

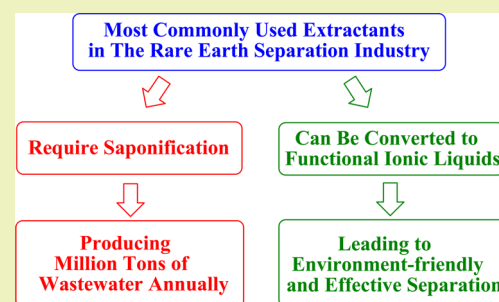
Development of Industrial Extractants into Functional Ionic Liquids for Environmentally Friendly Rare Earth Separation

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Supporting Information

ABSTRACT: Rare earth elements (REEs) are critical materials in many cutting-edge technology products. Di(2-ethylhexyl)phosphate (HDEHP) and 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) are the most commonly used industrial extractants in individual REE separation. However, acidic extractants, such as HDEHP and HEH[EHP], must be saponified for REEs separation, which often releases millions of tons of saponification wastewater into the environment annually. To develop effective and environmentally friendly extraction protocols for the REE separation industry, HDEHP and HEH[EHP] were prepared as acid–base coupling bifunctional ionic liquid extractants, and their extraction behavior and stripping properties for REEs were investigated.

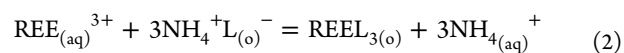
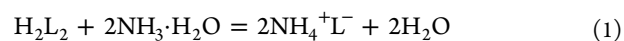
KEYWORDS: Rare earth elements, Ionic liquids, Separation, Acidic extractant, Saponification



INTRODUCTION

Rare earth elements (REEs) are a group of 17 elements in the periodic table, containing scandium, yttrium, and the 15 lanthanides. These elements have become critical materials in many cutting-edge technology products, such as catalysts, alloys, magnets, lasers, batteries, electronics, lighting, and telecommunications.¹ As the global demand for REEs increases, more and more attention is paid to REE separation.^{2,3} Among the numerous extractants for individual REE separation, di(2-ethylhexyl)phosphate (HDEHP) and 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) are most commonly used in industry.^{4,5} Tkac et al. indicated that in the presence of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), HDEHP dimer cleaved and interacted with CMPO through hydrogen bonding between POH and the phosphoryl group of CMPO. The formation of a new HDEHP–CMPO adduct significantly lowered the concentration of free CMPO available for complexation with lanthanide.⁶ Tasaki-Handa et al. studied the exchange of lanthanide(III) ions between a solution and a coordination polymer formed by HDEHP. Kinetic and selectivity studies suggested that a polymeric network of [Ln(DEHP)₃] had different characteristics to the corresponding monomeric complex.⁷ Braley et al. studied the extraction behavior of HEH[EHP] in the TALSPEAK (trivalent actinide–lanthanide separation by phosphorus reagent extraction from aqueous complexes) solvent extraction process.⁸ Wu et al. studied the adsorption behavior of La (III) with HEH[EHP] functionalized magnetic silica nanocomposite in batch experiments.⁹ To break hydrogen bonds in the dimers of extractant, and to avoid increasing the aqueous phase acidity by the H⁺ released during extraction, the acidic extractants (such as HDEHP and

HEH[EHP]), require saponification by NH₃·H₂O, NaOH, or Ca(OH)₂ in REEs separation, which often releases the corresponding ammonia-nitrogen, Na⁺ or Ca²⁺, wastewater into the environment. The following equations are the most used for ammonia saponification of acidic extractants for REE separation: eq 1 is the saponification of the acidic extractant; eq 2 is the extraction mechanism of the saponified acidic extractant for REE. It is seen that three NH₄⁺ ions will be released into the aqueous phase when one REE³⁺ ion is extracted by the saponified extractant.¹⁰



It has been reported that the REE industry produces over 20 million tons of wastewater annually, with ammonia nitrogen levels ranging from 300 to 5000 mg/L, exceeding the national emission standard by a dozen and even a hundred times in China, and more than 1.5 billion RMB (USD 0.24 billion) is required to deal with the environmental pollution each year.¹⁰ China produced 96 900 tons of separated rare earth products in 2011, accounting for more than 90% of the world's total output, which resulted in the creation of ten million tons of wastewater containing NH₄⁺ through the separation process. According to the China Ministry of Environmental Protection, rare earth producers must soon meet stricter environmental emission standards or be shut down.¹¹ In order to meet the worldwide

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need for REEs for high technology products, environmentally friendly and highly efficient separation technologies for REEs must be developed.

Ionic liquids (IL) are salts, generally liquid below 100 °C. Their potential as extractants is enhanced by the fact that their physical and chemical properties may be tuned by varying the structures of both the cations and anions that comprise the ILs. As demonstrated by the growing number of publications and patents, ILs are attracting interest in both academic research and industrial practice. Many applications of ILs at industrial scale have been established, e.g. BASF (BASIL, aluminum plating, cellulose dissolution), Institut Français du Pétrole (Difasol), Degussa (paint additives), Linde (hydraulic ionic liquid compressor), Pionics (batteries), and G24i (solar cells).¹² IL-based extraction is a novel separation strategy that applies ILs instead of VOCs as diluents and/or extractants. ILs have such properties that make them particularly suitable for solvent extraction, for example, their low volatility and combustibility, wide liquidus range, thermal stability, functional groups, high conductivity, and a wide electrochemical window. These all allow for high efficiency in both aqueous and nonaqueous processes such as extraction, adsorption, and electrodeposition.¹³ The application of IL-based extraction for metal ion separation has been investigated with interesting results.^{14–16} Sun et al. first reported the inner synergistic effect of acid–base coupling bifunctional ionic liquid extractant (ABC-BIL) for extracting Eu³⁺.¹⁷ The inner synergistic effect comes from both the cation and anion of ABC-BIL. Many ABC-BILs composed of quaternary ammonium cation and deprotonated organic (phosphoric) carboxylic anion were shown to possess an inner synergistic effect for Eu³⁺. The inner synergistic effect reveals some advantages. For example, extraction capacities of widely used extractants can be enhanced by converting them into ABC-BILs. Moreover, saponification wastewater from the application of acidic extractants can be avoided by using ABC-BILs, which is of great value to any environmentally friendly extraction process.¹⁷ The extraction performance of some novel functional IL extractants in IL diluents have been investigated for REEs separation with interesting results.^{18–20} However, the cost of the IL diluents are still too expensive to be used in REEs separation industry. To develop effectively and environment-friendly ABC-BIL based extraction protocol for REEs separation industry, this paper discusses the result of five ABC-BILs prepared using the most widely used REE extractants, namely HDEHP and HEH[EHP]. Cations of the ABC-BILs are different quaternary ammoniums, and anions of the ABC-BIL are deprotonated HDEHP and deprotonated HEH[EHP]. Extractivities and selectivities of the HDEHP and HEH[EHP] type ABC-BILs for REEs were studied in a traditional industrial diluent, heptane.

