

CrossMark
click for updatesCite this: *Dalton Trans.*, 2015, **44**,
1379

Influence of the ionic liquid cation on the solvent extraction of trivalent rare-earth ions by mixtures of Cyanex 923 and ionic liquids

Alok Rout and Koen Binnemans*

Trivalent rare-earth ions were extracted from nitric acid medium by the neutral phosphine oxide extractant Cyanex 923 into ionic liquid phases containing the bis(trifluoromethylsulfonyl)imide anion. Five different cations were considered: 1-butyl-3-methylimidazolium, 1-decyl-3-methylimidazolium, methyltributylammonium, methyltrioctylammonium and trihexyl(tetradecyl)phosphonium. The extraction behavior of neodymium(III) was investigated as a function of various parameters: pH, extractant concentration, concentration of the neodymium(III) ion in the aqueous feed and concentration of the salting-out agent. The loading capacity of the ionic liquid phase was studied. The extraction efficiency increased with increasing pH of the aqueous feed solution. The extraction occurred for all ionic liquids *via* an ion-exchange mechanism and the extraction efficiency could be related to the solubility of the ionic liquid cation in the aqueous phase: high distribution ratios for hydrophilic cations and low ones for hydrophobic cations. Addition of nitrate ions to the aqueous phase resulted in an increase in extraction efficiency for ionic liquids with hydrophobic cations due to extraction of neutral complexes. Neodymium(III) could be stripped from the ionic liquid phase by 0.5–1.0 M nitric acid solutions and the extracting phase could be reused. The extractability of other rare earths present in the mixture was compared for the five ionic liquids.

Received 10th September 2014,
Accepted 19th November 2014

DOI: 10.1039/c4dt02766c

www.rsc.org/dalton

Introduction

Ionic liquids (ILs) are alternatives for conventional diluents in solvent extraction processes.^{1–7} Since ionic liquids consist entirely of ions, they have a negligible vapor pressure and they are non-volatile.^{8,9} Replacement of volatile organic solvents in solvent extraction systems could lead to inherently safer extraction processes for metal ions. Many solvent extraction studies using ionic liquids as diluents and extractants have been carried out during the last 15 years.^{10–29} Ionic liquids that act as extractants can be considered as task-specific or functionalized ionic liquids. Most ionic liquids used as diluents contain either bis(trifluoromethylsulfonyl)imide or hexafluorophosphate anions. The bis(trifluoromethylsulfonyl)imide anion, [Tf₂N][–], is the preferred anion due to its better resistance to hydrolysis.³⁰ The extraction mechanism for transfer of a metal from the aqueous to the organic phase can be different for ionic liquids compared to molecular solvents. Metal ions are typically extracted together with their counter anions by neutral extractants dissolved in a molecular diluents (= ion-pair mechanism or neutral mechanism), whereas in

some ionic liquids extraction can also occur *via* an ion-exchange mechanism. This ion-exchange mechanism implies that ionic liquid cations are transferred from the organic phase to the aqueous phase during extraction of the metal ions. This ion-exchange mechanism for extraction of metal ions to an ionic liquid phase by neutral extractants has been well documented for extraction of alkali and alkaline earths metals by crown ethers.^{26,31–36} The extraction mechanism largely depends on the hydrophobic character of the ionic liquid: hydrophilic cations promote ion exchange, whereas hydrophobic cations suppress ion exchange. The hydrophobicity of the anion has an opposite effect: hydrophobic anions result in a greater tendency for cation exchange.^{37,38} The anion in the aqueous phase and its concentration have an effect on the mechanism, as evidenced by the extraction of Na⁺, Sr²⁺ and Ba²⁺ by crown ethers from HNO₃ and HCl solution.³⁹ A neutral crown ether nitrate complex is extracted from HNO₃ solution, whereas chloride-based systems have a stronger tendency towards ion exchange. For extraction of anionic metal complexes by ionic liquids, there is also a competition between ion exchange and extraction of neutral complexes. Knowledge of the mechanism of a solvent extraction process based on ionic liquids is of importance, because it allows tuning processes to such an extent that no ionic liquid cations or anions are lost to the aqueous phase upon transfer of the metal ion to the ionic liquid phase.^{40–42}

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P. O. Box 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@chem.kuleuven.be;
Fax: +32 16 32 7992; Tel: +32 16 32 7446

Examples on extraction studies in ionic liquids using neutral extractants other than crown ethers are those on tributyl phosphate (TBP) and octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide CMPO.^{11,43–50} Another example is Cyanex 923, which is an often used neutral extractant (solvent extractant) for solvent extraction of metal ions.^{51–62} The commercial Cyanex 923 extractant is a mixture of four trialkylphosphine oxides: $R_3P=O$, $R_2R'P=O$, $RR'_2P=O$ and $R'_3P=O$, where $R = n$ -octyl and $R' = n$ -hexyl, and with an average molecular weight of 348 g mol^{-1} .⁶³ Sun *et al.* described extraction with an imidazolium ionic liquid in combination with Cyanex 923 for the separation of yttrium from heavy rare earths in the presence of an aqueous complexant.⁶⁴ Zhu *et al.* investigated the extraction of Sc(III) by Cyanex 923/[C₈mim][PF₆] impregnated in a resin.⁶⁵ Cyanex 925, which has a composition similar to that of Cyanex 923 and consists mainly of bis(2,4,4-trimethylpentyl) octylphosphine oxide, was used in an ionic liquid for the separation of scandium from other rare earths.⁶⁶

In this paper, we describe the liquid–liquid extraction of neodymium(III) and other trivalent rare-earth ions with Cyanex 923 in five ionic liquid diluents: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₄mim][Tf₂N], 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁₀mim][Tf₂N], methyltributylammonium bis(trifluoromethylsulfonyl)imide [N₁₄₄₄][Tf₂N], methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [N₁₈₈₈][Tf₂N] and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [P₆₆₆₁₄][Tf₂N]. The aim of this systematic study was to investigate how the extraction mechanism depends on the type of ionic liquid cation and especially on the hydrophobicity of the cation.

Experimental

Materials and reagents

All chemicals and reagents used in this study were of analytical grade, and they were used as received without further purification. The ionic liquids: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (>98%), methyltributylammonium bis(trifluoromethylsulfonyl)imide (>98%) and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide (>98%) were purchased from IoLiTec (Heilbronn, Germany). 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide were synthesized following literature procedures.^{5,67} Sodium nitrate (99%) and nitric acid were purchased from Sigma-Aldrich (Diegem, Belgium). Sodium hydroxide (98%) was obtained from Alfa Aesar (Karlsruhe, Germany). Neodymium(III) nitrate hexahydrate and other rare-earth nitrate hydrates (purity >99%) were purchased from Acros Organics (Geel, Belgium). A 1000 ppm gallium standard was purchased from Merck (Overijse, Belgium). Cyanex 923 was kindly supplied by Cytec Industries, Canada.

