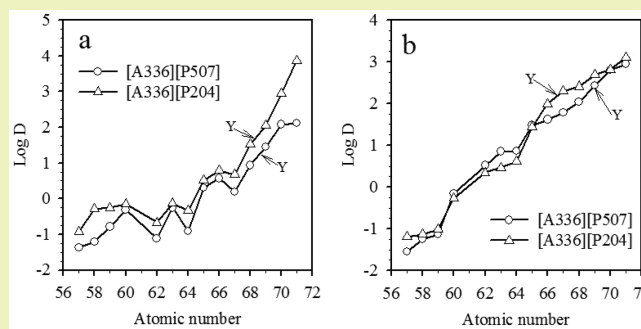


## Highly Selective Extraction and Separation of Rare Earths(III) Using Bifunctional Ionic Liquid Extractant

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**ABSTRACT:** The extraction and separation of rare earths (REs) from nitrate medium or chloride medium using bifunctional ionic liquid extractants (Bif-ILEs) [trialkylmethylammonium][di(2-ethylhexyl)orthophosphinate] ([A336]-[P507]) and [trialkylmethylammonium][di-2-ethylhexylphosphate] ([A336][P204]) in *n*-heptane were investigated in this report. The separation factor ( $\beta$ ) values indicated that [A336][P507] and [A336][P204] could be suitable for the separation of heavy REs(III) in nitrate medium and suitable for the separation of light REs(III) in chloride medium. Especially, in nitrate medium, the  $\beta$  values using [A336]-[P204] as the extractant were Tm/Er (3.36), Yb/Tm (7.92), and Lu/Yb (8.55), respectively, and in chloride medium, the  $\beta$  values using [A336][P507] as the extractant were Nd/Pr (9.52) and Sm/Nd (4.70), respectively. The  $\bar{\beta}_{z+1/z}$  values of REs(III) extracted by [A336][P507] and [A336][P204] in nitrate medium were 3.61 and 3.67, respectively, and in chloride medium, they were 2.75 and 2.59, respectively.

**KEYWORDS:** Rare earths, Bifunctional ionic liquid extractants, Extraction, Separation



## INTRODUCTION

Rare earths (REs) are composed of scandium, yttrium, and the lanthanides metallic elements. As one of the most important strategic and critical mineral resources, REs have a significant effect on luminescence, electronics, magnetism, catalysis, metallurgy, and the ceramic industry.<sup>1,2</sup> However, REs exist together in ore, e.g. bastnasite, monazite, xenotime, and oil shale residue.<sup>3,4</sup> The extraction and separation of each RE from the mixed REs is difficult due to their similar chemical and physical properties. In terms of ion adsorption, ore occurred in southern China in which the amount of Tm and Lu was less than 0.5% of the REs present.<sup>5</sup> And, Lu has a significant application in electromagnetic calorimeter equipment, e.g. future high energy physics accelerators.<sup>6</sup> Therefore, it is important to investigate the extraction and separation of REs from each other. China is the world's largest REs producer and exporter. Over 90% of the world's RE market comes from China, and the amount of resources in China have decreased to only one-third of the world's total.<sup>7</sup> "Emission Standards of Pollutants from Rare Earths Industry" was promulgated by China's Ministry of Environment Protection (MOP) in 2011 for protecting the resources and environment and limiting the amount of wastewater produced. With the huge consumption of RE resources, a greener and more efficient separation technique for extraction and separation of REs is urgently needed in China.

Up to now, there are many acidic organophosphorous extractants,<sup>8-16</sup> neutral organophosphorous extractants,<sup>17-20</sup>

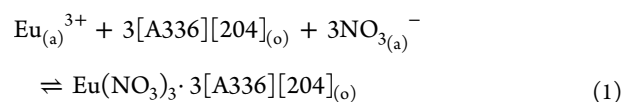
and amine extractants,<sup>21</sup> which are used for RE separation in hydrochloric acid, nitrate acid, or sulfuric acid systems. The extraction property and separation sequence was influenced by the extractant and different medium. The extractants 2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester (P507), di(2-ethylhexyl) phosphoric acid (P204), tributyl phosphate (TBP), naphthenic acid, and trialkylmethylammonium chloride (Aliquat 336) are widely investigated for REs extraction and separation. And the binary extractants system could also provide a good choice for RE extraction and separation.<sup>22-24</sup> In metallurgy industry of China, P507 is the main extractant which is used for extraction and separation of REs from each other. In P507 system, the separation factor ( $\beta$ ) values of light REs are higher. However, the  $\beta$  values of heavy REs are lower, e.g. the  $\beta$  values are Tm/Er (3.34), Yb/Tm (3.56), and Lu/Yb (1.78), respectively.<sup>3</sup> The stripping acidity is high and the heavy REs could not be completely stripped. Compared with P507, the  $\beta$  values of heavy REs using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) are enhanced.<sup>3</sup> When it is used for REs separation, the price of Cyanex 272 and the cost of equipment are high. And, the extraction and separation process is difficult to control, due to the easy emulsification phenomenon in the Cyanex 272 system. Li et al.<sup>25</sup> investigated the REs separation process using both P507 and alcohol as

