

DE LA RECHERCHE A L'INDUSTRIE
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Mass transfer kinetics of uranium(VI) and plutonium(IV) extracted by N,N- dialkylamides

Comparison of different techniques

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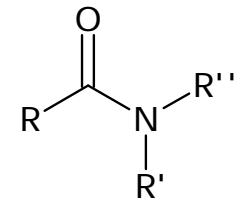
1- CEA Marcoule, 2- UPMC

CEA Marcoule, Nuclear Energy Division
Radiochemistry & Processes Department
Modelling and Process Chemistry Separation Service
Conception of Extraction Processes Laboratory



- Reprocessing of future spent fuels [1]
 - Need of innovative processes

- Extractant choice
 - Selection of the extracting molecule among N,N-dialkylamides [2-4]
 - Easy to synthesize and degradation products easily handled (C,H,O,N)
 - Low solubility in aqueous phase
 - High selectivity versus fission products



N,N dialkylamide

- Need of a full phenomenological model

Study of the scale-up

⇒ Mass transfer kinetics of U(VI) and Pu(IV) extraction

[1]: Treatment and Recycling of spent nuclear fuel, Nuclear Energy Division Monograph, Le Moniteur Ed., **2008**

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

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

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

- Existence of various techniques with constant interfacial area [5]
 - stirred cells, rotative cells, single drop method
 - ...

- Choice of single drop

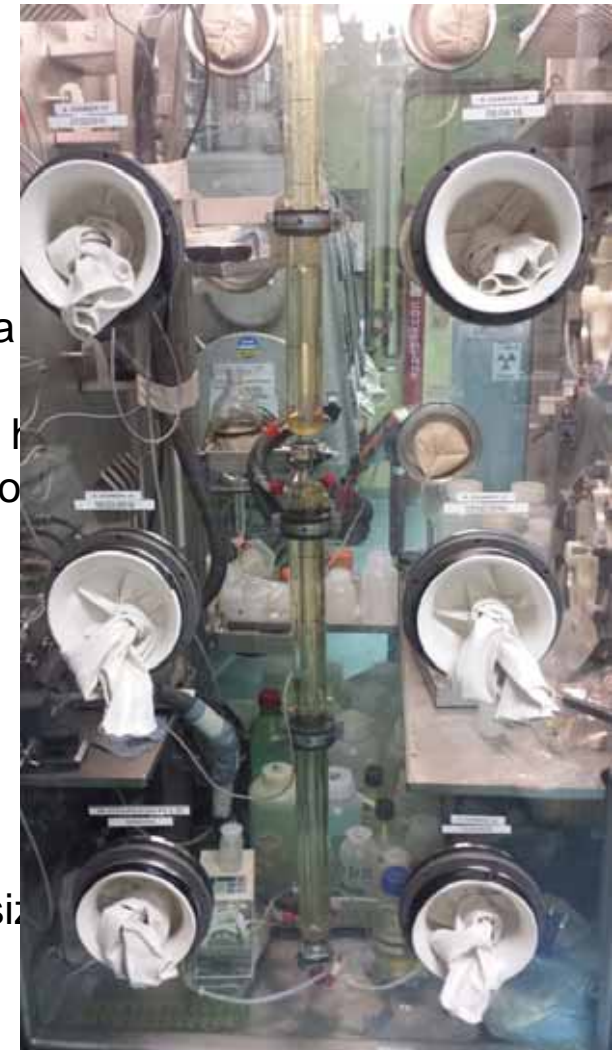
- Know-how in our team [6] and available in glove-box
- Principle: travel of a drop into a continuous phase from a

☹ End effects ⇒ work at different h
 Kinetics range $[10^{-7}-10^{-3}] \text{ m.s}^{-1}$ ⇒ not too slow or too fast

☺ Good control of drop size
 Easily handled

- Our system

- 15mm inner diameter
- 150 cm high
- 18mL/ h for the injection
- Hammered needle to control the drop size
- Organic or aqueous continuous phase



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

[6]: Dinh, B. *Investigation of the extraction kinetics of uranyl nitrate by tributylphosphate: Application of the single drop method in pulsed medium*. PhD Thesis. Ecole centrale des Arts et Manufactures, CEA R-S-414, 1987.

