

Recovery of Scandium(III) from Aqueous Solutions by Solvent Extraction with the Functionalized Ionic Liquid Betainium Bis(trifluoromethylsulfonyl)imide

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S Supporting Information

ABSTRACT: The ionic liquid betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf₂N] was used for the extraction of scandium from aqueous solutions. The influence of several extraction parameters on the extraction efficiency was investigated, including the initial metal concentration, phase ratio, and pH. The extraction kinetics was examined, and a comparison was made between conventional liquid–liquid extraction and homogeneous liquid–liquid extraction (HLLE). The stoichiometry of the extracted scandium complex was determined with slope analysis. Scandium(III) is extracted as a complex with zwitterionic betaine in a 1:3 stoichiometry, with three bis(trifluoromethylsulfonyl)imide counterions. Upon extraction of scandium(III), proton exchange occurs and three protons are transferred to the aqueous phase. Scandium is an important minor element present in bauxite residue (red mud), the waste product that results from the industrial production of alumina by the Bayer process. To evaluate the suitability of [Hbet][Tf₂N] for the selective recovery of scandium(III) from red mud leachates, the extraction of other metals present in the leachates (La(III), Ce(III), Nd(III), Dy(III), Y(III), Fe(III), Al(III), Ti(IV), Ca(II), Na(I)) was considered. It was shown that the trivalent lanthanide ions, yttrium(III) and the major elements aluminum(III), titanium(IV), calcium(II), and sodium(I), are all poorly extracted, which is advantageous for the selective recovery of scandium(III) from red mud. Iron(III) showed an extraction behavior similar to that of scandium(III). Scandium recovery was examined from a multielement rare-earth solution. Scandium could be separated from the other rare-earth elements by extraction with [Hbet][Tf₂N] and subsequent scrubbing of the loaded ionic liquid phase to remove coextracted metal ions. The extracted scandium was recovered from the ionic liquid phase by using back-extraction with hydrochloric acid or precipitation stripping with oxalic acid.

INTRODUCTION

Scandium is generally considered to be part of the group of the rare-earth elements since both scandium and the other rare-earth elements have a stable trivalent oxidation state. However, the chemical properties of scandium differ significantly from those of the other rare-earth elements. The ionic radius of scandium(III) is much smaller (0.745 Å for sixfold coordination) than any of the trivalent lanthanide ions. As a result, complexes of scandium(III) show higher stability constants than the corresponding lanthanide(III) complexes.^{1,2} The main application of scandium is aluminum–scandium alloy.³ Scandium-containing aluminum shows superior mechanical and physical properties compared to other high-strength alloys, such as higher strength, better corrosion resistance, and less hot cracking in welds.⁴ Other important applications of scandium include scandia-stabilized zirconia for solid oxide fuel cells (SOFC), analytical standards, high-intensity metal halide lamps, laser crystals, and oil-well tracers (radioactive isotope ⁴⁶Sc).^{3,5} The number of applications of scandium is increasing, resulting in a growing demand in scandium. The abundance of scandium in the earth's crust is relatively high (22 ppm),⁵ but deposits of minerals with high scandium concentrations are scarce and scandium mostly occurs as a trace element in different minerals. As a consequence, very little scandium is produced, resulting in high prices.³ In 2013, the global consumption of scandium was estimated to be less than 10 tons per year.³ Because of its low concentration in ores, scandium is not mined as a primary

product. It is produced exclusively as a byproduct during production of other metals or recovered from previously generated tailings or industrial process residues.⁶ Especially the residues resulting from the processing of tungsten ores are of interest for the recovery of scandium. After applying pressurized leaching with aqueous alkali to yield sodium wolframate from wolframite, scandium is left behind in the tungsten residue. Scandium can be recovered from this residue by leaching with a HCl solution, followed by solvent extraction. Scandium can also be recovered from the residues generated during the processing of uranium, tin, nickel, tantalum, and niobium ores.⁵ Another potential interesting scandium resource is bauxite residue (red mud).^{7–9} This is the industrial residue that is produced by the preparation of pure alumina from bauxite ore via the Bayer process. Bauxite residue from Greece contains about 130 ppm of scandium. Solvent extraction is the most often used method for the recovery and purification of scandium from aqueous solutions.^{10–18}

In this paper, we give a detailed description of the extraction behavior of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N] (Figure 1), toward various metal ions present in red mud leachates.

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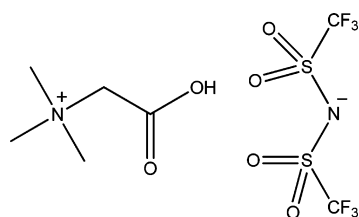


Figure 1. Chemical structure of [Hbet][Tf₂N].

These include ions of the major elements Fe(III), Al(III), Ti(IV), Ca(II), and Na(I), the minor elements Sc(III) and Y(III), and the trivalent lanthanides, with emphasis on the selective recovery of Sc(III) from aqueous solutions.

[Hbet][Tf₂N] was first developed for the dissolution of metal oxides.¹⁹ This ionic liquid is able to dissolve various metal oxides due to the coordinating ability of betaine.^{20,21} Taking this knowledge into account, [Hbet][Tf₂N] was recently applied by our group to the selective leaching of Y₂O₃·Eu³⁺ from lamp phosphor waste and the solvent extraction of rare-earth elements and other metals.^{22–24} Concerning the latter, it was shown that only low extraction efficiencies for the lanthanides were obtained with [Hbet][Tf₂N] (~10%). However, by addition of an excess of zwitterionic betaine to the aqueous phase, the extraction efficiency of the rare-earth ions was increased to >90%. It was also seen that the combination of betaine and [Hbet][Tf₂N] as the ionic liquid phase showed very good extraction efficiencies toward scandium.²³ This indicated that betaine and [Hbet][Tf₂N] have a higher affinity for scandium than for the other rare-earth elements. Sasaki et al. applied the ionic liquid [Hbet][Tf₂N] for the selective extraction of uranium and the precious metals palladium, rhodium, and ruthenium.^{25,26} Other authors have investigated the coordination chemistry of f-block elements in [Hbet][Tf₂N].^{27–30} On the basis of the difference in affinity between scandium and the lanthanides, [Hbet][Tf₂N] is applied in this paper to the selective extraction of scandium(III) from rare-earth mixtures. Furthermore, the extraction behavior of the ionic liquid toward the major metal ions present in red mud leachates is examined, namely, Fe(III), Al(III), Ti(IV), Ca(II), and Na(I), to evaluate whether [Hbet][Tf₂N] is suitable for the selective recovery of Sc(III) from red mud leachates.

EXPERIMENTAL SECTION

Products. Lithium bis(trifluoromethylsulfonyl)imide (99%) was obtained from IoLiTec (Heilbronn, Germany). Betainium hydrochloride (HbetCl) (99%), 1,4-dioxane (HPLC grade, 99.5%), and AlCl₃ (anhydrous, 98.5%) were purchased from ACROS Organics (Geel, Belgium). AgNO₃ (>99.8%), YCl₃·6H₂O (99.9%), TiCl₄ (≥98.0%), Sc(NO₃)₃ hydrate (99.9%), and NaCl (≥99.0%) were obtained from Sigma-Aldrich (Diegem, Belgium). HCl (36%) was obtained from VWR (Leuven, Belgium). HNO₃ (65%) and CaCl₂·2H₂O (>99.5%) were obtained from Chem-Lab (Zedelgem, Belgium). FeCl₃ (99%) was purchased from Honeywell Riedel-de-Haën (Seelze, Germany). Sc₂O₃ was kindly provided by Solvay (La Rochelle, France). LaCl₃·7H₂O (99.99%), CeCl₃ hydrate (99.9%), NdCl₃·6H₂O (99.9%), and DyCl₃ hydrate (99%) were obtained from Alfa Aesar. Oxalic acid (>99.5%) was obtained from JT Baker. The 1000 mg·L⁻¹ gallium ICP standard was purchased from Merck (Overijse, Belgium). The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH

(Heidelberg, Germany). All products were used as received, without further purifications.