Instrumentation

The concentrations of rare earths in the aqueous phase were determined with a bench top total reflection X-ray fluorescence

(TXRF) spectrometer (S2 Picofox, Bruker). A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction. The viscosities of the ionic liquid phase were measured using an automatic Brookfield plate cone viscometer, Model LVDV-II+P CP (Brookfield Engineering Laboratories, USA). pH measurements were performed with an S220 Seven-Compact™ pH/Ion meter (Mettler-Toledo) and a Slimtrode (Hamilton) electrode. Luminescence spectra were recorded on an Edinburgh Instruments FS-920P spectrofluorimeter.

Equilibration procedure

The extraction experiments were performed at 30 °C with a temperature-controlled thermo-shaker (model: TMS – 200, Hangzhou Allsheng Instrument Co. LTD, China). The ionic liquid phases were pre-equilibrated with the desired concentration of nitric acid to fix the pH. Extractions were performed by intensive shaking (2000 rpm) of the extraction mixture for 1.5 h (except for experiments on the time dependence of the extraction). After the extraction, separation of the phases was assisted by centrifugation for 5 min at 3000 rpm. The concentrations of neodymium distributed between the ionic liquid and the aqueous phases were measured by TXRF. The distribution ratio (D) was determined using the following equation:

$$D = \frac{[\text{Nd}]_{\text{IL}}}{[\text{Nd}]_{\text{aq}}} \quad (1)$$

$$= \frac{C_i - C_f}{C_f} \times \frac{V_{\text{aq}}}{V_{\text{IL}}}$$

C_i and C_f are the concentration of Nd(III) in the aqueous phase before and after extraction, respectively. Unless otherwise specified, C_i was $7 \times 10^{-4} \text{ M Nd(III)}$. V_{aq} and V_{IL} are the volumes of the aqueous and ionic liquid phase, respectively. A volume ratio of 1 : 1 was used for all the extraction experiments ($V_{\text{aq}} = V_{\text{IL}}$). The percentage extraction (% E) was determined using the following equation for ($V_{\text{aq}} = V_{\text{IL}}$):

$$\%E = \frac{D}{D + 1} \times 100 \quad (2)$$

The separation factor (α_{M_1, M_2}) was calculated as follows:

$$\alpha_{M_1, M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (3)$$

D_{M_1} and D_{M_2} are the distribution ratios of the metal ions M_1 and M_2 , respectively. The percentage stripping (% S) is defined by the equation:

$$\%S = \frac{[\text{M}]_{\text{aq}}}{[\text{M}]_{\text{IL}}} \times 100 \quad (4)$$

Results and discussion

Variation of equilibration time and pH

Neodymium(III) was extracted from a nitric acid solution by Cyanex 923 dissolved in the ionic liquids [C₄mim][Tf₂N], [N₁₄₄₄][Tf₂N] and [P₆₆₆₁₄][Tf₂N], with variation of different

extraction parameters. For these experiments, a Nd(III) concentration of 7×10^{-4} M and a Cyanex 923 concentration of 0.1 M was used. The volume ratio of the organic to the aqueous phase was 1 : 1. The temperature was 30 °C. The first parameter that was varied was the equilibration time, in order to determine the time required to reach the equilibrium condition (Fig. 1). Extraction was fastest for $[C_4mim][Tf_2N]$ and $[N_{1444}][Tf_2N]$: equilibrium was achieved within 30 to 40 min. In case of $[P_{66614}][Tf_2N]$, it took nearly 75 min to reach the equilibrium state. Thus in order to ensure reaching equilibrium conditions, the equilibration time of 1.5 h was used for all further extraction studies.

The distribution ratios D increased with increasing pH for the extraction of Nd(III) by 0.1 M Cyanex 923 diluted in ionic liquid diluents (Fig. 2). An analogous trend had been observed by Sun *et al.* for the extraction of Y(III) from heavy rare-earth ions using Cyanex 923 in the ionic liquid $[C_8mim][PF_6]$.⁶⁴ The pH dependence can be explained by the competition between the extraction of protons (or acid molecules) and the extraction of metal ions (or metal salts): neutral extractants are able to extract acids at low pH values. The distribution ratios depend on the type of ionic liquid: at all pH values, the distribution ratios for $[C_4mim][Tf_2N]$ and $[N_{1444}][Tf_2N]$ are much higher than those for $[P_{66614}][Tf_2N]$. Fig. 3 shows the variation of the distribution ratio as a function of pH for the ionic liquids $[C_{10}mim][Tf_2N]$ and $[N_{1888}][Tf_2N]$. When comparing these results with those presented in Fig. 2, it can be observed that the D values decrease with increase in the alkyl chain length. It should be noted that the D values for $[N_{1888}][Tf_2N]$ are higher than those for $[P_{66614}][Tf_2N]$ at all pH values.

To exclude that the difference in extraction mechanism is due to the type of cation rather than the length of the alkyl

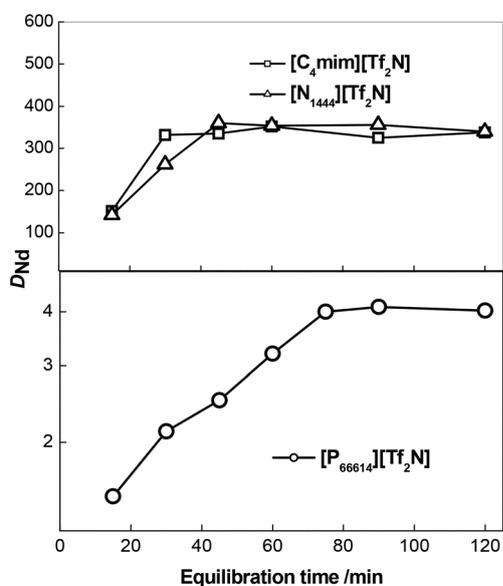


Fig. 1 Variation of distribution ratio of Nd(III) as a function of the equilibration time, for extraction with Cyanex 923 in $[C_4mim][Tf_2N]$, $[N_{1444}][Tf_2N]$ or $[P_{66614}][Tf_2N]$.

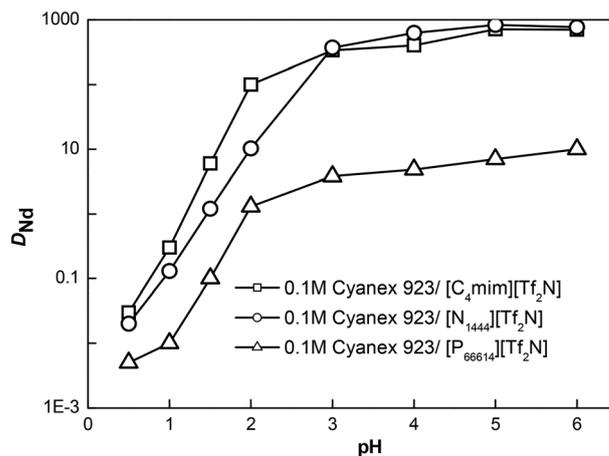


Fig. 2 Variation of the distribution ratio of Nd(III) as a function of the pH of the aqueous phase.

chains (hydrophobic), analogues of $[C_4mim][Tf_2N]$ and $[N_{1444}][Tf_2N]$ with longer alkyl chains were considered as diluents for extraction of Nd(III) with Cyanex 923: $[C_{10}mim][Tf_2N]$ and $[N_{1888}][Tf_2N]$.

