Green Chemistry

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ROYAL SOCIETY OF CHEMISTRY

rsc.li/green-chem

View Article Online
DOI: 10.1039/C7GC02958F

Journal Name

ARTICLE

Purification of crude In(OH)₃ using the functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide

0Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The recovery of indium from a crude indium(III) hydroxide using the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf$_2$N], was investigated. Leaching and solvent extraction were combined in one step using the thermomorphic properties of the [Hbet][Tf$_2$N]–H_2O system. During leaching (80 °C) a homogeneous phase was formed. Upon lowering the temperature below the lower critical solution temperature (UCST), the dissolved metals distributed themselves between the two phases. The optimal leaching/extraction conditions were determined to be a leaching time of 3 hours at 80 °C in a 1:1 wt/wt [Hbet][Tf$_2$N]–H_2O mixture. Large separation factors (>100) between In(III) and Al(III), Ca(II), Cd(II), Ni(II) and Zn(II) were obtained implying an easy separation. Fe(III), As(V) and Pb(II) are co-extracted. The separation factor between indium and iron was improved to >1000 by addition of ascorbic acid to reduce Fe(III) to Fe(II). The stripping was done very efficiently by HCl solution. The ionic liquid was regenerated during the stripping step. By combining a prehydrolysis and hydrolysis step, indium(III) hydroxide with a purity > 99% was obtained.

Introduction

Indium finds applications in many electronic devices *e.g.* photovoltaic cells, flat television screens, laptops and mobile phones, as metal, alloy or indium tin oxide (ITO). The demand of indium is expected to grow by more than 5% per year until 2020.[1] China dominates the indium supply from primary mining (>58% of the global production in 2013), and the worldwide recycling rate is still very low (<1%).[1,2] Indium is a scarce element with an abundance of only 0.1 ppm in the Earth's crust.[3-5] It is most commonly found in association with zinc ores such as sphalerite, although it also occurs in lead, copper, iron and tin ores.[3-5] The typical indium content of zinc deposits ranges from 10 to 20 ppm.[1,3,5] Thus, indium is a by-product of mining and refining operations of other metals. Indium is accumulated in low concentrations in residues formed during the processing of these ores. Possible primary sources of indium are by-products of refining, flue dusts, slags and metallic intermediates.[3,4] The recovery of indium from primary sources is often complex and difficult, and many of the flow sheets are proprietary to each producer.[5] Extractive metallurgy has been developed to recover indium from primary and secondary residues. Secondary indium sources comprise mostly e-waste and impure indium (<99%).[1,5] The recovery of indium from primary and secondary sources through extractive metallurgy makes use of pyrometallurgical and/or hydrometallurgical processes. It involves unit operations such as leaching, solvent extraction, cementation/precipitation, electrowinning and refining. Crude indium(III) hydroxide ($In(OH)_3$) is an intermediate that is often created during the processing of indium sources.[3,4,6-9]

Hydrometallurgical processes are very suitable for extracting indium from crude $In(OH)_3$. Typically, strong acids or bases are used to generate aqueous leachates by selective dissolution of the metals present in concentrates. The insoluble compounds can be readily separated from the leachate. Further purification is generally carried out by solvent extraction or ion exchange. Pure metals or metallic compounds can be produced once the metal salts have been prepared in a pure form by, for example, precipitation, cementation or electrowinning.

Advances in extractive metallurgy are mainly driven by environmental considerations, optimal metal recovery and reduction of in-process inventory.[9] Processes frequently involve multiple precipitation and dissolution steps with large volumes of waste water. Multiple processing steps lead to product losses in reject streams and high processing costs.[9] Among the approaches to overcome the disadvantages of the existing metal manufacturing technologies, ionic liquids can be alternative solvents in hydrometallurgy. Ionic liquids are solvents that consist entirely of ions.[10,11] Ionic liquids can be used either for replacing the aqueous phase in leaching processes or for replacing the molecular solvents in the organic phase of solvent extraction processes.[12-19] It is even possible to carry out solvent extraction with two mutually immiscible ionic liquid phases.[20] The term "ionometallurgy" has been coined by Abbott to describe processes in extractive metallurgy that make use of an ionic liquid phase instead of an aqueous phase.[21] More general, leaching with an ionic liquid can be considered a

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†Electronic Supplementary Information (ESI): Figures with additional leaching and distribution results available.

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DOI: 10.1039/C7GC02958F

solvometallurgical process.[22] Solvometallurgy makes use of processes involving nonaqueous solvents for the extraction of metals from ores, industrial process residues, production scrap, and urban waste.

To achieve selectivity and high metal loading upon leaching crude $In(OH)_3$, an alternative treatment is proposed that uses a reusable ionic liquid leaching agent, the carboxyl-functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf_2N], Fig. 1). [Hbet][Tf_2N] has been used to selectively dissolve different metal oxides,[23,24] to recycle rare earths from lamp phosphor waste and rare-earth permanent magnets,[25,26] and to recover rare earths from bauxite residue (red mud)[27]. In this paper, [Hbet][Tf_2N] was studied to purify crude $In(OH)_3$ by selective leaching. Crude $In(OH)_3$ was leached by water-saturated [Hbet][Tf_2N] and by taking the thermomorphic behavior of [Hbet][Tf_2N] into account. [Hbet][Tf_2N]–H_2O mixtures display thermomorphic behavior with an upper critical solution temperature (UCST) of 55 °C for a 1:1 wt/wt system.[23,26,28-30] The mixture forms one homogeneous phase above the UCST and two phases below that temperature. The metals might selectively distribute themselves between both phases, which can lead to the separation of metals upon cooling down the leachate below the critical temperature, and hence to phase separation. Metals dissolved in [Hbet][Tf_2N] can be stripped with an acidic solution while the ionic liquid is simultaneously regenerated. This leaching strategy has been studied previously for the selective dissolution of rare-earth elements.[25,26,27] Our process combines leaching and solvent extraction in a single step and can thus be considered as a form of process intensification. Contamination of the water phase by dissolved ionic liquid [Hbet][Tf_2N] is avoided during the process, by using a salting-out agent.

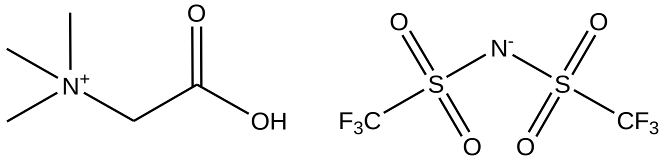

Fig. 1 Structure of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf_2N].

Experimental

Chemicals

$MgCl_2$ anhydrous (99%) and betaine hydrochloride (HbetCl) (99%) were obtained from Alfa Aesar (Karlsruhe Germany). Lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$) (>99%) and D_2O (99.9 atom% D) were purchased from Sigma-Aldrich (Diegem, Belgium). $Mg(NO_3)_2{\cdot}6H_2O$ (>99%) was obtained from Merck (Overijse, Belgium) and 1,4-dioxane (99.9 wt%) from Acros Organics (Geel, Belgium). L(+)-Ascorbic acid (technical grade) and NaOH pellets (>99%) were purchased from VWR (Leuven, Belgium). Hydrochloric acid solutions were prepared from concentrated HCl (37%, Acros Organics, Geel, Belgium) and water. All chemicals were used as received, without further purification. Water was always of ultrapure quality, deionized to a resistivity of >18.2 MΩ cm with a Milli-Q® Academic ultrapure water system. The crude $In(OH)_3$ was obtained from the Umicore Group Research & Development and its composition is shown in D2O (99.9 atom% D) were purchased from Sigma-Aldrich (Diegem, Belgium). Mg(NO3)2·6H2O (>99%) was obtained from Merck (Overijse, Belgium) and 1,4-dioxane (99.9 wt%) from Acros Organics (Geel, Belgium). l(+)-Ascorbic acid (technical grade) and NaOH pellets (>99%) were purchased from VWR (Leuven, Belgium). Hydrochloric acid solutions were prepared from concentrated HCl (37%, Acros Organics, Geel, Belgium) and water. All chemicals were used as received, without further purification. Water was always of ultrapure quality, deionized

Table 1. The crude $In(OH)_3$ was dried in a vacuum oven at 100 °C overnight before use.