Equipment. ¹H NMR spectra were recorded in D₂O on a Bruker Avance 300 spectrometer, operating at 300 MHz. FTIR spectra were recorded on a Bruker Vertex 70 spectrometer (Bruker Optics). The liquid samples were examined directly without further sample preparation using a platinum single reflection diamond attenuated total reflection (ATR) accessory. Analysis was performed with OPUS software. Carbon, hydrogen, and nitrogen content of the ionic liquid were determined using a CE Instruments EA-1110 element analyzer. Extraction experiments were performed in a TMS-200 thermoshaker (Nemus Life). The extraction vials were placed vertically in the thermoshaker. A Bruker Picofox S2 total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations (except for Na and Al) in both the aqueous and the ionic liquid phases. TXRF is an elemental analysis technique for the qualitative and quantitative determination of the metal content in multielement samples.^{31–33} A monochromatic X-ray beam impinges on a polished sample carrier at a very small angle (<0.1°) and is totally reflected. The characteristic fluorescence of the sample is emitted and measured in an energy dispersive X-ray detector. Due to the short distance to the carrier, the X-ray fluorescence yield is very high and the absorption by air is very low. The main difference between TXRF and conventional XRF spectrometers is the use of monochromatic radiation and total reflection optics. TXRF is much less sensitive to matrix effects than XRF and allows detecting much lower concentrations. TXRF is characterized by a very large dynamic range, from ppb to 100%. The sodium and aluminum content in both aqueous and ionic liquid phase was determined using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Electron X Series PQ2). Extraction mixtures were centrifuged using a Heraeus Labofuge 200. Thermogravimetric analysis (TGA) was performed on a TA Instruments T500 thermogravimeter in a nitrogen atmosphere (heating rate: 2 °C·min⁻¹, from 25 to 350 °C). The viscosity of water-saturated [Hbet][Tf₂N] at 25 °C was measured using a Brookfield cone plate viscometer (LV DV-II+ programmable viscometer) with a cone spindle CPE-40. The sample holder was kept at 25 °C by a circulating water bath.

Cloud-Point Titration. The mutual solubility of ionic liquid and water at room temperature (23 °C) was analyzed by cloud-point titration. To determine the maximum solubility of water in the ionic liquid, 1.5 g of dry ionic liquid was first mixed with 50 mg of water (to facilitate stirring), and the vial was closed with a septum. Next, using a syringe, small drops of distilled water were added to this mixture under constant stirring until the mixture became turbid. The amount of added water was determined by weighing the syringe before and after the experiment, and the maximum solubility of water in the ionic liquid was calculated. The same procedure was followed to determine the maximum solubility of the ionic liquid in water. Dry ionic liquid was mixed with 8 wt % of water to lower the viscosity and simplify the handling. This ionic liquid–water mixture was then added to distilled water under constant stirring using a syringe until phase separation occurred. The amount of added ionic liquid was determined by weighing the syringe before and after the experiment, and the maximum solubility of water in the ionic liquid was calculated.

Quantitative ¹H NMR. The concentration of ionic liquid in the aqueous phase was also determined using quantitative ¹H

NMR. A known amount of 1,4-dioxane was added in approximately equimolar concentrations to an aliquot of water, saturated with the ionic liquid. The ^1H NMR spectrum of 1,4-dioxane shows one peak at $\delta = 3.6$, corresponding to its 8 equiv protons. The ^1H NMR spectrum of 1,4-dioxane does not overlap with the ^1H NMR spectrum of $[\text{Hbet}][\text{Tf}_2\text{N}]$, making 1,4-dioxane a suitable internal standard. A ^1H NMR spectrum of the sample was recorded, and the relative concentration versus 1,4-dioxane and the absolute concentration of $[\text{Hbet}][\text{Tf}_2\text{N}]$ were calculated by integration of the peaks.

Synthesis of $\text{ScCl}_3 \cdot x\text{H}_2\text{O}$. $\text{ScCl}_3 \cdot x\text{H}_2\text{O}$ was prepared by dissolving Sc_2O_3 in an excess of hydrochloric acid (two equivalents). The mixture was stirred for 48 h at 60°C . Water was added, and the mixture was dried on a rotary evaporator to remove the water together with the excess of hydrochloric acid. This step was repeated several times until the majority of hydrochloric acid was removed and a crystalline material was obtained.

Extraction Experiments. The ionic liquid $[\text{Hbet}][\text{Tf}_2\text{N}]$ was prepared by following a literature method.¹⁹ Synthesis was confirmed with ^1H NMR, FTIR, and CHN elemental analysis. Prior to extraction, $[\text{Hbet}][\text{Tf}_2\text{N}]$ was presaturated with water to prevent uncontrollable uptake of water by the hygroscopic ionic liquid. Moreover, water-saturated $[\text{Hbet}][\text{Tf}_2\text{N}]$ is liquid and, thus, easier to dispense than solid $[\text{Hbet}][\text{Tf}_2\text{N}]$. Presaturation with water is performed by contacting the ionic liquid with an excess of water (more than 14 wt %), heating the mixture until one homogeneous phase is obtained, and cooling down until phase equilibrium is obtained at room temperature. In a typical extraction experiment, water-saturated ionic liquid was mixed with the aqueous feed solution. The feed solutions were prepared by dissolution of a certain amount of (hydrated) metal salt (chloride salt or nitrate salt) in water to obtain the required concentration. The pH of the solution was adjusted using small aliquots of HCl (1 M) or HNO_3 (1 M), respectively. The metal concentration was confirmed using TXRF. The composition of the extraction mixture was carefully chosen to obtain the required phase ratio of aqueous (ionic liquid lean) to organic (ionic liquid rich) phase, taking into account the mutual solubility of ionic liquid and water (determined experimentally, *vide infra*).¹⁹ For most extraction experiments 1150 mg of water-saturated ionic liquid was mixed with 850 mg of aqueous feed solution to obtain a final phase ratio of 1 at phase equilibrium. The phase ratio is defined as the mass of the ionic liquid phase divided by the mass of the aqueous phase:

$$\Theta = \frac{m_{\text{IL}}}{m_{\text{aq}}} \quad (1)$$

with m_{IL} and m_{aq} the masses of the ionic liquid phase and aqueous phase, respectively. It is preferred to work with the *mass* phase ratio, as defined in eq 1, instead of the *volume* phase ratio, since it is easier and more accurate to control the mass than the volume of a viscous solution such as the ionic liquid. As a consequence, all metal concentrations are expressed as molalities ($\text{mol} \cdot \text{kg}^{-1}$) instead of molarities ($\text{mol} \cdot \text{L}^{-1}$).

The extraction mixture was heated to 70°C and shaken at 700 rpm for 10 min in a thermoshaker. In this way, a homogeneous mixture and chemical equilibrium conditions were obtained. Next, the mixture was allowed to cool to room temperature for 1 h to induce settling of the phases. After 1 h of settling at room temperature, the mixture was completely clear with a flat interphase, indicating full phase separation. Finally, a

sample was taken from the aqueous phase to determine the metal concentration with a TXRF spectrometer (except for Na and Al, which were determined using ICP-MS). A small amount of gallium nitrate ICP standard solution ($1000 \text{ mg} \cdot \text{L}^{-1}$) was added to the sample as an internal standard. The gallium concentration should be similar to the unknown metal concentration to be measured. The sample was further diluted to 1 mL with Milli-Q water. A small droplet of the sample ($5 \mu\text{L}$) was dispensed on a quartz sample carrier, which was pretreated with a SERVA silicone solution in isopropanol ($10 \mu\text{L}$) to make the surface more hydrophobic and keep the sample droplet in the middle of the carrier. Finally, the carrier containing the sample was dried at 60°C for 30 min and measured with the TXRF spectrometer.

Metal ion extraction is evaluated by calculating the distribution ratio D and percentage extraction $\%E$ by following equations:

$$D = \frac{[M]_{\text{IL}}}{[M]_{\text{aq}}} \quad (2)$$

$$\%E = \frac{n_{\text{IL}}}{n_{\text{IL}} + n_{\text{aq}}} \cdot 100 \quad (3)$$

where n_{IL} and n_{aq} are the number of moles of the metal ion (in mmol) in the ionic liquid phase and the aqueous phase, respectively. n_{aq} was measured using TXRF (except for Na and Al, which were measured using ICP-MS), and the metal ion concentration in the ionic liquid phase was calculated as follows:

$$n_{\text{IL}} = n_{\text{aq, in}} - n_{\text{aq}} \quad (4)$$

where $n_{\text{aq, in}}$ and n_{aq} are the initial and final (measured) number of moles of metal ions in the aqueous phase, respectively.

Stripping. Back-extraction experiments were performed similarly as the extraction experiments. An ionic liquid phase loaded with $4.3 \text{ mmol} \cdot \text{kg}^{-1}$ of Sc(III) by extraction from a chloride solution was brought into contact with HCl solutions of different concentrations (0–2 M). The mixtures were heated and shaken at 70°C and 700 rpm for 10 min. The mixtures were allowed to cool down and phase separate at room temperature. After 1 h of settling, both the aqueous and the ionic liquid phases were analyzed by TXRF to measure the scandium content. The stripping efficiency was expressed using the percentage stripping $\%S$:

$$\%S = \frac{n_{\text{aq}}}{n_{\text{IL}} + n_{\text{aq}}} \cdot 100 \quad (5)$$

where n_{aq} and n_{IL} are the final number of moles of scandium in the aqueous phase and ionic liquid phase, respectively.

