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Short communication

Solvent extraction of rare-earth ions based on functionalized ionic liquids

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ABSTRACT

Three functionalized ionic liquids (ILs), tetrabutylammonium di(2-ethylhexyl)phosphate ([TBA][DEHP]), trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][DEHP]), and trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][DEHP]), are synthesized and characterized. These ILs are used as DEHP-based ionic extractants and are investigated for rare earth elements (REEs) separation in 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_6mim][NTf_2]) and diisopropylbenzene (DIPB) along with di(2-ethylhexyl)phosphoric acid (HDEHP). Solubilities of the DEHP-based ionic extractants in [C_6mim][NTf_2] are much better than that of HDEHP in [C_6mim][NTf_2]. We herein report the achievement of enhanced extractabilities and selectivities for separation of REEs using DEHP-based ionic extractants in [C_6mim][NTf_2]. This work highlights the potential of developing a comprehensive ionic liquid-based extraction strategy for REEs using ionic liquids as both extractant and diluent.

1. Introduction

Analytical and separation technologies for rare earth elements (REEs) are attracting more and more attentions worldwide because of their wide applications in many critical technological areas as well as nuclear fuel cycles (NFC) [1–3]. One prime example, trivalent actinide lanthanide separations by phosphorous-reagent extraction from aqueous complexes (TALSPEAK), was originally developed in the 1960s at Oak Ridge National Laboratory to separate minor actinides from rare-earth fission products [4–6]. In TALSPEAK, diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid (DTPA) was used as a complexing agent to selectively retain actinides; accordingly, REEs could be extracted into diisopropylbenzene (DIPB) containing HDEHP. Although TALSPEAK has been widely studied for separating actinides from REEs, less work has been reported for separations among REEs themselves using TALSPEAK. In our recent work, excellent extraction efficiencies and selectivities for some REEs using HDEHP as extractant were observed in a number of ionic liquids relative to those in DIPB [7]. However, the low solubility of HDEHP in ILs seemed to be a disadvantage. To bring this IL-based TALSPEAK into full play, herein we investigate the extraction behaviors of three ionic extractants containing di(2-ethylhexyl)phosphate (DEHP) as anions for REEs separation in an IL-based TALSPEAK process.

Ionic liquids are a family of molten salts that are unique from other such salts for various reasons. Their melting points are below 100 °C, oftentimes even below room temperature [8]. The IL-based extraction is a novel separation method that uses ILs rather than volatile organic compounds (VOCs) as diluents for extraction. Low volatility, low combustibility, and high thermal stability make ILs environmentally friendly for usage in solvent extraction [9–11]. The limited solubilities of ionic species in nonionic VOCs are the main problem associated with conventional solvent extractions. The ionic properties of ILs make them thermodynamically favorable solvents for the extraction of ionic species from aqueous solutions [12]. Up to now, many papers describe the large extractabilities and selectivities achieved using molecular extractants for metal ions in ILs [13–15]. In this report, three DEHP type ionic extractants, that is, tetrabutylammonium di(2-ethylhexyl)phosphate ([TBA][DEHP]), trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][DEHP]), and trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][DEHP])—are synthesized and investigated for REEs separation in 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_6mim][NTf_2]). These three ionic extractants are functionalized ILs. In contrast to most functionalized ILs with cations containing functional groups, the functionalities in our case are incorporated into the anion

