



## Solvent extraction of lithium from aqueous solution using non-fluorinated functionalized ionic liquids as extraction agents



Chenglong Shi <sup>a,b,c</sup>, Yan Jing <sup>a,b</sup>, Jiang Xiao <sup>a,b,c</sup>, Xingquan Wang <sup>a,b,c</sup>, Ying Yao <sup>a,b</sup>, Yongzhong Jia <sup>a,b,\*</sup>

<sup>a</sup> Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 810008 Xining, China

<sup>b</sup> Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Chinese Academy of Sciences, 810008 Xining, China

<sup>c</sup> University of Chinese Academy of Sciences, 100049 Beijing, China

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### ABSTRACT

Two non-fluorinated ionic liquids (ILs), namely tetrabutylammonium bis(2-ethylhexyl)-phosphate, [N<sub>4444</sub>][DEHP], and tetraoctylammonium bis(2-ethylhexyl)-phosphate, [N<sub>8888</sub>][DEHP], were synthesized and fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. These functionalized ILs were subsequently evaluated in terms of their ability to extract lithium ions from aqueous solution. The extraction efficiencies of these functionalized ILs for lithium ions were measured as a function of various extraction parameters, including aqueous acidity, temperature and extractant concentration. The extracted species were determined using a slope analysis method, which indicated that the ILs formed a 1:1 (metal:ligand) complex. Fourier transform infrared spectroscopy studies were conducted to better understand the nature of the extracted species. We also investigated the stripping of the lithium ions from the organic phase and the re-use of the ionic liquid in a subsequent extraction step.

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### 1. Introduction

Lithium, as the lightest metal element, is widely used in various fields, including lithium batteries, aerospace, ceramics, polymers and metal additives [1–5]. It is envisaged that the demand for lithium metal will increase considerably over the next decade with the continued development of modern industry. Lithium resources exist naturally in two forms: as a mineral and as a dissolved salt. The limited availability of lithium from mineral resources has steered the industry towards the use of liquid lithium resources, which have been estimated to contain >85% of the world's recoverable lithium [6]. Lithium ions can be recovered via a number of different processes, including precipitation, ion exchange, adsorption, extraction and supported liquid membrane [7–11]. Among these processes, solvent extraction is considered to be one of the most powerful techniques, offering several advantages over the other approaches, including continuous operation and the use of relatively simple equipment on the both laboratory and industrial scales. One of the most commonly used systems for the extraction of lithium ions is tributyl phosphate (TBP)/kerosene-FeCl<sub>3</sub> [12–14]. In this particular system, FeCl<sub>3</sub> acts as a co-extraction agent, where it plays a key role in the extraction of lithium ions. However, this

system must be used under strongly acidic conditions to avoid the hydrolysis of residual ferric ions in the aqueous phase. The use of this system therefore results in the generation of large amounts of acidic wastewater during the extraction and stripping process, representing a serious environmental pollution issue. Furthermore, the strongly acidic conditions required by this system may result in severe corrosion to the equipment. The development of innovative and green extraction processes for the extraction of lithium ions are therefore highly desired to address growing concerns about the environmental impact and safety issues associated with existing processes.

Ionic liquids (ILs) are organic salts composed entirely of ions that have melting points near or below room temperature. ILs have attracted considerable interest from researchers working towards the development of solvent extraction processes because of their many useful solvent properties, including their high thermal stability, negligible volatility, high selectivity and high solvent extraction efficiency [15–17]. ILs can be used to extract metals by simply adding conventional molecular extractants to commercially available ILs. The molecular extractants used in these systems interact with the metal ions to form hydrophobic complexes that readily dissolve in the hydrophobic IL phase. Most of the ILs typically used for solvent extraction processes contain fluorinated anions, such as hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) and bis(trifluoromethyl sulfonyl)imide (NTf<sub>2</sub><sup>-</sup>) anions, because these ILs tend to be immiscible with water, even in combination with small cations

\* Corresponding author at: Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 810008 Xining, China.

E-mail address: [qhislcas@126.com](mailto:qhislcas@126.com) (Y. Jia).