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extractants. In the mixed extractants system, the proportion of each reagent would be possibly changed due to the different solubility during long-time reuse. The extractants with changed composition have adverse effects on REs separation. Therefore, it is important to develop a new extraction system for the industry of RE separation. In most extraction processes, neutral extractants will consume less acid and base due to becoming the neutral target metal complex, while the selectivity will be lower than that of acidic extractants. On the contrary, the extraction of acidic extractants is cation exchange mechanism with high selectivity, but it will consume more acid or base.<sup>26</sup> Room temperature ionic liquid (IL) was an environmentally friendly green solvent and was widely applied as extractant in metal separation and extraction.<sup>27–29</sup> Nowadays, the neutral bifunctional ionic liquid extractants (Bif-ILEs) could provide a new choice for REs separation. The Bif-ILEs have been synthesized and applied in REs separation in our laboratory<sup>30–33</sup> since their advantages of high selectivity and extractability, good stability, good interfacial phenomena, and low consumption of acid and base. Sun et. al.<sup>33</sup> investigated the extraction mechanism of Eu(III) and [trialkylethylammonium]-[di-2-ethylhexylphosphate] ([A336][P204]) and showed the higher extraction ability of [A336][P204] than the mixture of Aliquat336 and P204. The phenomenon was attributed to the strong ion-pair interactions in IL, such as electrostatic interaction, van der Waals force, and induction interaction.<sup>34,35</sup> Sun et. al also reported both cation and anion of the Bif-ILEs complex with Eu(III) and ion association mechanism can be achieved. The extraction equation can be determined by the conventional slope analysis method. The main extraction process can be expressed as



Rogers et al.<sup>36,37</sup> found that, the physical, chemical, and biological properties of an IL drug of Active Pharmaceutical Ingredients (API) could be controlled and obtained by changing the cation or anion of IL, which provided a new method and concept for designing drugs rather than by covalent modification. The novel function and properties would be obtained when the designed IL was synthesized.

Since the extraction mechanism has been discussed in our past report,<sup>33</sup> we herein further investigated the extraction properties and extraction selectivity of these Bif-ILEs on RE separation in nitrate medium or in chloride medium. It would provide a potential application for REs separation in industry due to the high selectivity of novel Bif-ILEs.

## EXPERIMENTAL SECTION

**Reagent and Apparatus.** Aliquat 336 (>99.0% purity) was purchased from Sigma-Aldrich. P507 (>93.0% purity) and P204 (>95.0% purity) were supplied by Tianjin Beicheng Chemical Plant (China). Tributyl phosphate (TBP) was analytical reagent quality. Cyanex923 (mixture of four trialkylphosphine oxides) was kindly supplied by the Cytec Canada Inc. and purified according to the method of ref 30. The Bif-ILEs [trialkylmethylammonium][di(2-ethylhexyl)orthophosphinate] ([A336][P507]) and [A336][P204] were synthesized in our lab according to published method.<sup>38</sup> The synthesis process was combining the cation of A336 with phosphonic acid group as anions using acid/base neutralization method. The chemical structures of extractants are shown in Figure 1. All of the extractants were diluted with *n*-heptane. Stock solutions of REs(III) were prepared by dissolving their oxides (>99.9%) into concentrated

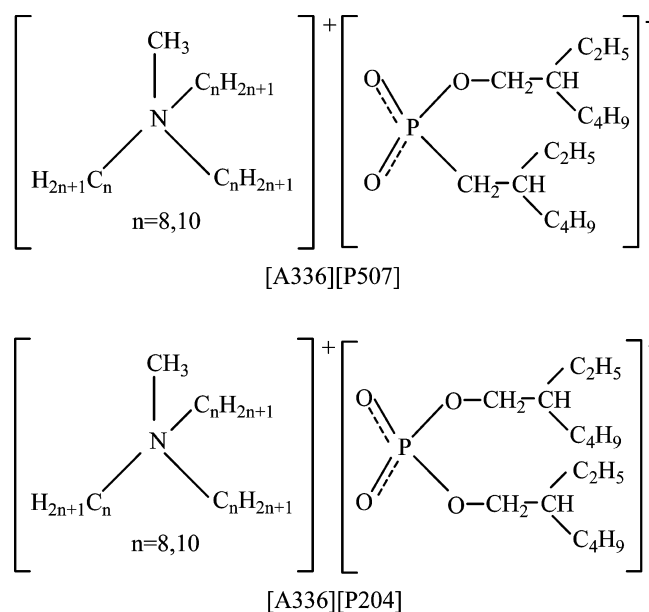


Figure 1. Chemical structures of the Bif-ILEs used in this study.

nitric acid or concentrated hydrochloric acid, respectively. All the other chemicals were analytical grade. The pH values of the aqueous phase were measured by a model PHS-3C pH meter (Leici, Shanghai, China). It was calibrated by 4.00 and 6.86 standard buffer solutions before measurement. The concentration of each RE(III) in REs(III) mixture was determined by inductively coupled plasma optical emission spectrometers (ICP-OES, Thermo iCAP 6000).