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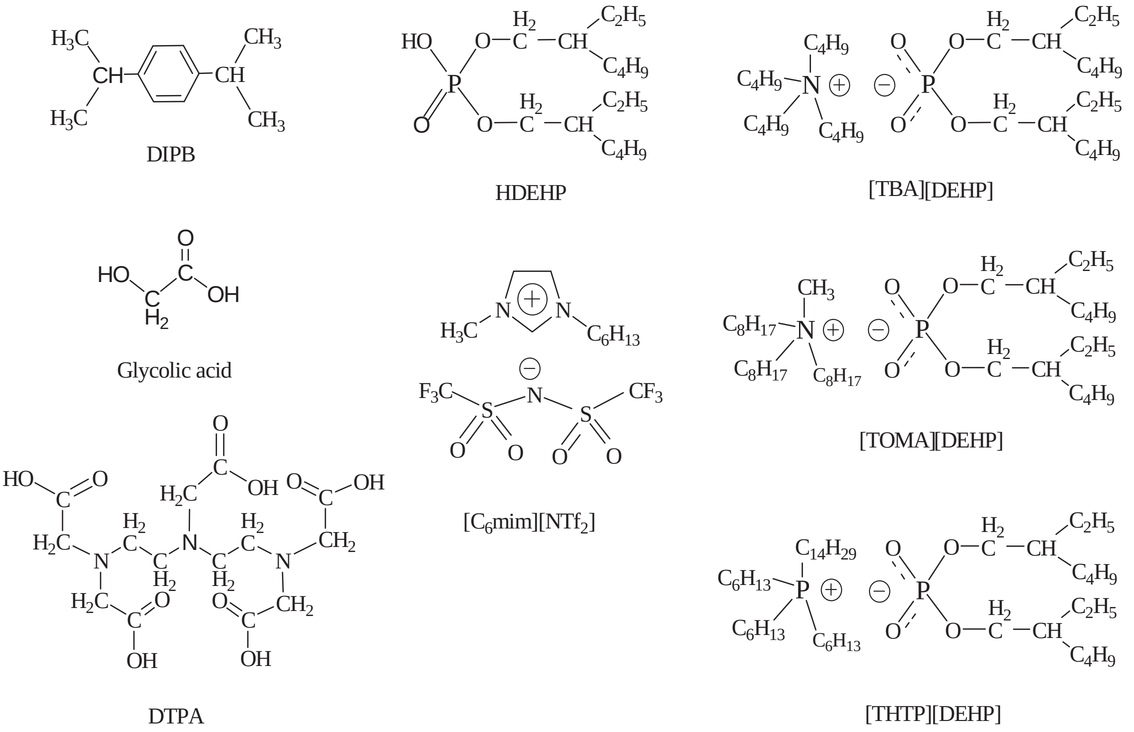

Fig. 1. Structures of components in IL-based TALSPEAK process.

structure of ILs. Recently, similar functionalized ILs were found to have obviously inner synergistic effect for Eu^{3+} in VOC [16]. The IL-based ionic extractants have the similar structural feature as those of ILs and therefore are highly miscible with other ILs. In this report, the extraction behaviors of series of REEs using the DEHP type functionalized ILs are investigated in IL. This comprehensive IL-based separation process using ILs as both extractants and diluents reveals surprising extraction and separation for REEs. To our knowledge, no such large extractabilities and selectivities from IL-based extraction systems have been reported in any other papers.

2. Experimental

2.1. Chemicals and reagents

All chemicals and solvents were reagent grade and used without further purification. Tetrabutylammonium chloride ([TBA]Cl) and trioctylmethylammonium chloride ([TOMA]Cl) were purchased from the Fluka. Trihexyltetradecylphosphonium bromide ([THTP]Br) was purchased from Aldrich. HDEHP was purchased from Alfa Aesar. [C_6mim][NTf_2] was prepared according to the previously published work [17]. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker MSL-400 at 400 MHz. TGA was carried out on a TA Instruments thermogravimetric analyzer. FT-IR spectra were measured using a Bio-Rad Excalibur FTS-3000 spectrometer. The water contents were determined using an AQUAPAL III Karl–Fisher titration. Thermo IRIS Intrepid III ICP-AES was used to determine the concentration of REEs in aqueous phase. The aqueous solutions containing 0.7 mM for each REE ion were prepared by dissolving their nitrate salts in the aqueous solutions with 0.1 M of DTPA and 1 M of glycolic acid. The deionized water used for preparing the aqueous solutions has a specific resistance of 18 MΩ-cm or greater. The pH of the aqueous solutions was adjusted using sodium hydroxide. The structures of the chemical components in our extraction study are given in Fig. 1.