Precipitation stripping was performed by adding different amounts of solid oxalic acid to an ionic liquid phase loaded with $83 \text{ mmol} \cdot \text{kg}^{-1}$ of Sc(III). The mixtures were heated and shaken for 1 h at 70°C and 1500 rpm. Next, the mixtures were cooled to room temperature and centrifuged for 15 min at 5000 rpm. The ionic liquid phase was separated from the precipitate and analyzed with TXRF to determine the scandium content. The percentage stripping was calculated as follows:

$$\%S = \frac{n_{\text{IL, in}} - n_{\text{IL}}}{n_{\text{IL, in}}} \cdot 100 \quad (6)$$

Table 1. Mutual Solubility (wt%) of [Hbet][Tf₂N] (IL) and Water at Room Temperature (23 ± 1 °C) Determined by ¹H-NMR and Cloud Point Titration and Compared to Literature Values

	TGA		¹ H NMR		cloud point titration		literature ¹⁹	
	IL	H ₂ O	IL	H ₂ O	IL	H ₂ O	IL	H ₂ O
aqueous phase	13.8	86.2	14 ± 0.5	85 ± 0.5	14.3 ± 0.5	85.7 ± 0.5	15	85
IL phase	87.1	12.9	92.4 ± 4.6	7.6 ± 4.6	84.5 ± 0.5	15.5 ± 0.5	87	13

with $n_{IL,in}$ the initial number of moles of scandium in the ionic liquid phase before stripping and n_{IL} the final number of moles of scandium in the ionic liquid phase after stripping.

Reusability Studies. The reusability of the ionic liquid phase was examined by first performing an extraction of Sc(III) from a ScCl₃ solution (100 mmol·kg⁻¹, pH 3.5) and subsequent stripping by back-extraction with 2 M HCl. Next, half of the ionic liquid phase was directly reused for the extraction of Sc(III), and the other half was first washed two times with distilled water (1:1 phase ratio) and then reused for extraction of Sc(III). All extraction and stripping steps were performed following the procedures described above. The reusability was checked by calculating the %E of the extraction of Sc(III) using eq 3.

Separation Experiments. The separation experiments were performed similarly as the extraction experiments. Water-saturated [Hbet][Tf₂N] (1150 mg) was mixed with a rare-earth chloride mixture (850 mg) prepared by dissolving the metal chlorides salts of Sc(III), Y(III), La(III), Ce(III), Nd(III), and Dy(III), all in a concentration of 1 mmol·kg⁻¹ (pH adjusted by addition of a small aliquot of 1 M HCl). The mixtures were heated and shaken at 70 °C and 700 rpm for 10 min. The mixtures were allowed to cool down and phase separate at room temperature. After 1 h of settling, the metal content in both the aqueous and the ionic liquid phases was analyzed by TXRF. The separation between metal A and metal B was expressed using the separation factor α_B^A :

$$\alpha_B^A = \frac{D_A}{D_B} \quad \text{with } D_A > D_B \quad (7)$$

Scrubbing of the Loaded Ionic Liquid Phase. Scrubbing of the loaded ionic liquid phase to selectively remove the coextracted rare-earth ions was performed similarly as the back-extraction experiments. An ionic liquid phase (1150 mg), which was loaded with rare-earth ions (Sc(III), Y(III), La(III), Ce(III), Nd(III), and Dy(III), approximately 7 mmol·kg⁻¹ of each element) by extraction following the procedure described elsewhere in this paper, was put into contact with HCl solutions (850 mg) of different concentrations (0–2 M). The mixtures were heated and shaken at 70 °C and 700 rpm for 10 min. The mixtures were allowed to cool down and phase-separate at room temperature. After 1 h of settling, the scandium content in both the aqueous and the ionic liquid phases was analyzed by TXRF. The scrubbing efficiency was expressed using the stripping percentage %S (eq 5).

RESULTS AND DISCUSSION

Mutual Solubility of [Hbet][Tf₂N] and Water. To perform extraction experiments, a metal feed solution is put into contact with [Hbet][Tf₂N]. This ionic liquid is solid at room temperature, very hygroscopic, and viscous. Therefore, [Hbet][Tf₂N] was always presaturated with water to prevent further uncontrolled uptake of water and to facilitate the handling, since water-saturated [Hbet][Tf₂N] is liquid at room

temperature and has a lower viscosity than dry [Hbet][Tf₂N]. It is preferable that the ionic liquid and aqueous phases in the extraction mixture, after phase equilibrium, are present in a 1:1 phase ratio, since this simplifies further calculations. For ionic liquids with a low solubility in the aqueous phase, the water-saturated ionic liquid can simply be mixed with the aqueous feed solution in an initial 1:1 phase ratio and no phase changes will occur during extraction. However, [Hbet][Tf₂N] partially dissolves in the aqueous phase, and this should be taken into account. The mutual solubility of [Hbet][Tf₂N] and water at room temperature (23 °C) was measured to determine the amount of water-saturated ionic liquid that had to be added to the aqueous feed solution to obtain a 1:1 phase ratio after reaching the phase equilibrium (Table 1). The mutual solubility at different temperatures was determined gravimetrically by Nockemann et al. (15 wt %).¹⁹ Both aqueous and ionic liquid phases were dried, and the composition of each phase was calculated by comparing the initial mass and remaining mass. To verify whether these literature results are a good estimate, the mutual solubility was measured experimentally with three other techniques, namely, TGA, quantitative ¹H NMR, and cloud point titration. The three techniques all resulted in a similar estimation of the ionic liquid content in the aqueous phase of around 14 wt %. This result is 1 wt % lower than the value reported in the literature.¹⁹ The estimation of the water content in the ionic liquid phase by TGA is the same as the result previously reported by Nockemann et al. Cloud point titration and quantitative ¹H NMR were found to be unsuitable for an accurate determination of the water content in the ionic liquid phase. Insufficient mixing resulted in an overestimation of the water content during cloud point titration. For quantitative ¹H NMR a 5% error exists on the concentration determination of the ionic liquid, making the quantification of large ionic liquid concentrations, like in the ionic liquid-rich phase, very inaccurate. Using the results of the TGA measurement, it was calculated that approximately 1150 mg of water-saturated ionic liquid should be mixed with 850 mg of water to obtain a 1:1 phase ratio in the final mixture of 2 g. This was confirmed when separating and weighing the two phases of a [Hbet][Tf₂N]–water mixture with this composition.

Extraction Parameters. The ionic liquid [Hbet][Tf₂N] was used for the extraction of scandium from acidic aqueous solution without the addition of any extractants or diluents. For the preparation of the scandium solutions, the hydrolysis of Sc(III) in aqueous media had to be taken into account. As a rule of thumb, for scandium concentrations up to 0.01 M, the pH should be kept below pH 4 to prevent precipitation of Sc(OH)₃ ($K_{sp} \sim 10^{-32}$).³⁴ The pH of the prepared Sc(III) stock solutions was set at pH 3.5 or lower by addition of a small amount of HCl.

Since [Hbet][Tf₂N] is a protic ionic liquid with a carboxylic acid function on the cation, extraction of metal ions will most likely occur via coordination of the carboxylic acid function, via a proton-exchange mechanism. Therefore, the influence of the initial pH of the feed solution on the extraction of Sc(III) was

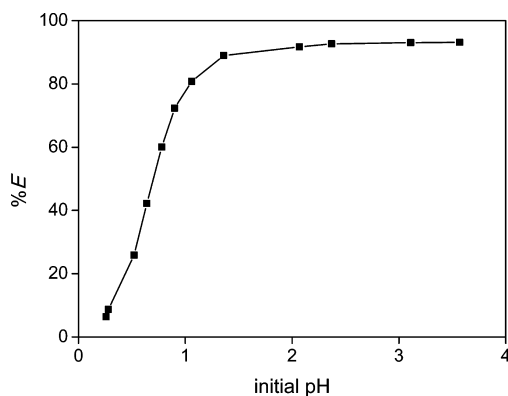


Figure 2. Influence of the initial pH of the feed on the extraction of scandium with [Hbet][Tf₂N]. Aqueous phase: initial scandium concentration 4.5 mmol·kg⁻¹ and initial pH 0.6–3.5.

investigated (Figure 2). %E was approximately constant at 95% in the pH range 1.5–3.5. This means that Sc(III) can be extracted efficiently from low and medium acidic solutions. However, at pH < 1.5, %E dropped sharply to less than 10% at pH 0.25. It must be noted that a small relative error exists on the scandium content measured by TXRF due to absorption effects of the ionic liquid matrix. The error depends on the amount of matrix present in the sample and results in an underestimation of the scandium content. The error is larger in absolute amounts when high scandium concentrations are measured, like in the aqueous phase when extracting at low pH. This results in a slight overestimation of the %E at low initial pH as it was seen that the scandium content in the ionic liquid phase of the extraction at pH 0.25 was negligible (below the detection limit of the TXRF spectrometer). It is preferred to plot the initial pH of the aqueous feed instead of the equilibrium pH. The equilibrium pH of the aqueous phase was mainly determined by the acidity of the ionic liquid. The pK_a of the [Hbet]⁺ cation is equal to 1.83.¹⁹ [Hbet][Tf₂N] dissolved in the aqueous phase partially deprotonates, creating a pH buffer around pH 1.3. Because of the presence of the buffer mixture, addition of a small amount of acid or base does not influence the aqueous equilibrium pH. However, aqueous feed solutions with an initial pH below 1.5 were able to significantly change the equilibrium pH, which was always approximately equal to the initial pH of these feed solutions. When using feed solutions with an initial pH of 1.5 or higher, an equilibrium pH around 1.3 was always obtained (Figure S1 in Supporting Information). Mixing of an aqueous solution with pH 7–10 with the ionic liquid also resulted in an aqueous equilibrium pH of only 1.3. Addition of high amounts of base to increase the aqueous equilibrium pH significantly was not considered because this resulted in the full deprotonation of the ionic liquid, followed by complete mixing of the ionic liquid phase with the aqueous phase. This made solvent extraction impossible.¹⁹ Therefore, it is generally not interesting to use alkaline feed solutions for extraction with [Hbet][Tf₂N]. It should be noted that it is possible to increase the equilibrium pH of the aqueous phase by addition of zwitterionic betaine to the aqueous phase. In this way, the composition of the buffer mixture is changed and the pH of the buffer mixture is increased.