Extraction mechanism

The two possible mechanisms for extraction of a Nd(III) ion from the aqueous phase to the ionic liquid phase are the *ion exchange mechanism* and the *neutral mechanism* (also called the *solvation mechanism*). In case of an ion exchange mechanism, the Nd^{3+} ion or a positively charged Nd(III) complex are extracted to the ionic liquid phase by cation exchange, while simultaneously ionic liquid cations are transferred to the water phase for the reasons of charge balance. Also solvating Cyanex 923 molecules are involved in the extraction process. The ion exchange mechanism can be represented by the following equations, depending on the type of positively charged Nd(III) complex that is formed.

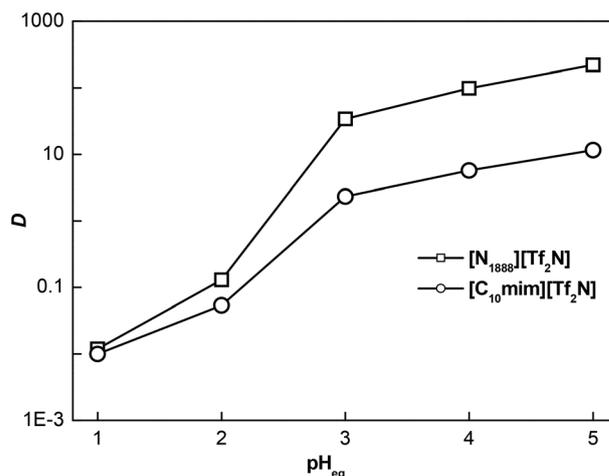
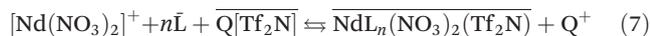
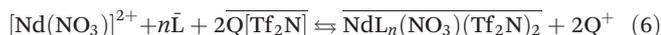


Fig. 3 Variation of the distribution ratio of Nd(III) as a function of the equilibrium pH of the aqueous phase.



The bar indicates molecules in the ionic liquid phase. L stands for a Cyanex 923 molecule and Q^+ is the ionic liquid cation. In case that the $\text{Nd}(\text{NO}_3)_3$ complex is formed, $\text{Nd}(\text{III})$ is extracted as a neutral complex (neutral mechanism):



Here the bar represents again molecules in the ionic liquid phase and L stands for a Cyanex 923 molecule. The main difference with the ion exchange mechanism shown in eqn (5)–(7), is that in the case of a neutral mechanism no ionic liquid cations are transferred to the aqueous phase. The extracted metal complexes can contain a different number of Cyanex 923 molecules. Moreover, there is a possibility that water molecules coordinate to $\text{Nd}(\text{III})$ in order to saturate the coordination sphere. The expected coordination number for this type of complexes is between 8 and 10. To find out what was the extraction mechanism in the ionic liquids at given conditions, different types of extraction experiments have been done.

The number of coordinated Cyanex 923 molecules was determined by variation of the concentration of Cyanex 923 in the ionic liquid phases. The distribution ratio D increased with an increase in the concentration of Cyanex 923 in the ionic liquid (Fig. 4). A linear regression analysis of $\log D$ versus $\log[\text{Cyanex 923}]$ of the extraction data gave a straight line with slope values of 2.80 for $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and 3.11 for $[\text{N}_{1444}][\text{Tf}_2\text{N}]$, whereas a slope value of 1.83 was obtained in case of $[\text{P}_{66614}][\text{Tf}_2\text{N}]$. This suggests that three molecules of Cyanex 923 are involved during extraction to the ionic liquids $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{N}_{1444}][\text{Tf}_2\text{N}]$ and two molecules are involved in case of the ionic liquid $[\text{P}_{66614}][\text{Tf}_2\text{N}]$.

To find evidence for an ion-exchange mechanism, the extraction of $\text{Nd}(\text{III})$ by 0.1 M Cyanex 923 in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ or $[\text{N}_{1444}][\text{Tf}_2\text{N}]$ was carried out from an aqueous phase (pH 3) containing various concentrations of $[\text{C}_4\text{mim}][\text{Cl}]$ and $[\text{N}_{1444}][\text{Cl}]$, respectively. Chloride rather than nitrate salts were used to avoid simultaneous change in the nitrate ion concentration while the ionic liquid cation concentration was varied. The use of a chloride salt is justified, because chloride ions do not form inner sphere complexes with rare-earth ions at chloride concentrations of lower than 5 M.⁶⁸ The distribution ratios decrease gradually with increase in the concentration of the ionic liquid cation in the aqueous phase (Fig. 5). These observations are an indication that $\text{Nd}(\text{III})$ gets extracted to the ionic liquid phase at the expense of $[\text{C}_4\text{mim}]^+$ or $[\text{N}_{1444}]^+$ cations, which are transferred to the aqueous phase. This decrease in distribution ratios is due to the *common-ion effect* in the aqueous phase. The concentration of $[\text{N}_{1444}]^+$ cations in the aqueous phase has a larger effect on the distribution ratios than the concentration of $[\text{C}_4\text{mim}]^+$ cations. A difference

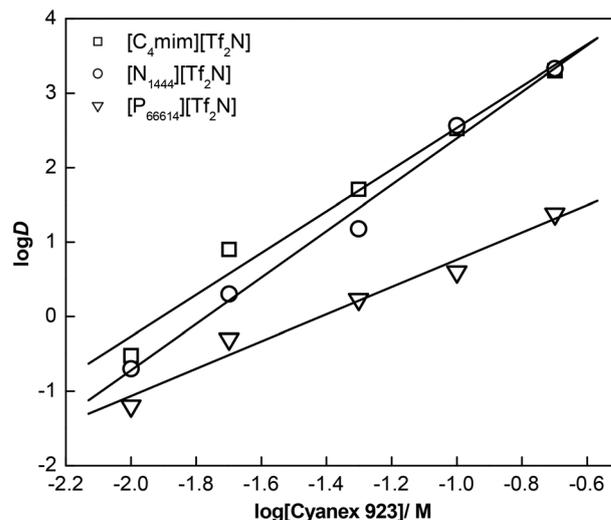


Fig. 4 Variation in the plot of $\log D$ as a function of $\log[\text{Cyanex 923}]$ for the extraction of $\text{Nd}(\text{III})$.

between the two cations is that $[\text{N}_{1444}]^+$ has a strongly localized positive charge, whereas $[\text{C}_4\text{mim}]^+$ has a delocalized positive charge. This leads to a stronger cation–anion interaction between cation and anion in the ionic liquid phase for $[\text{N}_{1444}]^+$ than for $[\text{C}_4\text{mim}]^+$, and thus to a stronger drive for the backward reaction in eqn (5). In the case of $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$ with addition of $[\text{C}_{10}\text{mim}]\text{Cl}$ to the aqueous, the distribution ratios remained within the experimental errors constant as a function of the $[\text{C}_{10}\text{mim}]^+_{\text{aq}}$ concentration but the distribution ratios are very small. A similar experiment with $[\text{P}_{66614}][\text{Cl}]$ was not possible, due to the very low solubility of $[\text{P}_{66614}][\text{Cl}]$ in the aqueous phase.

