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– *Notes* –

Extraction of Lithium from Salt Lake Brine with Tributyl Phosphate and an Ionic Liquid

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Solvent extraction of lithium (Li) from salt lake brine was investigated by employing tributyl phosphate (TBP) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMI-TFSI). High extraction efficiency of Li was obtained from the brine containing co-existed metals. The extraction of Li was proceeded by solvation of Li with TBP followed by cation exchange with the ionic liquid. The purity of Li was increased to 85.1% after two extraction – stripping processes of the present extraction system.

1. Introduction

Lithium (Li) is an important element used for lithium ion batteries (LIB), glass ceramics, medicine, aircraft alloys, catalyst, and nuclear fusion fuel [1-3]. Recently, demand of Li has rapidly increased with increase in demands of electric vehicles (EV) and plug-in hybrid vehicles (PHV). Most of Li resources are either salt lake brine-based or ore-based resources, and the current production ratio of Li from salt lake brine to that from ore is ca. 2 : 1 [4]. Generally, Li is currently produced from salt lake brine in the following way. Firstly, salt lake brine is evaporated for 1.5 to 2 years. Then, after neutralization and removal of impurities, soda ash is added into the concentrated brine to precipitate Li_2CO_3 [5]. In the case of Atacama in Chile, Li in salt lake brine is concentrated by evaporation in solar ponds. However, operation of this process is not easily applied to other salt lake brines, because salt lake brines containing low concentrations of sulfate ions like Atacama brine are seldom found and Li tends to precipitate as Li_2SO_4 in concentrated brine [6]. Therefore, development of a new recovery method is required for recovering Li from other salt lake brines like Uyuni in Bolivia which is the largest reservoir for Li in the world.

Solvent extraction is widely used as a hydrometallurgical separation process for metals, since it has the advantages of high capacity, fast production rate, simple equipment, and it is economical. In the case of Li, solvent extraction of Li by a cation exchange extractant is quite difficult, because the selectivity of the Li ion is lower than for the hydrogen ion. Thus, synergistic extraction systems have been applied to extract Li [7-9]. However, there are environmental pollution and safety issues in the extraction systems due to the use of a large amount of volatile organic solvent.

Recently, ionic liquids are found to be promising solvent alternatives to conventional organic solvents. An ionic liquid is a salt consisting of anions and cations, and is called a “Green solvent” due to their characteristics such as low volatility, flame retardation, and thermal stability [10,11]. Shi *et al.* have recently reported the extraction of Li using tri-*n*-butyl phosphate (TBP) and 1-butyl-3-metyl-imidazolium hexafluorophosphate (BMIM-PF_6, $[C_4min]^+,[PF_6]^-$) as an ionic liquid. The extraction of Li was achieved by solvation of Li with TBP, $[Li\cdot TBP]^+$, followed by cation exchange of $[Li\cdot TBP]^+$ with $[C_4min]^+$ [3,12,13]. However, the hexafluorophosphate anion in the ionic liquid is changed to hydrogen fluoride when the ionic liquid contacts water during liquid-liquid extraction. Particularly, in the case of acid conditions, the following reaction (1) occurs [14].

$$H^+ + PF_6^- + H_2O + HNO_3 \rightarrow H_3PO_4 + 6HF + HNO_3 + 2H_2O \quad (1)$$

In the present work, the cation of 1-butyl-3-methy-limidazolium bis(trifluoromethylsulfonyl)-imide (BMI-TFSI, $[C_4min]^+,[Tf_2N]^-$) was employed as a cation exchanger. The Uyuni Salt Lake brine in Bolivia was used as a target solution for recovery of Li. The extraction properties of Li from the brine with BMI-TFSI and TBP was firstly investigated to elucidate the effects of the concentration of BMI-TFSI and the pH of the aqueous solution. Stripping of the metals was then investigated. Finally, separation of Li by using repeated extraction was investigated for enhancement of the purity of Li.

