The Adjustable Synergistic Effects Between Acid–Base Coupling Bifunctional Ionic Liquid Extractants for Rare Earth Separation

Xiaoqi Sun
Dept. of Mining and Materials Engineering, McGill University, 3610 University, Montreal, Quebec, Canada H3A 0C5

Lab. of Rare Earth Separation Science and Engineering, Xiamen Institute of Rare Earth Materials, Chinese Academy of Sciences, Xiamen 361021, P. R. China

Kristian E. Waters
Dept. of Mining and Materials Engineering, McGill University, 3610 University, Montreal, Quebec, Canada H3A 0C5

DOI 10.1002/aic.14563

Two of the most widely used industrial extractants for rare earth elements (REEs), that is, di(2-ethylhexyl)phosphoric acid (HDEHP) and 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) were developed into [DEHP]$^-$ type acid–base coupling bifunctionalized ionic liquids (ABC-BILs) and [EHEHP]$^-$ type ABC-BILs, respectively. The combinations of ABC-BIL extractants revealed synergistic effects for REEs. Seven different combinations of ABC-BILs and five kinds of REEs confirmed the novel synergistic extraction. Some synergy coefficients of the combined ABC-BILs were bigger than those of mixed HDEHP and HEH[EHP] by two orders of magnitude. The first synergistic extraction produced by ionic liquid extractants in the field of solvent extraction was reported in this article. The novel synergistic extraction from combined ABC-BILs extractants revealed highly efficient and environmentally friendly potential in both of academic research and industrial application for REEs separation. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 3859–3868, 2014

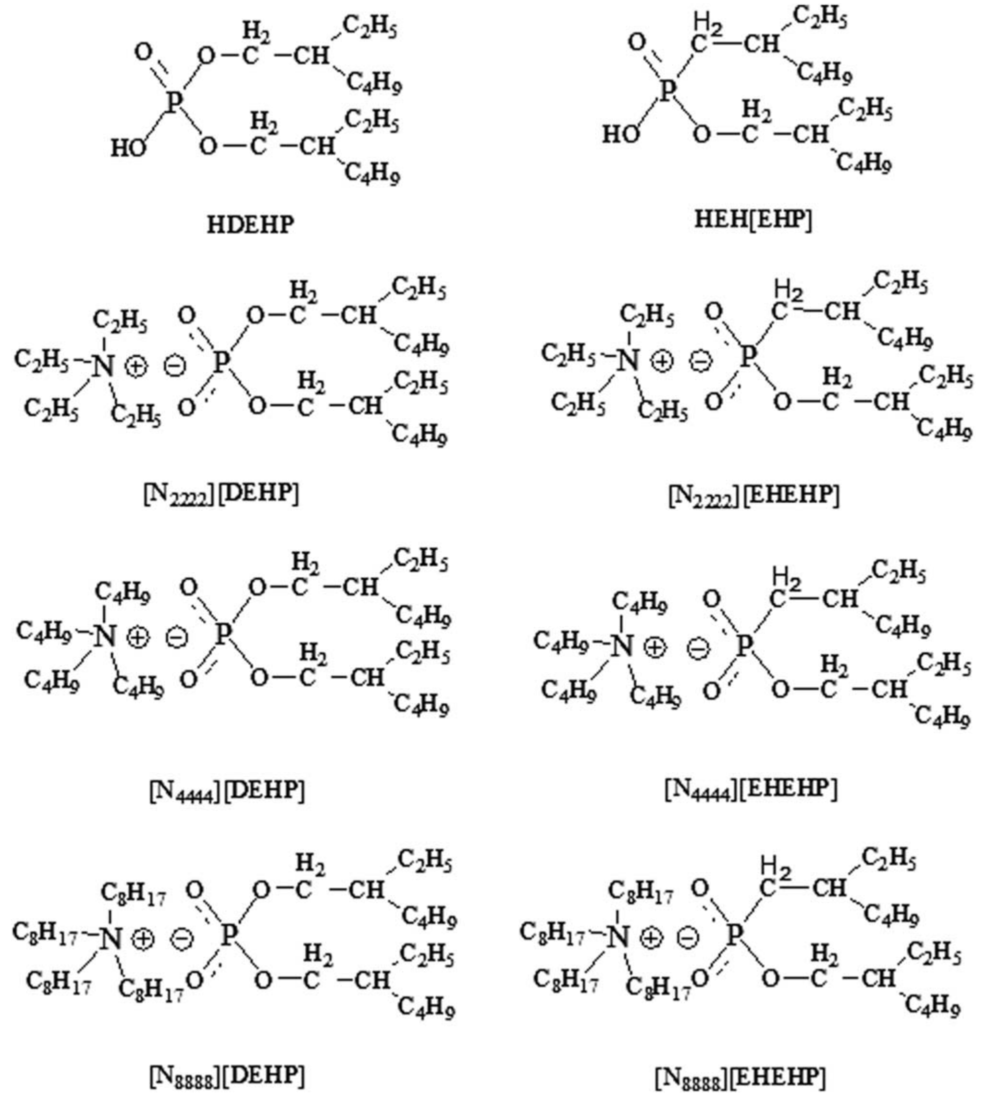
Keywords: ionic liquid, rare earth elements, extraction, synergistic effect, separation

Introduction

Rare earth elements (REEs) have been applied in many cutting-edge technology products, including telecommunications and lasers, solar energy conversion and photocatalysis, phosphors for displays and lighting, lanthanide luminescence in biosciences, and magnetic materials. However, separation of individual REEs is difficult due to their similar chemical properties. The separation operations of REEs can be lengthy, costly, and detrimental to the environment.[1] Very recently, the REE recovery and separation technologies have aroused wide attention from all over the world, such as mining REEs research from deep-sea mud in Japan[2] and the foundation of the Critical Materials Institute in United States.[3] Besides the importance of REEs separation for advanced materials, the separation of lanthanides were very important for nuclear fuel cycling.[4,5] Because of the high importance of REEs separation in materials and energy fields, many technologies have been developed for REEs separation such as extraction,[6] adsorption,[7] membrane,[8] and nano technology.[9] In the aforementioned methods, solvent extraction is the most widely used technology in the rare earth and nuclear industries due to its high processing capacity, fast reaction rate, and good separation. During the past few decades, many different extractants have been utilized for REEs separation, including ammonium,[10] phosphoric acid,[11] acetic acid,[12] phosphine oxide,[13] and phosphate.[14] Among the extractants, di(2-ethylhexyl)phosphoric acid (HDEHP, P204) and 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP], P507) are two of the most commonly used extractants. Up until now, much of the research concerning HDEHP and HEH[EHP] for REEs separation has been reported on hydrometallurgy[15,16] and nuclear fuel recycling.[17,18] As can be seen in Figure 1, there are two ester groups in HDEHP, and there is only one ester group in HEH[EHP]. The electronegativity of the ester groups in HDEHP and HEH[EHP] contribute to the coordination of P=O bond with REEs. However, the strong extraction capability of HDEHP hinders the separation and stripping of REEs. As a result, HEH[EHP] came to be the most commonly used extractant in REEs separation. However, the intermolecular hydrogen bonds from dimers and the hydrogen ions released in ion-exchange mechanism negatively affect the extractabilities of HEH[EHP] for REEs. HEH[EHP] requires saponification by $NH_3{\cdot}H_2O$ for industrial applications, which releases ammonia-nitrogen wastewater into the environment. Equation 1 describes the saponification of HEH[EHP], and Eq. 2 is the extraction

---

Correspondence concerning this article should be addressed to K. E Waters at kristian.waters@mcgill.ca.



