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# Homogeneous liquid–liquid extraction of neodymium(III) by choline hexafluoroacetylacetonate in the ionic liquid choline bis(trifluoromethylsulfonyl)imide†

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The ionic liquid choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf<sub>2</sub>N], was used for the extraction of neodymium(III), in combination with choline hexafluoroacetylacetonate, [Chol][hfac], as the extractant. The binary mixture of [Chol][Tf<sub>2</sub>N] and water shows temperature-dependent phase behavior, with an upper critical solution temperature of 72 °C. A novel extraction technique, homogeneous liquid–liquid extraction (HLL), was applied to this solvent system. HLL is based on the use of thermomorphic solvent mixtures and has the advantage of forming a homogeneous phase during mixing. Extraction is not kinetically hindered by an interface and the extraction equilibrium is reached faster than in the case of heterogeneous mixing in conventional solvent extraction. Several extraction parameters were studied for the extraction of neodymium(III) with [Chol][hfac]: temperature, pH, extractant concentration and loading of the ionic liquid phase. A speciation study was performed to determine the stoichiometry of the extracted neodymium(III) complex and a plausible extraction mechanism is proposed. Neodymium is extracted as a tetrakis hexafluoroacetylacetonate complex with one choline cation as counter ion. The crystal structure of the extracted complex showed the presence of a coordination bond between the choline counter ion and the neodymium(III) center, resulting in a coordination number of nine. The stripping of the loaded neodymium and the influence of acid and extractant concentrations on the phase behavior of the [Chol][Tf<sub>2</sub>N]–H<sub>2</sub>O system were investigated.

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## Introduction

Liquid–liquid extraction or solvent extraction is widely used in hydrometallurgy and is applied to the separation and processing of a wide range of metals, *e.g.* rare earths, hafnium–zirconium, niobium–tantalum and nickel–cobalt.<sup>1–3</sup> Solvent extraction is based on the preferential distribution of a solute between two immiscible phases, an aqueous phase and an organic phase, that are in contact with each other. The organic phase usually consists of a molecular solvent such as kerosene or toluene. Metal ions in the aqueous solution are generally hydrated and prefer to stay in the aqueous phase during solvent extraction because of the low solubility of the hydrated metal ion in the organic phase. Therefore, an extractant is added to the organic phase, which will coordinate to the metal ion to form a more hydrophobic and extractable complex.

Extractants can be termed acidic, basic (anion exchange) or solvating, depending on the type of complex that is formed.<sup>1</sup> Solvent extraction has the advantage that it can be implemented in a continuous mode and it is suitable for the processing of high metal feed concentrations.<sup>3</sup> Ionic liquids are intensively studied as an alternative organic solvent for solvent extraction.<sup>4–6</sup> Ionic liquids (ILs) are solvents that consist entirely of ions.<sup>7–14</sup> Properties such as low volatility, low flammability, wide liquidus range, good chemical stability and adjustable miscibility and polarity, make ionic liquids interesting replacements for the currently used noxious volatile organic solvents (VOCs). The specific properties of an ionic liquid depend both on the structure of the cation and the anion. Different cation–anion combinations result in different properties. Thus, the structure can be tuned according to the application. Ionic liquids are often highly viscous and this hampers their use in solvent extraction.<sup>15–18</sup> In a stirred two-phase mixture during solvent extraction, two stagnant films are formed near the interface, one at each side, in which movement of solute solely occurs *via* diffusion. The thickness of these films is correlated to the viscosity of the liquid, *i.e.* a higher viscosity results in a thicker film.<sup>1</sup> Since diffusion of

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the solute is also slower when the viscosity is higher, a higher viscosity slows down the extraction kinetics in two ways. Thus, longer stirring times are required for highly viscous solvent mixtures to reach equilibrium. Moreover, mixing of highly viscous ionic liquids requires a large energy input.

In our previous work, *homogeneous liquid-liquid extraction* (HLE) was introduced as an alternative technique to circumvent the issue of the high viscosity of ionic liquids.<sup>19,20</sup> It is a novel extraction technique that makes use of ionic liquid systems with thermomorphic behavior, *i.e.* with a temperature-dependent phase behavior and mutual solubility.<sup>21–26</sup> In an HLE process, an aqueous feed solution containing the metal to be extracted is mixed with a thermomorphic ionic liquid and heated above the upper critical solution temperature (UCST). At this temperature, the organic phase is completely miscible with water and a homogeneous solution is obtained (*homogeneous stage*). Complex formation can now occur over the entire volume of the solution and is no longer hindered by the interface. The speed of extraction only depends on the kinetics of the chemical reactions and extraction equilibrium is reached faster. Upon cooling, phase separation occurs and the metal complex is extracted to the organic phase (*settling stage*). HLE was first described by Murata *et al.* for the extraction of iron(III) thenoyltrifluoroacetate in propylene carbonate.<sup>27</sup> In the following decades, HLE has been mainly applied to the extraction and pre-concentration of metals for analytical purposes, extraction of organic compounds and extraction of biological material.<sup>28–36</sup> Examples of hydrometallurgical applications, however, are scarce and make use of molecular solvents only.<sup>37–41</sup> To the best of our knowledge, HLE has not yet been applied to hydrometallurgical applications with ionic liquids, besides the previous work by our group.<sup>19,20</sup>

In this paper, the potential of the ionic liquid choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf<sub>2</sub>N], for use in HLE of neodymium(III) is described (Fig. 1).<sup>26,42,43</sup> Neodymium is one of the most critical rare earths and is highly demanded for use in permanent magnets, so that efficient recovery methods for this element are being developed by several research groups.<sup>44–55</sup> [Chol][Tf<sub>2</sub>N] has been shown to exhibit thermomorphic behavior in water, with an UCST of 72 °C.<sup>26</sup> Since no specific chelating functions are present in the structure of [Chol][Tf<sub>2</sub>N], an extractant was added. Only polar extractants could be used in combination with [Chol][Tf<sub>2</sub>N], since this ionic liquid is quite polar and non-polar extractants have a poor solubility in this ionic liquid. Moreover, the complex formed between Nd(III) and the extractant upon extraction should have a higher affinity for the ionic liquid phase than

for the aqueous phase. As the  $\beta$ -diketone hexafluoroacetylacetone meets these requirements, it was used as extractant. The ionic liquid [Chol][hfac] was preferred instead of molecular hexafluoroacetylacetone (Hhfac) since the ionic liquid is much less volatile than Hhfac.<sup>56</sup> Moreover, the extractant moiety is already present in its deprotonated form, making it immediately available for coordination and no pH adjustments have to be made. In principle, hexafluoroacetylacetone ionic liquids with cations other than Chol<sup>+</sup> could also be used, such as 1-butyl-3-methylimidazolium or tetrabutylphosphonium.<sup>56,57</sup> However, the composition of the extraction system was kept as simple as possible by using the same Chol<sup>+</sup> cation for both extractant and diluent.  $\beta$ -Diketones, such as hexafluoroacetylacetone, are known for their coordination behavior with respect to lanthanide ions and are of general interest because of their luminescence properties.<sup>58</sup> Lanthanide  $\beta$ -diketonates have also been studied for liquid-liquid extraction, *e.g.* in the context of the separation of fission products from spent nuclear fuel, mostly with 2-thenoyltrifluoroacetone (Htta) as a ligand.<sup>58–62</sup>

## Experimental

### Products

Neodymium(III) chloride hexahydrate (99.9%), neodymium(III) nitrate hexahydrate (99.9%) and neodymium(III) oxide (99.99%) were purchased from Alfa Aesar (Karlsruhe, Germany). Lithium bis(trifluoromethylsulfonyl)imide (99%) was obtained from IoLiTec (Heilbronn, Germany). Hexafluoroacetylacetone (98%) was obtained from ABCR GmbH (Karlsruhe, Germany). Choline chloride (99%) was purchased from Acros Organics (Geel, Belgium). Choline hydroxide (46 wt% in water), sodium chloride (>98%), hydrogen bromide (48 wt%) and silver nitrate (>99.8%) were obtained from Sigma-Aldrich (Diegem, Belgium). HNO<sub>3</sub> (65%) was obtained from Chem-Lab (Zedelgem, Belgium) and absolute ethanol from VWR (Leuven, Belgium). A 1000 mg L<sup>-1</sup> dysprosium ICP standard was purchased from Merck (Overijse, Belgium). The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany).