Theory of mass transfer kinetic

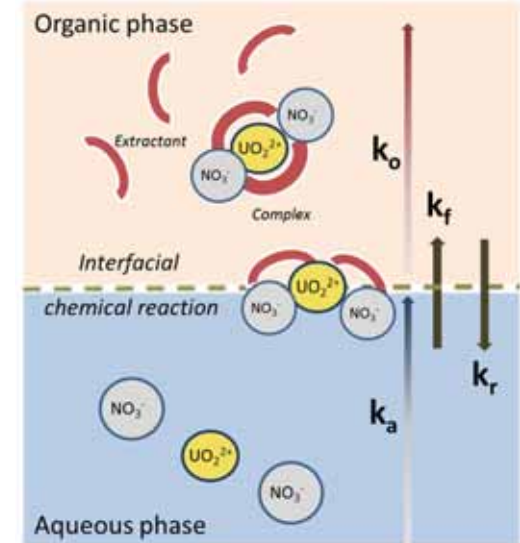
- Overall mass transfer could be described as

$$K_g \text{ (m/s)} = f(k_o, k_a, k_f)$$

$$\frac{1}{K_o} = \frac{D}{k_a} + \frac{1}{k_o} + \frac{1}{k_r}$$

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

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



- Kinetic regime: controlled by diffusion and/or chemical reaction
- Single drop method:

- Fick's law and double film theory

$$v \frac{dC}{dt} = aK^g (C - C^*)$$

- Graphic determination of K_g

Travel time

Injection flow

Drops number

⇒ Drop surface = interfacial area

C = concentration in the drop

C^* = initial concentration

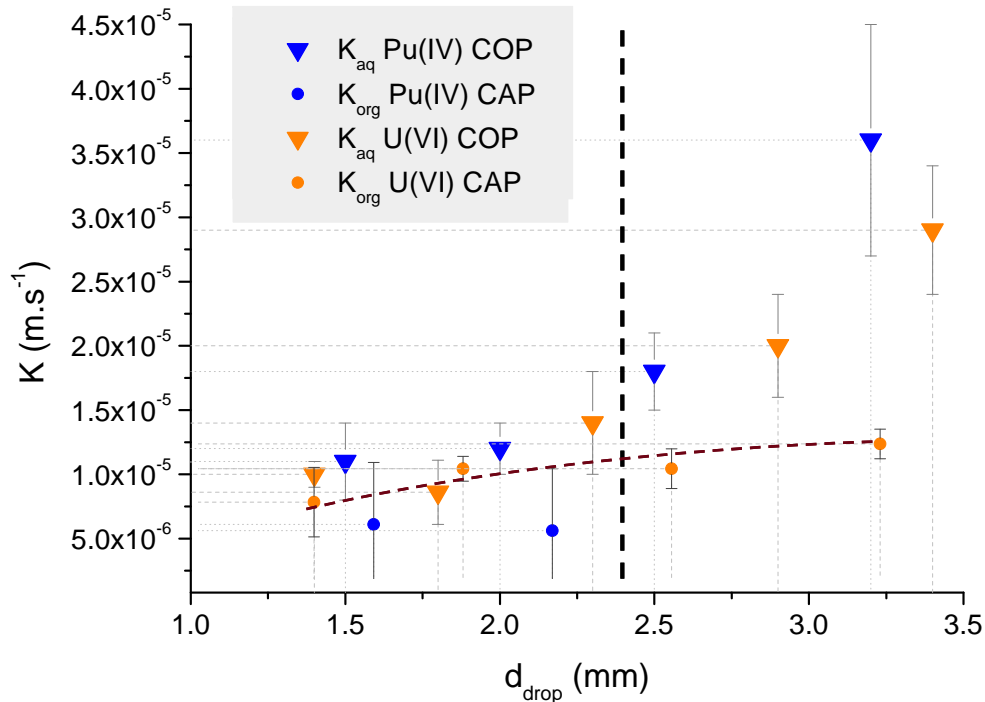
d = droplet diameter, t = travel time

K^g = global mass transfer constant

⇒ Droplet diameter

RESULTS: EXTRACTION KINETICS WITH U(VI) AND PU(IV)