Table 1 Metal composition of crude $In(OH)_3$ determined by ICP-OES.

Element	wt%	Element	wt%	Element	wt%
Al	1.4	Ga	0.0046	Se	0.0027
As	0.54	Ge	0.0095	Sn	0.0028
Bi	0.0018	In	58	Te	0.0015
Ca	0.20	Ni	0.027	Zn	5.0
Cd	0.18	Pb	0.26		
Fe	1.6	Sb	0.035		

Instrumentation and analysis methods

A Heraeus Labofuge 200 centrifuge was used to separate the undissolved flue dust particles from the ionic liquid after the leaching experiments. Metal concentrations were determined using inductively coupled plasma optical emission spectrometer (ICP-OES; Agilent, type E730) with an axial plasma configuration. For analysis of the aqueous phase by ICP-OES, a calibration curve was prepared with multi-element solutions over a concentration range of 0–10 mg L^{-1} with a quality control of 2 mg L^{-1} and scandium as an internal standard. The calibration solutions and the samples were diluted in 10 vol% HCl. The spectra were measured with a power of 1.4 kW, an argon flow of 15 L min^{-1} and an auxiliary argon flow of 1.5 L min^{-1}. For the organic phase, the sample was first digested with a mixture of H_2SO_4 and HNO_3 in a quartz beaker on a heating plate. H_2SO_4 and HNO_3 were evaporated (at 400 °C) and the residue was dissolved in 10 vol% HCl before measurement. The calibration and measuring procedure have been performed in the same way for the organic phase as described for the aqueous phase. pH and potential measurements of the aqueous phase after leaching were performed with an Protos® 3400 (X) pH/ORP/T meter (Knick) and a InPro® 3250i/SG/120 (Mettler-Toledo) electrode. A Mettler-Toledo DL38 volumetric Karl Fischer titrator (Hydranal® AG reagent) in combination with the oven sample changer Stromboli was used with to determine the water content of the ionic liquid.

Synthesis of [Hbet][Tf_2N]

The ionic liquid [Hbet][Tf_2N] was synthesized according to a one-step literature method based on the reaction between

DOI: 10.1039/C7GC02958F

[Hbet]Cl and $LiTf_2N$.[25] Chloride impurities were removed by several washing steps with ice water until the $AgNO_3$ test in the water phase after the washing step was negative. The level of chloride impurities in the ionic liquid phase after washing was below 1 ppm (Bench top total reflection X-ray fluorescence spectrometer; Bruker S2 Picofox). The water-saturated ionic liquid obtained after washing was used as such (water content: 13.25±0.04 wt% H_2O).

Leaching

Small glass vials (20 mL) were filled with 10 g of [Hbet][Tf_2N] and 700 mg sample of the crude $In(OH)_3$, resulting in a solid/liquid ratio of 70 mg g^{-1}. Water-saturated [Hbet][Tf_2N] (13 wt%) or a [Hbet][Tf_2N]–H_2O mixture (1:1 or 1:0.5 wt/wt) was used depending on the experiment. For the reduction of iron(III) to iron(II), a fixed amount of ascorbic acid was added to the aqueous phase to achieve a concentration of 0.010 M. This concentration was chosen based on the assumption that an iron leaching percentage of 100 % was obtained and all iron is present in the form of iron(III). A magnetic stirring bar was then added to each of the vials after which were closed using a plastic screw cap. The leaching experiments were carried out on a heating plate with an integrated magnetic stirrer and a temperature sensor. A copper block was placed on top as the vial container. The vials were placed in the copper block at the appropriate temperature and stirred at 500 rpm for a certain period of time. The content of the vials was then filtered through an MF-Millipore mixed cellulose membrane, pore size 0.45 µm, by means of a vacuum filtration to separate the undissolved crude $In(OH)_3$ from the ionic liquid before cooling took place. After leaching and filtration, the vials were cooling down in air to ambient temperature. Separation of the phases was assisted by centrifugation for 15 min at 3500 rpm. The metal contents dissolved in the ionic liquid and aqueous phase were determined using ICP-OES.

The *percentage leaching* (%L) is defined as the amount of metal leached to the ionic liquid or ionic liquid–water mixture over the initial amount of metal present in the crude $In(OH)_3$:

$$\%L = \frac{\mathrm{m_{IL}[M]_{IL}+m_{aq}[M]_{aq}}}{m_0} \times 100\% \quad (1)$$

where $[M]_{IL}$ (ppm) is the metal concentration in the ionic liquid after leaching/extraction, $[M]_{aq}$ (ppm) is the metal concentration in the aqueous phase after leaching/extraction and m_0 is the initial metal mass present in the crude $In(OH)_3$. m_{IL} and m_{aq} are the mass of the ionic liquid and aqueous phase, respectively.

The *distribution ratio D_M* of a metal is defined as:

$$D_{\mathrm{M}} = \frac{\mathrm{m_{IL}[M]_{IL}}}{\mathrm{m_{aq}[M]_{aq}}} \quad (2)$$

where $[M]_{IL}$ (ppm) is the metal concentration in the ionic liquid after leaching/extraction and $[M]_{aq}$ (ppm) is the metal concentration in the aqueous phase after leaching/extraction. m_{IL} and m_{aq} are the mass of the ionic liquid and aqueous phase, respectively.

The separation efficiency between two metals can be described by the *separation factor $\alpha_{M1,M2}$*, which is defined as the ratio of the respective distribution ratios of two extractable solutes measured under the same conditions:

$$\alpha_{M1,M2} = \frac{D_{M1}}{D_{M2}} \quad (3)$$

where D_{M1} and D_{M2} are the distribution ratios of metal M_1 and M_2, respectively. By definition, the value of the separation factor is always greater than unity.

Quantitative ^{1}H NMR

The concentration of ionic liquid in the aqueous phase was determined using quantitative ^{1}H NMR using 1,4-dioxane as an internal standard. A sample of the water phase was taken (100 mg) and a known amount of 1,4-dioxane–D_2O solution was added so that the concentration of 1,4-dioxane internal standard would be comparable to the concentration of ionic liquid in the sample. The ^{1}H NMR spectrum of 1,4-dioxane shows one resonance at δ = 3.7, corresponding to 8 equivalent protons, that does not overlap with the resonances of water or [Hbet][Tf_2N]. The relative concentration versus 1,4-dioxane and the absolute concentration of [Hbet][Tf_2N] were calculated by integration of the peaks by the Topspin software. Liquid-state ^{1}H NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer, operating at 400 MHz.

Scrubbing

Co-extracted metal ions are removed after extraction from the organic phase by a scrubbing agent, leaving the metal ions of interest in the loaded organic phase. First, leaching experiments were performed in which 700 mg sample of the crude $In(OH)_3$ was leached with a 1:1 wt/wt [Hbet][Tf_2N]–H_2O mixture (10 g [Hbet][Tf_2N]). The loaded ionic liquid phase obtained after leaching/extraction was contacted with an aqueous phase containing different stripping agents: Milli-Q water, HCl (1, 1.5 and 2 M), H_2SO_4 (0.75 and 1 M) and $MgSO_4$ (0.1 and 1 M) in a 1:1 wt/wt ratio. The scrubbing experiments were carried out in small glass vials (20 mL) on a heating plate with an integrated magnetic stirrer and a temperature sensor. A copper block was placed on top as the vial container. A magnetic stirring bar was added to each of the vials and they were closed using a plastic screw cap. The vials were placed in the copper block at the appropriate temperature and stirred at 500 rpm for 1 h. After scrubbing, separation of the phases was assisted by centrifugation for 15 min at 3500 rpm. The metal content dissolved in the ionic liquid and aqueous phase was determined using ICP-OES.