### Equipment

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in D<sub>2</sub>O on a Bruker Avance 300 spectrometer, operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C. <sup>19</sup>F NMR spectra were recorded on a Bruker Avance II+ 600 MHz spectrometer with a SCF F-H-D-05 probe (Bruker Biospin) at a frequency of 565 MHz. The temperature was controlled using a Bruker BCU 05 temperature controller, with a thermocouple type T. A 5 mL pycnometer was used to determine densities. FTIR spectra were recorded on a Bruker Vertex 70 spectrometer (Bruker Optics). Both solid and liquid samples were examined directly without further sample preparation using a Platinum ATR single reflection diamond attenuated total reflection (ATR) accessory. Analysis was performed with OPUS software. Carbon, hydrogen and nitrogen content were determined using a CE Instruments EA-1110 element analyzer. Water content was measured with a Mettler-Toledo

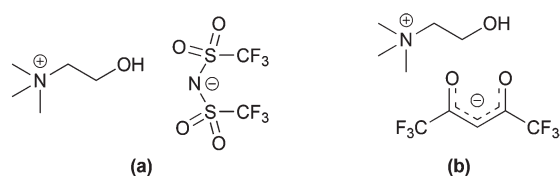


Fig. 1 Chemical structure of (a) [Chol][Tf<sub>2</sub>N] and (b) [Chol][hfac].

DL39 coulometric Karl Fischer titrator. Extraction experiments were performed in a TMS-200 thermoshaker (Nemus Life). A Bruker Picofox S2 total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations in both aqueous and organic (ionic liquid) phase and the chloride content of the synthesized  $[\text{Chol}][\text{TF}_2\text{N}]$ . Extraction mixtures were centrifuged using a Heraeus Labofuge 200. X-ray intensity data were collected at 100 K on an Agilent Supernova diffractometer, equipped with an Atlas CCD detector, using Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The images were interpreted and integrated with the CrysAlisPro software from Agilent Technologies. Using Olex2, the structure was solved with the SHELXS structure solution program using Direct Methods and refined with the SHELXL refinement package using full-matrix least squares minimization on  $F^2$ .<sup>63–65</sup>

### Synthesis of choline bis(trifluoromethylsulfonyl)imide

Choline bis(trifluoromethylsulfonyl)imide ( $[\text{Chol}][\text{TF}_2\text{N}]$ ) was prepared following a literature procedure.<sup>25</sup> Choline chloride (60.085 g, 0.430 mol) was mixed with an equimolar amount of lithium bis(trifluoromethylsulfonyl)imide (123.556 g, 0.430 mol) in 50 mL of distilled water. The mixture was stirred for one hour at room temperature. The ionic liquid phase-separated from the aqueous phase and was washed with small amounts of ice-cold water in order to remove chloride impurities. The presence of chloride in the water layer after washing was tested by the addition of a small aliquot of a concentrated silver nitrate solution to the washing solution. Finally, the ionic liquid was dried *in vacuo* on a rotary evaporator (60 °C). A white solid product was formed. Yield: 74% (67.225 g, 0.176 mol)  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_6]\text{DMSO}$ ,  $\delta$ ): 5.29 (t, 1H, OH,  $J = 5.0 \text{ Hz}$ ); 3.85 (m, 2H,  $\text{CH}_2$ ); 3.41 (m, 2H,  $\text{CH}_2$ ); 3.12 (s, 9H,  $3 \times \text{CH}_3$ ).  $^{13}\text{C}$  NMR (75.47 MHz,  $[\text{D}_6]\text{DMSO}$ ,  $\delta$ ): 119.63 (q,  $2 \times \text{CF}_3$ ,  $J = 322 \text{ Hz}$ ); 67.23 (N- $\text{CH}_2$ ); 55.29 ( $\text{CH}_2$ ); 53.34 ( $3 \times \text{CH}_3$ ). Elemental analysis: found (%): C, 21.49; H, 3.86; N, 7.20%; calc. for  $\text{C}_7\text{H}_{14}\text{N}_2\text{O}_5\text{F}_6\text{S}_2$ : C, 21.88; H, 3.67; N, 7.29%. Water content: 2200  $\text{mg kg}^{-1}$ . Chloride content:  $<10 \text{ mg kg}^{-1}$ . Density: 1.500  $\text{g cm}^{-3}$  (60 °C). FTIR ( $\text{cm}^{-1}$ ) 1477 ( $\text{CH}_2$ ); 1348 ( $\text{SO}_2$ ); 1181 ( $\text{CF}_3$ ); 1138 ( $\text{SO}_2$ ); 1050 ( $\text{SO}_2$ ); 953; 867; 791; 741 ( $\text{CF}_3$ ); 611; 570 ( $\text{CF}_3$ ); 513 ( $\text{CF}_3$ ).

### Preparation of the ionic liquid phase

As described in the literature,  $[\text{Chol}][\text{hfac}]$  is not stable at elevated temperatures and decomposition occurs fast.<sup>56</sup> Thus, special drying techniques are required to obtain a pure and dry product. However, since the extraction studies described in this paper do not require dry  $[\text{Chol}][\text{hfac}]$ , but  $[\text{Chol}][\text{hfac}]$  dissolved in the ionic liquid phase,  $[\text{Chol}][\text{hfac}]$  was prepared directly in the ionic liquid  $[\text{Chol}][\text{TF}_2\text{N}]$ . Choline hydroxide (46 wt% solution in water) and hexafluoroacetylacetone (Hhfac) were added to dry  $[\text{Chol}][\text{TF}_2\text{N}]$  in equimolar quantities. Water was added to this mixture to obtain a water content of 8 wt%. A small amount of this  $[\text{Chol}][\text{hfac}]-[\text{Chol}][\text{TF}_2\text{N}]$  mixture was then added to  $[\text{Chol}][\text{TF}_2\text{N}]$  (containing 8 wt% of water) to obtain the organic (ionic liquid) phase of the

extraction mixture. Because of its hygroscopic behavior, a  $[\text{Chol}][\text{TF}_2\text{N}]$  solution containing a certain amount of water (8 wt% in this case) was used instead of pure dry ionic liquid, in order to prevent further uncontrolled uptake of water. Moreover, water-containing  $[\text{Chol}][\text{TF}_2\text{N}]$  is liquid, thus easier to dispense than solid  $[\text{Chol}][\text{TF}_2\text{N}]$ .

### Extraction experiments

At a temperature of 20 °C, 12 wt% of  $[\text{Chol}][\text{TF}_2\text{N}]$  dissolves in water and 10 wt% of water dissolves in  $[\text{Chol}][\text{TF}_2\text{N}]$ .<sup>26</sup> During a typical extraction experiment, this mutual solubility was taken into account and the ionic liquid phase and water were always mixed in such proportions that two phases were obtained in a 1:1 mass ratio in the final extraction mixture after phase equilibration. A 1:1 mass ratio simplifies calculation of the distribution ratio  $D$  and percentage extraction % $E$  (eqn (1) and (2)). In order to obtain a 1:1 ratio, 1109 mg of ionic liquid phase, containing a certain amount of  $[\text{Chol}][\text{TF}_2\text{N}]$  extractant ( $50 \text{ mmol kg}^{-1}$ , unless otherwise specified) was mixed with 891 mg of metal feed solution (nitrate, chloride or bromide medium). The metal concentration in the aqueous feed was 15  $\text{mmol kg}^{-1}$  unless otherwise specified. The initial Nd(III) concentration in the aqueous phase was recalculated according to the phase equilibrium to 12  $\text{mmol kg}^{-1}$  (unless otherwise specified). The extraction mixture was heated and gently shaken in a thermoshaker at 700 rpm and 80 °C for 3 min to obtain one homogeneous phase. The mixture was cooled to room temperature to induce settling and two phases were again obtained. After waiting for 1 h to make sure settling was completed, a small sample (100 mg) was taken from the aqueous phase to determine the metal concentration in the aqueous phase with a TXRF spectrometer. A small amount (100 mg) of dysprosium nitrate ICP standard solution ( $1000 \text{ mg L}^{-1}$ ) was added to the sample as the reference for quantification and further diluted with 1 mL of MilliQ® water. A dysprosium standard was used because the detected dysprosium L-lines are close to those of neodymium, but there is no overlap. Thus, secondary absorption by the ionic liquid matrix on the carrier has a similar influence on the radiation of dysprosium and neodymium. The prepared sample solution was homogenized and a small droplet (5  $\mu\text{L}$ ) was dispensed on a quartz sample carrier. Finally, the carrier containing the sample was dried at 60 °C for 15 min. Prior to dispensing the sample droplet, the quartz carrier was pre-treated with a SERVA® silicone solution in isopropanol (10  $\mu\text{L}$ ) in order to make the surface more hydrophobic and keep the sample droplet in the middle of the carrier.

