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## A highly efficient solvent system containing ionic liquid in tributyl phosphate for lithium ion extraction

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### ABSTRACT

Application of a room temperature ionic liquid (RTILs), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[C_4mim][PF_6]$ ), in the extraction of lithium ion from salt lake brine using tributyl phosphate (TBP) as extractant was investigated. The effects of temperature, pH value of solution, phase ratio and other factors on the extraction were studied in detail. The preliminary experimental results had demonstrated that, compared with using conventional extraction system, the extraction efficiency had been increased greatly in this ionic liquid system. Study on the mechanism revealed that the extraction most likely occurred by a cation exchange mode in this system. This work highlights the vast opportunities in separation applications for ionic liquid.

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### 1. Introduction

Lithium is an important rare element and is known as the 21st century energy metal. Lithium and some lithium metal compounds are widely used in the fields of ceramics, lubricants, atomic energy, aerospace, pharmaceuticals, lithium battery and so forth [1–3]. Currently most lithium production comes from brine's sources. And the methods of separating lithium ion from salt lake brine mainly included salting-out method, precipitation, ion exchange, semipermeable membrane and extraction and so forth [4–7]. Among them, liquid–liquid extraction is an economical, efficient method for the separation of lithium ion especially for the brine sources of a high Mg/Li ratio. Zhou et al. [8] studied the extraction equilibrium of lithium ion with tributyl phosphate (TBP) in kerosene, TBP in methyl isobutyl ketone (MIBK), and TBP in 2-octanol. The results showed that the extraction capacity followed the sequence: TBP/MIBK > TBP/kerosene > TBP/2-octanol. The extraction mechanism for lithium ion with TBP in kerosene and  $FeCl_3$  as a co-extracting agent was investigated too. And they found that the extraction of the lithium ion is a cation exchange reaction [9]. Sun et al. [10] investigated tributyl phosphate (TBP)–kerosene– $FeCl_3$  extraction system by IR and NMR and found that lithium complex and TBP were associated by hydrogen bond. In these systems, tributyl phosphate played the role as extractant, which made a great contribution for extracting lithium ion. The lithium ion was extracted into the organic phase by forming a low polar  $LiFeCl_4 \cdot 2TBP$ . But the strong acidic condition in

these systems may result in severe corrosion to the equipment. And when the concentration of TBP in the TBP/kerosene system is low, the terrible third phase problem will appear. And it may attribute to the hydrolysis of residual ferric ions in the aqueous phase. Furthermore, lots of volatile organic solvents are used in these systems which may lead to serious environmental pollution.

Room temperature ionic liquids (RTILs) were considered as promising 'green' alternatives to the conventional diluents. Their properties, such as low volatility, low melting and high thermal stability, make them environmental friendly [11,12]. Due to their unique characteristics, RTILs are receiving an upsurge attention for their promising role as alternative media in organic synthesis, catalysis, separation and electrochemistry [13–17]. Panja et al. [18] had reported high distribution ratios for  $An^{n+}$  using N,N,N',N'-tetra-n-octyl diglycolamide (TODGA) in room temperature ionic liquids such as  $C_nmim^+ \cdot NTf_2^-$  from radioactive wastes. Okamura et al. [19] investigated the extraction behavior of lanthanoid(III) ions with  $\beta$ -diketones and trioctylphosphine oxide in an ionic liquid ( $[C_4mim][Tf_2N]$ ). The results suggested that special synergism for the enhancement of not only the extractability, but also the separability of Ln(III) ions occurs. Solvent extraction of  $UO_2^{2+}$  by ionic liquid ( $[C_4mim][PF_6]$ ) with dipicolinamide as extractant was investigated by Sun [20]. The results suggested that the imidazole-based ionic liquids had shown excellent radiation stability. Besides, this new system had exhibited large distribution ratio (D) of almost 100. In the previous studies, ionic liquids were used as extractants or solvents for the extraction of multi-valent metal ions, however, only relatively few reports about the extraction of lithium ion by ionic liquids. Song et al. [21] had used the TBP/ $FeCl_3$ /RTILs system for the extraction of lithium ion from salt lake brine. It revealed that the lithium ion was extracted into the

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organic phase by forming a low polar  $\text{LiFeCl}_4 \cdot 2\text{TBP}$ . This system with ionic liquid was of higher extraction efficiency and the capacity of lithium ion. In a follow-up study, the multi-stage countercurrent extraction was carried out. Total recovery of 97% was obtained by combination of three step extractions with two step back-extraction, and Mg/Li ratio was lower to about 2.2 [22]. Since the ferric ion was easy to hydrolyze, an effective extraction needs to be accomplished under high acidic conditions, which may cause severe corrosion to the equipment.

Herein, the extraction of lithium ion from salt lake brine was investigated using tributyl phosphate (TBP) as extractant in the room temperature ionic liquid, 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $\text{C}_4\text{mim}^+ \cdot \text{PF}_6^-$ ). The equipment corrosion and the environmental pollution had been avoided in this new extraction system. The TBP/ $[\text{C}_4\text{mim}][\text{PF}_6]$  extraction system was studied in detail with regard to different extraction parameters such as the pH, concentration of the ionic liquid, phase ratio and different diluents. Furthermore, an extraction mechanism had been proposed based on the slope analysis. Preliminary results indicate that the use of  $[\text{C}_4\text{mim}][\text{PF}_6]$  as an alternate solvent to replace traditional organic solvents (VOCs) in liquid/liquid extraction is very promising.