**Extraction Procedure.** Batch experiments were explored by adding one volume (1.0 mL) of organic phase and five volumes (5.0 mL) of aqueous phase in equilibrium tubes. The two-phase systems were shaken for 60 min with the help of a desktop constant temperature oscillator (TH2-318, Equipment Co., Ltd. Shanghai Jing Hong) at 20 °C to ensure complete equilibration. The mixture was then centrifuged for 5 min at 2000 r min<sup>-1</sup> to enhance phase separation. The concentration of REs(III) in aqueous phase was determined by UVmini-1240 UV-visible spectrophotometer (Shimadzu, Kyoto, Japan), and the concentration of REs(III) in organic phase was calculated by mass balance. The concentration of RE(III) in aqueous phase was determined by colorimetry with Arsenazo III as color developing agent. A 3 mL portion of ClCH<sub>2</sub>COOH–NaOH buffer solution (pH 2.8), 2 mL 0.05% Arsenazo III, and different amount of RE(III) solution were added to volumetric flask and diluted to 25 mL with deionized water. The absorbance of this solution was measured at 653 nm after 15 min. The extraction efficiency (*E*), distribution ratio (*D*), separation factor (*β*), and stripping ratio (*St*) were calculated by

$$E(\%) = \frac{C_{\text{org}} V_{\text{org}}}{C_{\text{aq},i} V_{\text{aq}}} \times 100 \quad (2)$$

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}} \quad (3)$$

$$\beta = \frac{D_1}{D_2} \quad (4)$$

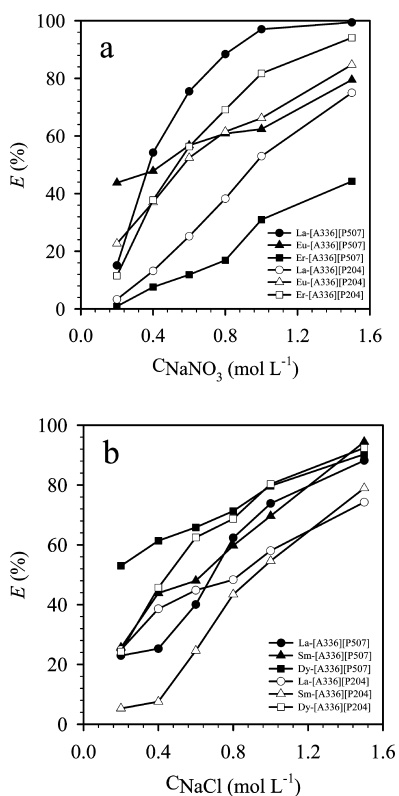
$$\text{St}(\%) = \frac{C_a}{C_o} \times 100 \quad (5)$$

where *C*<sub>aq,i</sub> and *C*<sub>aq</sub> are the initial and final concentrations of REs(III) in the aqueous phase, *C*<sub>org</sub> is the final concentrations of REs(III) in the organic phase, and *V*<sub>aq</sub> and *V*<sub>org</sub> are the aqueous and organic phase volumes, respectively. *D*<sub>1</sub> and *D*<sub>2</sub> are the distribution ratios of REs(III) 1 and 2, respectively. *C*<sub>a</sub> is the equilibrium concentration of REs(III) in

stripping acid, and  $C_0$  is the initial concentration of REs(III) in the organic phase. The experiments were conducted in duplicate under the same conditions, and the relative error between duplicates was less than 5%. The results were reported as mean values.

## RESULTS AND DISCUSSION

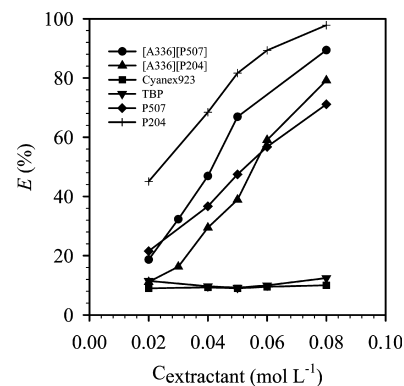
**Effect of Salting-Out Agent Concentration in Nitrate Medium and in Chloride Medium.** The effect of  $\text{NaNO}_3$  concentration on La(III), Eu(III), and Er(III) was explored with [A336][P507] or [A336][P204] as the extractant in nitrate medium (Figure 2a). And, the effect of NaCl



**Figure 2.** Effect of salting-out agent concentration on the extraction of REs(III) in different media. [extractant] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, the salting-out agent in parts a and b are  $\text{NaNO}_3$  and NaCl, respectively, La( $\text{NO}_3$ )<sub>3</sub> (pH = 2.9), Eu( $\text{NO}_3$ )<sub>3</sub> (pH = 1.73), Er( $\text{NO}_3$ )<sub>3</sub> (pH = 1.21). [A336][P507]:LaCl<sub>3</sub> (pH = 2.41), SmCl<sub>3</sub> (pH = 2.07), DyCl<sub>3</sub> (pH = 1.81). [A336][P204]:LaCl<sub>3</sub> (pH = 3.08), SmCl<sub>3</sub> (pH = 2.27), DyCl<sub>3</sub> (pH = 1.91).

