Influence of organic ligands on actinides(V) in natural waters

---

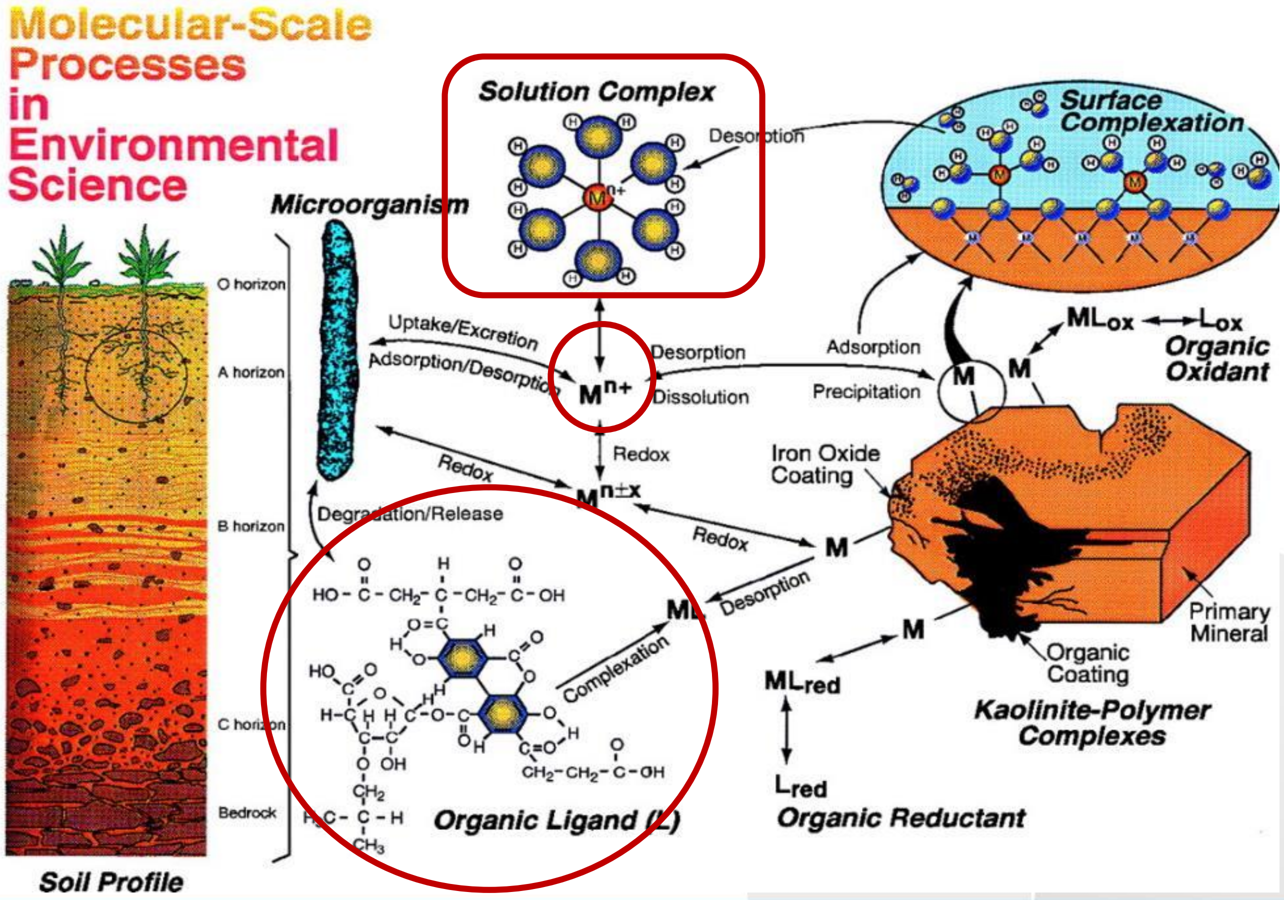
Meng LUO

Supervisors
M. Maloubier, C. Le Naour
Pôle
Énergie et Environnement/RAPHYNEE

Université Paris-Saclay, CNRS/IN2P3-IJCLab,
91405 Orsay, France,
e-mail: meng.luo@ijclab.in2p3.fr

