

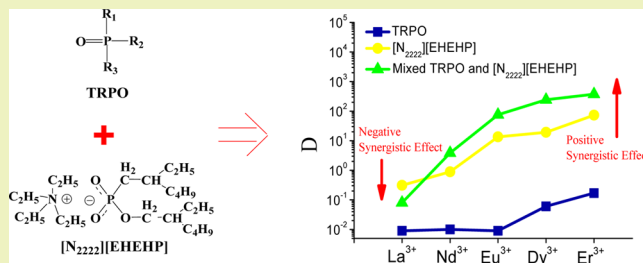
## Synergistic Effect between Bifunctional Ionic Liquids and a Molecular Extractant for Lanthanide Separation

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## Supporting Information

**ABSTRACT:** A novel form of synergistic extraction using both ionic liquid extractants and a molecular extractant is reported. The molecular extractant (TRPO, a mixture of four trialkylphosphine oxides) and anion precursors of the ionic liquid extractants (HDEHP and HEH[EHP]) are the most commonly used industrial extractants for f-block element separation. Development of acid–base coupling bifunctional ionic liquids (ABC-BILs) for rare earth elements (REEs) separation offers a promising strategy to reduce the millions of tons of industrial saponification wastewater that are produced annually. The synergistic effects of the ABC-BILs with TRPO contributed to increased extractabilities and selectivities of middle and heavy lanthanides, revealing theoretical importance and engineering potential in REEs separation.

**KEYWORDS:** Ionic liquids, Synergistic extraction, Rare earth elements, Separation, Saponification wastewater



## INTRODUCTION

Rare earth elements (REEs) are critical elements, vital to many cutting-edge technology products. The economic impact of the growing scarcity of REEs has been the reason for the United States and the European Union to address their strategic positions on the criticality of these elements.<sup>1</sup> The nuclear fuel cycle (NFC) is an important process in nuclear power. The lessons from the Fukushima accident reveal that the disposal of spent nuclear fuel is crucial for the safety and development of nuclear power.<sup>2</sup> Due to the importance of REEs and the NFC, it would be highly desirable to develop effective methods for the separation of individual f-block elements, that is, lanthanides and actinides. Such separation is challenging because the chemical properties of f-block elements are quite similar. Solvent extraction is one, possibly the most effective, technology for separating f-block elements in the REEs<sup>3</sup> and NFC<sup>4</sup> industries. The advantage of solvent extraction lies in its simple operation, high treatment capacity, quick reaction rate, and good separating effect. Among the research being conducted into solvent extraction, synergistic extraction is an attractive topic. Using the synergistic effect of two extractants, the distribution ratios of their mixture may be different to the sum of their individual contributions. When the combined distribution ratio is greater than the sum of the individual ones, the synergistic effect is termed a positive synergistic effect. Conversely, when it is lower, it is a negative synergistic effect. Because of the importance in fundamental research and industrial application, significant effort has been devoted to the study of synergistic extraction over the past decades.<sup>5–7</sup> However, no synergistic extractions concerning functional ionic

liquid extractants and molecular extractants have as yet been published.

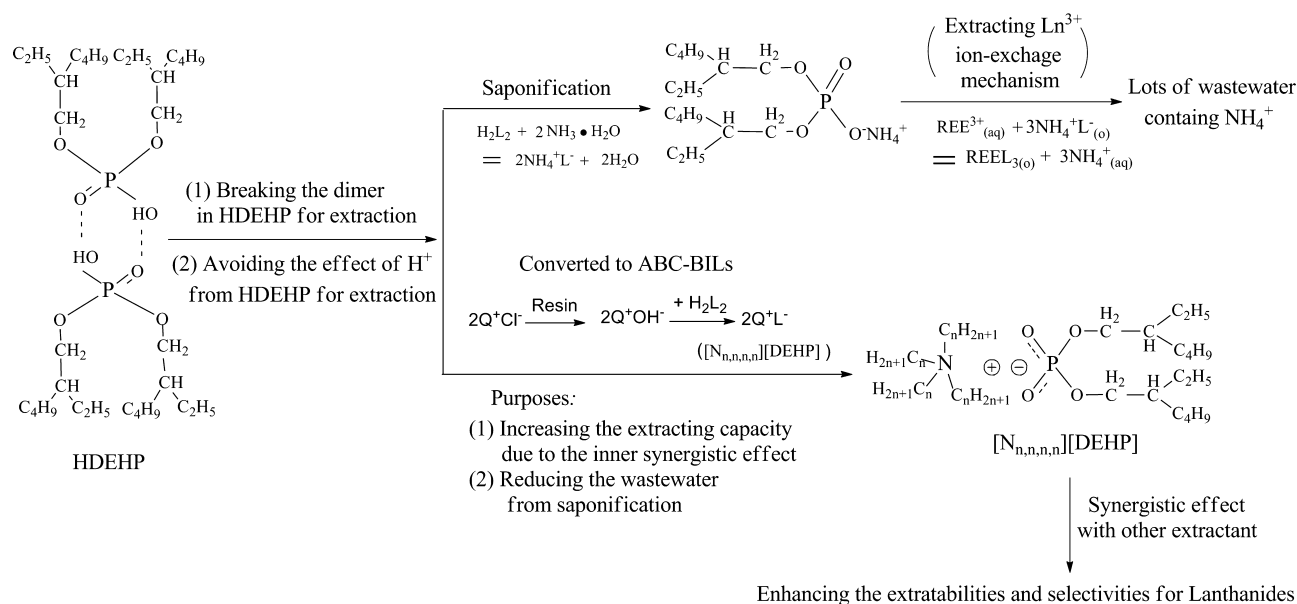
Ionic liquid (IL)-based extraction is a novel form of solvent extraction that applies ILs instead of VOCs as diluents and/or extractants. Ionic liquids are salts, generally in a liquid form below 100 °C. Some applications of ILs have been developed and applied at industrial scales.<sup>8</sup> The sustainable properties of ILs make them particularly suitable for solvent extraction, namely, low volatility, low combustibility, wide liquidus range, thermal stability, adjustable functional groups, high conductivity, and a wide electrochemical window.<sup>9</sup> Many interesting results from IL-based extraction for f-block element separation have been reported.<sup>10–13</sup> As shown in Figure 1, Sun et al. prepared ABC-BIL extractants,<sup>14</sup> revealing a noticeable inner synergistic effect between their cations and anions for REEs extraction.<sup>15</sup> Saponification wastewater is a severe environmental issue in the REEs separation industry, which results in the generation of tens of millions of tons of wastewater annually. Every year, China (the world's largest REEs producer) spends more than 1.5 billion RMB (US\$ 0.24 billion) dealing with wastewater pollution.<sup>16,17</sup> Thus, there is a pressing need, both environmentally and economically, to reduce the volume of polluted wastewater that is produced.

