INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

EMINANS – Evaluation et étude de Mélanges d'ammonIums quaterNaires pour l'extrAction sélective de l'uraNium en milieu Sulfurique

Evaluation and study of quaternary ammonium mix for selective extraction of uranium in sulfuric media

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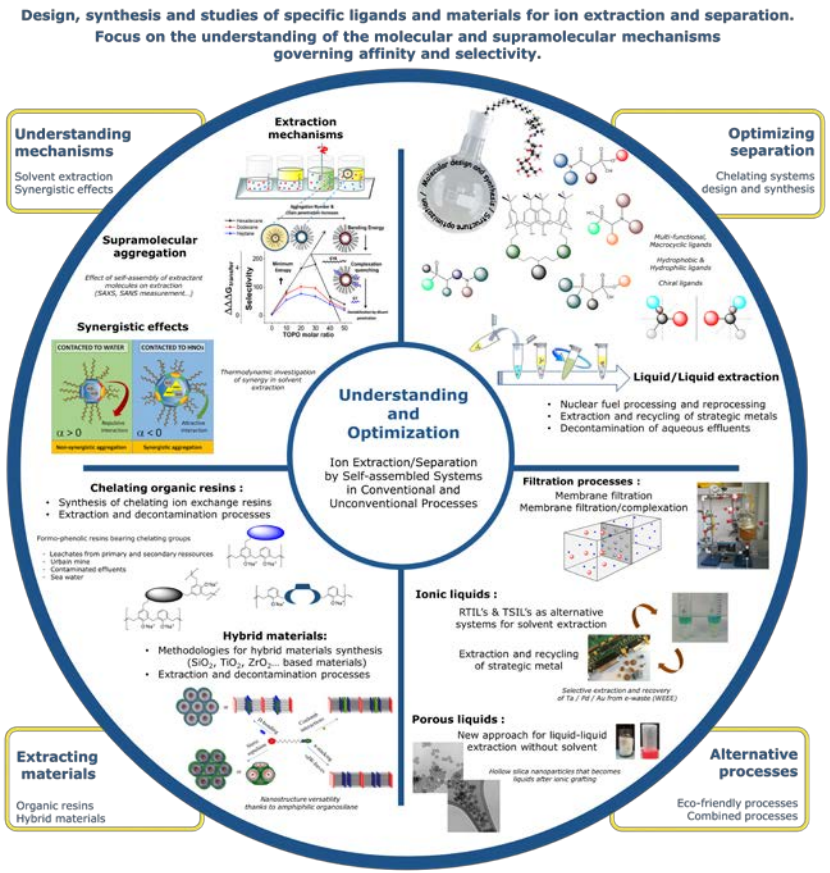
Elise GUERINONI

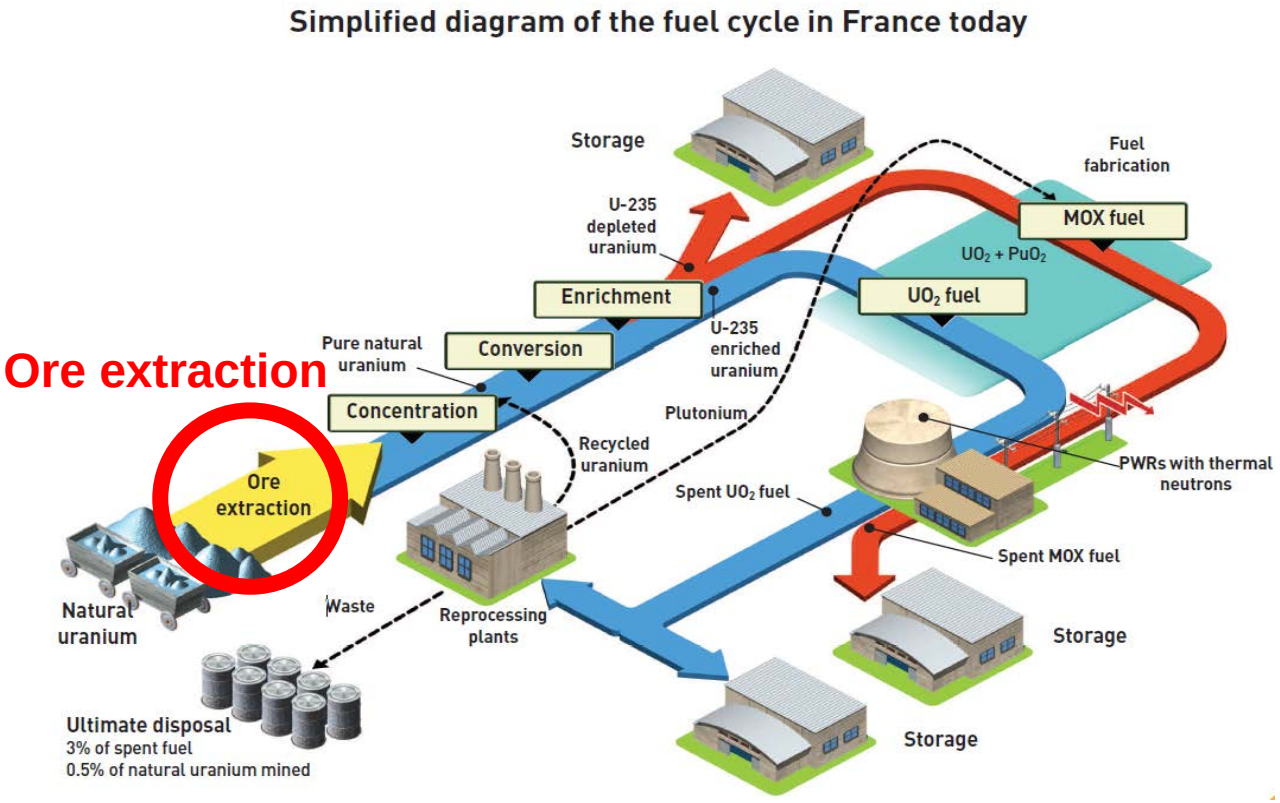
2022/01/21

LTSM – Laboratoire Tri ionique par les Systèmes Moléculaires auto-assemblés



FESTIVAL D'AVIGNON

Nuclear fuel cycle / Uranium production



COMMINUTION
PRE-CONCENTRATION

Mined ore

LEACHING

Oxidant

Lixiviant

Wash water

SOLID/LIQUID SEPARATION

TAILS TO WASTE

SOLVENT EXTRACTION

ION-EXCHANGE RESIN

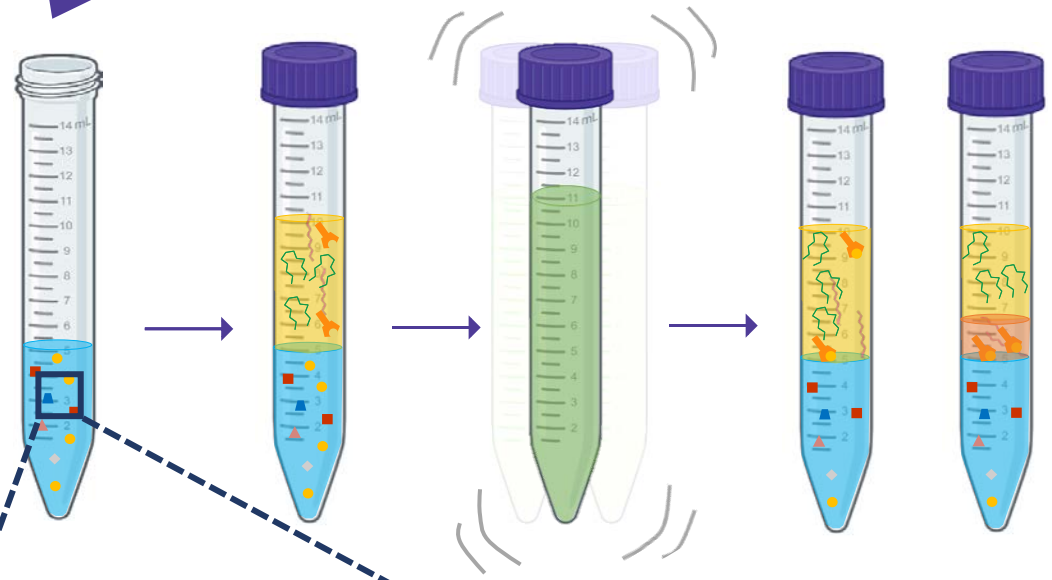
YELLOW CAKE PRECIPITATION AND DRYING

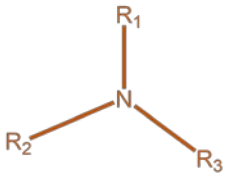
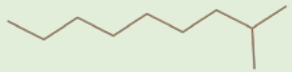
https://assets.rte-france.com/prod/public/2020-06/bilan-electrique-2019_1_0.pdf

IAEA, “Uranium 2018: Resources, Production and Demand.”