Extraction of Nd(III) is evaluated by calculating the distribution ratio  $D$  and percentage extraction % $E$  by using the following equations:

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

$$\%E = \frac{[\text{M}]_{\text{org}}}{[\text{M}]_{\text{org}} + [\text{M}]_{\text{aq}}} 100\% \quad (2)$$

where  $[M]_{\text{org}}$  and  $[M]_{\text{aq}}$  are the metal ion concentration (in  $\text{mol kg}^{-1}$ ) in the organic phase and the aqueous phase, respectively.  $[M]_{\text{aq}}$  was measured using TXRF. Since aqueous and organic phase were present in a 1 : 1 mass ratio, the metal ion concentration in the organic phase was calculated as follows:

$$[M]_{\text{org}} = [M]_{\text{aq, in}} - [M]_{\text{aq}} \quad (3)$$

where  $[M]_{\text{aq, in}}$  and  $[M]_{\text{aq}}$  are the initial and final (measured) metal ion concentration in the aqueous phase, respectively.

### Preparation of neodymium(III) bromide hydrate

Neodymium(III) bromide hydrate was prepared by adding  $\text{Nd}_2\text{O}_3$  (1 g, 3.0 mmol) to a HBr solution (48%, 3.006 g, 18 mmol), diluted in 10 mL of water. The mixture was stirred for 1 h and  $\text{NdBr}_3 \cdot x\text{H}_2\text{O}$  was crystallized out of solution by drying on a rotary evaporator.

### Study of temperature influence on extraction

The influence of temperature on extraction was studied using four identical extraction mixtures (same procedure as above for the extraction experiments). All mixtures were heated at different temperatures (30 to 80 °C) for 2 min. The last 5 s of heating, the mixtures were shaken (600 rpm). Next, the mixtures were quenched in an ice bath and centrifuged (5000 rpm, 1 min). The aqueous phase was isolated and its neodymium content was determined by TXRF (same procedure as above for the extraction experiments).

### Stripping experiments

Stripping experiments were performed by mixing 1.0 g of  $[\text{Chol}][\text{Tf}_2\text{N}]$  phase obtained after extraction of  $\text{Nd(III)}$ , with 1.0 g of diluted  $\text{HNO}_3$  solution (concentration ranging from 0 to 2  $\text{mol L}^{-1}$ ). The mixtures were heated to 80 °C and shaken for 3 min to obtain one homogeneous solution and again cooled to room temperature to induce phase separation. After 1 h of settling, the metal content in the aqueous and organic phase was measured with TXRF. The sample preparation of the aqueous phase proceeded according to the method described above. Samples of the organic phase were prepared by adding a small amount of dysprosium standard solution (1000  $\text{mg L}^{-1}$ ) to 100 mg of the organic phase and diluting it with 1 mL of pure ethanol. Approximately 2  $\mu\text{L}$  of the prepared sample solution was dispensed on the quartz glass carrier.

Stripping was evaluated using the stripping efficiency %S, which is calculated as follows:

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

where  $[M]_{\text{aq, str}}$  is the metal concentration in the aqueous phase after stripping and  $[M]_{\text{org, str}}$  the metal concentration in the organic phase after stripping.

### Cloud point determination

Cloud point determinations were performed by placing a 4 mL vial, closed with a cap and containing the solvent

mixture to be studied, in a temperature-controlled water bath. The solvent mixture was heated and stirred until the mixture turned homogeneous. Next, the heating was turned off and the mixture was slowly cooled. The transparency of the mixture was monitored visually and the temperature at which the homogeneous mixture became cloudy was recorded. The determination of this cloud point temperature was repeated three times to get an accurate result. The mixtures all contained 1109 mg of  $[\text{Chol}][\text{Tf}_2\text{N}]$  solution (water content of 8 wt% and a varying amount of  $[\text{Chol}][\text{hfac}]$ ) and 891 mg of water or diluted  $\text{HNO}_3$  (concentration varying between 0 and 2  $\text{mol L}^{-1}$ ).

### Study of decomposition $[\text{Chol}][\text{hfac}]$

$^{19}\text{F}$  NMR spectroscopy was applied to monitor the decomposition reaction of  $[\text{Chol}][\text{hfac}]$  with water.  $[\text{Chol}][\text{hfac}]$  was prepared by adding choline hydroxide (46 wt% in water) to pure hexafluoroacetylacetone. Immediately after mixing, a sample was taken and diluted in deuterated methanol ( $\text{CD}_3\text{OD}$ ). The sample was placed inside the NMR spectrometer and heated to 80 °C using the temperature controller of the NMR device. Every 26 s, a  $^{19}\text{F}$  NMR spectrum was recorded. The sample was not locked or shimmed before the start of the measurements since the decomposition reaction of the pure  $[\text{Chol}][\text{hfac}]$  in water occurred fast and locking and shimming would require too much time. The spectrum reference (SR) was used because standard  $^{19}\text{F}$  references evaporated at 80 °C and could not be applied.

### Crystallography

Single crystals of  $[\text{Chol}][\text{Nd}(\text{hfac})_4]$  suitable for X-ray diffraction were obtained by crystallization upon cooling of an extraction mixture (Nd concentration in feed was 0.1  $\text{mol kg}^{-1}$ , extractant concentration in organic phase was 144  $\text{mmol kg}^{-1}$ ). The choline ligand was modeled in two positions with an occupancy of 0.605(9):0.395(9). The second orientation binds to an extra water molecule O52 (occupancy 0.395(9)). The choline ligand and O52 were isotropically refined with DFIX restraints on both choline orientations. Non-hydrogen atoms of other parts were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times  $U_{\text{eq}}$  of the parent atoms (1.5 for methyl groups). The anisotropic displacement parameters of the fluorine atoms were restrained to be approximately isotropic and components of the displacement parameters in the directions of the C–F bond were restrained to be equal.

Crystal data for  $[\text{Chol}][\text{Nd}(\text{hfac})_4]$ :  $\text{C}_{25}\text{H}_{17}\text{F}_{24}\text{NNdO}_{9.395}$ ,  $M = 1081.96 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 11.03826(19) \text{ \AA}$ ,  $b = 18.5663(5) \text{ \AA}$ ,  $c = 17.8663(3) \text{ \AA}$ ,  $\beta = 92.0479(17)^\circ$ ,  $V = 3659.18(13) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.964 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 1.592 \text{ mm}^{-1}$ ,  $F(000) = 2101.0$ , crystal size  $0.27 \times 0.22 \times 0.16 \text{ mm}^3$ , 26 960 reflections measured, 7466 unique ( $R_{\text{int}} = 0.0266$ ) which were used in all calculations. The final  $wR_2$  was 0.1290 (all data) and  $R_1$  was 0.0481 ( $I > 2\sigma(I)$ ).



## Results and discussion

### Variation of extraction parameters

Homogeneous liquid–liquid extraction was carried out with the [Chol][Tf<sub>2</sub>N]–[Chol][hfac] extraction system (Fig. 2). [Chol]–[Tf<sub>2</sub>N] shows thermomorphic behavior with an UCST of 72.1 °C.<sup>26</sup> Some additives to the aqueous phase of a [Chol]–[Tf<sub>2</sub>N]–H<sub>2</sub>O mixture increase the UCST, such as inorganic salts like Nd(NO<sub>3</sub>)<sub>3</sub> in this case. Therefore, the extraction mixtures were heated to 80 °C to assure that a homogeneous solution is formed during the mixing stage.

For HLE, it is in principle sufficient to just heat the extraction mixture above the UCST to obtain a homogeneous phase, without applying any agitation. However, similarly to [Hbet]–[Tf<sub>2</sub>N], diffusion of the [Chol][Tf<sub>2</sub>N] molecules into the aqueous phase is too slow to obtain a homogeneous phase in a short time scale.<sup>19,20</sup> Thus, the mixture should be gently shaken (5 s) to obtain a homogeneous phase. To show the advantage of the formation of a homogeneous phase during extraction, this procedure (heating the extraction mixture to the required temperature and shaking it for 5 s) was applied to the extraction of Nd(III) from a nitrate solution at different temperatures between 30 and 80 °C (Fig. 3). To obtain the required temperature, the mixtures were heated for 2 min. Next, they were shaken for 5 s and immediately quenched in an ice bath. At low temperatures (30–45 °C), almost no Nd(III) was extracted. At higher temperatures (60 °C), but still below the UCST, extraction of Nd(III) occurred to some extent, but still less than 50% of Nd(III) was extracted. The extracted amount is a little higher at 60 °C compared to 30 °C, since an increase in temperature lowers the viscosity of the ionic liquid phase, thus facilitating diffusion of ions through the films near the interface. Extraction at 80 °C (above the UCST) clearly showed the positive effect of the formation of a homogeneous stage. After shaking for 5 s, a homogeneous phase was obtained and immediately, the extractable complex was formed resulting in almost 100% extraction. To obtain the same %E at temperatures below the UCST, the extraction mixture had to be shaken for 2 min at 65 °C and up to 10 min at 30 °C. So, it can be concluded that HLE can be

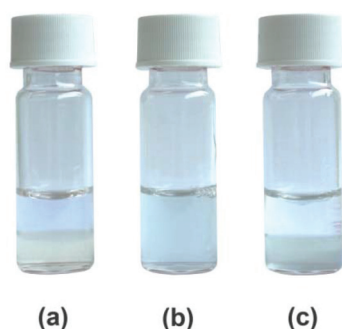


Fig. 2 Homogeneous liquid–liquid extraction of Nd(III) (purple color) from a nitrate solution with [Chol][hfac] (yellow color) dissolved in [Chol][Tf<sub>2</sub>N]. Left: before extraction (20 °C), middle: during homogeneous stage (80 °C), right: after settling (20 °C). The upper phase is the aqueous phase, the lower phase is the ionic liquid phase.

