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Recovery of Fe and Mn from aqueous solution with solvent extraction and liquid membrane permeation using ionic liquids

Pius Dore Ola, Michiaki Matsumoto*, Kazuo Kondo

Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto, 610-0321 Japan, Tel./Fax: +81-774-656655; emails: mmatsumo@mail.doshisha.ac.jp (M. Matsumoto), puskomundana@yahoo.com (P.D. Ola), kkondo@mail.doshisha.ac.jp (K. Kondo)

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ABSTRACT

In the hydrometallurgical recovery process of Fe(III) and Mn(II) from ores and scrap, solvent extraction and liquid membrane processes, which combine extraction and stripping into a single stage, are one of the promising separation process. In this study, ionic liquid such as Aliquat 336, Cyphos IL 101, and Cyphos IL 102 were used as complexing reagents to recover Fe(III) and Mn(II) in the solvent extraction and liquid membrane permeation. 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 large extractability for the recovery of Fe(III) and Mn(II). In the liquid membrane permeation with ionic liquids, 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 suggest that the kinetic separation of Fe(III) and Mn(II) is possible.

Keywords: Recovery; Solvent extraction; Membrane permeation; Ionic liquid; Fe; Mn

1. Introduction

Fe and Mn are the fourth and twelfth most abundant elements in the earth's crust, respectively, and are naturally present in rocks. In the hydrometallurgical recovery process of these metals from ores and scrap, hydrochloric acid was used to leach these metals in the aqueous solution [1,2]. Following this, precipitation and solvent extraction techniques were employed to recover these metals from the chloride-rich solution. In the precipitation process, selective separation proved difficult due to co-precipitation with other metals [3]. However, in the solvent extraction process, the selection of the extractant is the determining step in achieving the high efficiency and selectivity of metal separation. In general, the extractants used to separate Fe and Mn include: organophosphorus acid derivatives, high-molecular amines and ammonium salts, and neutral solvation extractants. Among them, organophosphorus acid derivatives, high-molecular amines and ammonium salts, especially di(2-ethylhexyl phosphoric) acid (D2EHPA), are studied extensively in order to extract these metals. Difficulties have been reported in the stripping of Fe(III) from loaded D2EHPA even using concentrated acid [3].

Ionic liquids (ILs) have been widely employed in solvent extraction [4,5]. ILs are organic salts remaining as liquids under ambient temperatures. They normally consist of an organic cation (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium), and a polyatomic inorganic anion (e.g., tetrafluoroborate, hexafluorophosphate, chloride) or an organic anion (e.g., trifluoromethylsulfonate, bis[(trifluoromethyl)sulfonyl]imide). There has been growing interest in the use of ILs in separation using a two-phase system. This is not only due to their negligible volatility, but also the other

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* Corresponding author.

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properties of ILs such as their non-flammability, non-toxicity, good solvation ability, wide liquid range, and tunable polarity. There are two approaches in the use of ILs in the solvent extraction of metal ions [6]. The first is that ILs are used as a diluent instead of conventional organic solvents. The second is that ILs themselves serve as a complexing reagent, much like the quaternary ammonium salts mentioned above. Recently, phosphonium-based ILs have become regarded as a new subclass of complexing reagents for transition metal extraction due to their good miscibility with non-polar diluents and low solubility in aqueous phases [7–9].

Liquid membrane (LM) processes have been applied to the separation of metal ions, as LM processes combine extraction and stripping into a single stage. Although the supported LMs among the several configurations of LMs have advantages such as simple scale-up, very low energy requirements, low capital and operating costs, and high separation factors, there are concerns regarding their stability and long-term performance in the supported LM processes [10]. However, because of the negligible volatility, relatively high viscosity, and interfacial tension of ILs, ILs have recently been used as stable impregnated liquids in the supported LM process. Moreover, in our previous study, it was found that polymer inclusion membrane (PIM) including ILs, which has a similar configuration to supported IL membranes, became more stable than supported IL membrane [11]. In this paper, PIMs were formed by casting a solution containing IL and base polymer polyvinyl chloride (PVC) in the absence of plasticizer to form a thin, flexible, and stable film.

