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Contribution of various techniques to U(VI) and Pu(IV) mass transfer kinetics in liquid-liquid extraction

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Extraction kinetics of uranium(VI) and plutonium(IV) by N,N-dialkylamide

towards the kinetics regime determination

thanks to 3 technics

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DE LA RECHERCHE À L'INDUSTRIE

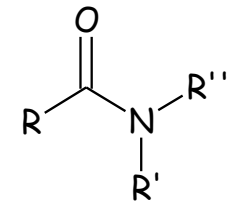
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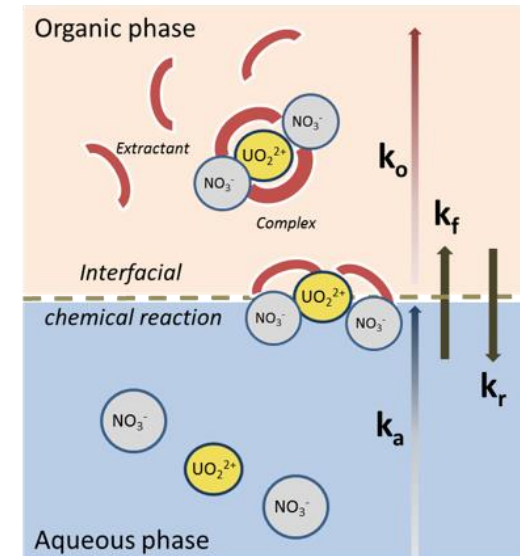
- Innovative processes for Plutonium multi-recycling based on a monoamide extractant [1-3]
 - Thermodynamical data acquired
 - Hydrodynamic and hot tests carried out
- Simulation of counter-current test in mixer-settlers or pulsed columns
 - ⇒ Determination of mass transfer coefficients of U(VI) and Pu(IV) extraction
 - ⇒ Determination of the kinetics regime
- Mass transfer theory applied to liquid-liquid extraction

$$J = k_o(C_o^i - C_o) = k_a(C_a - C_a^i) = k_f C_a^i - k_r C_o^i$$

$$\frac{1}{K_a} = \frac{1}{k_a} + \frac{1}{D \cdot k_o} + \frac{1}{k_f}$$



N,N dialkylamide



k_o, k_a : diffusion rate constants
 k_f, k_r : chemical rate constants
 D: distribution ratio