Furthermore, it was observed that extraction of Sc(III) is not influenced by the counterion present in the aqueous feed, being nitrate or chloride. Similar %E were obtained for extraction

from ScCl₃ and Sc(NO₃)₃ solutions with different concentrations (Figure S2 in Supporting Information). Extraction of Sc(III) was also tested from feed solutions with different initial Sc(III) concentrations ranging from 0.04 to 450 mmol·kg⁻¹ (Figure 3). At low initial concentrations (0.04–4 mmol·kg⁻¹),

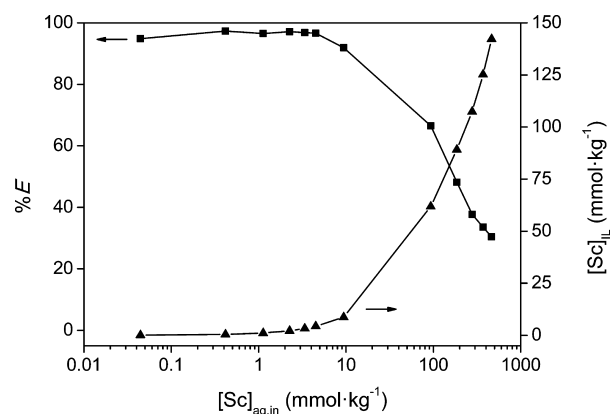


Figure 3. Influence of the initial Sc(III) concentration on %E of Sc(III) (■) and the Sc(III) concentration in the ionic liquid phase [Sc(III)]_{IL} (▲), after extraction with [Hbet][Tf₂N]. Aqueous phase: initial Sc(III) concentration 0.04–450 mmol·kg⁻¹.

the %E remained rather constant as a function of concentration (around 95%). This indicates that the distribution of the Sc(III)–[Hbet][Tf₂N] complex is solely controlled by the difference in solubility in the aqueous phase and the ionic liquid phase. At these low Sc(III) concentrations, the ionic liquid is present in excess, and loading of the ionic liquid phase does not influence the distribution of Sc(III). Extraction of Sc(III) from diluted feed solutions is relevant for the recovery of scandium from industrial process residues such as red mud, since the Sc(III) concentration in the mineral leachates is also very low.^{5,7,8,35–37} At higher Sc(III) concentrations, the ionic liquid is no longer present in a large excess and the extraction equilibrium is shifted due to loading effects. At an initial Sc(III) concentration of 450 mmol·kg⁻¹ in the aqueous phase, only 30% of the Sc(III) ions is extracted. However, the absolute amount of Sc(III) extracted to the ionic liquid phase increases sharply with increasing initial Sc(III) concentration in the ionic liquid phase and does not stabilize to a constant value at high initial concentrations for the tested concentration range (Figure 3). This is because the maximum loading of the ionic liquid phase is not reached within the tested concentration range due to the low %E.

In order to determine the maximum loading capacity, the phase ratio Θ of ionic liquid to aqueous phase was lowered (Figure 4). Because the extraction equilibrium is shifted due to the decrease in the concentration of ionic liquid in the mixture, lowering of Θ resulted in a decrease in %E. However, [Sc(III)]_{IL} increased with decreasing Θ . This can be explained by the fact that the increase in [Sc(III)]_{IL} due to the concentration effect by the lowering of Θ (decrease in mass of ionic liquid phase compared to aqueous phase), was more important than the decreasing %E. Sc(III) concentrations in the ionic liquid phase up to 85 mmol·kg⁻¹ were obtained for a phase ratio of 0.01. At these low phase ratios, the Sc(III) concentration in the ionic liquid phase stabilized. This could be caused either by saturation of the ionic liquid phase by reaching the maximum loading or because the decrease in ionic liquid

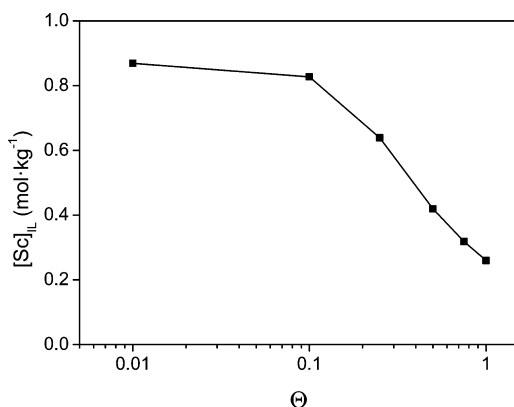


Figure 4. Maximum loading of Sc(III) in the ionic liquid phase: influence of the phase ratio Θ on the concentration of extracted Sc(III) in the ionic liquid phase. $\Theta = 0.01$ – 1 . Aqueous phase: initial Sc(III) concentration $1.8 \text{ mol}\cdot\text{kg}^{-1}$, initial pH 1.6.

concentration has a significant influence on the %*E* and the amount of extracted scandium ions $[\text{Sc(III)}]_{\text{IL}}$.

The kinetics of the extraction of Sc(III) was examined by testing different temperatures (from 25 to 40 °C) and shaking times (from 1 to 30 min) at a shaking speed of 700 rpm. It was seen that the extraction is fast, even at 25 °C where equilibrium was reached within 5 min (Figure 5). The fast extraction kinetics are due to the low viscosity of water-saturated [Hbet][Tf₂N], which is around 30 cP at room temperature (25 °C).

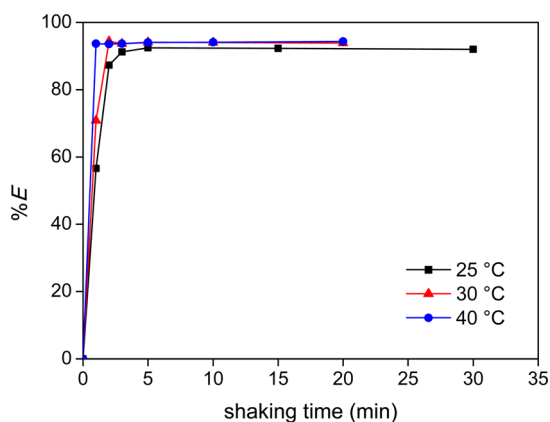


Figure 5. Influence of temperature and shaking time on the extraction of Sc(III) with [Hbet][Tf₂N]. Initial aqueous phase: $4.5 \text{ mmol}\cdot\text{kg}^{-1}$ Sc(III), pH 3.5.

[Hbet][Tf₂N] shows thermomorphic behavior with an upper critical solution temperature (UCST) of 55 °C and can be used in *homogeneous liquid–liquid extraction* (HLL).^{19,22,23,38} In principle, HLL can be performed by heating the thermomorphic extraction mixture above the UCST without extra shaking. However, it was seen that the formation of a homogeneous phase above the UCST is kinetically slow for an unstirred/unshaken [Hbet][Tf₂N]–H₂O mixture and can be accelerated by shaking for a few seconds at a low shaking speed (5 s at 700 rpm in this case). After the formation of the homogeneous phase (homogeneous stage), the extraction mixture was cooled to room temperature to initiate phase separation again (settling stage), upon which the metal complex was extracted to the ionic liquid phase. It was observed that the mixture should be

heated without shaking for approximately 120 s at 60 °C to reach the required temperature of 60 °C inside the extraction mixture and obtain a homogeneous phase (Figure S3 in Supporting Information). By shaking the mixture while heating, the required temperature was reached faster because of better heat transfer. However, shaking also accelerated extraction, so full extraction was reached already before the required temperature of 60 °C is obtained in the extraction mixture. Therefore, it can be concluded that HLL is possible for the extraction of scandium with [Hbet][Tf₂N], but it has no added value on a lab scale in terms of energy consumption or time benefit compared to conventional solvent extraction at room temperature. However, HLL might be beneficial on an industrial scale and further research on this matter is required.