Experiments were carried out under similar experimental conditions (0.1 M Cyanex 923 dissolved in the ionic liquid), but with varying nitrate concentrations in the aqueous phase at pH 3 (Fig. 6). The distribution ratios remain almost constant

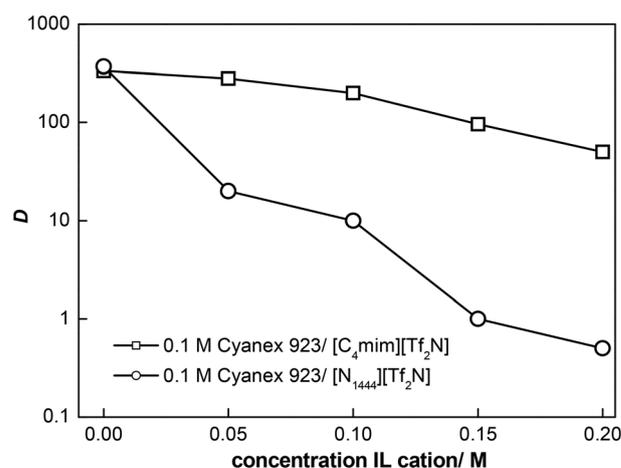


Fig. 5 Variation of the distribution ratio D of $\text{Nd}(\text{III})$ as a function of the concentration of $[\text{C}_4\text{mim}][\text{Cl}]$ or $[\text{N}_{1444}][\text{Cl}]$ concentration in the aqueous phase.

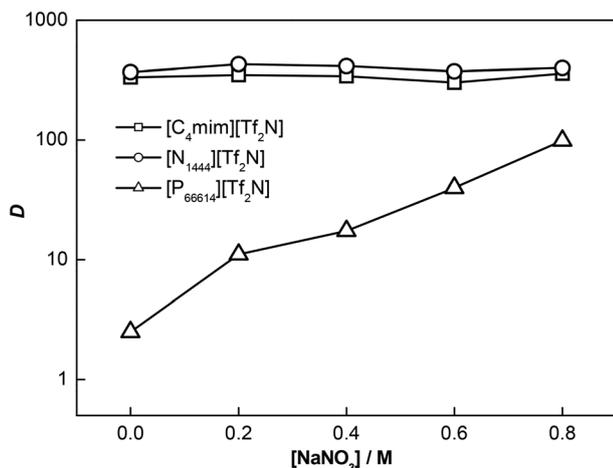


Fig. 6 Variation of the distribution ratio of Nd(III) for extraction with Cyanex 923 as a function of the nitrate concentration in the aqueous phase.

as a function of the nitrate concentration in the case of [C₄mim][Tf₂N] and [N₁₄₄₄][Tf₂N]. This suggests that nitrate ions are not involved in the extraction mechanism and that these ionic liquids do not promote the uptake of Nd(NO₃)₃, [Nd(NO₃)₂]⁺ or [Nd(NO₃)₂]²⁺; but that Nd³⁺ is extracted by the cation exchange mechanism shown in eqn (5). On the other hand, the distribution ratios increase sharply with an increase in the nitrate concentration in the aqueous phase in the case of 0.1 M Cyanex 923 in [P₆₆₆₁₄][Tf₂N]. This indicates that the metal ion is extracted in the form of a Nd(III) nitrate complex, as represented by equations (6), (7) or (8). For [N₁₈₈₈][Tf₂N] and [C₁₀mim][Tf₂N], the *D* values also increase with increase in nitrate ion concentration and show that nitrate ions are involved in the extraction process (Fig. 7). The cation in [N₁₈₈₈][Tf₂N] is a major component of Aliquat 336, which has been used in its chloride or nitrate form for solvent extraction studies.^{21,23,69} Since the [N₁₈₈₈]⁺ cation is more hydrophobic

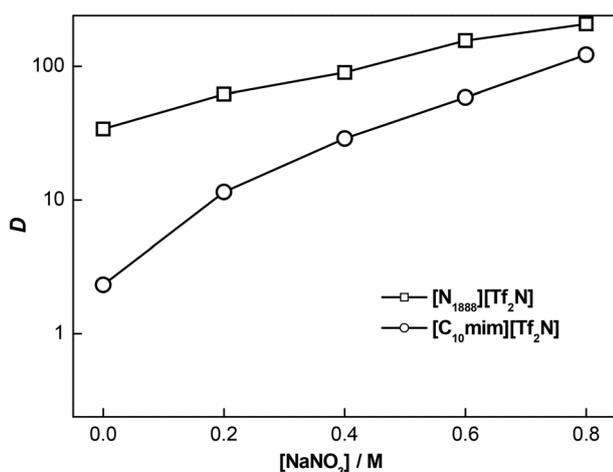


Fig. 7 Variation of the distribution ratio of Nd(III) for extraction with Cyanex 923 as a function of nitrate concentration in the aqueous phase.

than the [N₁₄₄₄]⁺ cation, the ion-exchange mechanism is suppressed, similarly to what was observed for [P₆₆₆₁₄][Tf₂N]. The low *D* values for the ionic liquids [C₁₀mim][Tf₂N], [N₁₈₈₈][Tf₂N] and [P₆₆₆₁₄][Tf₂N] in the absence of extra added nitrate ions in the aqueous solutions, indicate that these ionic liquids also extract *via* an ion exchange mechanism under these circumstances and that the low *D* values are due to the limited solubility of the ionic liquid cation in the aqueous phase. This also explains why the *D* values are smaller for [P₆₆₆₁₄][Tf₂N] than for [N₁₈₈₈][Tf₂N]: the [P₆₆₆₁₄]⁺ cation has a lower solubility in the aqueous phase than the [N₁₈₈₈]⁺.²³ The increase in *D* values upon addition of nitrate ions are an indication for a gradual shift from an ion exchange to a neutral mechanism, *i.e.* extraction *via* the mechanism shown in equations (5)–(7) to finally extraction *via* the mechanism shown in eqn (8).