The inner synergistic effect between the cations and anions of ABC-BILs contribute to a significant increasing in the extractabilities of their industrial precursors. The application of ABC-BILs offers a promising strategy to reduce the volume of

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**Figure 1.** Schematic illustration of the development of ABC-BILs for lanthanide separation.

industrial wastewater produced from REEs separation processes.<sup>9,16</sup> ABC-BIL extractants can not only reveal inner synergistic effects, but recently the synergistic effect between different ABC-BIL extractants were reported.<sup>18</sup> As further demonstrated in the current work, a synergistic effect with a molecular extractant, such as TRPO, can be revealed. To the authors' knowledge, this study is the first to report on synergistic extraction concerning bifunctional ionic liquid extractants and a molecular extractant, which contribute to the theoretical investigation and potential industrial application of ionic liquids in f-block element separation for REEs hydrometallurgy and potentially for the NFC.

## MATERIALS AND METHODS

**Reagents.** TRPO (Cyanex 923) was supplied by Cytec Canada, Inc. and used without further purification. Tetraethylammonium chloride ( $[N_{2222}]Cl$ ) was purchased from Aldrich. An anion exchange resin (Dowex Monosphere 550A (OH)) was obtained from the Dow Chemical Company. HDEHP was purchased from Alfa Aesar. HEH[EHP] was supplied by Luoyang Aoda Chemical Co., Ltd., China (95% purity). Rare earth chlorides were purchased from Aldrich.

**Synthesis of ABC-BILs.** The ABC-BILs were prepared using a combination of ion exchange and neutralizing reactions.<sup>19</sup>  $^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR) spectra were obtained in  $CDCl_3$  with a Bruker AV III 400HD NMR spectrometer.

**Tetraethylammonium Di-(2-ethylhexyl)phosphate  $\{[N_{2222}][DEHP]\}$ .** A solution of  $[N_{2222}]OH$  in ethanol was prepared from 1 g of  $[N_{2222}]Cl$  (0.006 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A total of 1.94 g of HDEHP (0.006 mol) was added to the  $[N_{2222}]OH$  solution. The mixture was then stirred at room temperature for 6 h until the solution became neutral. The ethanol and water were distilled off with an IKA RV10 rotary evaporator, and the product was dried at 70 °C under vacuum for 12 h to yield  $[N_{2222}][DEHP]$  as a viscous liquid (2.48 g, 0.0055 mol, yield: 92%).

$^1H$  NMR ( $CDCl_3$ , ppm): 0.70–0.76 (m, 12H, 4CH<sub>3</sub>), 1.12–1.15 (m, 12H, 4CH<sub>3</sub>), 1.17–1.26 (m, 16H, 8CH<sub>2</sub>), 1.34 (m, 2H, 2CH), 3.32 (m, 8H, 4NCH<sub>2</sub>), 3.55 (m, 4H, 2OCH<sub>2</sub>).

$^{13}C$  NMR ( $CDCl_3$ , ppm): 7.57 (4CH<sub>3</sub>), 10.91 (2CH<sub>3</sub>), 14.02 (2CH<sub>3</sub>), 23.05 (2CH<sub>2</sub>), 23.30 (2CH<sub>2</sub>), 28.98 (2CH<sub>2</sub>), 30.09 (2CH<sub>2</sub>), 40.40 (2CH), 52.32 (4NCH<sub>2</sub>), 67.19 (2OCH<sub>2</sub>).