In principle, the critical temperature at which the extraction mixture becomes homogeneous depends on the phase ratio Θ . By lowering the phase ratio below 1, thus by lowering the mass of the ionic liquid phase compared to the aqueous phase, the critical temperature can be lowered. From the phase diagram of [Hbet][Tf₂N]–H₂O, it can be deduced that the critical temperature is only reduced significantly to below 50 °C when Θ is smaller than 0.1 and the aqueous phase is 10 times larger in mass than the ionic liquid phase.¹⁹ As described above, lowering of Θ reduces the %*E* of Sc(III). For instance, at $\Theta = 0.1$, for a feed solution with an initial Sc(III) concentration of $4.5 \text{ mmol}\cdot\text{kg}^{-1}$, only 70% of the Sc(III) ions were extracted to the ionic liquid phase compared to >90% at $\Theta = 1$ (Figure S4 in Supporting Information). However, the Sc(III) concentration in the ionic liquid phase increased by a factor of almost 10 at $\Theta = 0.1$ compared to $\Theta = 1$ (from 4 to 34 $\text{mmol}\cdot\text{kg}^{-1}$). This concentration effect is useful when considering the recovery of scandium and other rare-earth elements from red mud leachates. The concentrations of these metals in such leachates are very low (<10 ppm) because of a dilution effect due to the high liquid-to-solid ratios (up to 50:1) used when leaching red mud.^{7,36}

Besides Sc(III), the affinity of [Hbet][Tf₂N] toward other metals was also examined, with a focus on the metal ions present in red mud leachates. Red mud consists of the major elements iron, aluminum, titanium, calcium, sodium, and silicon and some minor constituents including scandium and the other rare-earth elements. Most of these elements also end up in the leachate when leaching with mineral acids.^{7,36} Scandium is the most interesting minor element, since it represents more than 90% of the economic value of the minor elements present in red mud.³⁵ Extraction of different metals from single-element solutions was examined as a function of the initial pH. It is preferable to plot the initial pH instead of the equilibrium pH in order to visualize the ability of [Hbet][Tf₂N] to extract the different metals from feed solutions with varying acidity. The tested metal ions include the rare-earth elements Y(III), La(III), Ce(III), Nd(III), and Dy(III) and the major elements Al(III), Fe(III), Ca(II), Ti(IV), and Na(I) and were compared to the extraction of Sc(III). [Hbet][Tf₂N] shows a high affinity for Sc(III) (%*E* > 90%) but a much lower affinity for the other rare-earth ions (%*E* between 4% and 12% at initial pH 3, depending on the rare earth) (Figure 6). The behavior of [Hbet][Tf₂N] toward the rare-earth elements is similar to the other nonsterically hindered carboxylic acid extractants described in the literature, where the heavy rare-earth ions (Dy(III) in this case) have a slightly higher affinity for the extracting compound than the light rare-earth ions (La(III),

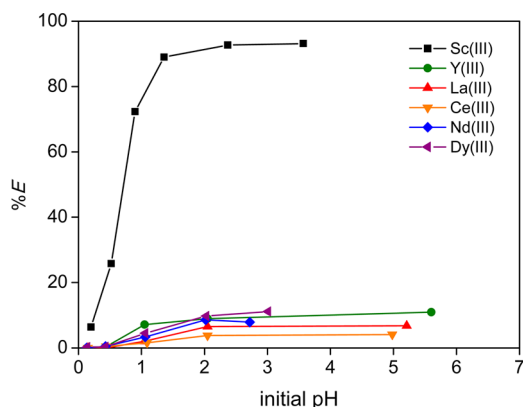


Figure 6. Percentage extraction of various trivalent rare-earth ions (Sc(III), Y(III), La(III), Ce(III), Nd(III), and Dy(III)) with [Hbet][Tf₂N] from single-element solutions as a function of initial aqueous pH. Initial concentration in the aqueous phase was 10 mmol·kg⁻¹ for rare-earth metal ion.

Ce(III), Nd(III) in this case).³⁹ Y(III) has approximately the same affinity for [Hbet][Tf₂N] as dysprosium.

[Hbet][Tf₂N] has a low affinity for almost all the major elements present in red mud, except for Fe(III) (Figure 7).

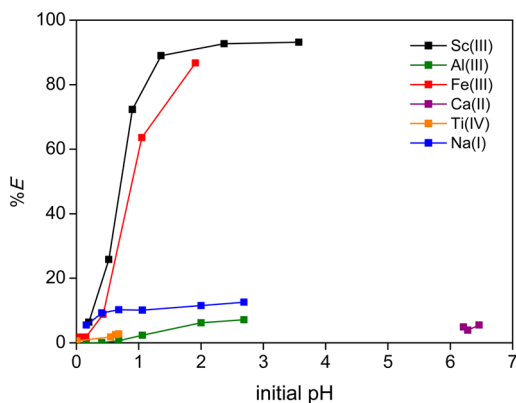


Figure 7. Percentage extraction of Sc(III), Al(III), Fe(III), Ca(II), Ti(IV), and Na(I) with [Hbet][Tf₂N] from single-element solution as a function of initial aqueous pH. Initial concentration in the aqueous phase was 10 mmol·kg⁻¹ for each metal ion.

Al(III), Ca(II), and Ti(IV) were extracted less than 5% at initial pH 3. Na(I) is extracted up to 10% at initial pH 3. The extraction behavior of Na(I) and Al(III) is similar to results obtained by Sasaki et al. for extraction from nitrate media.²⁵ However, the behavior of Fe(III) toward [Hbet][Tf₂N] is very similar to Sc(III). Up to 90% of Fe(III) is extracted to the ionic liquid phase at an initial aqueous pH of 2. From these results, it can be concluded that [Hbet][Tf₂N] shows a high affinity toward Sc(III) and Fe(III), whereas the other metal ions present in the red mud leachates are only poorly extracted. When considering the recovery of Sc(III) from red mud leachates, it is therefore preferable to perform a pretreatment to remove Fe(III) from solution before selectively recovering scandium by solvent extraction with [Hbet][Tf₂N].

The selectivity of [Hbet][Tf₂N] toward the tested metal ions, Sc(III), Fe(III), Al(III), Ca(II), Na(I), Ti(VI), Y(III), La(III), Ce(III), Nd(III), and Dy(III), is in line with the extraction behavior of carboxylic acid extractants described in the literature, where cations with a higher charge density and

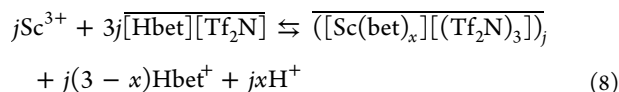
higher electronegativity generally form stronger complexes at more acidic conditions.^{40,41} One of the main reasons for the stronger extractability of Fe(III) and Sc(III) compared to the trivalent lanthanide ions and Y(III) is the fact that Fe(III) and Sc(III) have a smaller ionic radius and thus a higher charge density than the trivalent lanthanide ions and Y(III). This leads to the formation of more stable complexes with the carboxylate groups and hence to a more efficient extraction to the ionic liquid phase. Regarding the other metal ions, Al(III), Ca(II), Ti(IV), and Na(I), it is difficult to exactly determine the reason for the difference in selectivity of [Hbet][Tf₂N]. Many thermodynamic factors have an influence on the extractability, such as ionic radius, charge density, basicity, electronegativity, geometry of the complex, solvation effects, solvent type, hydrolysis, etc. Moreover, the extraction mechanism in ionic liquids often differs from that in molecular solvents.

Extraction Mechanism. The extraction mechanism was examined by slope analysis techniques to determine both the speciation of scandium(III) in the ionic liquid phase and the reaction that occurs between the aqueous and ionic liquid phase upon extraction. ATR-FTIR spectra of the ionic liquid phase of the extraction mixture, loaded with varying amounts of scandium (0–85 mmol·kg⁻¹), showed that coordination of the ionic liquid to the scandium ion occurs via the carboxylic acid function of the cation (peaks in the region 1580–1780 cm⁻¹) (Figure S5 in Supporting Information). This is in agreement with the speciation studies performed by Nockemann et al. on various metal complexes of [Hbet][Tf₂N].^{19,20}

