

Supporting Information (SI)

Extraction Behavior and Separation of Precious and Base Metals from Chloride, Bromide, and Iodide Media Using Undiluted Halide Ionic Liquids

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1 Properties of Synthesized Ionic Liquids

Table S1 contains the density, viscosity and water content of the synthesized, water-saturated ionic liquids [A336][Cl], [A336][Br] and [A336][I]. Karl Fischer titration was used to determine the water content of the synthesized ionic liquids. Measurements were performed on a Mettler–Toledo C30S coulometric titrator for [A336][Cl] and [A336][Br]. For [A336][I], the measurement was performed on a Mettler–Toledo V30S volumetric titrator coupled to a Stromboli oven sampler due to incompatibility of the titrant with the iodide. Densities and viscosities were measured on an Anton Paar DMA 4500 M density meter equipped with a Lovis 2000 ME microviscometer unit.

Table S1: Properties of synthesized and water-saturated ionic liquids at 25 °C.

	[A336][Cl]	[A336][Br]	[A336][I]
Density (g cm ⁻³)	0.90073	0.95285	1.01082
Viscosity (mPa s)	103	182	537
Water content (wt%)	19.90	9.81	3.37

2 TXRF Analysis after Scrubbing

Total reflection X-ray fluorescence (TXRF) was used to confirm the absence of both Cu(II) and Fe(III) in [A336][Cl] and [A336][Br] after the implementation of the three-stage scrubbing procedure with water using O/A 1/3. Using TXRF detection limits in the ppb range can be expected for both Cu(II) and Fe(II). The spectra are displayed in Figure S1 and Figure S2, respectively. In addition to the absence of Cu(II) and Fe(III), the presence of both Pd(II) and Au(III) can also be confirmed. The spectrum of [A336][Br] is largely dominated by the broad and intense $K\alpha_1$ and

$K\beta_1$ lines of bromide. A small amount of chloride contamination can be observed as well due to the presence of chlorides in the feed solutions.

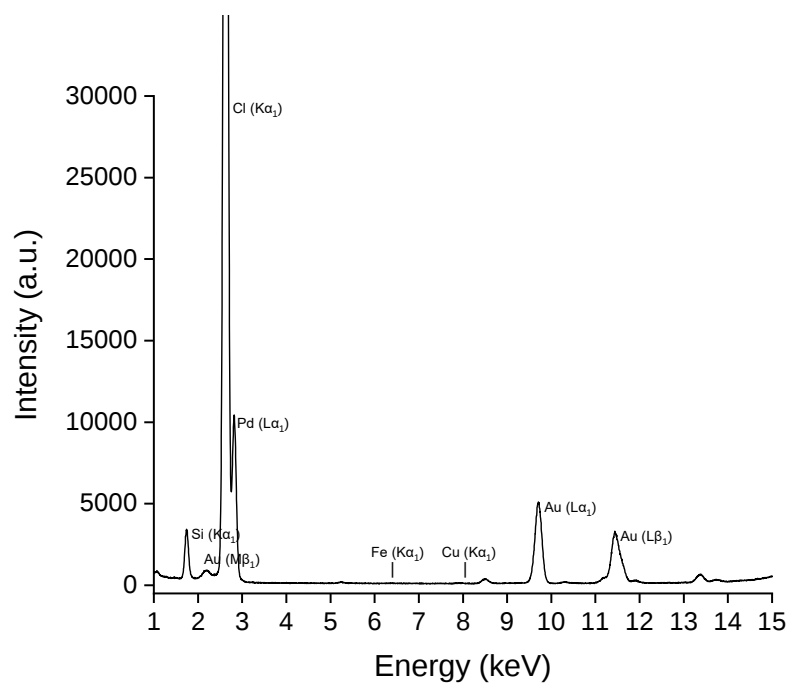


Figure S1: TXRF spectrum of the scrubbed [A336][Cl] ionic liquid.

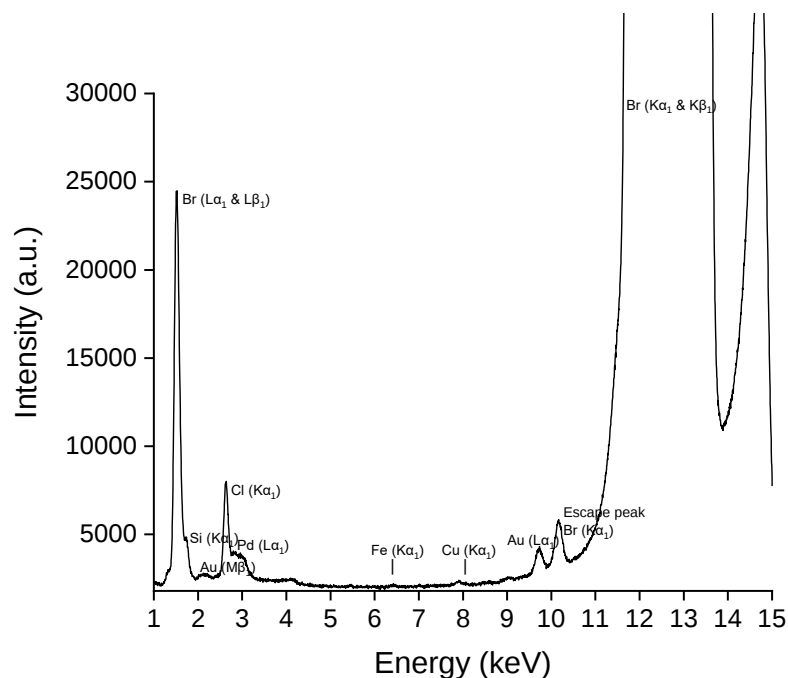


Figure S2: TXRF spectrum of the scrubbed [A336][Br] ionic liquid.