AMEX process and solvent extraction

- Extractant : Alamine
- Diluent : linear alcane
- Phase modifier : 1-octanol



Common Name	Composition		Nature of the amine
Alamine 336	Di-n-octyl monodecylamine	44 %	R_1, R_2  R_3 
	Tri-n-octyl-amine	28 %	R_1, R_2, R_3 
	Mono-octyl di-decyl-amine	23 %	R_1  R_2, R_3 
	Tri-n-decyl-amine	3 %	R_1, R_2, R_3 
Alamine 308	Tri-isooctyl-amine	100 %	R_1, R_2, R_3 
Alamine 304	Tri-n-dodecyl-amine	95-100 %	R_1, R_2, R_3 

Leaching containing :

- Uranium sulfate
- Impurities : Fe, Zr, Mo, V
- Sulfurique acid
- Ammonium sulfate

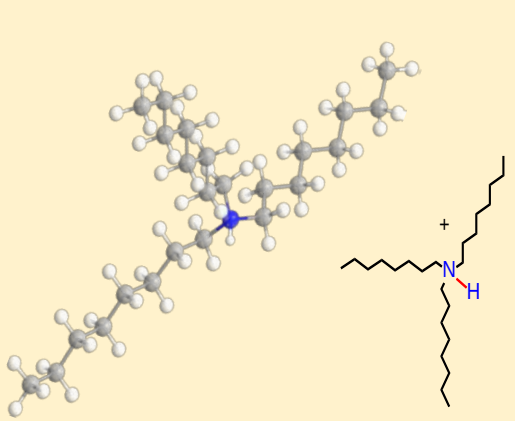
Problem:

- Non selective extraction
- 3rd phase formation
- Amines degradation due to combined presence of octanol and vanadium

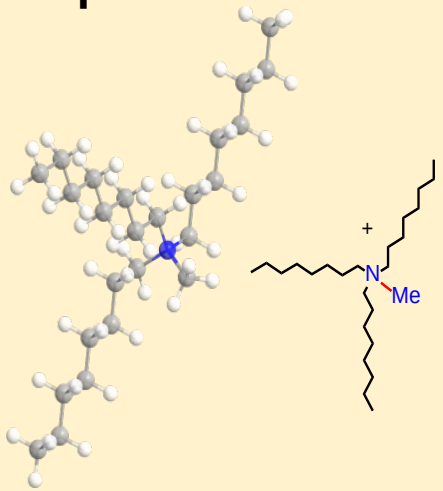
C. Boirie, “Extraction of uranyl sulfate with amines,” *Bull. soc. chim. France*, vol. No. 8-9, 1958
A. Chagnes *et.al.*, *Solvent Extraction and Ion Exchange*, vol. 30, no. 1, pp. 67–76, 2012

Ionic liquids

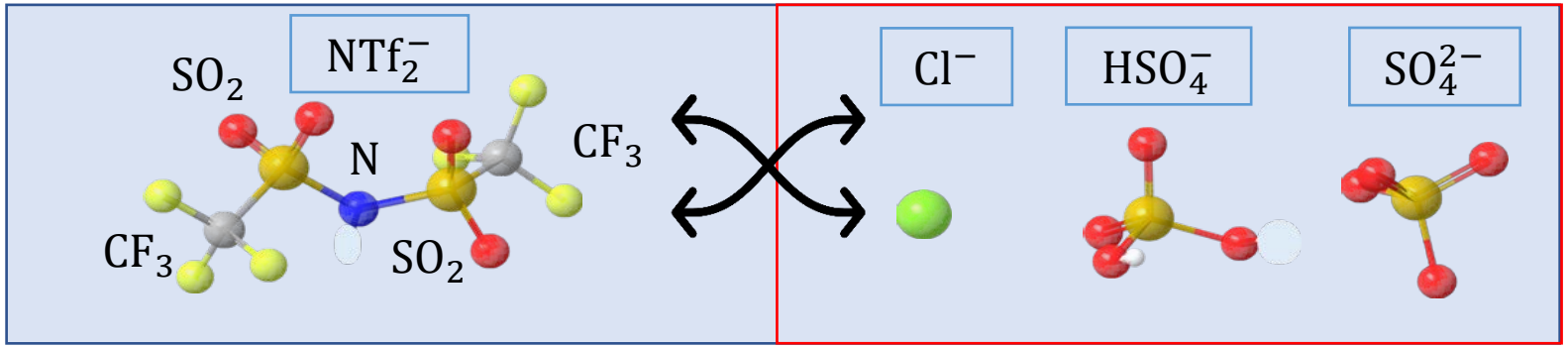
Ammonium-based Ionic Liquids



Trioctylammoniums ($TOAH^+$)



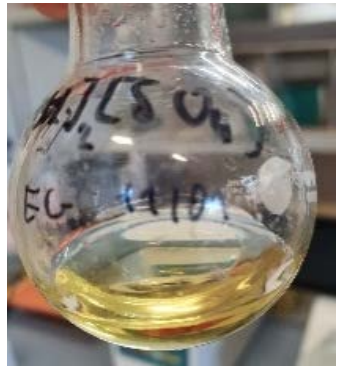
Methyltrioctylammoniums ($MTOA^+$)



Step 1: trialkylamine protonation

Step 2: uranyl extraction by anionic exchange

$[TOAH^+][NTf_2^-]$ $[TOAH^+]_2[SO_4^{2-}]$



$D_U = 0$

$D_U = 100$
viscous

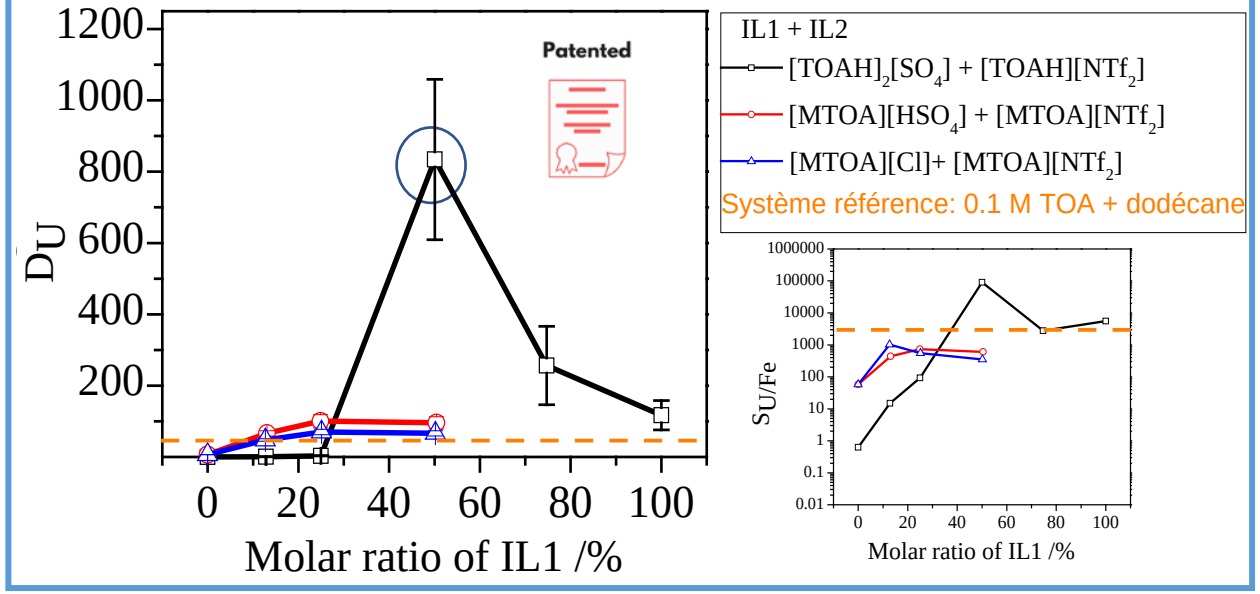
- Replace organic phase
- No dilution, no 3rd phase

