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# Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation†

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The ionic liquids 1-hexyl-3-methylimidazolium bis(2-ethylhexyl)phosphate, [$C_6$mim][DEHP], 1-hexyl-1-methylpyrrolidinium bis(2-ethylhexyl)phosphate, [$C_6$mpyr][DEHP], and tetrabutylammonium bis(2-ethylhexyl)-phosphate, [$N_{4444}$][DEHP], were prepared and characterized using $^1$H and $^{13}$C NMR spectroscopy. The extraction behavior of neodymium(III) from nitrate medium by these ionic liquids, diluted with the room temperature ionic liquids 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [$C_6$mim][$NTf_2$], 1-hexyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [$C_6$mpyr][$NTf_2$], and tributylmethylammonium bis(trifluoromethylsulfonyl)imide, [$N_{1444}$][$NTf_2$], was studied. The distribution ratio of neodymium(III) was measured as a function of various parameters, such as pH, concentration of the ionic liquid extractant, nature of diluents, concentration of ionic liquid cations and nitrate anions in the aqueous phase. The extraction behavior was compared with that obtained for a solution of the molecular extractant bis(2-ethylhexyl)phosphoric acid (DEHPA) in an ionic liquid diluent. The extraction of neodymium(III) in the ionic liquids [$C_6$mim][DEHP] and [$C_6$mpyr][DEHP] showed markedly different extraction properties in comparison with that of the quaternary ammonium analogue [$N_{4444}$][DEHP], especially concerning the pH dependence of the extraction process. These results show that the extraction process can be tuned by the selection of the ionic liquid cation. The extraction experiments also included the trivalent rare-earth ions lanthanum(III), cerium(III), praseodymium(III), ytterbium(III) and yttrium(III). Studies of the stripping behavior and the reusability of the ionic liquids were carried out, which indicate that the ionic liquids can be reused with no loss in activity.

## Introduction

Neodymium is one of the more abundant rare-earth elements and it is heavily used in neodymium–iron–boron permanent magnets.[1–4] The recovery of neodymium from End-of-Life consumer goods is essential for an efficient use of resources, to guarantee a sufficient supply of this critical element, and for the so-called "balance problem".[5] Solvent extraction (SX) is the most commonly used technique for the recovery of neodymium and other rare earths from waste streams containing these elements, and for the separation of mixtures of rare earths into the individual elements.[6] Different approaches have been followed to make the recovery of rare earths by solvent extraction more sustainable, and one of these is the use of ionic liquids (ILs).[7]

Ionic liquids are solvents that consist entirely of ions and are typically organic salts with melting points lower than 100 °C.[8–11] Room temperature ionic liquids (RTILs) are of special interest. Ionic liquids have a high potential for applications in hydrometallurgy.[12] Due to their useful solvent properties such as a negligible vapor pressure, a high thermal stability and high stability against nuclear radiation, high selectivity and efficiency for solvent extraction, they are attracting the attention of many researchers who are dealing with solvent extraction processes, and also of those working in the field of spent nuclear fuel reprocessing.[13–31] Ionic liquid extractants can be used in pure form, without diluents.[7,32,33] Ionic liquids with an organic functionality tethered to the cationic or the anionic part of the ionic liquid are known as functionalized ionic liquids (FILs) or task-specific ionic liquids (TSILs).[34] Functionalized ionic liquids may exhibit properties of both an ionic liquid and a complex-forming agent. Functionalized ionic liquids with the functional moiety as part of the anion were successfully applied as extractants for separation of metal ions from aqueous medium.[35–39] Mehdi *et al.* synthesized a new family of ionic liquids containing a β-diketonate anion combined with a 1-alkyl-3-methylimidazolium

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cation and they studied the coordination behavior of neodymium(III) and cobalt(II).[40] Similarly, Sun *et al.* synthesized some Aliquat® 336 based bi-functionalized ionic liquids with dialkylphosphate and carboxylate anions and studied the extraction and separation of rare-earth elements (REEs) from acidic medium.[41,42] They emphasized the "like dissolves like" principle to explain the remarkably higher distribution ratios of the REEs. They found that inner-synergism plays a dominant role when these bifunctional ionic liquids are being used as extractants as compared to the mixture of their corresponding precursors. In a recent study, these authors investigated the alkyl chain length of the cation and the anion of 1-alkyl-3-methylimidazolium bis(perfluoroalkanesulfonyl)imides used as diluents for tetraalkylammonium and phosphonium dialkylphosphate ionic liquids.[43] Rout *et al.* synthesized two ionic liquids derived of Aliquat® 336, namely tri-*n*-octyl-methylammonium bis(2-ethylhexyl)phosphate, [A336][DEHP], and tri-*n*-octyl-methylammonium bis(2-ethylhexyl)diglycolamate, [A336][DGA], and they highlighted their unusual miscibility in solvents used in the nuclear industry, *e.g.* *n*-dodecane and its higher homologues and their use for the separation of europium(III) from americium(III).[44] Another study by the same research group dealt with the extraction of plutonium(IV) by β-diketonate-based ionic liquids with ammonium and imidazolium cations.[45] Remarkably large distribution ratios and changes in the extraction mechanism were observed for extractions in ionic liquid media, compared to extractions in conventional molecular diluents. Wang *et al.* used the bifunctional ionic liquids tri-*n*-octyl-methylammonium *sec*-octylphenoxy acetate and tri-*n*-octyl-methylammonium *sec*-nonylphenoxy acetate for the extraction of rare earths from chloride medium.[46]

Although a few studies on the use of dialkylphosphate ionic liquids for the separation of rare earths have appeared in the literature, there was no focus on the changes in extraction behavior induced by the choice of the ionic liquid cation or the ionic liquid diluents. This paper deals with the synthesis of ionic liquids with the 1-hexyl-3-methylimidazolium cation $[C_6mim]^+$, the 1-hexyl-1-methylpyrrolidinium cation $[C_6mpyr]^+$ and the tetrabutylammonium cation $[N_{4444}]^+$ and with the bis(2-ethylhexyl)phosphate anion $[DEHP]^-$, as well as with the application of these ionic liquids for the extraction of neodymium(III) and other trivalent rare-earth ions from nitric acid medium under various experimental conditions. The extraction behavior of the ionic liquids $[C_6mim][DEHP]$ and $[C_6mpyr][DEHP]$ is compared with that of the molecular extractant bis(2-ethylhexyl)phosphoric acid (DEHPA) and the corresponding quaternary ammonium ionic liquid $[N_{4444}][DEHP]$.

