

Selective extraction and separation of Ce(IV) from thorium and trivalent rare earths in sulfate medium by an α -aminophosphonate extractant



Shengting Kuang^{a,b}, Zhifeng Zhang^a, Yanling Li^a, Guolong Wu^a, Haiqin Wei^a, Wuping Liao^{a,*}

^a State Key Laboratory of Rare Earth Resource Utilization, ERC for the Separation and Purification of REs and Thorium, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

^b University of Science and Technology of China, Hefei, 230026, China

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ABSTRACT

A novel extractant, di (2-ethylhexyl) (2-((2-ethylhexyl) amino) propan-2-yl) phosphonate (DEHAPP, abbreviated as **B**), was synthesized for the selective extraction of Ce(IV) in sulfate medium. The effect of contact time, the H_2SO_4 concentration, the DEHAPP concentration and temperature on the Ce(IV) extraction were studied systematically. DEHAPP exhibits a good extraction ability towards Ce(IV) when compared with other neutral organophosphorus extractants such as Cyanex 923, Cyanex 925 and DEHEHP. The extraction equilibrium constants and thermodynamic parameters (ΔG , ΔH and ΔS) were calculated. The extraction reaction of Ce(IV) is an endothermic process. The extracted complexes were determined to be $H_2SO_4 \cdot B_{(org)}$ and $Ce(HSO_4)_2SO_4 \cdot 2B_{(org)}$. A extraction process to selectively recover Ce(IV) from bastnaesite leaching was proposed, by which the purity of cerium product reached 99.5% with a yield of 90.7%.

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1. Introduction

Given their particular physicochemical properties, the cerium compounds have been widely used as polishing powders, fluorescent powders, magnets, catalysts and ceramic colorant (Sabot et al., 1996). Bastnaesite ($CeFCO_3$) is one of main resources of cerium in the world. For Panxi bastnaesite in China, the percentage of cerium oxide is about 50% by weight of the total rare earth oxides (Xu, 1995). The dominating methods of the enrichment and recovery of cerium from the acid leaching of bastnaesite include fractional crystallization, precipitation and ion exchange (Harris and Tompkins, 1947; Li, 1988; Ludek et al., 2006; Mayer and Tompkins, 1947; Spedding et al., 1947). However, these methods have some shortcomings such as low separation efficiency, high consumption of reagents, higher cost, troublesome operation and long separation period, which hinder their large-scale application (Shu and Yang, 2012).

Solvent extraction has been one of the most effective techniques for the metal separation and purification. Of course, solvent extraction was also applied for the selective recovery of cerium from the mineral acid leaching of the minerals (Abreu and Morais, 2010; Liao et al., 2001b; Wang and Chen, 2001; Wang et al., 2013a; Xu, 1995; Xu and Yuan, 1987). Many extractants such as organophosphorus acids (Preston et al., 1996; Wang et al., 2013a; Zhang et al., 2010; Zhang et al., 2008), neutral organophosphorus esters (Liao et al., 2001a; Liao et al., 2001b; Lu et

al., 1998; Zhang et al., 2007; Zhao et al., 2004a; Zhao et al., 2004b) and primary amine (Li et al., 1984), have been studied. Among these extractants, neutral organophosphorus esters have attracted much attention (Siddal, 1963; Soldenhoff, 1996). Warf (1949) studied the extraction of Ce(IV) by TBP from nitrate medium and determined the extraction complex being $Ce(NO_3)_4(TBP)_2$. Lu et al. (1998) investigated the Ce(IV) extraction from sulfate medium by Cyanex 923 and deduced the extraction complex being $Ce(HSO_4)_2(SO_4) \cdot 2(Cyanex\ 923)$. Liao et al. (2001a, 2001b) revealed that the extraction of Ce(IV) and F from sulfate solutions can be related to the formation of $Ce(HF)(HSO_4)_2(SO_4) \cdot 2(Cyanex\ 923)$. Zhao et al. (2004a) deduced the formation of the species of $Ce(NO_3)_4 \cdot 2(DEHEHP)$ in the Ce(IV) extraction from nitrate medium by DEHEHP. Sahu and Mishra (2015) studied the Ce(III) extraction from acidic nitrate medium by Cyanex923. However, the commercially available organophosphorus esters have some problems for the cerium extraction. For instance, the extractability of TBP and DEHEHP towards Ce(IV) is too low in sulfate medium. Cyanex923 is not widely used for the Ce(IV) separation due to its high price. Cyanex925 has strong reducibility towards Ce(IV) (Soldenhoff, 1996).

As a kind of interesting extractants, α -aminophosphonates have been used for the extraction of alkali metals, alkaline-earth metals, rare metals and noble metals (Davletshina et al., 2013; Garifzyanov et al., 2004; Koshimoto et al., 2011). However, there were few reports on the extraction and separation of rare earths (III) and Ce(IV) by α -aminophosphonates (Cherkasov et al., 2012; Cherkasov et al., 2009;

* Corresponding author.

E-mail address: wpliao@ciac.ac.cn (W. Liao).

