

## Extraction of Lithium Ion Using Ionic Liquids Dissolved in Tributyl Phosphate

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**Abstract.** Separation among lithium ion and magnesium ion remain challenging. In the present work, the solvent extraction of the lithium ions was performed using tributyl phosphate (TBP) as the extractant in a commonly used ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate ([C<sub>6</sub>mim][PF<sub>6</sub>]). The influence of several extraction parameters on the extraction efficiency was investigated, including the hydrochloric acid concentration, dosage of ionic liquid and phase ratio. The preliminary experimental results had demonstrated that this ionic liquid system shown considerable extraction ability for lithium ions from salt lake brine of a high Mg/Li ratio. Both the extraction efficiency and distribution coefficient were much larger than in conventional organic solvents. Therefore, this method is highly effective and selective to extract lithium ions from salt lake brine.

**Keywords:** Lithium; ionic liquid; tributyl phosphate; solvent extraction

### 1. Introduction

Lithium is an important rare element and is the lightest alkali metal. Lithium and lithium metal compounds are greatly used in the fields of batteries, aerospace, refrigerants, lubricants, atomic energy and so forth. And its application and consumption is steadily growing in recent years. Currently most lithium production comes from brine's sources. But many salt lakes exhibit characteristically high Mg to Li ratios, which make the efficient separation of lithium very difficult. Up to now, solvent extraction based on the tributyl phosphate is an effective method for separation of lithium and magnesium. However, it still suffers from one or more drawbacks including the volatility and toxicity of kerosene or chloroform as solvent. Therefore, looking for an alternative solvent for lithium extraction is in high demand.

Ionic liquids were considered as promising 'green' alternatives to the conventional diluents due to their characteristics such as low volatility, negligible volatility, thermal stability and benign nature [1]-[7]. Replacement of volatile organic solvents in solvent extraction systems could lead to inherently safer extraction processes for metal ions. In recent years, ionic liquid had been regarded as green solvents and functional liquid material for synthesis, separation, catalysis and material sciences [8]-[15]. Application of ionic liquid in the extraction of metal ions had also received increasing attention [16]-[22]. For example, iridium(IV) was found to be efficiently extracted using simple hydrophobic ionic liquids, exhibiting *D* values ranging up to 71[23]. Okamura et al. [24] investigated the extraction behavior of lanthanoid(III) ions with  $\beta$ -diketones and trioctylphosphine in ionic liquids. The results suggested special synergism for the enhancement of not only the extractability, but also the separability of Ln(III) ions. Comparable extraction behavior of several actinide ions from radioactive waste was reported by Panja et al. [25], employing N,N,N',N'-tetra-n-octyl diglycolamide (TODGA) in three different room temperature ionic liquids as the diluents. In the previous studies, ionic liquids were used as extractants or solvents for the extraction of

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multi-heavy metal ions, but there were few reports about the extraction of lithium from salt lake brine which exhibited a high Mg/Li ratio.

Herein, ionic liquids, 1-hexyl-3-methyl-imidazolium hexafluorophosphate ( $[C_6mim][PF_6]$ ), was exploited as a 'green' alternative to the commonly known organic solvents. The tributyl phosphate (TBP) was used as extractant in the ionic liquid, ( $[C_6mim][PF_6]$ ), for the extraction of lithium ions from salt lake brine which exhibited characteristically high Mg to Li ratios. Various parameters like the hydrochloric acid concentration, dosage of ionic liquid, etc. had been investigated in detail. In addition, to evaluate the potential use of ionic liquid to replace traditional volatile organic compounds (VOCs), the extractions of lithium ions with VOCs and ionic liquid were compared.

## 2. Experimental

### 2.1. Materials and apparatus

Tributyl phosphate (98.5% purity) was purchased from Tianjin Yongda Chemical Reagent Development Center (China) and used without further purification. Ionic liquid, viz. 1-hexyl-3-methyl-imidazolium hexafluorophosphate ( $C_6mim^+PF_6^-$ ) with purities >99% was procured from Lanzhou Institute of Chemical Physics, CAS. The ion concentration in Brine:  $Li^+(2.02g L^{-1}) + Mg^{2+}(92.14g L^{-1}) + Na^+(3.21g L^{-1}) + K^+(1.84g L^{-1})$ . Thermostatic water bath oscillators (THZ-82A, Changzhou Aohua Instrument Co., Ltd.);  $Li^+$  concentration was determined by atomic absorption spectroscopy using a GBC (Melbourne, Australia) GBC 908 atomic absorption spectrophotometer. All other reagents were of analytical grade.

