Extraction Mechanism of Ferric and Manganese Ions with Aqueous Two-phase System Formed by Ionic Liquid and Polyethylene Glycol

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In this work, we employed an aqueous two-phase system formed by an ionic liquid and polyethylene glycol for the separation of Fe(III), which is the most commonly used metal in the world, and Mn(II), which is currently used in many industries. We found that the extraction mechanisms of Fe(III) and Mn(II) were strongly influenced by the concentration of the hydrochloric acid that dissolved the metal salt. The ion pair reaction was the predominant mechanism that generated the Fe(III) and Mn(II) extractions. At a lower concentration of hydrochloric acid, metal ions were extracted because of the reaction between a metal cation and a dodecylsulfonate anion. At a higher concentration of hydrochloric acid, the reaction between a metal chlorocomplex anion and a hexylmethylimidazolium cation also proceeded. The aqueous two-phase system, composed of ionic liquid and polyethylene glycol, is promising for metal separation based on the difference in the affinity of metal with alkyl-sulfonate in a low HCl concentration and in the stability constant of metal chlorocomplex in a high HCl concentration. The maximum extractability of Fe(III) and Mn(III) was 57.8 and 75.3 %, respectively, with 0.3 mol dm^{-3} hydrochloric acid concentration.

Keywords:
solvent extraction, ionic liquid, aqueous two-phase system, iron, manganese

Introduction

Solvent extraction is the most commonly used method for the separation of metal ions, including Fe(III) and Mn(II). The simplicity with which such parameters (that control extraction as a diluent, pH, or extractant), can be changed is a major advantage of solvent extraction[1]. However, solvent extraction is not environmentally friendly because it requires a large volume of organic solvents that are often toxic and/or flammable. For the separation of Fe(III) and Mn(II), we investigated the use of ionic liquids (ILs) and deep eutectic solvent (DES) as an extractant[2–4]. However, the use of organic solvents such as heptane as a diluent agent could not be avoided, due to the very high viscosity of ILs and the formation of emulsion when DES itself interacted with the metal aqueous solution. In addition, GlaxoSmithKline (GLK) and Sanofi solvent selection guides categorized heptane itself as solvent with some issues and advised substitution[5]. For achieving green chemistry, solvent extraction without a conventional organic solvent (both as extractant and diluent) is the chemists' dream. Thus, an aqueous two-phase system (ATPS), which mainly consists of water at both the bottom and top phases, offers a promising solution for overcoming the toxicity and the flammability of organic solvents of a solvent extraction technique.

Under specific thermodynamic conditions, ATPS is formed spontaneously by mixing the aqueous solutions of two chemically different hydrophilic polymers or combining the aqueous solutions of a polymer and an electrolyte, which in turn separate two immiscible aqueous phases in equilibrium: a polymer-enriched top phase and an electrolyte-enriched bottom phase[6]. ATPS provides milder extraction conditions for biomaterials, since it requires no organic solvent[7]. It has also become an attractive separation technology due to the low cost of the phase-forming materials, the simplicity of the process, and its easy scaling-up to an industrial level[8]. ATPSs composed of polymer-polymer[9] and polymer-inorganic salts[10] have been widely used in the separation and purification of proteins, enzymes, blood cell antibiotics, and metal ions. However, application of this system is limited due to the similar polarity of the two phases.

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Ionic liquids (ILs) are new kinds of green solvents, and their unique properties, such as near-zero vapor pressure, good chemical and thermal stability, and physicochemical properties can be varied by altering the substitutive groups on a cation or a combined anion[11]. Those properties make ILs very attractive as extractants for the extraction of various metal ions. In the extraction process, hydrophobic ILs have been used to create an IL/water biphasic system[12]. However, the number of water-immiscible ILs is currently limited to a few cation/anion combinations, most notably with fluorinated anions, which can be expensive and environmentally non-benign[13].

