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PAPER

Selective alkaline stripping of metal ions after solvent extraction by base-stable 1,2,3-triazolium ionic liquids

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Novel 1,2,3-triazolium ionic liquids with a high base stability were synthesized for use in solvent extraction of first-row transition elements and rare earths from chloride media. The synthesis of these ionic liquids makes use of a recently reported, metal-free multicomponent reaction that allows full substitution of the 1,2,3-triazolium skeleton. The physical and chemical properties of these ionic liquids are compared with those of a trisubstituted analog. Peralkylation of the 1,2,3-triazolium skeleton leads to ionic liquids with superior properties, such as a low viscosity, a low solubility in water and a higher thermal and base stability. Iodide and thiocyanate ionic liquids with the peralkylated cation were applied to the solvent extraction of metal ions, and their stability in alkaline media was exploited in the selective stripping of the metals from the loaded ionic liquid phase by alkaline solutions. EXAFS and Raman spectroscopy were performed to gain insight into the extraction mechanism. The applicability of these extraction systems was demonstrated in separations relevant for the recovery of metals from ores and end-of-life products: Fe(III)/Cu(II)/Zn(II) (copper ores, brass scraps) and Fe(III)/Nd(III) (rare earth magnets).

Introduction

Ionic liquids are solvents that consist entirely of ions.^{1,2} Imidazolium ionic liquids are one of the most popular classes thereof and have been extensively studied for decades with applications in both laboratory and industrial chemistry.^{2–4} Unfortunately, their limited stability towards even weak bases (due to carbene formation) precludes their use in a variety of applications in which alkaline conditions are required.⁵ Highly substituted imidazolium cations are comparatively more resistant to alkaline solutions, but are generally obtained in relatively poor yields via complex synthetic procedures.^{3,5,6} 1,2,3-Triazolium ionic liquids constitute a rather new class of ionic liquids that feature improved stability in alkaline media.⁷ Functionalized 1,2,3-triazolium ionic liquids can easily be obtained in high yields using a variety of synthetic procedures, including multi-component reactions and the very popular ‘click’ reactions derived from the Huisgen cycloaddition.^{7–9} Regardless of these benefits, the state of art concerning these ionic liquids remains rather limited. Most 1,2,3-triazolium ionic liquids described in prior art feature low degrees of substitution and have been used as solvents in organic chemistry or as organocatalysts.⁵ For instance, the base-catalyzed Baylis-Hillman reaction can efficiently be carried out in 1,3-dialkylated 1,2,3-triazolium ionic liquids.^{7,10} Tetrasubstituted 1,2,3-triazolium ionic liquids do exist in prior art, in the form of fused

A[−] = I[−], SCN[−]

Fig. 1. Structure of the 1,2,3-triazolium ionic liquids with cations [T1]⁺ (3,5-diethyl-1-(2-ethylhexyl)-4-methyl-1,2,3-triazolium) and [T2]⁺ (3-ethyl-1-(2-ethylhexyl)-5-methyl-1,2,3-triazolium).

bicyclic systems or chiral spiro tetracyclic systems and they are finding applications as reaction solvents or platforms for asymmetric catalysts.¹⁰ In addition, various poly(triazolium) ionic liquids have been described as well, as ion-conduction materials for electrochemical applications.^{10,11}

Imidazolium ionic liquids, along with quaternary phosphonium and ammonium ionic liquids, have been extensively used as environmentally benign solvents for the extraction of metal ions from aqueous solutions, both neatly and as diluents for conventional extractants.^{12,13} Their negligible vapor pressure, low flammability and high thermal and electrochemical stability have earned them a reputation as safe and sustainable replacements for volatile organic solvents.³ However, in many cases stripping of metal ions from undiluted ionic liquids is challenging, especially if the extraction mechanism involves the loss of ionic liquid cations to the aqueous phase or if metal-anion pairs are too strongly extracted by the ionic liquid phase.^{12,14–17} Stripping of the metal ions from the loaded ionic liquid phase, which is a requirement for the

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extraction process to be of any practical value, is often neglected in extraction studies with ionic liquids or is accomplished using expensive and difficult to recycle agents such as EDTA.^{12,16} If the affinity of the metal for the ionic liquid is sufficiently low, back-extraction is sometimes accomplished using several consecutive equilibrations with water or with weakly acidic solutions.^{12,16–18} While alkaline stripping agents can bind strongly to metals, base-induced precipitation of metals is complicated by the base-sensitivity of most of the ionic liquids currently used for solvent extraction. Stripping using alkaline solutions has been accomplished from quaternary phosphonium and ammonium ionic liquids with long alkyl chains, but these ionic liquids suffer from a high viscosity, and heating them to reduce the viscosity drastically increases the rate of degradation in basic conditions.^{19–23} These ionic liquids also have a lower inherent loading capacity than ionic liquids with shorter alkyl chains because of their large hydrophobic cations, although losses of ionic liquid to the aqueous phase are small.^{19,24,25}