## Experimental

### Materials and reagents

All the chemicals and reagents used in the study were of analytical grade. The chemicals, nitric acid (Aldrich), dichloromethane (Aldrich), bis(2-ethylhexyl)phosphoric acid (DEHPA) (99%; Sigma Aldrich), tributylmethylammonium bis(trifluoromethylsulfonyl)imide (99%; IoLiTec), phosphorus trichloride (Alfa Aeser), 2-ethylhexanol (Alfa Aeser), 1-hexyl-3-methylimidazolium chloride (99%; IoLiTec), tetrabutylammonium chloride (99%; IoLiTec) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6mim][NTf_2]$ (99%; IoLiTec), were used as received. $Nd(NO_3)_3\cdot 6H_2O$ (>99%) and other metal nitrates (purity ≥ 99%) used in this study were purchased from ACROS Organics (Geel, Belgium). A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium).

### Instrumentation and analysis

The concentrations of rare earths in the aqueous phase were determined using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). The extraction experiments were performed using small vials in a temperature-controllable compact benchtop Turbo Thermo Shaker (Model: TMS – 200), Hangzhou Allsheng Instrument Co. Ltd, China. After 1 hour of equilibration, part of the aqueous phase was removed and an internal gallium standard was added until a total volume of 1 mL was obtained. The quartz glass sample carriers were first treated with 20 μL of silicone solution in isopropanol in order to bind the sample droplet by its polar sites and thus avoid spreading of the droplet on the sample carrier. Then, the sample carriers were dried for 5 minutes in a hot air oven at 60 °C, followed by the addition of 5 μL of the sample and a drying process of 20 minutes at the same temperature. The metal concentrations were measured for 200 seconds. All samples were diluted with water (MilliQ50) if necessary. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of samples after extraction. $^1H$ NMR and $^{13}C$ NMR spectra of ionic liquids were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for $^1H$. $^{31}P$ NMR spectra were recorded using a Bruker Avance 400 spectrometer, operating at 121.49 MHz for $^{31}P$, and using a $H_3PO_4$ (85%) external standard as a reference. $CDCl_3$ was used as the solvent for recording the NMR spectra and the data were analyzed with the SPINWORKS software package. The viscosity of the ionic liquids was measured using an automatic Brookfield plate cone viscometer, Model LVDV-II+P CP (Brookfield Engineering Laboratories, USA). The pH measurements were performed using an S220 SevenCompact™ pH/Ion meter (Mettler-Toledo) and a Slimtrode (Hamilton) electrode.

### Synthesis of ionic liquids

1-Hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_6mpyr][NTf_2]$ was prepared as described elsewhere.[47] The procedure for the synthesis of ionic liquids $[C_6mim][DEHP]$, $[C_6mpyr][DEHP]$ and $[N_{4444}][DEHP]$ and the structure of their precursors are summarized in Fig. 1. Briefly, the first step involved the refluxing of $PCl_3$ with 2-ethylhexanol at 50–70 °C for 5 hours. The formed H-phosphonate (1 eq.) was dissolved in dichloromethane and added to the solution of desired ionic liquid cation precursors (1.5 eq.) 1-hexyl-3-methylimidazolium chloride, 1-hexyl-1-methylpyrrolidinium chloride and tetra-*n*-butylammonium chloride in dichloromethane. This solution was stirred for 24 hours with 2M NaOH solution (1.5 eq.) and 35% $H_2O_2$ (3 eq.). Then, the organic phase was separated,

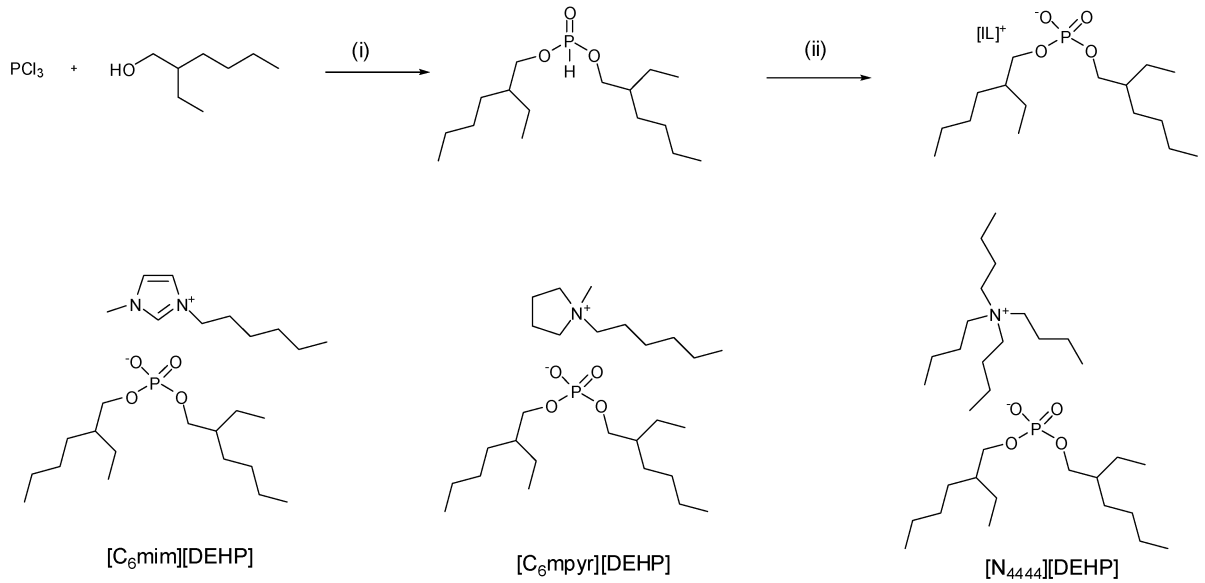

**Fig. 1** Synthetic pathway and structures of various dialkylphosphate ionic liquids. Synthetic conditions: (i) 50–70 °C, 5 hours; (ii) $H_2O_2$, NaOH, DCM, IL precursor. The IL precursors were 1-hexyl-3-methylimidazolium chloride, 1-hexyl-1-methylpyrrolidnium chloride and tetra-*n*-butylammonium chloride.

washed thoroughly with water, dried and evaporated under reduced pressure. The yields for the prepared ionic liquids were 82% for [$C_6$mim][DEHP], 56% for [$C_6$mpyr][DEHP] and 70% for [$N_{4444}$][DEHP]. NMR spectral data of synthesized ionic liquids are given below. A more detailed description of the synthesis of these compounds will be published in a separate paper.