The separation of Fe(III) from hydrochloric acid solution has been studied with ILs such as Aliquat 336 (a mixture of tri-octyl/decyl ammonium chloride), Cyphos IL 101 (trihexyl(tetradecyl)phosphonium chloride), and Cyphos IL 104 (trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate) as an anion exchanger in solvent extraction and LMs [7–9,12]. However, there are few reports on the separation of Mn with ILs as complexing reagents and on the comparative study of IL even in the extraction of Fe(III).

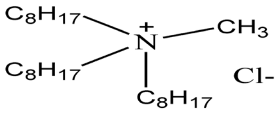
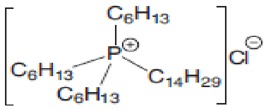
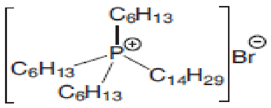
In this study, we examined ILs as complexing agents such as Aliquat 336, Cyphos IL 101, and Cyphos IL 102 (trihexyl(tetradecyl)phosphonium bromide) to extract Fe(III) and Mn(II) from hydrochloric acid solution. First, solvent extraction with these ILs diluted in *n*-heptane was examined. In previous papers [7,8], the harmful solvents chloroform and toluene were used as diluents for phosphonium-based ILs. In the case of LM permeation, we applied PIMs including ILs for the recovery of Fe(III) and Mn(II).

2. Materials and methods

2.1. Chemicals

Aliquat 336, and Cyphos IL 101 and 102 (used as ILs) were purchased from Strem Chemicals Inc. (Newburyport, MA, USA) and Cytec Industries Inc. (Woodlandpark, NJ, USA), respectively, and their molecular structures are shown in Table 1. 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. Concentrated hydrochloric acid solutions (Wako Pure Chemical Industries, Ltd., Osaka) were used in preparing the feed solution. All chemicals were used without further purification.

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	

2.2. Solvent extraction

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 (5 cm^3) 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 Eqs. (1) and (2).

$$\%\text{Extraction} = \frac{\left[\text{M}\right]_{\text{org.eq}}}{\left[\text{M}\right]_{\text{aq.int}}} \times 100 = \frac{\left[\text{M}\right]_{\text{aq.int}} - \left[\text{M}\right]_{\text{aq.eq}}}{\left[\text{M}\right]_{\text{aq.int}}} \times 100 \qquad (1)$$

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

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

2.3. Polymer inclusion membrane permeation

The PIMs used to permeate the metals were prepared by means of the solution casting method described in previous papers [11,13]. The polymer solution was prepared by dissolving 1.5 g of IL 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 h 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 as shown in Fig. 1.

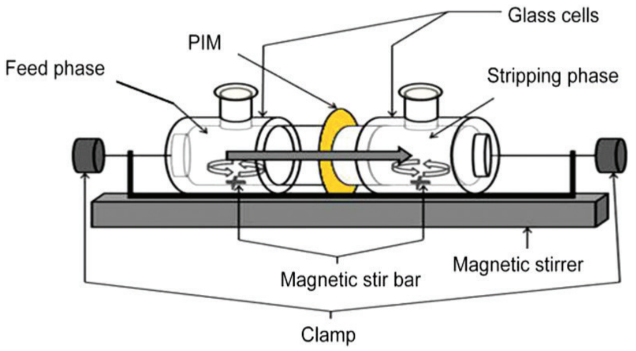


Fig. 1. Schematic diagram of the experimental setup for the permeation experiment.

