



# The development of sustainable yttrium separation process from rare earth enrichments using bifunctional ionic liquid



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## ABSTRACT

Organic phases consisting of acidic extractants, such as naphthenic acid (HA) and sec-octylphenoxy acetic acid (CA12), need to be saponified by ammonia or sodium hydroxide during each cycle in the conventional process for the separation of yttrium. The resulting acid and base consumption as well as wastewater salinity were serious in industry. In this paper, the extraction mechanism and stripping property of bifunctional ionic liquid [methyltrioctyl ammonium][CA12] ([N1888][CA12]) for yttrium separation were investigated. The extraction mechanism of rare earth elements (REEs) could be deduced as neutral mechanism combined with ion association via slope analysis and mass balance methods. The extraction order of heavy rare earth elements (HREEs) in [N1888][CA12] system followed a positive sequence, which is in contrast to that in the CA12 system. The quantitative stripping of yttrium and other HREEs from loaded organic phase was achieved with water rather than hydrochloric acid. Furthermore, a novel sustainable process for the separation of yttrium from rare earth enrichments using [N1888][CA12] as extractant was developed. Yttrium-enriched rare earth solution containing 0.16 mol/L yttrium and 0.20 mol/L total REEs was adopted as practical feed. 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 by using separating funnel array. The organic phase consisting of [N1888][CA12] was stable after regeneration. Neither acid nor base was consumed during the extraction, scrubbing and stripping steps.

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## 1. Introduction

As one of the most common heavy rare earth elements (HREEs), yttrium is widely used in rare earth aluminum alloy, rare earth ceramics, laser crystal and other rare earth functional materials. China is abundant in ion-absorbed rare earth deposits, specifically the concentrated yttrium and middle yttrium-concentrated europium ores [1–3]. The main extractant for high-purity yttrium separation from enriched yttrium feed is saponified naphthenic acid (HA), which has the advantages of low cost and high efficiency [4]. Yttrium with purity of 99.999% was produced via separation process based on HA with 90 stages of extraction section, 20 stages of scrubbing section and 10 stages of stripping section by using the mixer-settler extraction columns [5]. Also, yttrium with a purity of 99.99% was obtained through a two-step process; these extraction steps include HA (45 extraction, 10 scrubbing and 9 stripping) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP, P507 or PC88A) (5 extraction, 7 scrubbing and 8 stripping) steps

using annular centrifugal contactors in the pilot plant test at the Institute of Nuclear and New Energy Technology, Tsinghua University [6]. As a by-product of petroleum industry, the production of HA decreases sharply with the implementation of the fifth stage of vehicle emission standards in China, the decrease results in serious shortage of HA for yttrium separation of rare earth enterprises [7]. Two novel extractants for yttrium separation, namely, (2-ethylhexyl) oxymethyl bis(2-ethylhexyl) phosphonate (PT-28) and sec-octylphenoxy acetic acid (CA12), have been developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. In a PT-28 system, the separation factors ( $\beta$ ) between yttrium and other HREEs are 2.53, 2.98, 3.93, 2.71, 2.18, 2.87, 5.18 and 3.55 for  $\beta_{Cd/Y}$ ,  $\beta_{Tb/Y}$ ,  $\beta_{Dy/Y}$ ,  $\beta_{Ho/Y}$ ,  $\beta_{Er/Y}$ ,  $\beta_{Tm/Y}$ ,  $\beta_{Yb/Y}$  and  $\beta_{Lu/Y}$ , respectively [8]. Considering the easy synthesis and high performance of CA12, new attempts of mixed system based on CA12, including CA12–HEHEHP [9], CA12–Cyanex 272 [10,11] and CA12–TBP [12] have been released, and the corresponding yttrium products were obtained with purity of 99.95%, 99.94% and 99.5%. However, conventional acidic extractants, such as HA, Cyanex 272 and HEHEHP, should be saponified previously by ammonia or sodium hydroxide.

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Room-temperature ionic liquids (ILs), which are non-flammable and non-volatile as well as good thermal and radiation stability, can be used as alternative diluents or extractants of volatile organic compounds in the extraction process [13]. Many advances in ILs for separations of REEs via solvent extraction have been recently reported [14–22]. A solvent extraction system based on methylimidazole in ILs of [Cnmim][NTf<sub>2</sub>] (*n* = 2, 4 or 8) were investigated, and extraction order of the REEs follows the positive sequence: La < Nd < Eu < Gd < Tm < Yb < Lu [23]. A series of functionalized ILs were synthesized which have high selectivity, good stability and good interfacial phenomena [24–26]. The extraction thermodynamics and kinetics of [trialkylethylammonium][A336][CA12] for lanthanum extraction in dilute solutions were investigated [27,28]. The results indicated that the mass transfer kinetics of La(III) is a mixed-controlled process influenced by interfacial reaction. Sun et al. [29–33] synthesized five new bifunctional ionic liquids (bif-ILs), including [N2222][P204], [N4444][P204], [N6666][P204], [N8888][P204] and [N1888][P204], which can extract REEs in the Trivalent Actinide-Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Complexes (TALSPEAK) process. The distribution ratios and separation selectivities for REEs decreased with increasing sizes of their cations. Zhao et al. [34] developed an IL-based system for the extraction of rare earth nitrates utilizing the mixture of [A336][NO<sub>3</sub>] and P507. The mixed IL extraction system exhibited a synergistic extraction effect for light REEs (La–Eu), but an anti-synergistic effect for HREEs (Gd–Lu, Y). This result indicates that the synergistic extraction system is helpful for the separation of LREEs from HREEs.