Extraction kinetics in aqueous and continuous organic phase



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

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

Organic phase: N,N-dialkylamides/TPH, HNO₃ 1M

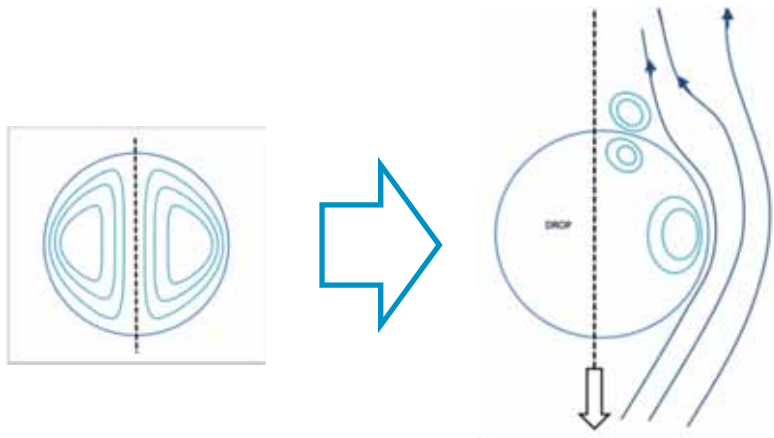
Temperature: 25°C

Falling drop configuration (COP)

- ✓ Similar transfer between U(VI) and Pu(IV)
- ✓ Increase of the K_g U(VI), Pu(IV) with the drop size
- Mass transfer probably influenced by the **internal circulation** inside the aqueous droplets

Rising drop configuration (CAP)

- ✓ Organic drop size has a lower effect on K_g U(VI), Pu(IV)
- **diffusional resistance in organic phase**
- **diffusional control** supposed

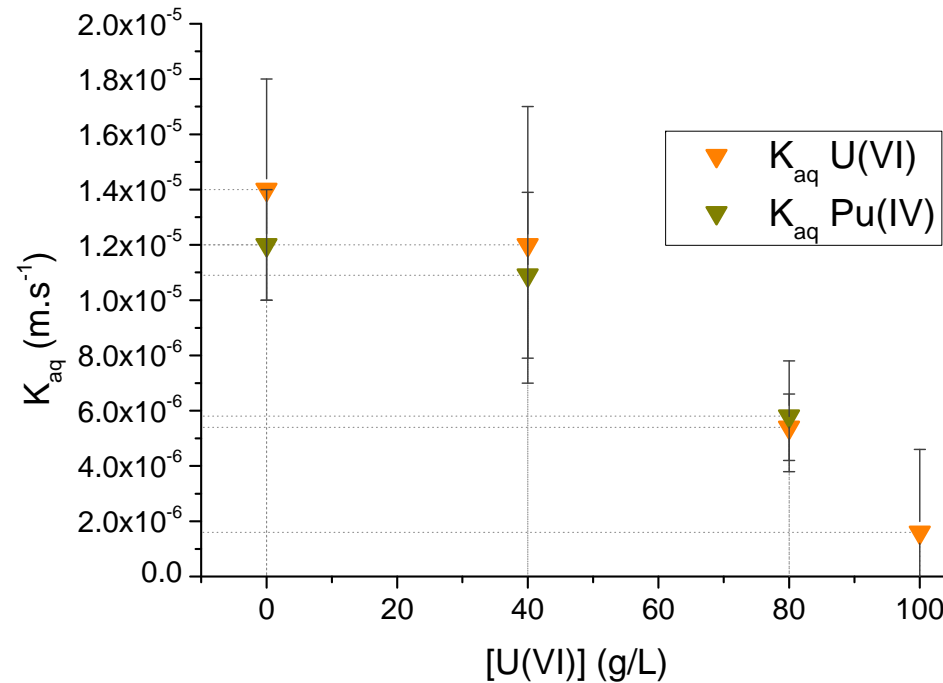
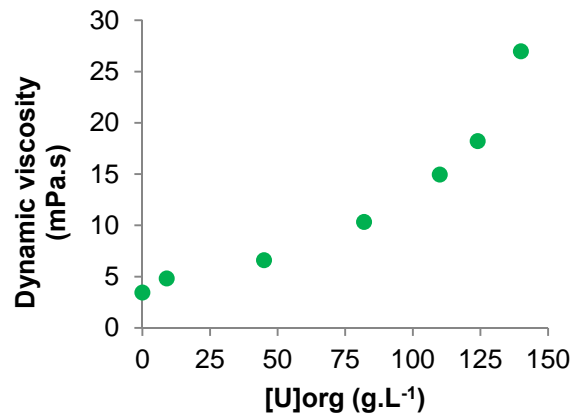