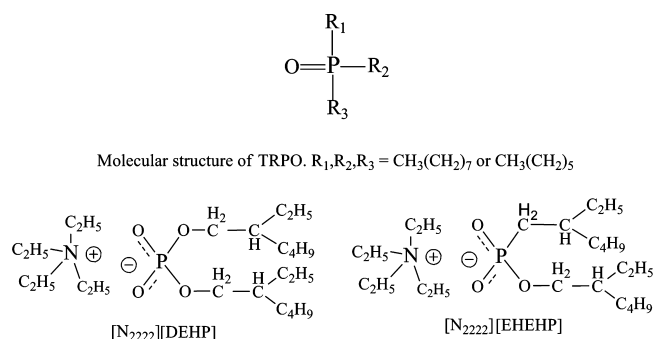
**Tetraethylammonium Mono-(2-ethylhexyl)2-ethylhexyl phosphonate  $\{[N_{2222}][EHEHP]\}$ .** A solution of  $[N_{2222}]OH$  in ethanol was prepared from 1 g of  $[N_{2222}]Cl$  (0.006 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A total of 1.84 g of HEH[EHP] (0.006 mol) was added to the  $[N_{2222}]OH$  solution. The mixture was then stirred at room temperature for 6 h until the solution became neutral. The ethanol and water were distilled off with an IKA RV10 rotary evaporator, and the product was dried at 70 °C under vacuum for 12 h to yield  $[N_{2222}][EHEHP]$  as a viscous liquid (2.39 g, 0.0055 mol, yield: 92%).

$^1H$  NMR ( $CDCl_3$ , ppm): 0.72–0.78 (m, 12H, 4CH<sub>3</sub>), 0.89–0.92 (m, 12H, 4CH<sub>3</sub>), 1.16–1.18 (m, 16H, 8CH<sub>2</sub>), 1.37 (m, 2H, 2CH), 3.31 (m, 8H, 4NCH<sub>2</sub>), 3.56 (m, 2H, CH<sub>2</sub>), 3.57 (m, 2H, OCH<sub>2</sub>).

$^{13}C$  NMR ( $CDCl_3$ , ppm): 7.63 (4CH<sub>3</sub>), 10.38 (CH<sub>3</sub>), 10.97 (CH<sub>3</sub>), 14.07 (CH<sub>3</sub>), 14.19 (CH<sub>3</sub>), 23.09 (CH<sub>2</sub>), 23.14 (CH<sub>2</sub>), 23.32 (CH<sub>2</sub>), 26.50 (CH<sub>2</sub>), 28.67 (CH<sub>2</sub>), 29.03 (CH<sub>2</sub>), 30.12 (CH<sub>2</sub>), 31.62 (CH<sub>2</sub>), 33.69 (CH<sub>2</sub>), 34.94 (CH), 40.69 (CH), 52.43 (4NCH<sub>2</sub>), 66.06 (OCH<sub>2</sub>).

**Extraction Experiments.** The extracting phases were prepared by dissolving the ABC-BILs in HPLC grade heptane (Aldrich). The aqueous lanthanide solutions were prepared by dissolving chloride salts in deionized water. Thermo Scientific iCAP 6500 Series inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was used to determine the concentration of lanthanide in the aqueous phase. Figure 2 indicates the structures of extractants investigated.

The extraction experiments were performed by mixing 5 mL of heptane containing ABC-BILs with 5 mL of aqueous lanthanide



**Figure 2.** Structures of the extractants used in this study.

solution for 60 min in a vibrating mixer. After centrifugation at 5000 rpm for 5 min, the aqueous phase was separated, and the concentration of the lanthanide ions was determined using ICP-AES. The concentration of lanthanide ion in the IL phase was calculated by a mass balance. The distribution coefficients ( $D_M$ ), synergy coefficient ( $R$ ), separation factor ( $SF$ ), and stripping ratio ( $S$ ) are defined as follows

$$D_M = \frac{C_i - C_f}{C_f} \quad (1)$$

$$R = \frac{D_{\text{mixture}}}{D_{\text{extractant-1}} + D_{\text{extractant-2}}} \quad (2)$$

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

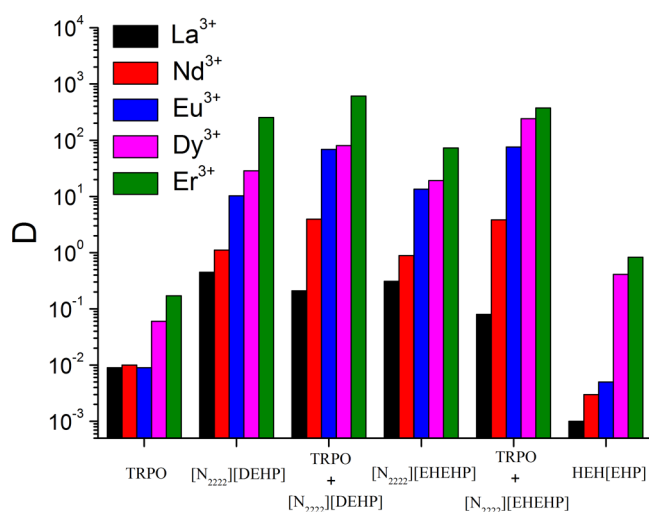
$$S = \frac{[M]_{\text{aq}}}{[M]_{\text{extr}}} \quad (4)$$

where  $C_i$  and  $C_f$  represent the initial and final concentration of lanthanide in aqueous phase,  $D_1$  and  $D_2$  are the distribution ratio of lanthanide 1 and 2,  $D_{\text{extractant-1}}$ ,  $D_{\text{extractant-2}}$ , and  $D_{\text{mixture}}$  are the distribution ratio of extractant 1, extractant 2, and their mixture, respectively.  $[M]_{\text{aq}}$  is the equilibrium concentration of metal ion in the stripping acid, and  $[M]_{\text{extr}}$  is initial concentration of metal ion in extracting phase, respectively. All the concentration values of REEs were measured in duplicate with the uncertainty within 5%.