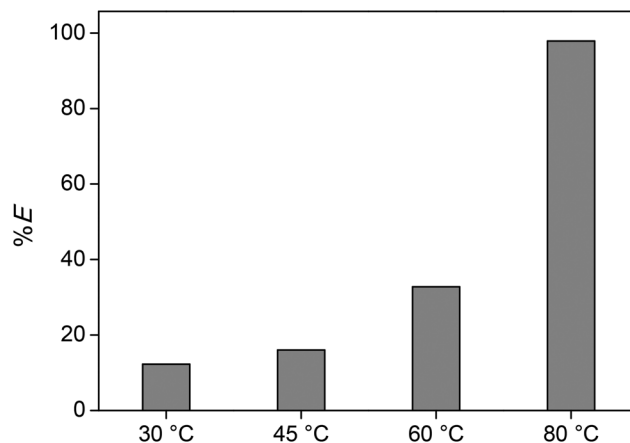


Fig. 3 Influence of temperature on %E of Nd(III) from a nitrate solution with [Chol][hfac]–[Chol][Tf<sub>2</sub>N]. 50 mmol kg<sup>−1</sup> [Chol][hfac] in organic phase, 12 mmol kg<sup>−1</sup> Nd(III) in aqueous phase.

performed on a shorter time scale compared to conventional liquid–liquid extraction and the extraction mixtures have to be shaken for a much shorter time.

The influence of several extraction parameters on %E was examined: the extractant concentration, pH and metal feed concentration. The percentage extraction increased when the amount of [Chol][hfac] extractant in the extraction mixture was raised (Fig. 4). Almost 100% extraction was achieved with 60 mmol kg<sup>−1</sup> [Chol][hfac] in the organic phase. The same extraction behavior as a function of [Chol][hfac] concentration was observed for extraction from chloride solution, meaning that the counter ion in the aqueous metal solution (being chloride or nitrate) has no influence on the extraction behavior. Extraction from both types of feed solution proceeded equally well. From Fig. 4, it can be seen that the pH increased

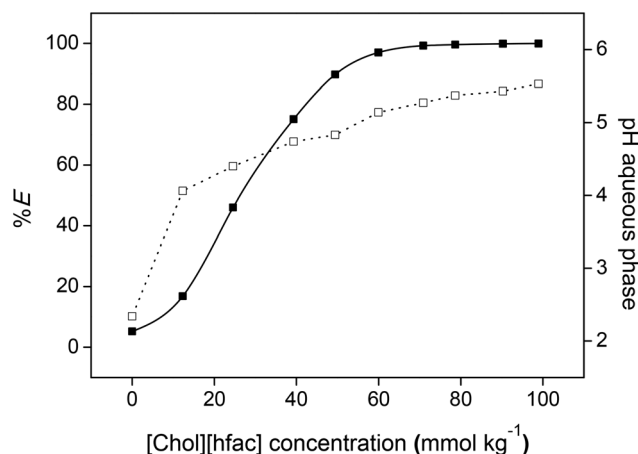
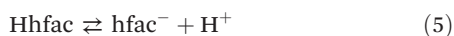


Fig. 4 %E (■) of Nd(III) from a nitrate solution with [Chol][hfac]–[Chol]–[Tf<sub>2</sub>N] as a function of the [Chol][hfac] concentration in the organic phase. 12 mmol kg<sup>−1</sup> Nd(III) and 0.01 M HNO<sub>3</sub> in aqueous phase, equilibrium pH is indicated with □.

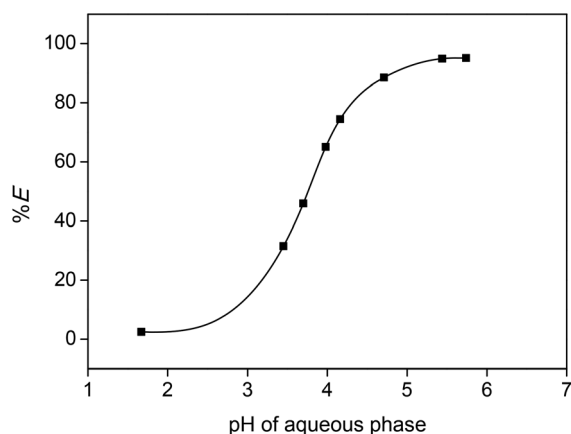
with increasing [Chol][hfac] concentration. This can be rationalized considering the following acid dissociation equilibrium:



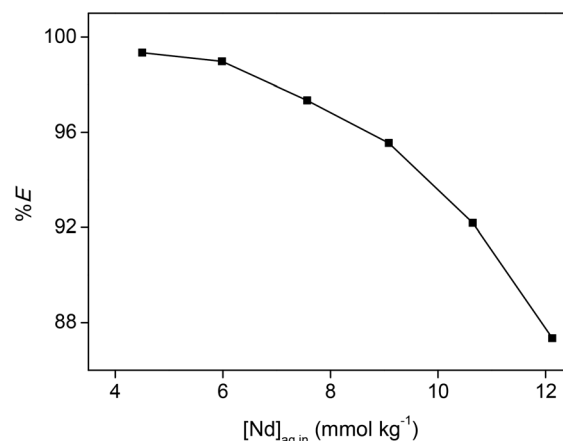
$\text{HNO}_3$  was initially added to the extraction mixtures to keep the pH low enough to prevent hydrolysis of Nd(III) ions. The amount of protons ( $\text{H}^+$ ) present in the aqueous start solution was the same in every extraction mixture (0.01 mmol). When  $\text{hfac}^-$  is added (e.g. as [Chol][hfac]), the acid dissociation equilibrium of Hhfac shown in eqn (5) was shifted to the left and the equilibrium proton concentration decreased, resulting in an increasing pH value.

Hexafluoroacetylacetone (Hhfac) is an organic acid, with  $\text{hfac}^-$  as its conjugated base. The acid concentration in the aqueous phase is expected to influence the extraction, since part of the  $\text{hfac}^-$  anions are protonated when acid is present. It was shown that at pH 5.5 (which corresponds to an extraction mixture without extra  $\text{HNO}_3$  added to the aqueous phase), nearly all Nd(III) ions were removed from the aqueous phase (Fig. 5). No precipitation was observed, so the removal of Nd(III) from solution was completely due to extraction to the organic phase. Moreover, it can be concluded that no non-extractable hydrolysis products were formed, since all metals are extracted and a %E of almost 100% was obtained. So, it is not necessary to add extra acid to the feed of the extraction mixture to prevent hydrolysis. Additionally, from Fig. 5 it can be seen that by lowering the equilibrium pH after addition of  $\text{HNO}_3$  to the aqueous phase, the percentage extraction decreased sharply between pH 3–5. At pH < 2, extraction of Nd(III) is almost negligible since all  $[\text{hfac}]^-$  anion are protonated and the ionic liquid [Chol][hfac] is destroyed.

The influence of the metal ion concentration in the aqueous feed on %E was also investigated, at constant pH and at constant extractant concentration. As expected, the percentage extraction decreased with increasing metal feed concen-



**Fig. 5** %E of Nd(III) from a nitrate solution with [Chol][hfac]–[Chol]–[Tf<sub>2</sub>N] as a function of the equilibrium pH of the aqueous phase at room temperature. 50 mmol kg<sup>−1</sup> [Chol][hfac] in organic phase, 12 mmol kg<sup>−1</sup> Nd(III) and 0–0.1 M  $\text{HNO}_3$  in aqueous phase.



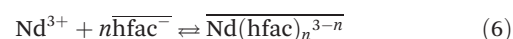
**Fig. 6** %E of Nd(III) with [Chol][hfac]–[Chol][Tf<sub>2</sub>N] as a function of the initial Nd(III) concentration in the aqueous phase. 50 mmol kg<sup>−1</sup> [Chol]–[hfac] in organic phase, 4–12 mmol kg<sup>−1</sup> Nd(III) and 0.01 M  $\text{HNO}_3$  in aqueous phase.

tration because the amount of extracted metal ions is always approximately constant (Fig. 6).