In this paper, we present the solvent extraction of metal ions by novel, highly substituted 1,2,3-triazolium ionic liquids and subsequent selective stripping of metal ions from the loaded ionic liquid phase by alkaline aqueous solutions, resulting in the selective recovery of metals from mixed feeds. These 1,2,3-triazolium ionic liquids (structures shown in Fig. 1) retain the benefits of imidazolium ionic liquids over hydrophobic quaternary ammonium and phosphonium ionic liquids: relatively low viscosity and low molecular mass.²⁶ Moreover, it is shown that peralkylation of the 1,2,3-triazolium core results in ionic liquids with superior physical and chemical properties. These peralkylated 1,2,3-triazolium salts can conveniently be synthesized via a recent multi-component reaction developed by Dehaen and coworkers.⁹

Experimental section

Chemicals

4-Nitroaniline (98%) and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (99.99%) were purchased from Alfa Aesar (Karlsruhe, Germany). NaN_3 (99%), 3-pentanone (98%), 2-ethylhexylamine (99%), iodoethane (99%), anhydrous CuCl_2 (99%) and 4 Å molecular sieves were purchased from Acros Organics (Geel, Belgium). Sodium nitrite (99%), anhydrous FeCl_3 (98%) and anhydrous ZnCl_2 (98%) were purchased from Honeywell Riedel-de-Haën (Seelze, Germany). Acetone (99.98%) and toluene (99.99%) were purchased from Fisher Scientific Limited (Longborough, UK). Potassium thiocyanate (99%), NH_3 (25% in water), isopropanol (99.8%), $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (98%), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (99%) and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Sigma-Aldrich (Diegem, Belgium). $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (98.5%) was purchased from Baker Chemicals (Deventer, Netherlands). $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%) was purchased from Merck (Overijse, Belgium). $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), and $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Strem Chemicals Inc. (Newburyport, USA). $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) was purchased from Abcr GmbH (Karlsruhe, Germany). Single-element aqueous ICP standard solutions (1000 $\mu\text{g mL}^{-1}$), heptane (99%) and

anhydrous NaH_2PO_4 (98%) were purchased from Chem-Lab (Zedelgem, Belgium). Acetic acid (100.0%) and HCl 37% were purchased from VWR Chemicals (Leuven, Belgium). Silicone solution in isopropanol was purchased from Serva Electrophoresis (Heidelberg, Germany). All chemicals were used as received without further purification.

Instrumentation

Viscosities of the ionic liquids were determined using an Anton Paar Lovis 2000 M/ME rolling-ball viscometer. Densities were measured using an Anton Paar DMA 4500 ME densitometer. Elemental concentrations in the aqueous phase before and after extraction were measured using a total reflection X-ray (TXRF) spectrometer (Bruker S2 Picofox).²⁷ Thermogravimetric analysis (TGA) was performed using a TA instruments TGA Q500. The thermal regime comprised a ramp up to 120–130 °C, an isothermal drying phase for 30–60 minutes and a ramp at either 3 or 10 °C min^{-1} up to a final temperature of 350 or 550 °C. Infrared spectra were recorded on a Bruker Vertex 70 ATR-FTIR spectrometer with RAMIII Raman module, equipped with a 1064 nm laser source. The OPUS software package was used for analysis of the spectra. NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer or Bruker Avance 400 MHz spectrometer (operating at 75 MHz and 100 MHz for ^{13}C respectively). Samples for NMR spectroscopy were dissolved in deuterated chloroform purchased from Sigma-Aldrich (Diegem, Belgium). The Spinworks software package was used for analysis of the spectra. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements (used when matrix effects prevented accurate TXRF measurements) were performed on a PerkinElmer Optima 8300 device. Samples were shaken using a Nemus Life TMS-200 thermoshaker and centrifuged in a Heraeus Labofuge 200 centrifuge. pH measurements were performed with a Mettler Toledo SevenCompact pH-meter equipped with an InLab micro electrode. Ultrapure water (18 $\text{M}\Omega \text{ cm}^{-1}$) was used for TXRF sample preparation and was generated using a Sartorius Arium Pro system.

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the Cu K-edge (8978.9 eV) and Ni K-edge (8332.8 eV) were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were done in transmission mode using Ar/He gas filled ionization chambers. A brass sample holder with Kapton® windows and a flexible polymeric spacer (VITON®) with a thickness of 2 mm was used as a sample holder.

Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the Viper software package²⁸, were k^4 -weighted and Fourier transformed over the k -range from 2 to 13.7 Å⁻¹ (for Cu) and 2.65 to 12.125 Å⁻¹ (for Ni). The data were fitted using the ab initio code FEFF 7.0²⁹, which was

used to calculate the theoretical phase and amplitude functions that subsequently were used in the non-linear least-squares refinement of the experimental data. Fitting of the data with the model was performed in R-space. Estimated standard deviations are shown between parentheses and calculated by VIPER. S_0 was fixed for both fits at 0.95.

Synthesis

Triazolium iodide ionic liquids were synthesized by alkylation of the corresponding neutral 1,2,3-triazoles, which in turn were synthesized using a metal-free multicomponent reaction.⁹ 1,2,3-Triazolium thiocyanate ionic liquids were synthesized *via* a metathesis reaction of the corresponding iodide ionic liquid and aqueous potassium thiocyanate solution. A detailed description of the synthesis of these compounds is provided in the supplementary information.