MATERIALS AND METHODS

Reagents. Tetraethylammonium chloride ([N₂₂₂₂]Cl), tetrabutylammonium chloride ([N₄₄₄₄]Cl), tetrahexylammonium bromide ([N₆₆₆₆]Br), and tetraoctylammonium bromide ([N₈₈₈₈]Br) were 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). The ABC-BILs were prepared according to previously published work,¹⁹ with detailed procedures for the preparation given in section 2.3. Rare earth chlorides were purchased from Aldrich.

Analysis. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained in CDCl₃ with a Bruker AV III 400HD NMR

spectrometer. The extracting phases were prepared by dissolving the ABC-BILs in HPLC grade heptane (Aldrich). The aqueous REE solutions were prepared by dissolving chloride salts in the deionized water. A Thermo Scientific iCAP 6500 Series inductively coupled plasma–atomic emission spectroscopy (ICP-AES) instrument was used to determine the concentration of REEs in the aqueous phase. Figure 1 shows the structure and abbreviations of different ABC-BILs in this study.

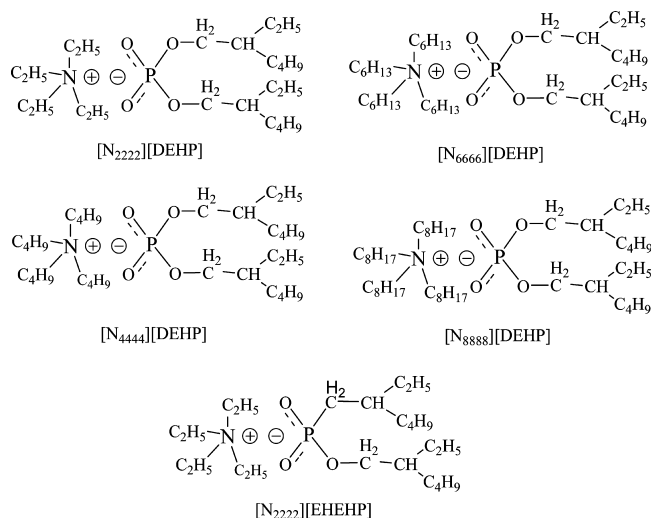


Figure 1. Structures of the ABC-BILs investigated in this study.

Synthesis of ABC-BILs. The ABC-BILs were prepared using a combination of ion-exchange and neutralizing reactions.¹⁹

Tetraethylammonium Di(2-ethylhexyl)phosphate {[N₂₂₂₂]-[DEHP]}. A solution of [N₂₂₂₂]OH in ethanol was prepared from 1 g of [N₂₂₂₂]Cl (0.006 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A 1.94 g portion of HDEHP (0.006 mol) was added to the [N₂₂₂₂]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 [N₂₂₂₂][DEHP] as a viscous liquid (2.48 g, 0.0055 mol, yield: 92%).

- ¹H NMR (CDCl₃, ppm): 0.70–0.76 (m, 12H, 4CH₃), 1.12–1.15 (m, 12H, 4CH₃), 1.17–1.26 (m, 16H, 8CH₂), 1.34 (m, 2H, 2CH), 3.32 (m, 8H, 4NCH₂), 3.55 (m, 4H, 2OCH₂).
- ¹³C NMR (CDCl₃, ppm): 7.57 (4CH₃), 10.91 (2CH₃), 14.02 (2CH₃), 23.05 (2CH₂), 23.30 (2CH₂), 28.98 (2CH₂), 30.09 (2CH₂), 40.40 (2CH), 52.32 (4NCH₂), 67.19 (2OCH₂).

Tetrabutylammonium Di(2-ethylhexyl)phosphate {[N₄₄₄₄]-[DEHP]}. A solution of [N₄₄₄₄]OH in ethanol was prepared from 1.39 g of [N₄₄₄₄]Cl (0.005 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A 1.61 g portion of HDEHP (0.005 mol) was added to the [N₄₄₄₄]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 [N₄₄₄₄][DEHP] as a colorless viscous liquid (2.59 g, 0.0046 mol, yield: 92%).

- ¹H NMR (CDCl₃, ppm): 0.80–0.81 (m, 12H, 4CH₃), 0.91–0.91 (m, 12H, 4CH₃), 1.19–1.44 (m, 32H, 16CH₂), 1.59 (m, 2H, 2CH), 3.31 (m, 8H, 4NCH₂), 3.63 (m, 4H, 2OCH₂).
- ¹³C NMR (CDCl₃, ppm): 10.95 (4CH₃), 13.66 (2CH₃), 14.01 (2CH₃), 19.71 (4CH₂), 23.14 (2CH₂), 23.32 (2CH₂), 24.07 (4CH₂), 29.06 (2CH₃), 30.12 (2CH₂), 40.43 (2CH), 58.70 (4NCH₂), 67.27 (2OCH₂).