2. Experimental

2.1 Reagents

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMI-TFSI) was supplied by Toyo Gosei Co., Ltd (Tokyo, Japan), and Amberlite IRA-400 was supplied by Sigma-Aldrich (St. Louis, Missouri, USA). Potassium chloride was supplied by Kanto Chemical Co., Inc. (Tokyo, Japan). All other organic and inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents. Amberlite IRA-400 was treated with 1 mol/L sodium hydroxide solution, followed by washing with Milli-Q water, prior to use.

2.2 Extraction and stripping of Li

In this study, a simulated solution (pH = 6.00) of brine of Uyuni Salt Lake was prepared using LiCl, NaCl, $MgCl_2$, KCl and H_3BO_3 as shown in Table 1 [15], and was used as the aqueous feed solution after pH adjustment with HCl. When the effect of the chloride ion concentration on the extraction properties of Li was investigated, a single Li solution ($[Li]_{feed}$ = 1500 mg/L) of which the chloride ion concentration was adjusted by HCl was used. Organic solutions were prepared by mixing BMI-TFSI and TBP. A typical volume ratio of BMI-TFSI to TBP was 10 vol%, and was changed from 0 to 30 vol% when the effect of the concentration of BMI-TFSI was investigated. Extraction of Li was carried out by mixing the organic solution (10 mL) and the simulated brine (10 – 40 mL), and then the mixture was shaken vigorously at 25°C for more than 3 h. After phase separation, stripping was carried out with hydrochloric acid at an organic and aqueous phase ratio (O/A) = 1. Concentrations of the metals in the resultant aqueous solutions were determined by atomic absorption spectroscopy (AAS, Shimadzu AA-6300) and inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPE-9000) and the pH was measured by a pH meter (Horiba F-23). Concentration of the chloride ion was determined by ion chromatography (IC, Shimadzu Prominence).

Table 1. Composition of the simulated Uyuni Salt Lake brine, Bolivia [15].

	Li^+	Na^+	Mg^{2+}	K^+	B
Concentration (mg/L)	1410	60560	19140	23320	850
Concentration (mmol/L)	203.1	2634	787.3	596.4	78.6

2.3 Purification of Li

Purification of Li after extraction from the simulated brine with the mixture of BMI-TFSI and TBP was investigated. In this case, the extraction of Li was firstly carried out using 10 vol% BMI-TFSI/TBP at an O/A = 1, and then the resultant organic phase was stripped with 1 mol/L hydrochloric acid solution at an O/A = 1. The extraction of Li was again carried out, after removal of chloride ions from the stripping solution by using a column containing Amberlite IRA-400. The column operation with Amberlite IRA-400 was carried out by feeding the stripping solution to the column (I.D. = 10 mm) packed with 1.5 g (wet volume 1.5 mL) of the adsorbent at a flow velocity of 0.25 mL/min (S.V. = 10 h^{-1}). The 2nd extraction was carried out by using the effluent solution at a bed volume = 0 – 2 as the feed solution.

3. Results and Discussion

3.1 Extraction of Li with BMI-TFSI and TBP

Firstly, comparison of PF_6^- and Tf_2N^- was carried out, and the extraction efficiency and selectivity were found to be almost the same. Therefore, BMI-TFSI was used for the extraction of Li from the salt lake brine.

The effect of the concentration of BMI-TFSI on the extraction of metals was investigated. Figure 1 shows the effect of the volume ratio of BMI-TFSI to TBP on the extraction percentage of the metals. Li was poorly extracted without BMI-TFSI. The extraction percentage of Li sharply increased with an increase in the concentration of BMI-TFSI until 20 vol%, and thereafter slightly decreased. These results indicate that both BMI-TFSI and TBP were required for the extraction of Li. When the concentration of BMI-TFSI was higher than 20 vol%, extractability of Li decreased due to a decrease in the TBP content. Based on these results, 10 vol% BMI-TFSI was used hereafter.

