Simulating of synergistic phenomena in ionic solutions encountered in extraction uranium process

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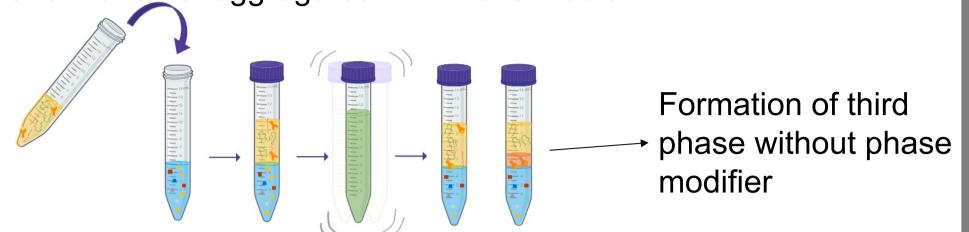
Context

Current AMEX process, a liquid-liquid extraction

The leachate is an aqueous solution obtained after the mining process. It contains uranium sulfate, sulfuric acid and impurities.

It is further contacted with an **organic phase** containing an extractant, $(TOAH^+)_2SO_4^{2-}$, a linear alkane and a phase modifier: 1-octanol .

After **demixtion**, uranyl is transferred in the organic phase thanks to the formation of aggregates with the extractant.

Formation of third phase without phase modifier

Problems of this process are the selectivity toward the others species, the need of a phase modifier to avoid 3rd phase formation, and the loss of the diluent due to evaporation.
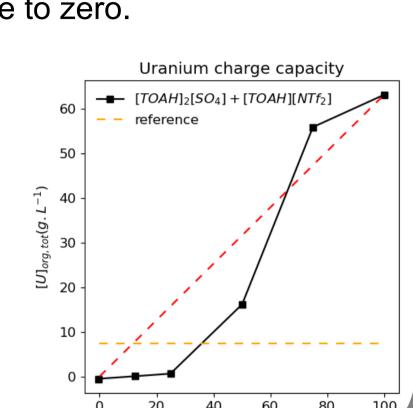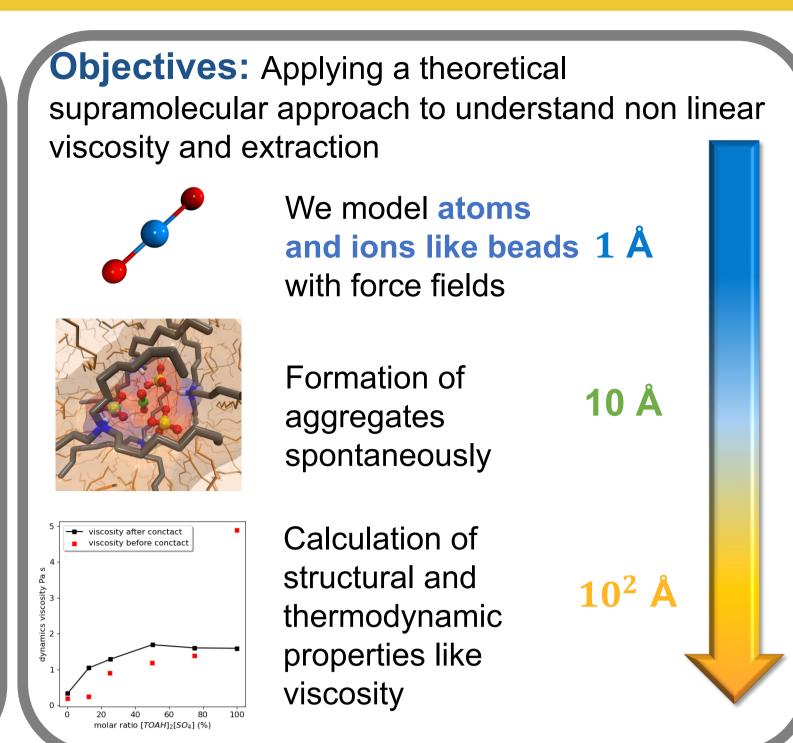
New process proposed by LTSM (1)

Contacting the leachate with an **ionic liquid** of $(TOAH^+)_2SO_4^{2-}$, without diluent and phase modifier.
With this new process, loading capacity of uranyl in the ionic phase is significantly increased. We obtain better separation factors towards the impurities like vanadium, iron, zirconium, molybdenum … and due to the absence of linear alkane, the solvent loss is close to zero.