Compared to traditional ATPSs composed of polymer and salt, the use of ILs instead of salts can adjust the phases' polarities more adequately[14,15]. However, in most cases, ATPS including ionic liquid has been used in a combination of ionic liquid and salt in ATPS, due to the weak salting-out ability of ionic liquids[16,17]. Recently, an ATPS, composed of ionic liquid and a polymer, was developed to extract gold (III), and its extraction mechanism was proposed[18]. However, to the best of our knowledge, using an ATPS based on IL (ILATPS) has not been applied in the separation of Fe, which is the most commonly used metal, and Mn, which is currently used in many manufacturing processes, such as ferroalloy or steel industries, dry-cell batteries, chemicals, fertilizers, glass, ceramics, paint, and numerous medicinal and chemical purposes[19]. In this work, an ILATPS, composed of an ionic liquid and a polyethylene glycol, was used for Fe(III) and Mn(II) extractions, with a focus on their extraction mechanisms.

Materials and methods

Chemicals

1-Hexyl-3-methylimidazolium chloride ([C_6mim]Cl), sodium dodecyl sulfonate ($C_{12}SO_3Na$), and polyethylene glycol (PEG 4000, 6000, 8000) were purchased from Wako Pure Chemicals (Osaka, Japan). Analytical grade $MnCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Nacalai Tesque (Kyoto, Japan). The molecular structures of [C_6mim]Cl and $C_{12}SO_3Na$ are shown in Fig. 1. All the chemicals were of analytical grade and used without further purification.

Preparation of ionic liquid

The ionic liquid, 1-hexyl-3-methyl imidazolium dodecyl sulfonate, ([C_6mim][$C_{12}SO_3$]), was synthesized based on procedures described by Zheng *et al*[17]. Equal moles of [C_6mim]Cl and $C_{12}SO_3Na$
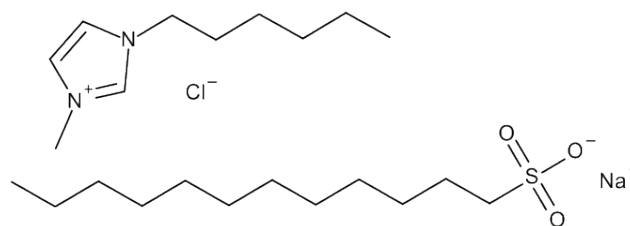

Fig. 1 – *Molecule structure of 1-hexyl-3-methylimidazolium chloride [C_6mim]Cl (a) and sodium dodecyl sulfonate $C_{12}SO_3Na$ (b)*

were dissolved in dichloromethane and stirred at room temperature and atmospheric pressure for four hours. The filtrate was washed with water until no chloride ion was detected by $AgNO_3$, and dried *in vacuo* to obtain [C_6mim][$C_{12}SO_3$].

FTIR spectrum of ionic liquid prepared is shown in Fig. 2. This spectrum was almost the same as that reported previously[18]. The existence of S–O sulfonate stretching at 1175 cm^{-1} indicated that ionic liquid [C_6mim][$C_{12}SO_3$] was formed.

Preparation of binodal curve

Binodal curve was prepared by turbidimetric titration. A PEG stock solution of 50 % (w/w) was prepared by mixing an equal mass of PEG and distilled water. Ionic liquid stock solution of 50 % (w/w) was prepared in the similar way with PEG stock solution. Ionic liquid solution was added drop-wise to a PEG solution until two phases were formed. The procedure was repeated using the larger mass of PEG or ionic liquid. The composition of the mixture that formed two phases was noted, and a binodal curve was constructed using these compositions.

