Metal extraction with a short-chain imidazolium nitrate ionic liquid

Daphne Depuydt, Arne Van den Bossche, Wim Dehaen, and Koen Binnemans

Supporting Information
Experimental

Chemicals

Glyoxal (40 wt% in water), sodium nitrate (+99%), nickel nitrate hexahydrate (99%), cobalt nitrate hexahydrate (99%) and Triton X-100 were purchased from Acros Organics (Geel, Belgium). Sodium hydroxide (Normapur) and ethanol absolute were obtained from VWR (Heverlee, Belgium). n-Hexylamine (99%), nitric acid (65% in water), chloroform-d (99.8 atom% D), deuterium oxide (99.9 atom% D), zinc(II) nitrate hexahydrate (≥98%) and yttrium nitrate hexahydrate (99.9%) were bought from Sigma-Aldrich (Diegem, Belgium). Dichloromethane (analytical reagent grade), acetic acid (analytical reagent grade) and formaldehyde (37-40 wt% in water) were obtained from Fisher Scientific Limited (Loughborough, UK). Ammonium nitrate (+99%) was purchased from Chempur (Karlsruhe, Germany). Samarium(III) nitrate hexahydrate (99.9%), lanthanum(III) nitrate hexahydrate (99.9%) and neodymium(III) nitrate hexahydrate (99.9%) were purchased from Alfa Aesar (Karlsruhe, Germany). Copper(II) nitrate trihydrate (≥99.5%) was purchased from Merck (Leuven, Belgium). Scandium(III) nitrate hydrate was synthesized from scandium(III) oxide which was kindly provided by Solvay (La Rochelle, France). All chemicals were used as received without any further purification.

General techniques

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for $^1$H and 75 MHz for $^{13}$C). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane. All solutions were made in CDCl$_3$ or D$_2$O. The spectra were analyzed with SpinWorks software. Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer, via the attenuated total reflectance (ATR) technique with a Bruker Platinum ATR accessory. The OPUS software package was used for analysis of the FTIR spectra. The water content of the dry, water-saturated and 6 M NaNO$_3$-saturated ionic liquid was determined by respective coulometric and volumetric Karl Fischer (KF) titration using a Mettler-Toledo C30S coulometric KF titrator and a Mettler-Toledo V30S volumetric titrator equipped with a Stromboli Oven. TGA measurements were performed on a TGA-Q500 (TA Instruments). For these TGA measurements, about 10 mg of a
water-saturated ionic liquid sample was heated at 10 °C min\(^{-1}\) to 120 °C, this temperature was kept for one hour to remove all water, and subsequently the dry ionic liquid was further heated to 500 °C at the same rate of 10 °C min\(^{-1}\). The elemental analysis of carbon, hydrogen and nitrogen (CHN analysis) was performed on a flash 2000 Elemental analyzer of Thermo Scientific Interscience. In order to presaturate the ionic liquid, dry ionic liquid and water or 6 M NaNO\(_3\) solution (1:1 w/w) were shaken with an Eppendorf Thermomixer C with a 15 mL SmartBlock (25 °C, 1000 rpm). Extraction mixtures in 2 mL Eppendorf vials were shaken with an Eppendorf Thermomixer C with a 2 mL SmartBlock (25 °C, 2000 rpm). A VWR MiniStar silverline microcentrifuge was used for the centrifugation of the samples. pH measurements were performed with an S220 SevenCompact™ pH/ion meter (Mettler-Toledo) and a Slimtrode (Hamilton) electrode. A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations in both aqueous and organic (ionic liquid) phase.\(^1\) For the determination of the metal content in experiments involving the Sm/Co and La/Ni pairs, both neodymium and gallium standard solutions were added to the sample as internal references for quantification, in the multi-element screening test only gallium standard solution was used. The sample was diluted to 1 mL with Triton 100 5 wt% in water for aqueous samples, and with ethanol for the ionic liquid phase. The prepared sample solutions were homogenized by vortex mixing and a small droplet (3 µL) was dispensed on a quartz sample carrier. Finally, the carrier containing the sample was dried at 60 °C for 30 min. Prior to dispensing the sample droplet, the quartz carrier was pretreated with a SERVA\(^*\) silicone solution in isopropanol (30 µL) which was dried at 60 °C for 30 min, in order to make the surface hydrophobic, to avoid spreading of the sample droplet.