concentration on La(III), Sm(III), and Dy(III) was explored in chloride medium (Figure 2b). As shown in Figure 2a and b, with the increasing of salting-out agent concentration from 0.20 to 1.50 mol L<sup>-1</sup>, the extraction efficiency of every RE(III) increased both in the [A336][P507] and [A336][P204] systems. The salting-out agent had a beneficial effect on RE(III) extraction using neutral extractants. When the anion of the salting-out agent was the same as the anion of RE(III) in the aqueous phase, adding a salting-out agent was equal to increasing the anion concentration of the target metal. Then  $E$  of RE(III) would be enhanced.<sup>3</sup> The neutral Bif-ILEs [A336][CA-12] and [A336][CA-100] were to demonstrate the same phenomenon on RE(III) extraction in chloride medium. With the increasing NaCl concentration in aqueous solution, the  $D$  of the REs(III) increased sharply.<sup>32</sup>

**Extraction of REs(III) with Different Extractants.** The comparison of the extractability of several extractants was investigated by the following experiment. As shown in Figure 3,



**Figure 3.** Comparison of different extractants for the extraction of REs(III). [Sm(III)]<sub>initial</sub> = 1.44 × 10<sup>-3</sup> mol L<sup>-1</sup>, [NaCl]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>initial</sub> = 2.04.

in chloride medium, Sm(III) was extracted by [A336][P507], [A336][P204], Cyanex923, TBP, 50% saponified P507, and P204, respectively. Under the same conditions, the extraction efficiencies of Cyanex923 and TBP were lower than that of the other extractants. With the increasing extractant concentration, the  $E$  of Sm(III) increased for [A336][P507], [A336][P204], 50% saponified P507, or P204. Especially, the extractability of P204 is better than [A336][P507], [A336][P204], and 50% saponified P507. This indicated that, under the lower acidity conditions, the extractability of neutral extractants Cyanex923 and TBP was low. The extraction of RE(III) by TBP needs more than 6 mol L<sup>-1</sup> HCl in chloride medium.<sup>39</sup> On the other hand, the extractability of neutral Bif-ILEs [A336][P507] and [A336][P204] was similar to that of acidic extractants P507 and P204 (Figure 3). These extractants could obtain higher extraction efficiency of RE(III) at lower acidity.

**Separation Factor ( $\beta$ ) of REs(III).** The  $\beta$  values of REs(III) extracted by [A336][P507] and [A336][P204] in nitrate medium were investigated, and the  $\beta$  values of heavy REs(III) are shown in Tables 1 and 2, respectively. The  $\beta$  values of heavy

**Table 1.** Separation Factor ( $\beta$ ) of Heavy REs(III) Extracted by [A336][P507] in Nitrate Medium<sup>a</sup>

RE(III)	Er	Tm	Yb	Lu
Ho	5.63	18.1	78.1	83.5
Er		3.22	13.9	14.8
Tm			4.31	4.61
Yb				1.07

<sup>a</sup>[A336][P507] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, [NaNO<sub>3</sub>]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>e</sub> = 1.82.

REs(III) indicated that the heavy REs(III) could be separated from each other. Compared with Tables 1 and 2, the  $\beta$  values between heavy REs(III) in the [A336][P204] extraction system were higher than those in the [A336][P507] extraction system. The phenomena indicated that the selectivity of Bif-ILE [A336][P204] was higher than that of [A336][P507] in nitrate medium. The inner synergistic effect and competition effect between [A336]<sup>+</sup> and [P507]<sup>-</sup> (or [P204]<sup>-</sup>) could enhance the  $\beta$  value of heavy REs(III). The  $\beta_{z+1/z}$  value was calculated to evaluate whether the extractant could apply in industry. In



**Table 2. Separation Factor ( $\beta$ ) of Heavy REs(III) Extracted by [A336][P204] in Nitrate Medium<sup>a</sup>**

RE(III)	Er	Tm	Yb	Lu
Ho	6.93	23.3	184	1577
Er		3.36	26.6	227
Tm			7.92	67.8
Yb				8.55

<sup>a</sup>[[A336][P204]] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, [NaNO<sub>3</sub>]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>e</sub> = 1.73.

nitrate medium, The  $\bar{\beta}_{z+1/z}$  values of REs(III) from La(III) to Lu(III) extracted by [A336][P507] and [A336][P204] were 3.61 and 3.67, respectively. The  $\bar{\beta}_{z+1/z}$  value of REs(III) extracted by P507 in the HNO<sub>3</sub> system ([HNO<sub>3</sub>] = 0.5 mol L<sup>-1</sup>) was 3.04, and the value was higher than that of P204.<sup>40</sup> The  $\bar{\beta}_{z+1/z}$  values of TBP and P350 (di(1-methylheptyl)methylphosphate) in the HNO<sub>3</sub> system were 1.56 and 1.16, respectively.<sup>3</sup> Therefore, the  $\bar{\beta}_{z+1/z}$  values of Bif-ILEs [A336]-[P507] and [A336][P204] in nitrate medium were higher than those of P507, P204, TBP, and P350. When P507 and P204 were used in REs(III) separation, the saponification procedure would break the intermolecular hydrogen bonds in dimers and enhance the extraction capacities of acidic extractants. However, ammonia-nitrogen or high content Ca<sup>2+</sup> or Mg<sup>2+</sup> wastewater was produced in the saponification procedure. On the other hand, the extraction of REs(III) by TBP and P350 occurred at high acid concentration (the nitrate acid concentration was always 3 M). Therefore, [A336][P507] and [A336][P204] would be suitable for heavy RE(III) separation at low acidity in industrial applications.