$(TOAH^+)NTf_2^-$ is added as it presents a smaller viscosity. The mixture $(TOAH^+)_2SO_4^{2-}$ + $(TOAH^+)NTf_2^-$ should give a linear response : it should decrease linearly the loading charge of uranyl and the viscosity, but it doesn't.

However, the **viscosity is 200 times higher** than the one of the current AMEX process, which is a problem for industrial application.

Uranium charge capacity

Objectives: Applying a theoretical supramolecular approach to understand non linear viscosity and extraction

We model **atoms and ions like beads** 1 Å with force fields

Formation of aggregates spontaneously 10 Å

Calculation of structural and thermodynamic properties like viscosity 10^2 Å
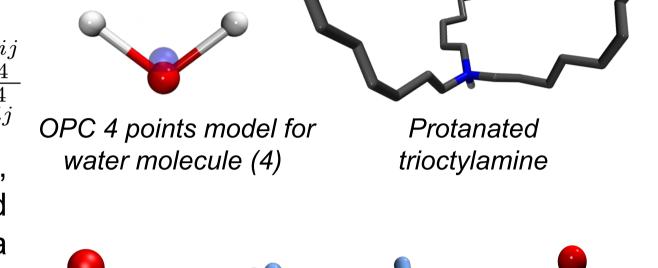
Methods

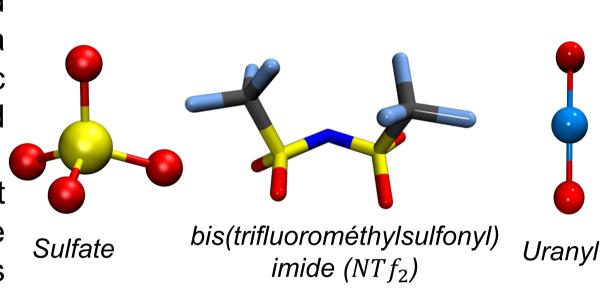We used **non polarizable classical molecular dynamics** with AMBER 20 and PMEMD package (3).
We used a 12-6-4 Lennard jones potential.

$$V(r_{ij}) = 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right) + \frac{e^2 q_i q_j}{r_{ij}} - \frac{C_4^{ij}}{r_{ij}^4}$$

OPC 4 points model for water molecule (4)

Protanated trioctylamine

Equilibration of the box in the **NPT ensemble**, the number of atoms (N), the pressure (P) and the temperature (T) are constant. We need a equilibration phase in this thermodynamic ensemble to have the correct density, energy and structure of the system.
Production runs in the **NVT ensemble**, at constant volume (V), in order to launch the simulations on graphical processing units GPUs which is 20 times faster.

Sulfate

bis(trifluorométhylsulfonyl) imide (NTf_2)

Uranyl

Small Angle X-ray Scattering (SAXS) by MD simulation (2)

The **SAXS intensity** is calculated from MD simulation

$$I(q) = \sum_\alpha \sum_\beta f_\alpha(q) f_\beta(q) \sqrt{N_\alpha N_\beta} S_{\alpha\beta}$$