The *percentage scrubbing (%S)* in the scrubbed phase can be defined as the amount of metal scrubbed from the ionic liquid phase to the total amount of metal in the ionic liquid phase before scrubbing:

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$$\%S = \frac{V_{aq}([M]_{IL,o} - [M]_{IL})}{V_{IL}[M]_{IL,o}} \times 100 \qquad (4)$$

where $[M]_{IL,0}$ is the metal concentration in the organic phase after extraction or before scrubbing.

Stripping

Stripping of the loaded ionic liquid phase to selectively recover the indium ions after scrubbing was performed in the same way as the scrubbing experiments. The stripping efficiency was expressed using the scrubbing percentage %S (eq 4).

Results and discussion

Leaching of crude $In(OH)_3$ in $[Hbet][Tf_2N]$

The protonated carboxyl-functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide $[Hbet][Tf_2N]$ can dissolve large quantities of metal oxides due to the carboxylic acid group (pK_a = 1.83) located on the cation of the ionic liquid.[23,31] This difference in solubility can be exploited to selectively recover indium from the crude $In(OH)_3$. The selectivity and kinetics of the dissolution process are affected by the water content in the ionic liquid. Water accelerates the dissolution of metal oxides because it lowers the viscosity, facilitates the exchange of protons from the betaine groups and enhances the solvation of ions in the ionic liquid.[23,25,26,28,31] Therefore, all the leaching tests were executed with a water-saturated ionic liquid (13 wt%).

First, the effect of temperature and reaction time were tested on the solubility of indium in the water-saturated ionic liquid. Crude $In(OH)_3$ particles were added to the ionic liquid (70 mg g^{-1}) and stirred (500 rpm) at various temperatures (20 °C, 40°C, 60 °C and 80 °C) for increasing periods of time (30 min, 1 h, 3 h). The percentages leaching for the various elements from dissolution of crude $In(OH)_3$ in water-saturated $[Hbet][Tf_2N]$ as a function of temperature and reaction time are shown in Fig. S1†. Overall, the percentages leaching of the elements are increasing with increasing temperature. Fig. 2 displays the percentages leaching for indium specifically as a function of temperature and reaction time. The percentages leaching of indium are increasing with time and temperature, reaching a maximum of 94% after 3 h at 80 °C (Fig. 2). 80 °C is the optimal indium leaching temperature since leaching results close to the maximum percentage leaching are already obtained after 30 min. However, no selectivity for indium was observed at this temperature (Fig. 3). All impurities, except for Pb and Ge, have percentages leaching above 50% at 80 °C.

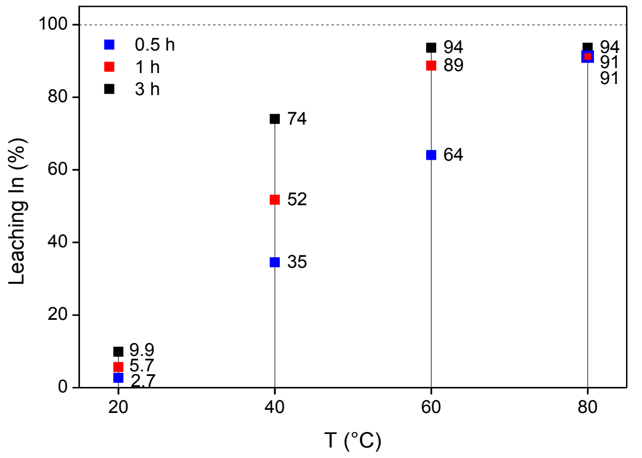

Fig. 2 Leaching of indium (%) from crude $In(OH)_3$ in water-saturated $[Hbet][Tf_2N]$ as a function of temperature and reaction time.

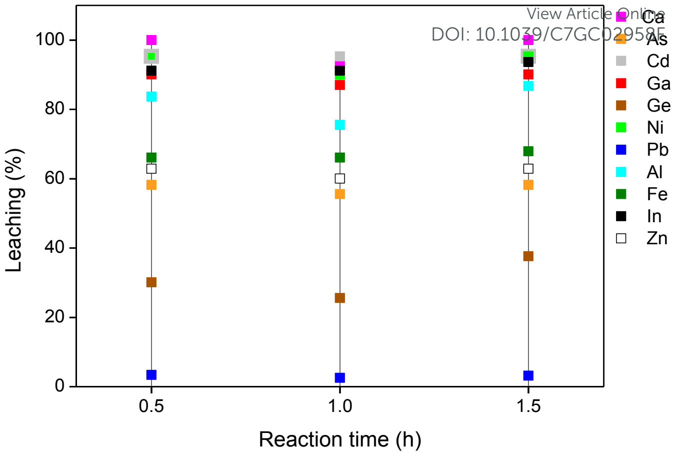

Fig. 3 Leaching (%) of different metals from crude $In(OH)_3$ in water-saturated $[Hbet][Tf_2N]$ as a function of reaction time at 80 °C. The concentrations of Sb, Se, Sn and Te were below the detection limit (<1 ppm) so these elements have been excluded from the graph.

Thermomorphic leaching/extraction in a $[Hbet][Tf_2N]–H_2O$ system

An alternative leaching system is proposed to improve the selectivity based on the same ionic liquid, but with an excess of water (>13 wt%) so that it forms a biphasic system at room temperature. This system combines leaching with metal extraction (separation) in one convenient step thanks to the thermomorphic properties of this ionic liquid-water system. The combined leaching/extraction process started by leaching the crude $In(OH)_3$ particles in a 1:0.5 or 1:1 wt/wt mixture of $[Hbet][Tf_2N]–H_2O$ at 60 or 80 °C (above the cloud point temperature) so that it formed one homogeneous phase. Afterwards, the solution was filtered at 60 or 80 °C and cooled again to room temperature so the mixture could phase separate. Besides varying the mass composition of the mixture and the temperature, the experiments were also executed for increasing periods of time (30 min, 1 h, 3 h). The total percentage leaching was determined by combining the measured metal content in the water phase and in the ionic liquid phase.

After cooling the filtered solution to room temperature, a gel-like precipitate appeared at the interphase under the

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following conditions: 1:0.5 wt/wt mixture of [Hbet][Tf_2N]–H_2O at 60 °C and 80 °C and 1:1 wt/wt mixture of [Hbet][Tf_2N]–H_2O at 60 °C after a 3h leaching (Fig. S2†). This precipitate was probably formed in the upper aqueous phase upon cooling. The pH of the aqueous phase was always between 1 and 1.5, excluding hydrolysis of the present metals. The composition of the precipitate on a piece of glass fiber filter was analyzed using SEM-EDS (Fig. S3†) and XRD (Fig. S4†). Two types of particles were observed on the SEM pictures: dark and bright. The dark particles consisted of Fe, As, In, Si, S and O. This can imply the formation of iron(III) arsenate ($FeAsO_4$) or indium(III) arsenate ($InAsO_4$).[32,33] The presence of sulfur cannot be explained by the formation of sulfides since the potential of the aqueous phase was always between 450 and 500 mV. According to Pourbaix, sulfides are present in solution below 223 mV at a pH of 1.[34] Crude $In(OH)_3$ contains 0.25 wt% of sulfur. The presence of silica (SiO_2) can explain the gel-like appearance of the precipitate.[35] Crude $In(OH)_3$ contains 0.17 wt% of silicon. It is also possible that the silica is attributed to the glass fiber filter. Another explanation for the gel-like appearance of the precipitate is the possibility that the metals form a metal complex with the betainium ligands that exhibit polymeric structures. Ag(I), Mn(II), Cu(II), Cd(II) and rare-earth complexes with betainium ligands that exhibit polymeric structures have already been reported in the literature.[23,31,36] When the filtered solution was cooled, phase separation occurred, consequently decreasing the water content of the ionic liquid phase, water that was previously preventing the indium from coordinating with the betainium ligands. The bright particles observed with SEM consisted of Pb, S and O, possibly indicating the presence of $PbSO_4$. The precipitate was further analyzed with XRD. The presence of $PbSO_4$ was confirmed alongside with an amorphous phase, $Fe((AsO_4)_{0.5}(SO_4)_{0.5}(OH)_{0.5}$ and compounds unable to identify with XRD.