Tetrahexylammonium Di(2-ethylhexyl)phosphate {[N₆₆₆₆]-[DEHP]}. A solution of [N₆₆₆₆]OH in ethanol was prepared from 2 g

of $[N_{666}]Br$ (0.0046 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A 1.49 g portion of HDEHP (0.0046 mol) was added to the $[N_{666}]OH$ 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 $[N_{666}][DEHP]$ as a viscous liquid (2.86 g, 0.0042 mol, yield: 92%).

- 1H NMR ($CDCl_3$, ppm): 0.85 (m, 24H, $8CH_3$), 1.21–1.35 (m, 40H, $20CH_2$), 1.42 (m, 2H, 2CH), 1.62 (m, 8H, $4CH_2$), 3.31 (m, 8H, $4NCH_2$), 3.64 (m, 4H, $2OCH_2$).
- ^{13}C NMR ($CDCl_3$, ppm): 10.95 ($4CH_3$), 13.85 ($2CH_3$), 14.11 ($2CH_3$), 22.18 ($4CH_2$), 22.38 ($2CH_2$), 23.17 ($4CH_2$), 23.33 ($2CH_2$), 26.05 ($4CH_2$), 29.08 ($2CH_2$), 30.12 ($2CH_2$), 31.27 ($4CH_2$), 40.44 ($2CH$), 58.91 ($4NCH_2$), 67.29 ($2OCH_2$).

Tetraoctylammonium Di(2-ethylhexyl)phosphate $\{[N_{888}][DEHP]\}$. A solution of $[N_{888}]OH$ in ethanol was prepared from 2.73 g of $[N_{888}]Br$ (0.005 mol) using a Dowex Monosphere 550A (OH) anion exchange resin. A 1.61 g portion of HDEHP (0.005 mol) was added to the $[N_{888}]OH$ 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 $[N_{888}][DEHP]$ as a viscous liquid (3.7 g, 0.0047 mol, yield: 94%).

- 1H NMR ($CDCl_3$, ppm): 0.84 (m, 24H, $8CH_3$), 1.20–1.34 (m, 56H, $28CH_2$), 1.38 (m, 2H, 2CH), 1.61 (m, 8H, $4CH_2$), 3.30 (m, 8H, $4NCH_2$), 3.64 (m, 4H, $2OCH_2$).
- ^{13}C NMR ($CDCl_3$, ppm): 10.95 ($4CH_3$), 13.98 ($2CH_3$), 14.11 ($2CH_3$), 22.02 ($4CH_2$), 22.54 ($4CH_2$), 23.18 ($2CH_2$), 23.32 ($2CH_2$), 26.36 ($4CH_2$), 29.00 ($2CH_2$), 29.08 ($2CH_2$), 29.12 ($4CH_2$), 30.11 ($4CH_2$), 31.63 ($4CH_2$), 40.43 ($2CH$), 58.88 ($4NCH_2$), 67.27 ($2OCH_2$).

Tetraethylammonium Mono-(2-ethylhexyl) 2-Ethylhexyl Phosphate $\{[N_{2222}][EHEHP]\}$. 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 1.84 g portion 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, $4CH_3$), 0.89–0.92 (m, 12H, $4CH_3$), 1.16–1.18 (m, 16H, $8CH_2$), 1.37 (m, 2H, 2CH), 3.31 (m, 8H, $4NCH_2$), 3.56 (m, 2H, CH_2), 3.57 (m, 2H, OCH_2).
- ^{13}C NMR ($CDCl_3$, ppm): 7.63 ($4CH_3$), 10.38 (CH_3), 10.97 (CH_3), 14.07 (CH_3), 14.19 (CH_3), 23.09 (CH_2), 23.14 (CH_2), 23.32 (CH_2), 26.50 (CH_2), 28.67 (CH_2), 29.03 (CH_2), 30.12 (CH_2), 31.62 (CH_2), 33.69 (CH_2), 34.94 (CH), 40.69 (CH), 52.43 ($4NCH_2$), 66.06 (OCH_2).

Extraction Experiments. The extraction experiments were performed by contacting 5 mL of heptane containing ABC-BILs with 5 mL of aqueous REE 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 REE ions was determined using ICP-AES. The concentration of REE ions in the IL phase was calculated by mass balance. The distribution coefficients (D_M), separation factor (SF), and stripping ratio (S) are defined as follows:

$$D_M = \frac{C_i - C_f}{C_f} \quad (3)$$

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

$$S = \frac{[M]_{aq}}{[M]_{Ext}} \quad (5)$$

Where, C_i and C_f represent the initial and final concentration of REE in aqueous phase, D_1 and D_2 are the distribution ratio of REE 1 and 2, $[M]_{aq}$ is the equilibrium concentration of the metal ion in the stripping acid, and $[M]_{Ext}$ is the initial concentration of the metal ion in the extracting phase, respectively. All the concentration values of REEs were measured in duplicate with the uncertainty within 5%.

RESULTS AND DISCUSSION

Effect of ABC-BIL Cation on REE Extractability and Selectivity. In the previous studies of ABC-BILs in organic molecule diluents,^{17,21–23} almost all the IL extractants were prepared with the same cation, tricaprylmethylammonium ($[A336]^+$). In this work, a comparison of the distribution ratios of REEs extracted by DEHP-type ABC-BILs containing different cations is made. As shown in Figure 1, the ammonium cations contain the same four alkyl groups, i.e., $[N_{2222}]^+$, $[N_{4444}]^+$, $[N_{6666}]^+$, and $[N_{8888}]^+$. All the anions of the ABC-BILs used in this section are $[DEHP]^-$, and the extractabilities of the DEHP-type ABC-BILs with different cations for REEs separations were quite different (Figure 2). The distribution

