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Solvent extraction of lithium from aqueous solution using a ammnoium ionic liquid

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Abstract

A new functionalized ionic liquid (FIL), tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate ([N₄₄₄₄][EHEHP]), was prepared and used in the extraction of lithium ion from aqueous solution. The factors affecting the extraction efficiencies, such as aqueous acidity, extractant concentration and temperature, were optimized. The mechanism involved in the extraction system was analyzed by slope analysis and FT-IR data. According to the Van't Hoff equation, the thermodynamic functions of the extraction reaction in ionic liquid system were obtained. Liquid/liquid extraction tests indicated that the ionic liquid system exhibited better selectivity towards lithium ions in the solution containing alkali metal ions. In addition, the quantitative stripping of lithium ions from the loaded ionic liquid phase was carried out and the effect of hydrochloric acid concentration on stripping rate was investigated in detail.

Keywords: Lithium, Solvent extraction, Ionic liquids.

1. Introduction

Ionic liquids (ILs) are organic salts molten at temperatures lower than 373 K [1]. Usually they are made up of a bulky, asymmetric organic cation, and an inorganic or organic anion. ILs are attracting increasing attention in various fields because they have some unique characteristics such as negligible vapor pressures, nonflammability, high polarity, high thermal stability and tunable properties [2-7]. Earlier studies on the extraction of metal ions with ILs made use of hydrophobic ILs containing imidazolium cations and fluorinated anions and the ILs was only used as a solvent for a molecular extractant [8-13]. These ionic liquids are usually involved in the extraction reaction by cation exchange. Although the extraction efficiency can be

increased, the ILs cations are lost to the aqueous solution. This not only contaminates the aqueous solution, but also decreases the stability of the organic phase. When the cationic or anionic part of the ILs tethered covalently with an organic functional moiety, they are known as functionalized ionic liquids (FILs). Due to the presence of coordinating groups, these FILs can be used as extractants for metal ions and not just diluents in extraction systems. FILs are enjoying a strong interest as novel extractants for solvent extraction of metal ions [14-17]. For example, Shen et al. [18] synthesized FIL trialkylmethylammonium di-(2-ethylhexyl)orthophosphinate a new ([A336][P507]) and studied the extraction behavior of mid-heavy rare earth metals (REs). The [A336][P507] showed high extractability towards mid-heavy REs from the simulated leach liquor. Dong et al. [19] reported the extraction of Y(III) using FIL [trihexyl(tetradecyl)-phosphonium] [sec-octylphenoxy acetate] ([P_{6,6,6,14}][SOPAA]). The extractability and selectivity of $[P_{6.6.6.14}]$ [SOPAA] for Y(III) are pronouncedly better than those of acidic extractant HSOPAA. The extraction mechanism and stripping of bifunctional [methyltrioctyl property ionic liquid ammonium][sec-octylphenoxy acetic acid] ([N₁₈₈₈][CA12]) for yttrium separation were investigated by Wang et al. [20]. Yttrium product with a purity of 99.1 mol.% was obtained via 13 stages of extraction section, 8 stages of scrubbing section and 5 stages of stripping section.

Lithium is currently a very important metal, largely as a result of its crucial role in energy production and storage, especially in the areas of Li ion battery technology and nuclear power [21-24]. Liquid-liquid extraction is an efficient and economical method for the separation of lithium ions from aqueous solutions. The extractants mainly includes alcohols, ketones, crown ethers, organophosphorus compounds and the like. Among them, the tributyl phosphate (TBP) is a popular neutral organophosphorus extractant with high selectivity to lithium ions. For example, the extraction of lithium by TBP-kerosene-FeCl₃ extraction system was reported by Sun et al. [25]. Under the optimal conditions, the single-stage extraction efficiency of lithium reached 88%. The extraction behavior of lithium ions using TBP in methyl isobutyl ketone (MIBK) with FeCl₃ was reported by Zhou et al. [26]. It was found that this extraction system can effectively extract lithium ions. In a follow-up study, the reaction mechanisms were proposed and the extracted species were ascertained based on the experimental data [27]. The formed complex was found to be LiFeCl₄·2MIBK. Though conventional extraction systems could obtain a satisfied separation, most of them must be used under strongly acidic conditions to avoid the hydrolysis of ferric ions in the aqueous phase. These systems often suffered from emulsification, equipment corrosion and other problems[28].