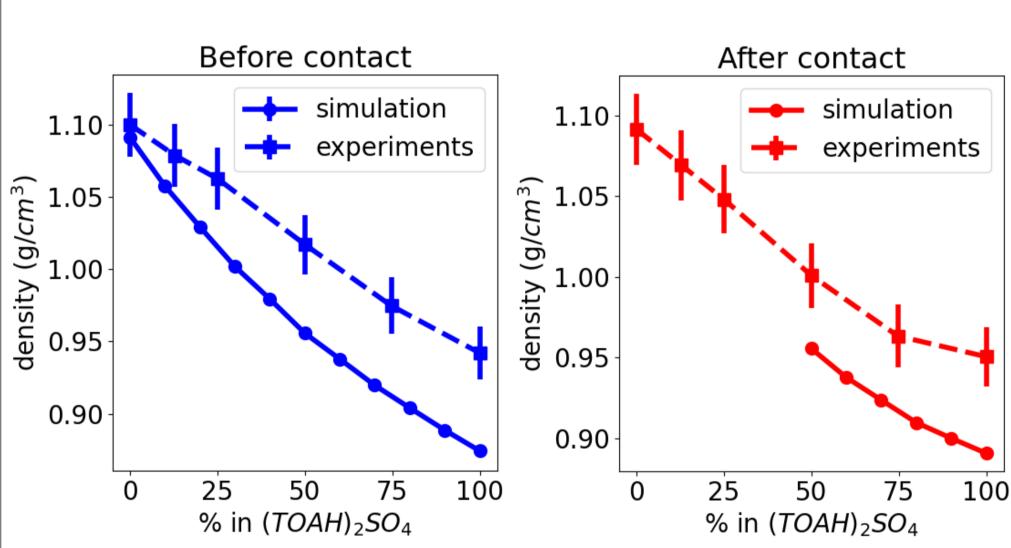With $S_{\alpha\beta}$ the structure factor between the species α and β

$$S_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\sqrt{\rho_\alpha \rho_\beta} \int_0^r (g(r)-1)\frac{\sin(qr)}{qr} r^2 dr$$

f_α(q) is the form factor of the species α
N_α is the number of atom α
ρ_α is the density of atom α
g(r) the radial distribution function
$\delta_{\alpha\beta}$ is the kronecker delta

➢ Theoretical intensity are **compared with experiment**
➢ Interpreting the **experimental results** by identifying which contribution gives a peak

Densities

Densities for different concentrations of $(TOAH^+)_2SO_4^{2-}$ and $(TOAH^+)NTf_2^-$
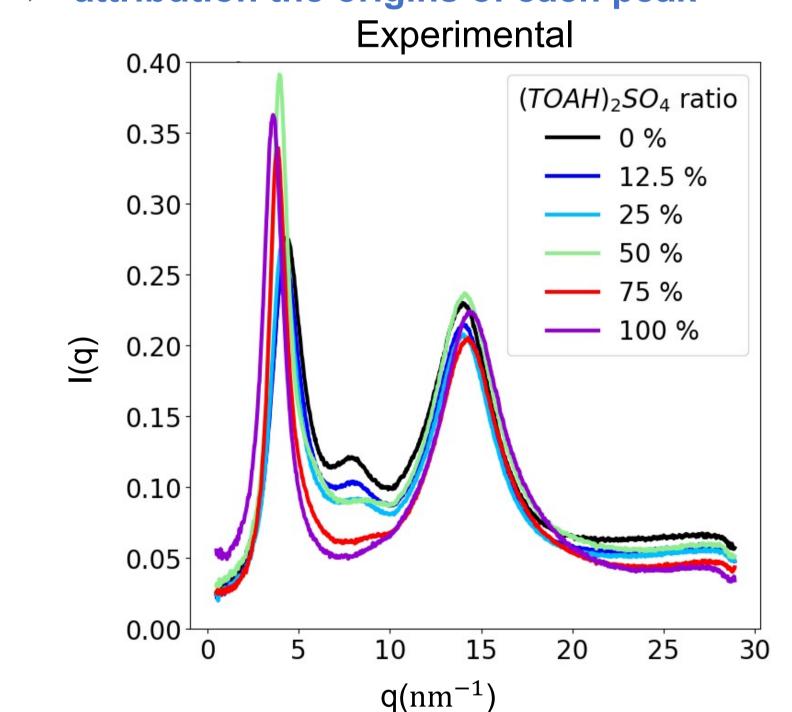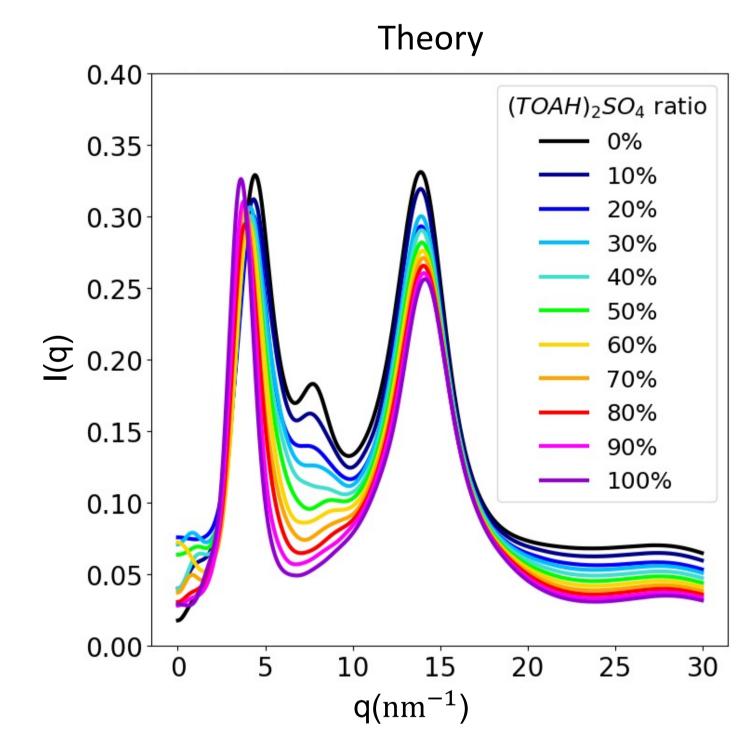
Before contact

