Journal of Molecular Liquids 215 (2016) 640–646

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Solvent extraction of lithium ions by tri-n-butyl phosphate using a room temperature ionic liquid

Chenglong Shi [a,b], Yan Jing [a], Yongzhong Jia [a,*]

[a] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 810008 Xining, China
[b] University of Chinese Academy of Sciences, 100049 Beijing, China

ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form 4 January 2016
Accepted 7 January 2016
Available online xxxx

Keywords:
Ionic liquid
Tri-n-butyl phosphate
Lithium
Extraction

ABSTRACT

Separation among lithium ion and magnesium ion remains challenging. In this work, solvent extraction of lithium ions from the Mg(II)-containing salt lake brine into a commonly used ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C_4mim][NTf_2]) using the neutral phosphorus compound tri-n-butyl phosphate (TBP) as the extractant was investigated. The extraction behavior of lithium ions was investigated as a function of various parameters: acidity of the salt lake brine, dosage of ionic liquid and phase ratio. Under the optimal conditions, the single extraction efficiency of lithium was 92.37%, which indicated that it was an efficient extraction system for the recovery of lithium ions. Based on the study of thermodynamics, thermodynamic parameters of the lithium ion extraction reaction were obtained. The extracted species were ascertained from slope analysis method which indicated 1:1 (metal:ligand) ratio in the complex. UV–visible and Fourier transform infrared spectroscopy (FTIR) studies were also carried out to understand the nature of the extracted species.

1. Introduction

Lithium, as the lightest metal element, is widely used in various fields such as lithium batteries, aerospace, ceramics, polymers, lithium-based lubricating greases and metal additives [1–5]. Its application and consumption is steadily growing in recent years. Lithium resources exist naturally in two forms: as a mineral and as a liquid. And the liquid state lithium mainly resides in salt lake brine. According to preliminary statistics, the worldwide reserves including lithium content in salt lakes are estimated to be 7.3×10^6 tons (as lithium) of which 60% in salt lakes [6]. However, lithium and magnesium are normally associated in the salt lake brine. And the magnesium presents a major challenge for lithium extraction because these two elements are located in diagonal positions within the periodic table, resulting in their many chemical similarities. The partition of Li^+ from Mg^{2+} has drawn considerable attention for a long time and lithium can be recovered from the salt lakes via a number of processes, including precipitation, ion exchange, adsorption, liquid–liquid extraction and supported liquid membrane [7–10]. Among them, liquid–liquid extraction has been widely studied as a hot technology for recovering lithium from the brine sources of a high Mg/Li ratio. Sometimes, traditional solvent extraction systems which used a large amount of volatile organic solvent can obtain a satisfied separation [11–13]. For example, the selective extraction of Li^+ with the phenylphosphonic (H-PHO), phenylphosphinic (H-PHI) and bis(2-ethylhexyl) phosphoric (H-BIS) acids dissolved in pentanol was investigated by El-Eswed et al. [14]. And the highest extraction efficiencies obtained in the case of H-PHO, H-PHI, and H-BIS were 43.2%, 45.7%, and 90.0%, respectively. The extraction of lithium from salt lake brine by tributyl phosphate–kerosene–$FeCl_3$ extraction system had been reported by Sun et al. [15]. The single-stage extraction has been conducted under the optimum conditions and the extraction efficiency reached 88%. However, almost all of traditional extraction systems used large amounts of volatile organic solvents, which may cause some of the environmental and workers' health problems. Furthermore, most of the systems were conducted under strong acidic condition and resulted in severe corrosion to the equipment. For sustainability of the liquid–liquid extraction, it is necessary to find “greener and safer” solvents to replace the traditional organic solvents.

Room temperature ionic liquids (RTILs) are a type of organic salts solely composed of ions and with the melting points near or below room temperature. They exhibit several properties that make them attractive as a potential solvent for ‘green’ separation processes, including high thermal stability, negligible volatility, nonflammability, tunable viscosity and good thermal and radiation stability for solvent extraction [16–18]. Based on the remarkable properties of ionic liquids, they have attracted considerable attention for metal extraction from aqueous solutions, since they can replace volatile organic solvents that have been widely used for this purpose [19–23]. For example, a solvent extraction system based on combination of ILs and 1-methylimidazole or 2-methylimidazole was investigated by Shen et al. [24]. Methylimidazole dissolved in ionic liquid ([$C_n$mim][NTf_2]) is able to extract lanthanides and yttrium. High selectivity for lanthanides compared to alkali metals and alkaline earth cations was demonstrated. The solvent extraction of

---

* Corresponding author.

http://dx.doi.org/10.1016/j.molliq.2016.01.025

U(VI) from aqueous solution through ionic liquids-based systems is also a hot topic. Yuan et al. [25] reported the extraction of U(VI) using trioctylphosphine oxide (TOPO) in ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The extraction efficiency of U(VI) in the TBP/IL system was comparable to that in the TBP/dichloromethane system. Raut et al. [26] demonstrated that 2-thenoyltrifluoroacetone (HTTA) in ionic liquids enhanced the extraction efficiency of U(VI) compared with that in a conventional organic solvent. In our previous studies, extraction of lithium ions using three different solvent systems containing TBP in ionic liquids such as $[C_n mim][PF_6]$ (where, n = 4, 6, 8) [27–30]. The trend of lithium ion extraction in the ionic liquids containing PF_6^- counter anion was: $[C_4mim][PF_6] > [C_6mim][PF_6] > [C_8mim][PF_6]$. The stripping test was performed using dilute hydrochloric acid. However, the HPF_6 that was formed during the stripping step can be lost to the aqueous phase due to the solubility of the acid HPF_6 in water. Ionic liquid $[C_4mim][NTf_2]$ has high hydrophobicity and the loss of ionic liquid will decrease during the extraction and stripping process.