Fourier transform-infrared spectroscopy (FT-IR) was carried out using a Bruker Tensor 27 IR spectrometer, and X-ray photoelectron spectroscopy (XPS) was carried out using a monochromatic X-ray photoelectron spectrometer (Thermo Fisher Scientific).

## RESULTS AND DISCUSSION

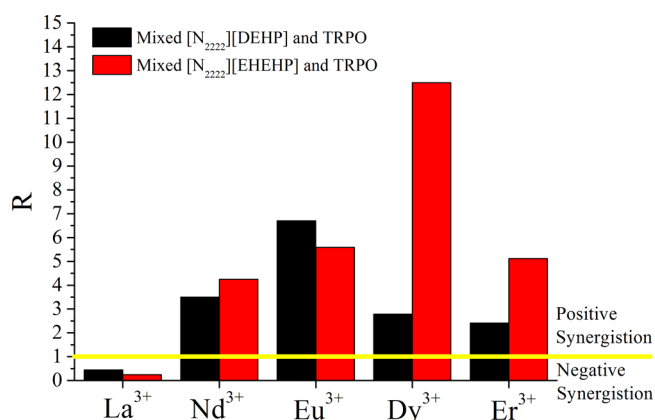
In this study, the extractabilities of individual  $[N_{2222}][\text{DEHP}]$ ,  $[N_{2222}][\text{EHEHP}]$ , and TRPO, HEH[EHP], together with mixed  $[N_{2222}][\text{DEHP}]$  and TRPO, mixed  $[N_{2222}][\text{EHEHP}]$ , and TRPO for lanthanides were compared. As shown in Figure 3, almost all the extracting sequences of lanthanides were from light to heavy lanthanide, which can be attributed to the ionic



**Figure 3.** Distribution coefficients of lanthanide extracted by TRPO,  $[N_{2222}][\text{DEHP}]$ , mixed  $[N_{2222}][\text{DEHP}]$  and TRPO,  $[N_{2222}][\text{EHEHP}]$ , mixed  $[N_{2222}][\text{EHEHP}]$  and TRPO, and HEH[EHP]. Molar concentration of the individual extractant was kept constant at 0.0045 mol/L,  $\text{REE}^{3+} = 0.0003$  mol/L for each lanthanide,  $\text{NaCl} = 0.2$  mol/L, and pH 4.76.