In view of this, the present study deals with the extraction behavior of lithium FIL, ions using novel namely tetrabutylammonium 2-ethylhexyl a hydrogen-2-ethylhexylphosphonate ($[N_{4444}][EHEHP]$). The ionic liquid is made up of a hydrophobic organic cation, and a long chain anion. There is a metal-coordinating group attached to the anion and the FIL could be used as a extractant. Ion association other than ion exchange may occur in this new extraction system. It was therefore envisaged that the loss of ILs to the aqueous phase would be reduced significantly, which was favorable for recycle utilization of the ionic liquid. The effects of various parameters such as aqueous acidity, concentration of ionic liquid and temperature on the extraction of lithium ions was studied. The extraction behavior of [N₄₄₄₄][EHEHP] is compared with that of the molecular extractant HEHEHP. The stripping of lithium ions from the loaded organic phase was also investigated.

2. Experimental

2.1. Reagents

The chemicals, tetrabutylammonium chloride ($[N_{4444}][Cl]$), barium chloride, cesium chloride, and silver nitrate, were procured from Sigma–Aldrich. The 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (HEHEHP) was procured from J&K Scientific Ltd. The lithium chloride, sodium hydroxide, sodium chloride and dichloromethane were procured from Aladdin Industrial Corporation. All reagents used in this study were of AR grade.

2.2. Instruments

NMR spectra were measured on an Inova-400 spectrometer (Agilent, USA) at 25°C. The metal contents of the aqueous phase were determined by inductively coupled plasma emission spectrometer (ICAP 6300, Thermo Fisher Scientific). The concentration of metal ions in the organic phase was obtained by mass balance. Fourier transform infrared spectroscopy (FTIR) measurements were performed with a Nexus 870 FTIR Spectrometer (Thermo Nicolet Corporation, USA).

2.3. Synthesis of FIL

Firstly, the tetrabutylammonium chloride was dissolved in dichloromethane. The

solution of $[N_{4444}][Cl]$ in dichloromethane and sodium hydroxide solution were thoroughly shaken and mixed. Ion exchange will occur between $[OH]^-$ and $[Cl]^-$ and $[N_{4444}][OH]$ was obtained. In order to verify the completeness of the ion exchange reaction, the acidified silver nitrate solution was used to test the $[Cl]^-$ in the aqueous phase after the reaction. Then, an acid-base neutralization reaction was carried out between 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (HEHEHP) and $[N_{4444}][OH]$. After rotary evaporation, stripping and drying, the $[N_{4444}][EHEHP]$ was finally obtained. It was observed that the resulting $[N_{4444}][EHEHP]$ was a pale yellow viscous liquid. Fig. 1 showed the structure of HEHEHP, $[N_{4444}][Cl]$ and $[N_{4444}][EHEHP]$. The $[N_{4444}][EHEHP]$ was characterized by NMR spectrometer, and the data of ¹H NMR and ¹³C NMR were given below.

 $[N_{4444}][EHEHP]$. ¹H NMR (300 MHz, CDCl₃): 0.95-1.03 (12H, 4CH₃), 1.14-1.18 (12H, 4CH₃), 1.24 (2H, PCH₂), 1.42-1.61(32H, 16CH₂), 1.793 (2H, 2CH), 3.419 (8H, 4NCH₂), 3.61 (2H, OCH₂); ¹³C NMR (CDCl₃, ppm): 10.41 (4CH₃), 11.72(1CH₃), 13.64 (1CH₃), 14.10(2CH₃), 19.58 (4CH₂), 23.14(PCH₂), 23.23 (1CH₂), 24.30 (1CH₂), 26.71(4CH₂), 28.81 (1CH₂), 29.11 (1CH₂), 30.15 (1CH₂), 31.30(1CH₂), 32.03(1CH₂), 33.95(1CH₂), 34.96(1CH), 41.42(1CH), 57.96(4NCH₂), 66.79 (OCH₂).