It is widely known that the separation and purification of Y(III) from heavy RE(III) by liquid–liquid extraction is difficult because of their similar chemical properties.<sup>13</sup> The  $\beta$  values of Y(III) and REs(III) extracted by [A336][P507] or [A336][P204] in nitrate medium system are shown in Table 3. The extraction of Y(III) was between that of Er(III) and Tm(III) with [A336][P507] or [A336][P204] as extractant. Liu et al. reported that in the HNO<sub>3</sub>–Cyphos IL 104 system, the  $\beta$  values were Y/Gd (6.17), Y/Tb (8.57), Y/Dy (40.81), Y/Ho (14.55), Er/Y (1.83), Tm/Y (2.06), Yb/Y (10.92), and Lu/Y (4.60), respectively.<sup>41</sup> Therefore, the  $\beta$  values indicated that Y(III) can be separated from other heavy REs(III) by [A336][P507] or [A336][P204] in nitrate medium. And compared with [A336][P507] and [A336][P204], [A336]-[P204] was more suitable for Y(III) separation from other heavy REs(III) in this study.

The  $\beta$  values of REs(III) extracted by [A336][P507] and [A336][P204] in chloride medium were explored; these and the  $\beta$  values of light REs(III) are shown in Tables 4 and 5, respectively. The  $\beta$  values of adjacent light REs(III) indicated that the light REs(III) could be separated from each other. Especially, when [A336][P507] was used as extractant, the

**Table 4. Separation Factor ( $\beta$ ) of Light REs(III) Extracted by [A336][P507] in Chloride Medium<sup>a</sup>**

RE(III)	Ce	Pr	Nd	Sm
La	2.03	2.62	24.9	117
Ce		1.29	12.3	57.7
Pr			9.52	44.7
Nd				4.70

<sup>a</sup>[[A336][P507]] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, [NaCl]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>e</sub> = 2.96.

**Table 5. Separation Factor ( $\beta$ ) of Light REs(III) Extracted by [A336][P204] in Chloride Medium**

RE(III)	Ce	Pr	Nd	Sm
La	1.14	1.49	8.35	34.6
Ce		1.31	7.34	30.4
Pr			5.61	23.3
Nd				4.14

<sup>a</sup>[[A336][P204]] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, [NaCl]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>e</sub> = 2.87.

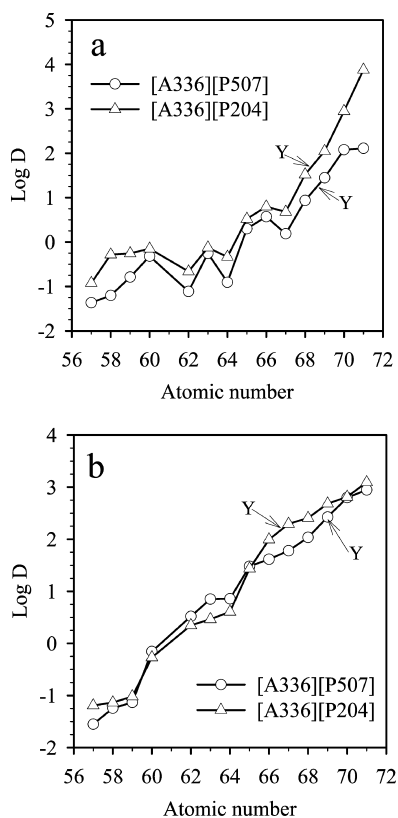
significantly large  $\beta$  values of Nd/Pr and Sm/Nd were obtained to be 9.52 and 4.70, respectively. However, these values were lower, 5.61 and 4.14, for the extractant [A336][P204]. Additionally in chloride medium, when acidic extractant P507 was utilized, both the corresponding  $\beta$  values were 1.17 and 2.00 which appeared to be similar to the values (4.86 and 1.06 for Nd/Pr and Sm/Nd, respectively) for the case of P204.<sup>26</sup> Therefore, the novel Bif-ILEs [A336][P507] and [A336]-[P204] could enhance the separation ability. [A336][P507] and [A336][P204] were suitable for light REs(III) separation in chloride medium. The  $\bar{\beta}_{z+1/z}$  values of REs(III) from La(III) to Lu(III) extracted by [A336][P507] and [A336][P204] were 2.75 and 2.59, respectively. Then in chloride medium, the selectivity of [A336][P507] for REs(III) separation was higher than [A336][P204]. When P507 or P204 was used solitarily as extractant for REs(III) separation in chloride medium, the corresponding  $\bar{\beta}_{z+1/z}$  value of REs(III) was 1.57 or 1.76.<sup>26</sup> The selectivity of Bif-ILEs [A336][P507] and [A336][P204] were higher than that of acidic extractants P507 and P204 in REs(III) separation.