The effect of the pH of the aqueous solution on the extraction percentage of the metals was then investigated. Figure 2 shows the effect of the equilibrium pH on the extraction percentage of the metals. Extraction of Li was almost constant against pH. In the case of the BMIM-PF_6-TBP system, the extraction mechanism of Li was reported to proceed *via* solvation of Li with TBP, followed by cation exchange with the cation species of the ionic liquid [3]. In the present extraction system, therefore, extraction of Li is considered to progress as reaction (2).

$$Li^+_{aq} + C_4min^+_{org} + 2TBP_{org} \rightarrow [Li\cdot 2TBP]^+_{org} + C_4min^+_{aq} \qquad (2)$$

Figures 1 and 2 indicate that the selective extraction of Li was possible, and the extraction percentage of the co-existed metals in the brine was much lower than that of Li. In addition, the extraction of Li was almost independent of pH. Therefore, the present extraction system has the potential to be applied for the recovery of Li from the salt lake brine.

The effect of the organic and aqueous phase ratio (O/A) was then investigated. Figure 3 shows the effect of O/A on the extraction percentage of the metals. The extraction percentage of Li increased with increasing O/A, and an extraction percentage of ca. 75% was achieved at an O/A = 3. B extraction also increased dramatically with increasing O/A because the selectivity for B is high. In fact, extraction from equal concentration solutions of the metals was carried out and a high extraction efficiency for B (ca. twice of Na, Mg, and K) following Li was found. Separation of Li became poorer due to an increase in the extraction percentage of the co-existed metals. An O/A of 1 was therefore used hereafter.

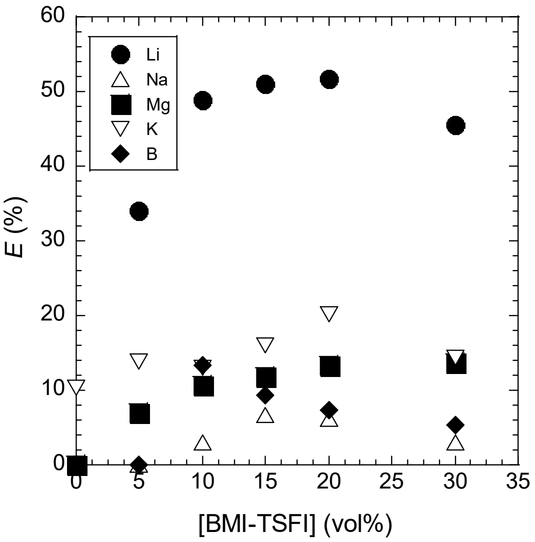

Figure 1. Effect of the concentration of BMI-TFSI on the extraction percentage of the metals. pH_{ini} = 6.00 and O/A = 1.

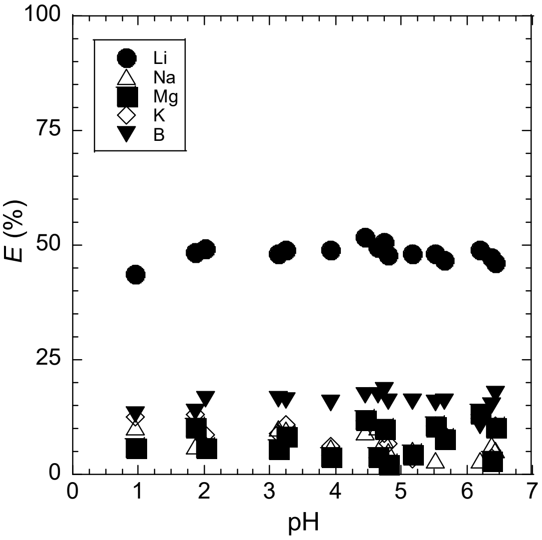

Figure 2. Effect of pH on the extraction percentage of the metals. [BMI-TFSI] = 10 vol% and O/A = 1.