### 2.2. Extraction experiments

Distribution studies were carried out by equilibrating suitable volumes of aqueous phase with suitable volumes of organic phase containing the required concentration ionic liquid in separating funnel. The biphasic system was shaken for 10min to ensure the phases were fully mixed and allowed it stand for 20min. After phase disengagement, the aqueous phase was properly diluted and the concentration of lithium ions was measured using an atomic absorption spectrometer. The concentration of  $Mg^{2+}$  in the aqueous phase was determined by using chrome black T as indicator and EDTA as titrant. The distribution ratio ( $D$ ), the extraction efficiency ( $E$ ) and separation factor ( $\beta$ ) were expressed as the following equations:  $V_{org}$  and  $V_{aq}$  are the volumes of the organic and aqueous phases, respectively. The  $C_0$  and  $C_e$  are the concentration of lithium ions in the aqueous phase before and after extraction, respectively.

$$D = \frac{C_0 - C_e}{C_0} \times \frac{V_{aq}}{V_{org}} \quad (1)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

$$\beta = \frac{D_{Li}}{D_{Mg}} \quad (3)$$

## 3. Results and Discussion

### 3.1. Effect of HCl concentration

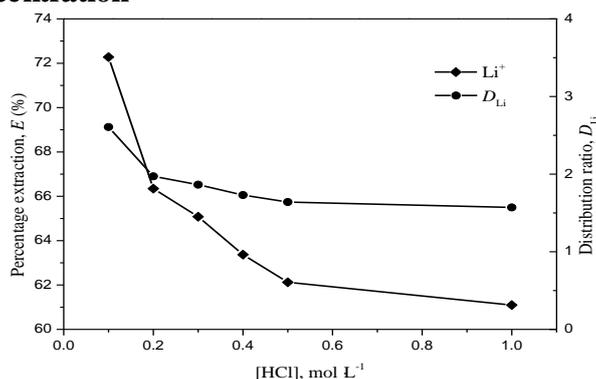


Fig. 1: The extraction efficiency of  $Li^+$  as the function of HCl concentration

Aqueous phase acidity played an important role in the extraction of lithium ions into neutral extractant like TBP. The effect of aqueous phase hydrochloric acid concentration on the extraction of the lithium ions was investigated. As shown in Fig. 1, the extraction efficiency and distribution ratio decreased with the increase in the acidity of the aqueous solution. At 0.1 mol L<sup>-1</sup> HCl, the distribution ratio of Li<sup>+</sup> was 2.61, but the distribution ratio gradually decreased to 1.57 at 1.0 mg L<sup>-1</sup> HCl. And the extraction efficiency decreased from 72.28 to 61.10%. The acidity dependence can be explained by the competition between the extraction of protons and the extraction of metal ions.

### 3.2. Effect of dosage of ionic liquid

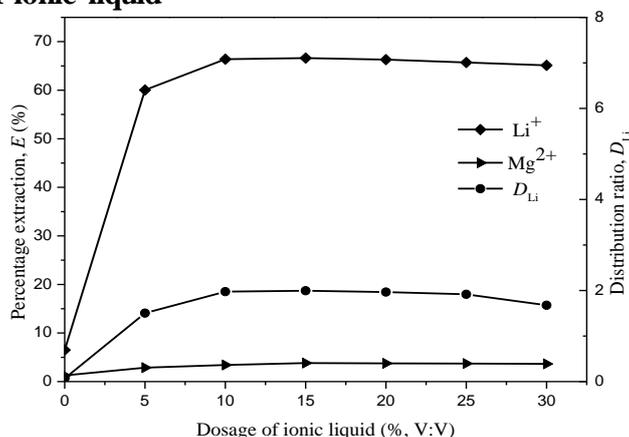


Fig. 2: Effects of RTILs volume in TBP on extraction efficiencies of metal ions

The organic phase was composed of ionic liquids and TBP. The volume of ionic liquids would affect the extraction efficiency of lithium directly. The effect of addition of ionic liquids in TBP was experimentally studied in the range of 0-30% (v/v). As you can see in Fig. 2, the extraction efficiency initially increased with an increase in ionic liquids concentration. When the volume fraction of ionic liquid was 10%, the extraction efficiency reached the maximum. And it decreased with further increasing in ionic liquid vol%. It may be due to the reduced probability of reaction between lithium ion and TBP with excessive ionic liquids diluted in the organic phase. From the results obtained, the volume percentage of ionic liquids in TBP 10% was chosen for further studies.