2.2. Synthesis and characterization of DEHP-type functionalized ILs

The DEHP-type ILs were prepared using the neutralizing method according to literature procedure [18].

2.2.1. [TBA][DEHP]

The solution of [TBA]OH in ethanol was prepared from [TBA]Cl (2.78 g, 0.01 mol) using a Doex monosphere 550A (OH) anion exchange resin. HDEHP (3.22 g, 0.01 mol) was added to the [TBA]OH solution. The mixture was then stirred at room temperature for 6 h till the solution became neutral. Ethanol and water were distilled off and the product was dried at 70 °C under vacuum for 12 h to yield [TBA][DEHP] as a colorless viscous liquid (5.29 g, 0.0094 mol, yield: 94%).

^{1}H NMR ($CDCl_3$, ppm): 0.86 (m, 6H, CH_3), 0.88 (m, 6H, CH_3), 0.98–1.02 (m, 12H, CH_3), 1.24–1.27 (m, 12H, CH_2), 1.32 (m, 2H, CH), 1.43–1.48 (m, 8H, CH_2), 1.51 (m, 4H, CH_2), 1.64 (m, 8H, CH_2), 3.36 (t, 8H, NCH_2), 3.70 (m, 4H, OCH_2); ^{13}C NMR ($CDCl_3$, ppm): 10.98 ($2CH_3$), 13.71 ($2CH_3$), 14.15 ($2CH_3$), 19.73 ($4CH_2$), 23.18 ($3CH_2$), 23.33 ($3CH_2$), 24.07 (2CH), 29.08 ($2CH_3$), 30.12 ($2CH_2$), 40.41 ($2CH_2$), 40.49 ($2CH_2$), 58.72 ($4CH_2$), 67.27 (CH_2), 67.32 (CH_2); IR (cm^{-1}): 2959, 2930, 2874, 1558, 1458, 1379, 1236, 1053.

2.2.2. [TOMA][DEHP]

The solution of [TOMA]OH in ethanol was prepared from [TOMA]Cl (4.04 g, 0.01 mol) using a Doex monosphere 550A (OH) anion exchange resin. HDEHP (3.22 g, 0.01 mol) was added to the [TOMA]OH solution. The mixture was then stirred at room temperature for 6 h till the solution became neutral. Ethanol and water were distilled off and the product was dried at 70 °C under reduced

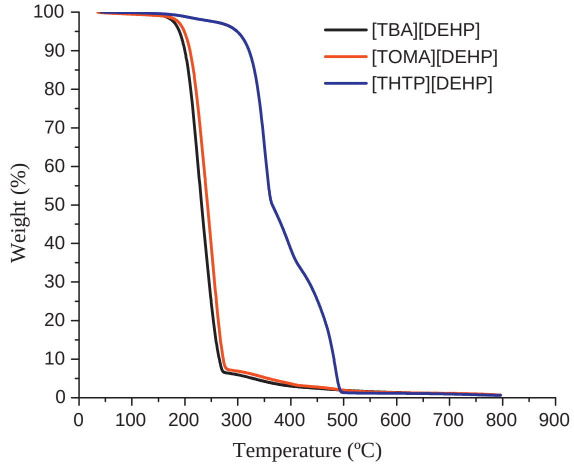

Fig. 2. TGA plots of [TBA][DEHP], [TOMA][DEHP] and [THTP][DEHP].

pressure for 12 h to yield [TOMA][DEHP] as a colorless viscous liquid (6.35 g, 0.0092 mol, yield: 92%).