The permeation experiment was conducted using the apparatus shown in Fig. 1. The feed phase was 2 M hydrochloric acid solution and the stripping phase was one of the following aqueous solutions: Na_2SO_4, $NaHSO_4$, and HCl. 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 Eq. (3).

$$\text{Permeation}(\%) = \frac{[\text{M}]_{s,t}}{[\text{M}]_{f,0}} \times 100 \tag{3}$$

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

3. Results and discussion

3.1. Solvent extraction

A key point for the effective application of solvent extraction in the selective recovery of valuable metals is to find an appropriate extractant and to design suitable separation procedures [14]. There are two parameters which absolutely affect the separation of metal using IL as a carrier: the concentration of ligand (form anion complex with metal) and the concentration of IL. This experiment was conducted in order to evaluate the influence of hydrochloric acid concentration and IL concentration on the recovery of Fe(III) and Mn(II). As reported by Wei et al. [14], the transport of metals from aqueous solution to organic solution containing IL occurs due to the anion exchange reaction between the anion of IL and the anionic form of metal which is produced by the reaction of metal cation with chloride anion as illustrated in Eq. (4).

$$\begin{aligned} &\text{M}^{n+} + (n+1)\text{HCl} \rightleftarrows \text{MCl}_{n+1}^{-} + (n+1)\text{H}^{+} \\ &\text{MCl}_{n+1}^{-} + \text{Q}^{+} \rightleftarrows \text{Q}^{+}\text{MCl}_{n+1}^{-} \end{aligned} \tag{4}$$

where M^{n+} is the metal ion with ion valence n and Q^+ is the cation of the IL. As seen in Eq. (4), Fe(III) and Mn(II) in the presence of excess hydrochloric acid form the anionic chlorocomplexes, $FeCl_4^-$ [7–9,12] and $MnCl_3^-$ [15]. Fig. 2 shows the effect of HCl concentration on the extractability and the distribution ratio of Fe(III) and Mn(II) with three ILs. As shown in Fig. 2(a), Fe(III) was not detected in the aqueous

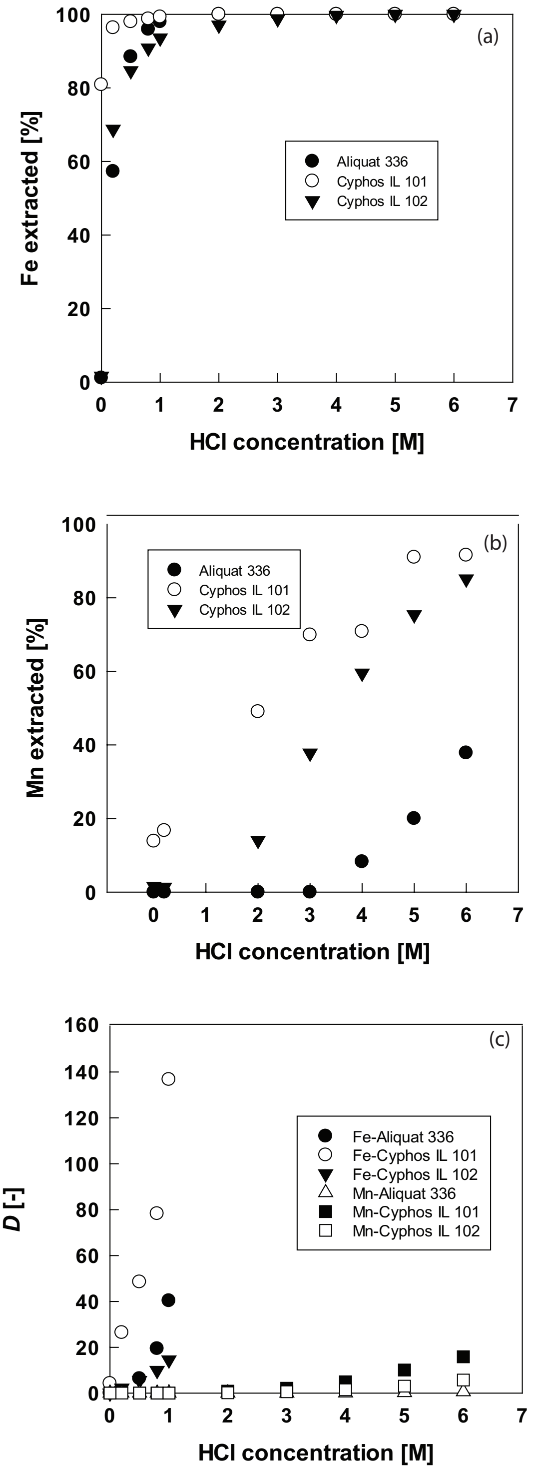


Fig. 2. Influence of HCl concentration on extractability of Fe(III) (a), Mn(II) (b), and the distribution ratio of Fe(III) and Mn(II) (c). Concentration of ionic liquid is 1.0 M.

