



# Lithium isotope separation by crown ethers of different nitrogen-containing derivatives in the ionic liquid-anisole system

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## ABSTRACT

A green and efficient ionic liquid-anisole extraction system was employed for the separation of lithium isotopes by comparing 4 aminobenzo 15 crown 5 (4 NH<sub>2</sub> B15C5), 4 nitrobenzo 15 crown 5 (4 NO<sub>2</sub> B15C5) and benzo 15 crown 5 (B15C5) extraction agents. The results of the effects of crown ether substituents, crown ether concentration and lithium salt anion on solvent extraction indicated that the molar ratio of crown ether and lithium ion complex is 2:1 and the order of the extraction efficiency in three extraction agents was 4 NH<sub>2</sub> B15C5 > B15C5 > 4 NO<sub>2</sub> B15C5. Furthermore, the single-stage separation factor  $\alpha$  for <sup>6</sup>Li/<sup>7</sup>Li obtained in present work was 1.032 and maximum abundance of <sup>6</sup>Li in organic phase was reached 7.762% in the extraction system of LiI/4 NO<sub>2</sub> B15C5 ILs.

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## 1. Introduction

With the development of global nuclear fusion industry, lithium element with two nature stable isotopes, lithium-6 (<sup>6</sup>Li) and lithium-7 (<sup>7</sup>Li), has attracted more attention due to its critical role in the process of nuclear fusion [1]. From our knowledge, <sup>6</sup>Li can be used as a reaction material to accept neutron bombardment to produce tritium, while <sup>7</sup>Li can be used as a molten salt reactor coolant and pH controller of pressurized water reactor in nuclear fusion reactors [2]. However, it is very difficult to separate lithium isotopes due to their extra-nuclear structure with only a tiny mass difference between <sup>6</sup>Li and <sup>7</sup>Li. Lots of efficient approaches were proposed to separate lithium isotopes such as lithium amalgam [3], chromatography [4,5], membrane separation [6], electro migration [7], laser [8] and solvent extraction [9,10]. Although the mercury amalgam approach has been utilized in large scale to enrich lithium isotopes because of its large and compelling single-stage separation factor ( $\alpha_{\max} = 1.054 \pm 0.002$ ) [11], the heavy use of mercury is not only detrimental to the environment that allows us to live but also directly threatens human health. Therefore, it is necessary to seek a green and efficient extraction system for lithium isotopes separation instead of the mercury amalgam. And at present, there was without experimental results show that the differences of crown ethers containing different

electron-donating or electron-withdrawing substituents in the separation of lithium isotopes.

Ionic liquids (ILs), a burgeoning type of green organic solvent [12], have attracted increasing attention in various fields due to their unique characteristics such as negligible vapor pressures, high polarity, high thermal stability and adjustable functional groups [13]. They were used for metal ions separation as both the organic solvent and extracting agents, such as Li(I) [14], U(VI) [15], Pb(II) [16], Sr(II) [17] and Pd(II) [18]. However, our research group had pioneered works that the ionic liquids were used for separation lithium isotopes [19,20]. 1 Butyl 3 methylimidazolium bis(trifluoromethylsulfonyl) imide ([C<sub>4</sub>mim][NTf<sub>2</sub>]) was selected as a synergistic extractant for the lithium isotope separation. And the conventional solvent was added as a diluent, anisole, in organic phase. There were two main reasons which were considered as following: (1) The relatively high viscosity of pure [C<sub>4</sub>mim][NTf<sub>2</sub>] results in low rate of diffusion mass transfer and difficulty in separate-phase. (2) The crown ether was partially dissolved in pure [C<sub>4</sub>mim][NTf<sub>2</sub>].

In this work, some promising solution extraction systems were studied, which contained relatively low viscosity room-temperature ILs and several kinds of crown ethers of different nitrogen-containing derivatives as part of extraction solution. In this system the ionic liquid with shorter carbon chain alkyl imidazole was used as organic solvent instead of traditional organic solvents such as chloroform and dichloroethane. The single-stage separation factor and extraction efficiency of the extraction process were optimized by tuning operating parameters, such as concentration of crown ether, lithium salt anionic and

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substituents of crown ether. In addition, the reasonable extraction mechanism by crown ethers of different nitrogen-containing derivatives was also explained.

## 2. Experimental

### 2.1. Chemical materials

ILs, [C<sub>4</sub>mim][NTf<sub>2</sub>], was produced from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). 4 NH<sub>2</sub> B15C5 (≥97%), 4 NO<sub>2</sub> B15C5 (≥97%) and B15C5 (≥97%) were purchased from J&K Scientific Ltd. (Shanghai, China). Lithium chloride (A.R., ≥99%), lithium bromide (A.R., ≥99%) and Lithium iodide (Anhydrous, ≥99.9%) were purchased from Shanghai Aladdin biological technology co., Ltd. (Shanghai, China). Lithium carbonate (A.R., 100%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. (Shanghai, China). Nitric acid (G.R., 65.0%–68.0%) and perchloric acid (A.R., 70.0%–72.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

### 2.2. Apparatus

The extracting phase and aqueous phase were mixed in a fully automatic multifunction thermostatic water bath oscillator (THZ-82A, Changzhou, China), followed by separation in high-speed centrifuge (TG16-WS, Hunan, China). Microwave digestion equipment (SH420, Shandong, China) was used to recovery lithium ions by wet digestion the extracting phase. The concentration of lithium ions in aqueous phase was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Fisher Scientific ICAP 6500 series). A double focusing inductively coupled plasma mass spectrometry (ICP-MS, Neptune Plus, Thermo Fisher Scientific, Bremen, Germany) was used to determine lithium isotopic ratio by sample-standard bracketing method. 2% HNO<sub>3</sub> solution and Li<sub>2</sub>CO<sub>3</sub> were used as blank and lithium isotope standard substance for correcting machinery bias.