Fig. 1. Chemical structure of the [N₄₄₄₄][EHEHP], [N₄₄₄₄][Cl] and HEHEHP.

2.4. Extraction experiments

The FIL in this paper was viscous, hence, the organic phase was prepared by dissolving FIL in dichloroethane. The extraction experiments were performed by contacting 2.5 mL of aqueous phase and 5 mL of organic phase in separatory funnels. The concentration of Li^+ in aqueous phase is 0.5 g·L⁻¹. The two-phase system was fully shaken for 30 minutes with the help of a mechanical shaker. The aqueous phase

was removed and properly diluted. The metal contents of the aqueous phase were determined by ICAP. The lithium ions were back-extracted from loaded organic phase with dilute hydrochloric acid. The stripping efficiency was calculated by measuring the concentration of lithium ions in the stripping acid. The extraction efficiency (E) and distribution ratio (D) were defined as followed:

$$D = \frac{[\text{Li}]_{\text{org}}}{[\text{Li}]_{\text{aq}}} = \frac{C_{\text{o}} - C_{\text{e}}}{C_{\text{e}}} \times \frac{V_{\text{aq}}}{V_{\text{org}}}$$
(1)

$$E(\%) = \frac{C_{o} - C_{e}}{C_{o}} \times 100$$
(2)

where C_o and C_e represent initial and equilibrated concentrations of metal ions in 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 hydrochloric acid concentration



Fig. 2. Effect of aqueous acidity on extraction efficiency of lithium. Aqueous phase: $[Li^+] = 0.5$ g·L⁻¹ and [HCl] = 0.0.5 mol·L⁻¹; temperature = 293 K.

Fig. 2 illustrated the extraction behavior of FIL and HEHEHP for Li⁺ as a function of aqueous acidity. Notably, quantitative extraction of Li⁺ was achieved over the whole pH range. When the hydrochloric acid was not added to the aqueous phase, the percentage extraction of lithium at equilibrium amounted to 94.61% with FIL. Increasing HCl concentration was not conducive to the extraction of lithium, and the

extraction efficiency in 0.5 mol·L⁻¹ HCl decreased to 64.50%. Obviously, the presence of HCl in the aqueous phase inhibited the lithium trapping by [N₄₄₄₄][EHEHP]. The decrease in extraction efficiency could be attributed to the stronger coordination ability between H⁺ and the extractant than that between Li⁺ and the extractant. With the H⁺ concentration in the aqueous phase increased, the amount of extractant combined with H⁺ was also increased. This resulted in a reduced probability of coordination between the extractant and Li⁺, which decreased the extraction efficiency of Li⁺. For comparison purposes, the extraction behavior of the acidic extractant HEHEHP was also investigated. As can be seen from Fig. 2, the extraction efficiency of Li⁺ by acidic extractant was very low, usually less than 10%. This could be explained by the lack of inner synergism in HEHEHP. There existed an inner synergism between the anion and cation of FIL, resulting in a higher extraction efficiency for the metal ions[29,30].

