

Hard-soft interactions in solvent extraction with basic extractants: comparing zinc and cadmium halides

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1. Synthesis of trioctylmethylammonium bromide and iodide

To produce trioctylmethylammonium bromide (TOMAB), trioctylmethylammonium chloride (TOMAC, 100 g) was mixed with toluene (200 mL) in a separatory funnel of 500 mL to speed up the mass transfer (by reduction of the viscosity) and to facilitate the phase disengagement. The organic phase was contacted five times with 200 mL of a 2 mol L⁻¹ KBr solution in the separatory funnel. Each time the funnel was intensively shaken for 15 minutes with an RS-1 separatory shaker from Lab Companion. Afterward, the phases were allowed to separate by gravity. After the conversion of TOMAC to TOMAB, the organic phase was washed two times with an aqueous 0.1 mol L⁻¹ Na₂SO₄ solution. The addition of Na₂SO₄ was required because no phase separation occurred when pure water was used for the washing step. Neither Na⁺ nor SO₄²⁻ are expected to significantly distribute to the organic phase.¹

To confirm that conversion of TOMAC to TOMAB was quantitative and to check whether no Na⁺ or K⁺ were present in the organic phase, the organic phase was measured with Total reflection X-ray fluorescence (TXRF) on a Bruker S2 Picofox TXRF spectrometer.² A qualitative measurement was sufficient because it was only necessary to check that the concentration of chloride in the organic phase was below the detection limit of 20 ppm. For this measurement, 2 μL of the organic phase was directly pipetted on a quartz glass sample carrier that was subsequently dried for 30 min at 60 °C. No Chloride, sodium, and potassium peaks were observed in the TXRF spectra.

After confirmation of full conversion of the chloride into the bromide salt, toluene was removed from the organic phase under reduced pressure with a rotary evaporator. Most of the remaining water was also removed by finishing the distillation for half an hour at 60 °C and below 1 mbar. The final product was solid, yellow TOMAB and was obtained in quantitative yield.

The procedure for the metathesis of TOMAC to trioctylmethylammonium iodide (TOMAI) was very similar to that for the synthesis of TOMAB. In this case, a 2 mol L^{-1} KI solution was used for the metathesis and three contacts with the organic phase turned out to be sufficient. Again, no chloride, sodium, or potassium peaks were observed by TXRF measurement. After removal of the solvent by rotary evaporation, a yellow-orange solid product, TOMAI, was obtained in quantitative yield.

2. Visual observation of TOMAI conversion to TOMAI₃



Figure S1. Color evolution of samples containing 0.2 mol L^{-1} TOMAI in toluene and aqueous solutions with 0.5 (left) to 5.0 (right) mol^{-1} HI and ZnI_2 (0.05 mol L^{-1}).

3. Raw Raman spectra of zinc(II) and cadmium(II) in aqueous HCl, HBr, and HI

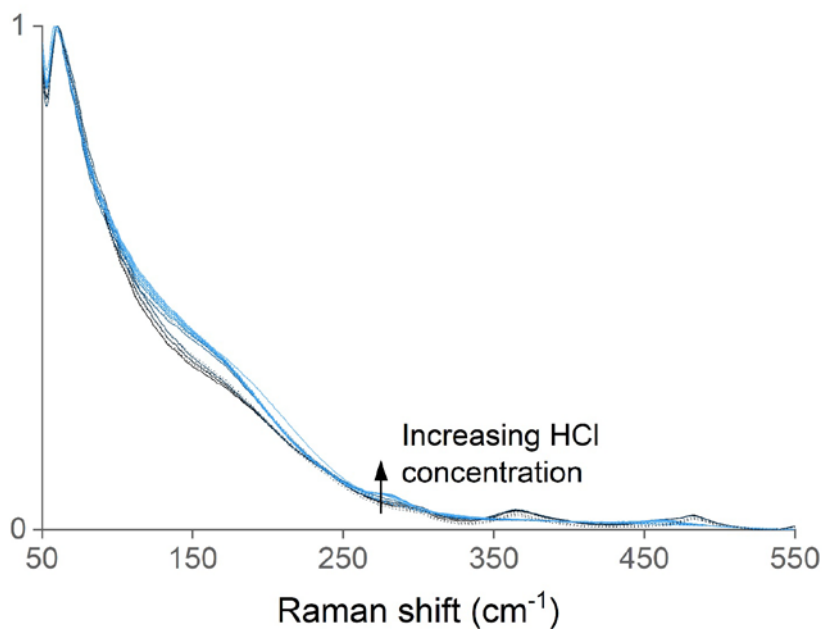


Figure S2. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Zn(ClO}_4)_2$ in 0 to 10.0 mol L^{-1} aqueous HCl. The full lines are the samples, while the dotted lines are the blanks that do not contain any zinc(II).