To probe the local environment of the rare-earth ion, luminescence spectra of Eu(III) in the aqueous phase and of the extracted Eu(III) complexes in the ionic liquid phases were recorded (Fig. 8). Eu(III) was selected instead of Nd(III), because Eu(III) is a well-known spectroscopic probe and emits in the visible range (red spectral region). Nd(III) is a near-infrared emitter and Nd(III) luminescence is totally quenched by co-ordinated water molecules. The splitting pattern, shape and relative intensities of the ⁵D₀→⁷F_{*J*} emission bands can provide information on the chemical environment of the Eu(III) ion. The transitions in the luminescence spectrum originate from the ⁵D₀ level and terminate at the various ⁷F_{*J*} levels (*J* from 0 to 6; only *J* = 0–4 observed in the operational wavelength range of the detector). The hypersensitive transition ⁵D₀→⁷F₂ is the most intense transition in the spectrum of the ionic liquid phases, but the magnetic dipole transition ⁵D₀→⁷F₁ is the most intense transition in the luminescence spectrum of the aqueous phase. These results show that the local environment of the Eu(III) ion is different in the ionic liquid phases compared to the aqueous phase due to the complex formation of

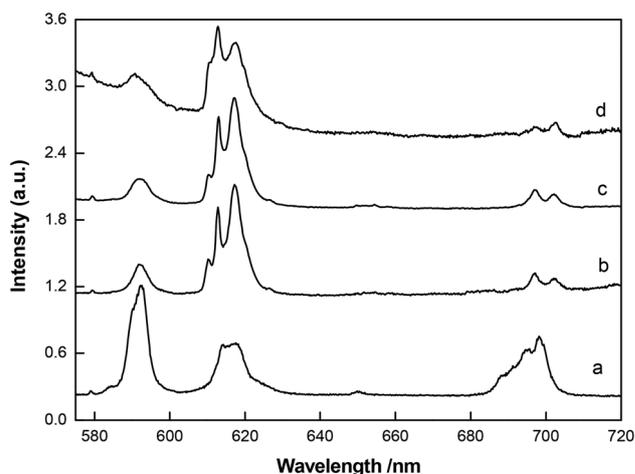


Fig. 8 Emission spectra of Eu(III) in the aqueous feed solution and of Eu(III) complexes extracted by Cyanex 923 to ionic liquid phases. ($\lambda_{\text{exc}} = 395$ nm, room temperature): (a) aqueous feed solution; (b) [P₆₆₆₁₄][Tf₂N]; (c) [N₁₄₄₄][Tf₂N]; (d) [C₄mim][Tf₂N].

Eu(III) in the ionic liquid phase. The relative intensities of the different transitions of the Eu(III) spectra in the three ionic liquids [C₄mim][Tf₂N], [N₁₄₄₄][Tf₂N] and [P₆₆₆₁₄][Tf₂N] are very comparable. Also the fine structure is quite similar, although some small differences are observed for [C₄mim][Tf₂N] compared to the other two ionic liquids. This indicates similarities in the structure of the extracted complexes. This is an indication for similar extraction mechanisms, as indicated by eqn (5). It also suggests that although three molecules of Cyanex 923 are involved in the extraction process in the ionic liquid [N₁₄₄₄][Tf₂N] only two of these molecules are in the first coordination sphere of Eu(III). The number of water molecules present in the inner-sphere (first coordination sphere) of the Eu(III) complex in different ionic liquids was determined by measuring the decay time of the ⁵D₀ emitting level (*via* monitoring the emission intensity of the hypersensitive transition ⁵D₀ → ⁷F₂ at 615 nm under excitation at 464 nm) and by applying the Horrocks–Sudnick equation:⁷⁰

$$q = 1.05 \left(\frac{1}{\tau_{\text{H}_2\text{O}}} - \frac{1}{\tau_{\text{D}_2\text{O}}} \right) \quad (9)$$

Here q is the number of water molecules in the first coordination sphere (inner-sphere) of the Eu³⁺ ion. $\tau_{\text{H}_2\text{O}}$ and $\tau_{\text{D}_2\text{O}}$ are the luminescence decay times measured in water and heavy water, respectively. The average life times were 1.63 ms in D₂O *versus* 0.56 ms in H₂O for [C₄mim][Tf₂N], 1.91 ms in D₂O *versus* 1.52 ms in H₂O for [N₁₄₄₄][Tf₂N] and 1.92 ms in D₂O *versus* 1.77 ms in H₂O for [P₆₆₆₁₄][Tf₂N], respectively. After filling in these values in eqn (9), a q value of 1.2 is obtained for [C₄mim][Tf₂N], a value of 0.14 for [N₁₄₄₄][Tf₂N] and a value of 0.04 for [P₆₆₆₁₄][Tf₂N]. These values indicate that there is no water molecule present in the inner coordination sphere of the Eu(III) complexes in [N₁₄₄₄][Tf₂N] or [P₆₆₆₁₄][Tf₂N] and that one molecule of water is present in [C₄mim][Tf₂N]. It should be noticed that we have used the Horrocks–Sudnick formula and not the modified Supkowski–Horrocks formula because the latter gave negative q values.^{71,72} This is due to the fact that the Supkowski–Horrocks formula should be used only in aqueous solutions and not in hydrated ionic liquids, since the modified formula takes in account water molecules in the second coordination sphere of the Eu(III) ion and the water concentration is lower in hydrated ionic liquids than in bulk water.⁷³

Loading of ionic liquid phase

The effect of metal concentration in the feed was investigated by using 0.1 M Cyanex 923 dissolved in all the [C₄mim][Tf₂N], [N₁₄₄₄][Tf₂N] and [P₆₆₆₁₄][Tf₂N] (Fig. 9). It was observed that the ionic liquid phase loading was in the order of [C₄mim]-[Tf₂N] > [N₁₄₄₄][Tf₂N] > [P₆₆₆₁₄][Tf₂N]: 16 mmol L⁻¹ Nd(III) could be loaded in [C₄mim][Tf₂N], 12 mmol L⁻¹ in [N₁₄₄₄]-[Tf₂N] and 5 mmol L⁻¹ in [P₆₆₆₁₄][Tf₂N]. The highest loadings are thus observed for ionic liquids with hydrophilic cations. However, the loading in the ionic liquid [P₆₆₆₁₄][Tf₂N] could be increased by increasing the nitrate concentration in the aqueous phase, as shown by adding 0.8 M NO₃⁻ to the

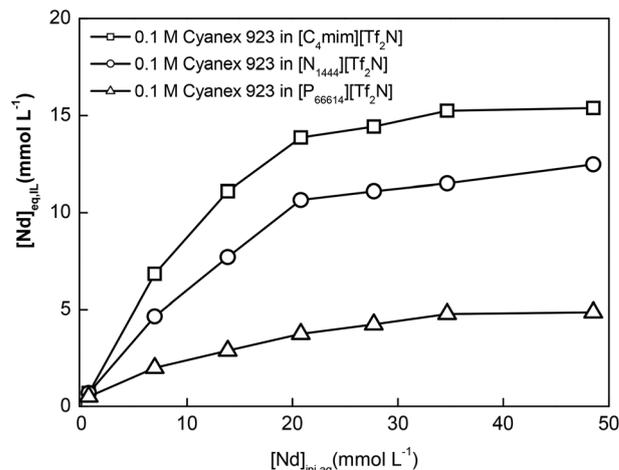


Fig. 9 Variation of [Nd]_{eq,IL} as a function of [Nd]_{ini,aq}. Aqueous phase: pH 3.