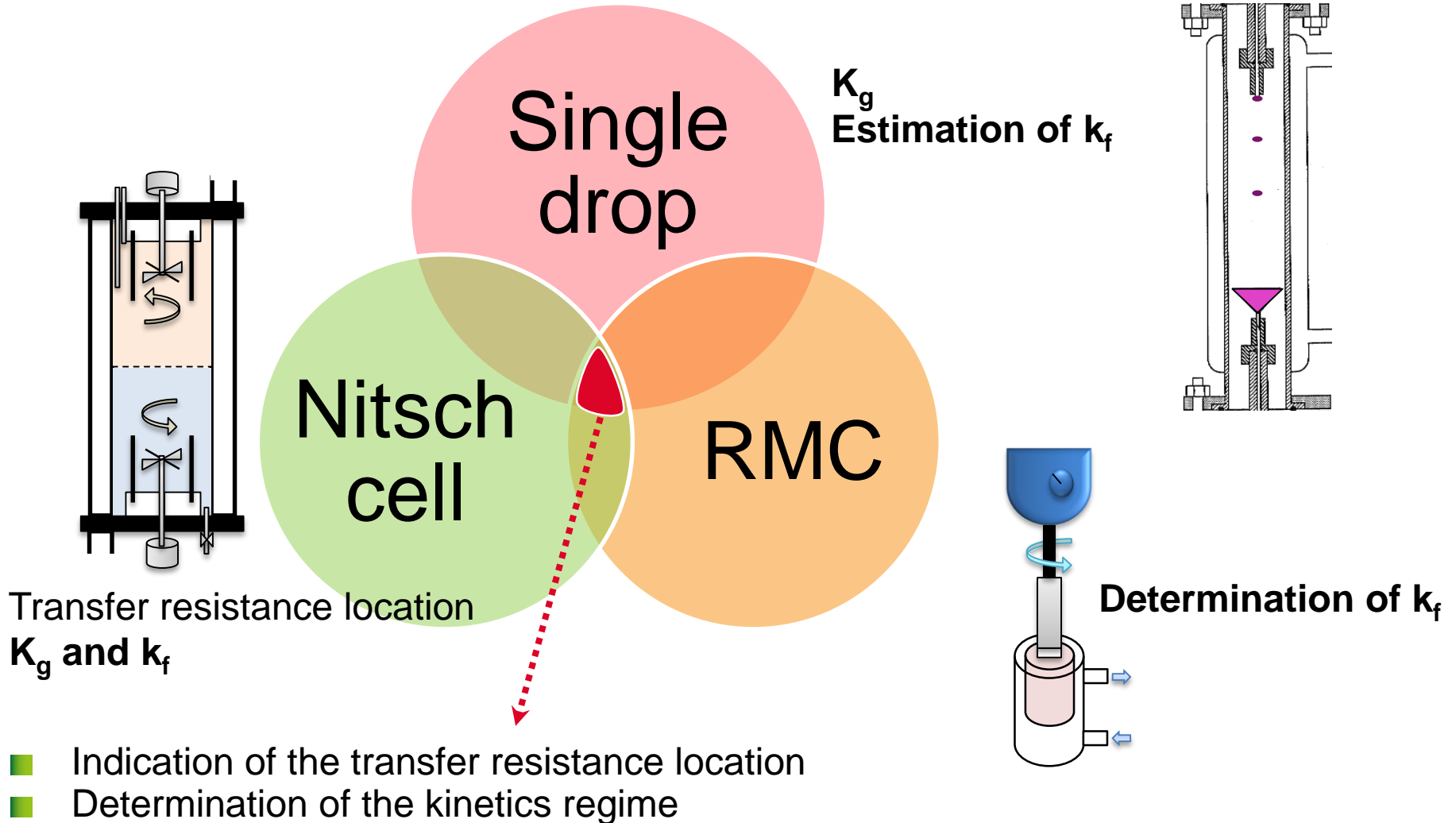
[1]: C. Musikas, P. Zorz, Process for the extraction of uranium (VI) and/or plutonium (IV), US 5132092, **1992**

[2]: Prabhu, D.R., et al., *J. Radioanal. Nucl. Chem.*, **1997**, 224(1-2) 113-117.

[3]: Pathak, P.N., et al., *Solvent Extr. Ion Exch.*, **2009**, 27(5-6) 683-694.

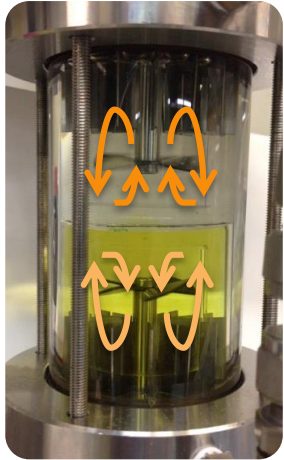
Comparison of 3 technics

- Techniques with constant interfacial area [4]

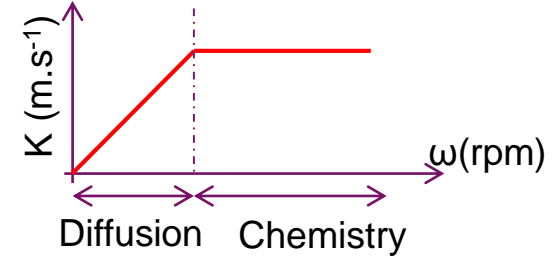


[4]: Hanna, G.J. and Noble, R.D., *Chem. Rev.*, 1985, 85(6) 583-598.