HDEHP HEH[EHP]

$[N_{2222}][DEHP]$ $[N_{2222}][EHEHP]$

$[N_{4444}][DEHP]$ $[N_{4444}][EHEHP]$

$[N_{8888}][DEHP]$ $[N_{8888}][EHEHP]$

Figure 1. Structures of the investigated ABC-BILs extractants.

mechanism of saponified HEH[EHP] for REE. Three NH_4^+ ions are released to the aqueous phase when one REE^{3+} ion is extracted.[19] In 2011, China produced 96,900 tons of rare earth products, accounting for more than 90% of the world's total output, which resulted in the creation of 10 million tons of wastewater containing NH_4^+ in the separation process.[20,21] More than 1.5 billion RMB (US$ 0.24 billion) is required to deal with the environmental pollution in China annually.[20] According to the China Ministry of Environmental Protection, rare earth producers must soon meet stricter environmental emission standards or be shut down.[21] Accordingly, environment friendly and highly efficient separation technologies for REEs should be developed as soon as possible

$$H_2L_2+2NH_3 \cdot H_2O=2NH_4^+L^-+2H_2O \tag{1}$$

$$REE^{3+}_{(aq)}+3NH_3^+L^-_{(o)}=REEL_{3(o)}+3NH^+_{4\,(aq)} \tag{2}$$

Ionic liquids (IL) are salts, which are generally a liquid below 100°C. Many applications of IL at industrial scale have been established, for example, BASF (BASIL, aluminium plating, cellulose dissolution), Institut Français du Pétrole (Difasol), Degussa (paint additives), Linde (hydraulic IL compressor), Pionics (batteries), and G24i (solar cells).[22] IL-based extraction is a novel separation strategy that applies ILs instead of volatile organic compounds (VOCs) as diluents and/or extractants. ILs have properties that make them particularly suitable for solvent extraction, including their low volatility and combustibility, wide liquidus range, thermal stability, adjustable functional groups, high conductivity, and wide electrochemical window.[23] Many papers have been published in the field of REEs separation using ILs.[24–26] Cytec Industries has produced some industrial IL extractants, such as Cyphos® IL 101 and Cyphos® IL 104, which have been widely studied for REEs separation.[27,28] In the numerous research on solvent extraction, synergistic extraction is an interesting research topic. When a combination of two extractants yields partitioning that is greater than the sum of their individual contributions, the system is synergistic and the enhanced extraction is most often attributed to the combined coordinating/solvating abilities of the two extractants.[29] The synergistic effect of two extractants for metal ions has been reported in a number of studies.[30–32] Stepinski et al.[33] reported that synergistic interactions between extractant molecules could occur in IL diluents, as was the case in many conventional organic diluents. This was the first article concerning IL and synergistic extraction. Unfortunately, the price of the diluents in that paper, that is, 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imides are still too high to be applied industrially. As for the synergistic effects from IL extractants in traditional industrial diluents, Sun et al. prepared some acid–base coupling bifunctional ionic liquid (ABC-BIL) extractants,[34] and reported the inner synergistic effect between the cation and anion of [tricaprylmethylammonium][di-2-ethylhexylphosphinate] for Eu^{3+} extraction. Many bifunctional IL extractants revealed such inner synergistic effects for Sm^{3+}, Eu^{3+}, and Gd^{3+} in cyclohexane, chloroform, and toluene. The inner synergistic effect of ABC-BIL highlighted some advantages, that is, extraction capacities of some quartary ammonium extractants and phosphoric (acetic) extractants could be enhanced by preparing them into ABC-BILs. In addition, saponification wastewater from the application of acidic extractants could be avoided by preparing them as ABC-BILs.[19] There is not only an inner synergistic effect in the ABC-BIL but also synergistic effect between the ABC-BILs. In this article, it is further reported that the synergistic effects between the combined ABC-BIL extractants for REEs, which is the first paper concerning the synergistic extraction effect between IL extractants.

Materials and Methods

Reagents

All the REEs were purchased from Aldrich as chloride salts. Tetraethylammonium chloride ([N$_{2222}$]Cl), tetrabutylammonium chloride ([N$_{4444}$]Cl), and tetraoctylammonium bromide ([N$_{8888}$]Br) were purchased from Aldrich. An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from the Dow Chemical Company. Di(2-ethylhexyl)phosphoric acid (HDEHP) was purchased from Alfa Aesar. HEH[EHP] was supplied by Luoyang Aoda Chemical Co., China (95% purity). The ABC-BILs were prepared according to previously published work,[35] detailed procedures for the preparation are given in the following section.

Analysis

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ with a Bruker AV III 400HD NMR spectrometer. Structures of extractants used in this study are shown in Figure 1. The extracting phases were prepared by dissolving the ABC-BILs (or HDEHP, HEH[EHP]) in heptane (HPLC grade, Aldrich). The aqueous REE solutions were prepared by dissolving the REE chloride salts in deionized water (18.2 MΩ cm) from a Barnstead DI water system. Thermo Scientific iCAP 6500 Series inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the concentration of REEs in the aqueous phase.

The preparation of ABC-BILs

The $[DEHP]^-$ type ABC-BILs and $[EHEHP]^-$ type ABC-BILs were prepared using the combination of ion-exchange and neutralizing reactions.[35] The study is the first time the novel $[EHEHP]^-$ type ABC-BILs were prepared.

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 Dowex Monosphere 550A (OH) anion-exchange resin. 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 a 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%).

- ^{1}H NMR ($CDCl_3$, ppm): 0.70–0.76 (m, 12H, $4CH_3$), 1.12–1.15 (m, 12H, $4CH_3$), 1.17–1.26 (m, 16H, $8CH_2$), 1.34 (m, 2H, 2CH), 3.32 (m, 8H, $4NCH_2$), 3.55 (m, 4H, $2OCH_2$);
- ^{13}C NMR ($CDCl_3$, ppm): 7.57 ($4CH_3$), 10.91 ($2CH_3$), 14.02 ($2CH_3$), 23.05 ($2CH_2$), 23.30 ($2CH_2$), 28.98 ($2CH_2$), 30.09 ($2CH_2$), 40.40 (2CH), 52.32 ($4NCH_2$), 67.19 ($2OCH_2$).

Tetrabutylammonium Di(2-ethylhexyl)phosphate {[N$_{4444}$][DEHP]}. A solution of [N$_{4444}$]OH in ethanol was prepared from 1.39 g of [N$_{4444}$]Cl (0.005 mol) using Dowex Monosphere 550A (OH) anion-exchange resin. HDEHP (0.005 mol) of 1.61 g was added to the [N$_{4444}$]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 a IKA RV10 rotary evaporator, and the product was dried at 70°C under vacuum for 12 h to yield [N$_{4444}$][DEHP] as a colorless viscous liquid (2.59 g, 0.0046 mol, yield: 92%).

- ^{1}H NMR ($CDCl_3$, ppm): 0.80–0.81 (m, 12H, $4CH_3$), 0.91–0.91 (m, 12H, $4CH_3$), 1.19–1.44 (m, 32H, $16CH_2$), 1.59 (m, 2H, 2CH), 3.31 (m, 8H, $4NCH_2$), 3.63 (m, 4H, $2OCH_2$);
- ^{13}C NMR ($CDCl_3$, ppm): 10.95 ($4CH_3$), 13.66 ($2CH_3$), 14.01 ($2CH_3$), 19.71 ($4CH_2$), 23.14 ($2CH_2$), 23.32 ($2CH_2$), 24.07 ($4CH_2$), 29.06 ($2CH_3$), 30.12 ($2CH_2$), 40.43 (2CH), 58.70 ($4NCH_2$), 67.27 ($2OCH_2$).