~~Dodecane~~

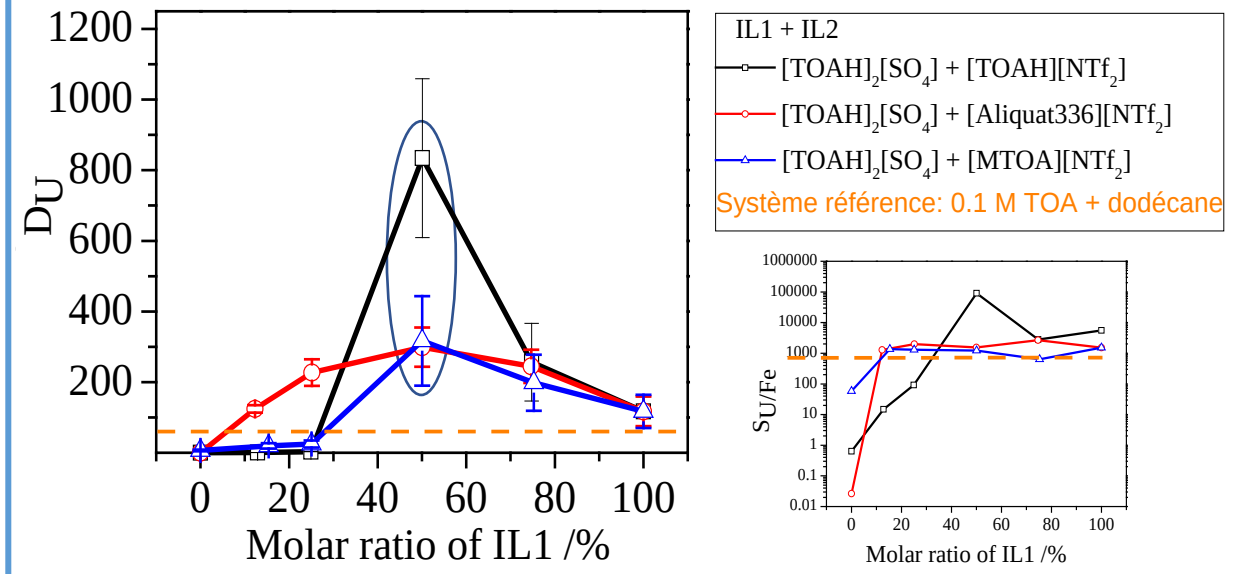
~~1-octanol~~

Synergistic mixture of anions

Mixtures with same anions and different cations



Mixtures with same cations and different anions



Organic phase
Mixtures of two ammoniums

Aqueous phase
0.1 M H_2SO_4 and 0.1 M$(NH_4)_2SO_4$ + 250 ppm U(VI) and 250 ppm Fe(III)
A/O = 2

Objectives:

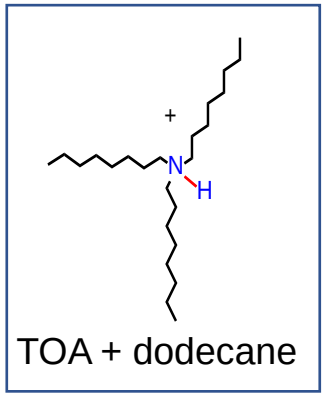
Comparisson of conventionnal and ionic liquid media for:

- Extraction capacity
- Extraction mechanism

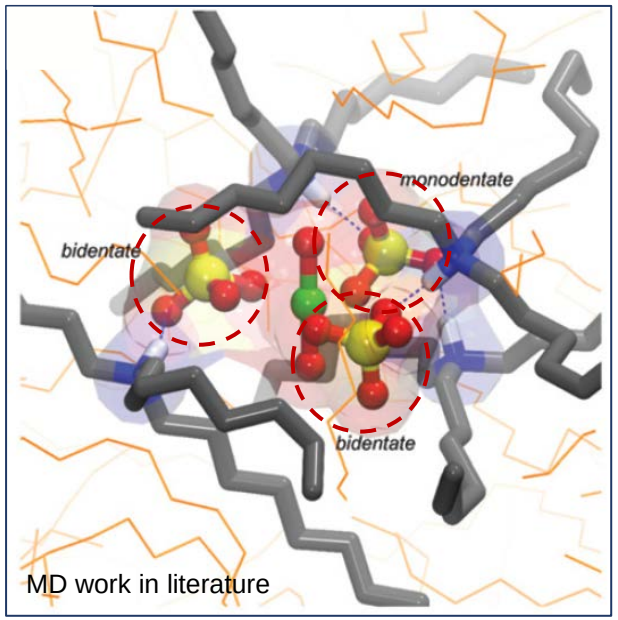
→ Explain the anionic synergy, not investigated in literature

Uranyl complexe caracterization

What we know:



TOA + dodecane

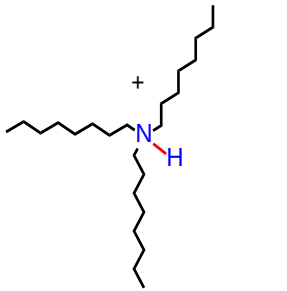


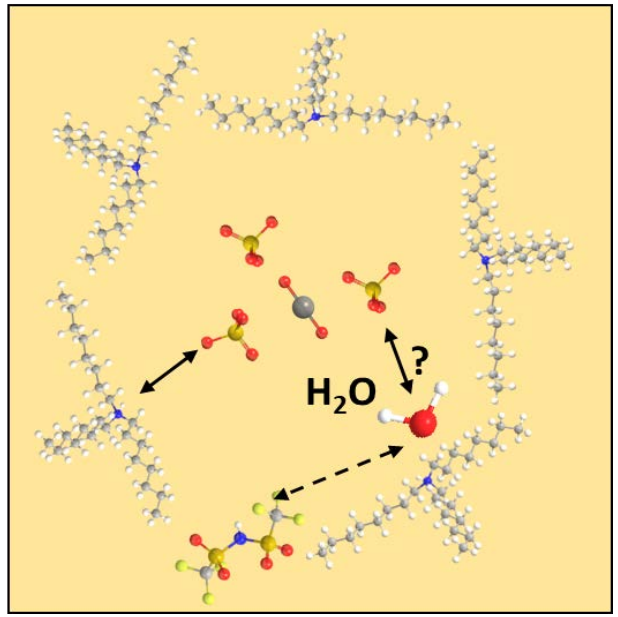
MD work in literature

- 3 SO_4^{2-} in inner sphere of UO_2^{2+}
- H-bonds created bewteen $TOAH^+$ and 3 SO_4^{2-}
- $[H_2O]_{org} \approx 0$

What we don't know:

$SO_4^{2-} + NTf_2^-$



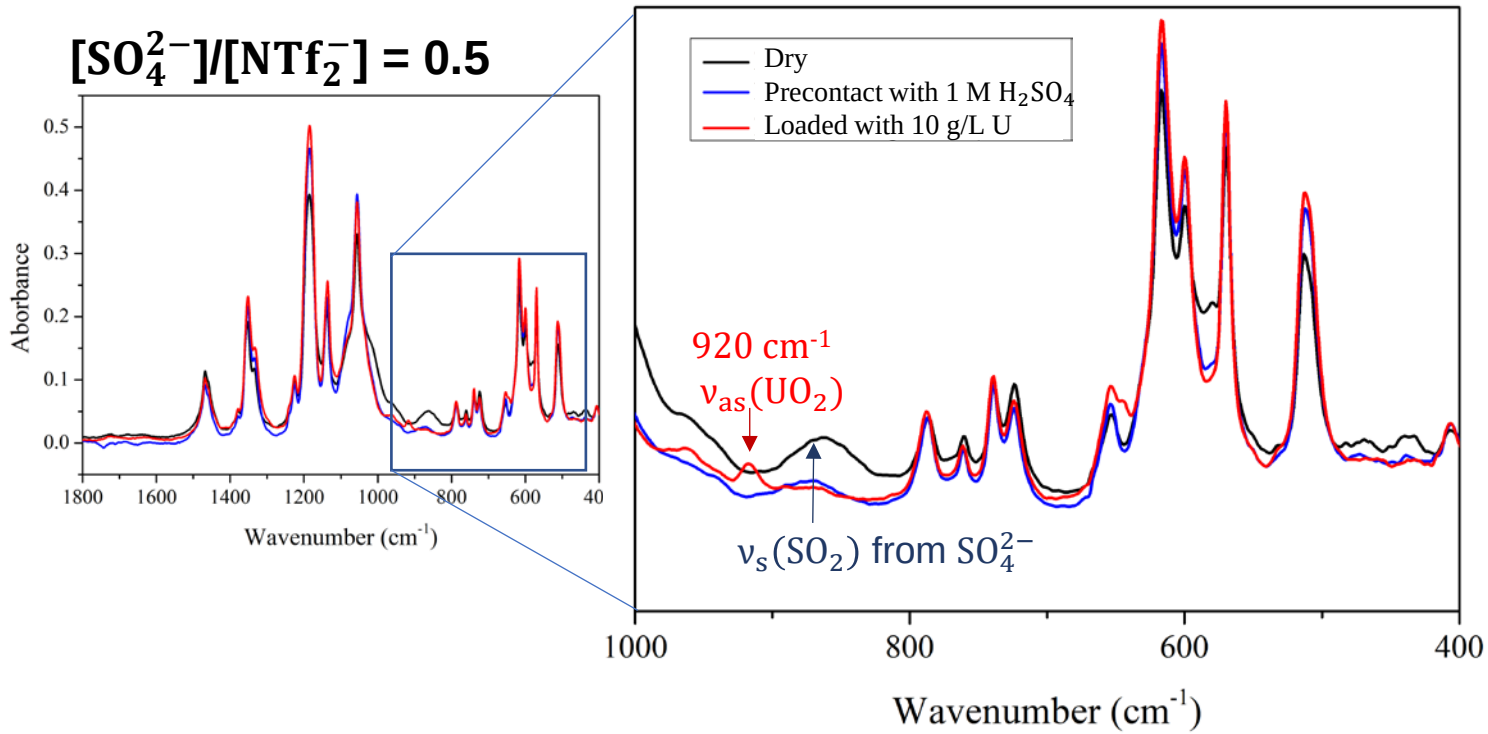


- Origin of synergy
- Role of SO_4^{2-} in UO_2^{2+} complexation?
- Role of NTf_2^- ?
- Role of H_2O? ($[H_2O]_{org} \gg 0$)

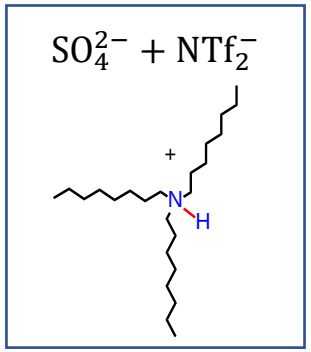
Uranyl complex in ILs mixture
Role of SO_4^{2-}

FT-IR

- Indentification of $\nu_{as}(UO_2)$ and vibrational modes of SO_4^{2-}



UO_2^{2+} complexed with SO_4^{2-}?



