



# Extraction of lithium from salt lake brine using room temperature ionic liquid in tributyl phosphate



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## HIGHLIGHTS

- We proposed a new system for Li recovery from salt lake brine by extraction using an ionic liquid.
- Cation exchange was proposed to be the mechanism of extraction followed in ionic liquid.
- This ionic liquid system shown considerable extraction ability for lithium and the single extraction efficiency of lithium reached 87.28% under the optimal conditions.

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## ABSTRACT

Lithium is known as the energy metal and it is a key raw material for preparing lithium isotopes which have important applications in nuclear energy source. In this work, a typical room temperature ionic liquid (RTILs), 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $[\text{C}_4\text{mim}][\text{PF}_6]$ ), was used as an alternative solvent to study liquid/liquid extraction of lithium from salt lake brine. In this system, the ionic liquid,  $\text{NaClO}_4$  and tributyl phosphate (TBP) were used as extraction medium, co-extraction reagent and extractant respectively. The effects of solution pH value, phase ratio,  $\text{ClO}_4^-$  amount and other factors on lithium extraction efficiency had been investigated. Optimal extraction conditions of this system include the ratio of TBP/IL at 4/1 (v/v), O/A at 2:1,  $n(\text{ClO}_4^-)/n(\text{Li}^+)$  at 2:1, the equilibration time of 10 min and unadjusted pH. Under the optimal conditions, the single extraction efficiency of lithium was 87.28% which was much higher than the conventional extraction system. Total extraction efficiency of 99.12% was obtained by triple-stage countercurrent extraction. Study on the mechanism revealed that the use of ionic liquid increased the extraction yield of lithium through cation exchange in this system. Preliminary results indicated 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 was very promising.

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## 1. Introduction

Lithium is known as the energy metal and consists of  $^6\text{Li}$  and  $^7\text{Li}$  two stable isotopes in nature.  $^6\text{Li}$  can be cracked into tritium (T) and helium (He) by bombarding with neutron, thus  $^6\text{Li}$  was used as nuclear raw materials for hydrogen bomb to rapidly proliferate tritium and protective materials of neutron for fission reactor to absorb neutron [1]. However, natural Li contains only about 7.6 at.%  $^6\text{Li}$  and, consequently, large amounts of lithium (Li) are needed to obtain the required 30–90% enrichment of  $^6\text{Li}$  for tritium breeding material in fusion reactors [2–4]. There is a great need to develop

efficient method for lithium separation. A salt lake is a landlocked body of water which has a concentration of salt and other dissolved minerals significantly higher than most lakes. Salt lakes are store houses of mineral salts. The productive elements (such as lithium, magnesium, potassium, boron, etc.) among salt lake brines, are precious resources with strategic interest for the development of economics and society. The amount of lithium resources in salt lakes occupies over 69% of its industrial reserves in the world, so the hot point in lithium industry is to exploit lithium resources in salt lakes. It is well known that many salt lakes exhibit characteristically high Mg to Li ratios, which render the efficient extraction of lithium very difficult. The salting-out method, precipitation, ion exchange, semipermeable membrane and extraction are the main methods of separating lithium from salt lake brine [5–8]. A hydrometallurgical process, for example, was developed by An et al. [9] to recover

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lithium from brine which contained saturated levels of Na, Cl and sulphate, low Li (0.7–0.9 g/L Li) and high Mg (15–18 g/L Mg). A high purity (99.55%) and well crystalline lithium carbonate was produced at 80–90 °C. In a follow-up study, they aimed to recover Ca and Mg separately using oxalate and to produce Mg oxalate as a precursor for high purity MgO production. And the high purity (99.5% grade) Mg precipitate was finally obtained [10]. The liquid–liquid extraction was also one of the most promising methods of separating lithium in salt lake containing high magnesium–lithium ratio using extractants of alcohols, esters, diketones, organophosphorus, quaternary ammonium salts and crown ethers. Tan et al. [11], for example, had studied the lithium distribution during the extraction with tributyl phosphate (TBP) diluted by kerosene from the solutions containing lithium and magnesium in the presence of FeCl<sub>3</sub>. It was found that a third phase was formed and lithium was mainly uplocated by the middle organic phase Zhang et al. [12] extracted lithium from salt lake brine with tributyl phosphate (TBP)–kerosene–FeCl<sub>3</sub> system. Effect of TBP concentration on extraction rate was investigated and experimental results showed that the optimum concentrations of TBP and sulfonated kerosene were 80% and 20% respectively. In addition, Sun et al. [13] investigated tributyl phosphate (TBP)–kerosene–FeCl<sub>3</sub> extraction system by IR and NMR and found that lithium complex and TBP were associated by hydrogen bond. In these systems, the equipment may be corroded severely under strong acidic condition during extraction and stripping process. What is more, lots of volatile organic solvents were used in these systems, which may result in serious environmental pollution.