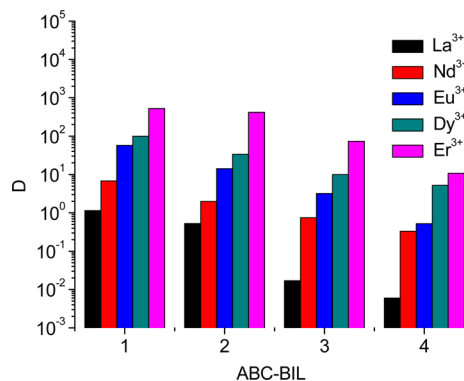


Figure 2. Distribution ratios of REEs extracted by (1) $[N_{2222}][DEHP]$, (2) $[N_{4444}][DEHP]$, (3) $[N_{6666}][DEHP]$, (4) $[N_{8888}][DEHP]$. The molar concentration of the ionic liquid was kept constant at 0.005 mol/L, and the REE³⁺ concentration was maintained at 0.0005 mol/L for each REE. NaCl = 0.1 mol/L. The equilibrium pH values of the aqueous phase were 4.98, 4.86, 4.92, and 4.95, respectively.

ratio sequence of the ABC-BILs for REEs was $[N_{2222}][DEHP] > [N_{4444}][DEHP] > [N_{6666}][DEHP] > [N_{8888}][DEHP]$. This sequence can be attributed to the different structures of the cations. As the cation's alkyl chain length increases, the steric hindrance of ABC-BILs increases accordingly, and the extractabilities of ABC-BILs for REEs decrease. As for the extraction sequence of REEs from the ABC-BILs, the REEs extraction sequence was $La^{3+} < Nd^{3+} < Eu^{3+} < Dy^{3+} < Er^{3+}$. The sequence is the inverse of the ionic radius of the REEs, i.e., La^{3+} (103 pm) $>$ Nd^{3+} (98.3 pm) $>$ Eu^{3+} (94.7 pm) $>$ Dy^{3+} (94.2 pm) $>$ Er^{3+} (89 pm).²⁴ The sequence can be attributed to the coordination abilities of the functional groups in the ABC-BILs. As the ionic radius of REEs decreases, the coordination strength of ABC-BILs with REE increases and the extractabilities of ABC-BILs for REEs increase.

Although the bigger steric hindrance decreases the distribution ratios of REEs, steric hindrance can increase the selectivity of REEs at the same time. The extractability and selectivity will always have an inverse relationship. As shown in

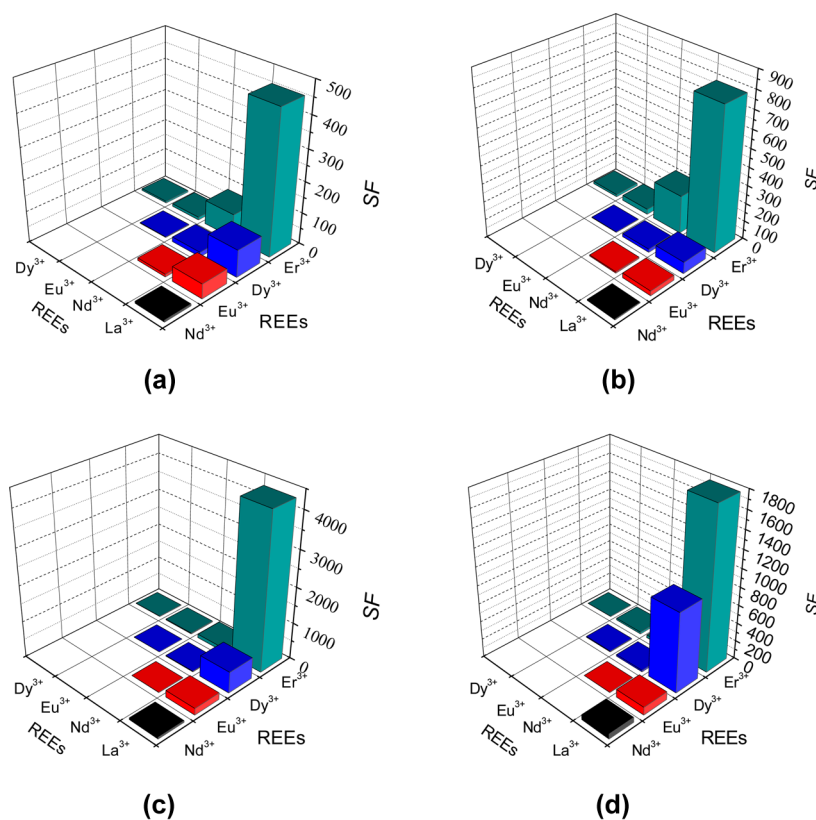


Figure 3. Separation factors of REEs extracted by (a) $[N_{2222}][DEHP]$, (b) $[N_{4444}][DEHP]$, (c) $[N_{6666}][DEHP]$, (d) $[N_{8888}][DEHP]$. The molar concentration of the ionic liquid was kept constant at 0.005 mol/L, and the REE^{3+} concentration was maintained at 0.0005 mol/L for each REE. $NaCl = 0.1$ mol/L. The equilibrium pH values of the aqueous phase were 4.98, 4.86, 4.92, and 4.95, respectively.

Figure 3, the separation factor sequence of REEs extracted by the ABC-BILs was $[N_{2222}][DEHP] < [N_{4444}][DEHP] < [N_{6666}][DEHP]$. It is worth mentioning that the selectivities of $[N_{8888}][DEHP]$ for REEs were less than those of $[N_{6666}][DEHP]$. It appears that $[N_{6666}][DEHP]$ possesses the best selectivities for the REEs. An initial conclusion that can be reached here is that the cations of ABC-BILs with the longest or shortest alkyl chains are all not good for the REE selectivities of ABC-BILs. The best structure of ABC-BILs for separating REEs must be optimized.