EXTRACTION KINETICS WITH U(VI): NITSCH CELL

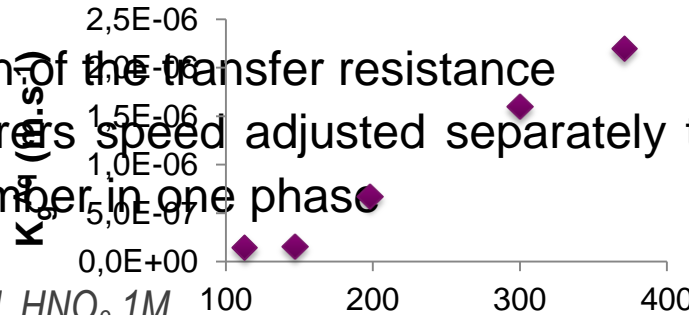


❑ Restricted stirring speed within the solvent : Chemical plateau unreached



❑ Location of the transfer resistance

➤ stirrer speed adjusted separately to keep a fixed Reynolds number in one phase



Organic phase: *N,N*-dialkylamide/TPH, HNO₃ 1M
 Aqueous phase: 40 g.L⁻¹ U(VI) HNO₃ 5M
 Temperature: 25°C

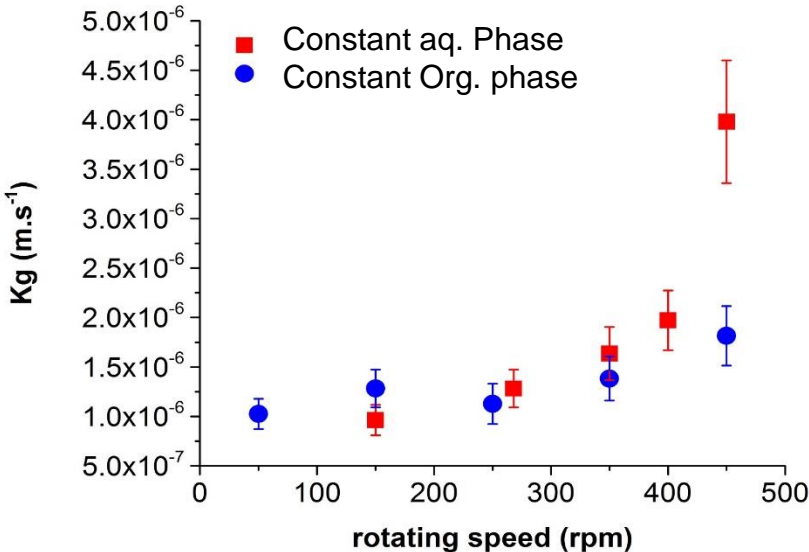
❑ Variation in aqueous phase

➤ low effect: $K_g^{aq} \approx 1.3 \pm 0.3 \cdot 10^{-6} \text{ m.s}^{-1}$

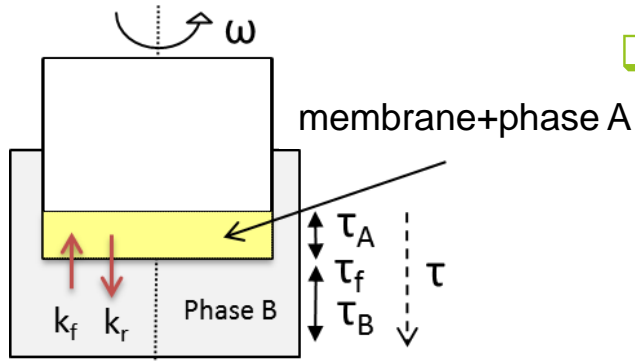
❑ Variation in organic phase

➤ High Impact: $K_g^{org} \approx 6.5 \pm 0.3 \cdot 10^{-6} \text{ m.s}^{-1}$

✓ Resistance of the U(VI) transfer located in the solvent



EXTRACTION KINETICS WITH U(VI) AND PU(IV): ROTATING MEMBRANE CELL



- Direct determination of the chemical constant, k_f :