3.2. Extraction mechanism

In solvent extraction, the slope analysis method was usually used to determine the mechanism of the extraction system. By plotting log*D* as a function of log[extractant], the slope of the line was obtained after fitting. And the slope indicated the number of molecules of the extractant in the complex formed in the organic phase. Since FIL contained functional groups that could coordinate with Li^+ , the extraction of Li^+ in this system may be realized by ion association rather than ion exchange. The extraction reaction equation, from available literature on analogous extraction systems [19], could be expressed by Eq. (3). The concentration of Li^+ in aqueous phase is 0.5 g \cdot L⁻¹ and the concentration of FIL in the organic phase was adjusted by using dichloroethane as a diluent. Fig. 3 showed the effect of the [N₄₄₄₄][EHEHP] concentration on the distribution coefficients of lithium ions at a phase ratio (O/A) of 2.

$$\operatorname{Li}_{(\mathrm{aq})}^{+} + n \left[N_{4444} \right] \left[\operatorname{EHEHP} \right]_{(\mathrm{org})} + \operatorname{Cl}_{(\mathrm{aq})}^{-} \rightarrow \operatorname{LiCl} \cdot n \left[N_{4444} \right] \left[\operatorname{EHEHP} \right]_{(\mathrm{org})}$$
(3)

The distribution ratio (D_{Li}) was equal to the ratio of the total concentration of lithium ions in organic phase to its total concentration in the aqueous phase. According to the Eq. (3), the D_{Li} and reaction equilibrium constant (*K*) can be calculated as:

$$\log D_{\text{Li}} = \log K + n \log[N_{4444} \cdot \text{EHEHP}]_{(\text{org})} + \log[\text{Cl}^-]_{(\text{aq})}$$
(4)

As can be seen from Fig. 3, the D_{Li} increased with increasing the concentration of FIL. A straight line with a slope of 1.16 was obtained by linear regression analysis of the extraction data. This showed that around one molecule of FIL was required to coordinated with one molecule of Li⁺ into the organic phase. This may be due to the large volume of the ionic liquid and steric hindrance, so that the complex formed by one molecule of FIL and Li⁺ was more stable. The plot of log D_{Li} versus log[Cl⁻] was also recorded (Fig.4). It was found that the plot of log D_{Li} versus log[Cl⁻] produced a straight line with a slope of 1.19, suggesting that only one chloride ion was included in the complex. In present system, therefore, a plausible mechanism of lithium extraction by the FIL dissolved in dichloroethane was considered to progress as Eq. (5).



Fig. 3. Plot of log D_{Li} as a function of log $[N_{4444} \cdot \text{EHEHP}]_{(\text{org})}$. Aqueous phase: $[\text{Li}^+] = 0.5 \text{ g} \cdot \text{L}^{-1}$; temperature = 293 K; organic phase: varying concentrations of $[N_{4444}]$ [EHEHP] in dichloroethane.



Fig. 4. Plot of log D_{Li} as a function of log [Cl⁻]. Aqueous phase: [Cl⁻] = 0.51 - 2.55 g·L⁻¹; organic phase: [N₄₄₄₄][EHEHP] in dichloroethane; temperature = 293 K; phase ratio O/A = 2.



Fig. 5. FTIR analysis of the organic phase.

The organic phases were characterized by an infrared spectrometer. Fig. 5 (a) and Fig. 5 (b) were the infrared spectra of the organic phase before and after extraction, respectively. The results showed that the characteristic peaks of most of the functional groups in FIL did not change after lithium extraction. For example, the peaks at 2960, 2874, 1463 and 1380 cm⁻¹ were considered to be the stretching vibration and

deformation vibration of -CH₃ groups in $[N_{4444}]^+$ cations. In the spectra of loaded organic phase (Fig. 5b), the typical peaks of -CH₃ groups still remained compared with the net organic phase (Fig. 5a). Furthermore, The [EHEHP]⁻ anions of FIL gave a symmetrical stretching vibration for the P-O-C bond at 1047 cm⁻¹, which was unchanged after extraction. Another important functional group of FIL was the P=O group. Its characteristic absorption peak occurred at 1186 cm⁻¹. After extraction, the corresponding peak was shift to 1164 cm⁻¹, indicating that P=O and Li⁺ interacted during the extraction process. The electron density of P=O groups decreased, causing the characteristic peak of P=O groups to move to a low wave number.