**[$C_6$mim][DEHP].** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.88 (m, 15H), 1.3 (m, 22H), 1.4 (m, 2H), 1.88 (m, 2H), 3.76 (m, 4H), 4.09 (s, 3H), 4.3 (t, $J$ = 7.3 Hz, 2H), 7.07 (s, 2H), 11.1 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.0, 13.9, 14.1, 22.4, 23.2, 23.4, 26.0, 29.1, 30.2, 31.2, 36.6, 40.4, 40.5, 50.1, 67.6, 120.7, 122.3, 141.0; $^{31}$P NMR (161.92 MHz, $CDCl_3$): $\delta$ = 1.17.

**[$C_6$mpyr][DEHP].** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.89 (m, 15H), 1.39 (m, 24H), 1.74 (m, 2H), 2.27 (m, 4H), 3.27 (s, 3H), 3.52 (m, 2H), 3.72 (m, 6H), 3.82 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.0, 13.9, 14.2, 21.7, 22.4, 23.2, 23.4, 24.0, 26.1, 29.1, 30.2, 31.4, 40.4 (d, $J$ = 8.2 Hz, 2H), 48.6, 63.9, 64.2, 67.4 (d, $J$ = 6 Hz, 2C), 67.6 (d, $J_{C-N}$ = 5.7 Hz); $^{31}$P NMR (161.92 MHz, $CDCl_3$): $\delta$ = 1.40.

**[$N_{4444}$][DEHP].** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 0.87 (t, $J$ = 4.3 Hz, 12H), 0.99 (t, $J$ = 7.1 Hz, 12H), 1.26 (m, 12H), 1.45 (m, 14H), 1.66 (m, 8H), 3.37 (m, 8H), 3.7 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 11.0, 13.7, 14.2, 19.8, 23.2, 23.4, 24.2, 29.1, 30.2, 40.5 (d, $J$ = 7.9 Hz, 2H), 58.9, 67.3 (d, $J$ = 6 Hz, 2H); $^{31}$P NMR (161.92 MHz, $CDCl_3$): $\delta$ = 0.76.

### Equilibration procedure

All the extraction studies were carried out at room temperature. Various solutions of [$C_6$mim][DEHP] or [$C_6$mpyr][DEHP] in their corresponding diluents, [$C_6$mim][$NTf_2$] or [$C_6$mpyr][$NTf_2$], were prepared. The organic phase was pre-equilibrated with the desired concentration of nitric acid to fix the equilibrium acidity. The extraction of neodymium(III) as a function of nitric acid concentration was studied by equilibrating the ionic liquid phase (1 mL) with the aqueous phase (1 mL) containing the neodymium(III) solution at the desired pH value. The concentration of Nd(III) was $7 \times 10^{-4}$ M. The pH of the aqueous solution was varied from 1 to 4, using 1M nitric acid. Extractions were performed with intensive stirring at 1500 rpm for 1 hour. After the extraction, separation of the phases was assisted by centrifugation for 2 minutes at 2200 rpm. The concentration of Nd(III) and other trivalent rare-earth ions Ln(III) distributed between ionic liquid and aqueous phases was measured using TXRF. The distribution ratio ($D$) was determined using the following equation:

$$D = \frac{[\mathrm{Ln}]_{\mathrm{IL}}}{[\mathrm{Ln}]_{\mathrm{aq}}} = \frac{C_{\mathrm{i}} - C_{\mathrm{f}}}{C_{\mathrm{f}}} \times \frac{V_{\mathrm{aq}}}{V_{\mathrm{IL}}} \tag{1}$$

$C_i$ and $C_f$ are the concentration of the metal ions in the aqueous phase before and after extraction, respectively. Ln is a trivalent rare-earth ion. $V_{aq}$ is the volume of the aqueous phase and $V_{IL}$ is the volume of the ionic liquid phase. The extraction efficiency (%$E$) was determined by using the following equation:

$$\%E = \frac{D}{D + \frac{V_{\mathrm{aq}}}{V_{\mathrm{IL}}}} \times 100\% \tag{2}$$

The stripping percentage (%$S$) is given by:

$$\%S = \frac{[\mathrm{Ln}]_{\mathrm{aq}}}{[\mathrm{Ln}]_{\mathrm{IL}}} \times 100\% \tag{3}$$

The separation factor ($\alpha_{\mathrm{Ln1,Ln2}}$) was calculated as follows:

$$\alpha_{\mathrm{Ln1,Ln2}} = \frac{D_{\mathrm{Ln1}}}{D_{\mathrm{Ln2}}} \tag{4}$$

$D_{Ln1}$ and $D_{Ln2}$ are the distribution ratios of the rare-earth ions $Ln_1$ and $Ln_2$, respectively. The effect of the concentration of [$C_6$mim][DEHP] and [$C_6$mpyr][DEHP] in the organic phase (ionic liquid diluents) was studied by varying the concentration of the functionalized ionic liquid from 0.002 M to 0.01 M.

## Results and discussions

### Extraction of neodymium(III) by DEHPA in an ionic liquid diluent

The first extraction experiments were to investigate the extraction behavior of Nd(III) from $HNO_3$ medium by bis(2-ethylhexyl)-phosphoric acid (DEHPA) in the ionic liquid diluents [$C_6$mim]-[$NTf_2$] and [$C_6$mpyr][$NTf_2$]. It is observed that the distribution ratio increases with increase in pH (Fig. 2). This is the characteristic behavior of extractions with the acidic molecular extractant DEHPA, wherein Nd(III) is coordinated to dialkylphosphate mainly by ion exchange mode with $H^+$ ions.[48] Rout *et al.* reported the complex formation of Eu(III) and Am(III) with DEHPA/[$C_8$mim][$NTf_2$] wherein three DEHP anions are involved in complex formation.[49] Based on these observations, the following mechanism can be proposed for the extraction of Nd(III) by DEHPA in the ionic liquids [$C_6$mim][$NTf_2$] and [$C_6$mpyr][$NTf_2$]:

$$\mathrm{Nd}^{3+} + \overline{3\mathrm{DEHPA}} \rightleftharpoons \overline{\mathrm{Nd(DEHP)_3}} + 3\mathrm{H}^+ \qquad (5)$$

The bar indicated compounds in the organic phase (ionic liquid phase). The ionic liquids [$C_6$mim][$NTf_2$] and [$C_6$mpyr][$NTf_2$] act solely as diluents and are not involved in the extraction mechanism. Fig. 2 also shows the extraction of Nd(III) by these (non-functionalized) ionic liquids, without added extractants. As expected, the $D_{Nd}$ values are very small ($\sim 10^{-2}$). It can be concluded that the extraction is solely due to the presence of the functional phosphate moiety in the extractant.