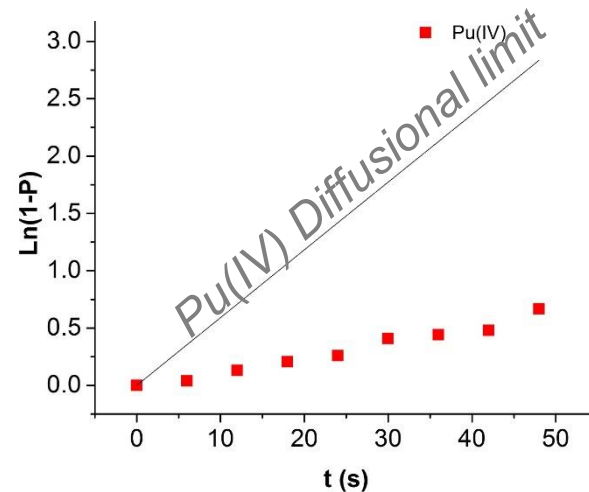
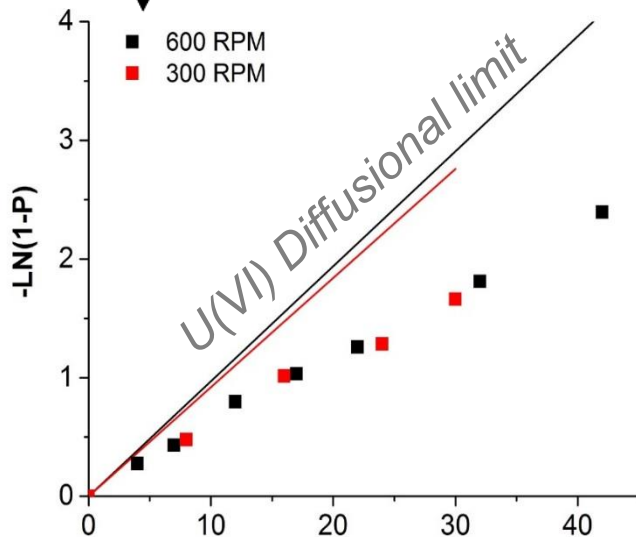
Measure of the proportion (P) of the solute transferred from A to B