Effect of ABC-BIL Anion on REE Extractability and Selectivity. As mentioned above, the extractabilities of $[N_{2222}][DEHP]$ for REEs were better than those of the other ABC-BILs with larger cations. Accordingly, $[N_{2222}][EHEHP]$ was prepared for a comparison with $[N_{2222}][DEHP]$ on REE separation. As can be seen in Figure 4, the extractabilities of $[N_{2222}][EHEHP]$ for REEs were less than those of $[N_{2222}][DEHP]$. The effect can be attributed to the fact that there are two ester groups in $[DEHP]^-$, however, there is only one ester group in $[EHEHP]^-$. The electronegativity of the ester group contributes to the coordination of the $P=O$ bond with REEs. As a result, the extraction abilities of $[N_{2222}][DEHP]$ for REEs were stronger than those of $[N_{2222}][EHEHP]$. In addition, the extraction sequences of $[N_{2222}][EHEHP]$ for REEs are the same as those of the DEHP-type ILs.

The selectivity of $[N_{2222}][EHEHP]$ for the REEs was better than those of the $[N_{2222}][DEHP]$. As shown in Figure 5, the separation factors of REEs extracted by $[N_{2222}][EHEHP]$ were almost twice as much as those extracted by $[N_{2222}][DEHP]$. The better separation performance reveals that $[N_{2222}][EHEHP]$ may be more useful for the REE separation industry

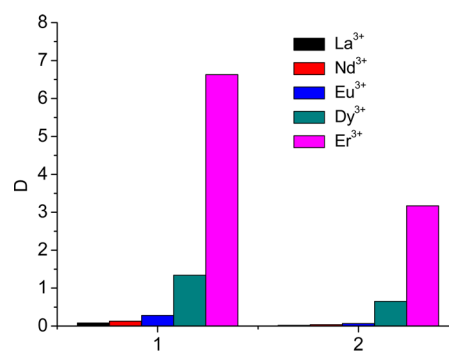


Figure 4. Distribution ratios of REEs extracted by (1) $[N_{2222}][DEHP]$ and (2) $[N_{2222}][EHEHP]$. $[N_{2222}][DEHP] = [N_{2222}][EHEHP] = 0.0035$ mol/L, $REE^{3+} = 0.0005$ mol/L for each REE ion, $NaCl = 0.1$ mol/L. The equilibrium pH values of the aqueous phase were 4.96 and 4.98, respectively.

since the higher separation factors contribute to decreasing the number of extraction stages for individual REEs.

Effect of pH on the Extractability and Selectivity of the ABC-BILs for REEs. To investigate the effect of acidity on the extraction behavior of ABC-BILs, the REE distribution ratios extracted by $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$ were studied at different initial pH values, i.e., 4.09, 2.82, 1.06. As can be seen in Figure 6, the distribution ratios of all the REE ions decrease as the acidities of the aqueous phase increased. The sequence is $Er^{3+} > Dy^{3+} > Eu^{3+} > Nd^{3+} > La^{3+}$; that is, the REEs extracted by ABC-BILs with higher distribution ratios decrease to a greater extent. The decrease of the REE distribution ratio can be attributed to the complexation competition between the

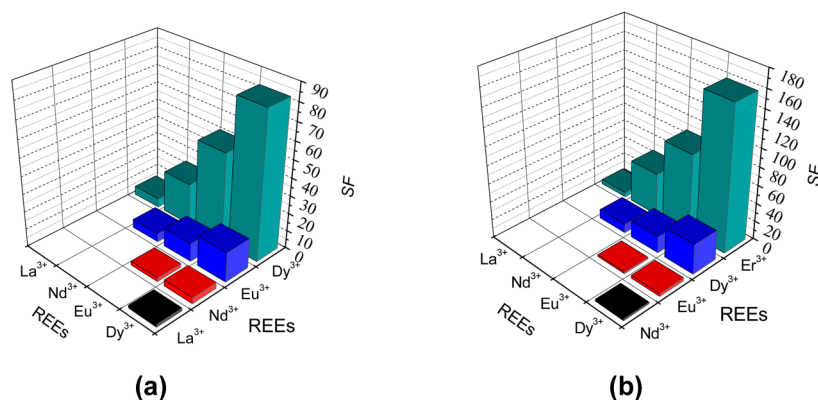


Figure 5. Separation factors of REEs extracted by (a) [N₂₂₂₂][DEHP] and (b) [N₂₂₂₂][EHEHP]. [N₂₂₂₂][DEHP] = [N₂₂₂₂][EHEHP] = 0.0035 mol/L, REE³⁺ = 0.0005 mol/L for each REE ion, NaCl = 0.1 mol/L. The equilibrium pH values of the aqueous phase were 4.96 and 4.98, respectively.

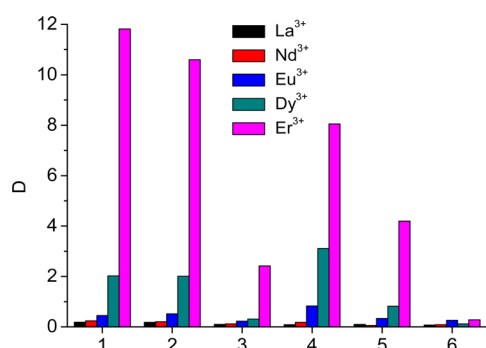


Figure 6. Acidity effect on distribution ratios of REEs extracted by [N₂₂₂₂][DEHP] and [N₂₂₂₂][EHEHP]. [N₂₂₂₂][DEHP] = [N₂₂₂₂][EHEHP] = 0.004 mol/L, REE³⁺ = 0.0005 mol/L for each rare earth ion, NaCl = 0.1 mol/L: (1) [N₂₂₂₂][DEHP], pH = 4.09; (2) [N₂₂₂₂][DEHP], pH = 2.82; (3) [N₂₂₂₂][DEHP], pH = 1.86; (4) [N₂₂₂₂][EHEHP], pH = 4.09; (5) [N₂₂₂₂][EHEHP], pH = 2.82; (6) [N₂₂₂₂][EHEHP], pH = 1.86. The equilibrium pH values of the aqueous phase were 4.38, 3.26, 2.16, 4.41, 3.28, and 2.19, respectively.