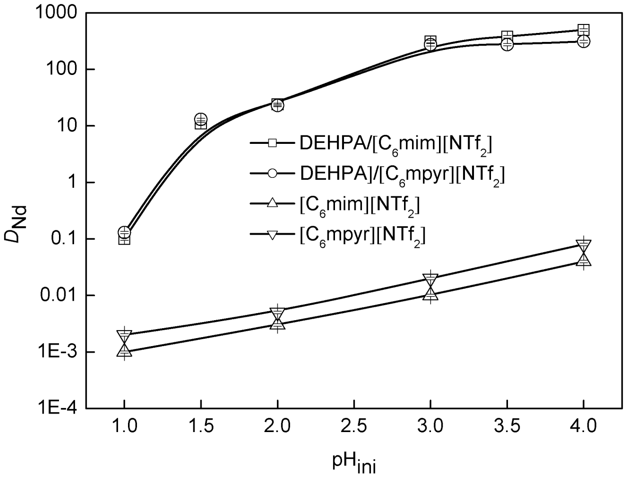

**Fig. 2** Extraction of Nd(III) as a function of pH. Organic phase: 0.01 M DEHPA in [$C_6$mim][$NTf_2$] or in [$C_6$mpyr][$NTf_2$]. $[\mathrm{Nd(III)}]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

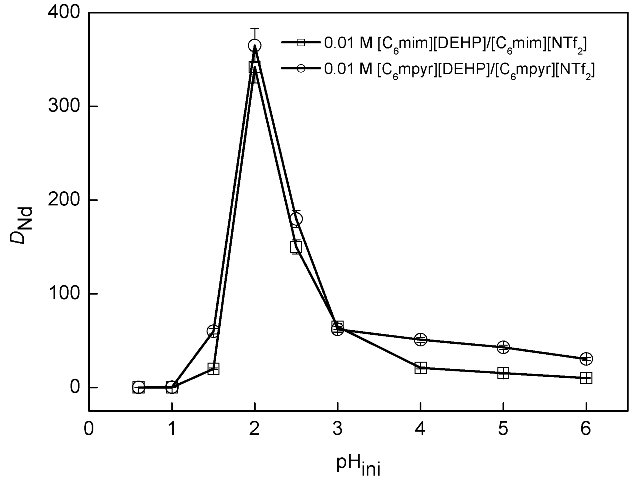

**Fig. 3** Variation of the distribution ratio of Nd(III) as a function of pH. Organic phase: 0.01 M [$C_6$mim][DEHP] in [$C_6$mim][$NTf_2$], or [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. $[\mathrm{Nd(III)}]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

### Extraction of neodymium(III) by [$C_6$mim][DEHP] and [$C_6$mpyr][DEHP]

The extraction of Nd(III) from $HNO_3$ medium was carried out using solutions of the ionic liquids with dialkylphosphate anions [$C_6$mim][DEHP] and [$C_6$mpyr][DEHP] in the ionic liquid diluents [$C_6$mim][$NTf_2$] or [$C_6$mpyr][$NTf_2$], respectively. The extraction of Nd(III) as a function of the equilibrium pH is shown in Fig. 3. In contrast to Fig. 2, it can be observed that the distribution ratio increases with decrease in pH, reaches a maximum at pH 2 and then decreases with further increase in pH. This unusual pH dependence of the extraction process was observed only when DEHP anions are combined with [$C_6$mim]$^+$ and [$C_6$mpyr]$^+$ cations, not with the tetrabutylammonium cation [$N_{4444}$]$^+$ (*vide infra*). This behavior can be attributed to a neutral solvation mechanism in the region from pH 2–6, wherein Nd(III) is extracted as a nitrate complex by the FIL in the ionic liquid phase. The probable stoichiometry of the complex formed during the extraction is $[\mathrm{Nd(NO_3)}_x\mathrm{(H_2O)_3}\cdot x\mathrm{(FIL)}]$. The involvement of the nitrate ion in the extraction process was confirmed by varying the nitrate ion concentration at pH 4 using different concentrations of sodium nitrate in the aqueous phase (Fig. 4). As expected, it is observed that the distribution ratio $D_{Nd}$ increases with increase in nitrate ion concentration and it is likely that the Nd(III) ion form complexes with the $NO_3^-$ ion, such as $[\mathrm{Nd(NO_3)}]^{2+}$, $[\mathrm{Nd(NO_3)_2}]^+$ and $[\mathrm{Nd(NO_3)_3}]$. The sharp decrease in the $D_{Nd}$ values at pH values lower than pH 2 could be due to the dominance of acid extraction over Nd(III) extraction and the extraction of $HNO_3$ blocks the coordinating site of the [DEHP]$^-$ anion. It can be expected that at pH 2, the [DEHP]$^-$ anion is protonated to DEHPA.[50]

Liquid–liquid extraction is strongly influenced by hydrodynamic parameters such as viscosity. Due to rather high viscosity of the ionic liquid diluents used (60–65 cP), equilibrium is reached after longer equilibration times compared to solvent extraction systems with molecular diluents. The distribution ratios of Nd(III) increase over time and remain almost constant