Moreover, the carboxylic acid function is the only important metal-coordinating function present in the structure of [Hbet][Tf₂N], since Tf₂N⁻ is a weakly coordinating anion. Water-saturated [Hbet][Tf₂N], without scandium, showed two IR bands in the 1580–1780 cm⁻¹ region, one absorption band at 1740 cm⁻¹ corresponding to the protonated acid function COOH, and one absorption band at 1625 cm⁻¹ corresponding to the deprotonated acid function (conjugated base) COO⁻. The presence of the absorption band of the COO⁻ vibration indicated that part of the ionic liquid is deprotonated in the ionic liquid phase. This was possible due to the presence of water in the ionic liquid phase. The liberated protons could bind to the water molecules, forming H₃O⁺. Upon extraction of scandium to the ionic liquid phase, the absorption band of COOH became narrower and the relative intensity of the COO⁻ absorption band increased. The FTIR spectrum of the ionic liquid phase loaded with 85 mmol·kg⁻¹ of scandium showed no absorption band corresponding to COOH, indicating that coordination occurs solely via the deprotonated carboxylate (COO⁻). This is to be expected, since coordination of the protonated Hbet⁺ cation to a positively charged metal ion is unlikely due to electrostatic repulsion. By deprotonation of the cation, a neutral zwitterionic compound is formed for which coordination is much less hindered by electrostatic interactions. However, when classical molecular acidic extractants (HA) are used for extraction of metal ions, coordination occurs mostly by deprotonated acid (conjugated base, A⁻) via an ion-exchange mechanism in combination with protonated acid itself (HA) via a solvating (neutral) mechanism.^{39–41} This generally occurs when the number of carboxylate ligands required for the formation of an electrically neutral complex is insufficient to saturate the coordination sphere of the metal. In case of [Hbet][Tf₂N], the deprotonated betaine ligand is a zwitterion, hence the overall charge of the ligand is zero and charge neutralization of the scandium(III) betaine complex is

obtained by counterions in the first or second coordination sphere. Furthermore, the absence of the COOH absorption bands indicates that maximum loading was reached, since no free carboxylic acid functions are present in the ionic liquid phase. This confirms the results depicted in Figure 4, which suggest a similar maximum loading at $85 \text{ mmol}\cdot\text{kg}^{-1} \text{ Sc(III)}$. By calculation of the number of moles of Sc(III) ions in the ionic liquid phase and the number of moles of ionic liquid present in a 2 g extraction mixture, a maximum loading of $85 \text{ mmol}\cdot\text{kg}^{-1}$ corresponds to three ionic liquid molecules per Sc(III) ion. This suggests a ligand-to-metal ratio of 3:1. An isosbestic point is detected in the FTIR spectrum at about 1700 cm^{-1} for the samples with a concentration of [Hbet][Tf₂N] from 0 to 63 mmol/kg (Supporting Information Figure S5). This indicates that only one equilibrium reaction exists in this concentration range.

To further elucidate the extraction mechanism and confirm the suggested 3:1 stoichiometry deduced from the maximum loading, the amount of betaine ligands and the nature of the counterions were determined. Two options are possible for the counterion, namely, the chloride ions present in the aqueous feed solution and the bis(trifluoromethylsulfonyl)imide anions of the ionic liquid. As described before, the nature of the anion of the metal salt in the aqueous phase did not influence the %E of Sc(III), suggesting that the anion of the metal salt did not act as a counterion in the extracted Sc(III) complex.²² To confirm this hypothesis, the chloride content of the ionic liquid phase after extraction of Sc(III) from a ScCl₃ solution ($4.5 \text{ mmol}\cdot\text{kg}^{-1}$) was measured by TXRF.³² The results showed no presence of chloride in the ionic liquid phase, meaning that chlorides are not coextracted. Thus, the charge of the extracted cationic scandium(III) betaine complex is neutralized by three Tf₂N⁻ anions of the ionic liquid. The general extraction mechanism is expressed in eq 8:



where the upper bar indicates the species in the organic phase. The coefficient j in eq 8 indicates the degree of polymerization of the extracted scandium(III) complex. The extraction equilibrium constant K is described by the following equation,

$$K = \frac{\overline{([\text{complex}]_j)}_{\text{IL}} \cdot [\text{Hbet}^+]^{j(3-x)} \cdot [\text{H}^+]^{jx}}{([\text{Sc(III)}]_{\text{aq}})^j \cdot [\text{IL}]^{3j}} \quad (9)$$

where "complex" indicates $[\text{Sc}(\text{bet})_x][(\text{Tf}_2\text{N})_3]$ and "[IL]" indicates the concentration of [Hbet][Tf₂N] in the ionic liquid phase. The distribution ratio for extraction of scandium is given by

$$D = \frac{j \cdot \overline{([\text{complex}]_j)}_{\text{IL}}}{[\text{Sc}]_{\text{aq}}} = j \cdot \frac{K \cdot ([\text{Sc(III)}]_{\text{aq}})^{j-1} [\text{IL}]^{3j}}{[\text{Hbet}^+]^{j(3-x)} [\text{H}^+]^{jx}} \quad (10)$$

which on taking the logarithms gives

$$\log D = \log j + \log K + (j-1) \cdot \log [\text{Sc(III)}]_{\text{aq}} + 3j \cdot \log [\text{IL}] - j(3-x) \cdot \log [\text{Hbet}^+] + jx \cdot \text{pH} \quad (11)$$

The degree of polymerization j was determined by plotting $\log D$ versus $\log [\text{Sc(III)}]_{\text{aq}}$ at constant equilibrium pH and [Hbet][Tf₂N] concentration (Figure 8). The Hbet⁺ concen-

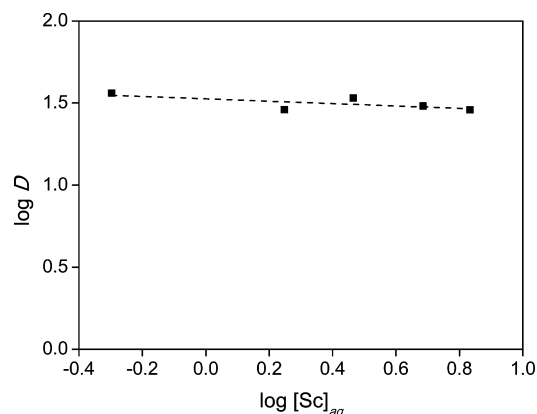


Figure 8. Plot of $\log D$ versus \log initial aqueous Sc(III) concentration. Initial aqueous phase: $0.04\text{--}4.5 \text{ mmol}\cdot\text{kg}^{-1} \text{ Sc(III)}$, initial pH 3–3.5. Slope of the linear fit (dashed line) is -0.07 ± 0.04 .

tration in the aqueous phase is relatively high due to the partial dissolution of the ionic liquid in the aqueous phase. Therefore, [Hbet⁺] will not change significantly upon extraction of scandium and is considered to be constant. Equation 11 is then simplified to

$$\log D = (j-1) \cdot \log [\text{Sc(III)}]_{\text{aq}} + C \quad (12)$$

where C indicates a constant term. The slope of $\log D$ versus $\log [\text{Sc(III)}]_{\text{aq}}$ is 0, resulting in a degree of polymerization j equal to 1. This means that no polymerization occurs and scandium is extracted as a mononuclear complex to the ionic liquid phase.

The slope of $\log D$ versus pH was plotted to determine the stoichiometry x of the betaine ligand in the extracted scandium(III) complex by keeping $[\text{Sc(III)}]_{\text{aq}}$ and the [Hbet][Tf₂N] concentration constant (Figure 9). Similar as before,

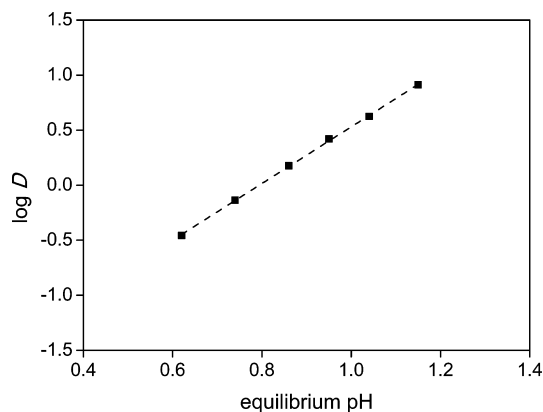


Figure 9. Plot of $\log D$ versus equilibrium pH for the extraction of Sc(III) with [Hbet][Tf₂N]. Initial aqueous phase: $3.6 \text{ mmol}\cdot\text{kg}^{-1} \text{ Sc(III)}$, pH 0.3–3.6. Slope of the linear fit (dashed line) is 2.57 ± 0.02 ($R^2 = 0.999$).

[Hbet⁺] was also considered to be constant because the potential exchange of Hbet⁺ upon extraction has no significant effect on its concentration in the aqueous phase. Equation 11 is then simplified to

$$\log D = x \cdot \text{pH} + C \quad (13)$$

The slope was equal to 2.57 ± 0.02 . This implies three possibilities for the stoichiometry, namely, $x = 2, 2.5,$ or 3 .

A stoichiometry of 2.5 would correspond to the formation of a binuclear Sc(III) complex with five betaine ligands. However, it was shown before that no dimerization occurred, so a stoichiometry of 2.5 is not possible. To distinguish between a stoichiometry of 2 or 3, the influence of the addition of Hbet⁺ to the aqueous phase in the extraction mixture was examined. In the case of stoichiometry 2 ($x = 2$), ion exchange would occur between Sc³⁺ and Hbet⁺ and one Hbet⁺ cation would transfer to the aqueous phase per extracted Sc³⁺. In the case of stoichiometry 3 ($x = 3$), no Hbet⁺ would transfer to the aqueous phase. When keeping the pH, the ionic liquid concentration and [Sc(III)]_{aq} constant, eq 11 is simplified to

$$\log D = (3 - x) \log[\text{Hbet}^+] + C \quad (14)$$

A plot of $\log D$ versus $\log [\text{HbetCl}]_{\text{aq,in}}$ showed a slope of 0, meaning that no Hbet⁺ transferred to the ionic liquid phase upon extraction of Sc(III) and x was equal to 3 (Figure 10).