REE ion and a proton in the aqueous phase with the ABC-BIL in the extracting phase. In addition, it is clear that the magnitude of the decrease in REE distribution ratio from pH 2.82 (Figure 6 (2, 5)) to pH 1.86 (Figure 6 (3, 6)) is larger than that from pH 4.09 (Figure 6 (1, 4)) to pH 2.82 (Figure 6 (2, 5)). The difference reveals that the decrease in distribution ratio is due to the increased concentration of protons in the aqueous phase. That is, the increase of protons in aqueous phase from $10^{-2.82}$ to $10^{-1.86}$ mol/L is greater than that from $10^{-4.09}$ to $10^{-2.82}$ mol/L. From the comparison of REE distribution coefficients extracted by [N₂₂₂₂][DEHP] and [N₂₂₂₂][EHEHP] at different acidity, almost all the distribution ratios extracted by [N₂₂₂₂][DEHP] are larger than those of [N₂₂₂₂][EHEHP]. This trend is the same as that shown in Figure 4.

As can be seen in Figure 7, the separation factors of REEs extracted by [N₂₂₂₂][DEHP] and [N₂₂₂₂][EHEHP] decrease with increasing acidity of the aqueous phase. At higher pH value (4.09), the separation factors of [N₂₂₂₂][EHEHP] for REEs were greater than those of [N₂₂₂₂][DEHP]. However, the separation factors of [N₂₂₂₂][EHEHP] for REEs were less than those of [N₂₂₂₂][DEHP] at the lower pH value of 1.86. The results indicate that selectivities of the ABC-BILs for REEs

depend not only on the structures of extractants but also the different aqueous phase acidity.

Effect of Salting on ABC-BILs' Extractability and Selectivity. To investigate the effect of a salting agent on the REE extraction, the distribution ratios of REEs extracted by [N₂₂₂₂][EHEHP] and [N₂₂₂₂][DEHP] with 0.5 and 1 mol/L sodium chloride were compared. As can be seen in Figure 8, almost all the distribution ratios of REEs extracted by the ABC-BILs increased as the salting agent concentration increased. The increase in distribution ratios may be attributed to the involvement of chloride ions in the extraction mechanism process. In addition, all the distribution ratios of REEs extracted by [N₂₂₂₂][EHEHP] were less than those extracted by [N₂₂₂₂][DEHP]. The tendency indicated that the addition of salting agents in aqueous phase could not change the different extraction behaviors of [N₂₂₂₂][EHEHP] and [N₂₂₂₂][DEHP].

As shown in Figure 9, the additional of sodium chloride decreased the separation factors between the REEs in both [N₂₂₂₂][EHEHP] and [N₂₂₂₂][DEHP] based extraction systems. Moreover, the decrease of the separation factors was significant, almost 3-fold in the ABC-BILs. The tendency revealed that the addition of more salting agents to aqueous phase was not a good method by which to improve the selectivities of ABC-BILs for REEs. Since selectivity is more important for REEs separation system than extractability, the high salting agent concentration seems not to be advantageous for the ABC-BIL based systems. More optimization of salting agent concentration needs to be conducted for differential REE separation systems based on ABC-BILs.

Stripping Properties of ABC-BILs for REEs. Stripping is an important property for evaluating an extractant for industrial REEs separation application. In this study, the REE loaded extracting phase was prepared using 0.0035 mol/L [N₂₂₂₂][EHEHP] and 0.0005 mol/L REEs, then the stripping acidities using HCl were investigated. As can be seen in Figures 10 and 11, the stripping of light REEs (La³⁺, Nd³⁺) was at lower concentrations of HCl than those of the middle (Eu³⁺, Dy³⁺) and heavy (Er³⁺) REEs in both [N₂₂₂₂][EHEHP] and [N₂₂₂₂][DEHP] systems. Such a tendency can be attributed to the fact that the coordination abilities of ABC-BILs with light REEs (La³⁺, Nd³⁺) are weaker than those of the middle (Eu³⁺, Dy³⁺) and heavy (Er³⁺) REEs. As a result, the extracting complexes formed by ABC-BILs with light REEs were easier to decompose at high acidity than those formed with middle and heavy REEs. In addition, the stripping acidities of the