Introduction

Behavior of actinide in the environment



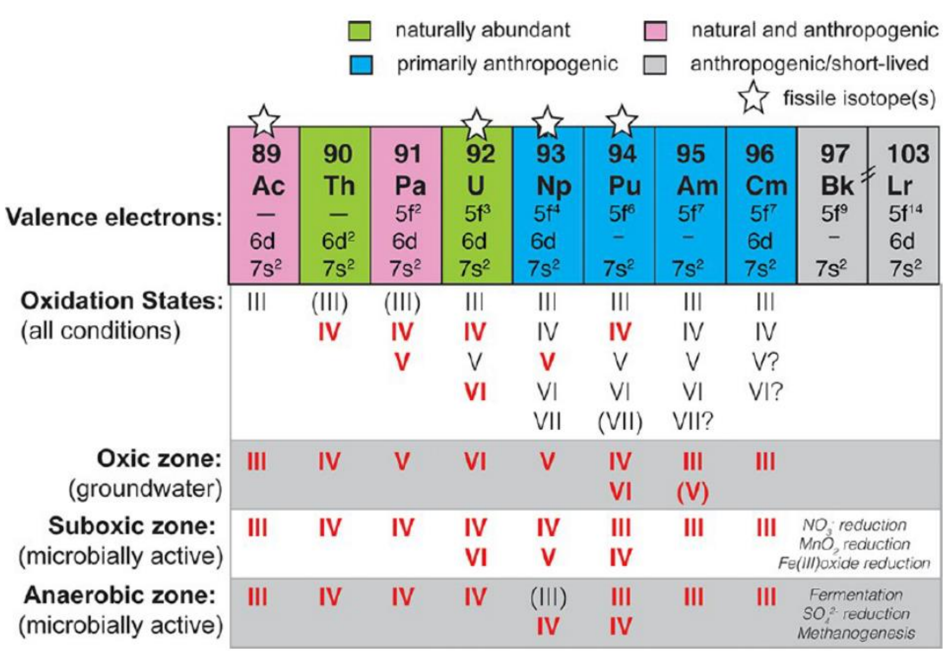
- Radionuclide contamination: a global, complex, and long lasting issue.
- The mobility of actinides depends on: pH, redox potential, soil and aquifer compositions.
- In particular, the presence of natural or anthropogenic organic ligands can modify the speciation and the solubility of these radioelements.

[1] Brown, G. E., Foster, A. L., Ostergren, J. D., *PNAS*, 1999, *96*, 3388-3395.

Introduction

Actinides

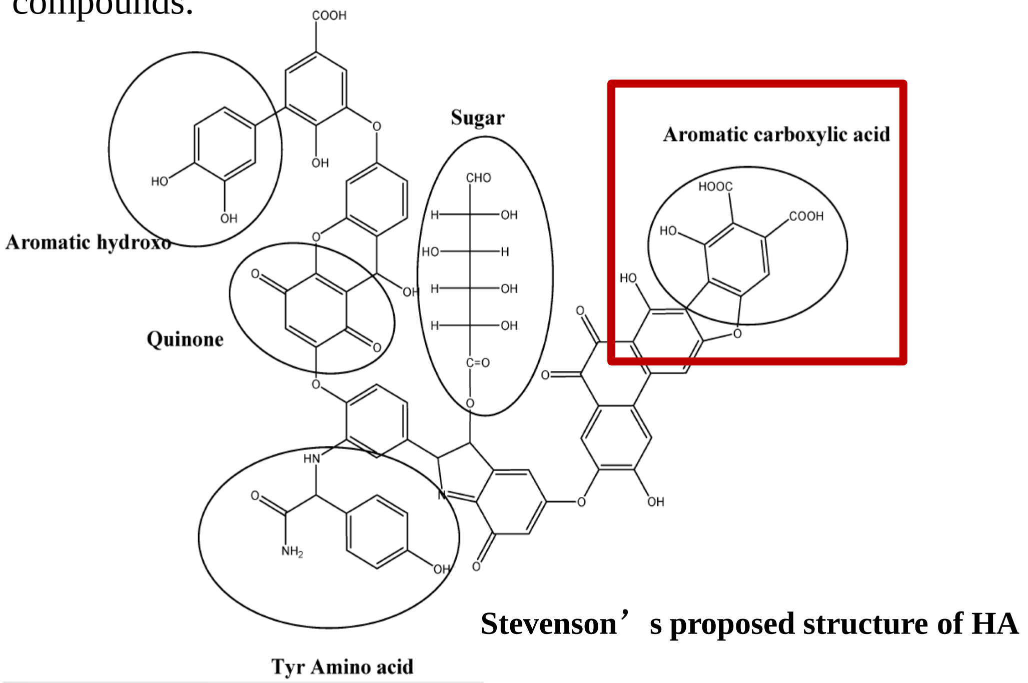
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	**Th**	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
227.028	232.038	231.036	238.029	237.048	244.064	243.061	247.070	247.070	251.080	[254]	257.095	258.1	259.101	[262]