Extraction of Fe(III) and Mn(II) with ATPS

Both metal solutions (10 mmol dm^{-3}) were prepared by dissolving metal chlorides in various concentrations of hydrochloric acid. An amount of 2 mL of PEG stock solution was mixed with 2 mL of IL stock solution to form an ATPS. Then, 2 mL of metal solution was added to the mixture in a calibrated tube, and the mixture was shaken at 55 °C and 150 rpm for 1 hour. The volumetric ratio of the PEG, IL, and metal solutions as operating parameters were changed. After shaking, the mixture was kept overnight to attain complete phase separation. The volume of each phase was recorded. The metal concentrations in the top and bottom phases were measured using ICP-AES (ICPS 8100, Shimadzu, Kyoto, Japan).

The percentage of extraction and the distribution ratio, D, were calculated using Eqs. (1) and (2).
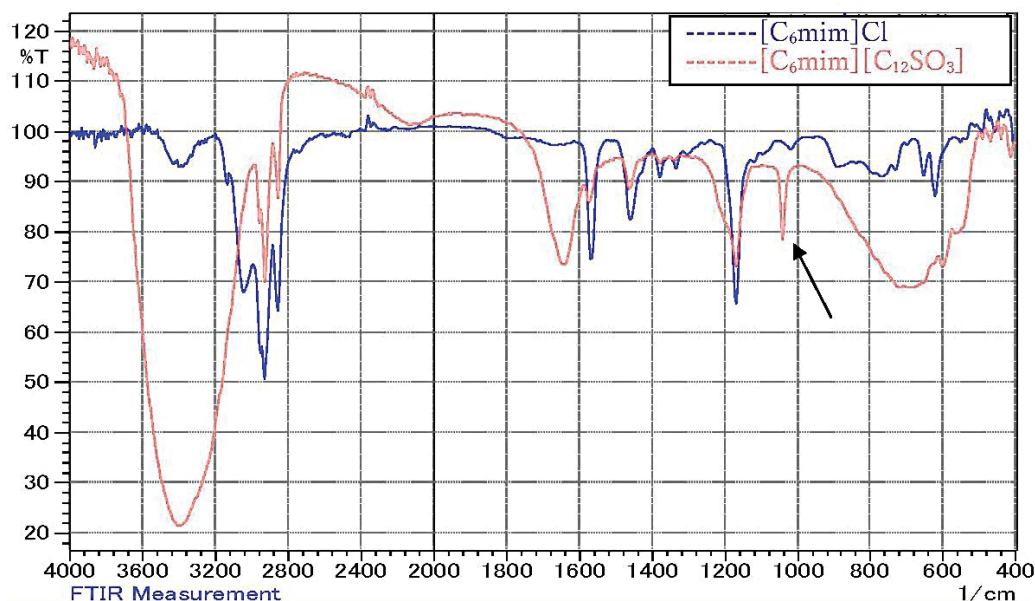
Fig. 2 – *FTIR spectra of $[C_6mim]^+ [C_{12}SO_3]^-$ and $[C_6mim]^+ [Cl]^-$*
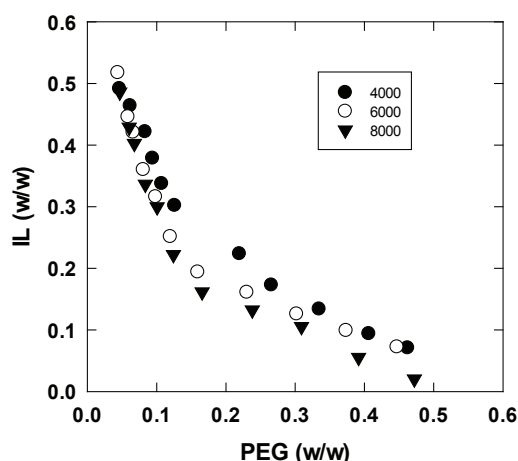

Fig. 3 – *Binodal curve of ATPS composed of $[C_6mim]^+$ $[C_{12}SO_3]^-$ (IL) and PEG*

$$\%E = \frac{C_T V_T}{c_O v_O} \cdot 100 \qquad (1)$$

$$D = \frac{C_T}{C_B} \qquad (2)$$

where, C and V are the metal concentration and the phase volume, subscripts 0 , T, and B represent the initial metal solution, the top and bottom phases, respectively. In this system, the top and bottom phases were IL- and PEG-rich.