With the increasing of atomic number of RE(III), the variation of log *D* extracted by [A336][P507] or [A336][P204] is shown in Figure 4. In nitrate medium, the *D* value of each RE(III) extracted by [A336][P204] was higher than that of [A336][P507] with the same extraction conditions (Figure 4a). The value of log *D* increased with the increasing of atomic number of RE(III) from Ho(III) to Lu(III). From Nd(III) to Sm(III), Eu(III) to Gd(III), and Dy(III) to Ho(III), the value of log *D* decreased. The sequence of Y(III) extracted by [A336][P507] or [A336][P204] was between Er(III) and Tm(III) in nitrate medium. In chloride medium, with the increasing of atomic number of RE(III), the log *D* of RE(III)

**Table 3. Separation Factor ( $\beta$ ) of Y(III) and REs(III) in Nitrate Medium<sup>a</sup>**

	Y/La	Y/Ce	Y/Pr	Y/Nd	Y/Sm	Y/Eu	Y/Gd	Y/Tb	Y/Dy	Y/Ho	Y/Er	Tm/Y	Yb/Y	Lu/Y
[A336][P507]	397	274	105	35.8	222	30.9	138	8.58	4.61	11.2	1.98	1.62	7.01	7.49
[A336][P204]	431	98.3	92.3	72.5	236	68.4	111	15.4	8.19	10.7	1.55	2.17	17.2	147

<sup>a</sup>[extractant] = 0.05 mol L<sup>-1</sup>, [RE(III)]<sub>initial</sub> = 7.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, [NaNO<sub>3</sub>]<sub>initial</sub> = 1.0 mol L<sup>-1</sup>, pH<sub>e</sub> = 1.79.



**Figure 4.** Relationship between the distribution ratio ( $D$ ) and atomic number of RE(III) ((a) extraction in nitrate medium, (b) extraction in chloride medium): (a) [extractant] =  $0.05 \text{ mol L}^{-1}$ ,  $[\text{RE(III)}]_{\text{initial}} = 7.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaNO}_3]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ ,  $\text{pH}_e = 1.50$ ; (b) [extractant] =  $0.05 \text{ mol L}^{-1}$ ,  $[\text{RE(III)}]_{\text{initial}} = 7.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaCl}]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ ,  $\text{pH}_e = 2.50$ .

increased (Figure 4b). The sequence of Y(III) extracted by [A336][P507] was between Er(III) and Tm(III), and that extracted by [A336][P204] was between Dy(III) and Ho(III). The variation trend of  $\log D$  using [A336][P507] or [A336][P204] as extractant in chloride medium was similar to that with solitary P507 or P204 as the extractant.<sup>26</sup> As shown in Figure 4, in the circumstance of different medium, the extraction sequence was different with the same extractant. The extraction sequence of RE(III) is closely related to the extractant and extraction medium. The sequence of RE(III) extracted by neutral extractant TBP in chloride medium was smooth, and the selectivity of TBP in chloride medium was not obvious.<sup>26</sup> In this work, in nitrate medium, the selectivity of neutral Bif-ILEs [A336][P507] and [A336][P204] on heavy RE(III) separation was higher. And in chloride medium, the selectivity of [A336][P507] and [A336][P204] on light RE(III) separation was higher. The value of  $\log D$  increased with the increasing of atomic number of RE(III) from La(III) to Lu(III) in P507 or P204 system. On the contrary, the value of  $\log D$  decreased with the increasing of atomic number of RE(III) from La(III) to Lu(III), when Aliquat 336 was the extractant in nitrate medium.<sup>26</sup> When P507 or P204 was used as the extractant in RE(III) separation,  $[\text{P507}]^-$  or  $[\text{P204}]^-$  combined with REs(III) and formed the extracted complex.<sup>9–11,40,42</sup> When the Bif-ILE [A336][P507] or [A336][P204] was used in RE(III) separation, both the cation and anion of Bif-ILE combined with REs(III) and formed the bigger extracted complex as mentioned above. Then both cation ( $[\text{A336}]^+$ ) and

anion ( $[\text{P507}]^-$  or  $[\text{P204}]^-$ ) had effects on the REs(III). Since this was an inner synergistic effect between the extractant cation and anion to the RE(III), the trend of  $\log D$  was changed. On the other hand, the extraction sequence of RE(III) was also attributed to the anion in aqueous phase. The variation of the extraction sequence in nitrate medium was different from that in chloride medium. The  $\text{NO}_3^-$  or  $\text{Cl}^-$  participated in forming the extracted complex. The property of  $\text{NO}_3^-$  or  $\text{Cl}^-$  could regulate the stability of the extracted complex and the selectivity of RE(III) extraction. Therefore, the extraction sequence of REs(III) was changed.

**Separation Properties of Bif-ILEs for RE(III) Mixtures.** The data of the  $\beta$  values of RE(III) pairs in nitrate medium showed that [A336][P204] was suitable for the heavy RE(III) separation. Therefore, the heavy RE(III) mixture was extracted by [A336][P204]. The ratios of Tm(III), Yb(III), and Lu(III) mixture were simulated by the Tm–Yb–Lu concentrate. As shown in Table 6, the  $\beta$  values of Yb/Tm, Lu/Tm, and Lu/Yb were 3.31, 6.13 and 1.85, respectively. The results may provide for potential industrial application for heavy RE(III) separation.