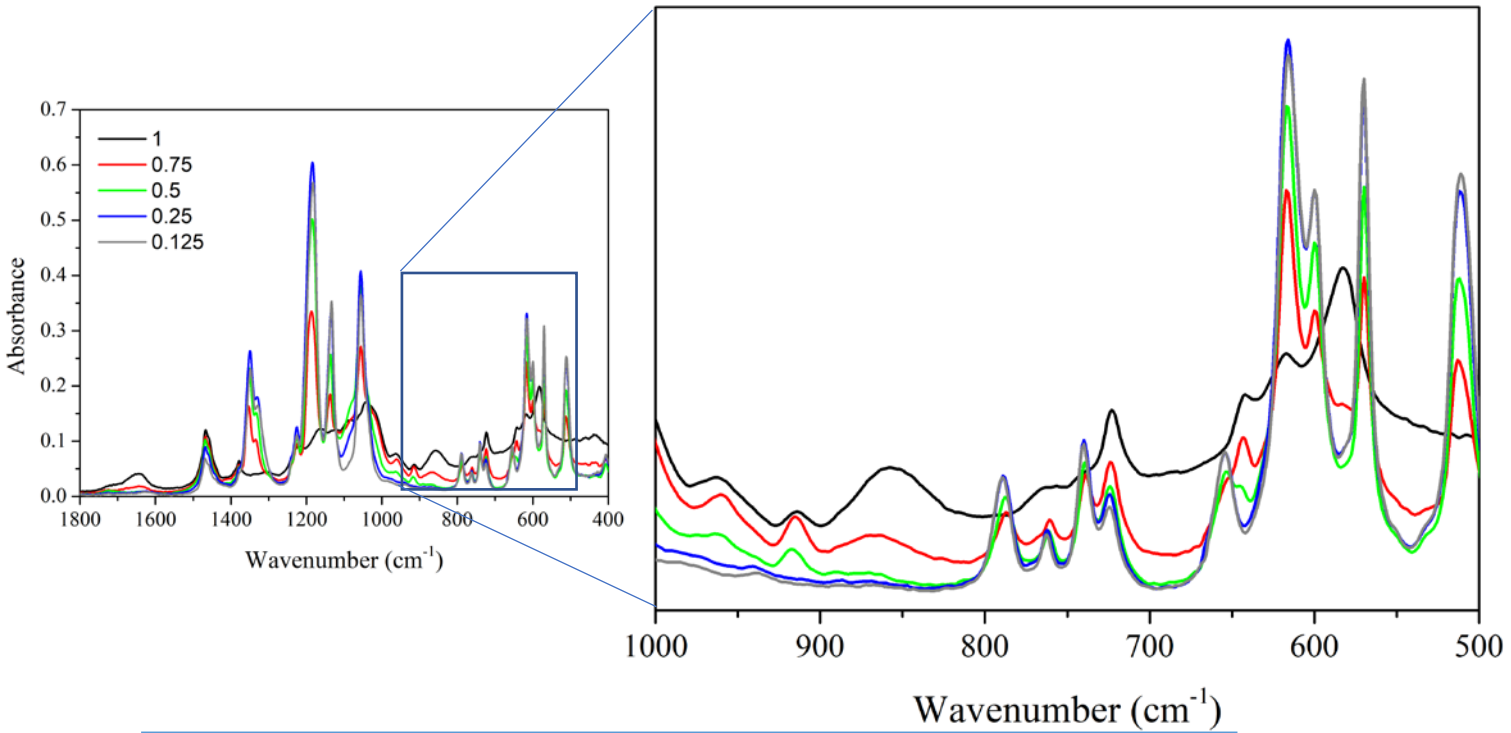
Organic phase
$[SO_4^{2-}]/[NTf_2^-]$ = 0.5,
loaded with 10 g/L U(VI)

Uranyl complex in ILs mixture
Role of NTf_2^-

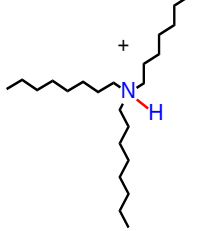
FT-IR

Indentification of $\nu_{as}(UO_2)$ and vibrational modes of NTf_2^-

$[SO_4^{2-}]/[NTf_2^-]$ = 0.125 – 1 loaded with U



$SO_4^{2-} + NTf_2^-$

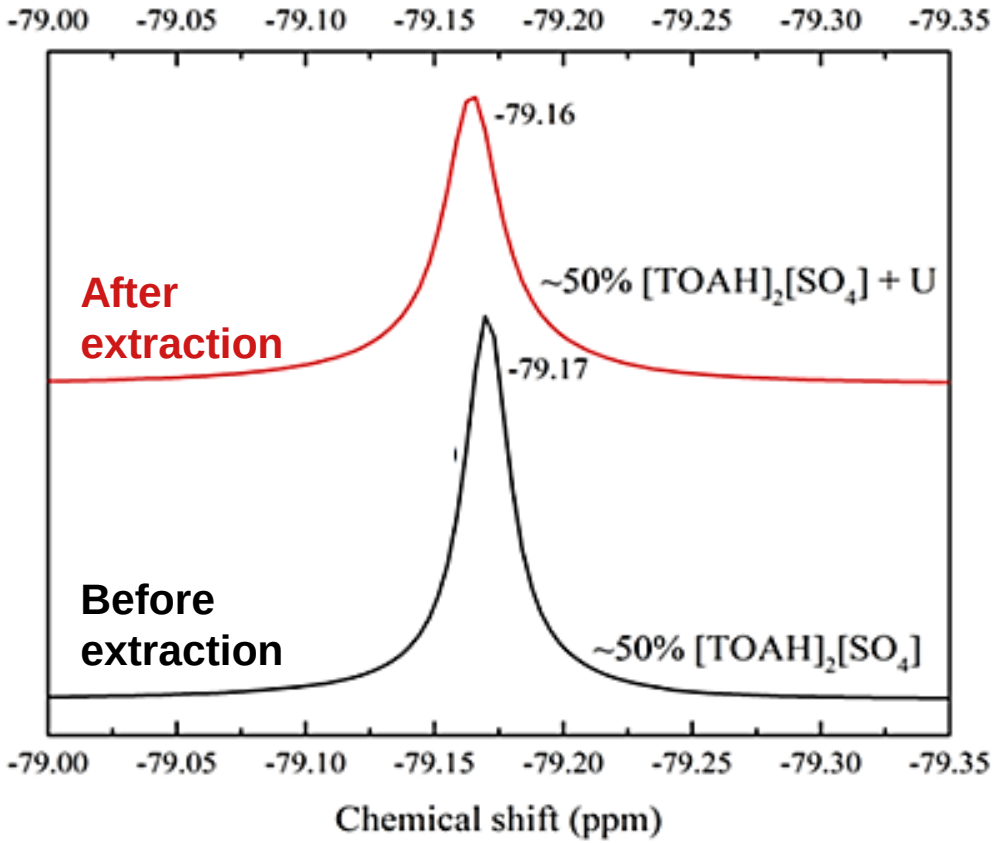


Organic phase
$[SO_4^{2-}]/[NTf_2^-]$ = 0.5, 0.75 and 1
loaded with 10 g/L U(VI)

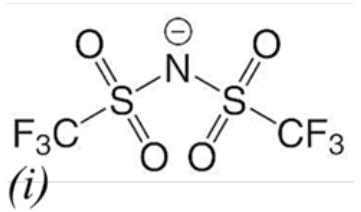
Structure of complex of UO_2 is not changed by presence of NTf_2^-.

Uranyl complex in ILs mixture
Role of NTf_2^-

^{19}F NMR



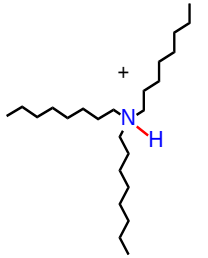
NTf_2^-



(i)

NTf_2^- chemical environment changed when mixed with SO_4^{2-}.