Organic phase: *N,N*-dialkylamide/TPH, HNO_3 1M

Aqueous phase 1: 40 g.L^{-1} U(VI) HNO_3 5M

Aqueous phase 2: 50 mg.L^{-1} Pu(IV) HNO_3 5M

Temperature: 25°C



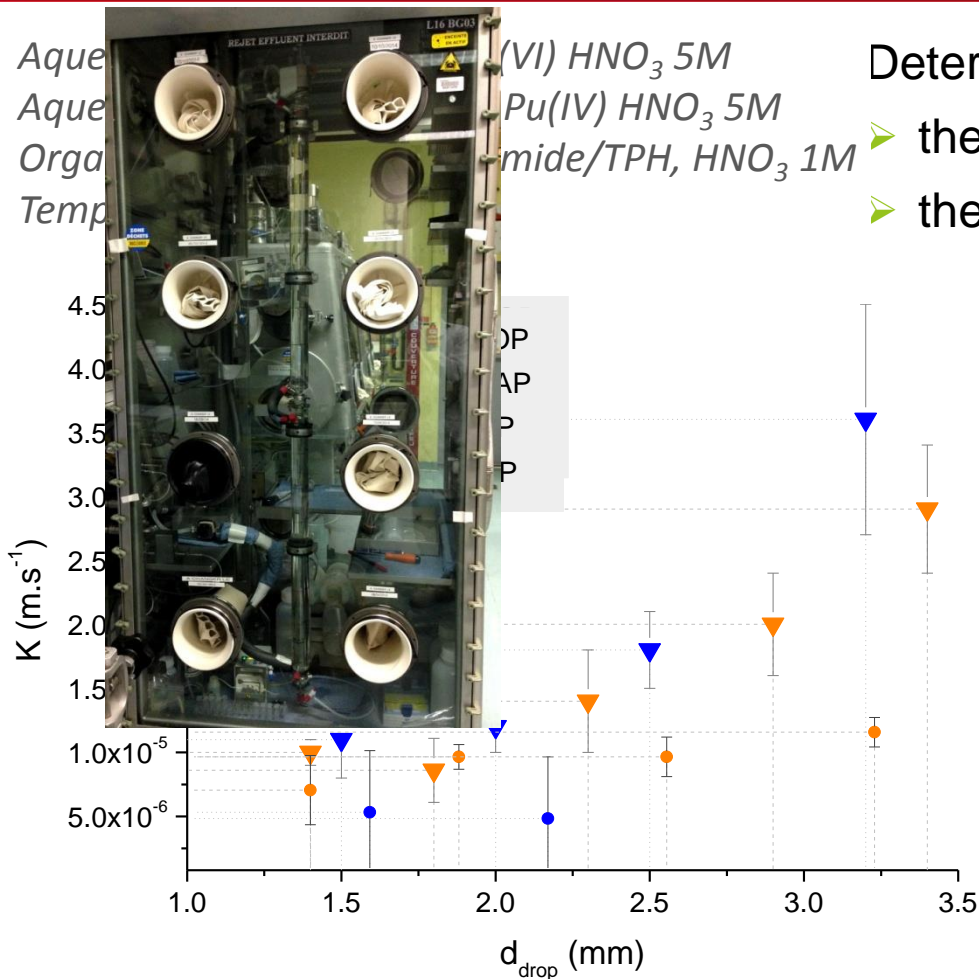
- Extraction of U(VI) at 300 and 600 rpm

✓ $k_f \text{ (m.s}^{-1}\text{)} = 1.9 \pm 0,5 \times 10^{-5}$

- Molecular diffusion seems to control the U(VI) transfer
- Pu(IV) under study but $\mathcal{D}(\text{Pu(IV)})$ to be acquired

EXTRACTION KINETICS WITH U(VI) AND PU(IV): SINGLE-DROP TECHNIQUE

Aque
Aque
Orga
Temp



Determination of K_g (Aq or Org) depending on

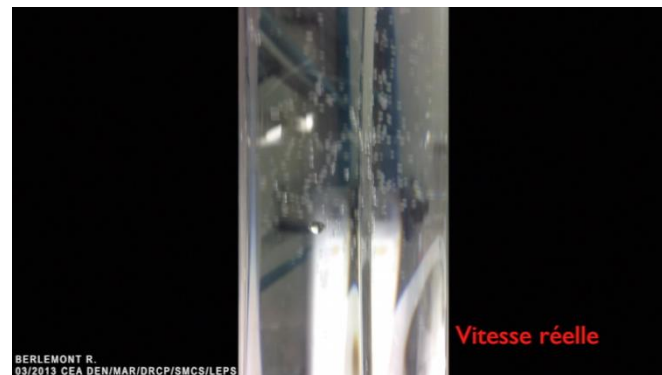
- the continuous phase
- the drop diameter

Falling drop configuration (COP)

- ✓ Increase of the K_g U(VI), Pu(IV) with the drop size
- **internal circulation** inside the aqueous droplets supposed

Rising drop configuration (CAP)

- ✓ Lower effect on K_g U(VI), Pu(IV) of the Organic drop size
- High resistance to the transfer



Vitesse réelle

- Similar transfer of U(VI) and Pu(IV) during extraction
- Diffusional resistance in organic phase
- Diffusional control supposed

- Solvent loaded with [U(VI)] in macro-concentration (40, 80 and 100g.L⁻¹)