*Synthesis of 1,3-dihexylimidazolium nitrate*

1,3-Dihexylimidazolium nitrate [HHIM][NO\(_3\)] was synthesized as described in a previous paper (Scheme S1).\(^2\) In a first step, 1,3-dihexylimidazolium acetate was prepared from readily available precursors: \(n\)-hexylamine, glyoxal, formaldehyde and acetic acid. 1,3-Dihexylimidazolium acetate (100 mmol) was then dissolved in water and nitric acid (65 wt% in water, 2 eq. 200 mmol, 13.94 mL) was added to the solution. After the addition of nitric acid, a water-insoluble product was formed. After two hours, dichloromethane was added to
the reaction mixture and the two phases were separated, the organic phase was washed two times with water. The dichloromethane was removed with a rotary evaporator and the last traces of solvent were removed on a Schlenk line at 50 °C.

![Scheme S1. Synthesis of [HHIM][NO₃].](image)

Brown, viscous liquid (26.56 g, 88.72 mmol, 89%). ¹H NMR: (300 MHz, CDCl₃, δ/ppm): 10.06 (s, 1H, CH), 7.35 (s, 2H, 2 CH), 4.26 (t, J = 7.5 Hz, 4H, 2 CH₂), 1.89 (m, 4H, 2 CH₂), 1.31 (m, 12H, 6 CH₂), 0.87 (t, J = 7.0 Hz, 6H, 2 CH₃). ¹³C NMR: (75 MHz, CDCl₃, δ/ppm): 137.81 (N-CH-N), 122.00 (2 CH-N), 50.14 (2 CH₂-N), 31.03 (2 CH₂), 30.19 (2 CH₂), 25.86 (2 CH₂), 22.38 (2 CH₂), 13.90 (2 CH₃). FTIR: (ν/cm⁻¹): 2956-2859 (C-H stretch), 1564 (N-C-N stretch), 1461 (C-C stretch), 1334 (N-O symmetric stretch), 830 (C-H bending). CHN analysis: (calculated for C₁₅H₂₉N₃O₃) (299.41 g mol⁻¹): C 59.63% (60.17%), H 9.57% (9.76%), N 14.72% (14.03%).

![Diagram of the synthesis of [HHIM][NO₃].](image)
$^1$H NMR Spectrum

$^{13}$C NMR Spectrum
Extraction experiments

Synthetic solutions of metal nitrates were used in the extraction experiments. All dilutions were made using ultrapure water (18.2 M Ω-cm) obtained from a Sartorius Arium Pro ultrapure water system. Presaturation of the ionic liquid [HHIM][NO₃] prior to extraction was necessary to minimize volume changes during the extraction experiments. Equal masses of ionic liquid and water were weighed in a 15 mL vial and shaken for 30 min. After centrifugation, approximately 1 g of the water-saturated IL and 1 g of an aqueous metal solution were added to a 2 mL Eppendorf tube and shaken at 25 °C at 2000 rpm for 30 min (unless stated otherwise). The tubes were centrifuged and a sample of both aqueous and ionic liquid phase was taken to measure the metal content by TXRF. To be noted, experiments involving a metal feed solution containing 6 M NaNO₃, were presaturated with a 6 M solution of NaNO₃, in other cases, water was used to presaturate the IL.