$SO_4^{2-} + NTf_2^-$



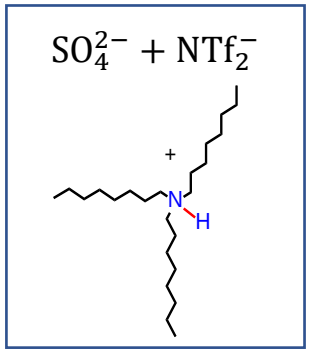
Organic phase
$[SO_4^{2-}]/[NTf_2^-]$ = 0.5
loaded with 10 g/L U(VI)

- No NTf_2^- in inner coordination sphere of UO_2^{2+}
  Peak broadening:

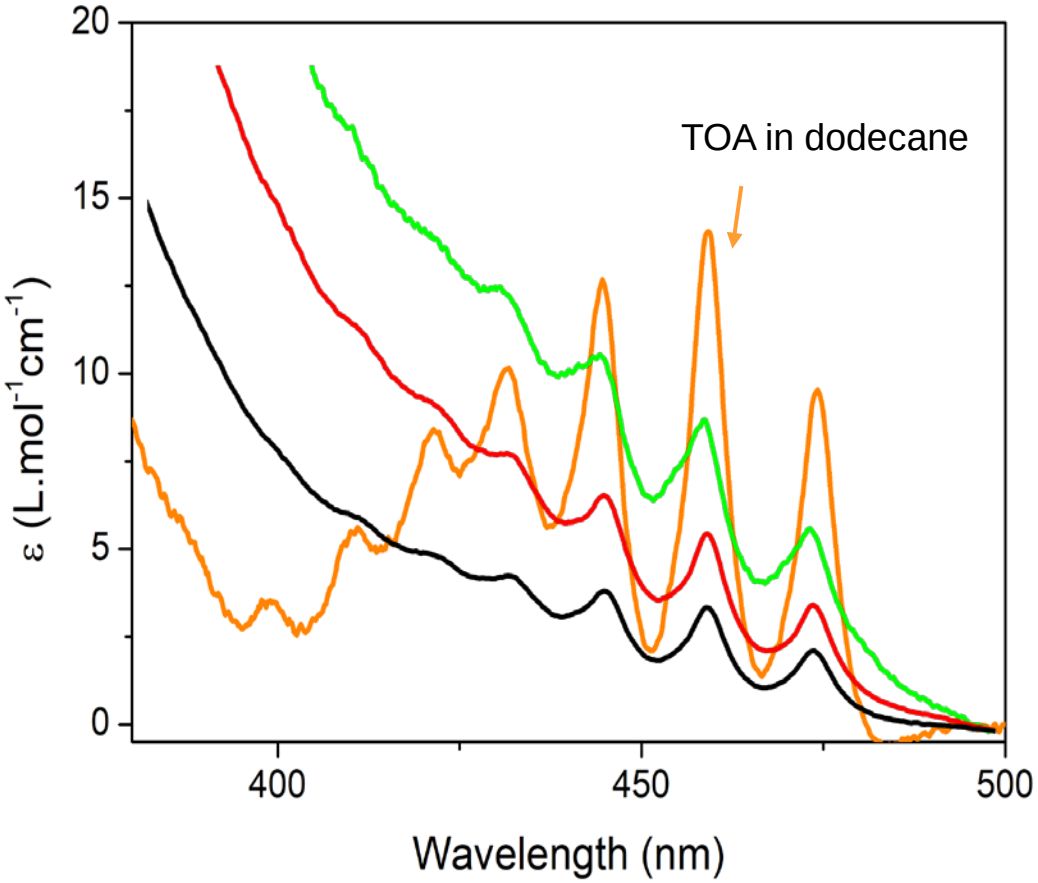
Concomitant with more water extracted

Uranyl complex in ILs mixture
Role of SO_4^{2-}

UV-vis



Organic phase
$[SO_4^{2-}]/[NTf_2^-]$ = 0.5, 0.75 and 1 or0.1 M TOA in dodecane + 5% oct. loaded with 2500 ppm U(VI)



$[SO_4^{2-}]/[NTf_2^-]$= 0.5
$[SO_4^{2-}]/[NTf_2^-]$= 0.75
$[SO_4^{2-}]/[NTf_2^-]$= 1

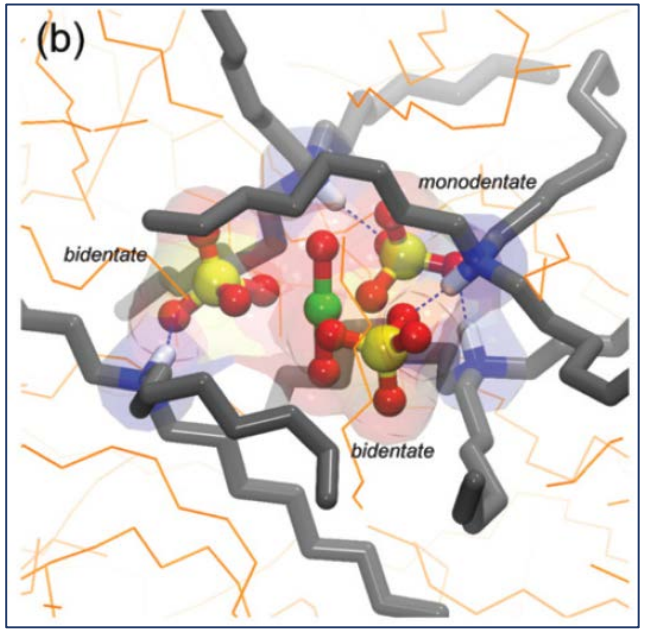
Similar D_{3h} trigonal symmetry* ⇒ 3 SO_4^{2-} in inner coordination sphere of uranyl in ILs system

*K. Servaes *et. al.*, *European Journal of Inorganic Chemistry*, no. 32, pp. 5120–5126, 2007