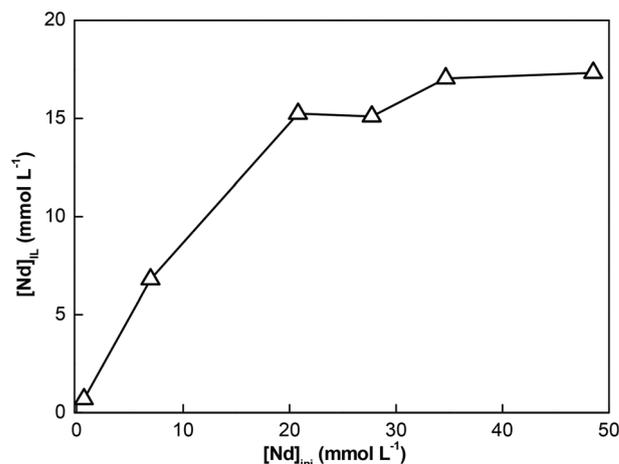


Fig. 10 Variation of [Nd]_{eq,IL} as a function of [Nd]_{ini,aq} for extraction with Cyanex 923 in [P₆₆₆₁₄][Tf₂N]. Aqueous phase: pH 3 + 0.8 M NO₃⁻ (as NaNO₃).

aqueous phase: the loading increased from 5 mmol L⁻¹ to 17 mmol L⁻¹ (Fig. 10).

Extraction of different rare-earth ions

The performance of Cyanex 923 for extraction of different rare-earth ions was investigated in the ionic liquids [C₄mim][Tf₂N], [N₁₄₄₄][Tf₂N] and [P₆₆₆₁₄][Tf₂N], using a mixture of different rare-earth nitrate salts in one aqueous feed solution (Fig. 11). As it can be noticed, the distribution ratios of all the rare earths increase across the lanthanide series and the extracting capacity of Cyanex 923 with respect to the type of ionic liquid follows the order [C₄mim][Tf₂N] > [N₁₄₄₄][Tf₂N] > [P₆₆₆₁₄][Tf₂N]. This order reflects the solubility of the ionic liquid cation in the aqueous phase. It was observed that the distribution ratios decreased when Nd(III) was mixed with other rare-earth ions, compared to extraction of Nd(III) from a solution in which only Nd(III) was present. This is due to competition of all the

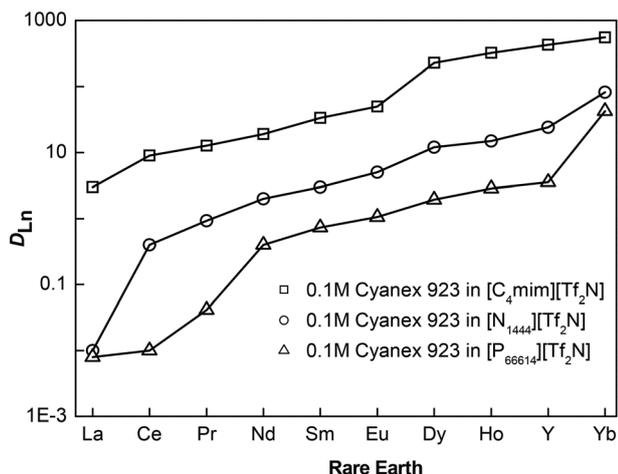


Fig. 11 Variation of the distribution ratios as a function of the rare-earth ion. Aqueous phase: pH 3 and rare-earth ion Ln(III) (7×10^{-4} M each).

different metal ions for complex formation with the extractant. From the distribution ratios, the separation factors were calculated using eqn (4). In Table 1, the separation factors for pairs of different rare-earth ions are shown. The separation factors

Table 1 Separation factors (β) of rare-earth ions of a mixture of different metal ions at a concentration of 7×10^{-4} M each

0.1 M Cyanex 923 in $[C_4mim][Tf_2N]$									
	Ce	Pr	Nd	Sm	Eu	Dy	Ho	Y	Yb
La	3	4.2	6.3	11	1.6	76	107	142	185
Ce		1.4	2	4	5.5	25	36	47	62
Pr			1.5	3.0	4.0	18	25	34	44
Nd				1.8	2.6	12	17	22	29
Sm					1.5	7.0	10	12.7	17
Eu						4.5	6.4	8.5	11
Dy							1.4	1.8	2.4
Ho								1.3	1.7
Y									1.3

0.1 M Cyanex 923 in $[N_{1444}][Tf_2N]$									
	Ce	Pr	Nd	Sm	Eu	Dy	Ho	Y	Yb
La	40	92	200	300	500	1200	1500	2400	8200
Ce		2.3	5	7.5	12.5	30	38	60	206
Pr			2.2	3.2	4.0	13	16	26	89
Nd				1.5	2.5	6.0	7.5	12	41
Sm					1.5	6.7	9.6	12.7	16.6
Eu						4.5	6.4	8.5	11
Dy							1.4	1.8	2.4
Ho								1.3	1.7
Y									3.0

0.1 M Cyanex 923 in $[P_{66614}][Tf_2N]$									
	Ce	Pr	Nd	Sm	Eu	Dy	Ho	Y	Yb
La	1.2	5	50	91	131	241	355	443	5200
Ce		4	40	73	105	193	284	355	4200
Pr			10	18	26	47	70	86	1000
Nd				1.8	2.6	5.0	7.0	9.0	105
Sm					1.4	2.6	4.0	5.0	58
Eu						1.8	2.7	3.4	40
Dy							1.4	2.0	22
Ho								1.2	15
Y									12

depend on the type of ionic liquids. The separation factors for Cyanex 923 in $[C_4mim][Tf_2N]$ are smaller than those for the other ionic liquids. From Table 1 and Fig. 11, it is evident that La(III) and to a lesser extent Ce(III) and Pr(III) are much less efficiently extracted than the other lanthanide ions. This suggests that these ionic liquids can be used to separate these elements from the heavier lanthanides. However, the separations factors between neighboring lanthanide ions are too small to be of practical use for separation of mixtures of heavy lanthanides. The position of Y(III) is between Ho(III) and Yb(III), irrespective of the type of ionic liquid.

Stripping studies

Since the combination of Cyanex 923 with the different ionic liquid diluents is able to extract Nd(III) even from solutions with a low pH value, it is likely that all the loaded metal ions have to be stripped from the ionic liquid phase by strongly acidic solutions. It was observed that 60% and 65% of Nd(III) was stripped back from $[C_4mim][Tf_2N]$ and $[N_{1444}][Tf_2N]$ phases with a 0.5 M HNO_3 solution. It was observed that the percentage stripping increased gradually by increasing the acidity of the stripping phase and 100% of metal ion could be stripped back by using 1 M nitric acid (Table 2). On the contrary, due to the lower loading of the $[P_{66614}][Tf_2N]$ phase (lower D value), complete stripping of Nd(III) from this ionic liquid was possible with 0.7 M HNO_3 . The mechanism of the stripping reaction is exchange of Nd^{3+} ions by H^+ ions in the ionic liquid phase. As mentioned earlier in the text, neutral extractants are able to extract acids. By working at high acid concentrations, the extraction of acids is favored over the extraction of metal ions and the extracted metal ions are released from the ionic liquid phase to the aqueous phase. However, HTf_2N formed in the ionic liquid phase during stripping of Nd^{3+} from the aqueous phase will be, at least partially, lost to the aqueous phase due to the high solubility of HTf_2N in water. This indicates that ionic liquid cations are lost to the aqueous phase to the extraction step and ionic liquid anions are lost to the aqueous phase during the stripping step. However, if the ionic liquid cations that are lost during the extraction step were recovered (for instance by reverse osmosis), they could be added as a solution with nitrate counter ions to the stripping solution and the ionic liquid cations would recombine with the Tf_2N^- anions in the aqueous phase to form new ionic liquid molecules that phase-separate of the aqueous phase and dissolve in the ionic