### 3.3. Effect of O/A phase ratio

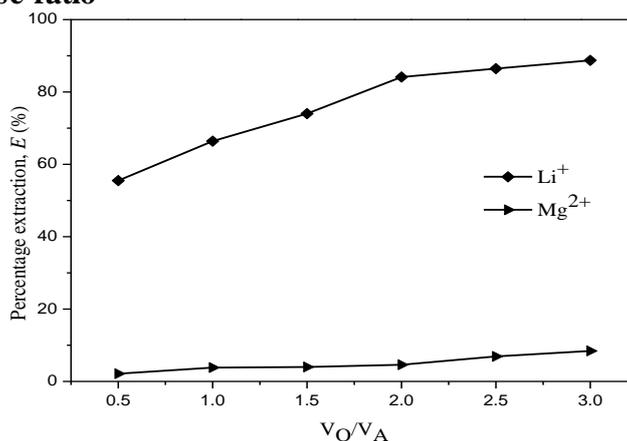


Fig. 3: Effects of phase ratio on the extraction efficiencies of metal ions

The influence of O/A phase ratio on the extraction of lithium ion between the aqueous phase and the organic phase was experimentally studied. Obviously, the extraction efficiency increased with the increasing of the O/A phase ratio by ionic liquid [C<sub>6</sub>mim] [PF<sub>6</sub>] diluted in TBP. When the O/A phase ratio was 2, the extraction efficiency reached 84.14%. At the same time, it was found that the extraction efficiency of magnesium ions was 4.61%. And the separation factor ( $\beta$ ) reached 109.77, which indicated that the TBP/[C<sub>6</sub>mim] [PF<sub>6</sub>] system is a really effective medium for liquid/liquid extraction of Li<sup>+</sup> from salt lake

brine of a high Mg/Li ratio. Considering the cost reduction and higher extraction efficiency, the O/A phase ratio of 2 was used for further studies.

### 3.4. Effect of TBP in various solvents

Table 1: Effect of different solvents on lithium ion extraction efficiency

solvent	none	sulfonated kerosene	chloroform	[C <sub>6</sub> mim][PF <sub>6</sub> ]
Extraction efficiencies/%	8.20	7.82	7.10	84.14

Experiments were conducted to study the extraction of lithium ions using tributyl phosphate (TBP) in various solvents like sulfonated kerosene, chloroform and ionic liquid. Obviously, the maximum extraction efficiency of lithium ion using TBP in ionic liquid was found. When chloroform or sulfonated kerosene was used as diluent at the same conditions, however, the extraction efficiency of lithium ions was not more than 10%. This result unambiguously indicated that Li<sup>+</sup> trapping was greatly enhanced by using [C<sub>6</sub>mim][PF<sub>6</sub>] as solvent, and that TBP/[C<sub>6</sub>mim][PF<sub>6</sub>] system was very effective medium for liquid/liquid extraction of Li<sup>+</sup>.

### 4. Multi-stage Countercurrent Extraction

In order to make the extraction efficiency of lithium ion over 99%, it's necessary to proceed with multi-stage countercurrent extraction. The extraction isotherm was studied to find out the number of stages required for a quantitative extraction of the substance at a chosen O/A phase ratio. The lithium ion extraction distribution isotherm and the McCabe-Thiele diagram obtained with fresh organic phase containing [C<sub>6</sub>mim][PF<sub>6</sub>] was showed in Fig. 4. And it indicated that the extraction efficiency will over 99% in three stages countercurrent extraction when O/A phase ratio was 2. In this work, a triple-stage countercurrent extraction experiment was carried out under the optimum conditions, and the results shown that the extraction efficiency of lithium ion had reached 99.60%. Subsequently, the distribution ratio ( $D_{Li}$ ) was calculated and it reached 124.50. The results demonstrated that this ionic liquid system had shown considerable extraction ability for lithium ions.