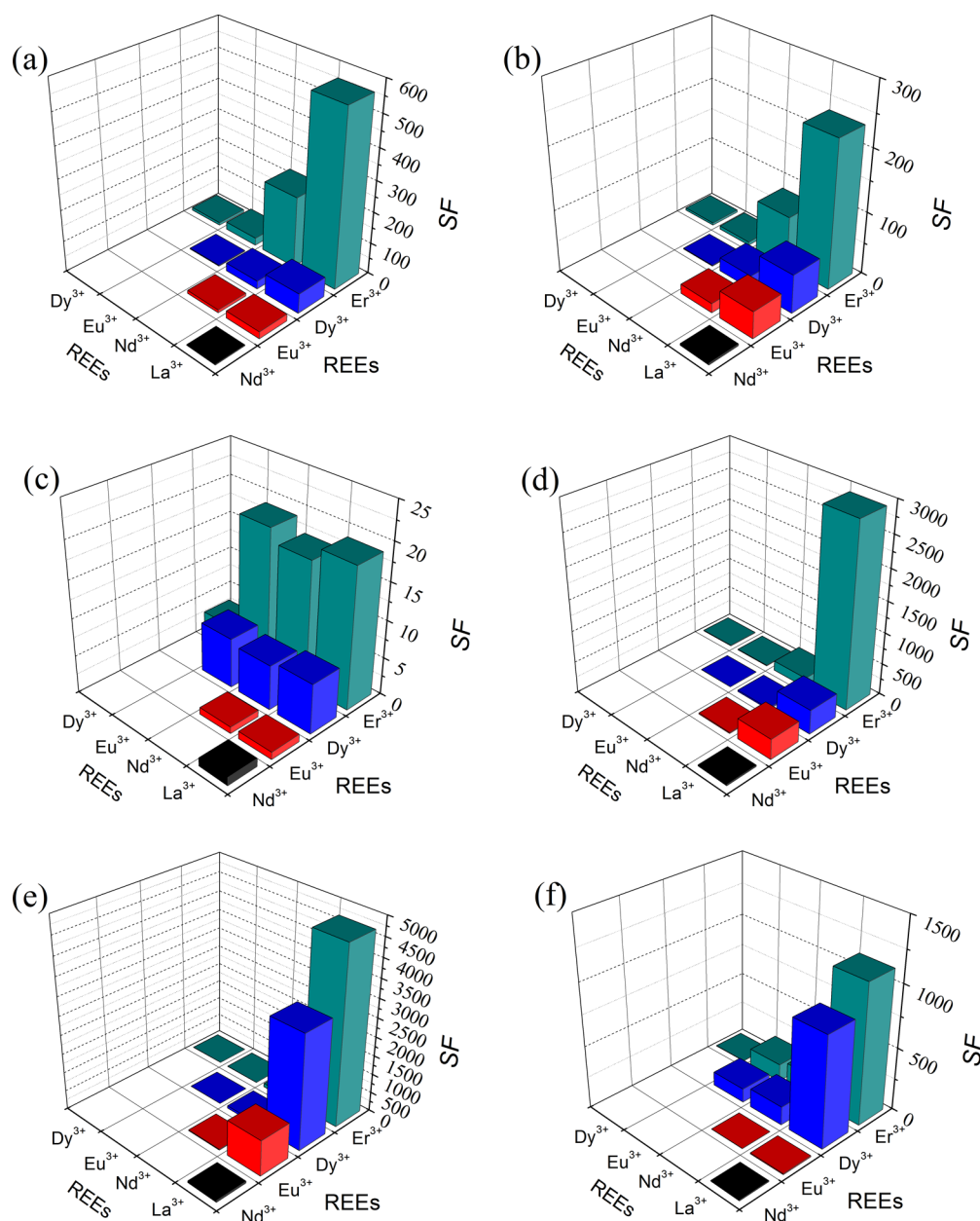
radius of each lanthanide.<sup>20</sup> As the ionic radius of the lanthanide decreases, the coordination strength of the functional group in the extractants for lanthanide increases, thus the extractability of the extractants for the lanthanide increased. Extracting capacities of the ABC-BILs for most lanthanides was  $[N_{2222}][\text{DEHP}] > [N_{2222}][\text{EHEHP}]$ . The sequences can be attributed to the fact that there are two ester groups in  $[\text{DEHP}]^-$ , whereas there is only one ester group in  $[\text{EHEHP}]^-$  (Figure 2). The electronegativity of the ester group contributed to the coordination of the P=O band with REEs.<sup>18</sup> For this extraction condition, TRPO revealed low distribution coefficients for all the lanthanides. Interestingly, distribution coefficients of the mixed ABC-BILs and TRPO were greater than those of individual extractants for almost all the lanthanides, except for  $\text{La}^{3+}$ , and even greater than the sum of distribution coefficients from contributions of individual extractants. This clearly reveals the positive synergistic extraction effects between the ABC-BILs and TRPO for  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Er}^{3+}$ . It is noticeable that extraction abilities of the synergistic systems for REEs were much higher than those from the most commonly used industrial extractants, that is, HEH[EHP].

Some synergistic extraction concerning TRPO for REEs have been reported. Synergistic extraction of trivalent rare earths from nitrate solutions using mixtures of bis(2,4,4-trimethylpentyl)dithiophosphinic acid and TRPO in xylene were investigated by Reddy et al.<sup>21</sup> Synergistic extraction and recovery of  $\text{Ce}^{4+}$  and fluorine from bastnaesite using a mixture of TRPO and HDEHP were discussed by Zhang et al.<sup>22</sup> In the current study, both of the mixed ABC-BILs and TRPO revealed positive synergistic effects for  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Er}^{3+}$  as shown in Figure 4. Synergistic coefficients of REEs can be



**Figure 4.** Synergy coefficients of lanthanide extracted by mixed  $[N_{2222}][\text{DEHP}]$  and TRPO and mixed  $[N_{2222}][\text{EHEHP}]$  and TRPO. Molar concentration of the individual extractant was kept constant at 0.0045 mol/L,  $\text{REE}^{3+} = 0.0003$  mol/L for each lanthanide,  $\text{NaCl} = 0.2$  mol/L, and pH 4.76.

attributed to the extractabilities of mixed extractants. As reported in previous work,<sup>15</sup> dimers of acidic extractants can be completely broken when the extractants are prepared as bifunctional ILs. The elimination of intermolecular hydrogen bonds from dimers will increase the coordination abilities of P=O bonds in HDEHP and HEH[EHP] to a considerable extent. Accordingly, the synergistic effects from P=O bonds in the mixed ABC-BILs are greater than those of mixed HDEHP and HEH[EHP].<sup>18</sup> Under the same extraction conditions, most



**Figure 5.** Separation factors of the extractants for lanthanides. (a)  $[N_{2222}][DEHP]$ , (b)  $[N_{2222}][EHEHP]$ , (c) TRPO, (d) mixed  $[N_{2222}][DEHP]$  and TRPO, (e) mixed  $[N_{2222}][EHEHP]$  and TRPO, and (f) HEH[EHP]. Molar concentration of the individual extractant was kept constant at 0.0045 mol/L,  $REE^{3+} = 0.0003$  mol/L for each lanthanide, NaCl = 0.2 mol/L, and pH 4.76.