Procedure for extraction experiments

Samples were prepared containing 500 μL of a 10 mM solution of the metal chloride of interest and 350 mg of the dry ionic liquid. Volume changes of the aqueous phase due to uptake of water by the ionic liquid were mathematically taken into account. Equilibration of the samples was achieved by shaking at 2000 rpm for 1 h at 60 °C. Phase separation after extraction was expedited by centrifugation. The aqueous phase of the sample before and after extraction was sampled (100 μL) and 20 μL of an 1000 $\mu\text{g mL}^{-1}$ internal standard was added (Ga(III) for Fe(III), Co(II), Ni(II), Cu(II) and Zn(II); Yb(III) for Y(III), La(III), Nd(III), Dy(III); Gd(III) for Yb(III)). The sample was diluted to 1 mL using ultrapure water. Sample carriers were pre-treated with a silicone solution in isopropanol (Serva) to avoid spreading of the droplet. A 2.5 μL aliquot of the sample was pipetted on the carrier and dried at 60 °C for 30 min. Each sample was measured for 500 s with the X-ray source operating at 50 kV and 300 mA. The percentage extraction (%E) is determined from the initial (n_i) and final (n_f) molar amounts of metal present in the aqueous phase:

$$\%E = \frac{n_i - n_f}{n_i} \times 100\% \quad (1)$$

The distribution ratio (D) is also determined from these results, according to:

$$D = \frac{c_{\text{IL},f}}{c_{\text{aq},f}} = \frac{(c_{\text{aq},i} - c_{\text{aq},f}) \cdot V_{\text{aq}}}{c_{\text{aq},f} \cdot V_{\text{IL}}} \quad (2)$$

Where $c_{\text{aq},i}$ and $c_{\text{aq},f}$ respectively represent the initial and final aqueous concentrations of the metal ion of interest, $c_{\text{IL},f}$ the final concentration of the metal ion in the ionic liquid, and V_{aq} and V_{IL} represent the aqueous and ionic liquid phase volumes, respectively. All extraction experiments were performed in duplicate.

Procedure for stripping experiments

Samples were prepared containing 500 μL of a 0.1 M solution of the analyte metal chloride and 350 mg of the dry ionic liquid. Equilibration and phase separation is performed as described for extraction experiments. The aqueous phase was pipetted off and 500 μL of a Na_2CO_3 (1 M or 3 M), NH_3 (1 M or ~13.4 M) or Na_2S (0.25 M) solution was added. Samples were equilibrated by shaking at 2000 rpm for 1 h at 60 °C. Samples with Cu(II) are equilibrated for 2 min when stripping with Na_2CO_3 (*vide infra*). The phases were then separated by centrifugation, also removing any precipitate from the liquid phase.

In case of back-extraction, the metal concentrations in the aqueous phase were measured using the procedure described above. If a precipitate was formed, the remaining metal concentration in the organic phase was determined by TXRF using standard addition to overcome matrix effects of the dense ionic liquid matrix. Isopropanol was used as a substitute for water to dilute the ionic liquid samples for TXRF, as the ionic liquids are not miscible with the aqueous standards used for the TXRF measurements. Two samples were prepared for each experiment. One contained 25 μL of the ionic liquid phase, diluted to 500 μL with isopropanol. The other sample also contained 20 μL of a 1000 $\mu\text{g mL}^{-1}$ standard solution of the analyte metal in addition to 25 μL of the ionic liquid phase, and was also diluted to 500 μL with isopropanol. The two samples were calibrated relative to each other using the iodide signals of the ionic liquid, by equating their intensity in each individual spectrum. Further sample preparation was identical to that for aqueous samples, as described above. The metal concentration in the ionic liquid before stripping was calculated from the concentration remaining after the extraction step, which was determined by TXRF using the procedure described above. The stripping percentage (%S) was finally calculated as follows:

$$\%S = \frac{n_i - n_f}{n_i} \times 100 \quad (3)$$

In equation (3), n_i and n_f are the molar amounts of metal present in the ionic liquid before and after stripping, respectively. The

Table 1. Physical properties of the 1,2,3-triazolium ionic liquids

	Kinematic viscosity (cSt) ^a	Water content (wt%)	TGA decomposition inflection point (°C) ^b	Solubility in water (wt%)	Density at 25 °C (g mL ⁻¹)
[T1][I]	19	21	240	3.3	1.173
[T1][SCN]	127	18	250	1.5 ^c	1.142 ^c
[T2][I]	195	12	231	7.0	n.d. ^e
[T2][SCN]	59	13	239	0.2 ^d	n.d.

^aAt 25 °C, water saturated. ^bRamp rate of 10 °C min⁻¹ 60 mol% solution in [T1][I], as used in extraction experiments. ^d60 mol% solution in [T2][I], as used in extraction experiments. ^eNot determined.

distribution ratio can again be defined according to equation (2). All extraction experiments were performed in duplicate.