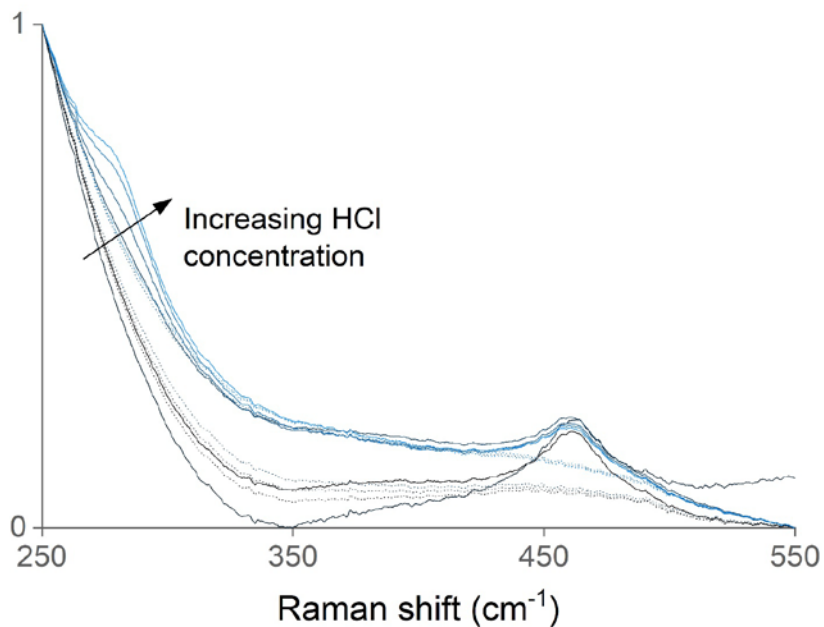


Figure S3. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Zn(ClO}_4)_2$ in 0 to 10.0 mol L^{-1} aqueous HCl. Remeasurement with emphasis on the octahedral region. The full lines are the samples, while the dotted lines are the blanks that do not contain any zinc(II).

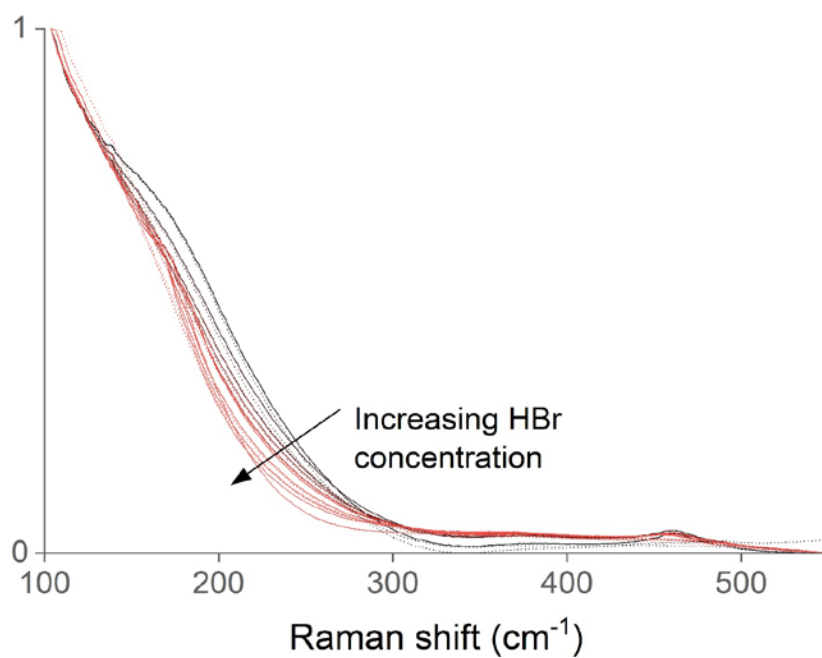


Figure S4. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Zn(ClO}_4)_2$ in 0 to 8.25 mol L^{-1} aqueous HBr. The full lines are the samples, while the dotted lines are the blanks that do not contain any zinc(II).