The distribution ratio $D$ and percentage extraction $%E$ were calculated according to equation S1 and S2, respectively:

$$D = \frac{c_{\text{org}}}{c_{\text{aq}}}$$  \hspace{1cm} (S1)

$$%E = \frac{c_{\text{org}} \cdot m_{\text{org}}}{c_{\text{org}} \cdot m_{\text{org}} + c_{\text{aq}} \cdot m_{\text{aq}}} \times 100\%$$  \hspace{1cm} (S2)

where $c_{\text{org}}$ and $c_{\text{aq}}$ are the metal concentration in the organic phase (i.e. ionic liquid phase) and in the aqueous phase, respectively and $m_{\text{org}}$ and $m_{\text{aq}}$ are the masses of the organic and the aqueous phase, respectively.

Scrubbing experiments

A larger extraction experiment was performed: equal masses of 6 M NaNO₃-saturated ionic liquid and 6 M NaNO₃ metal feed solution were weighed in a 15 mL vial and shaken for 30 min. After centrifugation, approximately 1 g of the loaded IL and 1 g of an aqueous NaNO₃ solution of varying concentration were added to a 2 mL Eppendorf tube and shaken at 25 °C.
at 2000 rpm for 30 min. Via TXRF, it was found that the IL was loaded with 13.2 g L\(^{-1}\) Sm(III) and 5.8 g L\(^{-1}\) Co(II) as nitrate salts. After the scrubbing, the percentage scrubbing %S was calculated according to equation S3:

\[
%S = \frac{\text{total amount of scrubbed metal}}{\text{total amount of extracted metal}} \times 100\%
\]  

(S3)

**Quantitative \(^1\)H NMR**

To determine the amount of IL lost into the water phase, quantitative \(^1\)H NMR measurements were performed. After presaturation of the ionic liquid, a 100 mg sample of the water layer was mixed with 10 mg of 1,4-dioxane to obtain approximately equimolar concentrations as the aliquot of water which was saturated with the ionic liquid. 1,4-Dioxane was chosen as internal standard since there is no overlap with the \(^1\)H NMR spectrum of the ionic liquid. Via the integration of the peaks in the \(^1\)H NMR spectrum of the water samples, the relative concentration versus 1,4-dioxane and the absolute concentration of the ionic liquid in the water layer were calculated. It is estimated that the measurement uncertainty is less than 1\%.\(^3\)
Results

Properties

Figure S1. Dynamic viscosity of [HHIM][NO₃], comparison dry, water-saturated (24 ±0.4 wt% H₂O) [HHIM][NO₃] and 6 M NaNO₃-saturated (11 ±0.1 wt% H₂O) [HHIM][NO₃].

Figure S2. Thermogravimetric analysis (TGA) of water-saturated [HHIM][NO₃] (heating rate: 10 °C min⁻¹, N₂ atmosphere).
Figure S3. Percentage extraction of Sm(III) and Co(II) as a function of varying NaNO₃ concentration in aqueous feed solution (1:1 w/w, feed solution: 15.5 g L⁻¹ Sm(III) and 36.9 g L⁻¹ Co(II) as nitrate salts, 25 °C, 30 min, pHₑq = 3).

Figure S4. Percentage extraction of Sm(III) and Co(II) as a function of the NH₄NO₃ concentration in the aqueous feed solution (1:1 w/w, feed solution: 15.5 g L⁻¹ Sm(III) and 36.9 g L⁻¹ Co(II) as nitrate salts, 25 °C, 30 min, pHₑq = 3).
Figure S5. Percentage extraction of Sm(III) and Co(II) as a function of time (1:1 w/w, feed solution: 15.5 g L\(^{-1}\) Sm(III) and 36.9 g L\(^{-1}\) Co(II) as nitrate salts, 25 °C, 6 M NaNO\(_3\), pH\(_{eq}\) = 3).

Figure S6. Percentage extraction of Sm(III) and Co(II) as a function of the equilibrium pH (pH\(_{eq}\)) (1:1 w/w, feed solution: approximately 14.0 g L\(^{-1}\) Sm(III) and 33.2 g L\(^{-1}\) Co(II) as nitrate salts, adjustment of pH by dilute solutions of HNO\(_3\) or NaOH, 25 °C, 30 min, 6 M NaNO\(_3\)).
References