Continuous organic phase (Falling drop) at 25°C

Aqueous drop 1: 40 g.L⁻¹ U(VI) HNO₃ 5M

Aqueous drop 2: 50 mg.L⁻¹ Pu(IV) HNO₃ 5M

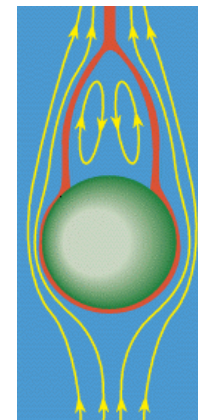
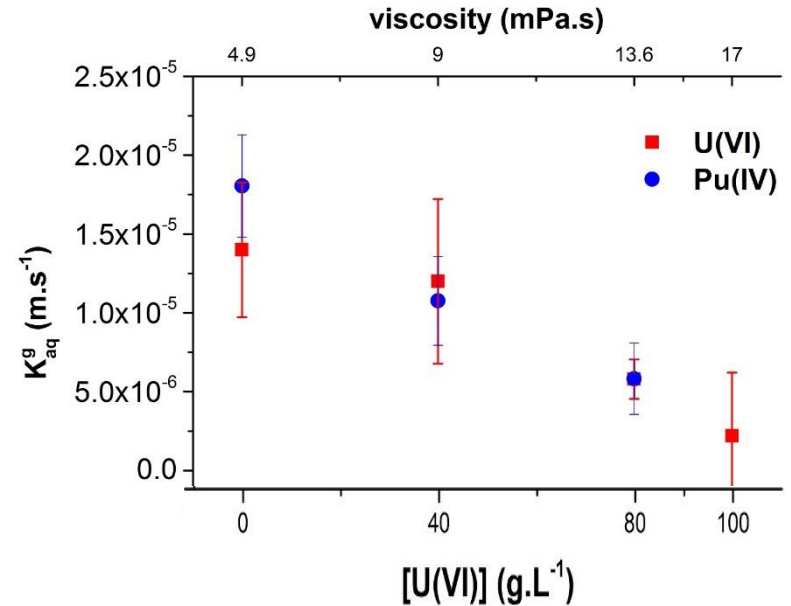
Drop size : 2.3 ± 0.1mm

- ✓ Similar trend of the mass transfer constants: the higher the organic uranium concentration, the lower the K^g of U(VI) and Pu(IV)

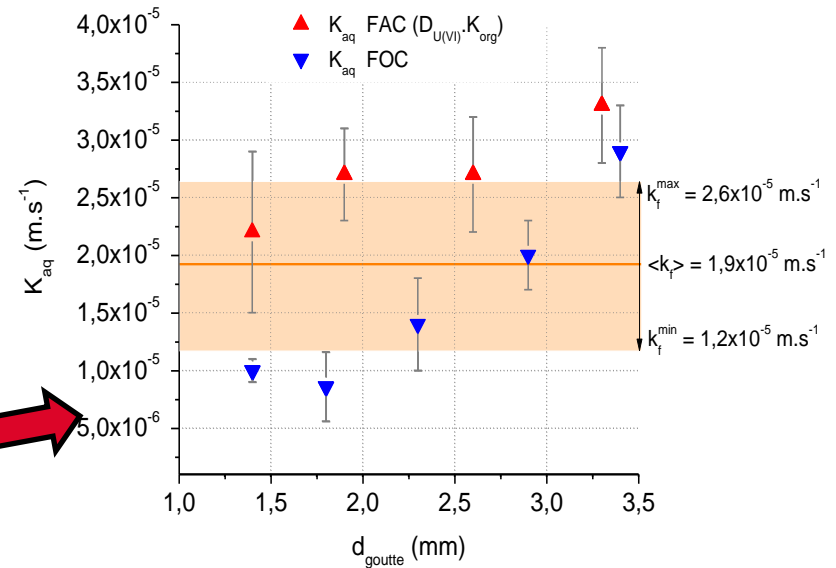
- Increase of the boundary layer of the organic phase (drop interface) with the organic phase viscosity (7 to 33 μm)