3 Additional Stripping Studies

3.1 Ethylenediaminetetraacetic acid (EDTA)

The influence of the EDTA concentration on the stripping efficiency of Pd(II) from [A336][Cl] is shown in Figure S3. A clear increase in efficiency is observed with increasing EDTA concentration, although quantitative stripping is not achieved. Also here, the use of EDTA shows a selectivity for Pd(II). In this experiment the equilibrium pH values were all below 9, which was the main cause for the relatively low stripping efficiencies. This highlights the importance of pH for the use of EDTA.

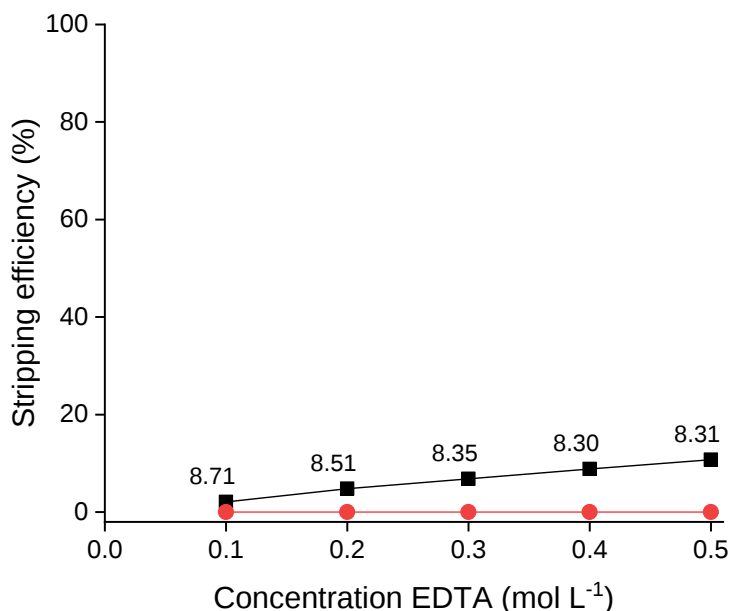


Figure S3: Stripping efficiency of 75 mg L⁻¹ Pd(II) (■) and 150 mg L⁻¹ Au(III) (●) from [A336][Cl] as a function of the EDTA concentration. The labels indicate equilibrium pH values. Conditions: 2500 rpm, 60 min, room temperature, O/A = 1.

3.2 Ammonia solution (NH_{3,aq})

The stripping behavior of Pd(II) and Au(III) from [A336][Cl] using NH_{3,aq} was studied more in detail. The stripping efficiencies of both elements as a function of NH_{3,aq} concentration are shown in Figure S4. A similar trend was observed as for [A336][Br] with Pd(II) being stripped first and Au(III) stripping occurring only at higher NH_{3,aq} concentrations. However, the stripping of Au(III) is significant at much lower NH_{3,aq} concentrations than for [A336][Br] due to the lower stability of the Au(III) chloride complexes compared to their bromide analogues.¹ This means that the operating window for the selective stripping of Pd(II) is more narrow for Aliquat 336 chloride. Pd(II) can be stripped relatively selectively using 0.1 mol L⁻¹ NH_{3,aq}, but the selectivity is very

sensitive to small changes in this concentration. As such, EDTA remains the best option for the selective stripping of Pd(II) from [A336][Cl].

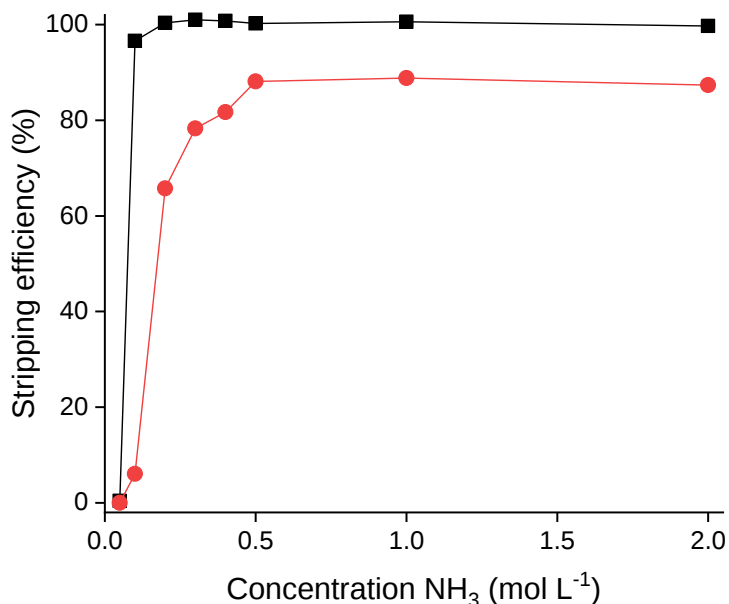


Figure S4: Stripping efficiency of 75 mg L^{-1} Pd(II) (■) and 150 mg L^{-1} Au(III) (●) from [A336][Cl] as a function of the NH_3 concentration. Conditions: 2500 rpm, 60 min, room temperature, O/A = 1.