Table 2 Percentage stripping of Nd(III) from the ionic liquid phase with different concentrations of HNO_3

$[HNO_3]/M$	Stripping percentage (%S)		
	$[N_{1444}][Tf_2N]$	$[C_4mim][Tf_2N]$	$[P_{66614}][Tf_2N]$
0.5	65	62	85
0.7	67	99	97
0.8	82	85	—
1.0	100	98	99.8

liquid phase. In this way it is possible to recover the ionic liquid molecules lost to the aqueous phases. It should be noticed that the losses of Tf_2N^- anions to the aqueous phase occur only if the extraction is *via* an ion exchange mechanism. In the case of extraction *via* a neutral mechanism, $\text{Ln}(\text{NO}_3)_3$ is transferred from the ionic liquid to the aqueous phase upon stripping and no Tf_2N^- anions are lost to the aqueous phase.

Conclusions

This systematic experimental study of the extraction of $\text{Nd}(\text{III})$ by the neutral extractant Cyanex 923 in five different ionic liquids with the bis(trifluoromethylsulfonyl)imide anion shows that the extraction efficiency depends on the type of ionic liquid cation. Ionic liquids with a small hydrophilic cation, such as $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{N}_{1444}][\text{Tf}_2\text{N}]$, extract $\text{Nd}(\text{III})$ efficiently *via* an ion-exchange mechanism from an aqueous nitrate solution with transfer of ionic liquid cations to the aqueous phase. Ionic liquids with a hydrophobic cation, such as $[\text{P}_{66614}][\text{Tf}_2\text{N}]$, $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$ or $[\text{N}_{1888}][\text{Tf}_2\text{N}]$, extract $\text{Nd}(\text{III})$ much less efficiently because the ion-exchange is suppressed by the low solubility of the ionic liquid cation in the aqueous phase. The extraction efficiency by these ionic liquids increases by addition of nitrate ions to the aqueous phase. At high nitrate concentrations, neutral $\text{Nd}(\text{III})$ complexes are extracted to the ionic liquid phase, without losses of the ionic liquid components to the aqueous phase. These findings are of importance for the development of solvent extraction processes for the separation of rare earths. For solvent extraction on an industrial scale with a neutral extractant in an ionic liquid diluent, a cation-exchange mechanism with loss of ionic liquid components to the aqueous phase has to be avoided because recovery of the ionic liquid cations from the aqueous waste streams adds costs. The ionic liquid diluent has to be chosen so that the rare-earth ions can be extracted *via* a neutral mechanism at high nitrate concentrations. Extraction studies on rare-earth ions other than $\text{Nd}(\text{III})$ show that the Cyanex 923 system in the bis(trifluoromethylsulfonyl)imide ionic liquids show potential for the separation of the lightest lanthanides $\text{La}(\text{III})$, $\text{Ce}(\text{III})$ and $\text{Pr}(\text{III})$ from the heavier one; however, the separation factors are too small for separation of mixtures of heavy lanthanides. The stripping of the rare-earth ions from the loaded ionic liquid phase has been investigated. The mechanism of the stripping reaction is exchange of rare-earth ions by protons in the ionic liquid phase. The HTf_2N that is formed in the ionic liquid during the stripping step can be lost to the aqueous phase due to the high solubility of the acid HTf_2N in water. Losses of Tf_2N^- anions to the aqueous phase occur only if the extraction is *via* an ion exchange mechanism. In the case of extraction *via* a neutral mechanism, $\text{Ln}(\text{NO}_3)_3$ is transferred from the ionic liquid to the aqueous phase upon stripping and no Tf_2N^- anions are lost to the aqueous phase.

Acknowledgements

This project has been supported by KU Leuven (projects GOA/13/008 and IOF-KP RARE³) and the FWO-Flanders (Pegasus Marie Curie Fellowship to AR). Support by IoLiTec (Heilbronn, Germany) is also gratefully acknowledged. The emission spectra and life time measurement studies were carried out with the help of Dr Ernesto Rezende Souza.

References

- 1 S. Dai, Y. H. Ju and C. E. Barnes, *J. Chem. Soc., Dalton Trans.*, 1999, 1201–1202.
- 2 X. Q. Sun, H. M. Luo and S. Dai, *Chem. Rev.*, 2012, **112**, 2100–2128.
- 3 P. R. Vasudeva Rao, K. A. Venkatesan, A. Rout, T. G. Srinivasan and K. Nagarajan, *Sep. Sci. Technol.*, 2012, **47**, 204–222.
- 4 I. Billard, Chapter 256 – Ionic Liquids: New Hopes for Efficient Lanthanide/Actinide Extraction and Separation? in *Handbook on the Physics and Chemistry of Rare Earths*, ed. J.-C. G. Bünzli and V. K. Pecharsky, Elsevier, 2013, pp. 213–273.
- 5 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.
- 6 Z. Kolarik, *Solvent Extr. Ion Exch.*, 2013, **31**, 24–60.
- 7 Y. H. Liu, J. Chen and D. Q. Li, *Sep. Sci. Technol.*, 2012, **47**, 223–232.
- 8 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- 9 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 10 A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596–3604.
- 11 I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard and S. Georg, *Solvent Extr. Ion Exch.*, 2011, **29**, 577–601.
- 12 N. Papaiconomou, G. Vite, N. Goujon, J. M. Leveque and I. Billard, *Green Chem.*, 2012, **14**, 2050–2056.
- 13 Y. Zuo, Y. Liu, J. Chen and D. Q. Li, *Ind. Eng. Chem. Res.*, 2008, **47**, 2349–2355.
- 14 K. Nakashima, F. Kubota, T. Maruyama and M. Goto, *Anal. Sci.*, 2003, **19**, 1097–1098.
- 15 M. P. Jensen, J. Neufeind, J. V. Beitz, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466–15473.
- 16 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.
- 17 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *J. Hazard. Mater.*, 2012, **221**, 62–67.
- 18 I. Billard, A. Ouadi and C. Gaillard, *Dalton Trans.*, 2013, **42**, 6203–6212.
- 19 Y. L. Shen, S. F. Wang, L. Zhu, J. J. Wang and W. S. Wu, *Ind. Eng. Chem. Res.*, 2011, **50**, 13990–13996.
- 20 A. Rout and K. Binnemans, *Dalton Trans.*, 2014, **43**, 1862–1872.