Separation of Cu(II), Fe(III) and Zn(II)

A stock solution of CuCl_2 (65.5 mM), FeCl_3 (38.8 mM) and ZnCl_2 (41.4 mM) was used. A 350 mg aliquot of the ionic liquid was added to two samples containing 500 μL of this stock solution. The samples were equilibrated at 60 °C for 1 h by shaking at 2000 rpm, after which the phases were separated and the ionic liquid was scrubbed with 500 μL of a 0.5 M Na_2CO_3 solution. An equilibration time of 1 h at 60 °C was also applied to the scrubbing step. A pale red precipitate developed after centrifugation of the equilibrated mixture. The concentration of each metal was evaluated in the raffinate, the aqueous phase after stripping, the precipitate and the ionic liquid. The former three phases were measured with TXRF, using the same sample preparation as for the samples of individual elements. As there were three analyte metals present in the ionic liquid rather than one, gallium was used as a standard to allow the simultaneous determination of Fe, Cu and Zn. It should be noted, however, that large errors are present on TXRF results obtained in a dense matrix using a standardization method other than standard addition. These results should be interpreted only as a general indication of the scale of the metal traces present in the ionic liquid. The precipitate was dissolved in 1 M HCl and qualitatively analyzed using standardless TXRF.

Separation of Nd(III) and Fe(III)

The feed used in this demonstration was an aqueous solution of FeCl_3 (100 mM) and NdCl_3 (15 mM). A 175 mg aliquot of mixed iodide/thiocyanate ionic liquid was added to each sample containing 250 μL of this stock solution. The samples were equilibrated at 60 °C for 1 h by shaking at 2000 rpm, after which the phases were separated and the ionic liquid was scrubbed with 250 μL of a 3 M Na_2CO_3 solution. An equilibration time of 1 h at 60 °C was also applied to the stripping step. A brown precipitate developed after centrifugation of the equilibrated mixture. The concentration of each metal was determined in the raffinate and the ionic liquid. The raffinate was analyzed using ICP-OES, using a Nd and Fe external standard solution. A 100 μL sample of the aqueous phase was diluted to 10 mL by a 0.25 M HNO_3 solution in ultrapure water. An external standard solution was used to calibrate for each analyte. A quality control solution with known concentration was measured to verify the calibration and to determine the optimal wavelength and measurement mode (axial vs. radial) for accurate results. The ionic liquid was evaluated with TXRF, using a Mn internal standard (measuring time 200 s, source at 50 kV and 600 mA). The sample preparation and measurement method was identical to what was applied in the Fe/Cu/Zn-separation.

Results and discussion

Characterization of the ionic liquids

The peralkylated 1,2,3-triazolium ionic liquids based on the $[\text{T1}]^+$ cation (structure shown in Fig. 1) were found to have

superior physical and chemical properties for application in solvent extraction compared to the trisubstituted ionic liquids based on the $[\text{T2}]^+$ cation (structure shown in Fig. 1). Firstly, the miscibility of the ionic liquid phase and the aqueous phase was determined. The solubility of the ionic liquid in water was determined gravimetrically by saturating demineralized water with the ionic liquid, collecting a measured volume of the aqueous phase and removing the water by evaporation using a rotary evaporator and a Schlenk line (70 °C). The residue after evaporation was then weighed. To determine the water content in the water-saturated ionic liquid phase, TGA was used. Somewhat counter-intuitively, the peralkylated ionic liquid $[\text{T1}][\text{I}]$ was less soluble in the aqueous phase, but had a higher capacity for water than its less hydrophobic trisubstituted analog $[\text{T2}][\text{I}]$. The lower solubility of the ionic liquid in water can be rationalized in terms of its higher hydrophobicity, but the higher water uptake by the ionic liquid is likely a result of decreased cation-anion interaction and thus stronger hydration, an effect which is also observed in the free energy of mixing in imidazolium ionic liquids.³⁰ This reduced interionic interaction can be expected for the peralkylated cation, due to its lack of hydrogen bonding ability and increased steric hindrance. Substitution of the thiocyanate anion for the iodide anion has both the effect of decreasing anion-cation interactions and increasing the hydrophobicity of the anion, as can be derived from their relative positions in the Hofmeister series.³¹ Thus, for the ionic liquids with the $[\text{T1}]^+$ cation, a decrease in water uptake is observed upon substitution of the anion, possibly due to the hydrophobicity increase, while an increase in water uptake is observed for the $[\text{T2}]^+$ cation, which may result from the reduced cation-anion coulombic force.

A high viscosity is often a limiting factor for the application of ionic liquids in solvent extraction. In binary water-ionic liquid systems, the relevant parameter is the viscosity of the water-saturated ionic liquid. The lowest attained value was 18 cSt for $[\text{T1}][\text{I}]$ at 25 °C, which compares favorably to those of the commercially available ionic liquids Aliquat® 336 and Cyphos® IL 101.²¹ The low value for ionic liquids with the $[\text{T1}]^+$ cation can be attributed to weak cation-anion interactions and high water uptake. In correspondence to what was observed for the water content in the ionic liquid phase, replacement of the iodide anion by the thiocyanate anion results in a higher viscosity for $[\text{T1}][\text{SCN}]$ and a lower viscosity for $[\text{T2}][\text{SCN}]$, compared to their iodide analogs.