Jagodić and Herak, 1970; Jagodić et al., 1971). In this study, a dialkylaminophosphonate extractant was synthesized for the selective extraction and separation of Ce(IV) from sulfate medium. Its extraction ability towards Ce(IV) would be different from other neutral organophosphorus extractants due to an additional amino moiety which would bind Ce(IV) along with the phosphoryl oxygen atom to form a more stable five-membered ring species (Cherkasov et al., 2009). The Ce(IV) extraction by the as-synthesized extractant was compared with those by Cyanex 923, Cyanex 925 and DEHEHP. The extraction mechanism of Ce(IV) and sulfuric acid were studied and the extraction equilibrium constants and thermodynamic parameters were calculated.

2. Experimental

2.1. Reagents and materials

Bis(2-ethylhexyl)phosphite (Shanghai Rare-earth Chemical Co., Ltd.), 2-ethylhexylamine (Shanghai Aladdin Industrial Co.) and acetone (Beijing Chemical Co., Ltd) were used as raw materials for the synthesis of DEHAPP without further purification. Cyanex 923 and Cyanex 925 were kindly supplied by CYTEC Canada Inc. and DEHEHP was kindly provided by Shanghai Rare-earth Chemical Co. Ltd. of China (their structures shown in Table 1). All extractants were purified by washing with 2% Na₂CO₃, 1.0 mol/L H₂SO₄ and distilled water in turn. n-Heptane of analytical grade was used as the diluent. All the other reagents and solvents were of analytical reagent grade.

Stock solutions of RE(III) and Ce(IV) were prepared by dissolving high-purity rare earth oxides in concentrated sulfuric acid and diluting to the required volume with distilled water. Stock solutions of Th(IV) were prepared by transforming Th(NO₃)₄·4H₂O of analytical grade into its hydroxide precipitate and then dissolving in sulfuric acid. The concentrations of RE(III) ions and Th(IV) were determined by titration with a standard solution of EDTA at pH 5.5 using xylenol orange as an indicator. The Ce(IV) solution was standardized by titration with a standard solution of (NH₄)₂Fe(SO₄)₂ using o-phenanthroline as an indicator.

The sulfuric acid concentration was determined by titration with standard NaOH solution using phenolphthalein as an indicator. All aqueous solutions were prepared with deionized water.

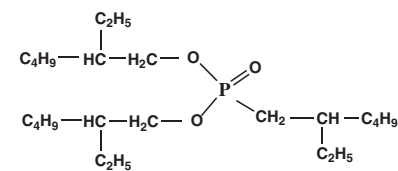
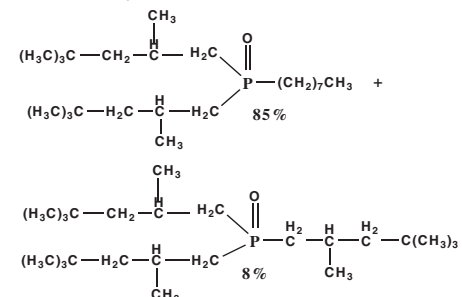
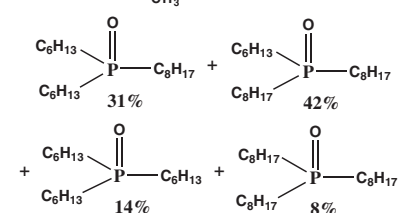
2.2. Apparatus

Nuclear magnetic resonance spectra were recorded on a Bruker AV600M for ¹H NMR (600 MHz). Infrared spectrum was measured by a Vector22/N spectrometer (Bruker Co., Fllanden, Switzerland). Mass spectra were obtained by a Bruker Daltonics Flex mass spectrum analyzer. Mixed solution was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optimal 8000).

2.3. Synthesis of di (2-ethylhexyl) (2-((2-ethylhexyl) amino) propan-2-yl) phosphonate (DEHAPP, B) (schemed in Fig. 1)

The general process was as follows: A mixture of 15.3 g (50 mmol) bis (2-ethylhexyl)phosphite, 7.1 g (55 mmol) 2-ethylhexylamine, 3.2 g (55 mmol) acetone, 40 mL anhydrous toluene and 100 mg *p*-toluenesulfonic acid were placed in a single-neck round-bottom flask (250 mL) equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser and heated with stirring for 10 h in an oil bath at 80 °C. The course of reaction was monitored by the method of TLC. At the end of the reaction 500 mg of K₂CO₃ was added into the solution, and the mixture was refluxed for 15 min for the removal of catalyst. The mixture was then cooled, washed with water (3 × 50 mL), and dried over anhydrous MgSO₄. The filtrate was evaporated in a vacuum on the rotary evaporator to remove the excess reagents and solvent until no fraction was steamed out. The obtained product was oily compound with a yield of 90% (21.40 g). ¹H NMR (600 MHz, CDCl₃) δ 3.98 (m, 4H, CH₂), 2.59 (d, 2H, CH₂), 2.01 (s, 1H, NH), 1.54 (m, 3H, CH), 1.45–1.27 (m, 24H, CH₂), 0.90–0.84 (m, 24H, CH₃); IR (KBr): ν/cm⁻¹: 1239 (P = O), 1010, 1043 (P–O–C), 3460, 1650 (N–H); MS–ESI *m/z*: [M + 1]⁺ 476.7, [M + 23]⁺ 498.7.

Table 1
Structures of neutral organophosphorus extractants.

Name	Full name	Structures of main components
DEHEHP	Di-(2-ethylhexyl) 2-ethylhexyl phosphonate	
Cyanex925	Trialkylphosphine oxides	
Cyanex923	Trialkylphosphine oxides	

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