

Solvent Extraction and Stripping of Fe and Mn from Aqueous Solution Using Ionic Liquids as Extractants

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In the hydrometallurgical recovery process of Fe and Mn from ores and scrap, hydrochloric acid was used to leach these metals in the aqueous solution. Following this, solvent extraction techniques were employed to recover these metals from the chloride-rich solution. Recently, ionic liquids (ILs) have been widely employed in solvent extraction because of their unique characteristics. In this study, recoveries of Fe and Mn were carried out by using solvent extraction and stripping with ionic liquids, Aliquat 336 and Cyphos IL 101. In the extraction process, the metals were extracted from aqueous solution to organic solution containing IL by the anion exchange reaction between the anion of ionic liquid and the anionic chlorocomplexes such as FeCl_4^- and MnCl_3^- . 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.

1. Introduction

In the recovery of iron and manganese using hydrometallurgical process, the metals are usually leached from ores and scraps with concentrated hydrochloric acid (Mao, 2015; Baba *et al.*, 2014). The Fe and Mn in the resultant chloride-rich solution can be extracted using several methods such as precipitation and solvent extraction. In the case of precipitation technique, the co-precipitation of the other metals, which are probably derived from the very close values of their solubility constants, could decrease the recovery of the targeted metals (Liu *et al.*, 2014). Solvent extraction is an economical and widely used process in hydrometallurgy for the recovery of valuable ions from aqueous solutions after the leaching process (Quijada-Maldonado *et al.*, 2016). 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 (Hoogerstraete *et al.*, 2013). This means that the selection of extractant is key point for the metal extraction in the term of efficiency and selectivity.

Conventionally, Fe and Mn can be extracted using many types of extractant such as di(2-ethylhexylphosphoric) acid (D2EHPA) (Pérez-Garibay *et al.*, 2012; Principe and Demopoulos, 2004), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) (Pérez-Garibay *et al.*, 2012; Biswas and Rahman 2011), 2-ethylexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) (Ahn *et al.*, 2002), *N,N*-dioctyl-1-octanamine (Alamine 336) (Lee and Filiz, 2008), octylphenyl acid phosphate (OPAP) (Principe and Demopoulos, 2004), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) (Alia *et al.*, 2011), tri-*n*-butyl phosphate (TBP) (Patnaik *et al.*, 2013) and others. However, those conventional liquid-liquid extraction systems use the organic diluents and extractants, which are often harmful and flammable (Parmentier *et al.*, 2015). 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 of their near-zero vapour pressure, their good chemical and thermal stability, and their physicochemical properties can be varied by altering the substitutive groups on the cation or the combined anion (Matsumoto, 2012). Solvent extraction with ILs of Fe (III) have been conducted using several ILs such as triethylpentylphosphonium (P₂₂₂₅) bis(trifluoromethyl-sulfonyl)amide (TFSA) (Matsumiya *et al.*, 2016), Aliquat 336, (de los Ríos *et al.*, 2010, Mishra *et al.*, 2011), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C₄mim][NTf₂] (Hussin *et al.*,

2014), trihexyl(tetradecyl) phosphonium chloride (Cyphos IL 101) (Kogelnig *et al.*, 2010), trihexyl(tetradecyl) phosphoniumbis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) (Regel-Rosocka *et al.*, 2012). However, there are few studies of Mn(II) extraction with ILs. In our previous paper (Ola *et al.*, in press), we studied the extraction of Fe(III) and Mn(II) with ILs including Aliquat 336, Cyphos IL 101 and 102, and the permeation of these metal ions through polymer inclusion membrane composed of IL and polyvinyl chloride.

In this work, we investigated mainly the stripping of Fe (III) and Mn (II) from the metal-loaded organic solution after the extraction of Fe (III) and Mn (II) from hydrochloric acid solution using of Aliquat 336 and Cyphos IL 101 as extractants. 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 specifically study how to strip the metal from metal-loaded organic solution (Liu *et al.*, 2014). Liu *et al.*, (2014) 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, we 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.

2. Materials and method

2.1 Chemicals

Aliquat 336 (*N*-Methyl-*N,N,N*-triethylammonium chloride) and Cyphos IL101 (Trihexyl(tetradecyl)phosphonium chloride) used as ionic liquid extractants were purchased from Strem Chemicals Inc. and Cytec Industry Inc. respectively. Ferric chloride, manganese chloride, sodium sulphate, nitric acid, sulphuric acid and sodium nitrate were purchased from Nacalai Tesque, Inc., Kyoto. Other reagents of G. R. grade were and purchased from Wako Pure Chemical, Industries, Ltd, Osaka. All chemicals were used without further purification.

2.2 Solvent extraction experiment

The aqueous solution was prepared by dissolving 10 mmol/L of metal solution in various concentrations of hydrochloric acid. The organic solution was prepared by dissolving ionic liquid in *n*-heptane. Equal volume (5 mL) of the aqueous and organic solutions were mixed and shaken (120 rpm) in a thermostat water bath at 303 K. After shaking for 3 hours to attain equilibrium, the concentration of metal in the aqueous phase was measured using ICP-AES (ICPS-8000). The percentage of extraction was calculated using Eq (1).

$$\% \text{Extraction} = \frac{[M]_{\text{org,eq}}}{[M]_{\text{aq,int}}} \times 100 = \frac{[M]_{\text{aq,int}} - [M]_{\text{aq,eq}}}{[M]_{\text{aq,int}}} \times 100 \quad (1)$$