⇒ **diffusional transfer**

- 3 times slower than TBP/TPH but reliable data to implement the model



U(VI)	Nitsch cell	RMC	Single drop
K_g^{Aq} (m.s ⁻¹)	1.3 $\times 10^{-6}$	/	0 – 2.9 $\times 10^{-5}$
k_f (m.s ⁻¹)		$1.9 \pm 0,$ $\times 10^{-5}$	



- ❑ Transfer resistance located in the organic phase
 - Nitsch cell unsuitable technique for the monoamide solvent
- ❑ Molecular diffusion seems to control the transfer
- ❑ Value of k_f of U(VI) on the same order of magnitude than the Single drop one
 - Mixed regime or data to be confirmed?
- ❑ Values in agreement with the extraction model

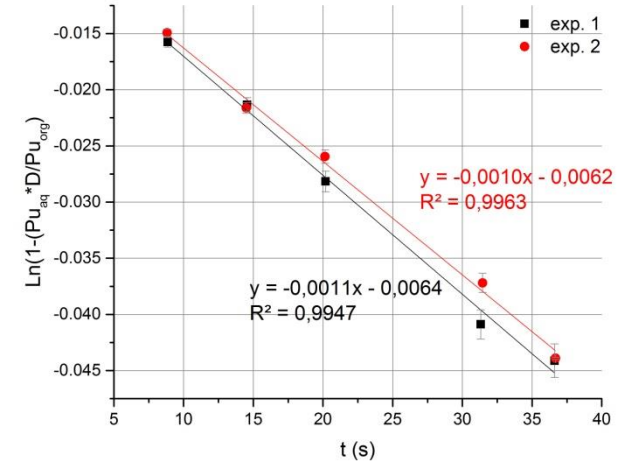
□ Pulsed column + mixer-settler tests in stripping conditions: U(VI) faster than Pu(IV)

Continuous organic phase (Falling drop) at 25°C

80 g.L⁻¹ U(VI), 40 mg.L⁻¹ Pu(IV) HNO₃ 0.15M

Aqueous drop: HNO₃ 0.1M; d=3.4 ± 0.1mm

	U(VI)	Pu(IV)	H ⁺
K_g^{Aq} (m.s ⁻¹)	6.2 x10 ⁻⁶	5.8 x10 ⁻⁷	6.8x10 ⁻⁷

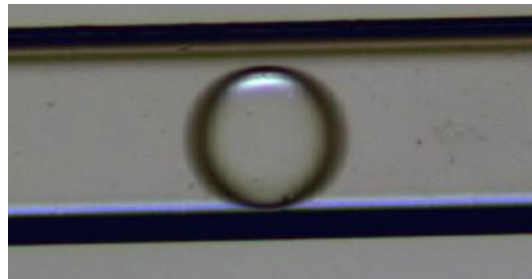
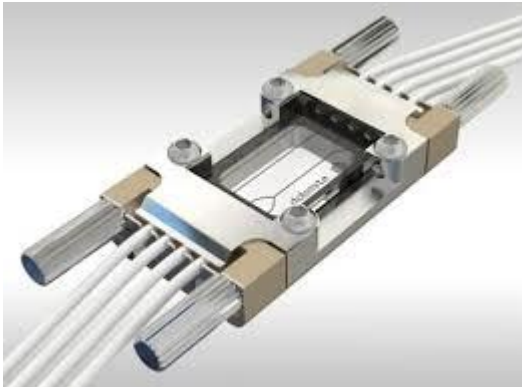


✓ U(VI) transfer 10 times faster

□ Consistency with counter-current test observations (CBP facility)

➤ More information with the Atal2016 – 236 and 241 presentations

- ❑ **Single drop method: most complete study**
- ❑ U(VI) and Pu(IV) seem to have **similar behavior** during the extraction process but new experiments have to confirm that trend
- ❑ **Mass transfer probably controlled by the diffusional resistance** in organic phase
- ❑ Data reliable enough to implement the **model**
 - Determination of the mass transfer constants by **micro devices**



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