The extraction capacity of the system was determined by examining the maximum loading of Nd(III) in the organic phase. It was shown earlier that 100% extraction could be obtained for an extractant concentration of 60 mmol kg<sup>−1</sup> or higher (Fig. 4). This counts for a Nd(III) feed solution of 15 mmol kg<sup>−1</sup>. To increase the loading of the organic phase, the metal feed concentration and the extractant concentration were increased. When testing the extraction from a 100 mmol kg<sup>−1</sup> Nd(III) solution (excess), precipitation of the extractable Nd(III) complex was observed for [Chol][hfac] concentrations of more than 144 mmol kg<sup>−1</sup>. To determine how much Nd(III) can maximally be extracted with 144 mmol kg<sup>−1</sup> of extractant, extraction was tested from different concentrations of Nd(III) feed solution, between 10 and 100 mmol kg<sup>−1</sup>. As expected, the percentage extraction %E decreased with increasing  $[\text{Nd}]_{\text{aq,in}}$  (Fig. 7), similarly as shown earlier in Fig. 6. The neodymium concentration in the organic phase  $[\text{Nd}]_{\text{org}}$  logically increases with increasing Nd(III) feed concentration, up to 43 mmol kg<sup>−1</sup>. Thus, it can be concluded that the maximum loading of the [Chol][Tf<sub>2</sub>N] ionic liquid with the Nd(III)–[Chol][hfac] complex is equal to 43 mmol kg<sup>−1</sup>. Beyond this point, the complex is no longer completely soluble in the organic phase and precipitates.

### Extraction stoichiometry

To get a better understanding of the extraction mechanism, a slope analysis was performed. The extraction equilibrium can be described by eqn (6):



The bar indicates species in the organic phase. During the homogeneous stage of the extraction, the dissociated hexafluoroacetylacetone anion coordinates to the Nd(III) ion. Upon phase separation during the settling stage, the formed

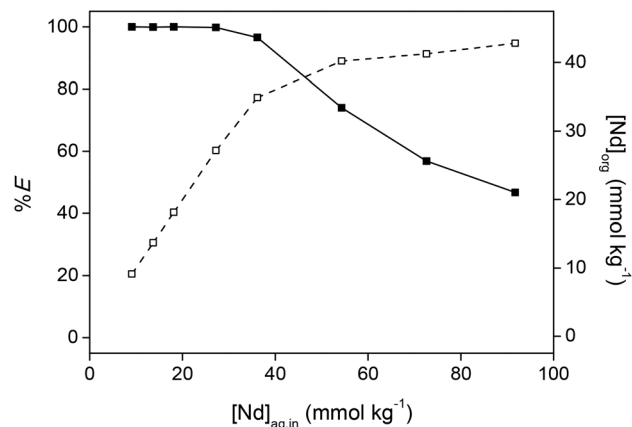


Fig. 7 Maximum loading of the organic phase: ■ %E and □ Nd concentration in the organic phase after extraction with [Chol][hfac]–[Chol]–[Tf<sub>2</sub>N] as a function of the initial Nd(III) concentration in the aqueous phase. 144 mmol kg<sup>−1</sup> [Chol][hfac] in organic phase. Equilibrium pH was constant at pH 6.

complex diffuses to the bulk of the organic phase. The corresponding equilibrium constant  $K_{\text{ex}}$  is expressed as:

$$K_{\text{ex}} = \frac{[\text{Nd}(\text{hfac})_n]_{\text{org}}}{[\text{Nd}^{3+}]_{\text{aq}} [\text{hfac}^-]_{\text{org}}^n} \quad (7)$$

In this equation, the equilibrium concentration of Nd–(hfac)<sub>n</sub><sup>3−n</sup> is equal to the analytical concentration of neodymium in the organic phase [Nd]<sub>org</sub> and [Nd<sup>3+</sup>] is equal to the analytical concentration of neodymium in the aqueous phase, [Nd]<sub>aq</sub>. Thus, the distribution ratio  $D$  can be written as:

$$D = \frac{[\text{Nd}]_{\text{org}}}{[\text{Nd}]_{\text{aq}}} = \frac{[\text{Nd}(\text{hfac})_n]_{\text{org}}}{[\text{Nd}^{3+}]_{\text{aq}}} \quad (8)$$

After substitution of (8) in (7) and taking the logarithm of both sides of eqn (7), log  $D$  is expressed as being linearly related to  $n$  times the logarithm of [hfac<sup>−</sup>]:

$$\log D = \log K_{\text{ex}} + n \log [\text{hfac}^-] \quad (9)$$

The slope of a plot of log  $D$  versus log [hfac<sup>−</sup>] is equal to  $n$ , which is the number of coordinated hfac<sup>−</sup> ligands per Nd(III) ion. Notice that [hfac<sup>−</sup>] is the equilibrium concentration of free hexafluoroacetylacetonate anions, which is an unknown parameter. It is approximated by the initial concentration of [Chol][hfac] (in mmol kg<sup>−1</sup>) in the ionic liquid phase.

Log  $D$  versus log [Chol][hfac] for the extraction of Nd(III) with [Chol][hfac]–[Chol][Tf<sub>2</sub>N] does not show a perfectly linear relation (Fig. 8). When drawing the tangent at different parts of the plot, it can be seen that the slope of the tangent varies between a value of 4 at low extractant concentrations and a value larger than 4 at high extractant concentrations. The same non-linear behavior was observed when extracting from an aqueous phase with a constant high ionic strength of 1 mol L<sup>−1</sup>, by addition of NaCl to the aqueous phase. Thus, it can be

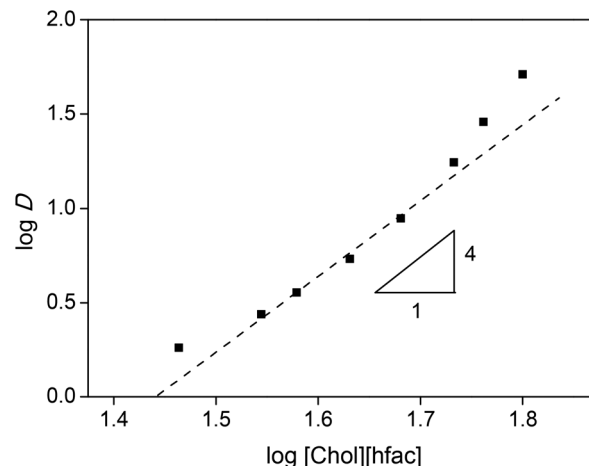


Fig. 8 Log  $D$  versus log [Chol][hfac] for the extraction of Nd(III) from a nitrate solution with [Chol][hfac]–[Chol][Tf<sub>2</sub>N]. 30–65 mmol kg<sup>−1</sup> [Chol]–[hfac] in organic phase, 12 mmol kg<sup>−1</sup> Nd(III) in aqueous phase initially. Equilibrium pH was constant at pH 6. Dashed line indicates a slope of 4. The deviations at low and high extractant concentrations are discussed in the text.

ruled out that the small deviation in slope is due to changes in the phase behavior which could influence the calculated percentage extraction. As will be described in the section ‘Phase behavior’ at the end this paper, it was observed that the presence of [Chol][hfac] in the ionic liquid phase had a lowering effect on the cloud point. However, at an ionic strength of 1 mol L<sup>−1</sup>, the mutual solubility of ionic liquid and water, and thus the mass of the phases, remains approximately constant regardless of the amount of [Chol][hfac] present. Thus, the increase in slope of the plot of log  $D$  versus log [Chol][hfac] in Fig. 8 is most likely due to the approximation of [hfac<sup>−</sup>] by the initial concentration of [Chol][hfac]. At low and intermediate extractant concentrations compared to the initial Nd(III) concentration, the equilibrium extractant concentration [hfac<sup>−</sup>] is proportional to the initial concentration of [Chol][hfac]. However, at higher concentrations (excess) of extractant compared to Nd(III), this no longer holds. The initial extractant concentration of [Chol][hfac] is no longer a good approximation of the equilibrium concentration [hfac<sup>−</sup>]. This explains the increase in slope in the plot of log  $D$  versus log [Chol][hfac] with higher [Chol][hfac] concentrations. Also, at very low extractant concentrations, almost no Nd(III) is extracted and the initial [Chol][hfac] concentration is not a good estimation of the equilibrium [hfac<sup>−</sup>] concentration.

When drawing a straight line with a slope of 4 in Fig. 8, it can be seen that this line fits well the middle part of the plot. This implies that Nd(III) is extracted by [Chol][hfac] in a 1 : 4 stoichiometry and a tetrakis Nd(III) hexafluoroacetylacetonate complex is formed upon extraction. The formation of anionic tetrakis β-diketonate complexes is often observed for the extraction of lanthanide ions into ionic liquids.<sup>66</sup> The availability of a counter ion and the possibility for ion exchange into a second phase enable the unexpected formation of a tetrakis complex in an aqueous system. However, the slope analysis

alone does provide valid proof for the extraction of a Nd(III) complex with a 1 : 4 stoichiometry.

