stripping precipitation. J. Chem. Technol. Biotechnol. (2015) 90, 1270–1280.

[5] Lozano, L. J., C. Godínez, A. P. de los Ríos, F. J. Hernández - Fernández, S.Sánchez - Segado and F. J. Alguacil. Recent advances in supported ionic liquid membrane technology. Journal of Membrane Science (2011) 376, 1–14.

[6] Kislik V. S. Introduction, general description, definitions, and classification. Overview. In: V.S. Kislik (ed.). Liquid membranes. Elsevier, Amsterdam, The Netherlands, (2010) pp. 1-15.

[7] Matsumoto, M. Ionic liquid-based supported liquid membranes. In: K. Mohanty and M. K. Purkait (eds.). Membrane technology and applications. CRC Press, Boca Raton, U.S.A. (2012). pp. 305–316.

[8] Parhi, P. K. Supported liquid membrane principle and its practices: A short review. Journal of Chemistry Volume 2013, Article ID 618236.

[9] Takeuchi, H., K. Takahashi and W. Goto. Some observations on the stability of supported liquid membranes. J. Membr. Sci. (1987) 34, 19–31.

[10]Brennecke, J.F. and E.J. Maginn. Ionic liquids: Innovative luids for chemical processing. AIChE Journal (2001) 47, 2384–2389.

[11]Carlisle T.K., J. E. Bara, C. J. Gabriel, R. D. Noble. and D. L. Gin. Interpretation of CO_2 solubility and selectivity in nitrile - functionalized room - temperature ionic liquids using a group contribution approach. Industrial and Engineering Chemical Research (2008) 47, 7005–7012.

[12]Smith, E. L., A. P. Abbott and K. S. Ryder. Deep eutectic solvents (DESs) and their applications. Chem. Rev. (2014) 114, 11060−11082.

[13]Matsumoto, M., Y. Murakami, Y. Minamidate and K. Kondo.Separation of lactic acid through polymer inclusion membranes containing ionic liquids. Sep. Sci. Technol. (2012) 47, 354–359.

[14]Pratiwi, A. I., T. Sato, M. Matsumoto and K. Kondo. Permeation mechanism of succinic acid through polymer inclusion membranes with ionic liquid Aliquat 336. J. Chem. Eng. Japan (2014) 47, 314–318.

[15]Regel-Rosocka, M., L. Nowak and M. Wiśniewski. Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. Sep. Purif. Technol. (2012) 97, 158–163.

CONCLUSION

CONCLUSION

Solvent extraction with organic solvent as extractant is the most commonly used technique in separation of metal ions. However the toxicity and/or flammability of the organic solvents is the main problem encountered by both researchers and practitioners. Therefore, a green solvent is needed to substitute the convetional organic solvents. Ionic liquids (ILs) and deep eutectic solvents (DES) which have character as green solvents were successfully used to extract Fe(III), Mn(II) and Co(II) from aqueous solution. In addition the metals from the metals-loaded organic phase were also successfully stripped. Another drawback of the solvent extraction technique is the use of large ammount of extractant. Therefore, the experiment of supported ionic liquid membrane (SILM) was conducted and successfully separate Fe(III) from Mn(II).