[18–22]. However, it is well known that the extraction mechanisms of ILs can differ from those observed in molecular solvents. In fact, ion exchange is often involved in the extraction mechanisms of ILs, which can lead to the loss of some of the components of the ILs. This process can also lead to the contamination of the water phase with hydrofluoric acid, following the hydrolysis of the fluorinated anions ( $\text{NTf}_2^-$ ,  $\text{PF}_6^-$ ). These issues can therefore complicate efforts to regenerate and reuse ILs, thereby limiting their recyclability. Subsequent developments in this area have led to the introduction of functionalized ionic liquids (FILs) or task-specific ionic liquids (TSILs), where a metal-coordinating group is attached to the cationic or the anionic part of the IL. FILs have been successfully applied as extractants for the separation of metal ions from aqueous medium [23–26]. For example, Onghena and Binnemans [27] synthesized betainium bis(trifluoromethylsulfonyl)imide as a new FIL, and studied its ability to coordinate scandium(III). The results revealed that this FIL allowed for the rapid extraction of Sc(III) ions from water, even at room temperature, with good extraction efficiencies (>95%). Similarly, Sun and Waters [28] synthesized five FILs and evaluated their use as extractants for the separation of rare earth elements. These novel FILs were reported to be highly efficient extraction extractants and showed excellent selectivity towards rare earth ions. Fang et al. [29] reported the development of a new thiol-FIL for the extraction of Cd(II). This system exhibited several good characteristics, including fast adsorption equilibrium and high efficiency, as well as, the interference-free extraction of trace Cd(II).

Here, we have examined the extraction of lithium ions using a solvent extraction system containing a novel non-fluorinated IL consisting of the functionalized IL extractant tetrabutylammonium bis(2-ethylhexyl)-phosphate or tetraoctylammonium bis(2-ethylhexyl)-phosphate in methylbenzene. The effects of several experimental parameters, including the aqueous acidity, temperature and extractant concentration, were also evaluated in terms of their impact on the extraction behavior of the lithium ions. Fourier transform infrared (FTIR) spectroscopy was used to investigate the interactions between the ligands and the lithium ions. Thermodynamic analysis was used to determine the thermodynamic parameters of the lithium ion extraction reaction. The stripping of the lithium ions from the loaded organic phase was also investigated as well as the recyclability and re-usability of the organic phase.

## 2. Experimental

### 2.1. Materials and apparatus

The chemicals, tetrabutylammonium chloride (99% purity), tetraoctylammonium bromide (99% purity) and bis(2-ethylhexyl)-phosphoric acid (99% purity), were purchased from Aladdin Industrial Corporation (China) and used without further purification. Lithium chloride (>99%) used in this study were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). The extraction experiments were performed in a THZ-82A thermostatic water bath oscillator (Changzhou, China). TG16-WS high-speed centrifuge (Hunan, China) was employed for sufficient disengagement of the organic phase and aqueous phase. Thermo scientific iCAP 6500 series inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the concentrations of metal ions in aqueous phase, and the concentration in organic phase was obtained from by mass balance.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of ILs were recorded on an Inova-400 spectrometer (Agilent, USA) and  $\text{CDCl}_3$  was used as the solvent for recording the NMR spectra. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Thermo Nicolet Corporation 670 Spectrometer (USA). Distilled water was used to prepare the

aqueous solutions in all experiments. All other chemicals used in this study were of analytical grade.

### 2.2. Synthesis of ionic liquids

The FILs were prepared using a combination of ion-exchange and neutralizing reactions. The first step of the synthesis of  $[\text{N}_{4444}][\text{DEHP}]$  involved the ion exchange of chloride ions present in tetrabutylammonium chloride,  $[\text{N}_{4444}][\text{Cl}]$ , by hydroxide ion to form  $[\text{N}_{4444}][\text{OH}]$ . This was done by equilibrating a solution of  $[\text{N}_{4444}][\text{Cl}]$  (1 eq.) in dichloromethane with an aqueous  $2 \text{ mol L}^{-1}$  NaOH solution (1.5 eq.) for 5 h. The aqueous phase was removed, and the organic phase was equilibrated again with a fresh sodium hydroxide solution. This procedure was repeated several times until the chloride content in organic phase was negligible (checked with an acidified silver nitrate solution). The second step involved refluxing the  $[\text{N}_{4444}][\text{OH}]$  with bis(2-ethylhexyl)phosphoric acid (DEHPA) in 1:1 mol ratio for about 10 h. The lower aqueous phase was separated and the organic phase was washed with distilled water several times. The solvent and water were removed with a rotary evaporator, and the product was dried at  $50^\circ\text{C}$  under vacuum for 4 h to yield  $[\text{N}_{4444}][\text{DEHP}]$  as a viscous liquid.