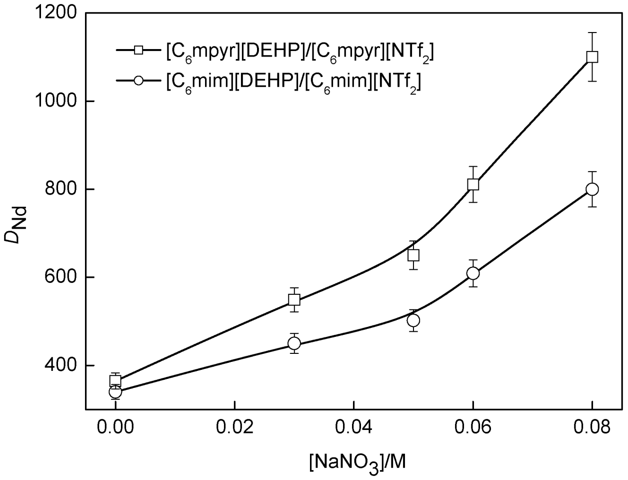

**Fig. 4** Variation of the distribution ratio of Nd(III) as a function of the nitrate concentration in the aqueous phase. Organic phase: 0.01 M [$C_6$mim][DEHP] in [$C_6$mim][$NTf_2$], or 0.01 M [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. Aqueous phase: pH 2 and varied concentration of the nitrate ion. $[Nd(III)]_{aq}$ = 7.6 $\times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

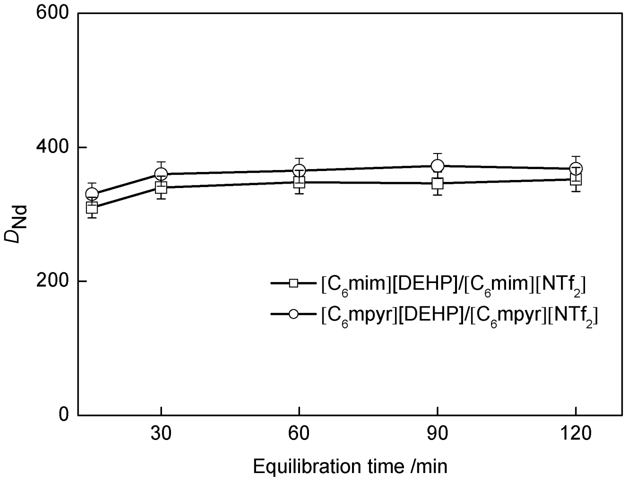

**Fig. 5** Variation of the distribution ratio of Nd(III) as a function of equilibration time. Organic phase: 0.01 M [$C_6$mim][DEHP] in [$C_6$mim][$NTf_2$], or [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. $[Nd(III)]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 15–120 minutes, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

after 30 minutes (Fig. 5). Therefore, it was assumed that it takes 30 minutes to reach the equilibrium state in these types of functionalized ionic liquids dissolved in an ionic liquid diluent. In order to ensure the complete extraction, all the studies have been carried out with an equilibration time of 1 hour.

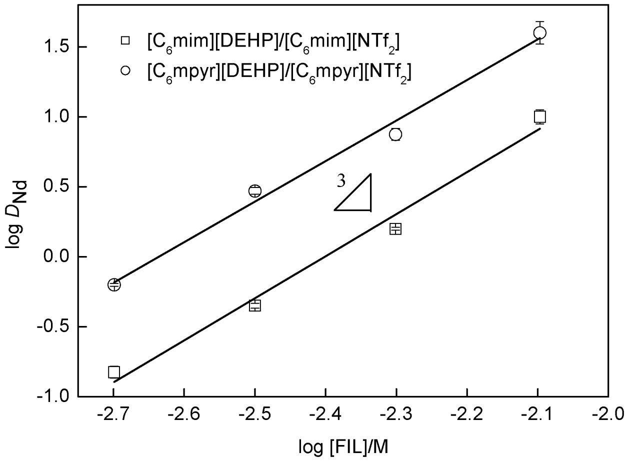

**Fig. 6** Variation of the distribution ratio of Nd(III) as a function of the concentration of functionalized ionic liquids. Organic phase: 0.002–0.008 M [$C_6$mim]-[DEHP] in [$C_6$mim][$NTf_2$], or [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. Aqueous phase: pH 2. $[Nd(III)]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

## Stoichiometry of extracted neodymium(III) complexes

Fig. 6 shows the variation in the distribution ratio of Nd(III) as a function of the concentration of the functionalized ionic liquid in the organic phase at pH 2. It is observed that the distribution ratio of Nd(III) increases with increase in the concentration of ionic liquid. Linear regression analysis of the extraction data results in a slope of 3 in both the ionic liquids, suggesting that three molecules of the functionalized ionic liquid are involved during the extraction process. This is in good agreement with the data obtained from the same class of functionalized ionic liquids with different cations.[41] The following mechanism is proposed for the extraction stoichiometry:

$$\begin{aligned} &Nd^{3+} + 3NO_3^{-} + \overline{3[C_6mim][DEHP]} \\ &\rightleftharpoons \overline{Nd(NO_3)_3{\cdot}3[C_6mim][DEHP]} \end{aligned} \quad (6)$$

A similar equation can be written for extraction of Nd(III) with the ionic liquid [$C_6$mpyr][DEHP]. The general formula of the extracted complex is $Nd(NO_3)_3{\cdot}3$(FIL), where FIL stands for either [$C_6$mim][DEHP] or [$C_6$mpyr][DEHP]. Fig. 7 shows the

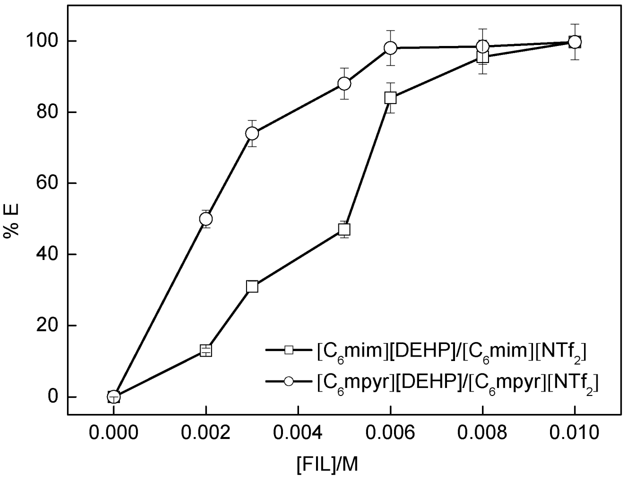

**Fig. 7** Variation of percentage extraction efficiency as a function of the ratio of the concentration of FIL. Organic phase: 0.002–0.01 M [$C_6$mim][DEHP] in [$C_6$mim][$NTf_2$] or [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. Aqueous phase: pH 2. $[Nd(III)]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