The percentages leaching of crude $In(OH)_3$ in a 1:1 wt/wt mixture of [Hbet][Tf_2N]–H_2O at 60 or 80 °C as a function of the reaction time for the various elements are shown in Fig. S5† and Table S1†. The percentages leaching of the elements increase with temperature and reaction time. The leaching process itself shows very poor selectivity towards indium. Fig. 4 displays the percentages leaching for indium as a function of temperature and reaction time. The percentages leaching increase with increasing reaction time and temperature. In general, a temperature of 80 °C and a reaction time of 3 h seems to be the optimal condition for dissolution of indium. A percentage leaching for indium of 100% was obtained under these conditions. The solubility of [Hbet][Tf_2N] in the aqueous phase was 2.56 g L^{-1} at 25 °C.

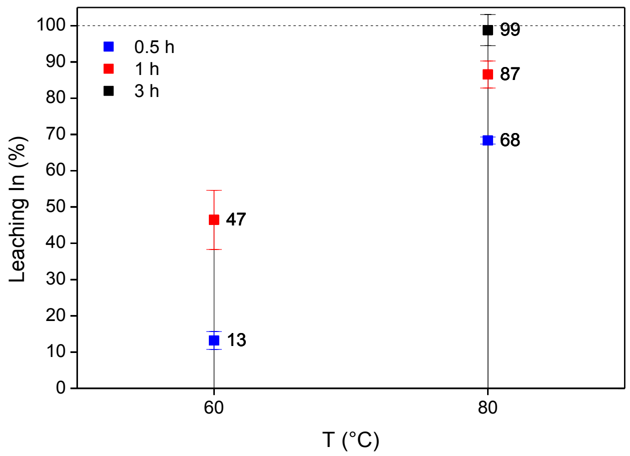

Fig. 4 Leaching indium (%) from dissolution of crude $In(OH)_3$ in a 1:1 wt/wt mixture of [Hbet][Tf_2N]–H_2O as a function of temperature and reaction time. The result at 60 °C after leaching 3 h is not shown because a precipitate was formed that contains indium.

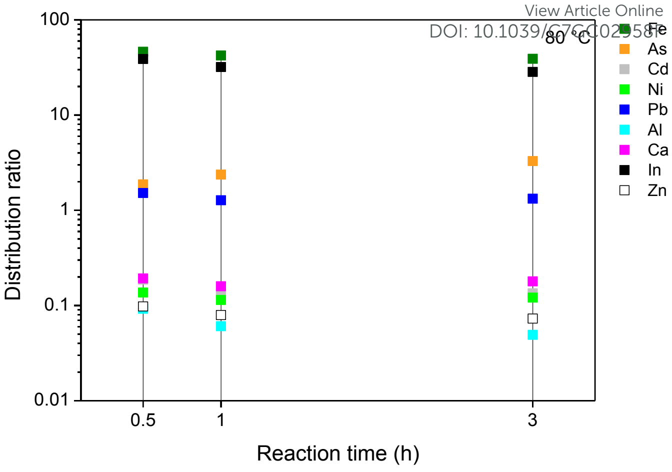

Fig. 5 Distribution ratio of the various elements in a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O system as a function of reaction time. A high distribution ratio corresponds to a greater affinity for the ionic liquid phase. The concentrations of Bi, Ga, Ge, Sb, Se, Sn and Te content were below the detection limit (<1 ppm) so these elements have been excluded from the graph.

Table 2 Separation factors (α) between indium and various elements for a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O system at 80 °C as a function of reaction time.

Element pair	1:1 wt/wt [Hbet][Tf_2N]–H_2O		
	0.5 h	1 h	3 h
In/Al	$(4.1 \pm 0.7)*10^2$	$(5.2 \pm 1)*10^2$	$(5.8 \pm 2)*10^2$
In/As	21 ± 8	13 ± 3	8.6 ± 1
In/Ca	$(2.0 \pm 0.8)*10^2$	$(2.1 \pm 1)*10^2$	$(1.6 \pm 0.3)*10^2$
In/Cd	$(2.0 \pm 0.5)*10^2$	$(2.5 \pm 0.2)*10^2$	$(2.1 \pm 0.1)*10^2$
Fe/In	1.2 ± 0.3[a]	1.4 ± 0.2[a]	$1.4 \pm 4*10^{-2}$[a]
In/Ni	$(2.8 \pm 1)*10^2$	$(2.8 \pm 0.6)*10^2$	$(2.4 \pm 0.3)*10^2$
In/Pb	26 ± 12	25 ± 8	22 ± 4
In/Zn	$(3.9 \pm 1.5)*10^2$	$(4.0 \pm 1.2)*10^2$	$(3.9 \pm 0.4)*10^2$

[a] These values represent the Fe/In ratio. According to IUPAC, by convention the ratio of the respective distribution ratios has to be chosen so that $\alpha > 1$.[46]

Next, the metal distribution over the two phases was studied by determining the distribution of the elements between the ionic liquid and the water phase. The leaching temperature of the process was set to 80 °C, because the leaching is sufficiently fast at this temperature in this water-saturated system. At 80 °C the thermomorphic ionic liquid-water system is also certainly homogeneous and the viscosity is also sufficiently low (0.87 ± 0.02 mPa s) and almost equal to pure water (0.89 mPa s at 25 °C).[26,37] Moreover, from previous results showed that 80 °C is the optimal leaching temperature for indium. Fig. 5 shows that the distribution ratios for the

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various elements are comparable across the reaction times. The low distribution ratios of aluminum, calcium, cadmium, nickel and zinc in combination with high separation factors ($\alpha \geq 100$) between these elements and indium(III), imply an easy separation (Fig. 5, Table 2, Table S2†). Separating indium completely from arsenic and lead is more difficult due to the lower separation factors between these elements and indium. Especially iron is very difficult to separate from indium. The separation factors between iron and indium are close to 1.

To improve the separation between indium and iron, iron(III) was reduced to iron(II). Ascorbic acid (vitamin C) was chosen as the reducing agent since it performs well in the Fe(III) reduction in aqueous solution and it has been used before in extraction systems with [Hbet][Tf_2N]. Moreover, ascorbic acid is cheap, non-toxic and from biological origin.[38-43] Addition of a stoichiometric amount of ascorbic acid reduces Fe(III) in an aqueous solution to Fe(II) (Fig. 6).

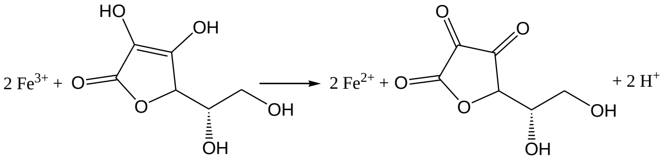

Fig. 6 Fe(III) to Fe(II) reduction by ascorbic acid with formation of dehydroascorbic acid.

Table 3 Percentages leaching (*%L*) and distribution ratios (*D*) of the elements and the corresponding separation factors (α) between indium and various elements for a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O and 1:1 wt/wt [Hbet][Tf_2N]– 0.01M ascorbic acid system at 80 °C and a reaction time of 3 h.