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

2.3 Stripping experiment

The metal-loaded organic solution was prepared by mixing of 50 mL of aqueous solution containing 10 mmol/L of metals in 5 mol/L of hydrochloric acid with 50 mL of organic solution containing 2 mol/L of Aliquat 336 or 1 mol/L of Cyphos IL 101 in *n*-heptane. Before and after mixing, the concentrations of the metals in the aqueous phase were measured to determine the initial concentration of metals in the organic phase ($[M]_{\text{org,int}}$). Two mL of metal-loaded organic solution was mixed with 2 mL of aqueous phase containing stripping agent. 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 Eq (2).

$$\% \text{Stripping} = \frac{[M]_{\text{aq,eq}}}{[M]_{\text{org,int}}} \times 100 \quad (2)$$

3. Result and discussion

3.1 Solvent extraction

In this experiment, Fe (III) and Mn (II) in hydrochloric acid solution, which is one of the most commonly used acids in hydrometallurgical process, were extracted to imitate the practical process of ores or scrap leaching. We used Aliquat 336 and Cyphos IL 101 as extractants because Aliquat 336 is the most commonly used ILs in the metals separation and Cyphos IL 101 was the best extractant of Fe (III) and Mn (II) in our previous experiment (Ola *et al.*, in press). To confirm our previous results, Fe (III) and Mn (II) in 2 and 5 mol/L hydrochloric acid were extracted with 1 mol/L Aliquat 336 or Cyphos IL 101. The results obtained were summarized in Table 1. As described in the previous paper (Ola *et al.*, in press), it was confirmed that the

extractability with Cyphos IL 101 was larger than that of Aliquat 336 and the extraction of Fe (III) was higher than that of Mn (II). Because the extractability strongly depends on the concentration of hydrochloric acid, the following mechanism was proposed. The transfer of metals from aqueous solution to organic solution containing ionic liquid occurs by the anion exchange reaction between the anion of ionic liquid and the anionic form of metal which is produced by the reaction of metal cation with chloride anion, as illustrated in Eqs (3) and 4.



where M is metal with valence n and Q^{+} is the cation of ILs. Eqs (3) and (4) show that the anionic chlorocomplexes such as $FeCl_4^{-}$ and $MnCl_3^{-}$ are formed under the excess amount of hydrochloric acid and then migrate to the organic phase.

Table 1 Extraction percentage of Fe(III) and Mn(II) from hydrochloric acid solution

Extractant	Aliquat 336		Cyphos IL 101	
	HCl conc. [mol/L]		HCl conc. [mol/L]	
	2	5	2	5
Fe (III) [%]	99.9	100	100	100
Mn (II) [%]	14.1	75.4	49.0	91.0

3.2 Stripping of Fe (III) and Mn (II)

In this work, the stripping of Fe (III) and Mn (II) from the Fe (III)- and Mn (II)-loaded organic solutions were investigated. In previous studies on the stripping of Fe (III) from organic solutions containing Aliquat 336 and Cyphos IL 101, water for Aliquat 336 (Mishra *et al.*, 2011) and 0.5 mol/L HCl and H_2SO_4 for Cyphos 101 (Kogelnig *et al.*, 2010, Regel-Rosocka *et al.*, 2012) were used for stripping agent. However there are no studies on the stripping of Mn (II) with Aliquat 336 and Cyphos IL 101. We investigated performances of a number of stripping agent including reductive or oxidative agents 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, we 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 (3). 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 occurred. Figure 1 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 mol/L 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 1, unlike stripping of Fe (III), Mn (II) was effectively stripped by water and neutral salt (Na_2SO_4) solution from the complex of $\text{Q}^+\text{MnCl}_3^-$ 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).



In metal-Cyphos IL 101 system shown in Figure 1, 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 mol/L and 0.5 mol/L, 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 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.

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	$\text{Na}_2\text{S}_2\text{O}_3$	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 mol/L except for water and Na_2SO_4 (0.3 mol/L).

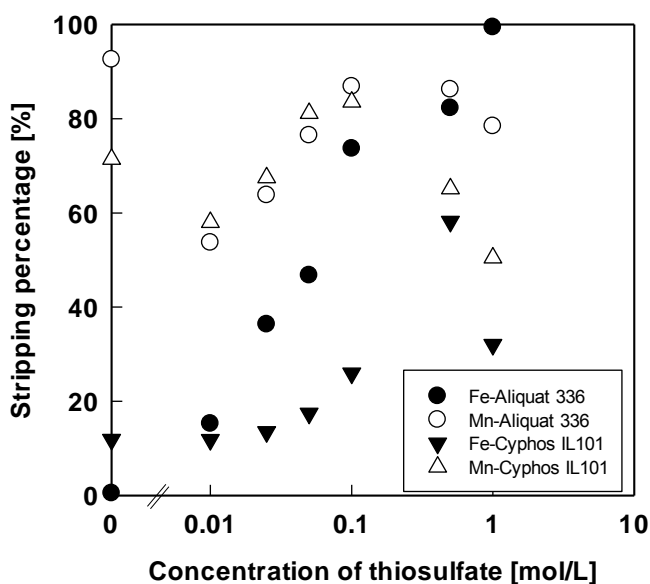


Figure 1: Effect of thiosulfate concentration on stripping of Fe (III) and Mn (II).

4. Conclusions

Solvent extractions of Fe (III) and Mn (II) from hydrochloric acid solution and stripping of their extracted metal complexes were carried out using ionic liquids as extractants. It was confirmed that the extractability with Cyphos IL 101 was larger than that of Aliquat 336 and the extraction of Fe (III) was higher than that of Mn (II). The metals from aqueous solution to organic solution containing ionic liquid were extracted by the anion exchange reaction between the anion of ionic liquid and the anionic chlorocomplexes such as FeCl_4^- and MnCl_3^- .

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. 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. This system is also promising to be applied in industrial process of Fe (III) and Mn (II) recovery where $\text{Na}_2\text{S}_2\text{O}_3$ 1.0 M and water are the best stripping agents for Fe (III) and Mn (II), respectively.

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