## 2. Experimental

### 2.1. Materials and apparatus

Tributyl phosphate (TBP) (T.G., 98.5%); room temperature ionic liquid, viz. 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $\text{C}_4\text{mim}^+ \cdot \text{PF}_6^-$ ) with purities >99% was procured from Lanzhou Institute of Chemical Physics, CAS. The ion concentration in brine is as follows:  $\text{Li}^+$  ( $2.088 \text{ g} \cdot \text{L}^{-1}$ ) +  $\text{Mg}^{2+}$  ( $92 \text{ g} \cdot \text{L}^{-1}$ ) +  $\text{Na}^+$  ( $3.2 \text{ g} \cdot \text{L}^{-1}$ ) +  $\text{K}^+$  ( $1.8 \text{ g} \cdot \text{L}^{-1}$ ). The following instruments were used: pH meter (pHS-3C, Shanghai INESA Scientific Instrument Co., Ltd.); thermostatic water bath oscillators (THZ-82A, Changzhou Aohua Instrument Co., Ltd.); atomic absorption spectrometer (GBC 908, GBC Scientific Equipment Pty. Ltd.); and FTIR spectrophotometer (670, Thermo Nicolet Corporation, Madison, USA).

### 2.2. Extraction experiments

Distribution studies were carried out by equilibrating suitable volumes of aqueous phase (usually 20 mL) with suitable volumes of organic phase containing the required concentration ionic liquid in separatory funnel. The biphasic system was shaken for 10 min to ensure that the phases were fully mixed and allowed it to stand for 20 min at 20 °C. Then the two phases were separate. After phase separation, the lower aqueous phase was taken out and measured with atomic absorption spectroscopy to determine the concentration of lithium ion that was left in the aqueous phase. The concentration of  $\text{Mg}^{2+}$  in the aqueous phase was determined by using chrome black T as indicator and EDTA as titrant. The extraction efficiency (E) and the distribution ratio (D) were calculated by

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$D = \frac{C_i - C_f}{C_f} \times \frac{\text{Volume of aqueous phase}}{\text{Volume of organic phase}} \quad (2)$$

where  $C_i$  and  $C_f$  represented the initial and ultimate concentration of lithium ion in the aqueous phase, respectively.

## 3. Results and discussion

### 3.1. Effect of TBP in various solvents

Experiments were conducted to study the extraction of lithium ion using tributyl phosphate (TBP) in various solvents like chloroform, sulfonated kerosene and ionic liquid, and 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $\text{C}_4\text{mim}^+ \cdot \text{PF}_6^-$ ). The volume percentage of diluent in TBP was 10% and other extraction conditions included O/A phase ratio of 1:1, constant duration of oscillation of 10 min and unadjusted pH. The extraction results are presented in Table 1. The maximum extraction percentage of lithium ion using TBP in ionic liquid was found. Based on the maximum extraction percentage of lithium ion from salt lake brine using TBP dissolved in different solvents, the following order was obtained: ionic liquid > sulfonated kerosene > chloroform. This highlights the vast opportunities in separation applications for ionic liquids with TBP.

### 3.2. Effect of pH value

The solution acidity was an important factor and could not be ignored for many extraction systems. Therefore, it was of interest to study the effect of the pH value of the aqueous phase on the extraction of lithium ion using TBP in  $[\text{C}_4\text{mim}][\text{PF}_6]$ . The pH value of the aqueous phase was adjusted by the hydrochloric acid and ammonia. In this paper, the pH value ranged from 1 to 7 and further increased in the pH value may result in the formation of the precipitation of  $\text{Mg}(\text{OH})_2$  as the brine contains a high level of magnesium ion.

As shown in Fig. 1, the extraction of lithium ion was independent of the pH value, which resulted in no significant variation in lithium ion extraction. The probable reason was the associated reaction competition between hydrogen ions and other metal ions was not very strong. Besides that, Fig. 1 shows that the extraction efficiency of lithium ion was much greater than that of the magnesium ions, which indicated high selectivity to lithium ion in this system. Since the pH of the brine is 5.58, the brine can be used for extracting directly without adjusting the pH value in this extraction system.

### 3.3. Effect of RTIL volume in TBP

As shown in Table 1, the experimental results showed that the ionic liquid played a key role in the extraction process. The volume of ionic liquid would affect the extraction efficiency of lithium ion directly. So the effect of addition of ionic liquid  $[\text{C}_4\text{mim}][\text{PF}_6]$  in TBP was experimentally studied in the range of 0–40% (v/v) and the results were shown in Fig. 2. It was observed from Fig. 2 that the extraction efficiency initially increased with an increase in ionic liquid concentration and it reached the maximum when the volume fraction of ionic liquid was 10%. And further increase in ionic liquid vol.% may result in the decrease in the extraction efficiency. The reason is mainly that the probability of reaction between lithium ions and TBP had been reduced as the excessive increase in the amount of ionic liquid diluted the organic phase. From the results obtained, the ionic liquid volume of 10% by total organic phase volume was chosen for further studies.

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

The effect of phase ratio on the lithium ion extraction was investigated covering different volume ratios of organic phase to aqueous phase

**Table 1**  
Effect of different solvents on lithium extraction efficiency.

Diluent	None	Sulfonated kerosene	Chloroform	$[\text{C}_4\text{mim}][\text{PF}_6]$
Extraction efficiencies/%	8.20	7.82	7.10	77.73

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