In contrast to the structurally similar imidazolium salts, 1,2,3-triazolium salts are inert towards bases of moderate strength. While the structures of the 1,2,3-triazolium salts discussed in this paper are optimized to attain low viscosities rather than high base stability, they are still sufficiently resistant to withstand long-term heating in contact with solutions of a pH of 12 to 13. ¹H NMR spectra showed that decomposition is due to dealkylation at the 3-position, presumably *via* a Hofmann elimination. The tetrasubstituted $[\text{T1}]^+$ ion was found to be more resistant, showing no decomposition after being heated to 60 °C for 24 hours at pH 13, whereas the $[\text{T2}]^+$ cation already displayed 12% 3-ethyl chain loss at 60 °C. When the temperature was raised to 90 °C, 9% of the $[\text{T1}]^+$ ionic liquid was

Fig. 2: Percentage extraction of various metal ions from 1 mM metal solutions in chloride medium, using [T1][I] (top) and [T1][SCN] (bottom) as extractants. A phase mass ratio of 7/10 organic/aqueous was used. The corresponding distribution ratios are indicated by blue diamonds.

found to lose its 3-ethyl chain. Nevertheless, this is a striking improvement over imidazolium ionic liquids. Dupont and coworkers used ^{13}C NMR spectroscopy to show that 3-ethyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide was virtually instantly and quantitatively deprotonated at the C-2 position upon addition of Cs_2CO_3 at 70 °C, yielding a non-ionic N-heterocyclic carbene.³²

Analogously, the $[\text{T1}]^+$ cation displayed a higher thermal stability than the $[\text{T2}]^+$ cation. TGA measurements on the iodide ionic liquids at a heating rate of 10 °C min⁻¹ produced a trace with two features: loss of water below 150 °C and a single sigmoidal loss of mass centered around 240 °C for [T1][I] and 231 °C for [T2][I]. The thiocyanate ionic liquids were more stable, with the mass loss respectively being centered around 250 °C and 239 °C for the tetrasubstituted and trisubstituted ionic liquids. Full TGA traces at ramp rates of 3 and 10 °C min⁻¹ are provided in the supplementary information (Fig. S5-S8).

Extraction studies

The four 1,2,3-triazolium ionic liquids were tested for solvent extraction of a series of first-row transition metals (Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)) and rare earths (Y(III), La(III), Nd(III),

Table 2. EXAFS data of $[\text{CuCl}_2]^-$ in $[\text{T2}][\text{I}]$.

Scattering path	N	r (Å)
Cu-Cl	2	2.11
Cu-Cl1-Cu-Cl2	2	4.22
Cu-Cl1-Cl2-Cu	2	4.22

Table 3. EXAFS data of $[\text{Ni}(\text{OH}_2)_2]^{2+}$ in $[\text{T2}][\text{I}]$.

Scattering path	N	r (Å)
Ni-O-Ni	6	2.05
Ni-O-Ni-O-Ni	6	4.10
Ni-O-O-Ni	6	4.10

Dy(III), Yb(III)). Extractions were carried out from feed solutions containing 10 mM of a single metal chloride, with a phase mass ratio of 7/10 organic/aqueous. The tri- and tetrasubstituted ionic liquids were found to give very similar results. Therefore, only the results of the tetrasubstituted ionic liquids, with favorable physical properties, are discussed in detail below. Data are shown in Fig. 2. Extraction data of the trisubstituted ionic liquids are provided in the supplementary information (Fig. S9 and S10).

The percentage extraction of the 3d transition metals by the iodide ionic liquids follows a trend correlating to the charge density of the species. With increasing atomic number, the ionic radius of the cation decreases and the charge density increases. Fe(III) has a higher charge density than Co(II) due to its higher oxidation state.

Cu(II) deviates from this trend, displaying the greatest extraction percentage in the series. Deviant behavior for Cu(II) is not uncommon in coordination chemistry: the Irving-Williams series predicts higher stability for Cu(II) complexes due to the Jahn-Teller effect.³³ However, Cu(II) is unstable in the presence of iodide, implying that Cu(II) is reduced to Cu(I) upon extraction.³⁴ This leads to the oxidation of I^- to I_2 , which readily adds to I^- to form I_3^- in iodide ionic liquids.³⁵ Raman spectroscopy of $[\text{T2}][\text{I}]$ loaded with CuCl_2 indicated the presence of oxidized iodine as the I_3^- ion, due to the appearance of a strong band centered around 113 cm⁻¹. The value of the X-ray absorption edge and EXAFS data for the ionic liquid $[\text{T2}][\text{I}]$ loaded with CuCl_2 correspondingly showed that copper is present as the $[\text{CuCl}_2]^-$ anion in the ionic liquid phase (see Table 2 and Fig. S11-S13, supplementary information). The stability and low charge density of this species most likely explains the efficient extraction of CuCl_2 . The extraction mechanism for CuCl_2 is thus postulated to be the following:

Trivalent rare-earth ions were, contrary to what is generally observed, preferentially extracted in reverse order of charge density.^{31,36} This is not entirely unique however, as this has been observed in several extraction systems before.^{36,37}

The extraction mechanism for most investigated non-redox-active metal ions is thought to be a simple ion-paired second-sphere solvation mechanism (*vide infra*):

It cannot be excluded that for some ions, such as Fe(III), chloro ligands may be bound to the extracted metal ion rather than being present as unbound anions.