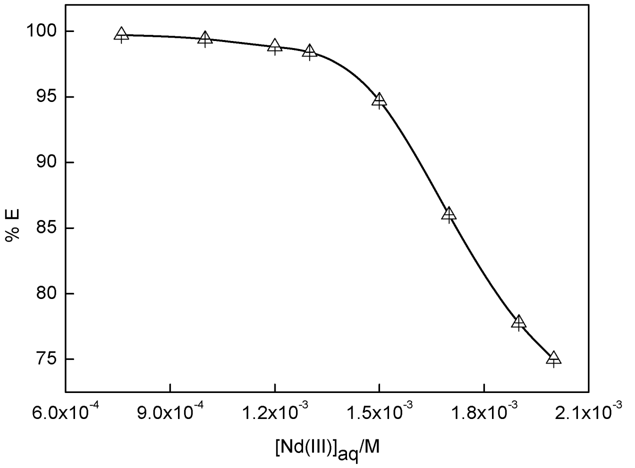

**Fig. 8** Variation of the distribution ratio of Nd(III) as a function of Nd(III) concentration in the aqueous phase. Organic phase: 0.01 M [$C_6$mim][DEHP] or 0.01 M [$C_6$mim][$NTf_2$]. Aqueous phase: pH 2 and concentration variation of Nd(III). Equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

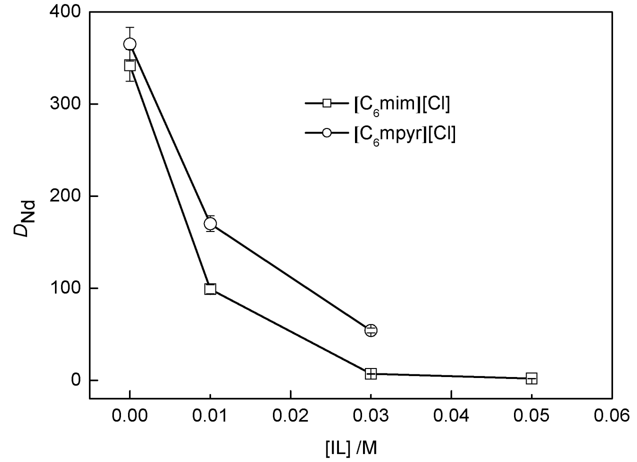

**Fig. 9** Variation of the distribution ratio of Nd(III) as a function of [$C_6$mim]$^+$ or [$C_6$mpyr$^+$] ion concentration in the aqueous phase. Organic phase: 0.01 M [$C_6$mim][DEHP] in [$C_6$mim][$NTf_2$], or 0.01 M [$C_6$mpyr][DEHP] in [$C_6$mpyr][$NTf_2$]. Aqueous phase: pH 2 and varied concentration of the [$C_6$mim]$^+$ or [$C_6$mpyr$^+$] ion. [Nd(III)]$_{aq}$ = 7.6 × $10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

variation of %$E$ (calculated using eqn (2)) as a function of [FIL]$_{IL}$. The extraction efficiency increases with increase in the concentration of the FIL and becomes almost constant >99%, which indicates that nearly complete extraction is possible by using this type of functionalized ionic liquids.

### Loading test

Fig. 8 displays the variation of extraction efficiency with respect to the initial Nd(III) feed concentration in the aqueous phase. It is observed that the extraction efficiency of Nd(III) decreases gradually from 99.7% to 75% with increase in Nd(III) loading in the aqueous phase. However, this decrease is very small up to a certain threshold concentration of Nd(III) in the aqueous phase (about 1.3 × $10^{-3}$ M), followed by sharp decrease. This could be due to the unavailability of coordinating sites of the functionalized ionic liquid to form complexes with Nd(III) at high feed concentration. The same behavior can also be expected for the ionic liquid [$C_6$mpyr][DEHP], since both the FILs have similar extraction patterns. However, a higher loading of Nd(III) is possible by increasing the [FIL] : [Nd] molar ratio.

### Effect of the ionic liquid cation

It is well known that an ion exchange mechanism often occurs during solvent extraction of rare earths using imidazolium-based ionic liquid diluents.[23,51,52] In order to confirm the existence of this ion-exchange mechanism, the extraction of Nd(III) as a function of the concentration of 1-hexyl-3-methylimidazolium chloride [$C_6$mim][Cl] and 1-hexyl-1-methylpyrrolidinium chloride [$C_6$mpyr][Cl] dissolved in the aqueous phase was studied (Fig. 9). As expected, the $D_{Nd}$ value decreases with an increase in the concentration of chloride ionic liquid dissolved in the aqueous feed. This observation seems to contradict the solvation mechanism (eqn (6)). It indicates that an ion exchange mechanism cannot be ruled out in the present solvent extraction system and that it operates along with the neutral solvation mechanism. However, it remains unclear to what extent the exchange of ionic liquid cations with the metal complex occurs.

### Extraction of neodymium(III) by a quaternary ammonium phosphate ionic liquid

The extraction of Nd(III) was carried out by tetrabutylammonium bis(2-ethylhexyl)phosphate [$N_{4444}$][DEHP], diluted in the ionic liquid tributylmethylammonium bis(trifluoromethanesulfonyl)-imide [$N_{1444}$][$NTf_2$] (Fig. 10). It is interesting to compare this result with that observed for the ionic liquids with imidazolium or pyrrolidinium cations. The extraction trend is similar to that of the neutral DEHPA extractant (Fig. 2). This type of observation has been studied and was reported in the case of extraction of Eu(III)