Continuous organic phase (Falling drop) at 25°C

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

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

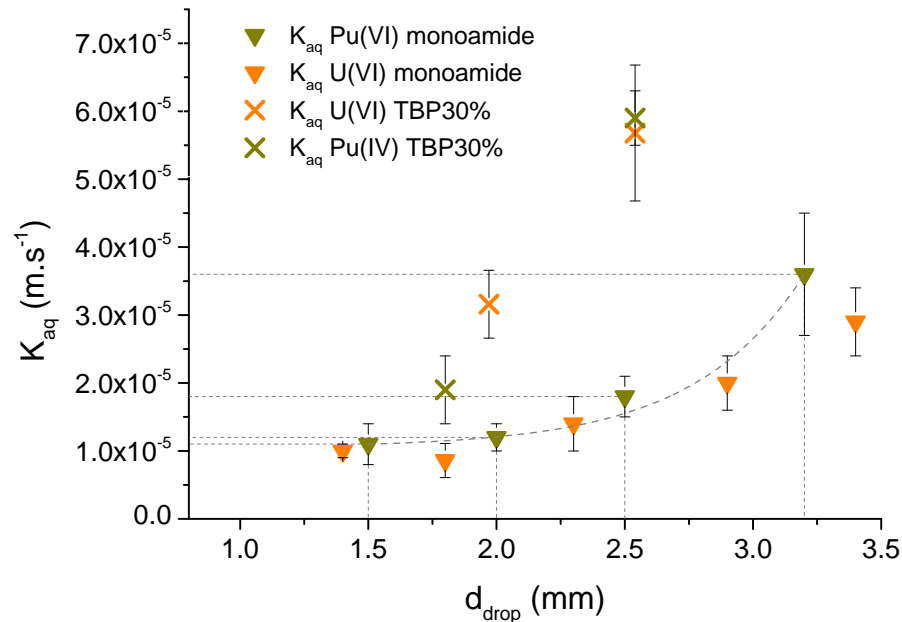
Drop size : 2.3 ± 0.1mm



- ✓ Similar trend of the mass transfer constants:
the higher the organic uranium concentration, the lower the K^g of U(VI) and Pu(IV) is
- Increase of the boundary layer of the organic phase (drop interface) with the organic phase viscosity
⇒ *diffusional transfer supposed*

RESULTS: EXTRACTION KINETICS WITH U(VI) AND PU(IV)

3- Comparison with classic extractant: TBP 30% diluted in TPH



Continuous organic phase (Falling drop), 25°C

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

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

Organic phase: TBP 30%/TPH or N,N-dialkylamides/TPH

- ✓ Transfer of U(VI) and Pu(IV) with the monoamide based solvent is slower than the transfer with TBP