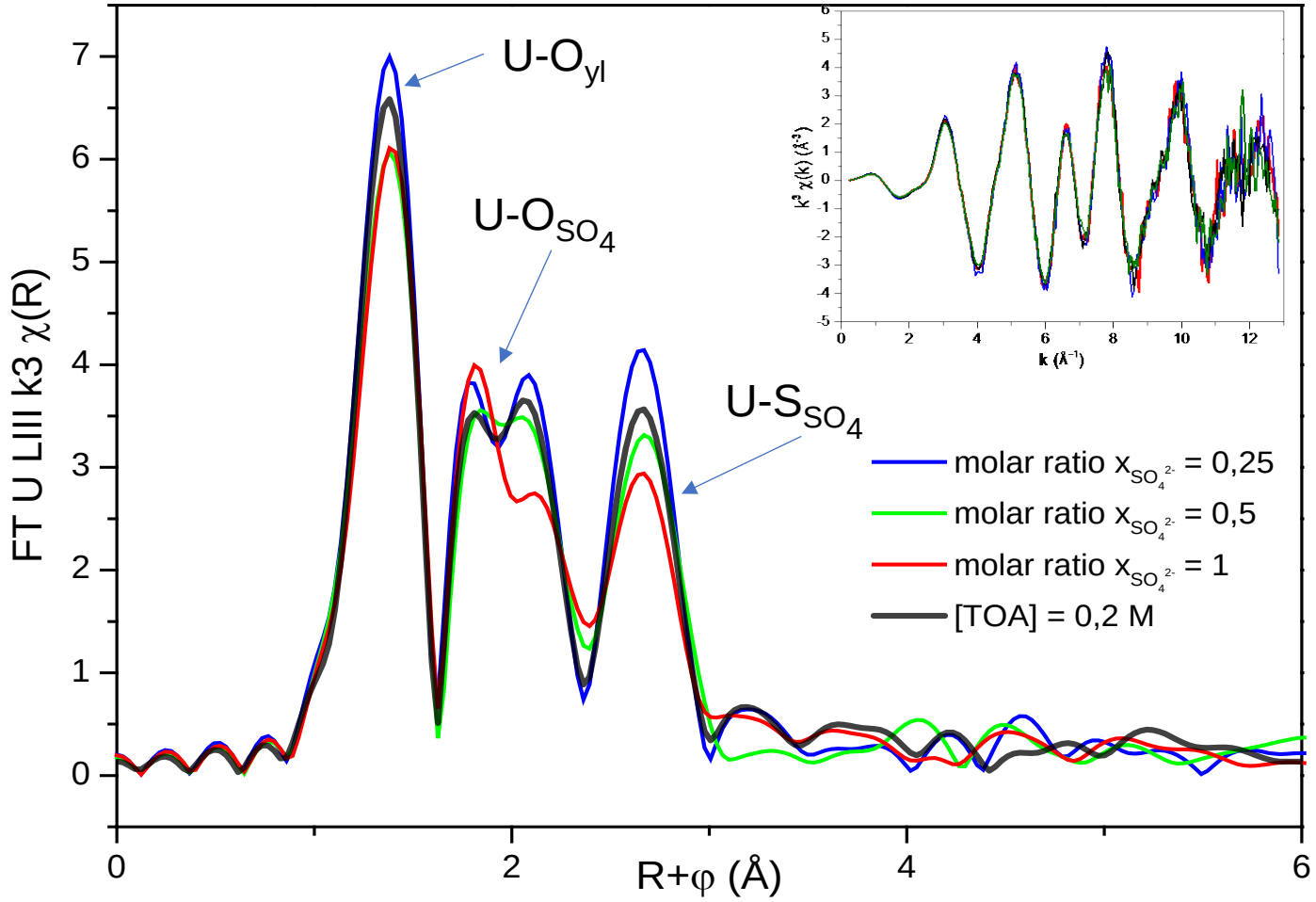
Uranyl complex in ILs mixture

EXAFS

Run EXAFS
Synchrotron Soleil
Mars beamtime
2 days - April 2021



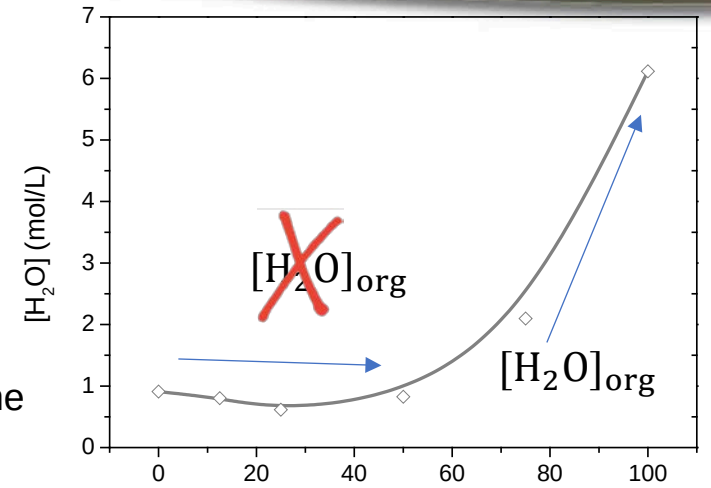
- In first coordination sphere:
  - 3 SO_4^{2-}
  - No NTf_2^- and no H_2O

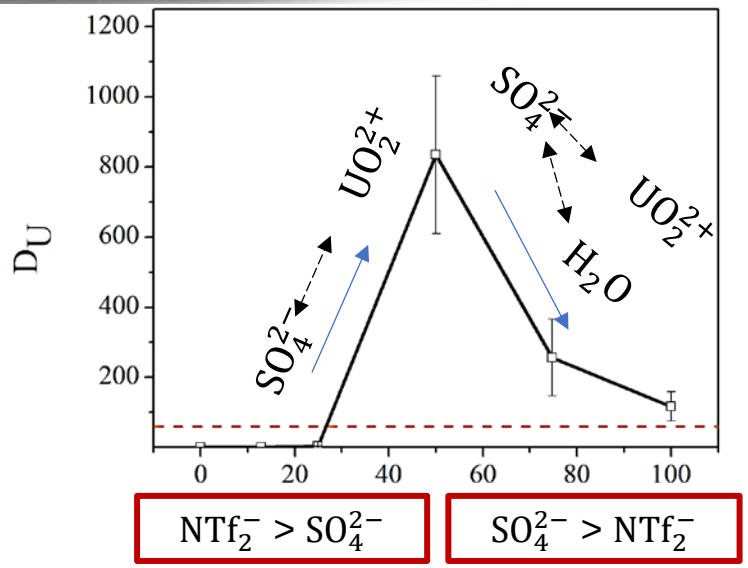


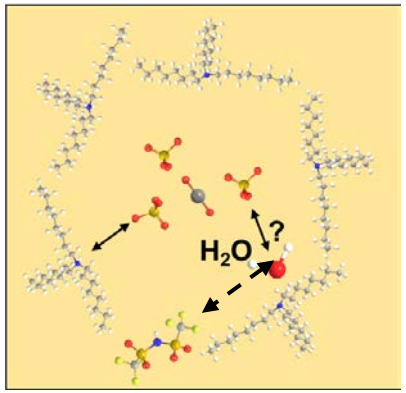
- Synergy origin?

Role of water on synergistic extraction?

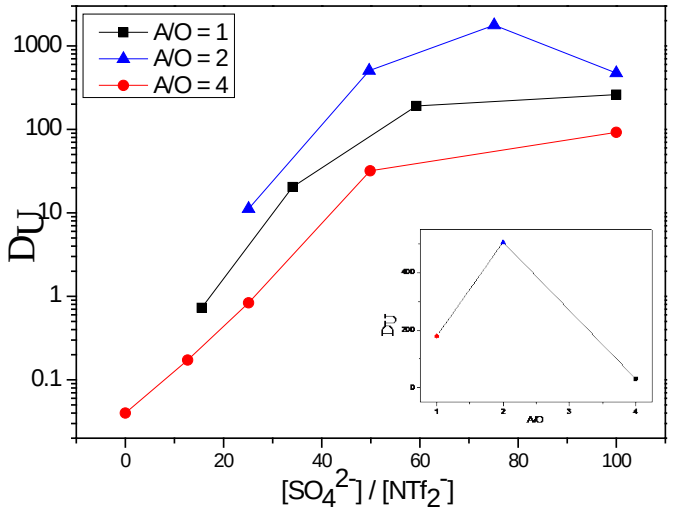
Reference:TOA + dodecane
$[H_2O]_{org}$ = 0.2 mol/L

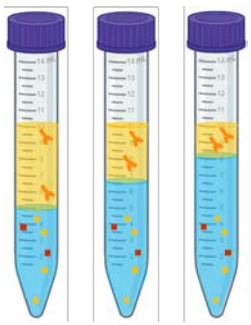




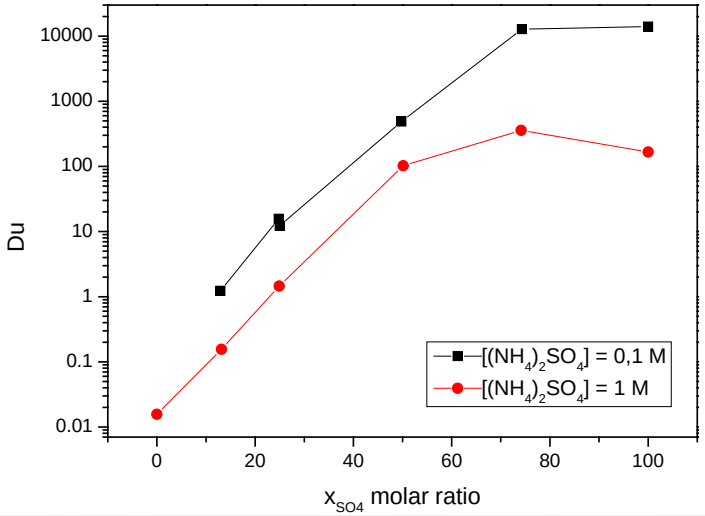


Different V_A/V_O ratio





Different $[(NH_4)_2SO_4]$



Conclusions / perspectives

- No dilution, no third phase
- Synergistic extraction of U

Patented

- 3 SO_4^{2-} in inner sphere of coordination
- NTf_2 not involved
- Role of water?

- Indentification of $\nu(SO_4)$ link with UO_2 and $\nu(SO_4)$ link with H_2O in FT-IR (DFT calculations)
- Determine the maximum sulfate and water quantites before lost of uranium extraction