In the present study, studies on lithium extraction from the Mg(II)-containing salt lake brine are carried out using TBP in imidazolium based ionic liquids $[C_4mim][NTf_2]$. The effects of several experimental parameters such as extractant concentration and phase ratio (O/A) on the extraction behavior of metal ions have been investigated and the results illustrated that $[C_4mim][NTf_2]$ was a promising solvent to replace traditional organic solvents (VOCs) in liquid/liquid extraction. The UV–visible and Fourier transform infrared spectroscopies have been performed to investigate the interactions between ligands and metal ions. Numerical treatments and graphical methods have been used to determine the stoichiometry of the complexes extracted, then the stoichiometry has been confirmed by slope analysis method and Fourier transform infrared spectra. The extraction equilibrium constants have also been calculated based on the solvent extraction data. The extraction mechanism was also studied and a cation exchange mechanism between $[C_4mim^+]$ and lithium ion was proposed.

2. Experimental

2.1. Materials and apparatus

Tributyl phosphate (98.5% purity) was purchased from Tianjin Yongda Chemical Reagents Development Center (China) and used without further purification. Room temperature ionic liquids, $[C_4mim]Cl$ (1-butyl-3-methylimidazolium chloride) and $[C_4mim][NTf_2]$ (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), were procured from Lanzhou Institute of Chemical Physics, CAS (Lanzhou, China) and used as received. Initial concentrations of Li^+ and Mg^{2+} in the salt lake brine were determined before extraction. And they were maintained at $2.02\ g \cdot L^{-1}$ and $92.34\ g \cdot L^{-1}$ for all the studies, respectively. Mg^{2+} concentration before extracted was determined by titration with standard EDTA using chrome black T as indicator. Li^+ concentration was determined by atomic absorption spectroscopy using a GBC (Melbourne, Australia) 908 atomic absorption spectrophotometer, and the concentration in organic phase was got by mass balance. UV–visible spectroscopic studies were carried out using a Shimadzu (Kyoto, Japan) UV-2600 single beam spectrophotometer using quartz cells and suitable reference solutions. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Thermo Nicolet Corporation 670 spectrometer. The slope analysis was used to determine the extraction equations. All other reagents were of analytical grade.

2.2. Liquid–liquid extraction

For the metal extractions, a required amount of $[C_4mim][NTf_2]$ was added into TBP to form the organic phase. The organic phase and the aqueous solution containing Li^+ or mixed metal ions (Mg^{2+}, Na^+ and K^+) were added to a separatory funnel and were shaken on a spectrophotometer at room temperature (303 ± 1 K) for 20 min to ensure equilibrium. Afterwards, the organic phase and the aqueous phase were separated. And the separated organic phase and aqueous phase were both clear and transparent. 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 metal concentrations in organic phase were calculated based on mass balances.

The extraction efficiency (E), the distribution ratio (D) and the separation factor (β) were calculated according to the following equations:

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

$$D = \frac{C_0 - C_e}{C_e} \times \frac{V_{aq}}{V_{org}} \tag{2}$$

$$\beta = \frac{D_{Li}}{D_{Mg}} \tag{3}$$

where C_0 and C_e ($mg \cdot L^{-1}$) are the initial and equilibrated concentrations of metal ion in the aqueous phase, respectively. V_{aq} and V_{org} (ml) represent the volume of the aqueous phase and organic phase, respectively.

3. Results and discussion

3.1. Effect of HCl concentration

The extraction behaviors of lithium ions by the $TBP/[C_4mim][NTf_2]$ system with various concentrations of hydrochloric acid in the aqueous phase were studied. The HCl concentration was varied over the range 0–1.0 $mol \cdot L^{-1}$. As shown in Fig. 1, the increasing HCl concentration showed a negative effect on the lithium ions' extraction performance. At 0.1 $mol \cdot L^{-1}$ HCl, the extraction efficiency of Li^+ was 76.06%, but the extraction efficiency gradually decreased to 34.62% at 1.0 $mg \cdot L^{-1}$ HCl. As a result, the distribution ratio (D) decreased from 3.18 to 0.53. The acidity dependence can be explained by the competition between the extraction of protons and the extraction of lithium ions. Extraction of hydrochloric acid by the TBP can lead to a decrease in the effective ligand concentration in the organic phase, thereby decreasing lithium ions' extraction. Since the pH of the brine is 5.58, the brine can be used for extracting directly without adding acid to the aqueous phase.

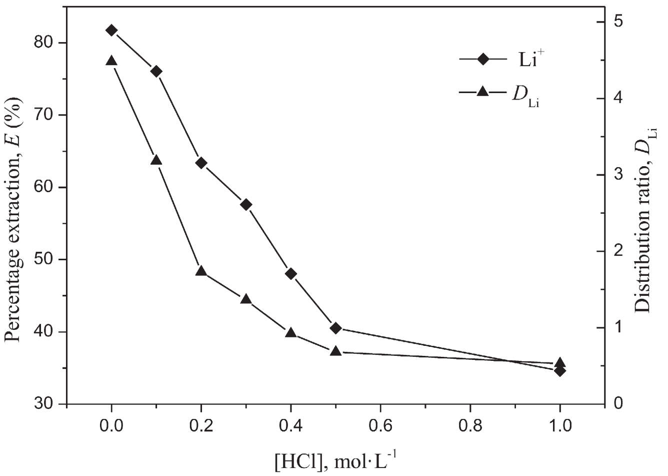

Fig. 1. Effect of HCl concentration on Li^+ extraction. Organic phase = 10% $[C_4mim][NTf_2]$; O/A = 1/1; T = 303 K; [HCl] = 0–1.0 $mol \cdot L^{-1}$.