Tetraoctylammonium Di(2-ethylhexyl)phosphate {[N$_{8888}$][DEHP]}. A solution of [N$_{8888}$]OH in ethanol was prepared from 2.73 g of [N$_{8888}$]Br (0.005 mol) using Dowex Monosphere 550A (OH) anion-exchange resin. HDEHP (0.005 mol) of 1.61 g was added to the [N$_{8888}$]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 a IKA RV10 rotary evaporator, and the product was dried at 70°C under vacuum for 12 h to yield [N$_{8888}$][DEHP] as a viscous liquid (3.7 g, 0.0047 mol, yield: 94%).

- ^{1}H 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 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 Dowex Monosphere 550A (OH) anion-exchange resin. 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 a 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).

Tetrabutylammonium Mono-(2-ethylhexyl) 2-ethylhexyl phosphonate {$[N_{4444}][EHEHP]$}. A solution of $[N_{4444}]OH$ in ethanol was prepared from 1.67 g of $[N_{4444}]Cl$ (0.006 mol) using Dowex Monosphere 550A (OH) anion-exchange resin. HEH[EHP] (0.006 mol) of 1.84 g of was added to the $[N_{4444}]OH$ solution. The mixture was, then, stirred at room temperature for 6 h until the solution became neutral. The ethanol and water were distilled off, and the product was dried at 70°C under vacuum for 12 h to yield $[N_{4444}][EHEHP]$ as a viscous liquid (3.01 g, 0.0055 mol, yield: 92%).

- ^1H NMR ($CDCl_3$, ppm): 0.72–0.79 (m, 12H, $4CH_3$), 0.89–0.92 (m, 12H, $4CH_3$), 1.17–1.38 (m, 32H, $16CH_2$), 1.57 (m, 2H, 2CH), 3.32 (m, 8H, $4NCH_2$), 3.56 (m, 4H, $2OCH_2$);
- ^{13}C NMR ($CDCl_3$, ppm): 10.36 ($4CH_3$), 10.96 (CH_3), 13.65 (CH_3), 14.08 (CH_3), 14.21 (CH_3), 19.71 ($4CH_2$), 23.13 (CH_2), 23.19 (CH_2), 24.11 (CH_2), 26.57 ($4CH_2$), 28.67 (CH_2), 29.06 (CH_2), 30.14 (CH_2), 31.35 (CH_2), 33.73 (CH_2), 33.81 (CH_2), 34.90 (CH), 40.63 (CH), 58.74 ($4NCH_2$), 65.92 (OCH_2).

Tetrahexylammonium Mono-(2-ethylhexyl) 2-ethylhexyl phosphonate {$[N_{8888}][EHEHP]$}. A solution of $[N_{8888}]OH$ in ethanol was prepared from 2.18 g of $[N_{8888}]Br$ (0.004 mol) using Dowex Monosphere 550A (OH) anion-exchange resin. HEH[EHP] (0.004 mol) of 1.23 g of was added to the $[N_{8888}]OH$ solution. The mixture was, then, stirred at room temperature for 6 h until the solution became neutral. The ethanol and water were distilled off, and the product was dried at 70°C under vacuum for 12 h to yield $[N_{8888}][EHEHP]$ as a viscous liquid (2.86 g, 0.0037 mol, yield: 93%).

- ^1H NMR ($CDCl_3$, ppm): 0.84 (m, 24H, $8CH_3$), 1.22–1.34 (m, 56H, $28CH_2$), 1.41 (m, 2H, 2CH), 1.62 (m, 8H, $4CH_2$),3.34 (m, 8H, $4NCH_2$), 3.62 (m, 2H, CH_2), 3.63 (m, 2H, OCH_2);
- ^{13}C NMR ($CDCl_3$, ppm): 10.40 ($4CH_3$), 11.01 (CH_3), 14.00 (CH_3), 14.14 (CH_3), 22.26 ($4CH_2$), 22.56 ($4CH_2$), 23.20 (CH_2), 23.27 (CH_2), 23.37 (CH_2), 26.42 (CH_2), 26.52 (CH_2), 26.59 (CH_2), 28.71 (CH_2), 29.04 ($4CH_2$), 29.11 (CH_2), 29.15 ($4CH_2$), 31.65 (CH_2), 33.79 ($4CH_2$), 33.87 (CH_2), 34.93 ($4CH_2$), 34.96 (CH), 40.66 (CH), 58.97 ($4NCH_2$), 66.06 (OCH_2).

Extraction experiments

The extraction experiments were performed by contacting 5 mL of heptane containing ABC-BIL (or HDEHP, HEH[EHP]) with 5 mL of REEs-containing aqueous solution for 60 min in a vibratory mixer. After centrifugation at 5,000 rpm for 5 min, the aqueous phase was separated, and the concentrations of REE ions were determined using ICP-AES. The concentrations of REE ions in the IL phase were calculated by a mass balance. The distribution ratio (D_M), separation factor (SF), and synergy coefficient (R) were defined as follows[35,36]

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

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

$$R=\frac{D_{mix}}{D_1+D_2} \quad (5)$$

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, D_1, D_2, and D_{mix} are the distribution ratio of extractant 1, extractant 2, and their mixture, respectively. Initial pH value of the aqueous REE solutions was adjusted to 4.65 using hydrochloric acid. All the concentration values of REE were measured in duplicate with the uncertainty within 5%.

Results and Discussion

The extractabilities of HDEHP, HEH[EHP], $[DEHP]^-$ type ILs and $[EHEHP]^-$ type ILs for REEs

As shown in Figure 2, the extraction sequence of REEs by HDEHP, HEH[EHP], and ABC-BILs were the same, namely $La^{3+} < Nd^{3+} < Eu^{3+} < Dy^{3+} < Er^{3+}$. The sequence can be attributed to the ionic radius of REEs. That is, La^{3+} (103pm) > Nd^{3+} (98.3pm) > Eu^{3+} (94.7pm) > Dy^{3+} (94.2pm) > Er^{3+} (89pm).[37] As the ionic radius of REEs decreases, the coordination strengths of functional groups in the extractants for REEs increases, accordingly the extractabilities of extractants for REEs increased. Some bifunctional ILs containing quaternary ammonium cations were investigated for REEs separation with interesting results.[24,38] In this study, the distribution ratios of RREs extracted by HDEHP, HEH[EHP], and ABC-BILs were quite different. The $[DEHP]^-$ type ILs revealed higher extractabilities for almost all the REEs than HDEHP, similarly, the $[EHEHP]^-$ type ILs revealed higher extractabilities for almost all the REEs than HEH[EHP]. The trend was the same as those previously published,[19] the ABC-BILs potentially exhibiting higher extractabilities for REE than the precursors due to the inner synergistic effects. As for the extractabilities of different ABC-BILs, different ABC-BILs might result in different distribution ratios of REEs. The distribution ratio sequence of $[DEHP]^-$ type ILs for REEs was $[N_{2222}][DEHP] > [N_{4444}][DEHP] > [N_{8888}][DEHP]$, and the distribution ratio sequence of $[EHEHP]^-$ type ILs for REEs was $[N_{2222}][EHEHP] > [N_{4444}][EHEHP] > [N_{8888}][EHEHP]$. Such sequences could be attributed to the different structure of the cation. As the alkyl chain length of the cation increases, the steric hindrances of ABC-BILs increases, and the extractabilities of ABC-BILs for REEs decreases, with the sequence being the same as those reported with imidazolium IL diluents.[39] As mentioned previously, the extractabilities of $[DEHP]^-$ type ILs were bigger than those of $[EHEHP]^-$ type ILs which could also be attributed to the fact that there are two ester groups in $[DEHP]^-$, whereas there is only one ester group in $[EHEHP]^-$. The electronegativity of the ester group contributed to the coordination of the P═O bond with REEs. As a result, the extraction abilities of ABC-BILs containing $[DEHP]^-$ for REEs were stronger than those of ABC-BILs