EXAFS data of Ni(II) dissolved in [T2][I] showed the presence of 6 oxygen atoms coordinated to the central nickel ion, indicating that the extracted species is the aqua complex (see Table 3 and Fig. S14-S15, supplementary information). In further support of mechanism (4), we present the following observations. No increase in the amount of organic matter dissolved in the aqueous phase was found after extraction of ZnCl₂ under the conditions described earlier in this paragraph, implying that no cation exchange takes place (determined gravimetrically). An increase of about 40 mg/mL would be expected for a cation exchange mechanism. A very modest pH decrease was observed for the extraction of both LaCl₃ (0.01 M) and NiCl₂ (0.05 M) by [T2][I], respectively a decrease from 5.86 to 4.77 and from 5.75 to 4.57. The increased acidity of the aqueous phase is too modest for this to be an integral part of the extraction mechanism, as this corresponds to a difference in proton concentration of about 2.5×10^{-5} M. If the charge balance is retained by proton release into the aqueous phase (e.g. by hydrolysis of the metal aqua ions), two or three moles of protons should be released per mole of extracted metal ions. The aforementioned observations directly contradict every possible means of preserving the charge balance during extraction other than the co-extraction of chloride anions. Thus, the extraction must occur via mechanism (4). In view of this mechanism, the correlation between the percentage extraction and the charge density of the evaluated transition metals is proposed to be a result of the aqua ligands being more tightly bound with increasing charge density, thereby stabilizing the metal ions' charge more effectively.

Instead of pure thiocyanate ionic liquids, 60 mol% dilutions of the thiocyanates in the corresponding iodide ionic liquids were used for extraction studies to reduce the viscosity and to facilitate stripping of late first-row transition metals, which are tightly coordinated by the thiocyanate anion. The trisubstituted thiocyanate ionic liquid [T2][SCN] shows similar trends and %E values for yttrium and the rare earths as its iodide analog. The first-row transition metal ions are all nearly quantitatively extracted. This is also the case for the tetrasubstituted [T1][SCN]. This high extraction efficiency is caused by the strong affinity of the transition metal ions for the thiocyanate ligand. Lanthanides and yttrium have far less affinity for this ligand, which explains the relatively modest observed percentages extraction for these elements. In spite of this, a very different trend is observed for extraction of these elements by [T1][SCN] compared to the results for [T1][I]. While La(III) and Yb(III) remain almost entirely in the aqueous phase, an extraction percentage of 42% was found for the intermediate lanthanide Nd(III). Maxima in extraction efficiency of rare earths have been

Fig. 3: Percentage extraction by and stripping from [T1][I] of various metal ions, using 3 M Na₂CO₃ (top) and 1 M NH₃ (bottom) as stripping agents. The feed was a 0.1 M solution in chloride medium. A phase mass ratio of 7/10 organic/aqueous was used. The corresponding distribution ratios are indicated by blue diamonds. Stripping by back-extraction and precipitation are cumulative, the total percentage stripping is thus indicated by the sum of the dark and light grey bars in the upper graph.

observed before and have been attributed by some authors to the interplay of two simultaneous effects occurring as the ionic radius decreases, where one effect decreases the percentage extraction and the other increases the percentage extraction.^{36,38}

Increasing the aqueous feed stock concentration from 10 mM to 100 mM (0.1 M) alters the percentage extraction of divalent metals relatively little. The loading capacity of the ionic liquid for the investigated trivalent metals, which are more difficult to stabilize in hydrophobic media, is much smaller. This causes the percentage extraction to drop more rapidly upon increase of the metal concentration. This effect improves selectivity in extractive separations from iron and separations of rare earths and transition metals.

Stripping studies – [T1][I]

Stripping was investigated after extraction of metals from 0.1 M solutions. To aid the solubility of trivalent metal ions in the water/[T1][I] system, about 0.05 M HCl was added to the feed solution. The use of concentrated sodium carbonate solutions as stripping agents is possible when stripping from [T1][I] due to its high base stability compared to imidazolium ionic liquids. The

results of precipitation experiments with 3 M Na_2CO_3 are shown in Fig. 3. The behavior of various metals in these media varied strongly, in spite of the poor solubility of all transition metal and rare earth carbonates. Some metals can form either carbonate or hydroxo complexes at high carbonate concentrations, causing these elements to remain in solution.^{39–42}

Fe(III), Zn(II) and Ni(II) precipitate from the ionic liquid when contacted with a 3 M solution of Na_2CO_3 . The speciation of transition metal complexes precipitated by alkali carbonate solutions is determined by a wide range of ligand exchange equilibria. In addition to $\text{M}(\text{OH})_x$ and $\text{M}(\text{CO}_3)_x$, complex carbonate anions of the form $[\text{M}_n\text{O}_x(\text{OH})_y(\text{CO}_3)_z]^{m-}$ may also precipitate as their alkali metal salts. However, due to the very high ratio of CO_3^{2-} to metal in the systems described here (≥ 30), these equilibria are probably driven towards the formation of carbonate-rich species, allowing the precipitate to be approximated as $\text{M}(\text{CO}_3)_x$.^{41,42}