Results and discussion

Preparation of binodal curves

Binodal curve was prepared using three kinds of PEGs, as shown in Fig. 3. A binodal curve can provide information about the concentration of the components of the top and bottom phases necessary to form a two-phase system. The area above the curve is a two-phase area, and the area below is a single-phase area. Therefore, the closer a curve is to the origin of the coordinates, the stronger is its ability to form a two-phase system. As shown in Fig. 3, the larger the molecular weight of PEG, the smaller is the concentration of both PEG and IL necessary to form a two-phase system, because the increase in the molecular weight increases the hydrophobicity of the phases. We prepared the ATPS consisting of aqueous solutions of $[C_6mim][C_{12}SO_3]$ and PEG 8000 mixed with aqueous metal solution for further experiment.

Effect of hydrochloric acid concentration on extractions of Fe(III) and Mn(II)

The aim of this work was to elucidate the extraction mechanisms of Fe(III) and Mn(II) using an ATPS formed by PEG and $[C_6mim][C_{12}SO_3]$. To that end, we investigated the effect of hydrochloric acid concentration on Fe(III) and Mn(II) extractions, as shown in Figs. 4 and 5.

The following are our general observations from the results shown in Fig. 4: 1) The larger the ratio of the top (IL-rich) phase to the bottom phase, the greater is the extractability; 2) The extractability of both Fe(III) and Mn(II) decreased with increasing HCl concentration; 3) The extractability of Mn(II) exceeded that of Fe(III), except at a HCl concentration of 12 mol dm^{-3}. For all tested ATPSs, the metal solution dissolved in 0.3 mol dm^{-3} hydrochloric acid gave the highest extractability of 57.77 % for Fe(III), and 75.35 % for Mn(II).
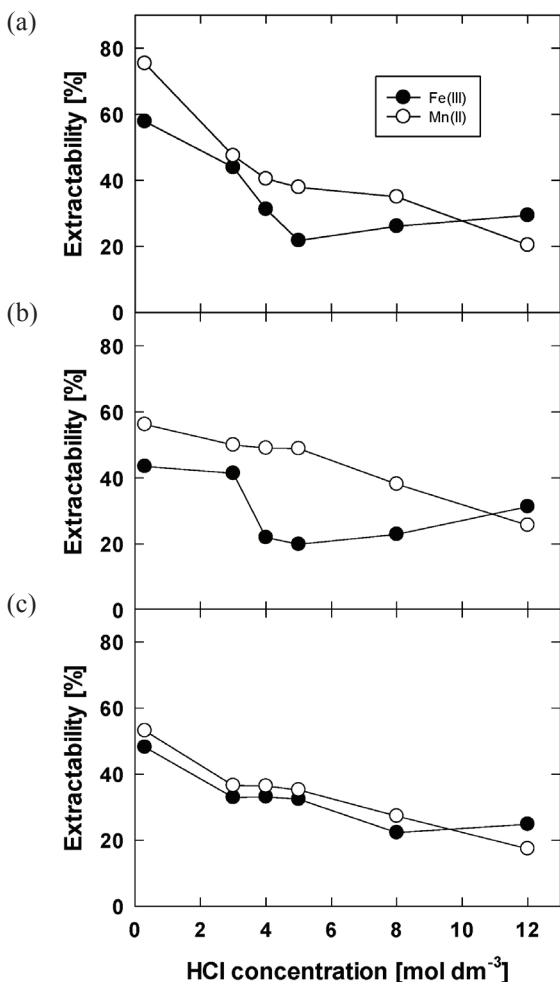
(a)

(b)

(c)