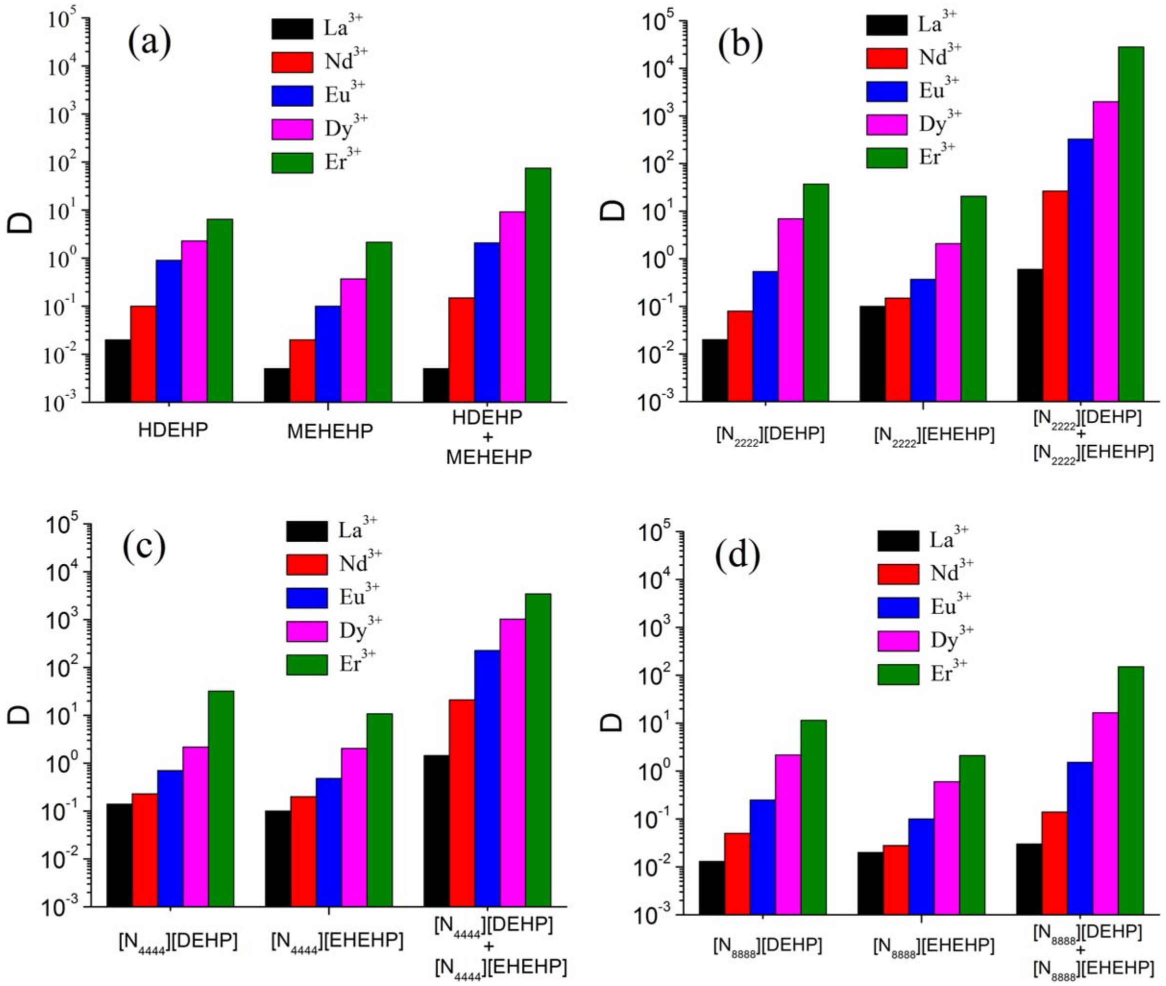


Figure 2. The distribution ratios of REEs extracted by (a) HDEHP and HEH[EHP], (b) $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$, (c) $[N_{4444}][DEHP]$ and $[N_{4444}][EHEHP]$, and (d) $[N_{8888}][DEHP]$ and $[N_{8888}][EHEHP]$.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing $[EHEHP]^-$. It is worthwhile to note that the extractabilities of mixed HDEHP and HEH[EHP] for REEs were greater than individual HDEHP or HEH[EHP]. Similarly, the extractabilities of mixed $[DEHP]^-$ type ILs and $[EHEHP]^-$ type ILs were greater than the corresponding $[DEHP]^-$ type ILs or $[EHEHP]^-$ type ILs. This interesting effect can be attributed to the synergistic extraction effects between the extractants.

Synergistic effects of $[DEHP]^-$ type ILs and $[EHEHP]^-$ type ILs with the same cations for REEs

Some studies concerning the synergistic extraction of HDEHP and HEH[EHP] for REE have been reported previously, such as Yb^{3+} in a hydrochloric acid medium,[40] and Sm^{3+} and Nd^{3+} in a sulfuric acid medium.[41] In this study, the HDEHP and HEH[EHP] also revealed synergistic effects for Eu^{3+}, Dy^{3+}, Er^{3+} as shown in Figure 3. Under the same extraction conditions, the synergy coefficients of REEs extracted by mixed ABC-BILs were higher than those of mixed HDEHP and HEH[EHP]. The combination of $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP]$ revealed synergy coefficients' two orders of magnitude greater than those of HDEHP and HEH[EHP] for REEs. For most of the REEs, the synergy-effect sequence was: a combination of $[N_{2222}][DEHP]$ and $[N_{2222}][EHEHP] >$ combination of $[N_{4444}][DEHP]$ and $[N_{4444}][EHEHP] >$ combination of $[N_{8888}][DEHP]$ and $[N_{8888}][EHEHP]$. The sequence indicated that the $[DEHP]^-$ type ILs and $[EHEHP]^-$ type ILs with smaller cations always revealed bigger synergy extraction effects. As well as the synergistic extraction of HDEHP and HEH[EHP], mostly synergy coefficients of the combined ABC-BILs increased from light REEs to heavy REEs. Synergistic coefficients of REEs can be attributed to the extractabilities of mixed extractants. As reported by Sun et al.,[19] dimers of acidic extractants could be absolutely broken when the extractants were prepared as bifuctional ILs. The elimination of intermolecular hydrogen bonds from dimers increased 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 were higher than those of mixed HDEHP and HEH[EHP]. The effect of ABC-BILs with smaller cations revealed higher synergistic effects could be attributed to the lower steric hindrance of ABC-BILs with smaller cations, the lower steric hindrances contributed to the higher coordination abilities of ABC-BILs with REEs. In traditional synergistic extraction investigations, the synergy coefficients were always adjusted by changing the mole fractions of extractants.[40,42] In this study, different cations and anions of ABC-BILs revealed different effects on the REEs synergy coefficients. The difference of synergy coefficients indicated that the synergistic

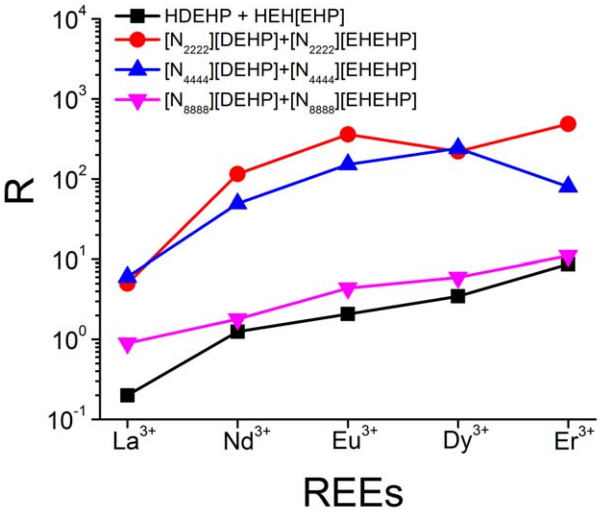


Figure 3. The synergy coefficients of combined extractants for REEs.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effects of ABC-BIL extractants could be optimized by adjusting their structures.