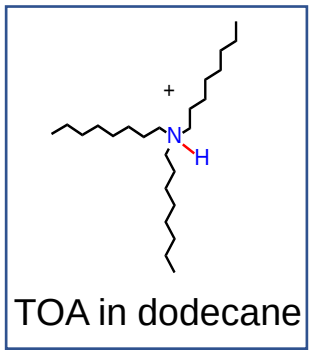
Thank you for your attention

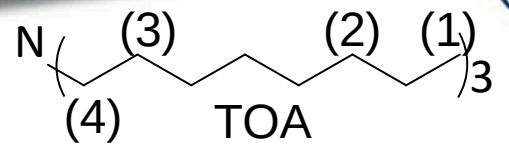
Récap data

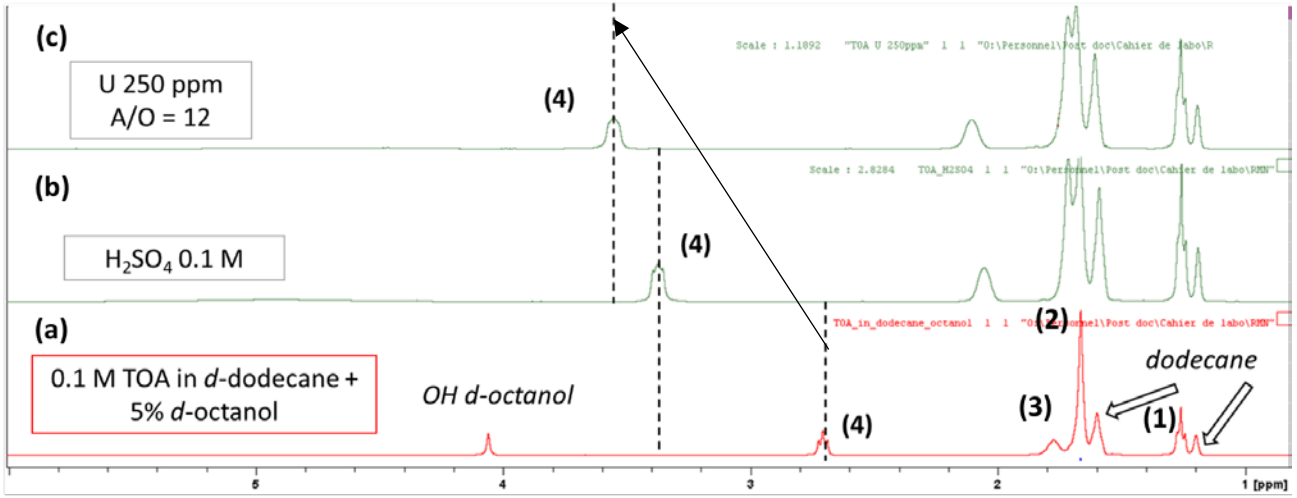
Uranyl complex in ILs mixture
Role of $TOAH^+$