### 2.3. Lithium isotope separation

The organic phase was prepared by dissolving appropriate amounts of 4 NH<sub>2</sub> B15C5, 4 NO<sub>2</sub> B15C5 and B15C5 in 2 mL organic phase, which contained a defined volume ratio of ILs and anisole. While the aqueous phase was prepared by dissolving different lithium salts in double-distilled water. The organic phase and the aqueous phase were mixed at a volume ratio of 1:1. After shaking for 60 min, the obtained mixture

was centrifuging at 7000 rpm for 4 min on a high-speed centrifuge for sufficient disengagement of the organic phase and aqueous phase. The upper aqueous phase was separated and diluted into low concentration samples, the under organic phase was heated to remove by wet digestion methods and was made into solution with double-distilled water. Fig. 1 shows the structures of ionic liquid and three crown ethers in this work.

The extraction efficiency (*E*%) and the distribution ratio (*D*) were calculated according to the following equations:

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$D = \frac{C_{org}}{C_e} = \frac{C_0 - C_e}{C_e} \quad (2)$$

where *C*<sub>0</sub> and *C*<sub>*e*</sub> (mg/L) are the initial and equilibrated concentrations of lithium ion in the aqueous phase, respectively. *C*<sub>org</sub> is the concentration of extracted lithium ion in the organic phase.

The single-stage separation factor (*α*) of lithium isotope is defined by Eq. (3):

$$\alpha = \frac{([{}^6\text{Li}]/[{}^7\text{Li}])_{org}}{([{}^6\text{Li}]/[{}^7\text{Li}])_{aq}} \quad (3)$$

where [<sup>6</sup>Li]/[<sup>7</sup>Li] represents the isotopic abundance ratio. The subscripts of *org* and *aq* refer to the organic phase and aqueous phase, respectively.

## 3. Results and discussion

### 3.1. Effect of the composition of the organic phase solution

Fig. 2 shows the extraction efficiency of Li ions at different volume ratios of ionic liquid and anisole in organic phase. Apparently, the extraction efficiency of Li ions is dramatically improved with increasing the volume ratio of ionic liquid. When the volume ratio of ionic liquid and anisole reached to 3:7, the extraction efficiency no longer improved significantly. The increasing extraction efficiency may attribute to the more ionic liquid involved in, which accelerated the extraction and exchange of lithium ions. However, with the ionic liquid volume ratio continues increasing, the exchange efficiency of the extraction process tends to balance the mass transfer process, which may ascribed the excessive ionic liquid ions can only exchange a limited number of lithium ions in the interface of water phase and organic phase.

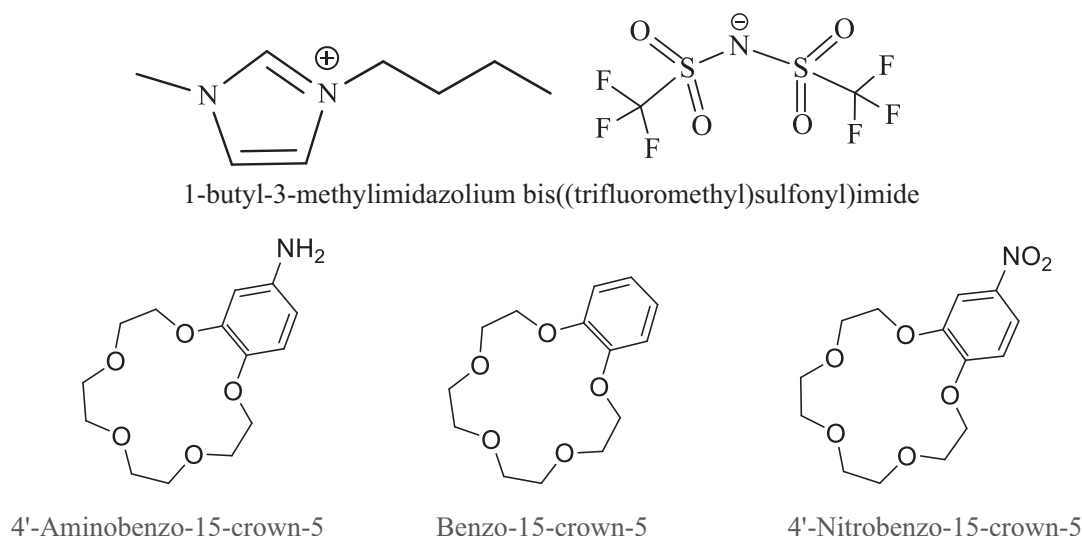


Fig. 1. The structures of ionic liquid and three crown ethers.

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