of the synergy coefficients of REEs extracted by mixed  $[N_{2222}][EHEHP]$  and TRPO were higher than those of mixed  $[N_{2222}][DEHP]$  and TRPO. The difference between the synergy coefficients indicates that the synergistic effects of the ABC-BILs and TRPO could be optimized by adjusting the structures of ABC-BILs. Synergistic effects of the systems are more noticeable for middle lanthanides, such that the synergy coefficient of  $Eu^{3+}$  is the largest in the mixed  $[N_{2222}][DEHP]$  and TRPO system, and the synergy coefficient of  $Dy^{3+}$  is the largest in the mixed  $[N_{2222}][EHEHP]$  and TRPO system. Both mixed systems indicate positive synergistic effects for  $Nd^{3+}$ ,  $Eu^{3+}$ ,  $Dy^{3+}$ , and  $Er^{3+}$  and a negative synergistic effect for  $La^{3+}$ . The trend can be attributed to the mixed systems revealing higher extractabilities for  $Nd^{3+}$ ,  $Eu^{3+}$ ,  $Dy^{3+}$ , and  $Er^{3+}$  and lower extractabilities for  $La^{3+}$ . Competition of the REEs with extractants reveals the reversed synergistic effects, which implies

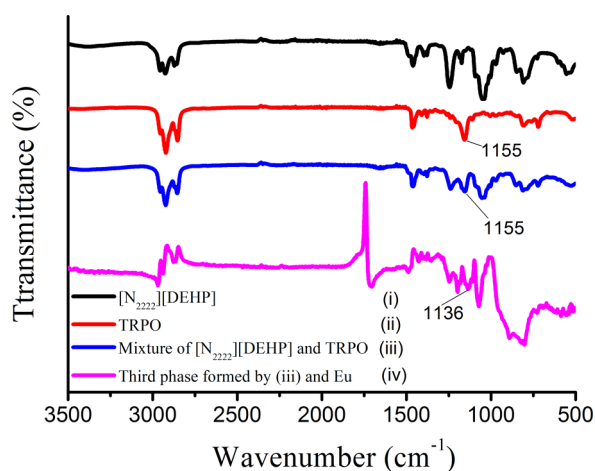
an advantage in the separation of light REEs ( $La^{3+}$ ) and middle to heavy REEs ( $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ).

According to the U.S. Department of Energy, short and medium-term criticality matrices,<sup>1</sup> the middle REEs and heavy REEs (such as  $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Nd^{3+}$ ), are far more important than light REEs (such as  $La^{3+}$ ) due to the current supply risk and importance to clean energy. Accordingly, the development of an effective extraction system for separating middle and heavy REEs from light REEs is very important. As mentioned above, the mixed ABC-BILs and TRPO systems reveal positive synergistic effects for  $Nd^{3+}$ ,  $Eu^{3+}$ ,  $Dy^{3+}$ , and  $Er^{3+}$  and a negative synergistic effect for  $La^{3+}$ . The reverse synergistic effects contribute to enhance the separation abilities between  $La^{3+}$  and the middle to heavy REEs ( $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ). To indicate the selectivities more clearly, separation factors of  $[N_{2222}][DEHP]$  (Figure 5a),  $[N_{2222}][EHEHP]$  (Figure 5b), TRPO (Figure 5c),

mixed  $[N_{2222}][DEHP]$  and TRPO (Figure 5d), mixed  $[N_{2222}][EHEHP]$  and TRPO (Figure 5e), and  $HEH[EHP]$  (Figure 5f) are compared.

As shown in Figure 5a and b, the separation factors of most REEs for the  $[N_{2222}][DEHP]$  system are greater than those of the  $[N_{2222}][EHEHP]$  system. Unlike the tendencies of  $[N_{2222}][DEHP]$  and  $[N_{2222}][EHEHP]$ , the sequence of separation factors in the mixed systems changes. As shown in Figure 5c, the lower extractabilities of the individual TRPO result in lower separation abilities for REEs. However, the combination of TRPO with the ABC-BILs contributes not only the extraction efficiencies but also the selectivities of REEs, especially for the separation factors between light REEs ( $La^{3+}$ ) and middle to heavy REEs ( $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ). As shown in Figure 5d and e, the mixed  $[N_{2222}][EHEHP]$  and TRPO reveals larger selectivities than the mixed  $[N_{2222}][DEHP]$  and TRPO. By comparing Figure 5a and b with Figure 5d and e, the increase in separation factors is 1 order of magnitude. In addition, the separation factors between light REEs and middle to heavy REEs from the synergistic systems formed by ABC-BILs and TRPO are mostly larger than those of  $HEH[EHP]$ .

The formation of a third phase is a common phenomenon in solvent extraction of lanthanides and actinide by neutral extractants.<sup>23,24</sup> The third phase occasionally appeared in this study when the concentrations of ABC-BILs were greatest. The formation of the third phase was attributed to the splitting of the organic phase into two phases, with the heavier one rich in metal-solvate and the lighter phase rich in diluent.<sup>23</sup> The formation of a third phase has also been reported in other IL-based extractions.<sup>25</sup> However, little investigation into the third phase for ABC-BIL-based extraction has been conducted. To investigate the structure of the third phase and obtain more information on the extracting complex, the third phase was prepared by equilibrating 0.02 mol/L  $[N_{2222}][DEHP]$  and 0.02 mol/L TRPO in heptane together with 0.02 mol/L  $Eu^{3+}$  in DI water under extraction conditions. Figure 6 shows the FTIR