Element	1: 1 wt/wt [Hbet][Tf_2N]–H_2O			1:1 wt/wt [Hbet][Tf_2N]–0.01 M ascorbic acid		
	%L	*D*	α	*%L*	*D*	α
Al	81	0.049	$5.8*10^2$	80	0.029	$1.2*10^3$
As	68	3.3	8.6	79	1.7	24
Ca	100	0.18	$1.6*10^2$	100	0.19	$2.1*10^2$
Cd	92	0.13	$2.1*10^2$	82	0.12	$3.8*10^2$
Fe	94	39	1.4	80	0.052	$9.1*10^2$
In	99	28	1.0	100	39	1.0
Ni	100	0.12	$2.4*10^2$	87	0.079	$5.3*10^2$
Pb	87	1.3	22	87	1.4	28
Zn	59	0.073	$3.9*10^2$	54	0.058	$9.2*10^2$

A 0.01 M ascorbic acid solution in water is mixed together with the saturated [Hbet][Tf_2N] in a 1:1 wt/wt mixture at 80 °C containing crude $In(OH)_3$ particles (70 mg g^{-1}). From previous tests, it was established that these are the optimal indium leaching conditions. The percentage leaching and distribution factors for the elements and the corresponding separation factors between indium and the elements are compared in Table 3 for the 1:1 wt/wt [Hbet][Tf_2N]–H_2O and 1:1 wt/wt [Hbet][Tf_2N]–0.01 M ascorbic acid system. As expected, the biggest difference in results is seen for iron. The distribution ratio of iron is reduced by almost three orders of magnitude and consequently the separation factor between indium and iron increased by almost three order of magnitude. The affinity of iron(II) for the ionic liquid phase is far less than of iron(III), implying an easy separation between indium and iron. The separation factors of arsenic and lead also increased slightly which is only beneficial to the separation of these elements from indium, but they are still insufficient to completely eliminate co-extraction. The solubility of the ionic liquid in the aqueous phase is 2.63 g L^{-1} at 25 °C.

The effect of inorganic salts in the aqueous phase on the distribution of the metals was also tested. According to its position in the Hofmeister series, Tf_2N^- is one of the most hydrophobic anions. Therefore, anion displacement from the ionic liquid is very unlikely to occur when using [Hbet][Tf_2N].[38] A high salt concentration can therefore be used in the water phase without exchanging anions. The addition of inorganic salts has a twofold advantage. First, the water-soluble salt anions can form complexes with the metal ions and therefore change their affinity of the metal ions for the aqueous phase. Secondly, salt anions and cations can influence the solubility of the ionic liquid in the aqueous phase.[26,45] The salting-out effect for cations follows the order $NH_4^+ < K^+ < Na^+ < Li^+ < Ca^{2+} < Mg^{2+}$, whereas the salting-out effect of anions follows the order $ClO_4^- < I^- < NO_3^- < Cl^- < SO_4^{2-}$. Furthermore, a higher salt concentration increases the salting-in or salting-out effect of a salt, respectively.[26] Therefore, it was interesting to investigate to what an extent salts could influence the betaine content in the aqueous phase, thereby influencing the distribution of the different metal ions. The above experiments concerning the combined leaching/extraction process were repeated with the addition of 1 M of $MgCl_2$ to the aqueous phase. Only one kind of cation was tested since they have a minor influence on the distribution of the metal ions but greatly influence the solubility of the ionic liquid in the aqueous phase. The magnesium(II) cation was chosen to insure the largest salting-out effect.

The percentages leaching of indium from crude $In(OH)_3$ in a 1:0.5 or 1:1 wt/wt mixture of [Hbet][Tf_2N]–1 M $MgCl_2$ at 60 or 80 °C as a function of reaction time for the various elements are shown in Fig. S6† and Fig. S7†. An average percentage leaching of 96% and 93% was obtained for indium, when the leaching took place in the 1:0.5 wt/wt mixture and in the 1:1 wt/wt mixture of [Hbet][Tf_2N]–1 M $MgCl_2$, respectively. Small differences were also observed between the percentage leaching of the impurities when comparing the 1:0.5 wt/wt with the 1:1 wt/wt mixture. Adding 1 M $MgCl_2$ to the 1:1 wt/wt [Hbet][Tf_2N]–H_2O system has a positive effect on the kinetics. Similar percentages leaching as for a 3 h leaching in the 1:1 wt/wt [Hbet][Tf_2N]–H_2O system, were obtained in the 1:1 wt/wt [Hbet][Tf_2N]–1 M $MgCl_2$ system after leaching for only 30 min.

Next, the metal separation capability of the [Hbet][Tf_2N]–1 M $MgCl_2$ mixture was examined by determining the distribution of the elements between the ionic liquid and the 1 M $MgCl_2$ aqueous phase. It has to be noted that no homogeneous phase was formed below 100 °C due to the salting-out effect, therefor it cannot be considered as a thermomorphic leaching/extraction system at temperatures lower than 100 °C. Small differences were observed for the distribution ratios and separation factors of the various elements when varying the temperature or reaction time (Fig. 7, Fig. 8, Table 4 and 5). However, increasing the ionic liquid : aqueous phase ratio has a

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positive effect on the distribution ratio (Fig. 7, Fig. 8). The higher distribution ratios are probably a consequence of the fact at more water was present when the leaching was performed in the 1:1 wt/wt mixture of [Hbet][Tf_2N]–1 M $MgCl_2$ instead of in the 1:0.5 wt/wt mixture (Fig. S6† and S7†). When comparing the [Hbet][Tf_2N]–1 M $MgCl_2$ system with the [Hbet][Tf_2N]–H_2O system, it was observed that the distribution ratios of some elements have decreased and for other increased (Fig. 5, Fig. 7, Fig. 8). Adding $MgCl_2$ to the aqueous phase increases the affinity of aluminum, calcium, iron, gallium, nickel and zinc for the ionic liquid phase. The affinity of indium, arsenic, cadmium and lead for the ionic liquid phase decreases upon addition of $MgCl_2$. These changes in distribution ratios have a direct effect on the separation factors. As the difference in distribution ratios between indium and the impurities decreases, so does the separation factor, making it more difficult to separate indium (Table 4, Table 5). No formation of a precipitate was observed at the interphase under all the studied conditions. Although the water content of the ionic liquid phase decreased due to the salting-out effect, no precipitate was formed due to a lower indium loading of the ionic liquid phase.

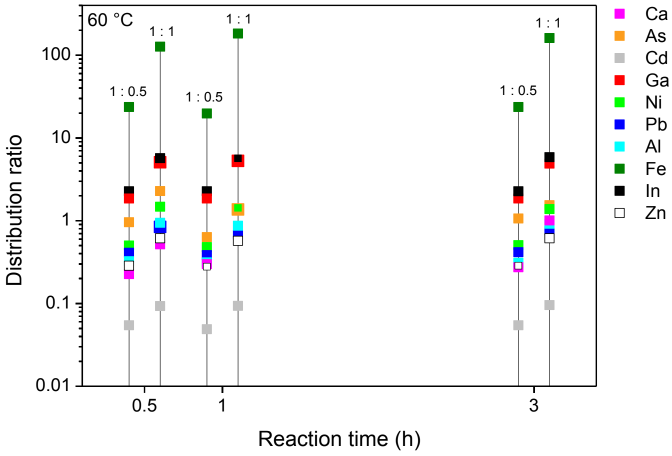

Fig. 7 Distribution ratio of the various elements in a biphasic 1:0.5 or 1:1 wt/wt [Hbet][Tf_2N]–1 M $MgCl_2$ system as a function of reaction time at 60 °C. A high distribution ratio corresponds to a greater affinity for the ionic liquid phase. The concentrations of Bi, Ge, Sb, Se, Sn and Te were below the detection limit (<1 ppm) so these elements have been excluded from the graph.

Table 4 Separation factors (α) between indium and various elements for biphasic 1:0.5 or 1:1 wt/wt [Hbet][Tf_2N]–H_2O system at 60 °C as a function of reaction time.