The FIL,  $[\text{N}_{8888}][\text{DEHP}]$ , was synthesized by stirring a solution of  $[\text{N}_{8888}][\text{Br}]$  (1 eq.) in dichloromethane with an aqueous  $2 \text{ mol L}^{-1}$  NaOH solution (1.5 eq.) for 5 h. After phase disengagement, the organic phase was equilibrated again with a fresh sodium hydroxide solution. This procedure was repeated several times until the chloride content in organic phase was negligible (checked with an acidified silver nitrate solution). Then, the resulting  $[\text{N}_{4444}][\text{OH}]$  (1 eq.) was refluxed with DEHPA (1 eq.) in dichloromethane medium for 10 h. The lower aqueous phase was separated and the organic phase was washed with distilled water several times. The product was evaporated to remove the solvent and water using a rotary evaporator. Then, the product was dried at  $50^\circ\text{C}$  under vacuum for 4 h to yield  $[\text{N}_{8888}][\text{DEHP}]$  as a viscous liquid. Fig. 1 showed the structure of the synthesized ILs and their precursors. NMR spectral data of synthesized ILs are given below.

$[\text{N}_{4444}][\text{DEHP}]$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 0.78 (m, 12H, 4 $\text{CH}_3$ ), 0.91 (m, 12H, 4 $\text{CH}_3$ ), 1.18–1.37 (m, 32H, 16 $\text{CH}_2$ ), 1.56 (m, 2H, 2CH), 3.22 (m, 8H, 4N $\text{CH}_2$ ), 3.61 (m, 4H, 2O $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 10.41 (4 $\text{CH}_3$ ), 13.55 (2 $\text{CH}_3$ ), 14.10(2 $\text{CH}_3$ ), 19.08 (4 $\text{CH}_2$ ), 22.66 (2 $\text{CH}_2$ ), 23.36 (2 $\text{CH}_2$ ), 24.07(4 $\text{CH}_2$ ), 28.52 (2 $\text{CH}_3$ ), 29.61 (2 $\text{CH}_2$ ), 39.93 (2CH), 57.96(4N $\text{CH}_2$ ), 66.89 (2O $\text{CH}_2$ ).

$[\text{N}_{8888}][\text{DEHP}]$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 0.84 (m, 24H, 8 $\text{CH}_3$ ), 1.17–1.31 (m, 56H, 28 $\text{CH}_2$ ), 1.34 (m, 2H, 2CH), 1.60 (m, 8H, 4 $\text{CH}_2$ ), 3.25 (m, 8H, 4N $\text{CH}_2$ ), 3.60 (m, 4H, 2O $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 11.12 (2 $\text{CH}_3$ ), 14.06 (6 $\text{CH}_3$ ), 22.60–23.49 (8 $\text{CH}_2$ ), 28.51–29.74 (22 $\text{CH}_2$ ), 30.23 (2 $\text{CH}_2$ ), 41.15 (2CH), 54.58 (4N $\text{CH}_2$ ), 69.37 (2O $\text{CH}_2$ ).

### 2.3. Extraction experiments

All the extraction studies were carried out at 293 K, with the exception of the experiments at variable temperatures for determination of the thermodynamic parameters, where the temperature was varied over the range 293–333 K. The extraction of lithium ions was studied by equilibrating 5 mL methylbenzene containing the FILs with 2.5 mL of the aqueous phase at the desired acidity. Extractions were performed by intensive shaking of the extraction mixture for 30 min. Separation of the phases was assisted by centrifugation for 10 min at 5000 rpm. After phase disengagement, the aqueous phase was properly diluted and the concentration of lithium ions was measured using an ICP-AES. The concentration of metal ions in organic phase was calculated from mass balance. For stripping experiments, the loaded organic phase was scrubbed with the dilute hydrochloric acid solution a few times. In the next

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