solution, when the concentration of HCl and IL were 1.0 M and higher, suggesting that it was completely extracted with each of the three ILs. The anion exchange ability of the ILs for $FeCl_4^-$ was as follows: Aliquat 336 ≈ Cyphos IL 102 < Cyphos IL 101. The extractability and distribution ratio of Mn(II) were lower than those of Fe(III) as shown in Fig. 2. The highest extractability of Mn(II), 91%, was reached 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) needed to form $MnCl_3^-$ [15]. This can also be seen in Fig. 2(b), which describes the anion exchange ability of the ILs for $MnCl_3^-$ as follows: Aliquat 336 < Cyphos IL 102 < Cyphos IL 101. The highest extractability of Mn(II) using conventional quaternary ammonium salt (Aliquat 336) was only approximately 37%. This suggests that phosphonium-based ILs have superior anion exchange ability than that of ammonium-based ILs and are preferable for the extraction of the meal anion species.

A similar trend was discovered when the concentrations of ILs were varied in the presence of 4.0 M of hydrochloric acid concentration as shown in Fig. 3.

3.2. Polymer inclusion membrane

Experiments regarding membrane permeation were conducted based on results concluded in the solvent extraction experiments. In the solvent extraction experiments, we found that the three ILs used were great carriers for the extraction of Fe(III). However, for Mn(II), Cyphos IL 101 was the best extractant. Hence, in the membrane permeation experiment we evaluated the recovery of Fe(III) and Mn(II) 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 Fig. 4. Sodium sulfate solution as a stripping reagent gave the better permeation rates than others. Fig. 4 shows that the recovery 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 IL 101 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 [8]. 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.