Element pair	1:0.5 wt/wt [Hbet][Tf_2N]–1 M $MgCl_2$			1:1 wt/wt [Hbet][Tf_2N]– 1 M $MgCl_2$		
	0.5 h	1 h	3 h	0.5 h	1 h	3 h
In/Al	7.0	7.3	7.3	6.1	6.5	6.4
In/As	2.4	3.6	2.1	2.5	4.2	3.8
In/Ca	10	7.6	8.3	11.0	10.0	5.8
In/Cd	42	47	42	61	61	61
Fe/In	10[a]	8.7[a]	10[a]	22[a]	32[a]	28[a]
In/Ga	1.2	1.2	1.2	1.1	1.1	1.2
In/Ni	4.5	4.7	4.5	3.9	4.0	4.2
In/Pb	5.5	5.9	5.5	6.8	8.4	7.7
In/Zn	7.9	8.2	7.9	9.3	9.9	9.5

[a] According to IUPAC, by convention the ratio of the respective distribution ratios has to be chosen so that α > 1.[46]

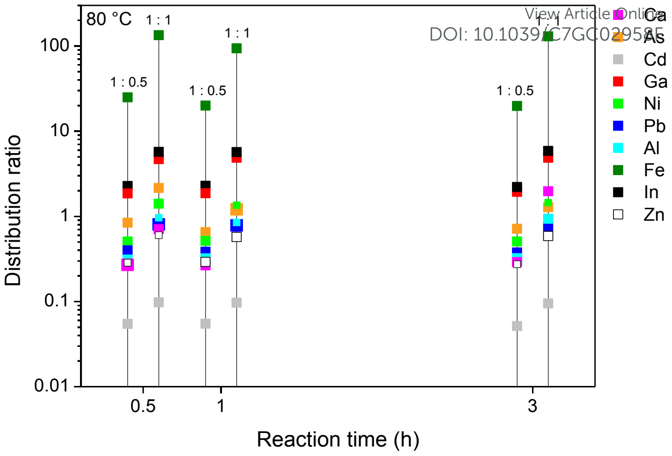

Fig. 8 Distribution ratio of the various elements in a biphasic 1:0.5 or 1:1 wt/wt [Hbet][Tf_2N]–1 M $MgCl_2$ system as a function of reaction time at 80 °C. A high distribution ratio corresponds to a greater affinity for the ionic liquid phase. The concentrations of Bi, Ge, Sb, Se, Sn and Te were below the detection limit (<1 ppm) so these elements have been excluded from the graph.

Table 5 Separation factors (α) between indium and various elements for biphasic 1:0.5 or 1:1 wt/wt [Hbet][Tf_2N]–H_2O system at 80 °C as a function of reaction time.

Element pair	1:0.5 wt/wt [Hbet][Tf_2N]–H_2O			1:1 wt/wt [Hbet][Tf_2N]–H_2O		
	0.5 h	1 h	3 h	0.5 h	1 h	3 h
In/Al	7.3	7.1	6.9	5.9	6.7	6.1
In/As	2.7	3.5	3.1	2.6	4.7	4.4
In/Ca	8.4	8.6	7.6	8.1	9.9	2.9
In/Cd	42	42	43	58	59	60
In/Fe	11[a]	8.8[a]	9.0[a]	23[a]	17[a]	23[a]
In/Ga	1.2	1.2	1.1	1.2	1.2	1.2
In/Ni	4.5	4.4	4.4	4.0	4.2	4.0
In/Pb	5.7	5.9	5.9	7.1	7.3	7.5
In/Zn	7.9	7.8	8.1	9.5	9.9	9.7

[a] According to IUPAC, by convention the ratio of the respective distribution ratios has to be chosen so that α> 1.[46]

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DOI: 10.1039/C7GC02958B

Adding a salt to the aqueous phase is necessary to decrease the loss of ionic liquid to the aqueous phase. Adding 1 M of $MgCl_2$ to the [Hbet][Tf_2N]–H_2O system has a negative effect on its separation capabilities. By decreasing the concentration of this magnesium salt, precipitation can still be avoided without losing significant amounts of indium to the aqueous phase. Also, changing the anion of the magnesium salt can change the distribution of indium across both phases. A 1 M $Mg(NO_3)_2$ solution was added to the aqueous phase, replacing the chloride salt. Under all conditions studied, a precipitate was formed at the interphase after cooling, probably due to the low water content of the ionic liquid phase as a consequence of the salting-out effect in combination with a high indium loading.

Metal scrubbing/stripping and recovery of ionic liquid

Scrubbing of the co-extracted metal ions and stripping of the indium was investigated after loading the [Hbet][Tf_2N] phase with metal ions by leaching crude $In(OH)_3$ in the 1:1 wt/wt [Hbet][Tf_2N]–H_2O system and 1:1 wt/wt [Hbet][Tf_2N]–0.01 M ascorbic acid system for 3 h. The 1:1 wt/wt [Hbet][Tf_2N]–1 M $MgCl_2$ system was not investigated due to the small separation factors obtained between indium and the impurities. First, scrubbing/stripping experiments were executed on the loaded ionic liquid phase obtained after leaching in the 1:1 wt/wt [Hbet][Tf_2N]–H_2O for 3 h. The scrubbing of the metal ions and the stripping of indium from the ionic liquid phase was tested by contacting the loaded ionic liquid phase obtained after leaching/extraction with different stripping agents: Milli-Q water, HCl (1.5 and 2 M), H_2SO_4 (0.75 and 1 M) and $MgSO_4$ (0.1 and 1 M) in a 1:1 wt/wt ratio. By contacting the ionic liquid phase with an acidic solution, the extraction equilibrium is shifted and (part of) the extracted complexes are decomposed and transferred to the aqueous phase. First, the effect of temperature was studied.

Table 6 shows the percentage scrubbing of the elements with Milli-Q water as a function of the temperature. Little difference in percentages scrubbing of the elements is observed with varying temperature. Next, the effect of acid concentration on the scrubbing percentages was tested using HCl and H_2SO_4 as scrubbing agents. From previous tests it was concluded that co-extraction of Pb was unavoidable. Scrubbing the ionic liquid phase with H_2SO_4 can lead to the formation of $PbSO_4$, which has a lower solubility in H_2SO_4 (mg L^{-1} range in 1 M H_2SO_4) than $PbCl_2$ in HCl (g L^{-1} range in 2 M HCl).[47] The precipitated $PbSO_4$ can be easily separated from the solution by filtration. Table 6 andTable 7 show the indium percentages stripping as a function of the HCl and H_2SO_4 acid concentration. It was noticed that 9.9% of the indium was stripped from the ionic liquid phase with Milli-Q water at 25 °C. Thus, acid-free scrubbing already accounts for a substantial indium loss. Although high percentages scrubbing were obtained for aluminum, cadmium, nickel and zinc, low concentrations (1-110 ppm) of these elements are present in the ionic liquid phase (Table 6). Among the co-extracted elements, arsenic and lead were only partly scrubbed, whereas iron is not scrubbed at all (Table 6). Table 7 shows the percentages scrubbing (*%S*) of the elements with HCl or H_2SO_4 as a function of the acid concentration. The percentages stripping of indium increased with increasing acid concentration. Indium is almost completely stripped at an acid concentration of 2 N. When indium is fully stripped, the other elements are also almost fully stripped. Upon scrubbing with H_2SO_4, a white $PbSO_4$ precipitate was formed, leaving only 4 ppm of lead in the aqueous phase. The scrubbing/stripping with an acid leads to higher losses of the ionic liquid to the aqueous phase than scrubbing/stripping with water (Table 8).

Table 6 The metal concentration in the organic phase after extraction or before scrubbing $[M]_{IL,0}$ and the percentages scrubbing (*%S*) of the elements with Milli-Q water as a function of the temperature. Scrubbing of the IL phase after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O system.

Element	$[M]_{IL,0}$ (ppm)	*%S*	
		25 °C	80 °C
Al	30±7	37	58
As	$2.0*10^{2}\pm7$	23	23
Cd	11±2	92	92
Fe	$1.1*10^{3}\pm0$	0	0
In	$(42\pm2)*10^{3}$	9.9	6.5
Pb	84±6	53	59
Zn	$1.1*10^{2}\pm0$	95	95

The concentration of Ca and Ni were below the detection limit (<20 ppm for Ca and <1 ppm for Ni) in the loaded ionic liquid phase so these elements have been excluded from the table.

Table 7 Percentages stripping/scrubbing (*%S*) of the elements with HCl or H_2SO_4 as a function of the acid concentration. Scrubbing of the IL phase obtained after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O system.

Element	*%S*			
	1.5 N HCl	2 N HCl	1.5 N H_2SO_4	2 N H_2SO_4
Al	85	64	94	94
As	95	98	99	99
Cd	92	92	93	93
Fe	58	97	98	99
In	96	99	92	98
Pb	92	97	99	99
Zn	98	98	99	99

Table 8 Solubility of the ionic liquid in the aqueous phase dependent on the scrubbing/stripping agent. Scrubbing of the IL phase after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf_2N]–H_2O system.