F i g . 4 – *Effect of HCl concentration on extractability of Fe(III) and Mn(II) at various ratios of 50 % IL solution: 50 % PEG solution: metal solution: (a) 4: 1: 1 (b) 2: 1: 1 and (c) 1: 1: 1*
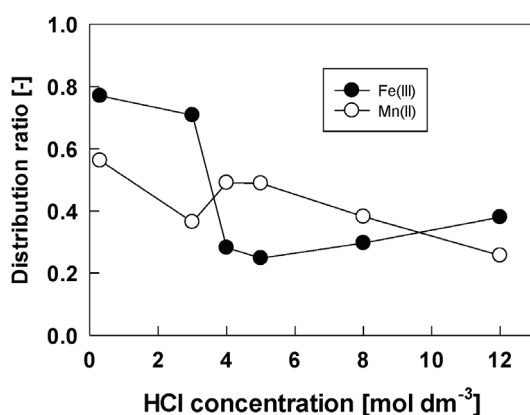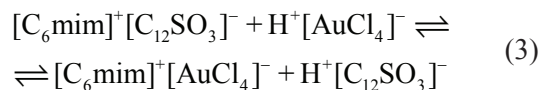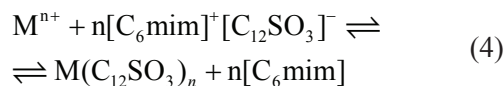

F i g . 5 – *Effect of HCl concentration on distribution ratio of Fe(III) and Mn(II) at various ratios of 50 % IL solution: 50 % PEG solution: metal solution: 2: 1: 1*
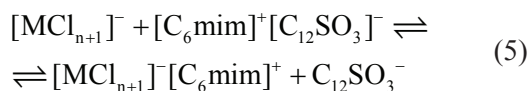
The following extraction reaction was proposed for the extraction of Au(III) with an ATPS composed of PEG6000 and $[C_6mim][C_{12}SO_3]$[18].

$$[C_6mim]^+[C_{12}SO_3]^- + H^+[AuCl_4]^- \rightleftharpoons$$
$$\rightleftharpoons [C_6mim]^+[AuCl_4]^- + H^+[C_{12}SO_3]^- \qquad (3)$$

If this extraction mechanism were applied to the present system, the extractability of the metallic ions would be strongly dependent on the formation of metal-chlorocomplex, such as $FeCl_4^-$ and $MnCl_3^-$. An increase in chloride concentration causes greater formation of metal chlorocomplex, and the extractability of Fe(III) is expected to be higher than that of Mn(II), because the stability constant of $FeCl_4^-$ is much higher than that of $MnCl_3^{-2}$. Our observations did not support the extraction reaction based on Eq. (3). Under a lower concentration of hydrochloric acid, the extraction mechanism was probably dominated by the ion pair reaction between the metal cation and the dodecylsulfonate anion, expressed by Eq. (4):

$$M^{n+} + n[C_6mim]^+[C_{12}SO_3]^- \rightleftharpoons$$
$$\rightleftharpoons M(C_{12}SO_3)_n + n[C_6mim] \qquad (4)$$

Therefore, the decrease in extractability due to the increase in hydrochloric acid concentration was generated by the decrease in concentration of the metal cation due to the formation of a metal chlorocomplex anion, $[MCl_{n+1}]^-$. In the absence of hydrochloric acid, the formation of precipitation of $[M(OH)_n]$ was observed, suggesting that a small amount of chloride ion (as a counter anion of a C_6mim cation produced in Eq. 4) was essential for this extraction system. Unlike at a lower concentration of hydrochloric acid, the extractability of the metal at a higher concentration of hydrochloric acid was derived partially from the reaction between a metal chlorocomplex anion and a cation of an ionic liquid, as in Eq. 3.

$$[MCl_{n+1}]^- + [C_6mim]^+[C_{12}SO_3]^- \rightleftharpoons$$
$$\rightleftharpoons [MCl_{n+1}]^-[C_6mim]^+ + C_{12}SO_3^- \qquad (5)$$