With the advancement of China's rare earth industry, sustainable processes for rare earth separation are urgently needed. In this paper, we investigated the extraction mechanism and stripping property of IL [N1888][CA12] by using Y(III) and Yb(III) as the model HREE in high concentration. We also presented a new approach for the separation of yttrium from practical yttrium-enriched rare earth feed using [N1888][CA12] as an extractant. The separation process for industrial application can contribute to eliminating the saponification process and avoiding the acid/base consumption.

## 2. Experimental

### 2.1. Reagents and apparatus

Methyltrioctylammonium chloride ([N1888]Cl, purity > 99%) was purchased from Anhui Benma Pioneer Technology Co., Ltd., China. CA12 and 260# kerosene were kindly provided by Shanghai Rare-earth Chemical Co., Ltd., China. An anion exchange resin of Dowex Monosphere 550A (OH) was obtained from Dow Chemical Company, USA. Individual REE stock solutions, including La–Lu plus Y, were prepared by dissolving the corresponding oxide (>99.99%, Ganzhou Rare Earth Group Co., Ltd., China) with hydrochloric acid and diluting with deionized water. Yttrium-enriched rare earth feed was provided by Fujian Changting Golden Dragon Rare Earth Co., Ltd., China, and its ingredients are shown in Table 1. All the chemicals were used without further purification.

Inductively coupled plasma optical emission spectroscopy (ICP–OES) Horiba Ultima 2 was used to determine the concentrations of REEs. The total concentrations of mixed REEs and free H<sup>+</sup> were

determined by volumetric titration with standard solutions of EDTA and NaOH, respectively [11]. Chloride was determined via titration with AgNO<sub>3</sub> and KCrO<sub>4</sub> as indicator (GB/T 6905.1-1986). IR spectra were measured with a Nicolet iS50 spectrometer in transmission mode. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained in CDCl<sub>3</sub> with an AV III-500 BRUKER spectrometer. Total ammonia nitrogen (TAN) was measured using the spectrophotometric method (723 N, Shanghai Precision & Scientific Instrument Co., Ltd.).

### 2.2. Synthesis of [N1888][CA12]

The [N1888][CA12] used without fractional extraction part was prepared in laboratory scale by combining ion-exchange and neutralizing reactions [35]. Fig. 1 shows the molecular structure of [N1888][CA12]. The amount of residual Cl<sup>−</sup> was determined as lower than 0.05 wt%. Yield 98.9%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.78–0.88 (m, 17H), 1.14–1.23 (m, 21H), 1.25–1.30 (m, 24H), 3.14 (s, 3H), 3.27 (t, *J*<sub>1</sub> = 6.8 Hz, 6H), 4.39 (s, 2H), 6.81–7.01 (m, 2H), 7.02–7.11 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.2, 14.3, 14.4, 21.3, 22.5, 22.9, 26.5, 27.9, 29.2, 29.3, 29.9, 30.0, 31.8, 32.0, 32.1, 48.9, 61.5, 68.5, 114.7, 114.8, 120.2, 126.3, 126.3, 127.6, 174.0.

### 2.3. Solvent extraction process

Extraction experiments were performed by contacting equal volumes (except specifically defined) of organic phase with aqueous solution for 30 min in a vibrating mixer at 30 °C. The stripping experiment was conducted by contacting 4 mL of loaded organic phase with 4 mL of stripping reagents for 30 min in a vibrating mixer at 30 °C. The concentration of the REEs in the aqueous phase was determined using ICP–OES after centrifugation at 2500 rpm for 5 min.

The extraction rate (*E*), distribution ratio (*D*), separation factor (*β*) and stripping ratio (*S*) are defined as follows.

$$E\% = \frac{[M]_{org}}{[M]_{org} + [M]_{aq}} \times 100 \quad (1)$$

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad (2)$$

$$\beta = \frac{D_1}{D_2} \quad (3)$$

$$S\% = \frac{[M]_{aq,a} \times V_{aq}}{[M]_{org,t} \times V_{org}} \times 100 \quad (4)$$

where  $[M]_{aq,a}$  is the equilibrium concentration of REE in stripping acid, and  $[M]_{org,t}$  is the initial concentration of REE in loaded organic phase. *D*<sub>1</sub> and *D*<sub>2</sub> are the distribution ratios of REE<sub>1</sub> and REE<sub>2</sub>, respectively.

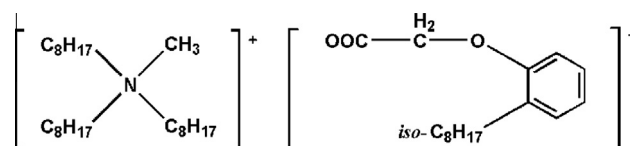


Fig. 1. Molecular structure of [N1888][CA12].

Table 1  
Composition of yttrium-enriched rare earth concentrate.

Ingredients	Y	La–Dy	Ho	Er	Tm	Yb	Lu
Mole fraction	0.873	<0.0001	0.0360	0.0473	0.0135	0.027	0.0030

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