Srubbing/stripping agent	Solubility of the Ionic liquid at 25 °C (g L^{-1})
H_2O	2.1
1.5 N HCl	4.4
2 N HCl	4.4
1.5 N H_2SO_4	4.5
2 N H_2SO_4	4.9

Since the Pb(II) ions can be removed via formation of $PbSO_4$, the addition of $MgSO_4$ to the stripping reagent can be sufficient to shift the equilibrium of lead to the aqueous phase without the presence of acids. Stripping experiments were performed using 0.1 M and 1 M $MgSO_4$ solutions. Unfortunately, the ionic liquid had a gel-like appearance after stripping. The high water-content in this ionic liquid phase impeded proper phase separation and analysis.

Similar scrubbing/stripping experiments were also executed on the loaded ionic liquid phase obtained after leaching in the 1:1 wt/wt [Hbet][Tf$_2$N]–0.01 M ascorbic acid system. The loaded ionic liquid phase was contacted with different stripping agents: Milli-Q water, 2 M HCl and 1 M H_2SO_4 in a 1:1 wt/wt ratio. The percentages stripping as a function of the acid concentration are presented in Table 9. As seen in the 1:1 wt/wt [Hbet][Tf$_2$N]–H_2O system, scrubbing with water led to a substantial loss of indium (11%) considering that only elements present in low concentrations in the ionic liquid phase are scrubbed. Again, an acid concentration of 2 N was sufficient to ensure an almost quantitative stripping of indium. Upon scrubbing with H_2SO_4, a white $PbSO_4$ precipitate was formed, leaving only 3 ppm of lead in the aqueous phase. The solubility of the ionic liquid in the aqueous phase is shown in Table 10. Slightly higher values were obtained in comparison with the 1:1 wt/wt [Hbet][Tf$_2$N]–H_2O system.

Table 9 The metal concentration in the organic phase after extraction or before scrubbing [M]IL,0 and the percentages stripping/scrubbing (%S) of the elements with H_2O, 2 N HCl or 2 N H_2SO_4. Scrubbing of the IL phase after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf$_2$N]–0.01 M ascorbic acid system.

Element	$[M]_{IL,0}$ (ppm)	*%S*		
		H_2O	2 N HCl	2 N H_2SO_4
Al	23±5	92	95	97
As	$1.8*10^2±0$	44	98	99
Cd	9.6±3.5	>94	>95	>94
Fe	37±15	62	97	91
In	$(43±0.7)*10^3$	11	99	98
Pb	88±1	71	99	99
Zn	86±48	98	98	99

The concentration of Ca and Ni were below the detection limit (<20 ppm for Ca and <1 ppm for Ni) in the loaded ionic liquid phase so these elements have been excluded from the table. The concentrations of these elements in the ionic liquid phase were below the detection limit (<1ppm).

Table 10 Solubility of the ionic liquid in the aqueous phase dependent on the scrubbing/stripping agent. Scrubbing of the IL phase after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf$_2$N]–0.01 M ascorbic acid system.

Srubbing/stripping agent	Solubility of the Ionic liquid at 25 °C (g L^{-1})
H_2O	2.4
2 N HCl	5.9
2 N H_2SO_4	6.0

Since the stripping of indium with an acid is not selective in neither of the two systems, the pH of the aqueous phase after stripping was increased up to the point where indium hydrolysis starts, pH 3 according to Pourbaix,[34] for the given indium concentration. It should also be possible to remove some iron(III) as iron(III) hydroxide. Furthermore, arsenic is also prone to sorption on iron(III) hydroxides or can be precipitated as $FeAsO_4$.[48,49] The composition of the aqueous phase after prehydrolysis to pH 3 and the hydrolysis yield is shown in precipitated during Table 11. A pH of 3 is clearly too high when performing a prehydrolysis step on the aqueous phase obtained after stripping with 2 N H_2SO_4, since over 40% of indium is removed. A Pourbaix diagram considers pure, single metal, aqueous solutions at standard conditions and does not take into account non-ideal behavior of aqueous solutions, so in reality the behavior of systems can deviate from the one predicted by the Pourbaix diagram as seen for the aqueous phase obtained after stripping with 2 N H_2SO_4. Lowering the pH is an evident choice to decrease the amount of indium precipitated, but this in turn also lowers the prehydrolysis yield of the impurities. Contrary to the prehydrolysis of the aqueous phase obtained after stripping with 2 N H_2SO_4, none or a small amount of indium was precipitated when prehydrolysis was performed on the aqueous phase obtained after stripping with 2 N HCl. If the leaching/extraction prior to stripping and prehydrolysis was executed under reducing conditions (1:1 wt/wt [Hbet][Tf$_2$N]–0.01 M ascorbic acid system), less arsenic is precipitated during prehydrolysis. The amount of iron extracted to the ionic liquid phase under reducing conditions was much lower than without the addition of ascorbic acid. Since almost everything got stripped, the iron concentration in the aqueous phase after stripping was consequently also lower and less iron was present to precipitate arsenic as $FeAsO_4$ or for the sorption of arsenic onto iron. The arsenic yield may be lower, but no indium is lost when prehydrolysis was executed on the aqueous phase obtained after stripping the ionic liquid phase, originating from

Table 11 Metal concentration in the aqueous phase after prehydrolysis to pH 3 ([M]Aq,ph) and the hydrolysis yield. Aqueous phase obtained after scrubbing/stripping the loaded ionic liquid phase with an acid concentration of 2 N. Loaded ionic liquid phase obtained after 3 h leaching in a biphasic 1:1 wt/wt [Hbet][Tf$_2$N]–H_2O or 1:1 wt/wt [Hbet][Tf2N]–0.01 M ascorbic acid system.

Element	1:1 wt/wt [Hbet][Tf$_2$N]–H_2O system			
	2 N HCl		2 N H_2SO_4	
	[M]Aq,ph (mg L^{-1})	Yield (%)	[M]Aq,ph (mg L^{-1})	Yield (%)
Al	26	0	18	9.7
As	29	80	130	7.9
Cd	8	0	7	23
Fe	61	93	250	63
In	28000	6.9	17000	45
Pb	41	20	4	0
Zn	74	7.7	18	22

Element	1:1 wt/wt [Hbet][Tf$_2$N]–0.01 M ascorbic acid system			
	2 N HCl		2 N H_2SO_4	
	[M]Aq,ph (mg L^{-1})	Yield (%)	[M]Aq,ph (mg L^{-1})	Yield (%)
Al	23	0	29	0
As	100	32	150	0
Cd	9.7	0	11	0
Fe	32	96	41	94
In	33000	0	18000	42
Pb	44	0	3	10
Zn	85	10	120	0

The concentration of Ni was below the detection limit (<1 ppm) in the aqueous phase after stripping so this element has been excluded from the table.

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DOI: 10.1039/C7GC02958F

a leaching/extraction under reducing conditions, with 2 N HCl. Therefore, leaching/extraction under reducing conditions, stripping with 2 N HCl and prehydrolysis to a pH of 3 were preferred. The amount of indium precipitated during prehydrolysis on the aqueous phase obtained after stripping the ionic liquid phase, originating from a leaching/extraction under non-reducing conditions, with 2 N HCl can be reduced by fine-tuning the prehydrolysis pH.

