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The synergistic extraction by combined ammonium and phosphonium type ionic liquids for rare earth elements separation

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ABSTRACT

A novel synergistic system of combined ammonium and phosphonium type ionic liquids is reported for the first time, which displays pronounced synergistic effect in the extraction of Lu(III). The synergistic enhancement coefficients from different mole fractions of [P₆₆₆₁₄][EHEHP] and [N₁₈₈₈][BTMPP] were calculated. Extraction mechanism of the combined functionalized ionic liquids for Lu(III) was shown to be ion association. Thermodynamic functions of the synergistic extraction system were obtained. The loaded Lu(III) in the synergistic system could be fully stripped using hydrochloric acid. The novel synergistic extraction provides the possibility of separating heavy lanthanides, which reveals theoretical and practical importance in REEs separation.

1. Introduction

Rare earth elements (REEs) are critical materials in many products of cutting-edge technology, such as catalysts, alloys, magnets, lasers, batteries, electronics, lightings, and communications (Eliseeva and Bünzli, 2011). The separation of REEs is difficult due to their similar chemical properties (Kumar et al., 2010). Because of the high importance of REEs, some separation technologies have been developed for REEs, such as solvent extraction, adsorption, membrane, and nanotechnology. Among the technologies, solvent extraction is one of the most often used industrial separation technology for REEs, because of its high processing capacity, fast reaction rate, and good separation (Nasab et al., 2011; Quinn et al., 2015; Wang et al., 2011a, b). Many investigations on solvent extraction for REEs separation have been reported in the past decades. The extraction behaviors of lanthanides and Y(III) using Cyanex 925 (mixture of branched chain alkylated phosphine oxides) in n-heptane from nitrate medium were studied (Li et al., 2007). The extraction and recovery of Ce, F, and Th from a bastnaesite sulfuric leaching solution by 2-ethylhexylphosphonic mono-2-ethylhexyl ester were reported (Wang et al., 2013).

Ionic liquids (ILs) are salts, generally liquid below 100 °C. Their potentials as extractants are enhanced by the fact that their physical and chemical properties such as low volatility and combustibility, wide liquidus range, thermal stability, functional groups, high conductivity, and wide electrochemical window (Sun et al., 2012). Up until now,

many IL-based extractions for REEs separation have been reported with interesting results listed in Table 1 (Dietz and Dzielawa, 2001; Dong et al., 2015; Tunsu et al., 2015; Sun et al., 2007, 2011; Rout and Binnemans, 2014, 2015). The ionic liquid technologies for separation and extraction of REEs allow optimization and improvement in developing new hydrometallurgical processes (Onghena et al., 2014). It has been reported that the Chinese REE industry produces over 20 million tons of wastewater annually, with ammonia nitrogen levels ranging from 300 to 5000 mg/L (Liu et al., 2012). Saponification wastewater may be avoided by using acid-base coupling bifunctional ionic liquid extractant (ABC-BIL), which is of great value to an environment-friendly extraction process (Sun and Waters, 2014a).

Mixtures of two extractants are used because this imparts enhanced separating properties compared to either extractant on their own, the phenomenon is known as synergistic extraction. Many synergistic extraction systems on REEs separation have been studied (Ellis et al., 2013; Reddy et al., 1999; Sun et al., 2005), and very recently, the adjustable synergistic effects between ABC-BIL extractants for REEs separation were reported (Sun and Waters, 2014b). Some synergistic extraction systems for REEs are presented in Table 2. In view of extending the understanding of synergistic extraction by IL extractant, a novel form of synergistic extraction by an ammonium type ABC-BIL ([N₁₈₈₈][BTMPP]) and a phosphonium type ABC-BIL ([P₆₆₆₁₄][EHEHP]) was tested. The synergistic extraction reveals potential in both of academic research and industrial application for the separation of REEs.