Co(II) and Cu(II) are not precipitated from the ionic liquid by Na_2CO_3 . Cu(II) is not stripped by precipitation, but is back-extracted to a significant extent (31%) when the loaded ionic liquid phase is treated with 3 M Na_2CO_3 . The blue, water-soluble complex, presumably $[\text{Cu}(\text{CO}_3)_2]^{2-}$, was only metastable in a sealed system, presumably due to slow reduction of the Cu(II) complex to a Cu(I) species. Samples with Cu(II) are thus equilibrated for only 2 min instead of 1 h, in order to prevent the decomposition of the Cu(II) species in solution. Back-extraction of Co(II) was comparatively poor in 3 M Na_2CO_3 : as little as 9% of the cobalt present in the ionic liquid was recovered.

As shown in Fig. 3, more efficient back-extraction of Cu(II) (59%) was obtained when an aqueous 1 M solution of ammonia was used as the stripping agent. After a second stripping step, a total of $65 \pm 4\%$ was recovered from the ionic liquid. The apparent distribution ratio (organic to aqueous) rapidly increases with the number of steps, preventing the final 30% of the remaining copper from being recovered using this method. It is assumed that initially, $[\text{CuCl}_2]^-$ is oxidized by I_3^- in this process. In ammoniacal media, the +II oxidation state is stabilized due to the formation of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex, of which the characteristic dark blue color was observed. The presumed mechanism for the stripping of copper with ammonia is shown in equation 6 below:

Stripping of cobalt using 1 M ammonia was even poorer (6%) and was not investigated further.

Near-quantitative stripping ($\%S = 97 \pm 1\%$) of copper was possible by contacting the ionic liquid with a 0.25 M Na_2S solution, which precipitates copper as Cu_2S . Raman spectroscopic analysis of $[\text{T2}][\text{I}]$ sequentially contacted with 0.1 M CuCl_2 and 0.25 M Na_2S solutions indicated that S(-II) is capable of reducing I_3^- back to iodide (see Fig. S12, supplementary information). The ionic liquid is thus restored to its initial state upon equilibration with Na_2S solution, *via* the following net reaction:

Stripping studies – $[\text{T1}][\text{SCN}]$ in $[\text{T1}][\text{I}]$

Stripping from 60 mol% $[\text{T1}][\text{SCN}]$ in $[\text{T1}][\text{I}]$ was evaluated using ammonia solutions. The results are shown in Fig. 4. Rare earths are omitted from these stripping studies due to low percentages extraction at high loadings, making quantization of the stripping percentage difficult. We propose the use of Na_2CO_3 solution as scrubbing agent to remove rare earth traces from ionic liquids (this is demonstrated for Nd(III) in a later paragraph). Fe(III) is also omitted from the series investigated in this paragraph. We demonstrate that Fe(III) can be stripped with Na_2CO_3 -solution in a following paragraph.

The stripping efficiencies of transition metals using a 1 M solution of ammonia was generally very low, with the exception of Zn(II) (68%). In order to achieve better stripping of transition metals, a higher concentration of ammonia (25%, ~13.4 M) was

Fig. 4: Percentage extraction and stripping from $[\text{T1}][\text{SCN}]$ (60 mol% dilution in $[\text{T1}][\text{I}]$) of various metal ions, using 1 M NH_3 (top) and 14 M NH_3 (bottom) as stripping agents. The feed was a 0.1 M solution in chloride medium. A phase mass ratio of 7/10 organic/aqueous was used. The corresponding distribution ratios are indicated by blue diamonds.

Fig. 5: Percentage extraction and stripping in the separation of Fe(III), Cu(II) and Zn(II) using the ionic liquid [T1][I] by extraction and selective stripping with 0.5 M Na_2CO_3 . The feed was a solution of CuCl_2 (65.5 mM), FeCl_3 (38.8 mM) and ZnCl_2 (41.4 mM). A phase mass ratio of 7/10 organic/aqueous was used. Stripping by back-extraction and precipitation are cumulative, the total percentage stripping is thus indicated by the sum of the dark and light grey bars.

used. However, only for Cu(II) an improvement in the percentage stripping was observed (46% vs. 2%). The percentage stripping of Co(II) and Ni(II) did not improve significantly upon increase of the ammonia concentration. This result suggests that these metals are probably already entirely present as ammine complexes at 1 M NH_3 , but that these complexes are more soluble in the ionic liquid than the aqueous phase. Increasing the concentration of ammonia is only expected to result in improved stripping if the speciation is not entirely shifted towards the ammine complex at low ammonia concentrations. The observation that Co(II) and Ni(II) undergo the thiocyanate to ammine ligand exchange reaction more readily than Cu(II) appears to conflict with literature data.^{34,43} However, one must take into consideration that the stability of complexes can be strongly affected by the medium in which they are dissolved, and that Co(II) is readily oxidized to Co(III) in ammoniacal media.^{34,43}

Recovery of Cu(II) from Fe(III) and Zn(II) chloride solutions

Zinc and iron are commonly present in copper sources. For instance, the common copper ore chalcopyrite (CuFeS_2)⁴⁴ often occurs in tandem with the zinc mineral sphalerite ($(\text{Zn,Fe})\text{S}$). This association is close to such an extent that it is referred to as the “chalcopyrite disease” by metallurgists wishing to extract the most valuable component of the minerals, namely copper.⁴⁵ Scrap copper in the form of brass will mainly contain zinc as an impurity, while iron is a common structural material which may also be present in secondary copper sources. The efficient separation of copper from iron and zinc is thus of utmost importance for copper mining from both primary and secondary sources.