After the prehydrolysis step to pH 3, the solution was filtered and the pH was increased further to fully precipitate the indium as indium(III) hydroxide. According to Pourbaix,[34] at a pH of 4.6 the indium concentration in solution should be equal to the detection limit of the ICP-OES, 1 ppm. However, 77 and 79 ppm of indium still resided in the aqueous solution after hydrolysis when stripping was performed using 2 N HCl and 2 N H_2SO_4, respectively, after extraction under non-reducing conditions. 130 and 1600 ppm of indium still resided in the aqueous solution after hydrolysis when stripping was performed using 2 N HCl and 2 N H_2SO_4, respectively, after extraction under reducing conditions. Fine-tuning the hydrolysis pH can decrease the amount of indium still present in the aqueous phase after hydrolysis, but care must be taken not to increase the coprecipitation of impurities. The composition of the indium(III) hydroxide produced is compared with that of crude indium(III) hydroxide in Table 12. The indium(III) hydroxide produced from an aqueous solution which has its origin in stripping the ionic liquid phase with 2 N HCl, has a higher purity than the one produced from an aqueous solution which has its origin in stripping the ionic liquid phase with 2 N H_2SO_4. A higher concentration of impurities was precipitated during prehydrolysis and less impurities were coprecipitated during hydrolysis. Also, the purity of the indium(III) hydroxide produced from an aqueous solution which has its origin in stripping the ionic liquid phase with 2 N HCl was very similar, independent if leaching/extraction was performed under reducing or non-reducing conditions. But as stated before, less indium is lost during prehydrolysis of an aqueous solution obtained after stripping the ionic liquid phase with 2 N HCl, when the ionic liquid phase was obtained after extraction under reducing conditions.

The ideal system comprises of a leaching/extraction of crude $In(OH)_3$ using a 1:1 wt/wt [Hbet][Tf2N]–0.01 M ascorbic acid system, followed by a stripping of the loaded ionic liquid phase with a 2 N HCl solution. A prehydrolysis step to a pH of 3 was performed on the aqueous phase obtained after stripping and ending with a hydrolysis step to a pH of 4.6 on the solution obtained after prehydrolysis. The purity of the crude $In(OH)_3$ was improved from 86.2% to 99.4%. A flowsheet of the proposed process is shown in Fig. 9.

Element	1:1 wt/wt [Hbet][Tf_2N]–H_2O system		
	2 N HCl	2 N H_2SO_4	
	Produced $In(OH)_3$	Produced $In(OH)_3$	Crude $In(OH)_3$
	wt%	wt%	wt%
Al	0.024	0.045	1.4
As	0.065	0.31	0.54
Bi	0.0007	0.0007	0.0018
Ca	0.0022	0.0094	0.20
Cd	0.0037	0.013	0.18
Fe	0.13	1.4	1.6
Ga	0.0016	0.0023	0.0046
Ge	0.0001	0.0002	0.0095
In	61	61	58
Ni	0.0002	0.0017	0.027
Pb	0.028	0.0052	0.26
Sb	0.0026	0.0046	0.035
Se	0.0002	0.0006	0.0027
Sn	<0.0001	0.0006	0.0028
Te	<0.0001	<0.0001	0.0015
Zn	0.058	0.13	5.0
Purity	99.48%	96.94%	86.23%

Element	1:1 wt/wt [Hbet][Tf_2N]–0.01 M ascorbic acid system		
	2 N HCl	2 N H_2SO_4	
	Produced $In(OH)_3$	Produced $In(OH)_3$	Crude $In(OH)_3$
	wt%	wt%	wt%
Al	0.030	0.057	1.4
As	0.19	0.24	0.54
Bi	0.0013	0.0009	0.0018
Ca	0.0030	0.0019	0.20
Cd	0.0046	0.010	0.18
Fe	0.056	0.071	1.6
Ga	0.0019	0.0019	0.0046
Ge	<0.0001	<0.0001	0.0095
In	57	51	58
Ni	0.0004	0.0004	0.027
Pb	0.016	0.0042	0.26
Sb	0.0011	0.0010	0.035
Se	0.0004	0.0001	0.0027
Sn	0.0004	0.0015	0.0028
Te	0.0001	0.0004	0.0015
Zn	0.065	0.088	5.0
Purity	99.36%	99.07 %	86.23%

Table 12 Metal composition of the produced and crude $In(OH)_3$ determined by ICP-OES in combination with the purity on metal basis.

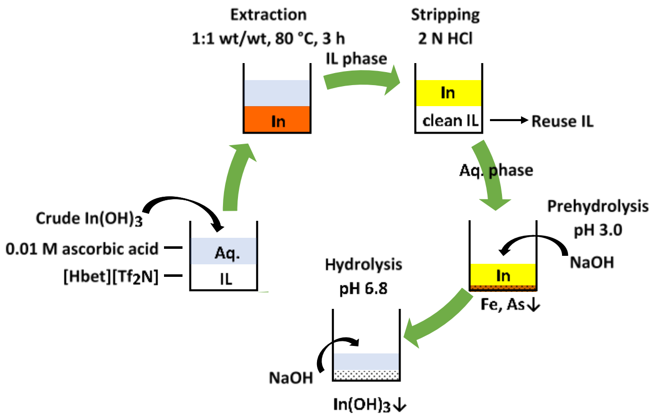

Fig. 9 Overview of the proposed purifying process for crude $In(OH)_3$, based on the selective dissolution and revalorization of indium with the protonated functionalized ionic liquid $[Hbet][Tf_2N]$.

Conclusions

The combined use of ionic liquid leaching and extraction described in this work provides a sustainable and efficient alternative for the recovery of indium from crude $In(OH)_3$ using the ionic liquid $[Hbet][Tf_2N]$. Leaching and solvent extraction were combined in one step by taking advantage of the thermomorphic properties of the $[Hbet][Tf_2N]–H_2O$ system. The mixture is homogeneous during leaching at 80 °C (temperature above the UCST) and biphasic with cooling to room temperature. This causes the dissolved metal ions to distribute themselves amongst the two phases. The optimal leaching/extraction conditions were determined to be a leaching time of 3 hours at 80 °C in a 1:1 wt/wt $[Hbet][Tf_2N]–H_2O$ mixture. The formation of a biphasic system induces metal separation where In(III) is extracted to the ionic liquid phase, whereas Al(III), Ca(II), Cd(II), Ni(II) and Zn(II) ions remain in the aqueous phase with high separation factors (α>100). Fe(III), As(V) and Pb(II) are co-extracted to the ionic liquid phase. The separation factor between indium and iron can be increased (α>1000) by addition of ascorbic acid to the aqueous phase, thereby reducing Fe(III) to Fe(II). A HCl solution was used to strip In(III) to the aqueous phase. The stripping step also regenerated at the same time the ionic liquid. Attempts to exclude any loss of ionic liquid to the aqueous phase using a salting-out method resulted in the formation of a gel-like precipitate. The solubility of the ionic liquid in the aqueous phase after leaching/extraction was 2.6 g L^{-1}. Depending on the conditions the solubility of the ionic liquid in the aqueous phase after stripping/scrubbing ranged between 2.1 and 6.0 g L^{-1}. This minor loss of the ionic liquid guarantees an almost full recovery of the ionic liquid which is required to avoid contamination of the aqueous phase. Therefore, this closed-loop system generates only small volumes of waste and offers selectivity, mild conditions and reusability. By combining a prehydrolysis and hydrolysis step on the aqueous phase obtained after stripping, the purity of the crude $In(OH)_3$ was improved from 86.2% to 99.4%.

Acknowledgements

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DOI: 10.1039/C7GC02958F

This research was supported by the Flemish Institute for the Promotion of Innovation by Science and Technology (IWT Vlaanderen) via a Baekeland PhD fellowship to Clio Deferm (IWT 130305) and by the Umicore Group Research & Development. ICP-OES analyses were executed in the analytical laboratory of Umicore Group Research & Development.

Conflicts of interest

There are no conflicts of interest to declare.

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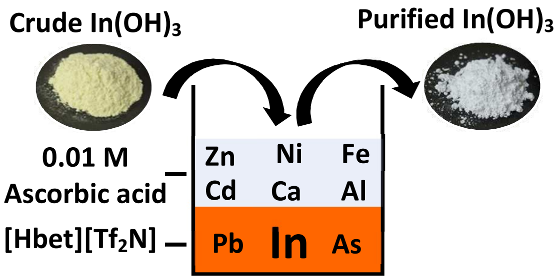
Table of Contents Graphic



A process was developed to purify crude $In(OH)_3$ using a combined leaching/extraction system based on the thermomorphic and acidic properties of the ionic liquid $[Hbet][Tf_2N]$.