^{1}H NMR ($CDCl_3$, ppm): 0.85 (m, 6H, CH_3), 0.88 (m, 9H, CH_3), 1.23–1.27 (m, 30H, CH_3 and CH_2), 1.32 (m, 6H, CH_2), 1.35 (m, 12H, CH_2), 1.43 (m, 4H, CH_2), 1.49 (m, 2H, CH), 1.58 (m, 6H, CH_2), 3.28 (s, 3H, NCH_3), 3.37 (t, 6H, NCH_2), 3.72 (m, 4H, OCH_2); ^{13}C NMR ($CDCl_3$, ppm): 10.22 (CH_3), 14.26 (CH_3), 14.37 (CH_3), 22.59 (CH_2), 22.80 (CH_2), 23.40 (CH_2), 23.59 (CH_2), 26.55 (CH_2), 29.25 ($2CH_2$), 29.31 (CH_2), 29.41 (CH_2), 30.36 (CH_3), 31.88 (CH_2), 40.63 (CH), 49.08 (CH_2), 61.37 (CH_3), 67.74 (CH_2); IR (cm^{-1}): 2957, 2926, 2858, 1466, 1379, 1244, 1051.

2.2.3. [THTP][DEHP]

The solution of [THTP]OH in ethanol was prepared from [THTP]Br (4.50 g, 0.008 mol) using a Doex monosphere 550A (OH) anion exchange resin. HDEHP (2.58 g, 0.008 mol) was added to the [THTP]OH solution. The mixture was then stirred at room temperature for 6 h till the solution became neutral. Ethanol and water were distilled off and the product was dried at 70 °C under vacuum for 12 h to yield [THTP][DEHP] as a colorless viscous liquid (5.96 g, 0.0074 mol, yield: 93%).

^{1}H NMR ($CDCl_3$, ppm): 0.85–0.91 (m, 24H, CH_3), 1.26–1.31 (m, 48H, CH_2), 1.37–1.49 (m, 18H), 2.37–2.41 (m, 8H, PCH_2), 3.70 (m, 4H, OCH_2); ^{13}C NMR ($CDCl_3$, ppm): 11.23 (CH_3), 14.18 (CH_3), 14.38 (CH_3), 18.95 (CH_3), 19.41 (CH_3), 22.21 (CH_2), 22.59 (CH_2), 22.90 (CH_2), 23.42 (CH_2), 23.59 (CH), 29.33 (CH_2), 29.56 (CH_2), 29.86 (CH_2), 30.38 (CH_2), 30.67 (CH_2), 30.82 (CH_2), 31.00 (CH_2), 31.14 (CH_2), 31.42 (CH_2), 32.13 (CH_2), 40.66 ($3CH_2$), 40.73 (CH_2), 67.63 ($2CH_2$); IR (cm^{-1}): 2957, 2924, 2855, 1458, 1377, 1240, 1055.

2.2.4. TGA of DEHP-type functionalized ILs

Thermal gravimetric analysis (TGA) was carried out in a nitrogen atmosphere with a 10 °C/min temperature ramping rate to 800 °C. The TGA plots of three functionalized ILs are illustrated in Fig. 2. As seen in Fig. 2, all three ILs are thermally stable up to ~250 °C, phosphonium based IL ([THTP][DEHP]) is about 100 °C more stable than ammonium based-ILs ([TBA][DEHP] and [TOMA][DEHP]).

2.2.5. Water contents of DEHP-type functionalized ILs

The water contents of [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] have been determined using the Karl–Fisher titration. They are 1.2%, 1.0%, and 0.3%, respectively. The water contents of these functionalized ILs follow a consistent trend. The phosphonium-based IL ([THTP][DEHP]) is more hydrophobic than the ammonium based-ILs ([TBA][DEHP] and [TOMA][DEHP]) and the longer carbon chain length increases hydrophobicity.