- 21 A. Rout and K. Binnemans, *Ind. Eng. Chem. Res.*, 2014, **53**, 6500–6508.
- 22 A. Fortuny, M. T. Coll and A. M. Sastre, *Sep. Purif. Technol.*, 2012, **97**, 137–141.
- 23 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.
- 24 S. Wellens, R. Goovaerts, C. Möller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.
- 25 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.
- 26 S. Chun, S. V. Dzyuba and R. A. Bartsch, *Anal. Chem.*, 2001, **73**, 3737–3741.
- 27 X. Q. Sun and K. E. Waters, *ACS Sustainable Chem. Eng.*, 2014, **2**, 1910–1917.
- 28 X. Q. Sun, C. L. Do-Thanh, H. M. Luo and S. Dai, *Chem. Eng. J.*, 2014, **239**, 392–398.
- 29 Y. Baba, F. Kubota, N. Kamiya and M. Goto, *J. Chem. Eng. Jpn.*, 2011, **44**, 679–685.
- 30 R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *Green Chem.*, 2003, **5**, 361–363.
- 31 M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124–2125.
- 32 M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682–685.
- 33 M. P. Jensen, J. A. Dzielawa, P. Rickert and M. L. Dietz, *J. Am. Chem. Soc.*, 2002, **124**, 10664–10665.
- 34 M. L. Dietz and D. C. Stepinski, *Green Chem.*, 2005, **7**, 747–750.
- 35 C. A. Hawkins, S. L. Garvey and M. L. Dietz, *Sep. Purif. Technol.*, 2012, **89**, 31–38.
- 36 C. Xu, X. H. Shen, Q. D. Chen and H. C. Gao, *Sci. China, Ser. B: Chem.*, 2009, **52**, 1858–1864.
- 37 S. L. Garvey and M. L. Dietz, *Sep. Purif. Technol.*, 2014, **123**, 145–152.
- 38 H. Luo, S. Dai, P. V. Bonnesen, T. J. Haverlock, B. A. Moyer and A. C. Buchanan, *Solvent Extr. Ion Exch.*, 2006, **24**, 19–31.
- 39 S. L. Garvey, C. A. Hawkins and M. L. Dietz, *Talanta*, 2012, **95**, 25–30.
- 40 M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.
- 41 C. H. C. Janssen, A. Sanchez, G. J. Witkamp and M. N. Kobrak, *ChemPhysChem*, 2013, **14**, 3806–3813.
- 42 A. Messadi, A. Mohamadou, S. Boudesocque, L. Dupont and E. Guillon, *Sep. Purif. Technol.*, 2013, **107**, 172–178.
- 43 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Sep. Purif. Technol.*, 2011, **76**, 238–243.
- 44 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.*, 2011, **290**, 215–219.
- 45 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Radiochim. Acta*, 2009, **97**, 719–725.
- 46 P. Giridhar, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.*, 2005, **265**, 31–38.
- 47 K. Nakashima, F. Kubota, T. Maruyama and M. Goto, *Ind. Eng. Chem. Res.*, 2005, **44**, 4368–4372.
- 48 M. S. Murali, N. Bonville and G. R. Choppin, *Solvent Extr. Ion Exch.*, 2010, **28**, 495–509.
- 49 Y. Kikuchi, M. Matsumiya and S. Kawakami, *Solvent Extr. Res. Dev., Jpn.*, 2014, **21**, 137–145.
- 50 M. Matsumiya, Y. Kikuchi, T. Yamada and S. Kawakami, *Sep. Purif. Technol.*, 2014, **130**, 91–101.
- 51 D. Q. Li and C. Wang, *Hydrometallurgy*, 1998, **48**, 301–312.
- 52 W. W. Wang, X. L. Wang, S. L. Meng, H. F. Li and D. Q. Li, *J. Rare Earths*, 2006, **24**, 685–689.
- 53 I. M. Ahmed, Y. A. El-Nadi and N. E. El-Hefny, *Hydrometallurgy*, 2013, **131**, 24–28.
- 54 F. J. Alguacil, C. Caravaca, S. Martinez and A. Cobo, *Hydrometallurgy*, 1994, **36**, 369–383.
- 55 Y. A. El-Nadi, *J. Rare Earths*, 2010, **28**, 215–220.
- 56 B. Gupta, P. Malik and A. Deep, *J. Radioanal. Nucl. Chem.*, 2002, **251**, 451–456.
- 57 B. Gupta, P. Malik and A. Deep, *Solvent Extr. Ion Exch.*, 2003, **21**, 239–258.
- 58 J. Lu, Z. G. Wei, D. Q. Li, G. X. Ma and Z. C. Jiang, *Hydrometallurgy*, 1998, **50**, 77–87.
- 59 S. D. Pawar and P. M. Dhadke, *J. Serb. Chem. Soc.*, 2003, **68**, 581–591.
- 60 M. L. P. Reddy, R. L. Varma, T. R. Ramamohan, S. K. Sahu and V. Chakravorty, *Solvent Extr. Ion Exch.*, 1998, **16**, 795–812.
- 61 S. K. Sahu, M. L. P. Reddy, T. R. Ramamohan and V. Chakravorty, *Radiochim. Acta*, 2000, **88**, 33–37.
- 62 K. Larsson, C. Ekberg and A. Odegaard-Jensen, *Hydrometallurgy*, 2012, **129**, 35–42.
- 63 E. Dziwinski and J. Szymanowski, *Solvent Extr. Ion Exch.*, 1998, **16**, 1515–1525.
- 64 X. Q. Sun, B. Peng, J. Chen, D. Q. Li and F. Luo, *Talanta*, 2008, **74**, 1071–1074.
- 65 L. L. Zhu, Y. H. Liu, J. Chen and W. F. Liu, *J. Appl. Polym. Sci.*, 2011, **120**, 3284–3290.
- 66 X. Q. Sun, D. B. Wu, J. Chen and D. Q. Li, *J. Chem. Technol. Biotechnol.*, 2007, **82**, 267–272.
- 67 J. P. Mikkola, P. Virtanen and R. Sojholm, *Green Chem.*, 2006, **8**, 250–255.
- 68 C. Beuchat, D. Hagberg, R. Spezia and L. Gagliardi, *J. Phys. Chem. B*, 2010, **114**, 15590–15597.
- 69 X. Q. Sun, Y. Ji, L. Guo, J. Chen and D. Q. Li, *Sep. Purif. Technol.*, 2011, **81**, 25–30.
- 70 W. D. Horrocks and D. R. Sudnick, *J. Am. Chem. Soc.*, 1979, **101**, 334–340.
- 71 R. M. Supkowski and W. D. Horrocks, *Inorg. Chim. Acta*, 2002, **340**, 44–48.
- 72 A. Rout, E. R. Souza and K. Binnemans, *RSC Adv.*, 2014, **4**, 11899–11906.
- 73 A. Brandner, T. Kitahara, N. Beare, C. K. Lin, M. T. Berry and P. S. May, *Inorg. Chem.*, 2011, **50**, 6509–6520.