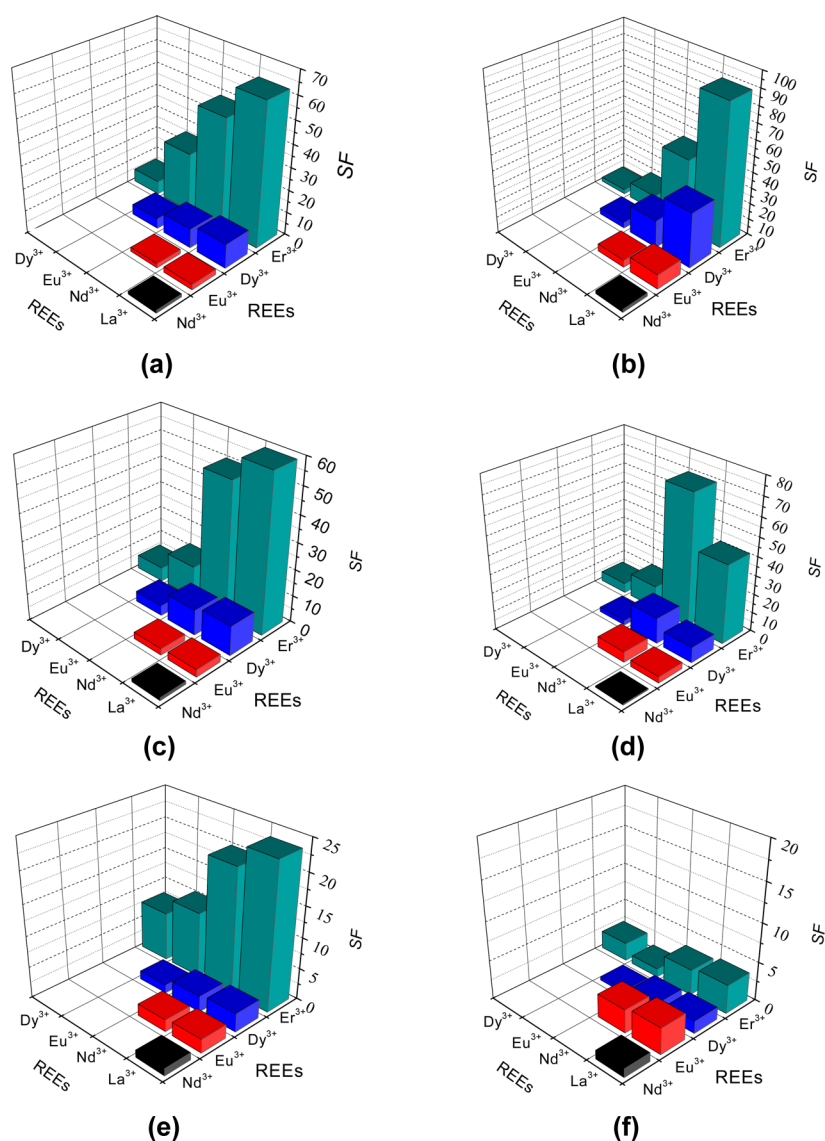


Figure 7. Acidity effect on separation factors of REEs extracted by [N₂₂₂₂][DEHP] and [N₂₂₂₂][EHEHP]. [N₂₂₂₂][DEHP] = [N₂₂₂₂][EHEHP] = 0.004 mol/L, REE³⁺ = 0.0005 mol/L for each rare earth ion, NaCl = 0.1 mol/L: (a) [N₂₂₂₂][DEHP], pH = 4.09; (b) [N₂₂₂₂][DEHP], pH = 2.82; (c) [N₂₂₂₂][DEHP], pH = 1.86; (d) [N₂₂₂₂][EHEHP], pH = 4.09; (e) [N₂₂₂₂][EHEHP], pH = 2.82; (f) [N₂₂₂₂][EHEHP], pH = 1.86. The equilibrium pH values of the aqueous phase were 4.38, 3.26, 2.16, 4.41, 3.28, and 2.19, respectively.

[N₂₂₂₂][EHEHP] based system for the REEs were less than those of the [N₂₂₂₂][DEHP] based system. All the REEs could be stripped at a HCl concentration of 0.09 mol/L in the [N₂₂₂₂][EHEHP] based system. In comparison with the [N₂₂₂₂][EHEHP] based system, Eu³⁺, Dy³⁺, and Er³⁺ cannot be fully stripped even at a HCl concentration of 0.09 mol/L in the [N₂₂₂₂][DEHP] based system. As mentioned previously, the lower stripping property of [N₂₂₂₂][DEHP] can be attributed to its coordination abilities with REEs from the P=O bond being stronger than those of [N₂₂₂₂][EHEHP]. In REE separation industry, the stripping ability of the extractant is very important. Since the stripping abilities of HEH[EHP] for REEs are better than HDEHP, HEH[EHP] is more widely used. However, the stripping of the heavy REE is still difficult for HEH[EHP]. As a result, the acid must be used in high concentrations for the REE stripping in the HEH[EHP] system.⁴ The application of acid at high concentration results in serious environmental concerns. In this study, all the loaded REEs could be stripped using 0.09 mol/L HCl. The low

stripping acidity is another important environmental advantage of the ABC-BIL extraction protocol.

CONCLUSIONS

To summarize this work, the most widely used industrial extractants for REEs, (i.e., HDEHP and HEH[EHP]) were prepared as ABC-BILs, and their extraction behaviors for REEs were investigated. The application of ABC-BILs can be used to reduce the pollution of saponification wastewater from the application of HDEHP and HEH[EHP] in industrial REE separations. The following conclusions can be reached from this study:

- (1) As the alkyl chains of cations in ILs increased, the steric hindrances of ABC-BILs increased. Accordingly, the distribution ratios of REEs decreased and the separation factors of REEs increased.
- (2) The extractabilities of [N₂₂₂₂][EHEHP] for REEs were less than those of [N₂₂₂₂][DEHP]; however, the

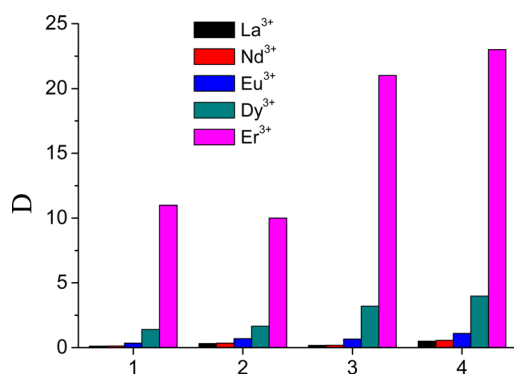


Figure 8. Effect of salting on the distribution ratios of REEs extracted by $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$. $[N_{2222}][DEHP] = [N_{2222}][EHEHP] = 0.004$ mol/L, $REE^{3+} = 0.0005$ mol/L for each rare earth ion: (1) $[N_{2222}][EHEHP]$, NaCl = 0.5 mol/L, equilibrium pH = 4.69; (2) $[N_{2222}][EHEHP]$, NaCl = 1 mol/L, equilibrium pH = 4.66; (3) $[N_{2222}][DEHP]$, NaCl = 0.5 mol/L, equilibrium pH = 4.64; (4) $[N_{2222}][DEHP]$, NaCl = 1 mol/L, equilibrium pH = 4.62.

selectivities of $[N_{2222}][EHEHP]$ for REEs were greater than those of $[N_{2222}][DEHP]$ for REEs at lower acidity.