2.3. Extraction experiments

The extraction experiments were performed by contacting 0.5 mL of DIPB or [C_6min][NTf_2] containing 0.8 M of HDEHP, [TBA][DEHP], [TOMA][DEHP], [THTP][DEHP] with 5 mL of REEs-containing aqueous solution for 60 min in a vibrating mixer. After centrifugation at 8500 rpm for 5 min, the aqueous phase was separated and the concentrations of REE ions in aqueous phases were determined using ICP-AES. The concentration of REE ions in IL phase was calculated by mass balance. The distribution coefficient (D) and separation factor (SF) are defined as follows:

$$D_M = \left\{ \frac{(C_i - C_f)}{(C_f)} \right\} \times \frac{\{\text{Volume of aqueous solution}\}}{\{\text{Volume of IL}\}} \tag{1}$$

$$SF = \frac{D_1}{D_2} \tag{2}$$

where C_i and C_f represent the initial and final concentrations of a metal ion in aqueous phase, D_1 and D_2 are the distribution ratio of metal 1 and 2.

2.4. Stripping experiments

To recover the REEs from extraction experiments, the IL phase was separated from the aqueous phase following the extraction experiment, 5 mL solution of nitric acid with different concentrations was added to the recovered IL phase. The mixtures were agitated for 60 min in a vibrating mixer. After centrifugation at 8500 rpm for 5 min, the aqueous phase was separated and the concentrations of REE ions in aqueous phases were determined using ICP-AES. The concentration of REE ions in IL phase was calculated by mass balance. The stripping ratio (S%) is defined as follows:

$$S\% = \frac{[M]_{\text{aq,a}}}{[M]_{\text{org,t}}} \times 100 \tag{3}$$

where $[M]_{\text{aq,a}}$ is an equilibrium concentration of the metal ion in stripping phase and $[M]_{\text{org,t}}$ is an initial concentration of the metal ion in IL phase, respectively.

3. Results and discussion

3.1. Comparison of extractabilities of HDEHP and DEHP-based ionic extractants for REEs

Three DEHP-type functionalized ILs are used as DEHP-based ionic extractants for separation of REEs. Fig. 3 compares the extraction results of three DEHP-based ionic extractants and HDEHP in [C_6mim][NTf_2] and DIPB. It is clear that the distribution coefficients (D_M) of HDEHP, [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] for REEs in [C_6mim][NTf_2] are much higher than those in DIPB. It worthwhile to mention that $D_{\text{IL}}/D_{\text{DIPB}}$ of [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] is larger than those of HDEHP for light and heavy REEs. For example, the largest $D_{\text{IL}}/D_{\text{DIPB}}$ values from [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] for Lu^{3+} are 3.95×10^2, 6.04×10^6, and 2.16×10^3, respectively. The largest $D_{\text{IL}}/D_{\text{DIPB}}$ from HDEHP for Lu^{3+} is 1.3. Obviously, the increased amounts of extractability of [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] for REEs in [C_6mim][NTf_2] versus DIPB are larger than those of HDEHP. The drastic increase in distribution coefficients for these ionic extractants in ILs other than DIPB reaches as high as 6 orders of magnitude. The interesting effect can be attributed to their different structures in nature. [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP] are ionic extractants; however, HDEHP is a molecular extractant. The better extraction abilities of ionic extractants in [C_6mim][NTf_2] can be attributed to the well-known “like-dissolves-like (LDL)” principle

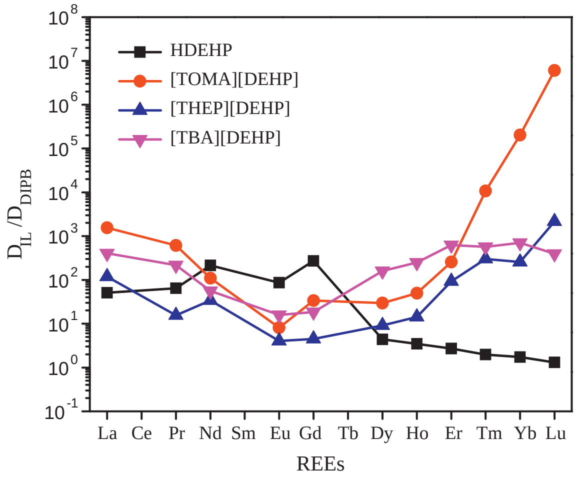

Fig. 3. Ratios of distribution coefficients of REEs in [C_6mim][NTf_2] versus DIPB. HDEHP = [TBA][DEHP] = [TOMA][DEHP] = [THTP][DEHP] = 0.8 M, REE^{3+} = 0.7 mM for each metal ion, DTPA = 0.1 M, glycolic acid = 1.0 M.