Selectivities of combined [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with same cations for REEs

To further investigate the synergistic extraction of ABC-BILs for REEs, the SFs of combined [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with the same cations were compared with mixtures of HDEHP and HEH[EHP] (Figure 4a). Some of the combined ABC-BILs, that is, [N$_{2222}$][DEHP] and [N$_{2222}$][EHEHP] (Figure 4b), revealed better selectivities for REEs. On the contrary, the selectivities of other combined ABC-BILs ([N$_{4444}$][DEHP] and [N$_{4444}$][EHEHP] (Figure 4c); [N$_{8888}$][DEHP] and [N$_{8888}$][EHEHP] (Figure 4d)) were worse than the mixture of HDEHP and HEH[EHP] (Figure 4a). Unlike the identical tendencies of extractabilities, the selectivities of combined ABC-BILs were not all better than those of the mixed HDEHP and HEH[EHP] for REEs. Extractability and selectivity is a pair of main factors for evaluating an extracting system. In this study, all the distribution ratios of REEs extracted by mixed ABC-BILs were higher than those extracted by HDEHP and HEH[EHP]. The higher extractability is an important advantage of the combined ABC-BILs. However, not all mixed ABC-BILs could reveal better selectivities than those of mixed HDEHP and HEH[EHP]. It is noticeable that combined ABC-BILs with smaller cations revealed higher selectivities for REEs. As the size of cations increased, the steric hindrances of ABC-BILs increased. The bigger steric hindrances decreased the selectivities of quaternary ammonium ions and P═O bonds in ABC-BILs for REEs.

The extractabilities of combined ABC-BILs with different cations for REEs

As shown in Figure 2, the mixed [N$_{2222}$][DEHP] and [N$_{2222}$][EHEHP] revealed better extractabilities for REEs than other combined ABC-BILs with large cations. Herein, the extractabilities of [N$_{2222}$][DEHP] and [N$_{2222}$][EHEHP] for REEs were further studied in other combinations of ABC-BIL systems with different cations. As illustrated in Figure 5, the extractabilities of four combined [DEHP]$^-$ type IL and [EHEHP]$^-$ type IL with different cations for REEs were compared. All REE extraction sequences were the same, that is, $La^{3+} < Nd^{3+} < Eu^{3+} < Dy^{3+} < Er^{3+}$ (the sequence being the same as that shown in Figure 2). The distribution ratios of REEs extracted by the four systems were different. The sequence being: the combination of [N$_{4444}$][DEHP] and N$_{2222}$][EHEHP] > combination of [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP] > combination of [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP] > combination of [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP]. It appears that the extractabilities of combined ABC-BIL extraction systems containing [N$_{2222}$][EHEHP] were greater than the combined ABC-BILs systems containing [N$_{2222}$][DEHP] for REEs.

Synergistic effects of [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with different cations for REEs

As can be seen from Figure 6, there were also synergistic effects of the combined [DEHP]$^-$ type and [EHEHP]$^-$ type ILs with different cations. The combination of [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP] revealed synergistic extraction effects for all the REEs, the other three combinations of mixed ABC-BILs revealed synergistic effects for some of the five REEs. When the total carbon chain numbers of cations were same, the synergy coefficients of combined [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP] system for REEs were greater than those of combined [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP] by two orders of magnitude. Similarly, synergy coefficients of combined [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP] systems for most REEs were larger than those of combined [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP]. In previous investigations on synergistic extractions of REEs using HDEHP and HEH[EHP], the maximum synergistic enhancement coefficients were obtained at a ratio of HEH[EHP] to HDEHP of 3 to 2.[40,41] In this study, a similar conclusion was reached in that the [N$_{2222}$][EHEHP] was more important than [N$_{2222}$][DEHP] for the synergistic extraction effects of REEs between the combined ABC-BILs with different cations, which meant that the effect of [EHEHP]$^-$ type IL was more pronounced for the synergistic extraction between the combined ABC-BILs.

The selectivities of combined [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with different cations for REEs

In this section of this study, the SFs of combined [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with different cations were compared. As shown in Figure 7, the SFs for most REEs extracted by a combination of [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP] (Figure 7c) were greater than those from [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP] (Figure 7a). At the same time, the SFs between mostly REEs extracted by combined [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP] (Figure 7d) were bigger than those of combined [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP] (Figure 7b). As mentioned above, total carbon chain numbers of cations were crucial for the extractability and selectivity of ABC-BILs with the same cations for REEs. When the cations were smaller, the extractabilities and selectivities were bigger. The comparison from Figures 6 and 7 indicates that lower total carbon chain numbers of cations were also important when cations of the combined ABC-BILs were different, such as most extractabilities and selectivities of combined [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP] for REEs were better than those of combined [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP]. In case of combined [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP] vs. combined [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP], the trends

