

Enhancing Uranium Extraction Efficiency Using Protonated Amines and Quaternary Ammoniums-Based Ionic Liquids: Mechanistic Insights and Nonlinearities Analysis

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ESI 1 Synthesis of protonated tertiary amines and quaternary ammoniums

- Synthesis of [TOAH]₂[SO₄] and [Aliquat336]₂[SO₄]

In a 100 mL round bottom flask cooled at 0 °C (ice bath), 98% mass. sulphuric acid (1.19 mL, 18.6 mol.L⁻¹) was added dropwise to a 98% pure TOA solution (20 mL, 2.22 mol.L⁻¹) or an Aliquat 336 solution (20 mL) under stirring. The remaining solution was solubilized in absolute ethanol (50 mL) in order to remove water. Alcohol and solubilized water were further removed using a rotary evaporator. The residual liquid was dried at 60 °C under vacuum (50 mbar) for 24 hours to obtain each compound, [TOAH]₂[SO₄] as a pale-yellow viscous (η = 4.9 Pa.s at 25 °C) oil and [Aliquat336]₂[SO₄] as a colorless viscous oil, with 100% yield.

- Synthesis of [TOAH][NTf₂] and [Aliquat336][NTf₂] by anionic metathesis.

10 g of [TOAH]₂[SO₄] (0.012 mol) or 10 g of [Aliquat336][Cl] (0.024 mol) was mixed with an aqueous solution of 1 mol.L⁻¹ LiNTf₂ (25 mL) in a 50 mL tube by mechanical stirring at room temperature, after which two phases were separated from each other by centrifugation (8000 rpm) for 20 minutes at 25 °C. The anion exchange is quantitative. The ionic liquid phase separated from the aqueous phase was washed 10 times with deionized water. Evaporation steps indicated above were further applied. The product was finally dried at 60 °C under vacuum for 24 hours to obtain [Aliquat336][NTf₂] and [TOAH][NTf₂] as, respectively, pale and brown liquid in quantitative yield. The [TOAH][NTf₂] product was not further purified in order to avoid additional step making the process more cumbersome.

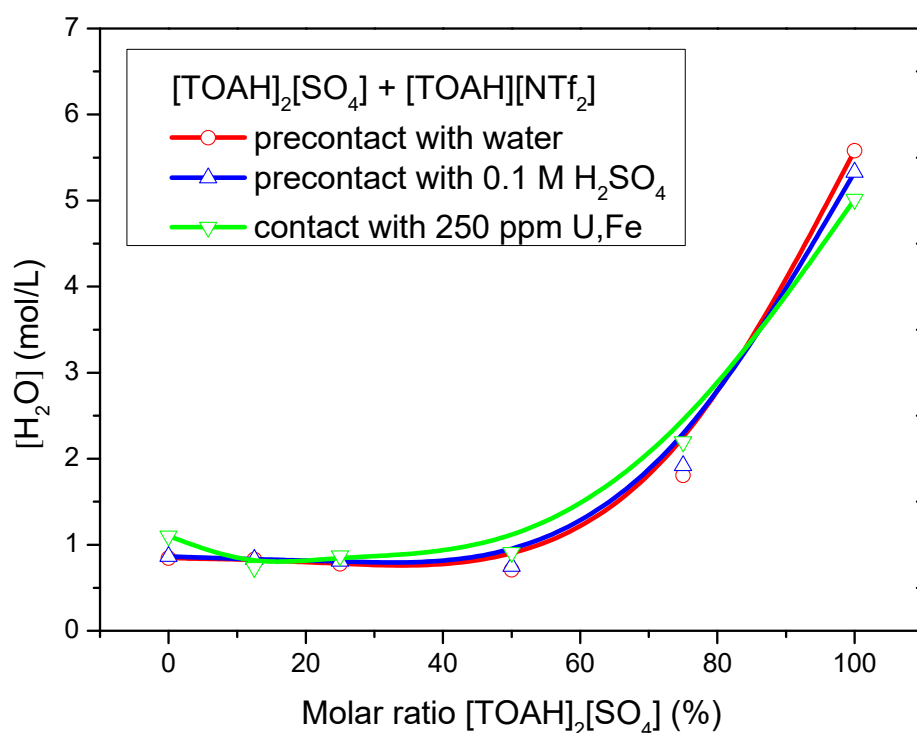


Figure S1. Water content of $[\text{TOAH}]_2[\text{SO}_4] + [\text{TOAH}][\text{NTf}_2]$ as a function of $x[\text{TOAH}]_2[\text{SO}_4]$ estimated after contact with water (red), after contact with 0.1 mol/L sulfuric acid containing 0.1 mol/L ammonium sulfate (blue) and after contact with 0.1 mol/L sulfuric acid containing 250 ppm U(VI), 250 ppm Fe(III) and 0.1 mol/L ammonium sulfate (green).