[19,20]. This principle states that a solute can dissolve best in a diluent that has a similar chemical structure to itself. According to the principle, the polar compounds are more likely to be extracted by polar extracting phases. In this study, the ionic extracting complexes formed by REEs and ionic extractants have better solubilities and stabilities in ILs than in DIPB. There are strong ion-pair interactions in ILs, such as electrostatic interaction, van der Waals forces, and induction interaction [21]. The strength of the ion–ion interaction depends on the IL structure and may strongly affect the ability of anions and/or cations to interact with dissolved species. It is clear that the ion-pair interactions are effective for REEs extraction in ILs containing both ammonium and phosphonium cations with DEHP anion.

3.2. *Different extraction phenomena*

The photographs of extraction solutions using HDEHP and [TOMA][DEHP] in DIPB and [C_6mim][NTf_2] after extraction in IL-based TALSPEAK process for REEs are given in Fig. 4. As can be seen in Fig. 4, the DIPB extracting phases containing HDEHP [Fig. 4(1)] and [TOMA][DEHP] [Fig. 4(3)] are quite clear. However, the extraction solutions of HDEHP in [C_6mim][NTf_2] [Fig. 4(2)] and [TOMA][DEHP] in [C_6mim][NTf_2] [Fig. 4(4)] are different, where small white droplets can be seen for Fig. 4(2) and the clear lower extracting phase can be seen for [Fig. 4(4)]. This difference reveals clearly the different extraction abilities of HDEHP and [TOMA][DEHP] in DIPB and in [C_6mim][NTf_2]. Moreover, the extracting complexes formed by HDEHP and REEs are distributed onto [C_6mim][NTf_2] as white liquid drops [Fig. 4(2)] suggesting that such extracting complexes are not well solubilized by [C_6mim][NTf_2] and the emulsification phenomenon is observed here. In contrast, the extracting complexes formed by [TOMA][DEHP] and REEs are all homogeneously distributed into [C_6mim][NTf_2] to form a nice clear phase [lower phase in Fig. 4(4)]. In fact, HDEHP can only be dissolved in [C_6mim][NTf_2] up to ~0.04 M. However, [TOMA][DEHP] is basically miscible with [C_6mim][NTf_2]. For the sake of comparison, the same concentration (0.8 M) for HDEHP and [TOMA][DEHP] was used in our study under the typical conditions of TALSPEAK. The solubility differences of HDEHP and [TOMA][DEHP] in [C_6mim][NTf_2] before extraction and extracting complexes formed after extraction can be both attributed to the "like-dissolves-like" principle. Fig. 4(4) clearly shows that extracting complexes formed by [TOMA][DEHP] and REEs are well dissolved in [C_6mim][NTf_2] (lower phase). The visual comparison of the photographed extracting phases indicates that the "LDL" principle applies to the IL-based TALSPEAK process discussed above. In order to visually see the different extraction behaves of HDEHP and [TOMA][DEHP] in DIPB and [C_6mim][NTf_2], the extractant concentration as high as ~0.8 M was used in the extraction experiments (Fig. 4). The extracting complexes derived from [TOMA][DEHP] formed a homogeneous solution in the IL diluent [lower phase in Fig. 4(4)] while a emulsification phenomenon was observed for HDEHP in [C_6mim][NTf_2] [Fig. 4(2)]. It should be pointed out that no white droplets can be seen if less concentrated HDEHP is used in [C_6mim][NTf_2].