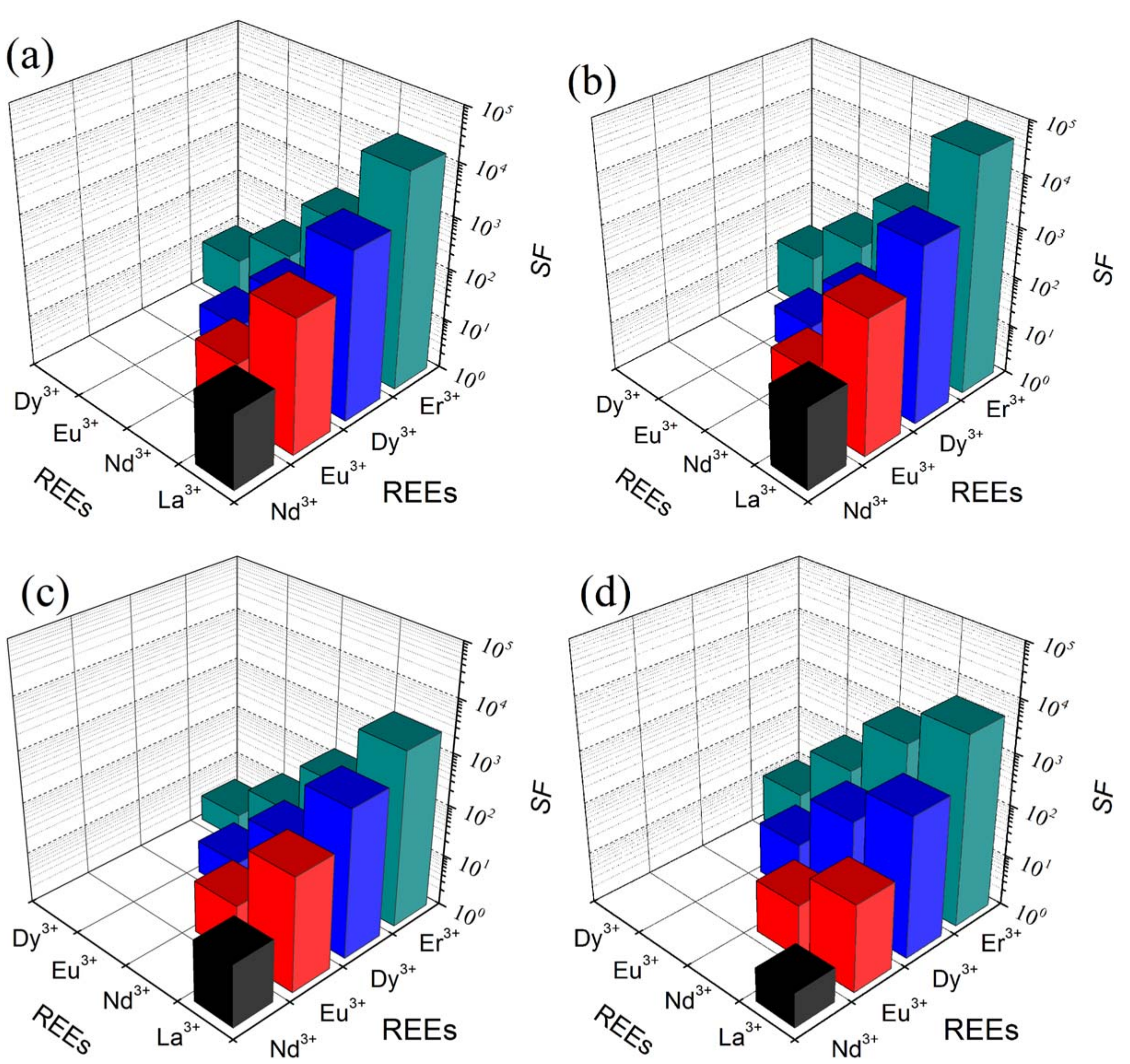


Figure 4. The separation factors of combined extractants for REEs.

(a) Mixed HDEHP and HEH[EHP]. (b) Mixed $[N_{2222}]$[DEHP] and $[N_{2222}]$[EHEHP]. (c) Mixed $[N_{4444}]$[DEHP] and $[N_{4444}]$[EHEHP]. (d) Mixed $[N_{8888}]$[DEHP] and $[N_{8888}]$[EHEHP]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

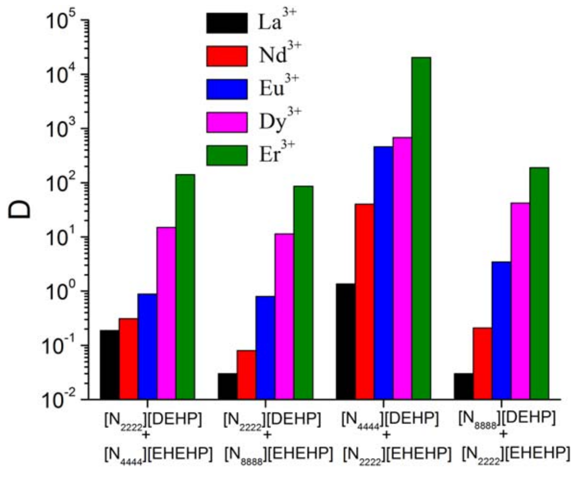


Figure 5. The distribution ratios of REEs extracted by combined DEHP-type ILs and EHEHP-type ILs with different cations for REEs.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

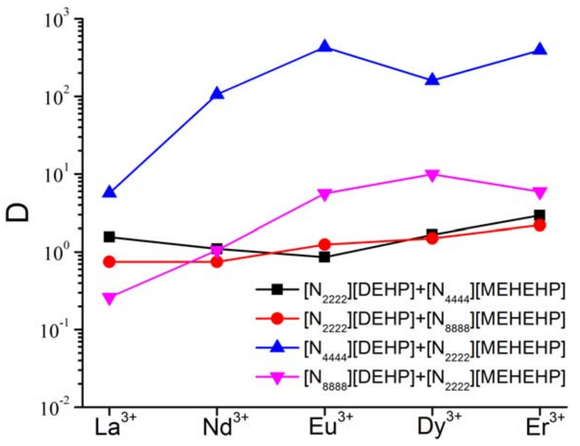


Figure 6. The synergy coefficients of combined ABC-BILs with different cations for REEs.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

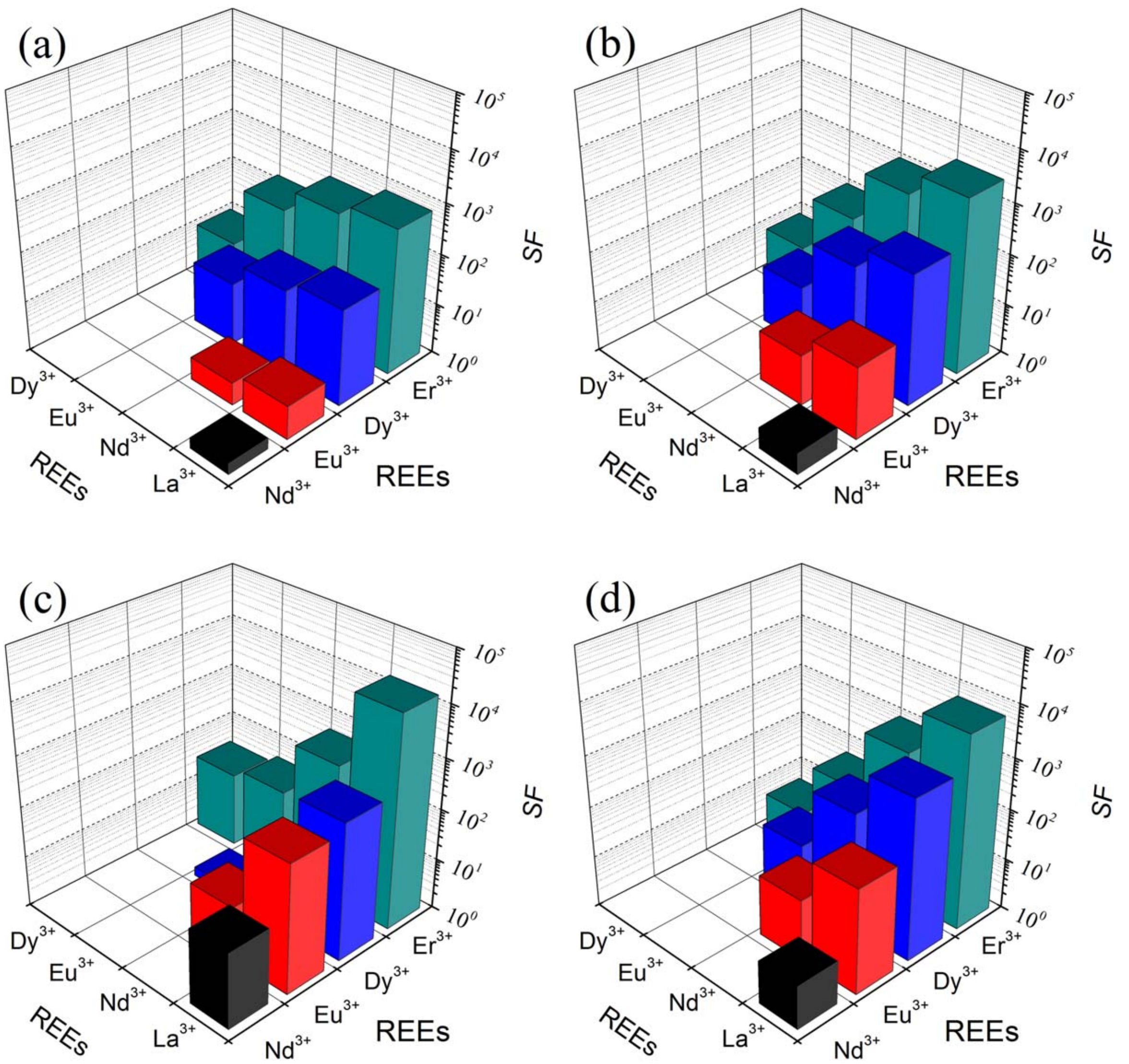


Figure 7. The separation factors of combined [DEHP]$^-$ type ILs and [EHEHP]$^-$ type ILs with different cations for REEs.