- (3) The distribution ratios of all the REE ions in the $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$ systems decreased as the acidities of the aqueous phase increased.
- (4) Almost all the distribution ratios of REEs extracted by ABC-BILs increased as the salting agent concentration in the aqueous phase increased. The increase of distribution

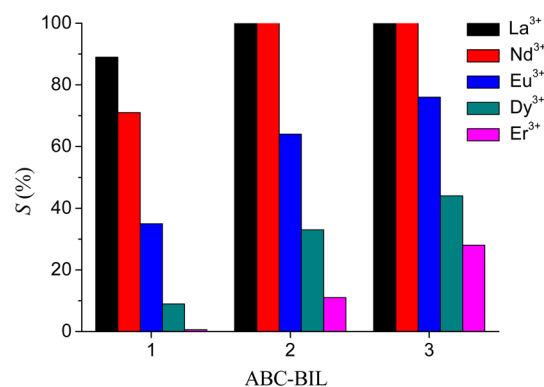


Figure 10. Stripping of REEs in $[N_{2222}][DEHP]$ system using HCl. (1) HCl = 0.03 mol/L; (2) HCl = 0.06 mol/L; (3) HCl = 0.09 mol/L.

ratios may be attributed to the involvement of chloride ion in the REE extraction mechanism by ABC-BILs.

- (5) The stripping property of $[N_{2222}][EHEHP]$ for REE was better than those of $[N_{2222}][DEHP]$. The low stripping acidity of $[N_{2222}][EHEHP]$ revealed another environmentally friendly implication for REE separation.

Since both cations and anions of the ABC-BILs revealed effects on the extraction behaviors of REEs, the extraction mechanisms of ABC-BILs for REEs seems to be complicated. This is an area that should be investigated in the future, to improve the understanding of ionic liquids as extractants which would then lead to improved industrial processes.

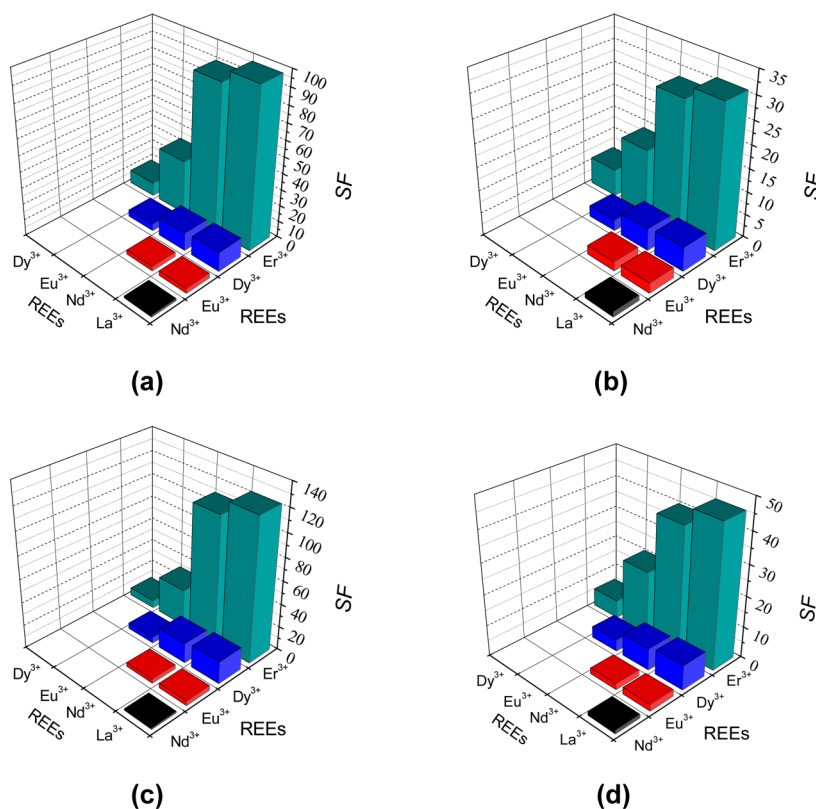


Figure 9. Effect of salting on the separation factors of REEs extracted by $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$. $[N_{2222}][DEHP] = [N_{2222}][EHEHP] = 0.004$ mol/L, $REE^{3+} = 0.0005$ mol/L for each rare earth ion: (a) $[N_{2222}][EHEHP]$, NaCl = 0.5 mol/L, equilibrium pH = 4.69; (b) $[N_{2222}][EHEHP]$, NaCl = 1 mol/L, equilibrium pH = 4.66; (c) $[N_{2222}][DEHP]$, NaCl = 0.5 mol/L, equilibrium pH = 4.64; (d) $[N_{2222}][DEHP]$, NaCl = 1 mol/L, equilibrium pH = 4.62.

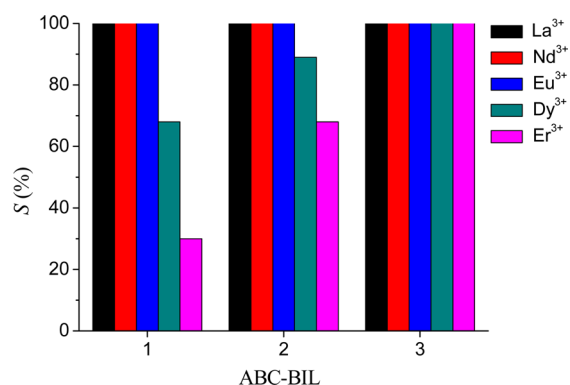


Figure 11. Stripping of REEs in $[N_{2222}][EHEHP]$ system using HCl. (1) HCl = 0.03 mol/L; (2) HCl = 0.06 mol/L; (3) HCl = 0.09 mol/L.

■ ASSOCIATED CONTENT

📄 Supporting Information

Numerical values associated with Figures 3, 5, 7, and 9. 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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