For $d_{\text{drop}} = 2.0$ mm, K^g are **3 to 1.6 times slower** respectively

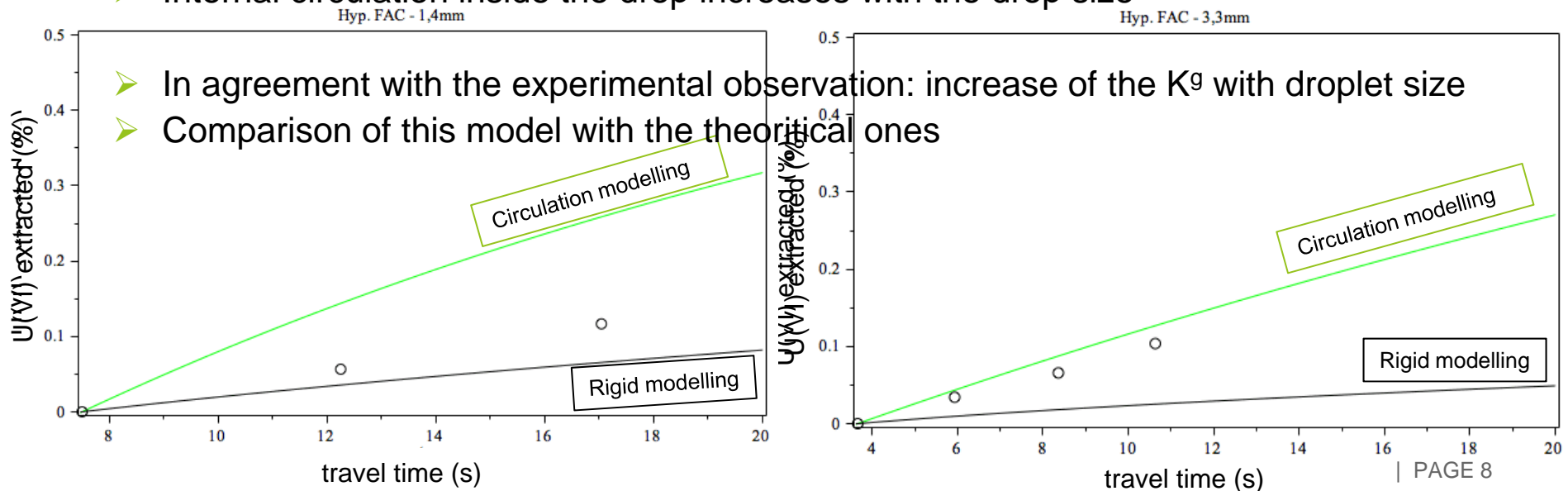
For $d_{\text{drop}} = 2.5$ mm, K^g are about **3 times slower**

- ✓ Related to the difference of the solvent viscosities ?

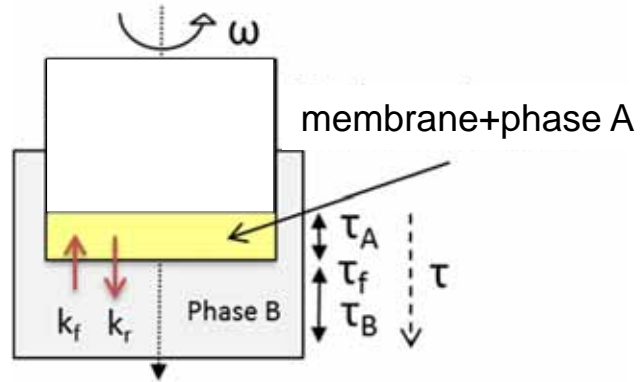
3.6 mPa.s for the monoamide-based solvent and **1.3 mPa.s** for TBP 30%/TPH

- ❑ Model for U(VI) based on literature's correlations
 - Supposing a diffusional transfer into the continuous phase
 - 2 hypothesis
 - 1- rigid droplet: transfer only controlled by diffusion
 - 2- perfect internal circulation: no diffusional resistance into the droplet
 - Study of 2 drop diameters in the both configurations