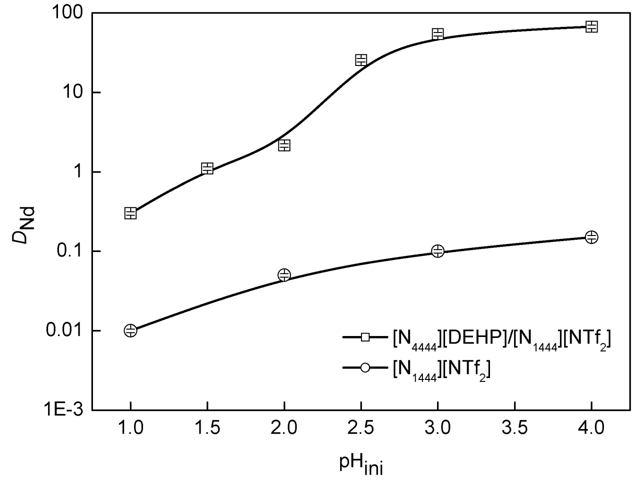

**Fig. 10** Variation of the distribution ratio of Nd(III) as a function of pH. Organic phase: 0.01 M [$N_{4444}$][DEHP] in [$N_{1444}$][$NTf_2$] or pure [$N_{1444}$][$NTf_2$]. [Nd(III)]$_{aq}$ = 7.6 × $10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

and Am(III) using [A336][DEHP]/*n*-dodecane.[44] Sun *et al.* also reported the same trend for Eu(III) using [A336][DEHP]/cyclohexane.[41] Eqn (7) and (8) explain the extraction mechanism:

$$HNO_3 + \overline{[N_{4444}][DEHP]} \rightleftharpoons \overline{[N_{4444}][NO_3]} + \overline{DEHPA} \qquad (7)$$

$$Nd^{3+} + \overline{3DEHPA} \rightleftharpoons \overline{Nd(DEHP)_3} + 3H^+ \qquad (8)$$

Since the ionic liquids contain different cations (imidazolium, pyrrolidinium and quaternary ammonium), their ionic strengths and dielectric constants are different.[53,54] Taking this assumption into consideration, the extraction of Nd(III) was carried out by exchanging the FIL–IL combination, *i.e.*, $[C_6mim][DEHP]$ or $[C_6mpyr][DEHP]$ in $[N_{1444}][NTf_2]$, or $[N_{4444}][DEHP]$ in $[C_6mim][NTf_2]$ or $[C_6mpyr][NTf_2]$. Surprisingly, it was observed that the extraction trend drastically changes when $[C_6mim][DEHP]$ or $[C_6mpyr][DEHP]$ was used in $[N_{1444}][NTf_2]$ (Fig. 11 and 12) and it followed the same pattern as in the case of DEHPA and $[N_{1444}][DEHP]$. This can be due to difference in mode of interaction (*i.e.* ionic, van der Waals and ionic interactions) in the corresponding ionic liquid mixtures. It is likely that ionic liquid extractants might be undergoing the following exchange reaction in the ionic liquid phase to form $[N_{1444}][DEHP]$:

$$\begin{aligned}&\overline{[C_6mim][DEHP]} + \overline{[N_{4444}][NTf_2]}\\ &\quad\rightleftharpoons \overline{[C_6mim][NTf_2]} + \overline{[N_{4444}][DEHP]}\end{aligned} \qquad (9)$$

A similar reaction can be written for $[C_6mpyr][DEHP]$ and $[N_{1444}][NTf_2]$. However, the extent of the conversion is not known. It can be concluded that by using such a type of functionalized ionic liquids (FILs) and tuning the FIL–IL combination in the extracting phase, it is possible to recover selectively the desired metal ions from feeds with different acidities.

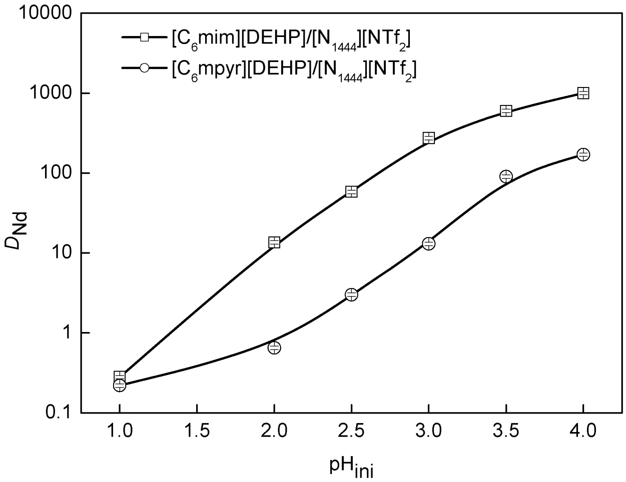

**Fig. 11** Variation of the distribution ratio of Nd(III) as a function of pH. Organic phase: 0.01 M $[C_6mim][DEHP]$ in $[N_{1444}][NTf_2]$ or 0.01 M $[C_6mpyr][DEHP]$ in $[N_{1444}][NTf_2]$. $[Nd(III)]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

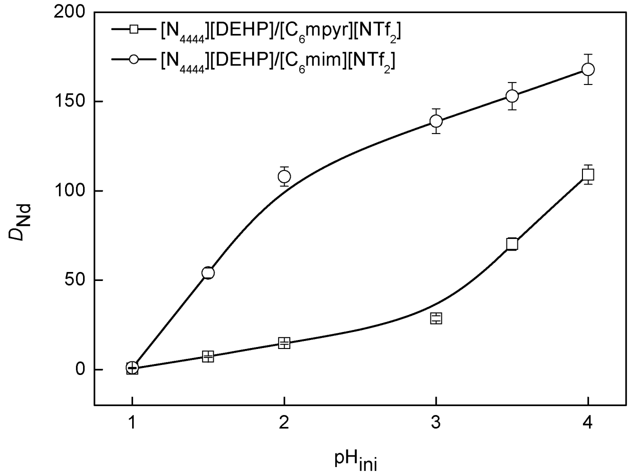

**Fig. 12** Variation of the distribution ratio of Nd(III) as a function of pH. Organic phase: 0.01 M $[N_{4444}][DEHP]$ in $[C_6mim][NTf_2]$, or 0.01 M $[N_{4444}][DEHP]$ in $[C_6mpyr][NTf_2]$. $[Nd(III)]_{aq} = 7.6 \times 10^{-4}$ M, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

### Stripping and reusability studies

After quantitative extraction of Nd(III) into the ionic liquid phase, the stripping was carried out using 1M nitric acid. Complete back extraction of Nd(III) into the aqueous phase was possible within four stages. Fig. 13 shows the stripping of Nd(III) from the $[C_6mim][DEHP]/[C_6mim][NTf_2]$ phase. The same stripping behavior can be anticipated for the corresponding pyrrolidinium ionic liquid $[C_6mpyr][DEHP]$, since the extraction pattern and distribution ratios are similar to that of the imidazolium ionic liquid $[C_6mim][DEHP]$. After complete stripping of the metal ion, the ionic liquid phase was washed four times with 1M NaOH, followed by washing with dilute nitric acid (0.01 M). It was observed that the extraction efficiency remained almost the same using the