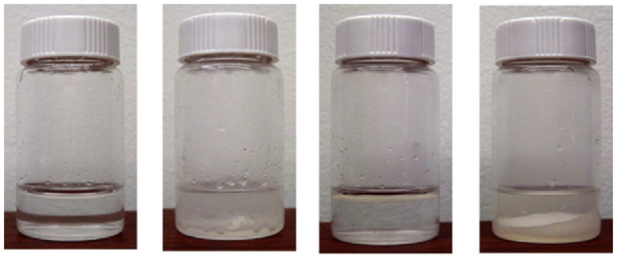
(1) (2) (3) (4)

Fig. 4. Photographs of extraction solutions using HDEHP and [TOMA][DEHP] in DIPB (1, 3) and in [C_6mim][NTf_2] (2, 4) after extraction in IL-based TALSPEAK process for REEs.

3.3. *Selectivity study of HDEHP and DEHP-based ionic extractants for REEs*

In addition to extractability, selectivity is another important factor in separation of REEs. The prepared DEHP-based ionic extractants are bifunctional ILs. Larger steric hindrance in cations is an eminent characteristic of these DEHP-based ionic extractants over HDEHP. Steric hindrance is a crucial property for extractants that increases selectivities in metal ions separations [22–24]. The conventional TALSPEAK process typically gave lower extraction abilities for middle REEs. Therefore, the selectivities of HDEHP and DEHP-based ionic extractants were investigated using other REEs to Eu^{3+}, one of the middle REEs. As illustrated in Fig. 5, the separation factors (*SFs*) of [TBA][DEHP], [TOMA][DEHP] and [THTP][DEHP] are obviously larger than those

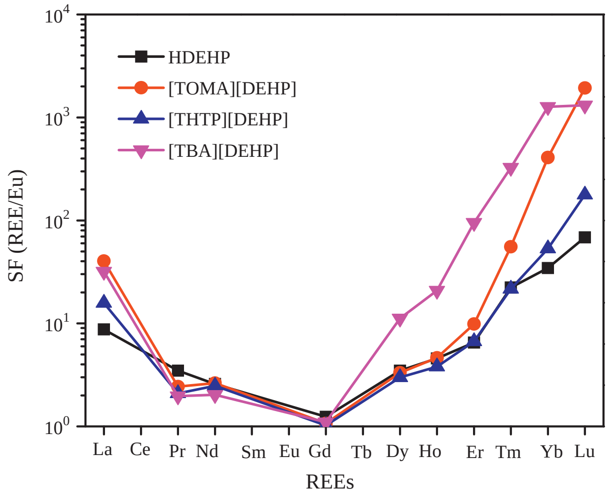

Fig. 5. Separation factors of REEs versus Eu^{3+} using HDEHP, [TBA][DEHP], [TOMA][DEHP] and [THTP][DEHP] in [C_6mim][NTf_2]. HDEHP = [TBA][DEHP] = [TOMA][DEHP] = [THTP][DEHP] = 0.8 M, REE^{3+} = 0.7 mM for each metal ion, DTPA = 0.1 M, glycolic acid = 1.0 M.

of HDEHP in [C_6mim][NTf_2]. To conserve space, more useful *SF* values between adjacent REEs in IL-based TALSPEAK process are calculated and given in Supporting Information. These results indicate that the greater steric hindrance of DEHP-based ionic extractants is an important advantage for increasing selectivities in the IL-based TALSPEAK process. DEHP-based ionic extractants containing ammonium {[TBA][DEHP], [TOMA][DEHP]} seem to have higher separation factors for heavy REEs than phosphonium-based extractant {[THTP][DEHP]}. In addition, the increased extraction sequences of REEs using HDEHP and DEHP-based ionic extractants are different. As Fig. 3 reveals, the better extraction abilities of REEs by HDEHP are for the middle REEs. However, the better extraction abilities of REEs by DEHP-based ionic extractants are the light and heavy REEs. Undoubtedly, the different extraction sequence of REEs is another explanation for the better selectivities of REEs from DEHP-based ionic extractants. From the extractabilities and selectivities discussed above, cations with different structures can have different effects on REEs extraction and separation.