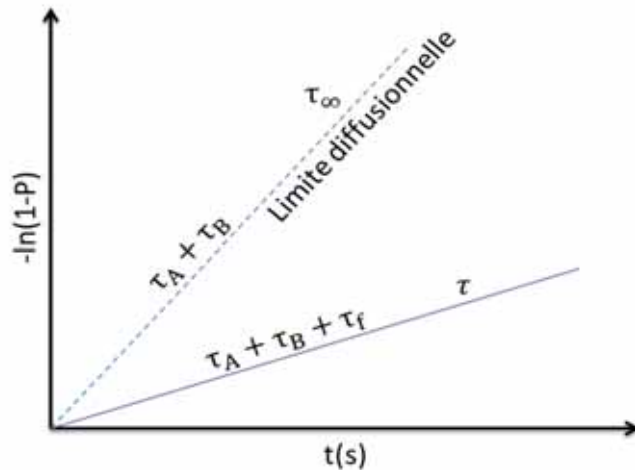
- ❑ Falling drop configuration
 - Model to be improved
- ❑ Rising drop configuration
 - Internal circulation inside the drop increases with the drop size



ROTATIVE MEMBRANE CELL: COMPARISON WITH AN INNOVATIVE KINETIC TECHNIQUE



- Adding a drop with solute on a membrane which is fixed on an stirring axle dived into a continuous phase
- Good control of the diffusion of the solute into the membrane
- Direct determination of the k_f (chemical constant)
 - ✓ Measure of the proportion (P) of the solute transferred into phase B



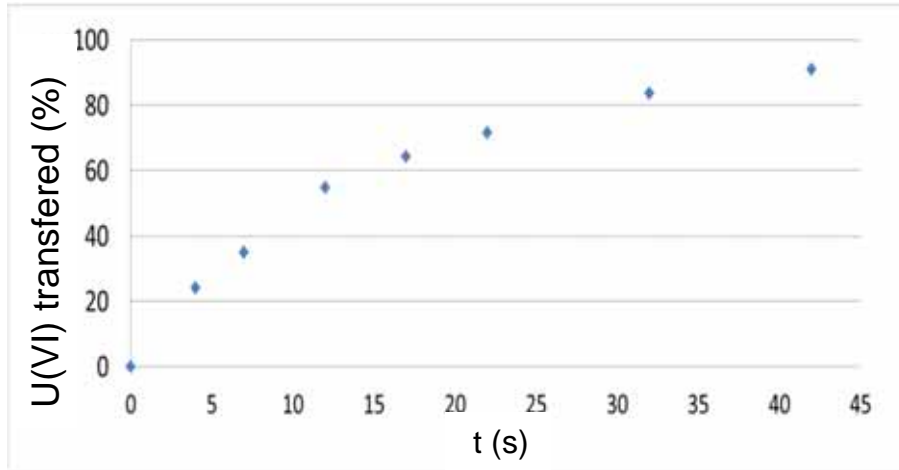
$$P(t) \approx 1 - e^{-\frac{t}{\tau}} \quad \text{with } \tau = \tau_A + \tau_B + \tau_f$$

$$\text{and } \tau_A = \frac{L^2}{3D_m} \quad \tau_B = \frac{L\sigma\delta}{DD_B} \quad \tau_f = \frac{L}{k_f}$$