Figure S5 shows the influence of the O/A volume ratio on the stripping of Pd(II) from [A336][Br] using $0.2 \text{ mol L}^{-1} \text{ NH}_{3,\text{aq}}$. At a phase ratio of 2/1, Pd(II) was stripped with 99% efficiency. At small O/A ratios, some Au(III) stripping was observed as well.

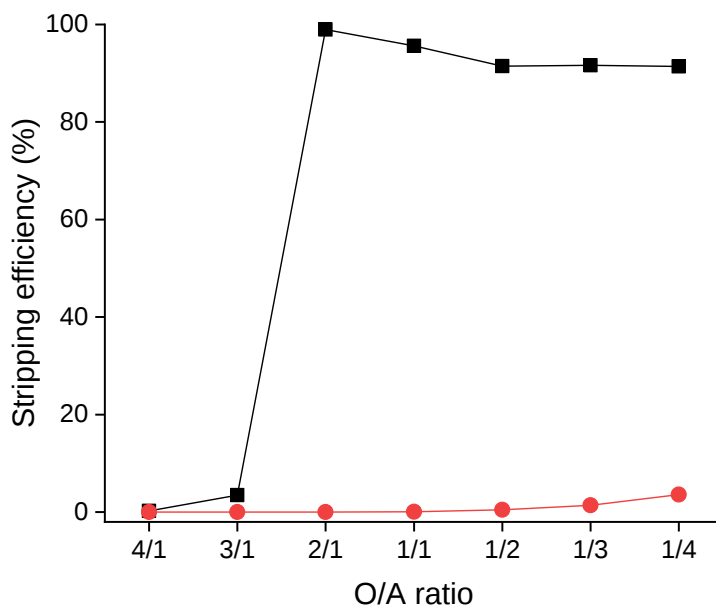


Figure S5: Stripping efficiency of 75 mg L^{-1} Pd(II) (■) and 150 mg L^{-1} Au(III) (●) from [A336][Br] using 0.2 mol L^{-1} $\text{NH}_{3,\text{aq}}$ as a function of the O/A ratio. Conditions: 2500 rpm, 60 min, room temperature.

3.3 Sodium sulfite (Na_2SO_3)

Figure S6 shows the influence of the O/A volume ratio on the stripping efficiency of Au(III) from both [A336][Cl] and [A336][Br] using 1.5 and 1.0 mol L^{-1} Na_2SO_3 , respectively. For [A336][Cl], the stripping of Au(III) is rather unaffected by the O/A volume ratio. In the case of [A336][Br], the stripping efficiency lowers at O/A ratios larger than 2/1.

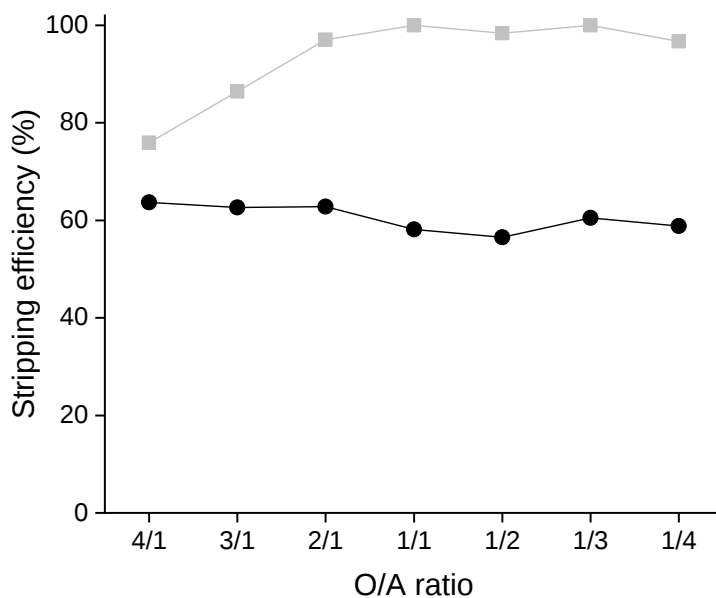


Figure S6: Stripping efficiency of 150 mg L^{-1} Au(III) from [A336][Cl] (●) and [A336][Br] (■) using 1.5 and 1.0 mol L^{-1} Na_2SO_3 respectively, as a function of the O/A volume ratio. Conditions: 2500 rpm , 60 min , room temperature.

4 References

- 1 A. Usher, D. C. McPhail and J. Brugger, *Geochim. Cosmochim. Acta*, 2009, **11**, 3359–3380.