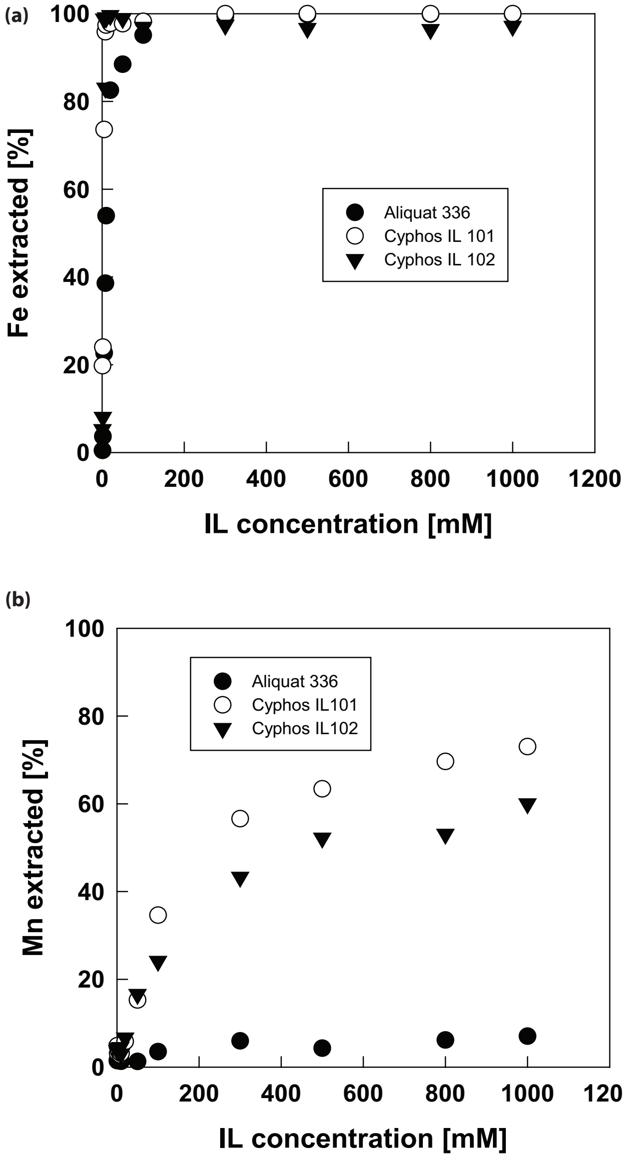


Fig. 3. Influence of ionic liquid concentration on the extractability of Fe(III) (a) and Mn(II) (b). Hydrochloric acid concentration is 4.0 M.

The recoveries of Mn(II) from 4 or 6 M hydrochloric acid solutions with PIM were carried out using Cyphos IL 101 as a carrier. In the case of Aliquat 336, Mn(II) was not permeated at all. Fig. 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 2 lists the effect of a stripping reagent on the permeation. Table 2 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 h of permeation. Usage of Na_2SO_4 and $NaHSO_4$ as stripping phases demonstrated excellent stability of membranes up to 72 h of permeation.

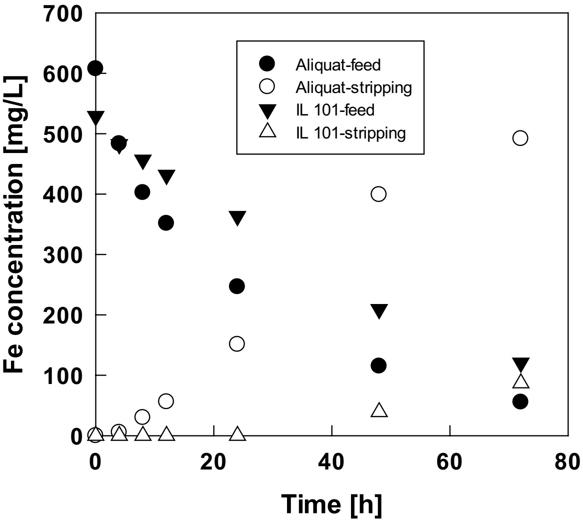


Fig. 4. Permeation of Fe(III) using Aliquat 336 and Cyphos IL 101 as carrier.

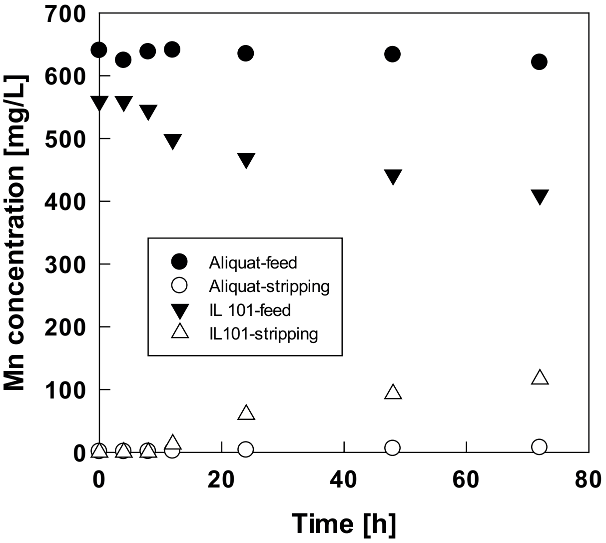


Fig. 5. Permeation of Mn(II) using Aliquat 336 and Cyphos IL 101 as carrier.

Table 2
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	

4. Conclusion

In this study, ILs such as Aliquat 336, Cyphos IL 101, and Cyphos IL 102 were used as complexing reagents to recover Fe(III) and Mn(II) in the processes of the solvent extraction and LM permeation. In the solvent extraction, the anionic chlorocomplexes, $FeCl_4^-$ and $MnCl_3^-$ formed in the presence of excess hydrochloric acid were extracted with all ILs via anion exchange reaction. Cyphos IL 101 among the ILs investigated was the largest extractability for recovery of Fe(III) and Mn(II).

In the LM permeation with ILs, 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.

Acknowledgments

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