🟩 naturally abundant
🟪 natural and anthropogenic
🟦 primarily anthropogenic
⬜ anthropogenic/short-lived
☆ fissile isotope(s)

	☆ 89 Ac	90 Th	91 Pa	☆ 92 U	☆ 93 Np	☆ 94 Pu	95 Am	96 Cm	97 Bk	103 Lr
Valence electrons:	— 6d $7s^2$	— $6d^2$ $7s^2$	$5f^2$ 6d $7s^2$	$5f^3$ 6d $7s^2$	$5f^4$ 6d $7s^2$	$5f^6$ – $7s^2$	$5f^7$ – $7s^2$	$5f^7$ 6d $7s^2$	$5f^9$ – $7s^2$	$5f^{14}$ 6d $7s^2$
Oxidation States: (all conditions)	III	(III) IV	(III) IV V	III IV V VI	III IV V VI VII	III IV V VI (VII)	III IV V VI VII?	III IV V? VI?		
Oxic zone: (groundwater)	III	IV	V	VI	V	IV VI	III (V)	III		
Suboxic zone: (microbially active)	III	IV	IV	IV VI	IV V	III IV	III	III	NO_3^- reduction MnO_2 reduction Fe(III)oxide reduction	
Anaerobic zone: (microbially active)	III	IV	IV	IV	(III) IV	III IV	III	III	Fermentation SO_4^{2-} reduction Methanogenesis	

- Natural organic matter : complex mixture of thousands of organic compounds.



Stevenson' s proposed structure of HA

$$An^{4+} > An^{3+} > AnO_2^{2+} > AnO_2^{+}$$

Low solubility
Strong sorption
Low mobility

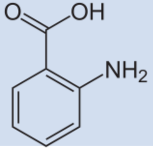
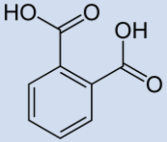
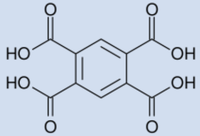
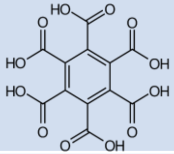
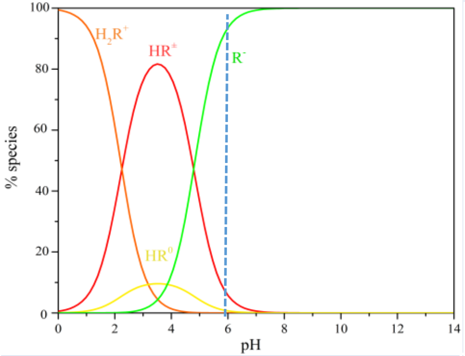
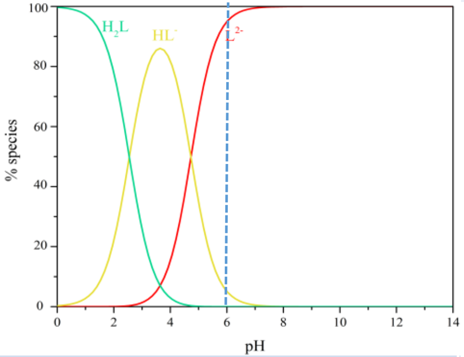
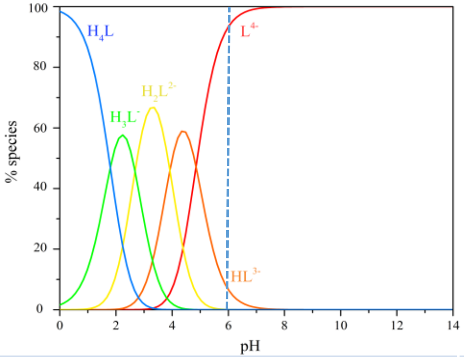
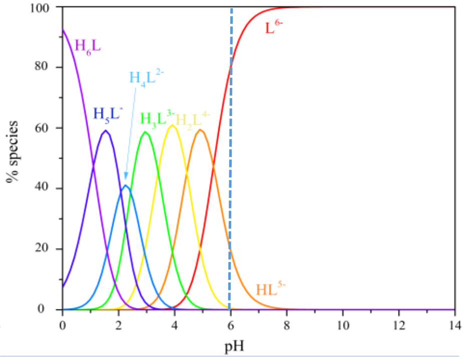
soluble
Weak sorption
High mobility

⇒ Use of simple ligand as model

[2] Maher, K. et al., Inorganic Chemistry **2013,** *52(7)*, 3510-3532.