3.3. Determination of thermodynamic parameters

To investigate the effect of temperature on the extraction behavior of Li⁺, extraction studies were performed at various temperatures in the range of 293–333 K using [N₄₄₄₄][EHEHP] / dichloroethane. As can be seen from Fig. 6, the extraction efficiency of lithium ion decreased significantly with the increase of temperature. At 293 K, the single-stage extraction efficiency of lithium ion was 94.64%. When the temperature was raised to 333 K, the extraction efficiency of lithium ions decreased to 86.09%. At the same time, the distribution ratio of lithium ions decreased from 8.83 to 3.10. The reason why the extraction efficiency of lithium ions decreased may be that the high temperature increased motion of molecules, which made the stability of the complex formed between lithium ion and the extractant decrease. According to the Vant Hoff's equation, a relationship between the enthalpy change (ΔH°), the distribution ratio of lithium ions, and the temperature can be obtained, and the equation is shown in Eq. (6). It can be seen that there is a linear relationship between $\log D$ and the extraction temperature. When $\log D$ is plotted against 1000/T, the slope of the line is $-\Delta H^{\circ}/2.303R$. The variation of log D as a function of reciprocal temperature was shown in Fig. 7. It can be seen from Fig. 7 that there is a good linear relationship between the distribution ratio and the reciprocal temperature. The slope of the fitted curve was 1.11, and the enthalpy of the extraction reaction was calculated to be $-21.25 \text{ kJ} \cdot \text{mol}^{-1}$. The change in enthalpy of extraction was negative, which indicated that the extraction of lithium ions was exothermic. An increase in temperature at constant pressure will shift the equilibrium (Eq. 5) to the left, so the extraction efficiency of lithium ions decreased.

$\partial \log D$	$-\Delta H^{o}$	
$\partial(1/T)$	2.303 <i>R</i>	

The relationship between the Gibbs energy change(ΔG°), the entropy (ΔS°), and the temperature can be expressed as follows:

$$\Delta G^{\circ} = -2.303 RT \log K \tag{7}$$

$$\Delta S^{\rm o} = \frac{\Delta H^{\rm o} - \Delta G^{\rm o}}{T} \tag{8}$$

The value of log *K* can be obtained from the intercept of the line in Fig. 3. According to Eq. (7), the Gibbs free energy of the extraction system was calculated to be $-5.89 \text{ kJ} \cdot \text{mol}^{-1}$. The value of Gibbs free energy was negative, indicating that the extraction reaction of lithium ion was spontaneous. By substituting the values of the enthalpy change and the Gibbs free energy into Eq. (8), the entropy change of the extraction reaction can be calculated at a fixed temperature. At 293 K, the entropy change of the extraction reaction reaction was $-52.42 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which indicated that the extraction was ordered in nature. The possible reason was that the butyl chains in ionic liquid became more crowded and the degrees of freedom were decreased when the extractant was complexed with lithium ions[31].



Fig. 6. Effect of temperature on extraction efficiency of lithium. Aqueous phase: $[Li^+] = 0.5 \text{ g} \cdot L^{-1}$; organic phase: $[N_{4444}]$ [EHEHP] in dichloroethane; temperature = 293–333 K.



Fig. 7. Plot of log *D* versus 1000/T for Li^+ extraction. Aqueous phase: $[\text{Li}^+] = 0.5 \text{ g} \cdot \text{L}^{-1}$; organic phase: $[N_{4444}][\text{EHEHP}]$ in dichloroethane; temperature = 293–333 K.

3.4. Extraction of lithium ions from multi-metal-ion solutions



Fig. 8. Extraction efficiencies of several alkali metal ions with $[N_{4444}][EHEHP]$ in dichloroethane. Aqueous phase: $[Li^+] = [Na^+] = [K^+] = [Rb^+] = [Cs^+] = 0.5 \text{ g} \cdot L^{-1}$; organic phase: $[N_{4444}][EHEHP]$ in dichloroethane; phase ratio O/A=1/1; temperature = 293 K.