**Table 6.** Separation Factors ( $\beta$ ) of Heavy RE(III) Mixtures in Nitrate Medium

RE(III)	Yb	Lu
Tm	3.31	6.13
Yb		1.85

$^a$ [A336][P204] =  $0.05 \text{ mol L}^{-1}$ ,  $[\text{Tm(III)}]_{\text{initial}} = 1.1 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Yb(III)}]_{\text{initial}} = 7.2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Lu(III)}]_{\text{initial}} = 1.3 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaNO}_3]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ ,  $[\text{H}^+] = 0.15 \text{ mol L}^{-1}$ .

The data of the  $\beta$  values of RE(III) pairs in chloride medium revealed that [A336][P507] was suitable for the light RE(III) separation. The main components of the Baotou Rare Earth Mine was La, Ce, Pr, and Nd. Therefore, [A336][P507] for the light RE(III) mixture separation was investigated. The ratios of La(III), Ce(III), Pr(III), and Nd(III) mixtures were simulated by the components of the Baotou Rare Earth Mine. As shown in Table 7, the  $\beta$  values of Ce/La, Pr/Ce, and Nd/Pr were

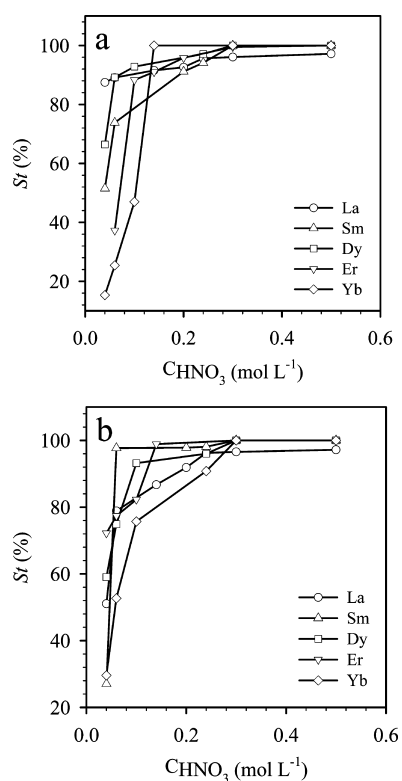
**Table 7.** Separation Factors ( $\beta$ ) of Light RE(III) Mixtures in Chloride Medium

RE(III)	Ce	Pr	Nd
La	23.5	26.6	154
Ce		1.13	6.55
Pr			5.79

$^a$ [A336][P507] =  $0.05 \text{ mol L}^{-1}$ ,  $[\text{La(III)}]_{\text{initial}} = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Ce(III)}]_{\text{initial}} = 4.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Pr(III)}]_{\text{initial}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Nd(III)}]_{\text{initial}} = 2.1 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaCl}]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ ,  $\text{pH}_e = 2.52$ .

23.49, 1.13, and 5.79, respectively. The  $\beta$  value of Nd/Pr was higher than the one with P507 as extractant. The results may provide the potential industrial application for the light REs(III) separation.

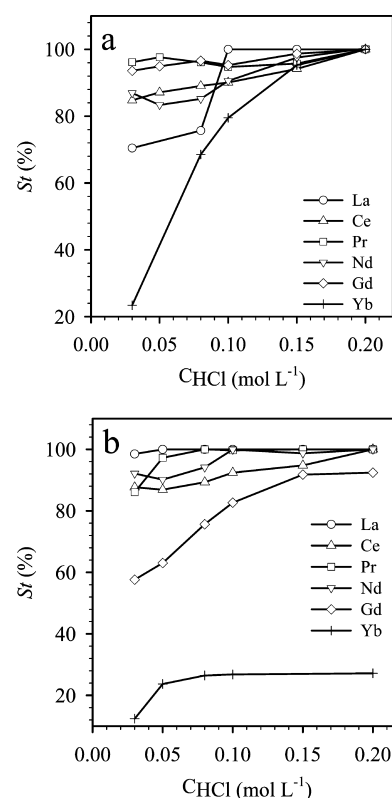
**Stripping Properties.** The stripping experiments of extractant loaded RE(III) in nitrate medium were explored. As shown in Figure 5a and b, the extractants were [A336][P507] and [A336][P204], respectively, and different concentrations of  $\text{HNO}_3$  were the stripping solutions. With the increasing of  $\text{HNO}_3$  concentration from 0.04 to  $0.50 \text{ mol L}^{-1}$ , stripping ratio of RE(III) increased both in [A336][P507] and



**Figure 5.** Stripping of RE(III) with  $\text{HNO}_3$  from the loaded organic phase.  $[\text{extractant}] = 0.05 \text{ mol L}^{-1}$ ,  $[\text{RE(III)}]_{\text{initial}} = 7.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaNO}_3]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ , extractants in parts a and b are  $[\text{A336}][\text{P507}]$  and  $[\text{A336}][\text{P204}]$ , respectively.