(a) Mixed [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP], (b) Mixed [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP], (c) Mixed [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP], (d) Mixed [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were similar. It is worthwhile to mention that the contributions of [EHEHP]$^-$ ILs with smaller cations were more important than those of [DEHP]$^-$ ILs with smaller cations for the synergistic effects when the total carbon chain numbers of cations were the same, for example, most extractabilities and selectivities of combined [N$_{4444}$][DEHP] and [N$_{2222}$][EHEHP] were bigger than those of combined [N$_{2222}$][DEHP] and [N$_{4444}$][EHEHP]. In additional, most extractabilities and selectivities of combined [N$_{8888}$][DEHP] and [N$_{2222}$][EHEHP] were bigger than those of combined [N$_{2222}$][DEHP] and [N$_{8888}$][EHEHP]. Considering the size effect of cation, effect of [EHEHP]$^-$ type ABC-BIL with smaller cation was the most important to the synergistic extraction of REEs.

Stripping properties of the synergistic extraction system for REEs

To evaluate stripping properties of the synergistic effects between ABC-BILs for REEs, the loaded extracting phases were prepared using 0.005 mol/L [N$_{2222}$][DEHP], 0.005 mol/L [N$_{2222}$][EHEHP], and 0.0005 mol/L REEs, and the strip-

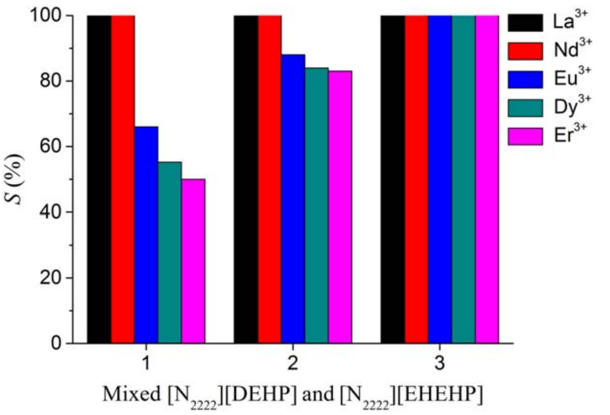


Figure 8. The stripping of REEs in mixed [N$_{2222}$][DEHP] and [N$_{2222}$][EHEHP] system using HCl.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ping by HCl were investigated at different acidities. Figure 8 reveals the stripping of light REEs (La^{3+}, Nd^{3+}) was at lower acidities than those of the middle (Eu^{3+}, Dy^{3+}) and heavy (Er^{3+}) REEs. As mentioned above, coordinating abilities of the mixed ABC-BILs synergistic system for REEs enhanced with the ionic radius of REEs decrease. Accordingly, extracting complexes formed by REEs with a larger ionic radius (i.e., La^{3+}, Nd^{3+}) were easier to be decomposed by acid than those with a lower ionic radius (i.e., Eu^{3+}, Dy^{3+}, Er^{3+}). The extracted REEs using the mixed ABC-BILs could be fully stripped when the acidity arrived at 0.18 mol/L.

Conclusions

Two of the most commonly used industrial extractants for REEs, that is, HDEHP and HEH[EHP] were developed into six types of ABC-BIL extractants. As with the mixture of HDEHP and HEH[EHP], the combined $[DEHP]^-$ type ABC-BILs and $[EHEHP]^-$ type ABC-BILs revealed synergistic extraction effects for REEs in seven different ABC-BILs combinations, regardless of whether or not their cations were the same. The synergy coefficients of five REEs from light to heavy, that is, La^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Er^{3+}, also confirmed the synergistic extraction effects from combined ABC-BILs. All combinations confirmed that the synergistic effects of $[DEHP]^-$ type ABC-BILs and $[EHEHP]^-$ type ABC-BILs for REEs were very strong. In some combinations, the synergy coefficients of REEs extracted by the ABC-BILs mixtures reached 10^2 to 10^3 in order of magnitude, far greater than those of mixed HDEHP and HEH[EHP] under the same conditions. The synergistic extraction effects of ABC-BILs were shown to be closely related to the structures of the ABC-BILs. When the cations of the combined ABC-BILs were the same, the combination of $[N_{2222}]$[DEHP] and $[N_{2222}]$[EHEHP] had the largest synergy coefficients for REEs. When cations of the combined ABC-BILs were different, the $[N_{2222}]$[EHEHP] was shown to be more important than $[N_{2222}]$[DEHP] for the combined ABC-BILs synergistic extraction. The extractabilities and selectivities of the combined ABC-BILs for REEs can be optimized by adjusting the structures of extractants. In this study, two basic rules could be concluded from the experimental results. First, the ABC-BILs with smaller cations contributed to the synergistic effect. Second, the contributions of $[EHEHP]^-$ type ABC-BILs were more important than those of $[DEHP]^-$ type ABC-BILs for the synergistic effect. Such synergistic extraction of REE from IL extractants is the first time that has been reported. As the synergistic effect concerns the combination of four functionalized cations and anions of ABC-BILs, extraction processing is complicated than the traditional mechanism of synergistic extraction from two molecular extractants, further investigations is required to elucidate the mechanism and optimization of the novel synergistic extraction.

Acknowledgments

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada (NSERC) in conjunction with SGS Canada Inc., Shell Canada, Barrick Gold Corp, COREM, Teck, Vale Base Metals, CheMIQA, and Xstrata Process Support for funding this work through the Collaborative Research and Development Grant Program (CRDPJ-445682-12). The authors are thankful to Dr. Frederick Morin for collecting and analyzing the NMR data (Department of Chemistry, McGill University) and Mr Andrew Golsztajn (Department of Chemical Engineering, McGill University) for his assistance with ICP-AES.