A competitive extraction of alkali metal ions by FIL in dichloroethane was carried out to assess the selectivity of the present system. The distribution ratios are plotted in Fig. 8. The lithium ions are effectively extracted under the extraction conditions. However, the ionic liquid system had very low distribution coefficients for

the other alkali metal ions. The possible reason for this selectivity could be that the cation [Li⁺] has higher surface charge density than other alkali metals (Na⁺, K⁺, Rb⁺ and Cs⁺) due to its smaller ionic radius. So the higher stability of the complexes formed from [N₄₄₄₄][EHEHP] with lithium ions. The results clearly showed that the ionic liquid system was found to be highly selective for the extraction of lithium in the solution containing alkali metal ions.

3.5. Stripping experiments

In traditional neutral phosphonium extraction systems, the back extraction of lithium ions from the loaded organic phase was usually carried out concentrated hydrochloric acid, which may cause serious equipment corrosion. For example, Zhang reported the extraction behavior of lithium ions with et al. [32] HBTA-TOPO-kerosene system. The lithium ions was stripped from the loaded organic phase by 3.0 mol $\cdot L^{-1}$ HCl solution. Shi et al. [33] studied the lithium ions extraction process using TBP - kerosene - FeCl₃ system. The 6.0 mol \cdot L⁻¹ HCl solution was chosen as the stripping agent, and the stripping efficiency of lithium ions was close to 100% at a phase ratio of 10/1 through a four – stage stripping process. In the present study, the effect of hydrochloric acid concentrations were experimentally studied in the range of 0.0 to 2.0 mol L^{-1} and the results were presented in Fig. 9. As shown in Fig. 9, the stripping efficiency of lithium ions initially increased with an increase in hydrochloric acid concentration. About 99.37% of the loaded lithium ions could be recovered using hydrochloric acid concentration above 0.5 mol \cdot L⁻¹ in a single contact. And further increase in hydrochloric acid concentration may result in no significant variation in the stripping efficiency. From the results obtained, the 0.5 $mol \cdot L^{-1}$ hydrochloric acid was a suitable choice for recovering lithium ion from the organic phase. In the ionic liquid extraction system, the lower concentration of hydrochloric acid was used as the stripping agent, which was beneficial to reduce the corrosion of the equipment.



Fig. 9. Stripping effect of different concentrations of hydrochloric acid on lithium ions in organic phase. Temperature = 293 K; $[HCl] = 0-2.0 \text{ mol } L^{-1}$; phase volume ratio = 1.

4. Conclusions

A new FIL, $[N_{4444}][EHEHP]$, was prepared and studied for the extraction of lithium ions from aqueous solution. The ionic liquid $[N_{4444}][EHEHP]$ shown stronger extractabilities in comparison to its acidic extractant HEHEHP. The mechanism involved in the extraction system was analyzed by slope analysis and FT-IR data, which indicated the interaction of one molecule of ionic liquid with each lithium ion through phosphate groups. The effect of temperature on the extraction of lithium ions was studied and it was found to be exothermic, spontaneous and ordered in nature. During the extraction of lithium ions from a mixed solution containing several alkali metal ions, the ionic liquid system exhibited better selectivity towards lithium ions. Quantitative stripping of lithium ions from the loaded ionic liquid phase was achieved with 0.5 mol·L⁻¹ hydrochloric acid. The present study highlighted the potential of FIL as an extractant for the extraction of valuable metal ions.

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CRediT author statement

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Declaration of interests

 \square The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Solution of the second second

Highlights:

- 1. A new functionalized ionic liquid was successfully synthesized and used for lithium extraction.
- 2. Nature of extracted species was found out to be 1:1.
- 3. The ionic liquid system exhibited better selectivity towards lithium ions in the solution containing alkali metal ions.