$[\text{A336}][\text{P204}]$  systems. When the  $\text{HNO}_3$  concentration increased to  $0.30 \text{ mol L}^{-1}$ , more than 95% of La(III) and almost the whole Sm(III) and Dy(III) were stripped from loaded organic phase. Both  $[\text{A336}][\text{P507}]$  loaded RE(III) and  $[\text{A336}][\text{P204}]$  loaded RE(III) were easily stripped, when the  $\text{HNO}_3$  concentration was higher than  $0.30 \text{ mol L}^{-1}$ .

The stripping experiments of La(III), Ce(III), Pr(III), Nd(III), Gd(III), and Yb(III) extracted by  $[\text{A336}][\text{P507}]$  and La(III), Ce(III), Pr(III), Nd(III), Gd(III), and Yb(III) extracted by  $[\text{A336}][\text{P204}]$  in chloride medium were explored. As shown in Figure 6a and b, different concentrations of HCl were the stripping solutions. From La(III) to Nd(III), the RE(III) loaded  $[\text{A336}][\text{P507}]$  and RE(III) loaded  $[\text{A336}][\text{P204}]$  could be easily stripped by HCl. The stripping of other RE(III) loaded  $[\text{A336}][\text{P507}]$  could be accomplished. However, other REs(III) loaded  $[\text{A336}][\text{P204}]$  could not be stripped completely. Although one of the main extraction mechanisms eq 1 of REs(III) by  $[\text{A336}][\text{P204}]$  in  $\text{HNO}_3$  was proposed in Sun's paper,<sup>33</sup> it is still far away from the complete and detailed understanding of the extraction process for the Bif-ILEs. For example, Yb(III) can be partly stripped at  $0.2 \text{ mol/L}$  HCl in Figure 6b, and this is possibly due to the forming of the new complex,  $\text{RE}(\text{Cl})_{3-n}[\text{P204}]_n \cdot (3-n)[\text{A336}][\text{P204}]$ , ( $n = 1, 2, \text{ or } 3$ ), and the interaction of  $\text{P}-\text{O} \cdots \text{RE}$  other than  $\text{P}=\text{O} \cdots \text{RE}$  from  $[\text{P204}]$  will greatly enhance the stability the new complex, while leading to the increased stripping acidity and decreased stripping ratio. The more detailed mechanism including sulfuric acid extraction system is being researched. With the increasing HCl concentration from  $0.03$  to  $0.20 \text{ mol L}^{-1}$ , all of La(III), Ce(III), Pr(III), or Nd(III) were stripped from the loaded organic phase and went into the HCl phase.



**Figure 6.** Stripping of RE(III) with HCl from the loaded organic phase.  $[\text{extractant}] = 0.05 \text{ mol L}^{-1}$ ,  $[\text{RE(III)}]_{\text{initial}} = 7.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaCl}]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ , extractants in parts a and b are  $[\text{A336}][\text{P507}]$  and  $[\text{A336}][\text{P204}]$ , respectively.

The stripping property of  $[\text{A336}][\text{P507}]$  was better than that of  $[\text{A336}][\text{P204}]$  in chloride medium.

**Recycling Property.** Stability and recycling of the extractants are the most important required factors for practical application. The stability and recycling of the Bif-ILEs  $[\text{A336}][\text{P507}]$  and  $[\text{A336}][\text{P204}]$  in chloride medium were studied by a repeated loading/stripping process. The extractant was reused four times. The result (Table 8) indicated that the loss of the extraction efficiency was almost negligible, and the extractants could be reused.

**Table 8.** Recycling Experiment of La(III) in Chloride Medium

number of cycle	1	2	3	4
$E_{[\text{A336}][\text{P507}]} (\%)$	87.6	86.3	86.4	86.1
$E_{[\text{A336}][\text{P204}]} (\%)$	64.5	65.1	64.5	64.2

$^a[\text{extractant}] = 0.05 \text{ mol L}^{-1}$ ,  $[\text{La(III)}]_{\text{initial}} = 7.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{NaCl}]_{\text{initial}} = 1.0 \text{ mol L}^{-1}$ ,  $[\text{HNO}_3]_{\text{stripping}} = 0.1 \text{ mol L}^{-1}$ ,  $[\text{HCl}]_{\text{stripping}} = 0.1 \text{ mol L}^{-1}$ .

## CONCLUSIONS

In this paper, the extraction and separation of REs(III) by  $[\text{A336}][\text{P507}]$  or  $[\text{A336}][\text{P204}]$  as extractant in nitrate medium or in chloride medium were investigated. Salting-out agent had a beneficial effect on RE(III) extraction. From the analysis of  $\beta$ , the separation of heavy REs(III) could be achieved using  $[\text{A336}][\text{P507}]$  or  $[\text{A336}][\text{P204}]$  as the extractant in nitrate medium, and the separation of light REs(III) could be achieved using  $[\text{A336}][\text{P507}]$  or  $[\text{A336}][\text{P204}]$  as the extractant in



chloride medium. Then, the advantages of [A336][P507] or [A336][P204] were high selectivity and low acid–base consumption. This would be a positive factor applied in industry. On the other hand, the molecular weight of the novel extractant [A336][P507] or [A336][P204] was higher than that of P507 or P204, which would decrease the maximum extraction capacity. In the future industry application, it is important to find the balance between the selectivity and extraction capacity of the extractant.

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### Notes

The authors declare no competing financial interest.

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