### Crystal structure of [Chol][Nd(hfac)<sub>4</sub>]

The assumption of the formation of a tetrakis Nd(III)hexafluoroacetylacetonate complex as derived above in the previous section, was confirmed with single-crystal X-ray diffraction. Upon increasing the loading of extracted Nd(III) in the ionic liquid phase, crystal formation occurred during the settling (cooling) stage. Compound [Chol][Nd(hfac)<sub>4</sub>] crystallizes in the centrosymmetric space group *P*<sub>2</sub><sub>1</sub>/*n* with one molecule in the asymmetric unit (Fig. 9). The central Nd(III) ion is coordinated by four hexafluoroacetylacetonate ligands and one choline ligand to form a nine-coordinate complex with a capped square antiprism as coordination polyhedron. The choline ligand is disordered over two positions with an occupancy of 0.605(9):0.395(9). The Nd–O distances between the Nd and the hfac<sup>−</sup> ligands range between 2.429(4) Å and 2.489(4) Å. The Nd–O distances of the choline ligand are significantly larger. The distances are respectively 2.550(8) Å for the first orientation and 2.618(16) Å for the second part. The second position of the choline ligand leaves room for a water solvent molecule, which interacts by hydrogen bonding with a nearby fluorine atom (O52...F24<sup>i</sup>: 2.651(7) Å, symmetry code: (i) [−*X*, −*Y*, −*Z*]) and the choline oxygen (O52...O51: 2.625(8) Å). In the crystal packing three intermolecular non-classical hydrogen bonds are noticeable. Their donor acceptor distances are respectively: C3...F11 3.352(7) Å, C44...F22 3.075(11) Å and C44...F3 3.172(9) Å. The crystal structure is remarkable, because it is one of the rare examples of a nine-coordinate lanthanide tetrakis β-diketonate complex.<sup>58</sup> In general, this type of complexes has an eight-coordinate lanthanide center, with the four bidentate β-diketonate ligands saturating

the first coordination sphere of the lanthanide ion.<sup>57,67–72</sup> Coordination of a water molecule to neodymium(III) tetrakis-hexafluoroacetylacetonate complexes has been reported.<sup>73,74</sup> Also in some lanthanide tetrakis 3-cyanopentane-2,4-dionate complexes additional coordination of water molecules occurs to give a nine-coordinate complex.<sup>75</sup> Recently, Nockemann and coworkers reported a crystal structure of a europium(III) tetrakis hexafluoroacetylacetonate complex with coordination of the oxygen atom of a imidazolium-functionalized diphenylphosphin oxide.<sup>76</sup> The structure of the [Chol][Nd(hfac)<sub>4</sub>] complex is somewhat similar to the latter complex, since the coordinated ligand also provides the counter cation for the anionic tetrakis complex. The unusual structure of [Chol]-[Nd(hfac)<sub>4</sub>] is most likely due to a combination of different factors: the increased Lewis acidity of the neodymium(III) ion due to the fluorinated ligands, sterically little demanding β-diketonate ligands and a small cation with a Lewis basic group (the choline cation with its primary alcohol function).

### Ion exchange

To preserve electrical neutrality upon extraction of the tetrakis-Nd(III) complex, ion exchange has to occur between the organic and the aqueous phase. Per extracted Nd(III) ion, one of the four dissociated Chol<sup>+</sup> cations neutralizes the extracted [Chol]-[Nd(hfac)<sub>4</sub>] complex. The other three Chol<sup>+</sup> cations either stay in the organic phase or diffuse to the aqueous phase. When the Chol<sup>+</sup> cations are staying in the organic phase, nitrate ions should be co-extracted to neutralize the three Chol<sup>+</sup> cations. To determine which hypothesis is valid, extraction was carried out from a bromide solution. As described in the beginning of the paper, it was seen that the type of neodymium salt, being nitrate or chloride, did not influence the extraction performance. Since measurement of nitrate or chloride content by TXRF is difficult, extraction was performed from a bromide solution. TXRF is a suitable technique to measure bromide content in ionic liquids.<sup>77</sup> It was observed that no bromide was co-extracted with the metal ions, which implies that the three Chol<sup>+</sup> cations diffuse to the aqueous phase. So, in exchange for one extracted Nd(III) ion, three Chol<sup>+</sup> are transferred to the aqueous phase. To confirm the ion-exchange mechanism, the influence of the addition of choline chloride to the aqueous phase was examined. It was observed that the %*E* decreased significantly with increasing choline chloride content (Fig. 10). Thus, addition of choline chloride to the aqueous phase pushes back the extraction equilibrium, which confirms that Chol<sup>+</sup> cations migrate to the aqueous phase upon Nd(III) extraction.

Ion exchange is a typical mechanism for extraction of metal ions into ionic liquids.<sup>59,78,79</sup> Depending on the type of extracted complex, being anionic or cationic, anions or cations of the ionic liquid diffuse to the aqueous phase in exchange for the extracted metal complex. In some extraction systems with ionic liquids, the occurrence of ion exchange enhances metal extraction to the ionic liquid phase compared to extraction to the organic phase with traditional molecular diluents and could be considered an advantage.<sup>59</sup> Still, loss of ions of the ionic liquid to the aqueous phase by the ion exchange

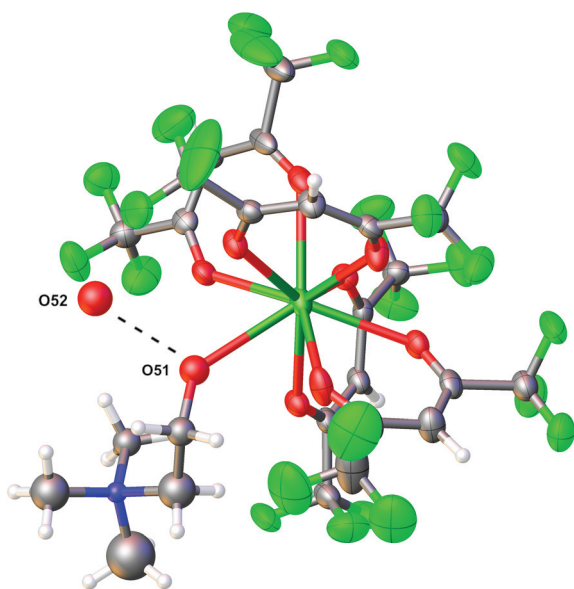
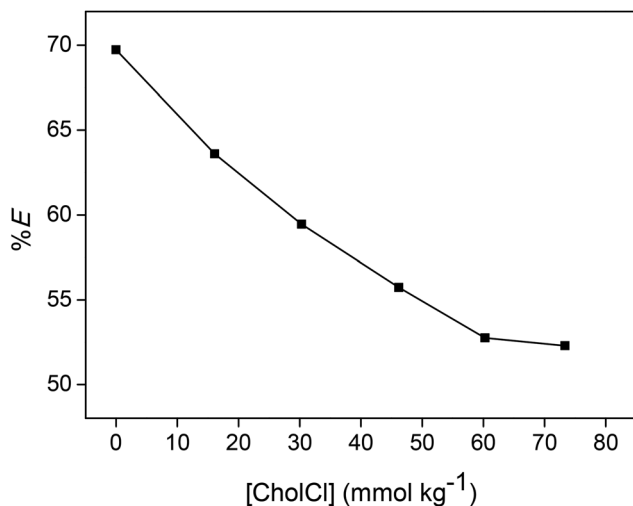


Fig. 9 Crystal structure of [Chol][Nd(hfac)<sub>4</sub>]. Only one part of the choline ligand orientation is shown.