Room temperature ionic liquids (RTILs) are reported to be promising green alternatives to the conventional solvents due to their characteristics such as low volatility, low melting temperature, low phase disengagement time and benign nature [14,15]. Therefore, there is no loss of solvent with ionic liquids and this will avoid environmental and safety problems due to volatilization, as is the case in traditional organic solvents. What is more, room temperature ionic liquids (RTILs) can dissolve a wide spectrum of organic, organometallic and inorganic compounds. In recent years, RTILs were regarded as green solvents and functional liquid material for separation, synthesis, catalysis and material sciences [16–18]. Application of RTILs in the extraction of metal ions had also received increasing attention. Panja et al. [19], for example, had investigated the extraction behavior of several actinide ions such as Am<sup>3+</sup>, Pu<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> in three different room temperature ionic liquids (RTILs). The solvent systems were found to result in higher distribution ratios for all the actinides as compared to that containing *n*-dodecane as the solvent. The investigation of solvent extraction of UO<sub>2</sub><sup>2+</sup> from aqueous solution using IL ([C<sub>4</sub>mim][PF<sub>6</sub>]) showed that the extractant exhibited excellent solubility in the tested RTILs [20]. The extraction of lanthanoid(III) ions with β-diketones and trioctylphosphine in an ionic liquid ([C<sub>4</sub>mim][Tf<sub>2</sub>N]) was analyzed by Okamura et al. [21]. The results suggested special synergism for the enhancement of not only the extractability, but also the separability of Ln(III) ions. A new non-fluorinated malonamide-based ionic liquid extractant synthesized by Rout et al. [22] was investigated for the extraction behavior of europium(III) and other trivalent rare-earth ions from nitric acid medium. A good separation of the rare earths from the transition metals could be achieved with the ionic liquid system. Chen et al. [23] had studied the extraction capability of Cu(II) in aqueous solution with imidazolium ionic liquids and found that the extraction efficiency was much higher compared to CCl<sub>4</sub> extraction system. Further more, Castillo et al. [24] analyzed the extraction of Cu(II) using quaternary ammonium and quaternary phosphonium based ionic liquids. The liquid/liquid extraction tests indicated that it was possible to remove Cu(II) from highly contaminated aqueous solutions using quaternary ammonium type ionic liquids in sulphate, chloride or mixed media. All these works

highlighted the vast opportunities of ILs as a novel media for the separation of metal ions from aqueous solutions.

In the present work, the extraction of lithium from salt lake brine using tributyl phosphate (TBP) as extractant and NaClO<sub>4</sub> as new co-extraction reagent in the room temperature ionic liquid, 1-butyl-3-methyl-imidazolium hexafluorophosphate (C<sub>4</sub>mim<sup>+</sup>.PF<sub>6</sub><sup>-</sup>). The effects of various parameters on the extraction of lithium were discussed in detail and an extraction mechanism is proposed. In addition, to evaluate the potential use of RTILs to replace traditional volatile organic compounds (VOCs) in liquid/liquid extraction of lithium, the extractions of lithium ions with VOCs and ionic liquid were compared.

## 2. Experimental

### 2.1. Materials and apparatus

Tributyl phosphate (TBP) (T.G., 98.5%); NaClO<sub>4</sub>·H<sub>2</sub>O (A.R., >99.0%) was supplied by Sinopharm Chemical Reagent Co., Ltd.; room temperature ionic liquid, viz. 1-butyl-3-methyl-imidazoliumhexafluorophosphate (C<sub>4</sub>mim<sup>+</sup>.PF<sub>6</sub><sup>-</sup>), 1-hexyl-3-methyl-imidazoliumhexafluorophosphate (C<sub>6</sub>mim<sup>+</sup>.PF<sub>6</sub><sup>-</sup>) and 1-octyl-3-methyl-imidazolium hexafluorophosphate (C<sub>8</sub>mim<sup>+</sup>.PF<sub>6</sub><sup>-</sup>) with purities >99% were procured from Lanzhou Institute of Chemical Physics, CAS. The ion concentration in Brine: Li<sup>+</sup>(2 g L<sup>-1</sup>)+Mg<sup>2+</sup>(92 g L<sup>-1</sup>)+Na<sup>+</sup>(3.2 g L<sup>-1</sup>)+K<sup>+</sup>(1.4 g L<sup>-1</sup>). 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); UV-VIS Spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd.).

### 2.2. Solvent extraction studies

Before the extraction, the co-extraction reagent was added to the aqueous phase with a 1:1 molar ratio of ClO<sub>4</sub><sup>-</sup> to Li<sup>+</sup>. The precipitation of NaCl will be found as the salt-out effect. The solids need to be filtered out and the aqueous phase will be used for extraction. Distribution studies were carried out by equilibrating suitable volumes of aqueous phase (usually 20 ml) with equal volumes of organic phase containing the required concentration ionic liquid in separating funnel. The biphasic system was shaken for 10 min and allowed it stand for 20 min at 20 °C. Then separate the two phases. 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 Mg<sup>2+</sup> in the aqueous phase was determined by using chrome black T as indicator and 0.03142 mol/L of EDTA as titrant. Extraction efficiency (*E*) and 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<sub>i</sub>* and *C<sub>f</sub>* represented the initial and ultimate concentrations of lithium ion in the aqueous phase, respectively.

## 3. Results and discussion

### 3.1. Effect of the equilibration time

Due to high viscosity of the ionic liquid, it was expected that the rate of mass transfer will be slower. But viscosity decreased greatly when the ionic liquid was mixed with TBP. The effect of the equilibration time was experimentally studied in the range of 2–12 min and the result was shown in Fig. 1. The results indicated that the

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