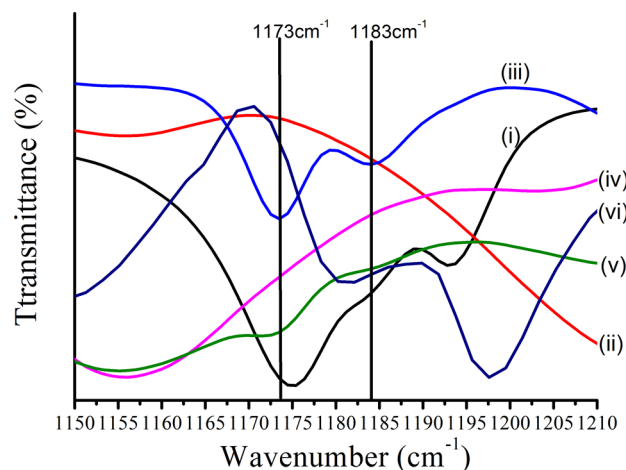


**Figure 6.** FTIR transmittance spectra of different reagent combinations.

spectra obtained from (i)  $[N_{2222}][DEHP]$ , (ii) TRPO, (iii) a mixture of  $[N_{2222}][DEHP]$  and TRPO, and (iv) the third phase formed by adding  $Eu^{3+}$  to the mixture of  $[N_{2222}][DEHP]$  and TRPO. A comparison of FTIR spectra reveals the stretching vibration of  $P=O$  from (iii)  $1155\text{ cm}^{-1}$  to (iv)  $1136\text{ cm}^{-1}$ . The

shift of FTIR reveals a strong interaction between  $P=O$  in  $[N_{2222}][DEHP]$  and TRPO with  $Eu^{3+}$ .

Figure 7 shows the FTIR spectra for different ABC-BILs, TRPO, and  $Eu^{3+}$  combinations. As shown in spectra (i) of



**Figure 7.** Part IR transmittance spectra of different systems: (i)  $[N_{2222}][Cl]$ , (ii) HDEHP, (iii)  $[N_{2222}][DEHP]$ , (iv) TOPO, (v) mixture of  $[N_{2222}][DEHP]$  and TOPO, and (vi) third phase formed by mixture of  $[N_{2222}][DEHP]$  and TOPO with  $Eu^{3+}$ .

Figure 7, there is mainly a stretching vibration of  $1175\text{ cm}^{-1}$  from  $[N_{2222}]^+$ . When the  $[N_{2222}][Cl]$  is prepared to  $[N_{2222}][DEHP]$ , as revealed in spectra (iii), the stretching vibration of  $1175\text{ cm}^{-1}$  from  $[N_{2222}]^+$  shifted to  $1183$  and  $1173\text{ cm}^{-1}$ . The two different stretching vibrations from  $[N_{2222}]^+$  in  $[N_{2222}][DEHP]$  can be attributed to the different electron distributions in  $[N_{2222}]^+$  due to the effect of  $[DEHP]^-$ . As shown in spectra (v), the stretching vibration at  $1183\text{ cm}^{-1}$  is weakened; however, the stretching vibration at  $1173\text{ cm}^{-1}$  is strengthened. This change can be attributed to the structure of mixed TRPO being similar to  $[DEHP]$ . In spectra (vi), both stretching vibrations at  $1183$  and  $1173\text{ cm}^{-1}$  disappeared, and a new stretching vibration at  $1180\text{ cm}^{-1}$  appeared, with the shift being attributed to the existence of complexation interactions between  $[N_{2222}]^+$  and  $Eu^{3+}$  in the third phase. It worth noting that there are no stretching vibrations of HDEHP (spectra (ii)) and TOPO (spectra (iv)) at  $1173$  and  $1183\text{ cm}^{-1}$ ; the shifts mentioned above reveal the importance of  $[N_{2222}]^+$  in the extraction process.

To investigate the individual effect of  $[N_{2222}][DEHP]$  on REEs extraction, 0.02 mol/L  $[N_{2222}][DEHP]$  in heptane and 0.02 mol/L  $Eu^{3+}$  in DI water were used to prepare the third phase. As indicated in Figure 8, XPS spectra indicate the existence of carbon, oxygen, and phosphorus, with just a slight amount of nitrogen in the third phase. The composition indicates that it was mainly the complexes formed by  $[DEHP]^-$  from the ABC-BILs that form the third phase. The IR and XPS spectra of the third phase clearly indicates the complexation between  $[DEHP]^-$  and rare earths. Unlike the ion association mechanism of ABC-BILs with quaternary ammonium with a longer carbon chain, the mechanism for  $[N_{2222}]^-$  type ABC-BILs may be a mixed mechanism due to the hydrophilicity of  $[N_{2222}]^-$ , that is, ion association and cation exchange.