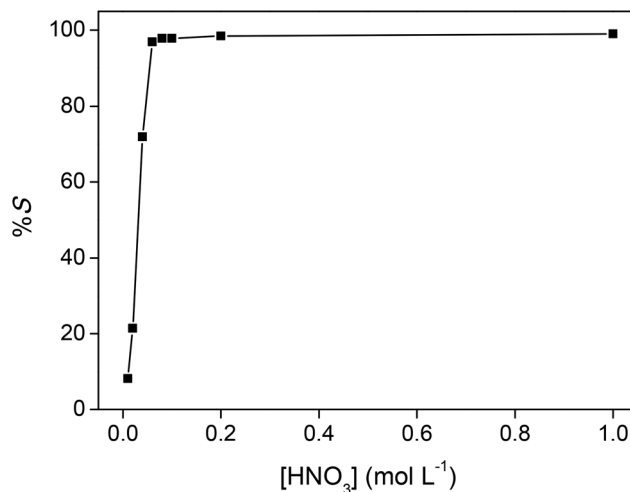
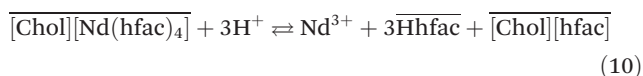


**Fig. 10** Influence of the addition of choline chloride to the aqueous phase on the %E of Nd(III) from a nitrate solution with [Chol][hfac]–[Chol][Tf<sub>2</sub>N]. 50 mmol kg<sup>-1</sup> [Chol][hfac] in organic phase, 12 mmol kg<sup>-1</sup> Nd(III) in aqueous phase. Equilibrium pH was constant.

mechanism is a major limitation for the practical application of ionic liquid solvent extraction systems. Part of the ionic liquid is lost and the aqueous phase is contaminated. Therefore, ion exchange should be avoided if possible.<sup>80</sup> A possibility to prevent the loss of Chol<sup>+</sup> to the aqueous phase when extracting Nd(III) with [Chol][hfac] is the replacement of three of the [Chol][hfac] ionic liquid molecules by the molecular acidic form of the extractant, namely hexafluoroacetylacetone (Hhfac). Upon extraction of one Nd(III) ion, Hhfac exchanges its protons to coordinate to the Nd(III) center. The fourth hfac<sup>-</sup> ligand is provided, together with the counter ion, by the [Chol][hfac] ionic liquid moiety. However, it was observed that about 50% less Nd(III) was extracted compared to extraction by [Chol][hfac] only. In order to compare the obtained results with the results of extraction with only [Chol][hfac], a small amount of NaOH (35 μL, 1 M) was added to the extraction mixture to obtain the same equilibrium pH as in previous experiments. The same amount of hfac<sup>-</sup> was used (50 mmol kg<sup>-1</sup>), but 75 mol% was added as Hhfac and 25 mol% as [Chol][hfac], instead of 100 mol% as [Chol][hfac]. This indicates that the diffusion of Chol<sup>+</sup> ions to the aqueous phase significantly enhances extraction, which is in line with observations described in the literature.<sup>78</sup>

### Stripping studies

The extracted Nd(III) ions were again stripped from the loaded [Chol][Tf<sub>2</sub>N] phase by mixing with a diluted HNO<sub>3</sub> solution. When acid was added to the loaded [Chol][Tf<sub>2</sub>N], the neodymium complex dissociated into free metal ion and protonated ligands:



**Fig. 11** Stripping of a [Chol][Tf<sub>2</sub>N] phase, loaded with Nd(III) (12 mmol kg<sup>-1</sup>) after extraction with [Chol][hfac], with varying HNO<sub>3</sub> concentration.

Mixing of the loaded [Chol][Tf<sub>2</sub>N] with a diluted HNO<sub>3</sub> solution with a concentration of 0.1 M resulted in 98% stripping efficiency of Nd(III) from the ionic liquid phase. All metal ions were removed by stripping with a 1 M HNO<sub>3</sub> solution (Fig. 11). It is preferable to perform stripping in one step. Each time the ionic liquid phase is brought in contact with an aqueous solution, part of the [Chol][Tf<sub>2</sub>N] diluent dissolves in the aqueous phase, which leads to significant losses of valuable ionic liquid. Determination of the loss of [Chol][Tf<sub>2</sub>N] is not straightforward, since these losses depend on the composition of the extraction mixture (acid concentration, metal concentration, extractant concentration). After stripping, the ionic liquid phase was available for a new extraction step. Some HNO<sub>3</sub> was dissolved in the ionic liquid phase, but this was easily neutralized with a base, such as NaOH.

### Decomposition of [Chol][hfac]

The extraction efficiency of the [Chol][hfac] extractant decreased when heated for a longer time at elevated temperature. Moreover, the extraction performance of the ionic liquid phase also decreased significantly with increasing storage time (Fig. 12). After 14 days of storage at room temperature (20 °C), %E for the extraction of Nd(III) was reduced to less than 50% of the percentage extraction at day 1. The degradation of the [Chol][hfac]–[Chol][Tf<sub>2</sub>N] mixture is slowed down by storing the mixture at lower temperatures (for instance in a refrigerator at 6 °C), but still %E decreased with more than 10% after 14 days of storage at 6 °C. The decrease in extraction performance was due to reactions between hexafluoroacetylacetone and water, forming decomposition products such as trifluoroacetic acid and trifluoroacetone (Fig. 13) or Hhfac–water adducts, such as the *gem*-diol product.<sup>81,82</sup>

It has also been described in the literature that dry [Chol][hfac] has a low thermal stability.<sup>56</sup> The decomposition temperature determined with TGA is stated to be equal to 83 ± 3 °C,

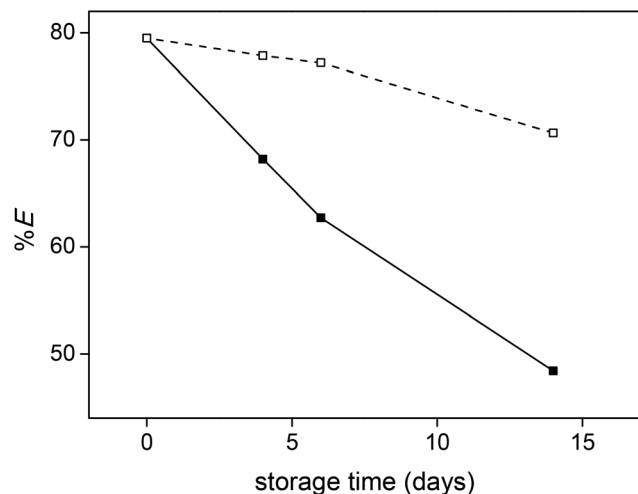


Fig. 12 Decrease in extraction performance of a [Chol][hfac]–[Chol]–[Tf<sub>2</sub>N] mixture containing 8 wt% water, as a function of storage time and storage temperature: 20 °C (solid line) and 6 °C (dashed line). Initial amount of HNO<sub>3</sub> in the aqueous phase is 0.01 mmol.

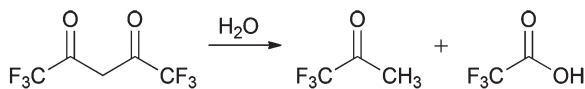


Fig. 13 Decomposition reaction of hexafluoroacetylacetone with water to trifluoroacetone and trifluoroacetic acid.

but it can be seen from the reported thermogram that a mass loss already occurs at temperatures below 80 °C.

Decomposition of [Chol][hfac] was monitored by <sup>19</sup>F NMR measurements. A mixture of [Chol][hfac] and water was kept at 80 °C and a <sup>19</sup>F NMR spectrum was recorded every 26 s. At the start of the experiment, only one peak (a, at –77.89 ppm) was visible in the <sup>19</sup>F NMR spectrum, which was contributed to the CF<sub>3</sub> groups of hfac<sup>–</sup>. Nearly immediately after the start of the experiment, it was seen that this peak slowly diminished. At the same time, a second peak appeared near the peak of hfac<sup>–</sup> (b, at –77.91 ppm) (Fig. 14), which is most likely caused by the formation of trifluoroacetic acid. Moreover, a third peak, most likely assigned to trifluoroacetone, and a fourth peak appeared at –85.48 ppm (d) and –76.29 ppm (c), respectively. These observations showed that decomposition is fast at 80 °C. Thus, it is preferable to perform extractions on a short time scale and to avoid long mixing times at elevated temperatures. This conclusion confirms that it is preferable to use HLE, since it can be executed on a very short time scale. In this way, the extraction process is fast and decomposition is avoided as much as possible.