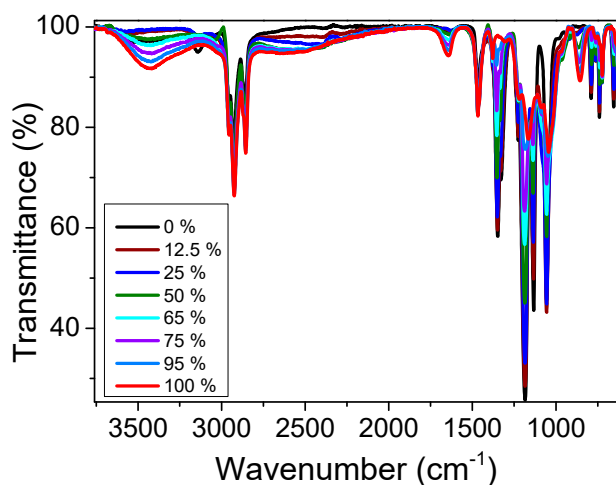


Figure S2 FT-IR spectra of different $x[\text{TOAH}]_2[\text{SO}_4]$ ratios brought into contact with aqueous phase containing 2500 ppm U(VI), 0.1 mol.L⁻¹ sulfuric acid and 1 mol.L⁻¹ ammonium sulphate. A/O = 4.

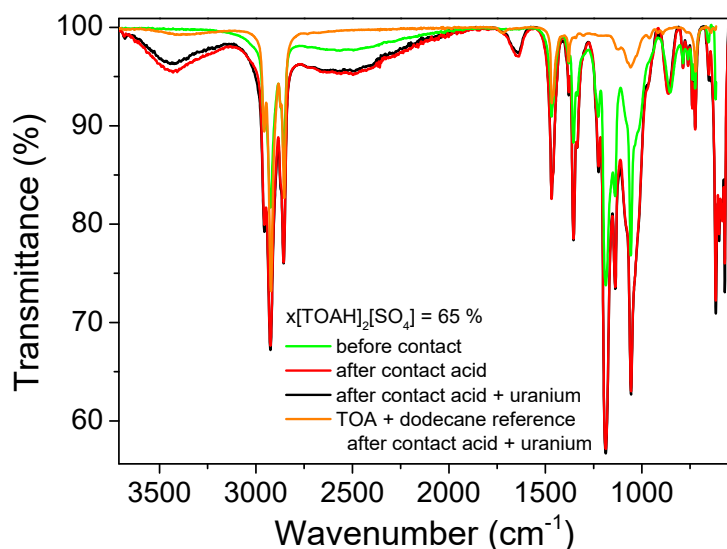


Figure S3. Infra-red spectra of $x[\text{TOAH}]_2[\text{SO}_4] = 65\%$ mixture before contact (dry), after contact with acid (0.1 mol/L sulfuric acid and 1 mol/L ammonium sulfate) and acid + uranium (0.1 mol/L sulfuric acid containing 2500 ppm U(VI), 250 ppm Fe(III) and 1 mol/L ammonium sulfate) aqueous solution. Orange spectra is TOA + dodecane reference system after contact with acid + uranium solution (0.1 mol/L sulfuric acid containing 2500 ppm U(VI), 250 ppm Fe(III) and 1 mol/L ammonium sulfate).

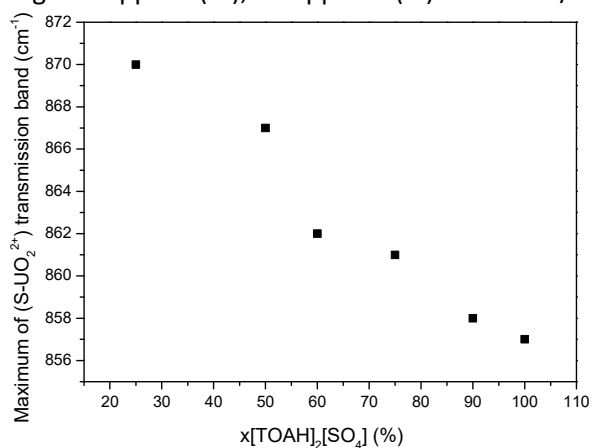


Figure S4. Illustration of linear shift towards the lower frequencies of the transmission band maximum with the molar ratio of sulphate, indicating that sulphate becomes increasingly free.