Literature Cited

1. Eliseeva SV, Bünzli JG. Rare earths: jewels for functional materials of the future. *New J Chem.* 2011;35:1165–1176.
2. Kato Y, Fujinaga K, Nakamura K, Takaya Y, Kitamura K, Ohta J, Toda R, Nakashima T, Iwamori H. Deep-sea mud in the pacific ocean as a potential resource for rare-earth elements. *Nat Geosci.* 2011;4:535–539.
3. de Boer MA, Lammertsma K. Scarcity of rare earth elements. *ChemSusChem.* 2013;6:2045–2055.
4. Grimes TS, Tian G, Rao L, Nash KL. Optical spectroscopy study of organic-phase lanthanide complexes in the TALSPEAK separations process. *Inorg Chem.* 2012;51:6299–6307.
5. Shkrob IA, Marin TW, Jensen MP. Ionic liquid based separations of trivalent lanthanide and actinide ions. *Ind Eng Chem Res.* 2014;53: 3641–3653.
6. Vander Hoogerstraete T, Wellens S, Verachtert K, Binnemans K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. *Green Chem.* 2013;15:919–927.
7. Xu Y, Kim SY, Ito T, Hitomi K, Kuraoka E, Usuda S, Ishii K. Adsorption behavior of trivalent americium and rare earth ions onto a macroporous silica-based *iso*butyl-BTP/SiO_2-P adsorbent in nitric acid solution. *J Radioanal Nucl Chem.* 2014;299:149–155.
8. Juang RS, Kao HC, Yen PS. Modeling extraction separation of Nd(III) and La(III) from nitrate media in hollow-fiber modules. *AIChE J.* 2007;53:561–571.
9. Li CR, Zhuang ZY, Huang F, Wu ZC, Hong YP, Lin Z. Recycling rare earth elements from industrial wastewater with flowerlike nano-$Mg(OH)_2$. *ACS Appl Mater Interfaces.* 2013;5:9719–9725.
10. Atanassova M, Jordanov VM, Dukov IL. Effect of the quaternary ammonium salt Aliquat- 336 on the solvent extraction of lanthanoid (III) ions with thenoyltrifluoroacetone. *Hydrometallurgy.* 2002;63: 41–47.
11. Preston JS, Cole PM, Craig WM, Feather AM. The recovery of rare earth oxides from a phosphoric acid by-product. Part 1" leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy.* 1996;41:1–19.
12. Li W, Wang XL, Meng SL, Li D, Xiong Y. Extraction and separation of yttrium from the rare earths with *sec*-octylphenoxy acetic acid in chloride media. *Sep Purif Technol.* 2007;54:164–169.
13. Yang F, Kubota F, Kamiya N, Goto M. A comparative study of ionic liquids and a conventional organic solvent on the extraction of rare-earth ions with TOPO. *Solvent Extr Res Dev, Jpn.* 2013;20:225–232.
14. Nasab ME, Sam A, Milani SA. Determination of optimum process conditions for the separation of thorium and rare earth elements by solvent extraction. *Hydrometallurgy.* 2011;106:141–147.
15. Liao CS, Wu S, Wang SL, Cheng FX, Zhang B, Yan CH. Extraction of rare earth sulfates using saponified HEH(EHP) with Mg^{2+} Ion as barrier agent. *Sep Sci Technol.* 2013;48:1572–1576.
16. Yin SH, Wu WY, Bian X, Zhang FY. Effect of complexing agent lactic acid on the extraction and separation of Pr(III)/Ce(III) with di-(2-ethylhexyl) phosphoric acid. *Hydrometallurgy.* 2013;131:133–137.
17. Braley JC, McAlister DR, Horwitz EP, Nash KL. Explorations of Talspeak chemistry in extraction chromatography: comparisons of TTHA with DTPA and HDEHP with HEH[EHP]. *Solvent Extr Ion Exch.* 2013;31:107–121.
18. Grimes TS, Tillotson RD, Martin LR. Trivalent#lanthanide/actinide separation using aqueous-modified TALSPEAK chemistry. *Solvent Extr Ion Exch.* 2014;32:378–390.
19. Sun XQ, Ji Y, Hu FC, He B, Chen J, Li DQ. The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. *Talanta.* 2010;81:1877–1883.
20. Liu YH, Chen J, Li DQ. Application and perspective of ionic liquids on rare earths green separation. *Sep Sci Technol.* 2012;47:223–232.
21. Wang LS, Huang XW, Yu Y, Xiao YF, Long ZQ, Cui DL. Eliminating ammonia emissions during rare earth separation through control of equilibrium acidity in a HEH(EHP)-Cl system. *Green Chem.* 2013;15:1889–1894.

22. Petkovic M, Seddon KS, Rebelo LPN, Pereira CS. Ionic liquids: a pathway to environmental acceptability. *Chem Soc Rev*. 2011;40: 1383–1403.
23. Sun XQ, Luo HM, Dai S. Ionic liquids-based extraction: a promising strategy for the advanced nuclear fuel cycle. *Chem Rev*. 2012;112: 2100–2128.
24. Sun XQ, Luo HM, Dai S. Solvent extraction of rare-earth ions based on functionalized ionic liquids. *Talanta*. 2012;90:132–137.
25. Odinets IL, Sharova EV, Artyshin OI, Lyssenko KA, Nelyubina YV, Myasoedova GV, Molochnikova NP, Zakharchenro EA. Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery. *Dalton Trans.* 2010;39:4170–4178.
26. Yang F, Kubota F, Baba Y, Kamiya N, Goto M. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. *J Hazard Mater*. 2013;254:79–88.
27. Liu YH, Zhu LL, Sun XQ, Chen J. Toward greener separations of rare earths: bifunctional ionic liquid extractants in biodiesel. *AIChE J*. 2010;56:2338–2346.
28. Hoogerstraete TV, Wellens S, Verachtert K, Binnemans K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. *Green Chem.* 2013;15:919–927.
29. Bond AH, Chiarizia R, Huber VJ, Dietz ML, Herlinger AW, Hay BP. Synergistic solvent extraction of alkaline earth cations by mixtures of di-n-octylphosphoric acid and stereoisomers of dicyclohexano-18-crown-6. *Anal Chem.* 1999;71:2757–2765.
30. Levitskaia TG, Bonnesen PV, Chambliss CK, Moyer BA. Synergistic pseudo-hydroxide extraction: synergism and anion selectivity in sodium extraction using a crown ether and a series of weak lipophilic acids. *Anal Chem.* 2003;75:405–412.
31. Hasegawaa Y, Tamaki S, Yajima H, Hashimoto B, Yaita T. Selective separation of samarium(III) by synergistic extraction with diketone and methylphenylphenanthroline carboxamide. *Talanta*. 2011;85:1543–1548.
32. Tong H, Wang YL, Liao W, Li D. Synergistic extraction of Ce(IV) and Th(IV) with mixtures of Cyanex 923 and organophosphorus acids in sulfuric acid media. *Sep Purif Technol*. 2013;118:487–491.
33. Stepinski DC, Jensen MP, Dzielawa JA, Dietz ML. Synergistic effects in the facilitated transfer of metal ions into room-temperature ionic liquids. *Green Chem.* 2005;7:151–158.
34. Sun XQ, Ji Y, Liu YH, Chen J, Li DQ. An engineering-purpose preparation strategy for ammonium-type ionic liquid with high purity. *AIChE J*. 2010;56:989–996.
35. Sun XQ, Luo HM, Dai S. Mechanistic investigation of solvent extraction based on anion-functionalized ionic liquids for selective separation of rare-earth ions. *Dalton Tran*. 2013;42:8270–8275.
36. Sun XB, Zhao JM, Meng SL, Li DQ. Synergistic extraction and separation of yttrium from heavy rare earths using mixture of sec-octylphenoxy acetic acid and bis(2,4,4-trimethylpentyl)phosphinic acid. *Anal Chim Acta*. 2005;533:83–88.
37. Greenwood NN, Earnshaw A. *Chemistry of the Elements*, 2nd ed. Oxford, U.K.: Butterworth-Heinemann, 1997.
38. Rout A, Kotlarska J, Dehaen W, Binnemans K. Liquid-liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: the non-innocence of the ionic liquid cation. *Phy Chem Chem Phy*. 2013;15:16533–16541.
39. Sun XQ, Do-Thanh CL, Luo HM, Dai S. The optimization of an ionic liquid-based TALSPEAK-like process for rare earth ions separation. *Chem Eng J*. 2014;239:392–398.
40. Wang XL, Li W, Meng SL, Li DQ. The extraction of rare earths using mixtures of acidic phosphorus-based reagents or their thio-analogues. *J Chem Technol Biotechnol*. 2006;81:761–766.
41. Huang XW, Li JN, Long ZQ, Zhang YQ, Xue XX, Zhu ZW. Synergistic extraction of rare earth by mixtures of 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester and di-(2-ethylhexyl) phosphoric acid from sulfuric acid medium. *J Rare Earths*. 2008; 26:410–413.
42. Zhao JM, Shen XY, Wang FC, Liu HZ. Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. *Sep Purif Technol*. 2011;78:345–351.

Manuscript received Apr. 16, 2014, and revision received July 10, 2014.