3.2 Stripping of metals from BMI-TFSI-TBP

Stripping of the metals was investigated with hydrochloric acid. Figure 4 shows the effect of the hydrochloric acid concentration on the stripping percentage of the metals, after extraction with 10 vol% BMI-TFSI at O/A = 1. Stripping of Li increased with increasing hydrochloric acid concentration achieving 100% with 1 mol/L hydrochloric acid. This is due to the influence of the chloride ion, but not the hydrogen ion, because the hydrogen ion is not included in the extraction reaction in eq.(2). Table 2 shows the concentration of the metals in the stripping solution of 1 mol/L hydrochloric acid. Despite the high extraction efficiency of Li and the low extraction efficiencies of co-existed metals, considerable amounts of co-existed metals, especially Na, were still found in the stripping solution due to their high concentration in the feed solution. Therefore, an increase in the purity of Li should be investigated.

Table 2. Concentration of the metals and chloride ion in the stripping solution.

	Li	Na	Mg	K	B	Cl^-
Before removal of Cl^- (mmol/L)	78.2	70.5	5.8	2.1	10.78	861.1
After removal of Cl^- (mmol/L)	75.5	65.6	5.5	2.1	7.54	226.4

3.3 Effect of chloride ion concentration

The effect of the chloride ion on the extraction of Li was investigated with a Li solution only. In this case, the concentration of the chloride ion was controlled by adding hydrochloric acid to the Li solution. Figure 5 shows the effect of the chloride ion concentration on the extraction percentage of Li. The extraction efficiency of Li decreased with an increase in the chloride ion concentration. Therefore, removal of chloride ion from the stripping solution is required before further extraction of Li for increasing the purity of Li.

3.4 Purification of Li

Purification of Li by a 2nd extraction step from the stripping solution, as shown in Table 2, was investigated. Removal of chloride ion from the stripping solution was firstly investigated using a column operation with Amberlite IRA-400. Figure 6 shows the breakthrough curve of the chloride ion. Complete removal of the chloride ion was difficult due to its high concentration in the stripping solution, and thus chloride ion immediately broke through. The 2nd extraction of Li was therefore carried out using the effluent solution until bed volume = 2.

Table 3 shows composition of the metals in the 2nd stripping solution. The purity of Li was improved by the 2nd extraction. The extraction system in the present work therefore possesses a potential for the separation of Li from salt lake brine.

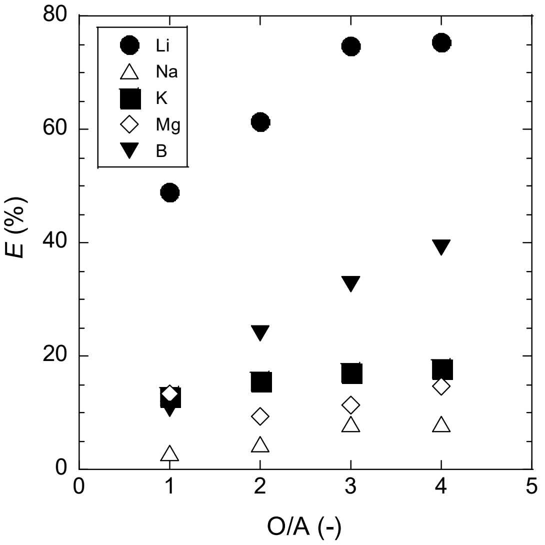

Figure 3. Effect of the organic and aqueous (O/A) phase ratio. pH_{ini} = 6.00 and [BMI-TFSI] = 10 vol%.