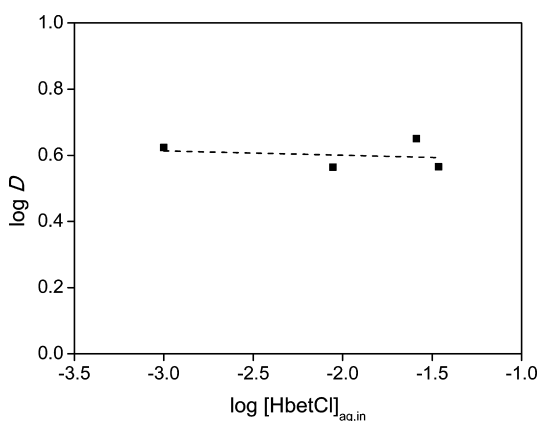
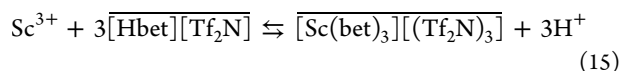


Figure 10. Influence of the addition of HbetCl to the aqueous phase on the extraction of Sc(III) with [Hbet][Tf₂N]. Initial aqueous phase: 4 mmol·kg⁻¹ Sc(III), 1 M NaCl, pH 3–3.5. Slope of the linear fit (dashed line) is -0.01 ± 0.04 .

The reason why the slope of the linear fit in Figure 9 is not exactly 3 is most likely due to the changes in phase behavior at higher HCl concentrations in the aqueous phase (low equilibrium pH). The presence of HCl increases the upper critical solution temperature (UCST) of the water–[Hbet]–[Tf₂N] system, which mostly likely results from a decrease in mutual solubility of [Hbet][Tf₂N] and water (salting-out effect).²³ Thus, the presence of HCl slightly alters the phase ratio of the extraction mixture, which is not taken into account in the calculation of D . Therefore, a small deviation on $\log D$ exists at increased HCl concentrations, resulting in a slope which is not exactly 3. From these results, it can finally be concluded that Sc(III) is extracted in a ligand-to-metal ratio of 3:1, as suggested from the calculations based on the maximum loading. The extraction mechanism is described by the following expression.



It must be noted that no ion exchange of ionic liquid components occurs, which is a major advantage. Ion exchange of ionic liquids often occurs upon extraction of metal ions and results in the loss of (part of) the ionic liquid to the aqueous phase.^{42,43}

Stripping. Stripping of the extracted Sc(III) was examined after loading [Hbet][Tf₂N] with Sc(III) by extraction from a ScCl₃ aqueous solution. As shown above, the extraction of scandium decreases with increasing acid concentration in the feed (Figure 11). Thus, stripping of Sc(III) by back-extraction

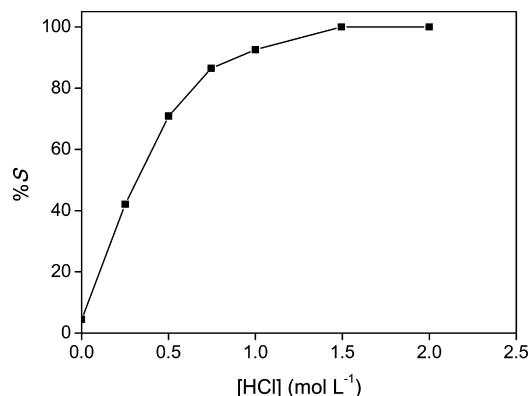
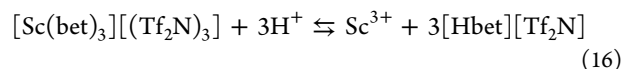


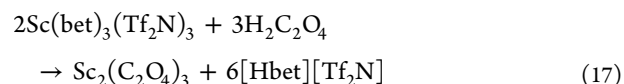
Figure 11. Stripping of Sc(III)-loaded [Hbet][Tf₂N], containing 4.3 mmol·kg⁻¹ Sc(III), by back-extraction with HCl solutions with varying concentrations (0–2 M).

was tested using HCl solutions with varying concentrations (0–2 M). The back-extraction reaction can be described with the following equation:



The coordinated ionic liquid is fully regenerated without any losses due to ion exchange. Sc(III) was fully removed from [Hbet][Tf₂N] loaded with 4.3 mmol·kg⁻¹ of Sc(III) by stripping with 1.5–2 M of HCl. The stripping efficiency drops when using more diluted HCl solution from 92% for 1 M HCl to 42% for 0.25 M HCl. By stripping with pure water, only 4% of the loaded scandium is stripped. For batch experiments, it is preferable to perform stripping in as few steps as possible by using more concentrated HCl solutions (e.g., 2 M) instead of applying several stripping steps with more diluted HCl solutions (e.g., 1 M), because [Hbet][Tf₂N] dissolves in the aqueous phase up to 14 wt %. So, every stripping step is accompanied by a loss of ionic liquid to the aqueous phase. However, the accumulation of losses to the aqueous phase when applying multiple stripping steps is not an issue in a counter-current continuous process. The aqueous phase from stripping step n , saturated with dissolved ionic liquid, flows back to stripping step $n - 1$, where no extra losses occur since the aqueous phase is already saturated with ionic liquid.

To avoid losses of ionic liquid to the aqueous phase during back extraction, stripping can also be performed by precipitation of the extracted metals as oxalates by addition of solid oxalic acid to the ionic liquid phase (precipitation stripping).^{44,45} It was observed that all extracted Sc(III) could be removed from an ionic liquid phase loaded with 83 mmol·kg⁻¹ Sc(III) by addition of a stoichiometric amount of oxalic acid (1.5 equiv) (eq 17, Figure 12).



A major advantage of precipitation stripping is the fact that this process does not make use of an aqueous phase and loss of the

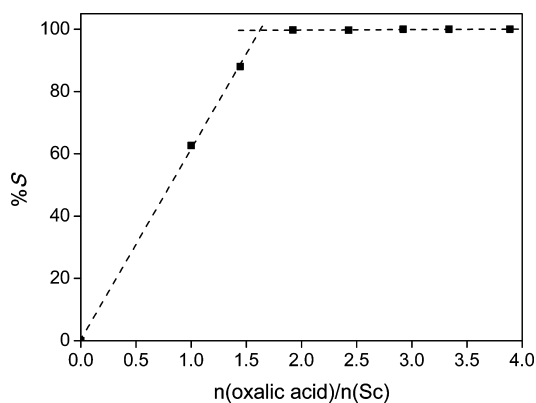


Figure 12. Precipitation stripping of scandium(III)-loaded [Hbet]-[Tf₂N], containing 83 mmol·kg⁻¹ Sc(III), with oxalic acid.

ionic liquid is limited. Furthermore, precipitation leads to purification of the product and automatically regenerates the ionic liquid by protonating the betaine groups (eq 17). Finally, the obtained scandium(III) oxalate can easily be converted to the corresponding oxide by calcination.

Reusability of the Ionic Liquid. After stripping, the ionic liquid phase was reused in a new extraction cycle. The ionic liquid phase obtained after full stripping with 2 M HCl was directly contacted with a fresh ScCl₃ solution (100 mmol·kg⁻¹, pH 2.6) to extract Sc(III), without any pretreatment of the ionic liquid phase (Table 2). In principle, by stripping with 2 M

Table 2. Reusability of the Ionic Liquid Phase after Stripping with a 2 M HCl Solution and %E of Sc(III) (10 mmol·kg⁻¹, pH 3.5) Using Fresh Water-Saturated [Hbet][Tf₂N] (EX1), Reused Water-Saturated [Hbet][Tf₂N] without Any Pretreatment (EX2.1), and Reused Water-Saturated [Hbet][Tf₂N] after Two Washing Steps with H₂O (EX2.2)

	treatment of reused IL phase	%E	pH _{aq,eq}
EX1	none (fresh IL)	>90	1.3
EX2.1	none	48	0.9
EX2.2	2× washing with H ₂ O	91	1.3

HCl, the original water-saturated ionic liquid phase is reobtained since all Sc(III) ions are removed and the ionic liquid [Hbet][Tf₂N] is again reformed. However, it was observed that the %E decreased when directly reusing the ionic liquid phase after stripping without any pretreatment. This is due to the higher acidity in the extraction mixture, as can be seen from the lower equilibrium pH of the aqueous phase. The ionic liquid phase is slightly acidified after the stripping step because an excess of HCl was used during the stripping. By washing the ionic liquid phase two times with water (1:1 phase ratio), the residual acid was removed and the same %E of Sc(III) was obtained as with fresh ionic liquid.