Stripping is a key factor in evaluating the potential value of applying novel synergistic extraction systems. The REE-loaded extracting phases were prepared using 0.0045 mol/L ABC-

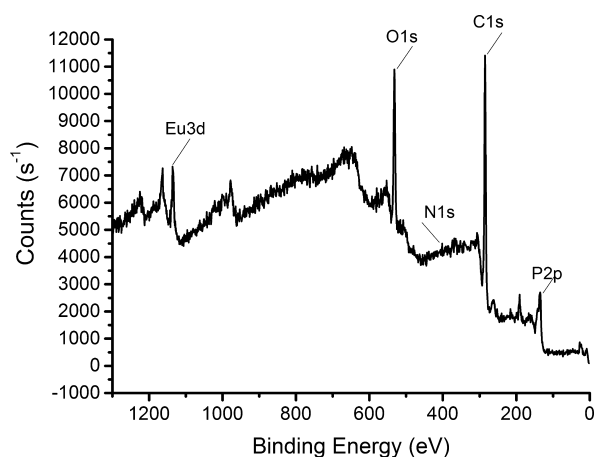


Figure 8. XPS spectra formed by  $[N_{2222}][DEHP]$  and  $Eu^{3+}$ .

BILs, 0.0045 mol/L TRPO, and 0.0003 mol/L REEs, and then the stripping by use of HCl was investigated. Figure 6 reveals that the stripping of  $La^{3+}$ ,  $Nd^{3+}$ , and  $Eu^{3+}$  can be achieved at lower acidities than those of  $Dy^{3+}$  and  $Er^{3+}$ . As mentioned above, the coordination strength of functional groups in the extractants for lanthanides increases with a decrease in lanthanide ionic radius. Hence, extracting complexes formed by the lanthanide with a larger ionic radius (i.e.,  $La^{3+}$ ,  $Nd^{3+}$ ,  $Eu^{3+}$ ) are easier to decompose using acid than those with a lower ionic radius (i.e.,  $Dy^{3+}$ ,  $Er^{3+}$ ). The stripping acidities of the mixed  $[N_{2222}][EHEHP]$  and TRPO system for the lanthanide are less than those of the mixed  $[N_{2222}][DEHP]$  and TRPO system. All the REEs could be fully stripped at a HCl concentration of 0.15 mol/L in the mixed  $[N_{2222}][EHEHP]$  and TRPO system. The stripping of REEs by  $H^+$  from HCl can be attributed to the competition between the complexation of REEs and  $H^+$  with the  $[N_{2222}][EHEHP]$  and TRPO. Lower stripping acidity of the system reveals advantages for potential industrial lanthanide separation.

## CONCLUSIONS

In summary, the synergistic extraction of ABC-BILs with TRPO for lanthanides was studied. This is the first report of synergistic extraction concerning a bifunctional IL extractant and a molecular extractant. Precursors of the ABC-BILs, that is, HDEHP and HEH[EHP], are the most commonly used industrial extractants for lanthanide separation. The development of ABC-BILs offers a promising strategy to reduce the annual production of millions of tons of saponification wastewater in the REEs separation industry. The combination of another industrial extractant, TRPO, with the ABC-BILs reveals interesting synergistic effects for lanthanide extraction and separation. Such synergistic effect contributes to increased abilities of the ABC-BILs for separating middle to heavy REEs ( $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ) from light REEs ( $La^{3+}$ ). The IR and XPS spectra of the third phase clearly confirms the complexation between  $[DEHP]^-$  from  $[N_{2222}][DEHP]$  and  $Eu^{3+}$ . The lanthanides extracted by mixed  $[N_{2222}][EHEHP]$  and TRPO can be effectively stripped at an acidity of 0.15 mol/L, which further confirms the applied potential of this novel kind of synergistic extraction for lanthanide separation.

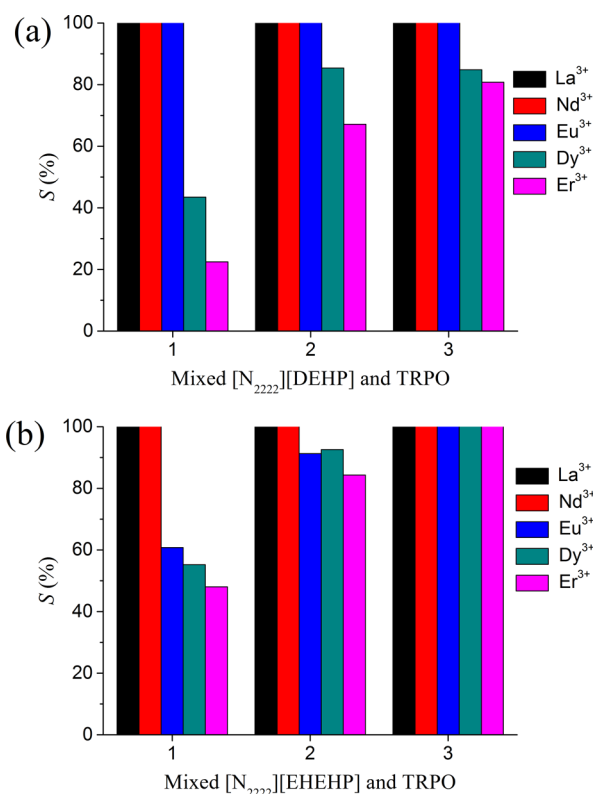


Figure 9. Stripping of lanthanide in synergistic extraction systems using HCl: (1) HCl = 0.05 mol/L, (2) HCl = 0.1 mol/L, and (3) HCl = 0.15 mol/L.

## ASSOCIATED CONTENT

### Supporting Information

The numerical data for Figure 5 a–f is shown in tabular format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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