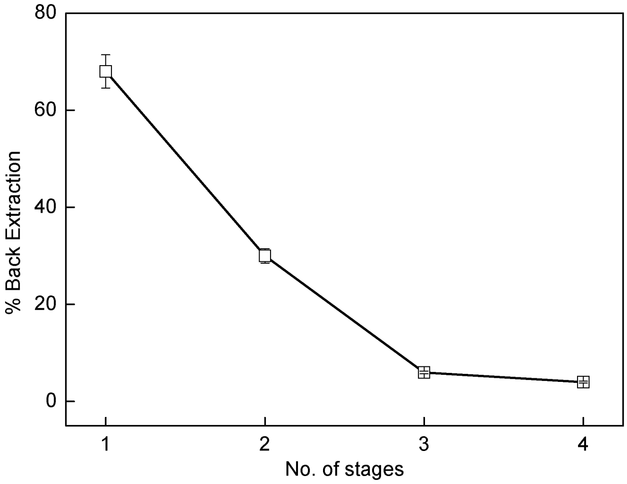

**Fig. 13** Stripping behavior of Nd(III) from an ionic liquid phase. Organic phase: 0.01 M $[C_6mim][DEHP]$ in $[C_6mim][NTf_2]$. Aqueous phase: 1 M nitric acid, equilibration time = 1 hour, temperature = 300 K, the volume ratio between organic and aqueous phases = 1.

**Table 1** Distribution ratio of some trivalent rare-earth Ln(III) ions for extraction by [C$_6$mim][DEHP] or [C$_6$mpyr][DEHP] in ionic liquid diluents[a]

| Ln(III) | $D_{Ln}$ in [C$_6$mim][DEHP]/[C$_6$mim][NTf$_2$] | $D_{Ln}$ in [C$_6$mpyr][DEHP]/[C$_6$mpyr][NTf$_2$] |
|---|---|---|
| La(III) | 1 ± 0.1 | 1 ± 0.06 |
| Ce(III) | 2 ± 0.12 | 2 ± 0.1 |
| Pr(III) | 95 ± 2 | 2 ± 0.14 |
| Nd(III) | 340 ± 17 | 365 ± 18 |
| Yb(III) | 136 ± 6.5 | 274 ± 8 |
| Y(III) | 12 ± 0.5 | 11 ± 0.3 |

[a] Extraction conditions: organic phase: 0.01 M [C$_6$mim][DEHP] in [C$_6$mim][NTf$_2$], or 0.01 M [C$_6$mpyr][DEHP] in [C$_6$mpyr][NTf$_2$]. Aqueous phase: pH = 2, the volume ratio between organic and aqueous phases = 1, $T$ = 300 K, equilibration time = 1 hour. The Ln(III) concentration was $7 \times 10^{-4}$ M.

recycled ionic liquid (99.7%, 99.8% and 99.5% for recycle number 1, 2 and 3, respectively). Thus, it can be concluded that the ionic liquid can be re-used at least three to four times without any change in extraction efficiency.

### Extraction of rare-earth ions other than neodymium(III)

The extraction studies were extended to trivalent rare-earth ions Ln(III) other than Nd(III) to explore the use of these type of functionalized ionic liquids for the separation of mixtures of rare earths. Table 1 summarizes the distribution ratio of some rare-earth ions by the [C$_6$mim][DEHP]/[C$_6$mim][NTf$_2$] and [C$_6$mpyr][DEHP]/[C$_6$mpyr][NTf$_2$] ionic liquid extraction systems. It is noticed that the light rare earths La(III) and Ce(III) are poorly extracted, whereas Nd(III) and Yb(III) are strongly extracted. The Pr(III) ion is a borderline case. It is weakly extracted by the [C$_6$mpyr][DEHP]/[C$_6$mpyr][NTf$_2$] system, but rather strongly by the [C$_6$mim][DEHP]/[C$_6$mim][NTf$_2$] system. This sharp cutoff between light and heavy rare earths is remarkable. A separation factor of 340 is obtained for Nd(III) over La(III) in the imidazolium ionic liquid [C$_6$mim][DEHP], and a similar separation factor is found for the pyrrolidinium ionic liquid [C$_6$mpyr][DEHP]. The distribution ratios seem to go through a maximum and then fall of towards the end of the lanthanide series. These ionic liquid systems could be useful for the splitting of the lanthanide series into two groups, but it is less suitable for the separation of mixtures of rare earths into the individual elements. It must be mentioned that the extraction experiments have been carried out with low concentrations of rare earths (tracer levels), about $7 \times 10^{-4}$ M. The extraction behavior from more concentrated rare-earth solutions could be different. The position of yttrium is also remarkable. Yttrium can behave different in different solvent extraction systems.[55] In some extraction systems, such as extraction with DEHPA, yttrium behaves like the heavy rare earths holmium or erbium, whereas it can be behave as a light rare earth in other extraction systems. This is the so-called itinerant behavior of yttrium.[55] In our ionic liquid systems, yttrium has a behavior close to praseodymium.

## Conclusions

The ionic liquids [C$_6$mim][DEHP], [C$_6$mpyr][DEHP] and [N$_{4444}$][DEHP] with bis(2-ethylhexyl)phosphate anions were prepared and studied for the liquid–liquid extraction of Nd(III) from nitric acid medium. The extraction of Nd(III) increased with increase of the initial pH value (pH$_{ini.}$), reaching a maximum at pH 2, followed by decrease with further increase in pH$_{ini}$. In the case of [C$_6$mim][DEHP] and [C$_6$mpyr][DEHP], this extraction trend is completely different from what was observed for the corresponding molecular extractant bis(2-ethylhexyl)phosphoric acid (DEHPA) dissolved in an ionic liquid diluent as well as for [N$_{4444}$][DEHP]. Complete stripping of Nd(III) was possible within four stages using 1M nitric acid. The extraction efficiency of the ionic liquid phase remained intact after recycling. The extraction studies were extended to trivalent rare-earth ions other than Nd(III). The light rare-earth ions are poorly extracted, whereas the heavier rare-earth ions are much better extracted. This type of extraction behavior allows splitting of the rare earths into two groups. The extraction behavior of yttrium resembles that of the light rare earths. The results presented in this paper clearly show that the ionic liquid cation has a distinct influence on the extraction properties of ionic liquid extractants with coordinating anions. Therefore, it is possible to tune the extractability of metal ions and the selectivity by a proper choice of the ionic liquid cation.

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