where $D_m = \frac{D_A}{\lambda}$, λ = membrane tortuosity

ROTATIVE MEMBRANE CELL

U(VI) extraction

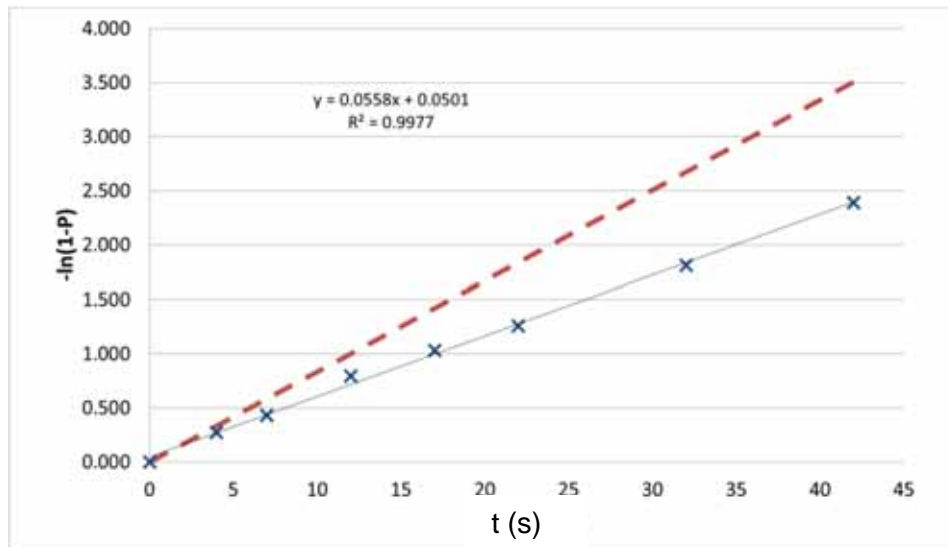


Organic phase: *N,N*-dialkylamides/TPH, HNO_3 1M
 Aqueous phase: 40 g.L^{-1} U(VI) HNO_3 5M
 Temperature: 25°C

- Work at 300 and 600 rpm
 - 80% of U(VI) transferred after 30s stirring
 - No differences between the stirring speed
- ✓ Control of the diffusion into the membrane

- Suitable technique for this study

Preliminary result: $k_f \approx 1.8 \pm 0,5 \cdot 10^{-5} \text{ m/s}$



- Molecular diffusion seems to control the transfer as in the Single drop technic
- Very similar value of the constant than with the single drop technique

2 complementary techniques studied

Single-drop technique

- U(VI) and Pu(IV) have similar behaviour during the extraction process

Falling drop configuration

$$K_g \text{ U(VI), Pu(IV)} \approx 1-2 \cdot 10^{-5} \text{ m.s}^{-1} \quad 1.5 < d < 2.5 \text{ mm}$$

Rising drop configuration

$$K_g \text{ U(VI)} \approx 10^{-5} \text{ m.s}^{-1} \quad \text{and} \quad K_g \text{ Pu(IV)} \approx 5 \cdot 10^{-6} \text{ m.s}^{-1}$$

- Mass transfer seems to be controlled by the diffusional resistance in organic phase
- Diffusional regime supposed but to be confirmed

Rotative membrane cell

- Suitable technique to measure mass transfer constants $k_f \approx 1.8 \cdot 10^{-5} \text{ m.s}^{-1}$
- Indication on the kinetic regime: under diffusion control

OUTLOOKS

- Comparison between the constant values obtained is on going
- Determination of the kinetic regime thanks to literature's model

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YOU for your attention



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Nuclear Energy Division
Radiochemistry and Processes Department
Separation Process Chemistry & Modelling Service
Elaboration of Separation Process Laboratory



- Two phases mixed independently in order to have a planar interface
 - constant interfacial area can be calculated [6]
 - stirrers speed adjusted separately to keep the same Reynolds number in both phases

$$Re = \frac{Nd^2\rho}{\eta}$$

- Global mass transfer coefficient in aqueous phase is obtained [6] following this equation
 - Graphic determination

$$\ln\left(\frac{C_{aq} - C_{aq}^{eq}}{C_{aq}^{ini} - C_{aq}^{eq}}\right) = \ln\left(\frac{C_{org}^{eq} - C_{org}}{C_{org}^{eq} - C_{org}^{ini}}\right) = -\frac{A}{V_{aq}} K_{aq} \left(1 + \frac{1}{\varepsilon}\right) t$$

with $\varepsilon = \frac{V_{org} D_m}{V_{aq}}$

FIRST RESULTS: EXTRACTION KINETICS WITH URANIUM(VI)

Determination of the phase limiting the mass transfer

□ Conditions

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

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

Temperature: 25°C

Variation of the stirring speed in only one of the phases

□ Variation of the Re in aqueous phase

- low effect on the global mass transfer

$$K_g^{\text{aq}} \approx 1.3 \pm 0.3 \cdot 10^{-6} \text{ m.s}^{-1} \text{ at same Re}$$

- At 450 rpm, increase of the global coefficient is due to the instability of the interface which might increase the interfacial area

□ Variation of the Re in organic phase

- impact on the global mass-transfer coefficient

- **At 450 rpm**, the interface remains stable

$$K_g^{\text{aq}} \approx 6.5 \pm 0.3 \cdot 10^{-6} \text{ m.s}^{-1}$$

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