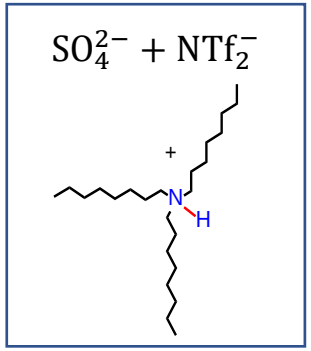
^1H NMR

Reference system: TOA in dodecane



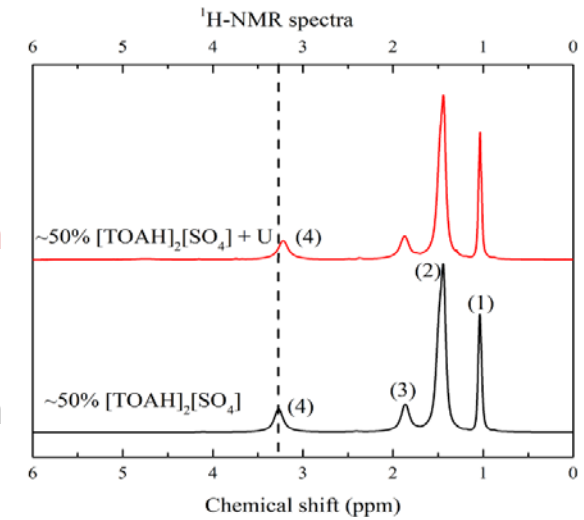


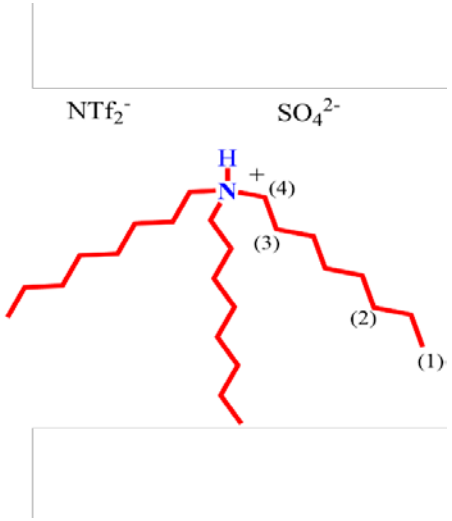




After extration

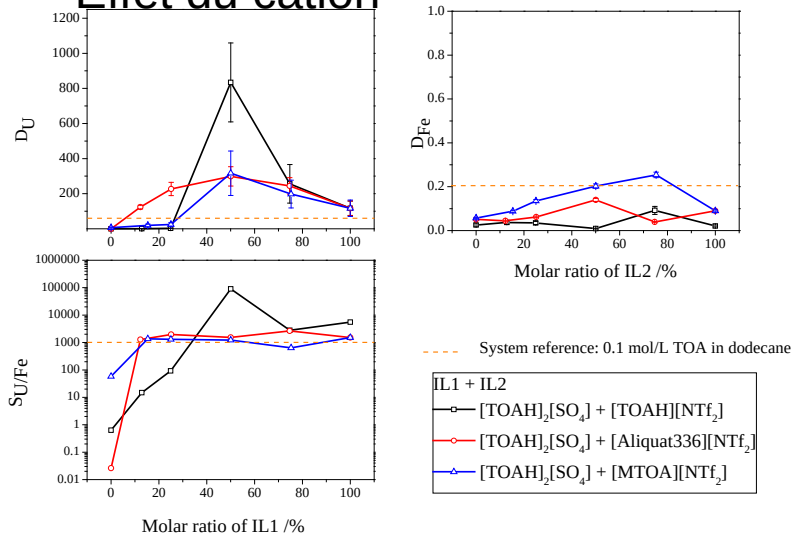
Before extration

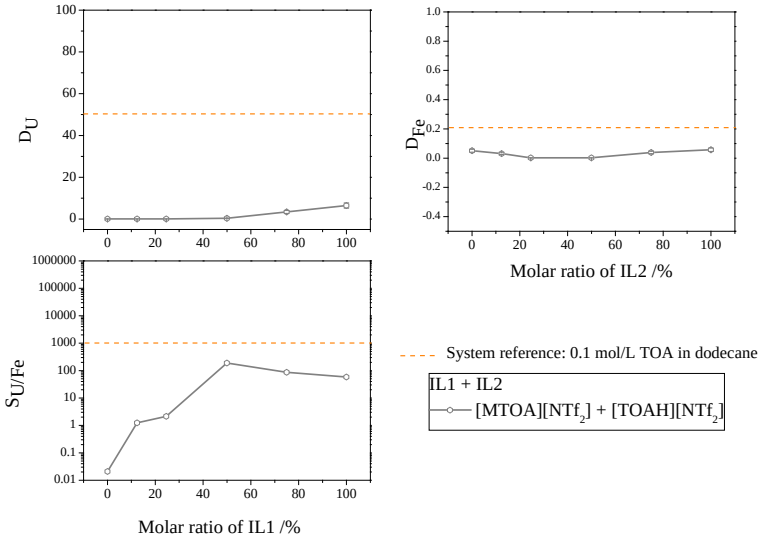




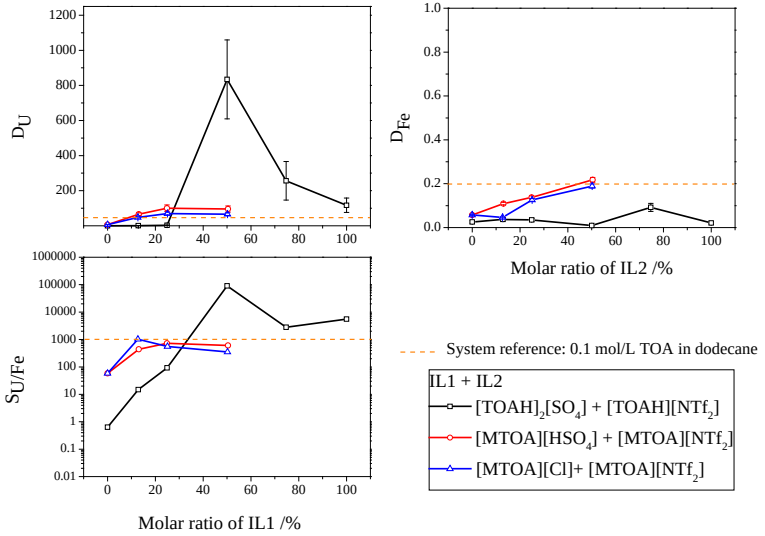
Synergie anionique et pas cationique

Effet du cation



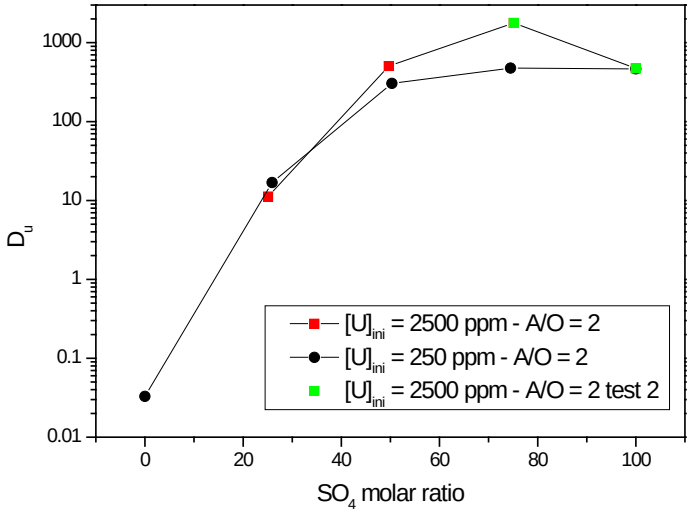


Effet de l'anion

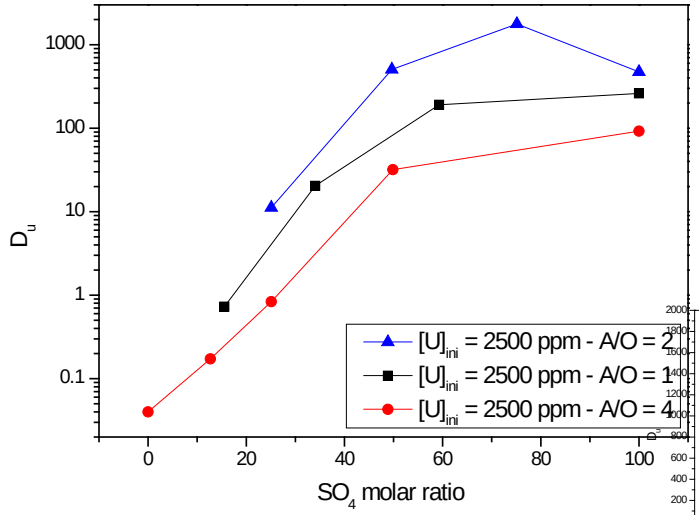


On a choisi le système et on essaye de voir les para qui changent

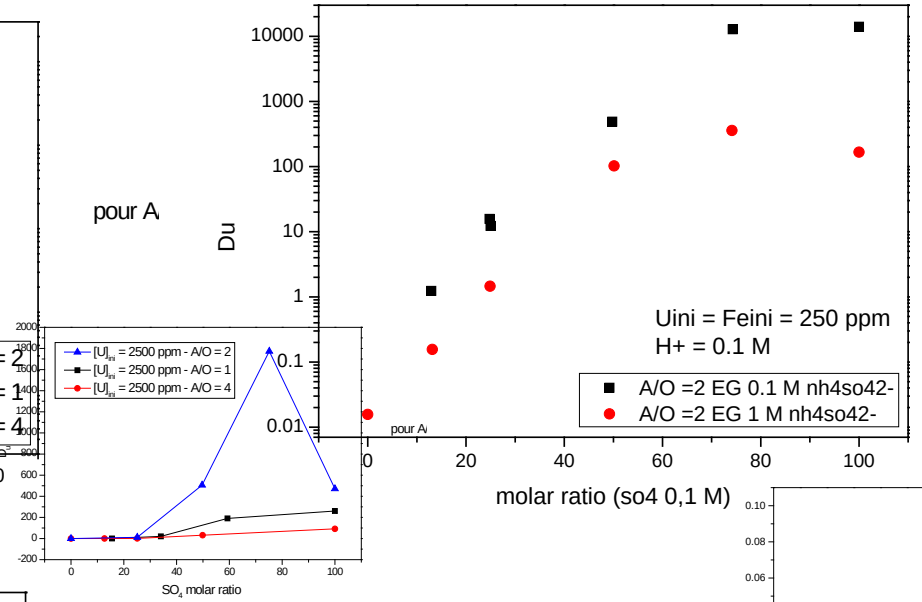
Effet de [U]initiale

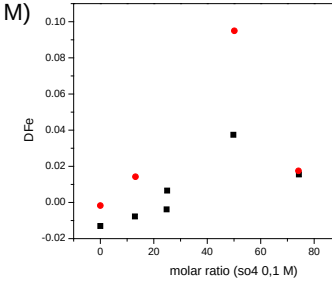


Effet de A/O

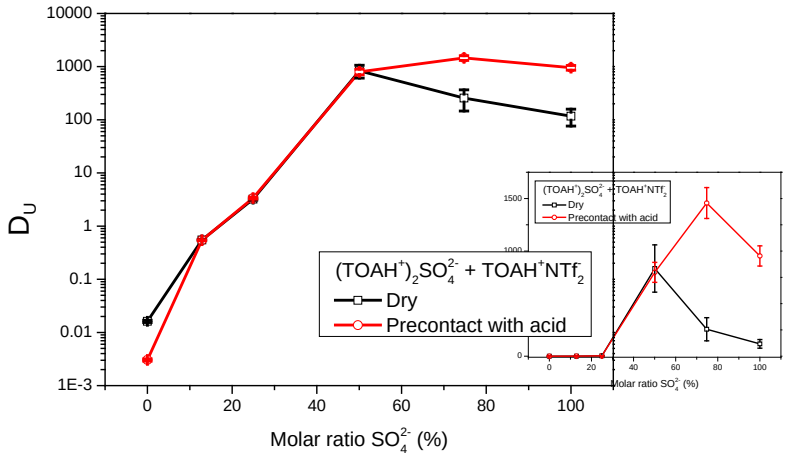


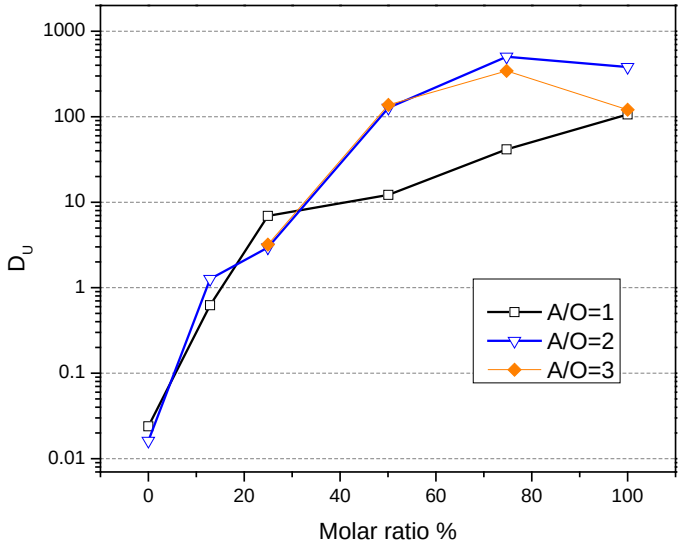
Effet sulfate

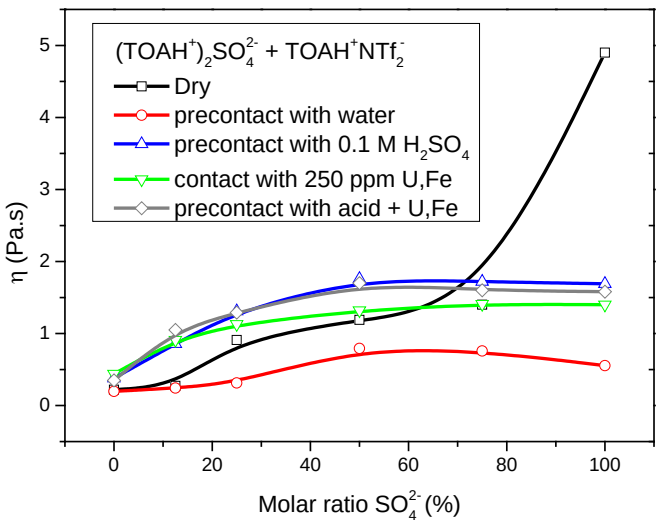


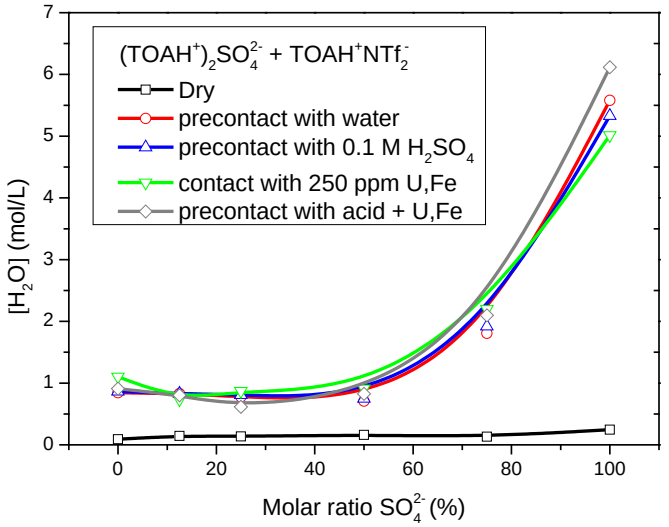


Effet du précontact zl






(TOAH+)2SO4 2- + TOAH+NTf2-
Dry
precontact with water
precontact with 0.1 M H2SO4
contact with 250 ppm U,Fe
precontact with acid + U,Fe
η (Pa.s)
Molar ratio SO4 2- (%)


(TOAH+)2SO4 2- + TOAH+NTf2-
Dry
precontact with water
precontact with 0.1 M H2SO4
contact with 250 ppm U,Fe
precontact with acid + U,Fe
[H2O] (mol/L)
Molar ratio SO4 2- (%)