[T1][I] is the most suitable of the synthesized ionic liquids for the extraction process. This ionic liquid has a higher affinity for Cu(II) than for the other metal cations due to a change in extraction mechanism, described above and shown in equation

Fig. 6: Separation of Fe(III) and Nd(III) using various ratios of ionic liquid [T1][SCN] in ionic liquid [T1][I] by extraction and stripping with 3 M Na_2CO_3 solution. The feed was a solution of FeCl_3 (0.1 M) and NdCl_3 (0.015 M). A phase mass ratio of 7/10 organic/aqueous was used.

4. The resulting Cu(I) complex in the ionic liquid is sufficiently stable to prevent the precipitation or back-extraction of Cu(II) when the loaded ionic liquid is contacted with 0.5 M Na_2CO_3 . Under these conditions, Fe(III) and Zn(II) do precipitate, leading to the near-quantitative removal of both. Subsequently, Cu(II) can be precipitated using Na_2S as described above, concurrently regenerating the ionic liquid in its reduced state (*vide supra*). The Cu_2S precipitate is a chemically idealized chalcocite copper ore and can thus be reduced to Cu^0 using current copper extraction techniques. Alternatively, a solvometallurgical process developed by Parker can be employed.⁴⁶

The results of this separation are summarized in Fig. 5. The extraction step already provides a certain degree of selectivity for copper, displaying an %E of 97%, as opposed to 77% for both Fe(III) and Zn(II). The Na_2CO_3 scrub is selective for Fe(III) and Zn(II), with no copper being detected in the precipitate. After scrubbing, the ionic liquid contained traces of Fe(III) and Zn(II), although 98% of both Fe(III) and Zn(II) had been removed.

Separation of Fe(III) and Nd(III)

Neodymium-iron-boron magnets are strong permanent magnets with a wide array of technological applications. As of 2007, they represent the majority of the market value for all permanent magnets (65%).⁴⁷ However, neodymium is included in the critical materials list published by the European Commission in 2010 as part of the light rare-earth group of elements.⁴⁸ Furthermore, the U.S. Department of Energy has categorized only three elements as having the highest short-term supply risk, a category which includes neodymium.⁴⁹

Various dilutions of the ionic liquid [T1][SCN] in the ionic liquid [T1][I] were used for the extraction and separation of Fe(III) and Nd(III). The extraction step provides the selectivity: the thiocyanate ionic liquids extract first-row transition metals efficiently *via* a mechanism likely involving coordination of the thiocyanate anion to the metal cation. Conversely, the rare earths display a much lower affinity for this ligand, resulting in lower percentages extraction. They are especially poorly

extracted from concentrated feed solutions. An aqueous 3 M solution of Na_2CO_3 was used as a non-selective stripping/scrubbing agent. The results are shown in Fig. 6.

The extraction step was found to be highly selective for Fe(III) over Nd(III). The highest selectivity was found for a 75 mol% dilution of $[\text{T}1][\text{SCN}]$ in $[\text{T}1][\text{I}]$. The scrubbing/stripping procedure removed a large fraction ($\geq 80\%$) of the extracted Fe(III) and nearly all of the extracted Nd(III). A linear decline in the efficiency of Fe(III) stripping is observed as a function of the mole fraction of thiocyanate salt in the ionic liquid. This can easily be rationalized by the strong coordinating nature of the thiocyanate anion. However, variation in the extraction efficiency of Fe(III) is not monotonous: a synergism is observed, and iron is quantitatively extracted by 75 mol% thiocyanate ionic liquid in iodide ionic liquid.

Conclusions

Tetrasubstituted 1,2,3-triazolium ionic liquids were prepared using the new multi-component reaction developed by Dehaen and coworkers.⁹ These 1,2,3-triazolium ionic liquids have more favorable properties than their trisubstituted analogues, including lower viscosity, higher thermal and base stability, and lower solubility in water. Furthermore, 1,2,3-triazolium ionic liquids feature improved base stability over the structurally similar and often studied imidazolium ionic liquids, while retaining their relatively low viscosity and low molar volume. It was demonstrated that tetrasubstituted 1,2,3-triazolium ionic liquids can be used for solvent extraction of first-row transition metals and rare-earth elements without dilution or the need of an additional extractant. Due to the resistance of the ionic liquids towards bases, the ionic liquid can be contacted with concentrated Na_2CO_3 and NH_3 solutions without degradation of the ionic liquid. Sodium carbonate, ammonia and sodium sulfide were used to demonstrate the selectivities and stripping percentages that can be obtained using basic stripping agents. Finally, the performance of the ionic liquid/base systems was established by applying a suitable ionic liquid/base combination to two industrially relevant separations: copper from iron and zinc and neodymium from iron.

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