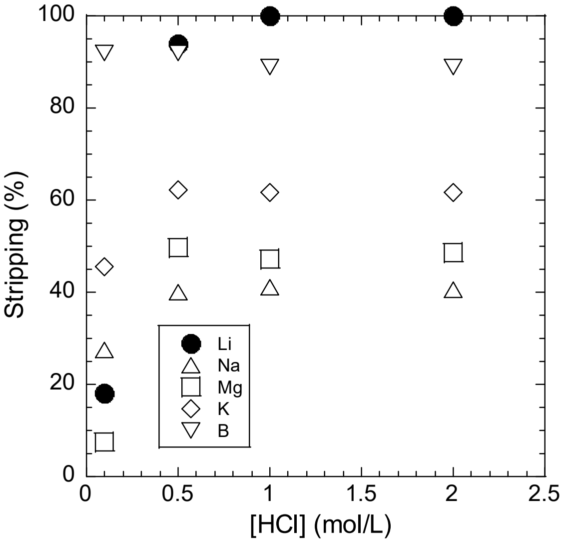

Figure 4. Effect of the HCl concentration on the stripping of metals.

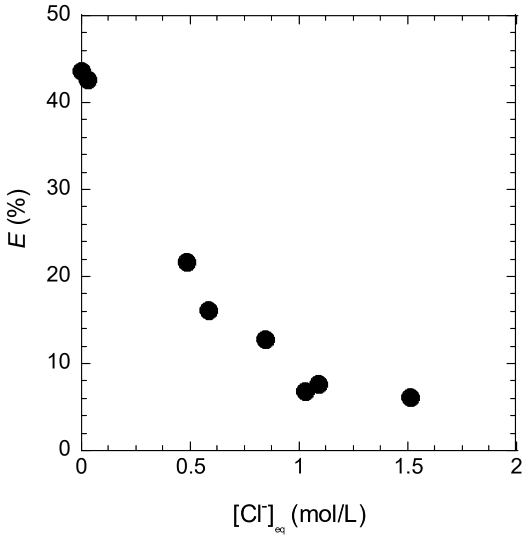

Figure 5. Effect of chloride ion concentration on the extraction efficiency of Li. O/A = 1, and [BMI-TFSI] = 10 vol%

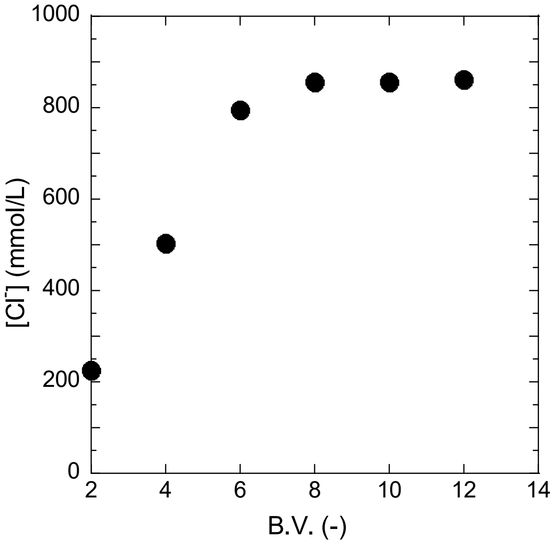

Figure 6. Breakthrough curve of the chloride ion.

Table 3. Concentration and composition of the metals in the 2nd stripping solution.

	Li	Na	Mg	K	B
Concentration (mmol/L)	46.2	6.4	N.D.	1.1	0.7
Composition (mol%)	85.1	11.7	0	2.0	1.2

4. Conclusion

Solvent extraction of Li with the synergistic extractant system of BMI-TFSI plus TBP was investigated, with the following results. Extraction of Li was possible in the presence of BMI-TFSI, and selective extraction of Li was achieved from the brine. The extraction of Li was affected by the chloride ion concentration in the aqueous solution, and thus successful stripping of loaded Li was achieved by hydrochloric acid. The purity of Li could be increased by a second extraction – stripping processing after removal of the chloride ions in the 1st stripping solution. The ionic liquid has a high potential, but it is currently quite expensive. If this issue can be solved, the present study may be used for Li recovery in the future.

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