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2. Experimental

2.1. Reagents and apparatus

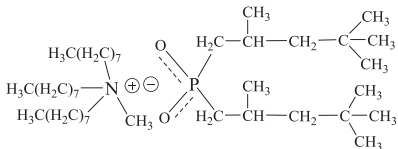
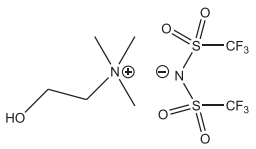
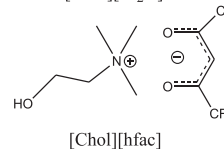
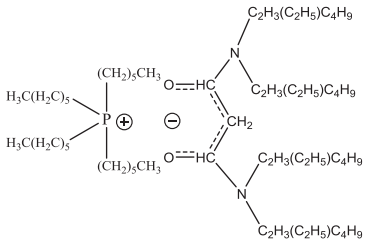
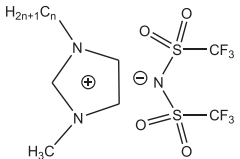
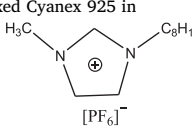
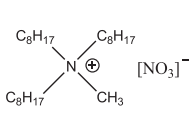
Trihexyl(tetradecyl)phosphonium chloride (CyphosIL101, [P₆₆₆₁₄]Cl) and bis(2,4,4-trimethylpentyl)phosphonic acid (Cyanex272, HBTMPP) were obtained from Cytec Industries Inc. The anion-exchange resin (Dowex Monosphere 550A (OH)) was purchased from Dow Chemical Company. 2-ethylhexylphosphonic acid and mono-(2-ethylhexyl) ester (P507, HEH[EHP]) were purified by washing with 2% Na₂CO₃, 0.2 mol L⁻¹ H₂SO₄ and deionized water. The REE oxides were purchased from Fujian Changting Golden Dragon Rare-Earth Co., Ltd. (China). Stock solutions of REEs were prepared by dissolving their oxides (> 99.99%) in concentrated hydrochloric acid and diluted with distilled water. All chemicals were used as received without further purification. Trihexyl(tetradecyl) phosphonium mono-(2-ethylhexyl) 2-ethylhexyl phosphonate ([P₆₆₆₁₄][EHEHP]) and trioctylmethylammonium bis

(2,4,4-trimethylpentyl) phosphonate ([N₁₈₈₈][BTMPP]) were prepared using the combination of ion-exchange and neutralizing reactions (Sun and Waters, 2014a). The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the ILs were obtained in CDCl₃ with an AV III-500 BRUKER spectrometer. The detailed synthetic procedures of [P₆₆₆₁₄][EHEHP] and [N₁₈₈₈][BTMPP] are given as follows.

(a) [P₆₆₆₁₄][EHEHP]

A solution of [P₆₆₆₁₄]OH in 60 mL methanol was prepared from 5.1931 g (0.01 mol) [P₆₆₆₁₄]Cl using a Dowex Monosphere 550A (OH) anion exchange resin. A 3.0642 g portion of HEH[EHP] (0.01 mol) was added to the [P₆₆₆₁₄]OH solution. The mixed solution was stirred at 40 °C for 6 h until the solution became neutral. The methanol and water were distilled off with a RE-52AA rotary evaporator at 70 °C for 2 h. Finally, the product was dried at 70 °C under vacuum for 12 h to yield [P₆₆₆₁₄][EHEHP] as a viscous liquid (7.25 g, yield: 91.9%). The ¹H and

Table 1
Ionic Liquid based extraction for REE separation.

Ionic liquids (ILs)	Important aspect	Ref.
 <p>[N₁₈₈₈][BTMPP]</p>	<ul style="list-style-type: none"> The extractabilities of [N₁₈₈₈][EHEHP] were stronger than those of HEH[EHP] for all the heavy REEs. 	Dong et al., 2015
 <p>[Chol][Tf₂N]</p>	<ul style="list-style-type: none"> [Chol][Tf₂N] was a suitable diluent for the homogeneous liquid-liquid extraction of Nd(III) from aqueous solution with [Chol][hfac] as extractant 	Tunsu et al., 2015
 <p>[Chol][hfac]</p>		
 <p>[P₆₆₆₁₄][MA]</p>	<ul style="list-style-type: none"> REE extraction from nitrate medium was far superior to that from chloride medium. The salting-out agent had a dramatic effect on the distribution ratio and loading capacity. 	Rout and Binnemans, 2014
<p>Mixed dicyclohexano-18crown-6 (DCH18C6) in</p>  <p>[C_nmim][Tf₂N] (n=2, 4, 5, 6)</p>	<ul style="list-style-type: none"> ILs enhanced extraction efficiency and reduced volatility vs. conventional organic solvents. ILs had significant implications for the 'greenness' in the area of liquid-liquid extraction. 	Dietz and Dzielawa, 2001;
<p>Mixed Cyanex 925 in</p>  <p>[C₈mim][Tf₂N]</p>  <p>[N₁₈₈₈][NO₃]</p>	<ul style="list-style-type: none"> Extraction mechanism of Sc(III) was indicated to be cation exchange. The extraction system was efficient and sustainable in the extraction-stripping-regeneration-recycling process. 	Sun et al., 2007 Sun et al., 2011

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