Separation of Scandium and the Rare-Earth Elements.

As shown in the extraction studies of single-element solutions of the different rare-earth elements described above, the ionic liquid [Hbet][Tf₂N] has a high selectivity for scandium compared to the other rare-earth elements (including yttrium). This property was exploited for the recovery of Sc(III) from a multielement solution containing Sc(III), Y(III), La(III), Ce(III), Nd(III), and Dy(III). The separation of Sc(III) from Y(III), La(III), Ce(III), Nd(III), and Dy(III) was tested as a function of the initial aqueous pH, adjusted by addition of small

amounts of HCl. The results showed that at low acid concentrations, Y(III), La(III), Ce(III), Nd(III), and Dy(III) were extracted up to 10–18% and Sc(III) up to 85% (Table 3).

Table 3. Percentage Extraction (%E) of La(III), Ce(III), Nd(III), Dy(III), Y(III), and Sc(III) by [Hbet][Tf₂N] as a Function of the pH of the Feed Solution^a

	pH 0.1	pH 0.4	pH 1.1	pH 2.0	pH 3.1
La(III)	0.0%	0.5%	3.9%	8.7%	11.6%
Ce(III)	0.0%	1.4%	7.8%	12.4%	15.2%
Nd(III)	0.0%	0.3%	7.9%	15.6%	19.0%
Dy(III)	0.0%	0.8%	7.6%	17.3%	18.1%
Y(III)	0.0%	0.0%	6.8%	14.3%	18.0%
Sc(III)	0.6%	7.3%	53.0%	18.6%	82.9%

^aThe feed solution contained a mixture of all the elements. Initial concentration of aqueous phase: 1 mmol·kg⁻¹ of each element.

The extraction selectivity follows the series La(III) < Ce(III) < Nd(III) < Dy(III) ~ Y(III) < Sc(III). It must be noted that both the aqueous metal content and the ionic liquid metal content were measured by TXRF and used for the calculation of the %E during the separation studies. This was required since high HCl concentrations significantly influenced the phase equilibrium of [Hbet][Tf₂N], as described before, resulting in a decrease in mass of the aqueous phase and an increase in mass of the ionic liquid phase. Using only the measured metal content in the aqueous phase for the calculation of %E would result in a strong underestimation of %E for the poorly extracting metal ions. On the other hand, because of the use of Ga as an internal standard in the TXRF measurements, the concentration of light elements, such as scandium, in a large organic matrix, such as in the ionic liquid phase, is also underestimated due to absorption effects of the secondary X-rays by the organic matrix. Therefore, the %E of Sc(III) is slightly underestimated (85% determined using the measurement of both the aqueous and the ionic liquid phases, compared to >90% when using only the measured aqueous scandium content). For the separation experiments performed from feed solutions with a pH of 3, separation factors of approximately 50 for the Dy(III)/Sc(III) couple and up to 85 for the La(III)/Sc(III) couple, were obtained. The selectivity for Sc(III) decreased slightly with increasing acid concentration in the aqueous feed, but remained fairly constant. Below pH 1, the %E of both Sc(III) and the other rare-earth ions decreased sharply with increasing acidity to zero at pH 0. Therefore, it is preferable to recover scandium from rare-earth solutions with moderate acidity (>pH 1.5) to combine both the high %E and high selectivity for Sc(III).

To purify the loaded ionic liquid phase and remove the coextracted lanthanide and yttrium ions, scrubbing was examined. In the case of [Hbet][Tf₂N], scrubbing can be performed by contacting the ionic liquid phase with a HCl solution. The process of removal of metal ions by scrubbing is based on the same principle as the stripping, namely, that by contacting the ionic liquid phase with an acidic solution, the extraction equilibrium is shifted and (part of) the extracted metal complexes are decomposed. The ionic liquid is regenerated and the metal ions transfer to the aqueous phase (eq 16). By using more diluted acid solutions than in the case of stripping, selectivity can be obtained between the coextracted metal ions and Sc(III). HCl solutions with concentrations between 0 and 1 M were tested to determine the optimal

conditions for scrubbing and the scrubbing efficiency (expressed as percentage stripping %S) was calculated. It can be seen that both scandium and the coextracted rare-earth ions are all fully stripped from the ionic liquid phase when using a 1 M HCl solution (Figure 13). By lowering the concentration, the

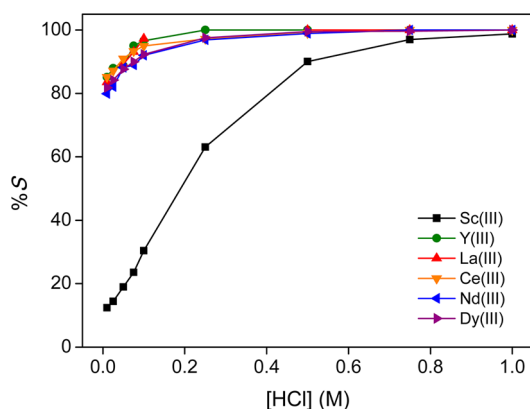


Figure 13. Scrubbing of a [Hbet][Tf₂N] phase obtained after extraction of a multielement solution containing Sc(III), Y(III), La(III), Ce(III), Nd(III), and Dy(III) (7 mmol·kg⁻¹ of each element) by different HCl concentrations (0–1 M). The initial concentration of Y(III), La(III), Ce(III), Nd(III), and Dy(III) in the IL phase was around 0.5 mmol·kg⁻¹, and the initial Sc(III) concentration in the IL phase was 6 mmol·kg⁻¹.

%S of Sc(III) decreases, but the %S of the coextracted rare-earth ions remains fairly constant at >95%. Scrubbing with HCl solutions with a concentration ≤0.25 M resulted in a decreasing scrubbing efficiency compared to the more concentrated scrub solutions. However, the scrubbing efficiency for the coextracted rare-earth ions still remains higher than 80% when using pure water, while the %S of scandium drops to <15%. Therefore, it is preferable to perform multiple scrubbing steps with more diluted HCl solutions (<0.1 M) to selectively remove the coextracted rare-earth ions and prevent high losses of Sc(III) during the scrubbing stage.

CONCLUSIONS

The ionic liquid [Hbet][Tf₂N] is suitable for the extraction of Sc(III) from both chloride and nitrate aqueous solutions. Extraction is fast, even at room temperature, and good extraction efficiencies (>95%) are obtained when extracting from feed solution with a moderate acidity (pH ≥ 1.5). Because of the thermomorphic behavior of [Hbet][Tf₂N], both conventional liquid–liquid extraction and homogeneous liquid–liquid extraction (HLL) were applied. Extraction is possible from a broad initial concentration range. Extraction from highly diluted feed solutions is useful for the selective recovery of scandium from red mud leachates. Because of the high liquid-to-solid ratio applied during the leaching, the concentration of scandium in the leachate is very low (<10 ppm). Furthermore, it was shown that the concentration of extracted Sc(III) in the ionic liquid phase can be increased by lowering the mass of the ionic liquid phase compared to the mass of the aqueous phase. In this way, Sc(III) is concentrated in the ionic liquid phase, which is again interesting for the recovery of scandium from red mud leachates. The mechanism for extraction of Sc(III) was investigated by slope analysis. It was concluded that Sc(III) is extracted by coordination of three zwitterionic betaine ligands and charge neutralization with three

Tf₂N⁻ anions as counterions. Three protons of the ionic liquid are exchanged per extracted Sc(III) ion. Besides scandium, the extraction behavior toward the minor elements yttrium(III) and the trivalent lanthanides and the ions of the major elements Fe(III), Al(III), Ti(IV), Ca(II), and Na(I) present in red mud was also examined. It was shown that all the tested elements have a low affinity for the ionic liquid, except for Fe(III) which has a similar extraction behavior as Sc(III) in these conditions. Therefore, a pretreatment to remove Fe(III) is recommended when applying [Hbet][Tf₂N] for the selective recovery of scandium from red mud leachates. Furthermore, the separation of Sc(III) from a mixture of rare-earth ions was considered. Selective recovery of Sc(III) is possible by a combination of extraction and scrubbing with diluted HCl solutions. Finally, Sc(III) can be fully stripped from the loaded ionic liquid phase by back-extraction with a HCl solution (1.5–2 M) or by precipitation with oxalic acid. Stripping by back-extraction with HCl results in a slight acidification of the ionic liquid phase. The ionic liquid phase can be reused again for extraction of Sc(III) after washing off the residual acid with water.

ASSOCIATED CONTENT

Supporting Information

A plot of the initial versus the equilibrium pH for extraction of scandium (S1), plot of the comparison of the extraction from nitrate and chloride solution (S2), influence of heating time on the extraction of scandium with HLL (S3), influence of phase ratio on the extraction of scandium (S4), and FTIR spectra of loaded ionic liquid (S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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