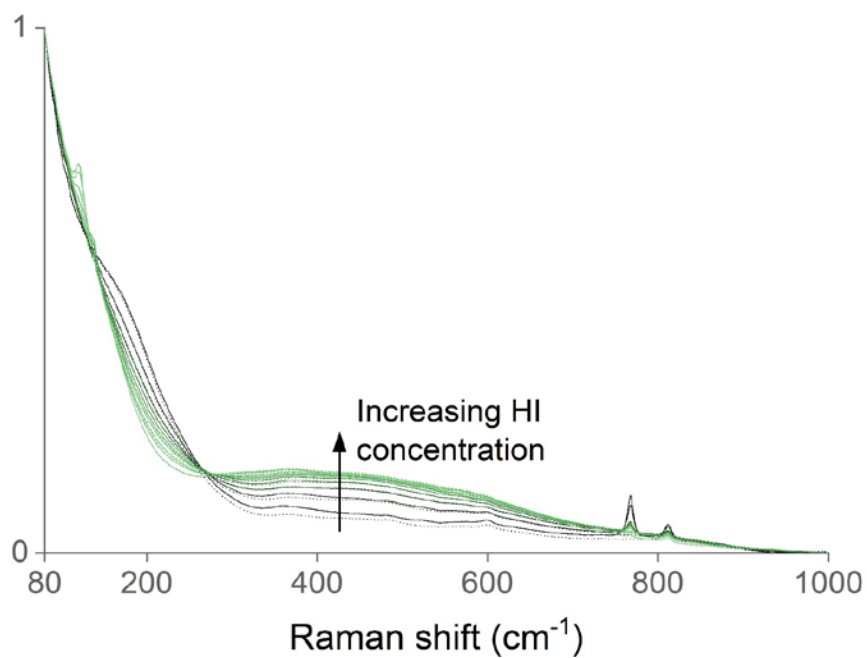


Figure S5. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Zn(BF}_4)_2$ in 0 to 7.20 mol L^{-1} aqueous HI. The full lines are the samples, while the dotted lines are the blanks that do not contain any zinc(II).

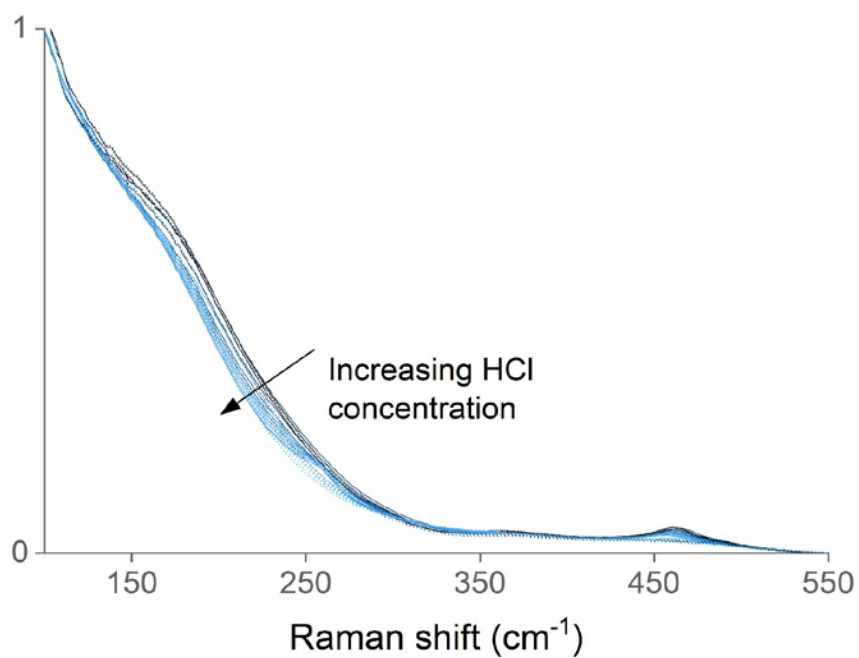


Figure S6. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Cd}(\text{ClO}_4)_2$ in 0 to 10.0 mol L^{-1} aqueous HCl. The full lines are the samples, while the dotted lines are the blanks that do not contain any cadmium(II).