After contact

❑ No simulation yet at **low concentration** of uranyl due to the need of a big simulation box for the ratio between 0 and 50% of $(TOAH^+)_2SO_4^{2-}$.

❑ **Same trend**: the density decreases for high percentage of $(TOAH^+)_2SO_4^{2-}$.

❑ **Small differences** between simulations and experiments. There are several possible explanation:
- An experimental systematic error due to the measure
- Different composition because of impurities and water
- The force fields for the different molecules are not good
- The protonation states of species as a function of the percentage of $(TOAH^+)_2SO_4^{2-}$.

SAXS

Comparison of **the experimental** and **theoretical SAXS intensity** without uranyl
➢ **attribution the origins of each peak**

Experimental

Theory

We obtain the **same 3 peaks around 4, 8 and 14 nm^{-1}** and the same shift for the peak around 8 nm^{-1}.

Box with low concentration of uranyl

We need a **big box to simulate low concentrations**
Because the $(TOAH^+)NTf_2^-$ doesn't extract, the ratio with 0% of $(TOAH^+)_2SO_4^{2-}$ has a very low concentration of uranyl : 5.80×10^{-6} mol/L . To simulate this concentration, we need a cubic box of 550 Å with 50 000 TOAH : **It's too much!**
For now, we tried to simulate a cubic box of 200 Å with 10 000 TOAH, but we have no uranyl in the box at the lowest concentration. We **glue 8 small boxes together to fasten the calculations**.

Outlook and conclusions

❑ We made a lot of **simulation with and without uranyl** to **compare the MD results with experiments**

❑ We obtained the **same trend for the density** with a small difference with experiment

❑ We calculated the **same SAXS** intensities with 3 peaks at the same positions allowing to explain the structure of the solution

❑ The next step will be to **compare theoretical and experimental EXAFS spectra** in order to look at the first coordination shell of the uranyl complexes.

❑ All these results **confirm the 12-6-4 force field** of the uranyl

References

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(2) A. Coste et al, *J. Phys. Chem. B* , **2019**, 123, 5121-5130
(3) D.A Case et al, *Amber 2022,* University of California, San Francisco, **2022**
(4) S.Izadi et al, *J. Chem. Phys. Lett.,* **2014**, 5(21), 3863-3871

Acknowledgements