### Phase behavior

The addition of extractants and the presence of acids and ions in the aqueous phase have an influence on the phase behavior and the mutual solubility of the ionic liquid and water.<sup>83–85</sup> To examine the effect of the addition of [Chol][hfac] and HNO<sub>3</sub> to

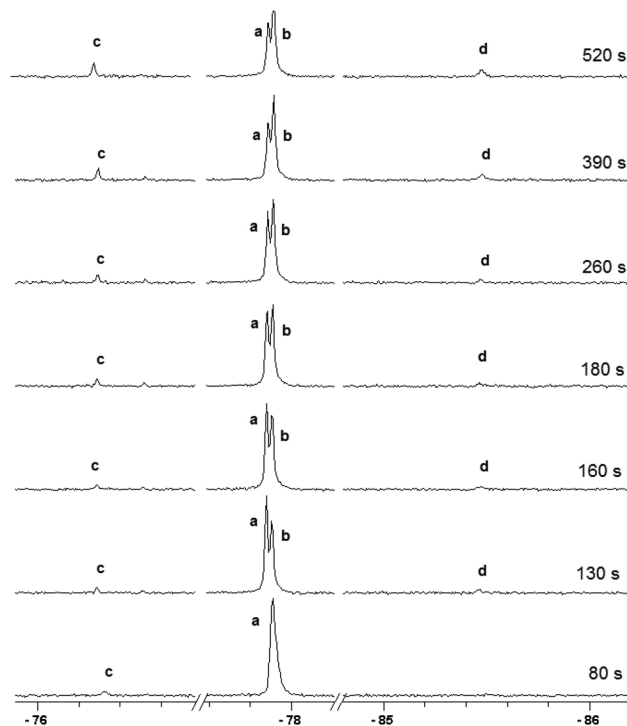


Fig. 14 Decomposition reaction of [Chol][hfac] with water at 80 °C monitored by <sup>19</sup>F NMR spectroscopy.

the extraction mixture, the cloud point of [Chol][Tf<sub>2</sub>N]–H<sub>2</sub>O mixtures containing varying amounts of HNO<sub>3</sub> and [Chol]–[hfac] was determined. The cloud point is the temperature at which the mixture becomes cloudy upon cooling. At this point, water and the ionic liquid are no longer completely miscible and they will phase separate. An ionic liquid rich organic phase is formed, together with an ionic liquid lean aqueous phase. The presence of HNO<sub>3</sub> at low concentrations (<0.5 M) in the IL–H<sub>2</sub>O mixture increased the cloud point with approximately 1 °C. At higher HNO<sub>3</sub> concentrations (>1 M) however, the cloud point decreased several degrees Celsius (Fig. 15). These observations are similar to the phase behavior of imidazolium ionic liquids described in the literature.<sup>83,85</sup> The change in water solubility of a solute upon addition of certain ions is related to salting-in/salting-out effects. A decrease in water solubility is known as salting-out, an increase in solubility is known as salting-in. The properties of different ions with respect to the salting of ionic liquids follow the Hofmeister series.<sup>85</sup> It must be noted that these salting phenomena are complex and depend both on the type of solute and the concentration of the salting ion. The nitrate ion is located at the end of the Hofmeister series, *i.e.* it generally has a weak salting-out or even a salting-in effect on the solubility of organic compounds in water. Thus, the slight increase in cloud point at low HNO<sub>3</sub> concentrations, corresponding to a slight decrease in water solubility of the ionic liquid and thus a small salting-out effect is also in line with observations described in the literature, where it was stated that the salting effect (in or out) of a certain ion depends on the concentration of the corres-

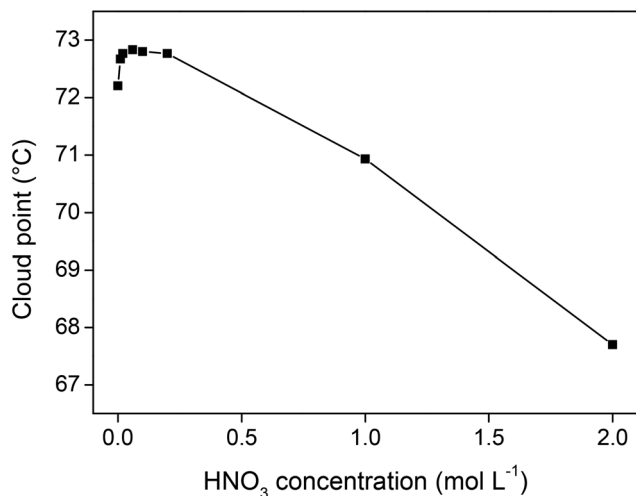


Fig. 15 Influence of the concentration of HNO<sub>3</sub> in the aqueous feed on the cloud point of a [Chol][Tf<sub>2</sub>N]–H<sub>2</sub>O mixture. Standard deviation on cloud point is 0.2 °C.

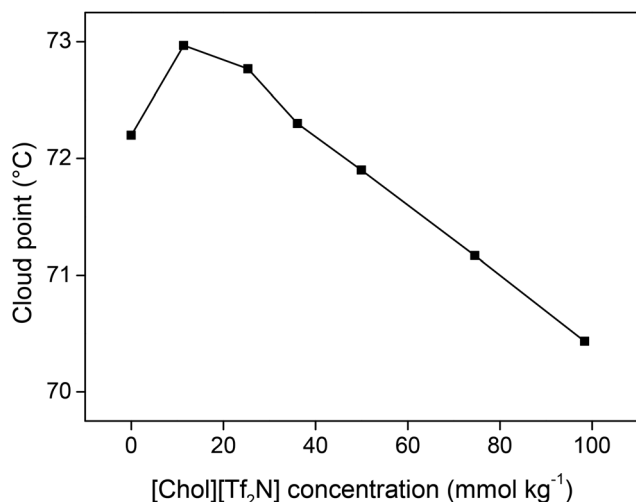


Fig. 16 Influence of the concentration of [Chol][hfac] in the organic phase on the cloud point of a [Chol][Tf<sub>2</sub>N]–H<sub>2</sub>O mixture. Standard deviation on cloud point is 0.2 °C.

ponding salt.<sup>83</sup> The addition of the extractant [Chol][hfac] to the [Chol][Tf<sub>2</sub>N]–H<sub>2</sub>O mixture had a similar effect on the cloud point. At low [Chol][hfac] concentrations, the cloud point increased 1 °C (Fig. 16). At higher concentrations (>50 mmol kg<sup>-1</sup>), the cloud point decreased again below 72.2 °C, which is the cloud point of a mixture without the presence of any additives.

#### Comparison with the [Hbet][Tf<sub>2</sub>N] system

In previous work, the protic ionic liquid [Hbet][Tf<sub>2</sub>N] was presented for HLE of rare-earth ions.<sup>19,20</sup> Because pure [Hbet][Tf<sub>2</sub>N] only poorly extracts rare-earth ions, an extractant was added. [Hbet][Tf<sub>2</sub>N] has a high acidity due to the presence of the carboxyl function on the cation and typical acidic extrac-

tants could not be used. Thus, zwitterionic betaine was added as an extractant. However, relatively high amounts of betaine (200 g kg<sup>-1</sup>) were required to obtain good extraction efficiencies. The [Chol][Tf<sub>2</sub>N] ionic liquid described in this paper is similar to [Hbet][Tf<sub>2</sub>N]. It has a similar chemical structure as [Hbet][Tf<sub>2</sub>N], but with a hydroxyl function on the cation instead of a carboxyl function, making it less acidic. They both show a UCST-type of phase behavior with water. The critical temperature of [Chol][Tf<sub>2</sub>N] (72 °C) is higher than [Hbet][Tf<sub>2</sub>N] (55 °C), so higher temperatures are required during HLE to reach the homogeneous stage. Because of the lower acidity of [Chol][Tf<sub>2</sub>N] in water, it is possible to use this ionic liquid as a diluent in combination with (polar) acidic extractants, such as  $\beta$ -diketones. In the extraction system described in this paper, the [Chol][hfac] extractant is added to the organic phase in stoichiometric amounts to obtain almost full extraction of Nd(III), whereas an excess of zwitterionic betaine was required to obtain high extraction efficiencies of Nd(III) in [Hbet][Tf<sub>2</sub>N].

## Conclusions

It was shown that the ionic liquid [Chol][Tf<sub>2</sub>N] is a suitable diluent for the homogeneous liquid–liquid extraction of Nd(III) from aqueous solution with [Chol][hfac] as extractant. Homogeneous liquid–liquid extraction is a novel energy-efficient technique to perform ionic liquid solvent extraction, which is based on the formation of a homogeneous phase during mixing. [Chol][Tf<sub>2</sub>N] shows thermomorphic behavior in water, with an UCST of 72 °C. The influence of several extraction parameters was studied, including extractant concentration, pH and Nd(III) feed concentration. At stoichiometric ratios of Nd(III) and [Chol][hfac], nearly all metal ions were extracted and loadings in the ionic liquid phase up to 43 mmol kg<sup>-1</sup> were achieved. A speciation study was performed to determine the extraction mechanism. *Via* slope analysis and crystal structure determination, it was shown that Nd(III) was extracted *via* an anionic tetrakis(hexafluoroacetylacetonato)neodymate(III) complex, with a choline cation as counter ion. Upon extraction, ion exchange occurred and three Chol<sup>+</sup> ions were transferred to the aqueous phase. The crystal structure determination of the extracted [Chol][Nd(hfac)<sub>4</sub>] complex showed that the Chol<sup>+</sup> counter ion was coordinated to the Nd(III) center, forming a nine-coordinate complex. This is one of the rare examples of coordination of the counter ion in tetrakis lanthanide  $\beta$ -diketonate complexes to the lanthanide(III) ion. Finally, Nd(III) was successfully stripped from the loaded ionic liquid phase with a 1 M HNO<sub>3</sub> solution.

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