3.4. *Stripping characteristics of REEs*

Stripping is an important feature for evaluating an extraction system. As can be seen in Fig. 6, the stripping characteristics of REEs were studied using nitric acid under three different acidities (2 M, 4 M, and 6 M). In this IL-based TALSPEAK system, the extractabilities of [TOMA][DEHP] for REEs are different. Light REEs (e.g. La^{3+}) and heavy REEs (e.g. Lu^{3+}) are easier to be extracted than middle REEs (e.g. Eu^{3+}). Accordingly, there are more light REEs and heavy REEs than middle REEs in extracting phase before stripping. As a result, the stripping ratios (*S*%) of middle REEs are greater than those of light and heavy REEs at the lower acidity (2 M) because of less amount of middle REEs existed in the IL phase. As acidities increased to 4 M and 6 M, the *S*% values increase and the difference between the *S*% values decreases. At the acidity of 6 M HNO_3, all the REEs can be stripped with satisfactory results.

The extraction mechanism is very important for the new DEHP-based ionic extractants. The systems are very complicated and therefore it is difficult to determine which species exist based on our current experimental data. The objective of this short communication is to report the advantage of our comprehensive IL-based TALSPEAK approach using IL as both extractant and diluent so as to achieve the high solubilities of DEHP-ILs in [C_6mim][NTf_2], high extractabilities, and high selectivities of the IL-based TALSPEAK for REEs. Detailed investigations of the extraction mechanism and process optimization of this comprehensive IL-based extraction for REEs separation are underway in our laboratory, which will be a subject of a full paper. Our preliminary results indicate that it is a solvation mechanism and it seems not to involve the exchange of either cation or anion from ILs into the aqueous phase.

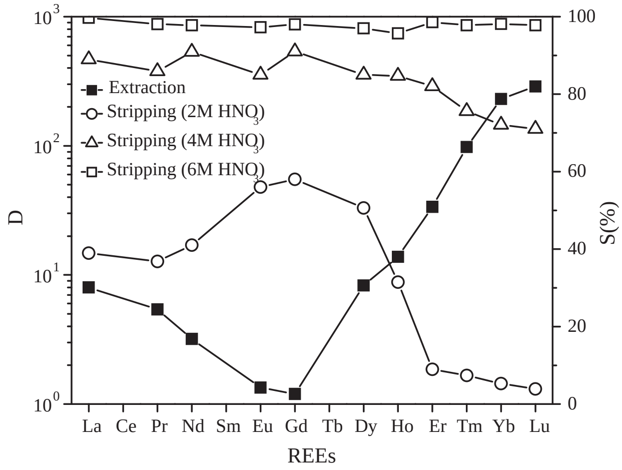

Fig. 6. The extraction of REEs in IL-based TALSPEAK and stripping characteristics of REEs using HNO_3. [TOMA][DEHP] = 0.2 M, REE^{3+} = 0.84 mM for each metal ion, DTPA = 0.02 M, glycolic acid = 1.0 M.

4. Conclusions

In conclusion, the IL-based separation process for separation of REEs using IL as both extractant and diluent was developed. Ionicity is a crucial characteristic of this strategy. The novel functionalized ILs—that is, [TBA][DEHP], [TOMA][DEHP], and [THTP][DEHP]—used as extractants revealed much higher extractabilities for REEs in [C_6mim][NTF_2] than in DIPB. The high extraction efficiency can be attributed to the “like-dissolves-like” principle. The ionic extracting complexes formed by REEs and ionic extractants have better solubilities and stabilities in IL than in DIPB. The DEHP-based ionic extractants demonstrate better selectivities for REEs than HDEHP because of the larger steric hindrance in cations. In addition, REEs can be effectively stripped using nitric acid in the IL-based TALSPEAK. This work highlights the potential of developing a comprehensive IL-based extraction strategy for REEs using IL as both extractant and diluent. The comprehensive IL-based extraction strategy also reveals dramatic potential to be applied in microextraction, adsorption, membrane for preconcentration and separation of REEs.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.12.069.

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