In Chapter 2, three kinds of ILs experimented that are Aliquat 336, Cyphos IL 101 and Cyphos IL 102 indicated the great ability to extract Fe(III) and Mn(II) from aqueous solution. These metals were extracted probably as metal chlorocomplexes formed in the presence of excess hydrochloric acid due to the anion exchange reaction between metal chlorocomplex anion with ILs anion. Cyphos IL 101 among the ionic liquids investigated showed the largest extractability for recovery of Fe(III) and Mn(II). A number of stripping agents were tested for recovery of Fe(III) and Mn(II). Sodium thiosulfate which is a reductive stripping agent was the only one stripping agent, giving the quantitative recovery of Fe(III) from Aliquat 336 solution. Mn(II) was effectively stripped by water and neutral salt (Na_2SO_4) solution from Aliquat 336 solution. Stripping for Fe(III) and Mn(II) by neutral salt was derived by anion exchange reaction between anion of metal chlorocomplex of metal-loaded organic solution with anion of stripping agents of aqueous solution. On the other hand, the stripping of Mn(II) with water is caused by decomposition of metal chlorocomplex ($MnCl_3^-$). The stripping percentages in metal-Cyphos IL 101 system were lower than those of metal-Aliquat 336 system because extractabilities of Fe(III) and Mn(II) with Cyphos IL 101 were larger than those of Aliquat 336. Considering both extraction and stripping processes of Fe(III) and Mn(II), Aliquat 336 is better extractant than Cyphos IL 101 because of its high stripping performance.

In Chapter 3, Fe(III), Mn(II) and Co(II) were successfully extracted from aqueous solution using solvent extraction technique with the more superior extractant namely deep eutectic solvent (DES) composed of decanoic acid and lidocaine as extractant. The extraction of metals was highly influenced by the pH of metal slution. In the case of Fe(III), extraction mechanism involved the ion pair reaction between Fe^{3+} and decanoic anion at the pH of lower than 2.0, while at the larger pH the precipitation was formed at the aqueous phase causing the effect of pH cannot be evaluated. The similar mechanism was observed for Mn(II) and Co(II) at the pH of lower than 2.5 and 1.5 respectively. This mechanism was also occured at pH of higher than 3.5 for Mn(II) and 2.5 for Co(II). Between these two ranges of pH, the most possible mechanism was probably the cation exchange reaction between metal cations with lidocaine cation. In the case of Fe(III), the separation was complete at the concentration of DES about 25 g/L whereas the complete separation of Mn(II) and Co(II) was reached at the concentration of DES about 300 g/L. Hydrochloric acid successfully stripped these three metal ions from the metal-loaded organic phase.

Fe(III) was also separated from Mn(II) using polymer inclusion membrane (PIM) reported in Chapter 4. Aliquat-336 as a carrier and 0.1 M Na_2SO_4 as a stripping phase gave a largest permeability of Fe(III) (approximately 80 %). In the case of Cyphos IL-101, the stripping rate was found to be considerably slow. The permeation rate of Mn(II) in membrane permeation using Aliquat 336 was smaller than that of Fe(III). This suggests that the kinetic separation of Fe(III) and Mn(II) is possible. DES composed of decanoic acid and tetrabutylammonium bromide was not compatible for separation of Mn(II).

In conclusion, solvent extraction and supported liquid membrane were the great technique to extract metal ions from aqueous solution. ILs can be employed as extractant in both techniques, while DES was only suitable to be used in solvent extraction tecnique. Considering the cost of the extraction process, SILM is suggested for separation of metals as it consumes very small amount of ILs and the extraction and re-extraction carried out in one technological step. Between ILs and DES, DES is recomended to be applied in solvent extraction technique for metal separation because it does not involve the use of concentrated hydrochloric acid which is highly corrosive.

List of Publications

Recovery of Fe and Mn from aqueous solution with solvent extraction and liquid membrane permeation using ionic liquids.
Pius Dore Ola, Michiaki Matsumoto and Kazuo Kondo.
Desalination and Water Treatment, 75 (2017) p.325–330

Solvent Extraction and Stripping of Fe and Mn from Aqueous Solution Using Ionic Liquids as Extractants.
Pius Dore Ola, Yusuke Kurobe and Michiaki Matsumoto.
CHEMICAL ENGINEERING TRANSACTIONS, VOL. 57, (2017) p. 1135-1140.

Supported Ionic Liquid Membrane for Metal Separation.
Pius Dore Ola and Michiaki Matsumoto.
Progress and Developments in Ionic Liquids, 1st edition. Editor: Scott Handy.
INTECH (2017) pp. 539-555.

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