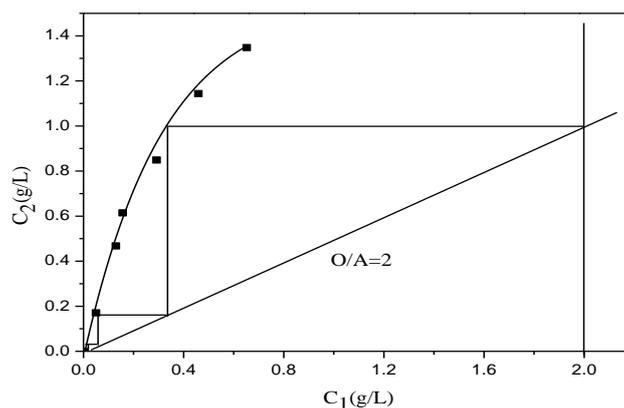


Fig. 4: McCabe-Thiele diagram for lithium ion extraction: C<sub>1</sub> was the concentration of Li<sup>+</sup> in aqueous phase in equilibrium, and C<sub>2</sub> for in organic phase in equilibrium. O/A = 1/2 to 3/1; T = 303 K.

### 5. Stripping

The single-stage extraction had been conducted under the optimum conditions and the organic phase was taken out for stripping. After one stage extraction, the concentration of lithium ion and magnesium ion in the organic phase was 0.85g/L and 2.12g/L, respectively. The stripping test for Li<sup>+</sup> extracted by TBP in [C<sub>6</sub>mim][PF<sub>6</sub>] was performed using different concentrations of dilute hydrochloric acid at 303 K. The HCl concentration was varied over the range 0.1-2.0 mol L<sup>-1</sup> and the results were shown in Fig. 5. The single

stripping efficiency of lithium ions increased with increasing the acidity of the aqueous solution. At 0.1 mol L<sup>-1</sup> HCl, the single stripping efficiency of lithium ions was 43.45%, but the stripping efficiency gradually increased to 97.84% at 2.0 mol L<sup>-1</sup> HCl. At 1.0 mol L<sup>-1</sup> HCl, it was found that the stripping efficiencies of lithium ions and magnesium ions were 95.80% and 91.33%, respectively. The Mg/Li ratio was 2.38 in the aqueous phase after stripping, which have dropped 94.78% when it compared with the initial value. After concentrating the aqueous phase and precipitating the magnesium ion with alkali, the magnesium hydroxide could be separated after filtration. Lithium carbonate will be obtained by adding sodium carbonate to the aqueous phase.

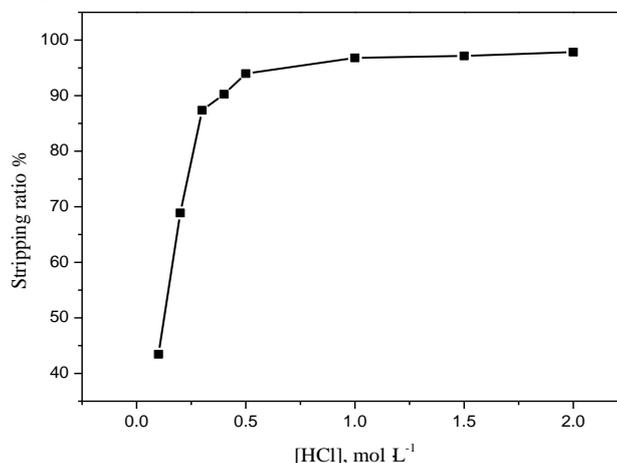


Fig. 5: Percentage stripping of lithium ions from the ionic liquid phase with different concentrations of hydrochloric acid. (T=303 K)

## 6. Conclusion

The ionic liquid, [C<sub>6</sub>mim][PF<sub>6</sub>], was explored as a solvent for the separation of lithium ions from salt lake brine. The results confirmed that the TBP in conjunction with ionic liquids provided extraordinary extraction of lithium ion. The single extraction efficiency of 84.14% was obtained under the optimal conditions. And total extraction efficiency of 99.60% was obtained by triple-stage countercurrent extraction. The single stripping rate of lithium ion had reached 95.80% at 1.0 mol L<sup>-1</sup> HCl. The Mg/Li ratio was 2.38 in the aqueous phase after stripping which have dropped 94.78% when it compared with the initial value. Preliminary results indicated that the use of ionic liquid as an alternate solvent to replace traditional organic solvents in liquid/liquid extraction was very promising.

## 7. Acknowledgements

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