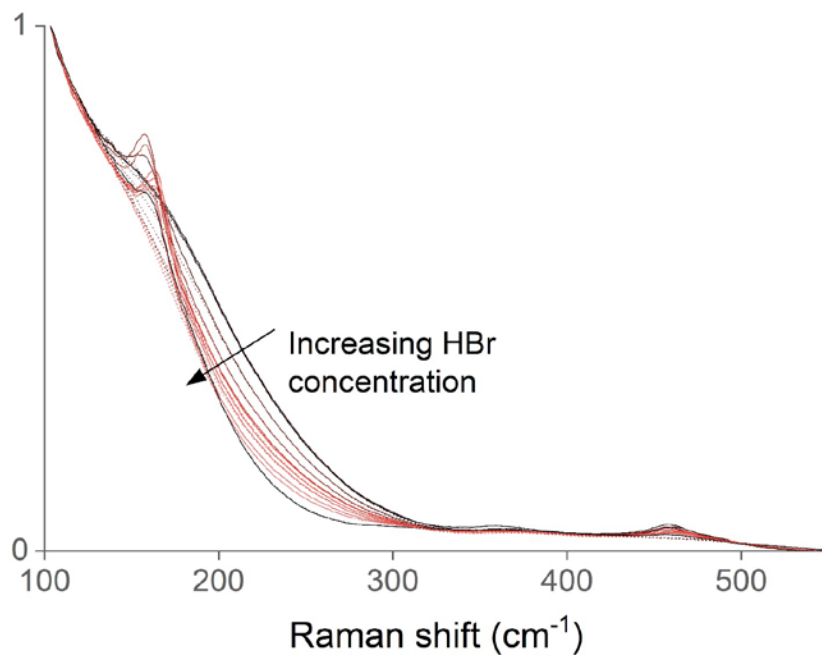


Figure S7. Normalized Raman spectra of $0.05 \text{ mol L}^{-1} \text{ Cd}(\text{ClO}_4)_2$ in 0 to 8.25 mol L^{-1} aqueous HBr. The full lines are the samples, while the dotted lines are the blanks that do not contain any cadmium(II).

4. UV-VIS absorption quantification of TOMAI conversion to TOMAI₃

The conversion of TOMAI to its triiodide form (TOMAI₃) was quantified by UV-VIS absorption spectroscopy on an Agilent Cary 6000i spectrophotometer and Cary WinUV software. All spectra were recorded with 1 mm quartz suprasil cuvettes. An external calibration curve was created by dissolving I₂ (99.5%; Acros Organic, Geel – Belgium) in 0.2 mol L⁻¹ TOMAI in toluene. The samples were measured directly after the extraction of 0.05 mol L⁻¹ ZnI₂ in different HI concentrations by 0.2 mol L⁻¹ TOMAI in toluene. These samples were diluted with 0.2 mol L⁻¹ TOMAI in toluene until an acceptable absorbance was reached for quantitative analysis. The dilution factor and results can be found in Table S1.

Table S1. UV-VIS absorption results for the conversion of TOMAI to TOMAI₃ after extraction of 0.05 mol L⁻¹ ZnI₂ from different HI concentrations by 0.2 mol L⁻¹ TOMAI in toluene.

[HI] _{aq,initial} (mol L ⁻¹)	Dilution factor	Absorbance at 367 nm	[TOMAI ₃] (mol L ⁻¹)	TOMAI conversion (%)
0.5	1	1.3109	0.0005	0.26
1.0	10	0.5877	0.0023	1.17
2.5	100	0.4290	0.0171	8.53
4.0	100	0.7045	0.0280	14.0
4.5	100	0.7942	0.0316	15.8
5.0	200	0.4406	0.0351	17.5

5. ¹³C NMR of TOMAI organic phase after phase splitting

The *in-situ* formed I₂ can react with toluene under certain conditions, forming a iodotoluene. This changes the structure of the solvent, which might influence the extraction characteristics and phase behavior of the system. The occurrence of such reactions was investigated in the SX experiments with 4 or more mol L⁻¹ HI because of the unexpected phase disengagement in these systems. ¹³C NMR was used to detect any presence of iodinated toluene, but no relevant NMR

peaks were identified in both the top and bottom organic phase. A Bruker Avance III HD with Ascend 400 magnet operating at 100 MHz was used for the measurements. The samples (400 μL) were mixed with CDCl_3 (100 μL) and internally referenced to tetramethylsilane. The inverse gated zgig30 program was used for the measurements of and the Spinworks 4.2.9 software was used to analyze the spectra.

5. References

- (1) Dupont, D.; Depuydt, D.; Binnemans, K. Overview of the Effect of Salts on Biphasic Ionic Liquid/Water Solvent Extraction Systems: Anion Exchange, Mutual Solubility, and Thermomorphic Properties. *J. Phys. Chem. B* **2015**, *119* (22), 6747–6757.
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- (2) Vander Hoogerstraete, T.; Jamar, S.; Wellens, S.; Binnemans, K. Determination of Halide Ions in Solution by Total Reflection X-Ray Fluorescence (TXRF) Spectrometry. *Anal. Chem.* **2014**, *86* (3), 1391–1394. <https://doi.org/10.1021/ac403583u>.