This mechanism was confirmed by the fact that the extractability of Fe(III) was higher than that of Mn(II) at a hydrochloric acid concentration of 12 mol dm^{-3}, which was the highest concentration applied in this work. This was because the stability constant of $FeCl_4^-$ is higher than that of $MnCl_3^-$, as described above. The stability constant of $FeCl_4^-$, which is higher than that of $MnCl_3^-$, also explains why the extractability of Fe(III) at a lower concentration of hydrochloric acid is lower than the extractability of Mn(II). In addition, the extractabilities of both Fe(III) and Mn(II) at a lower hydrochloric acid concentration exceeded those at a higher hydrochloric acid concentration, indicating that the extraction constant of Eq. 4 was higher than that of Eq. 5.
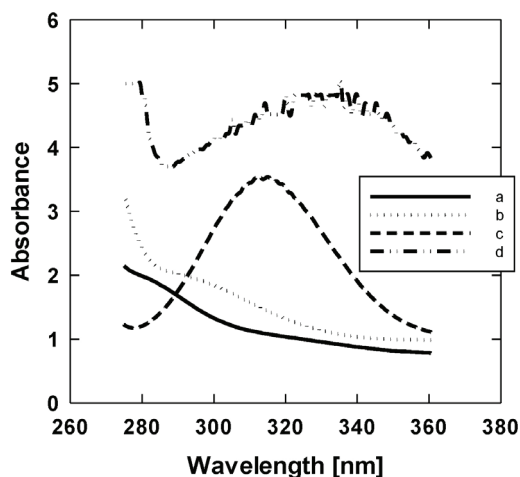
Fig. 6 – *UV-Vis spectra of FeCl₃ dissolved in HCl 0.1 mol dm⁻³ (a) and 12 mol dm⁻³ (c), and in top phase of ATPS in contact with bottom phase composed of PEG solution and FeCl₃ dissolved in HCl 0.1 mol dm⁻³ (b) and 12 mol dm⁻³ (d)*

To clarify the above mechanism, the UV-Vis spectra of the initial hydrochloric acid solution, by dissolving FeCl$_3$ and the top phase after extraction, were measured, and are shown in Fig. 6. Before extraction, an adsorption band at 315 nm in a 12 mol dm^{-3} HCl solution (curve c) was attributable to FeCl$_4^{-}$[20], and in the 0.1 mol dm^{-3} HCl solution (curve a), the peak disappeared, suggesting that FeCl$_4^{-}$ was not a dominant species. Fig. 6 also shows the spectrum of the top phase in ATPS with FeCl$_3$ dissolved in 0.1 mol dm^{-3} (curve b) and 12 mol dm^{-3} (curve d) hydrochloric acid after extraction. In curve b, the FeCl$_4^{-}$ peak did not appear, and in curve d, the maximum absorption wavelength of FeCl$_4^{-}$ shifted to a longer wavelength because of the difference in the dielectric constant between the aqueous and organic media[20]. Consequently, the extraction mechanism described above was supported strongly by the results of the UV-Vis spectra measurements.

Conclusions

The possibility of using an ionic-liquid-based aqueous two-phase system for the extraction of Fe(III) and Mn(II) was studied in this work. We found that the extraction mechanisms of the metals were influenced by the concentration of the hydrochloric acid. At a lower concentration of hydrochloric acid, Fe(III) and Mn(II) were extracted due to the reaction between a metal cation and a dodecyl-sulfonate anion. The extraction reaction between [C$_6$mim]$^+$ and a metal chlorocomplex anion also proceeded at a higher concentration of hydrochloric acid. For both metals, the extractabilities at a lower concentration of hydrochloric acid were larger than those at a higher concentration. This mechanism

was supported by UV-Vis spectra measurement. An ILATPS composed of ionic liquid and polyethylene glycol is promising for metal separation based on the difference in the affinity of metal with alkyl-sulfonate in a low HCl concentration and in the stability constant of metal chlorocomplex in a high HCl concentration.

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