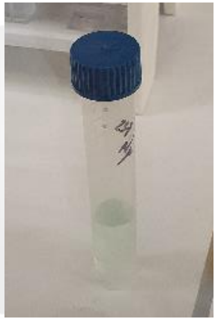
Studied systems

Aromatic carboxylic acid

	Anthranilic acid	Phthalic acid	Pyromellitic acid	Mellitic acid
structure				
Speciation diagram				
Source	metabolite produced in L-tryptophan-kynurenine pathway in the central nervous system	major pollutants of purified terephthalic acid wastewater	intermediate products of the biochemical processes of the humic substances	end product of exhaustive oxidation of graphite, coal, ...

Complexation of Np(V) with aromatic carboxylic acid

^{237}Np



Methodology

- **Stock solutions (cNp=10^{-2} M)**

  Dissolution of $NpO_2(OH)\cdot 2.5H_2O$ in 1M HCl

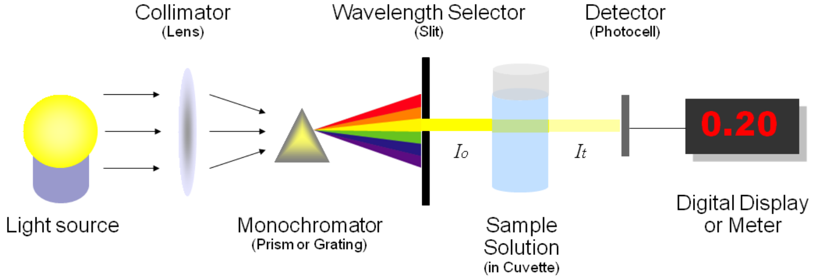
- **Complexation of Np(V)-ligand by UV-Vis-NIR spectrophotometry**

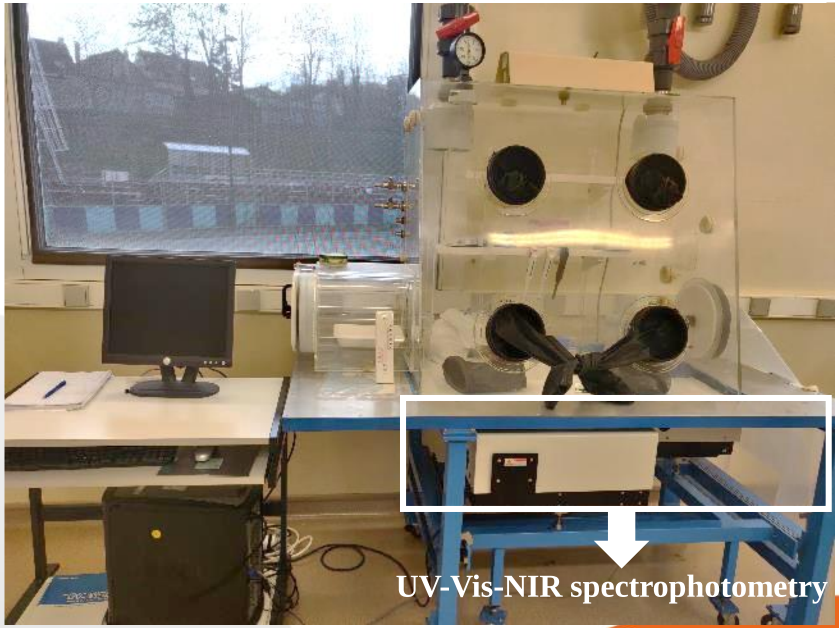
$$M + nL \overset{\beta n}{\leftrightarrow} ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

To determine the stability constants, the ligand concentration is increased in actinide solutions.

Spectra analyzed by HypSpec. exe software

Schematic diagram of UV-visible spectrophotometer

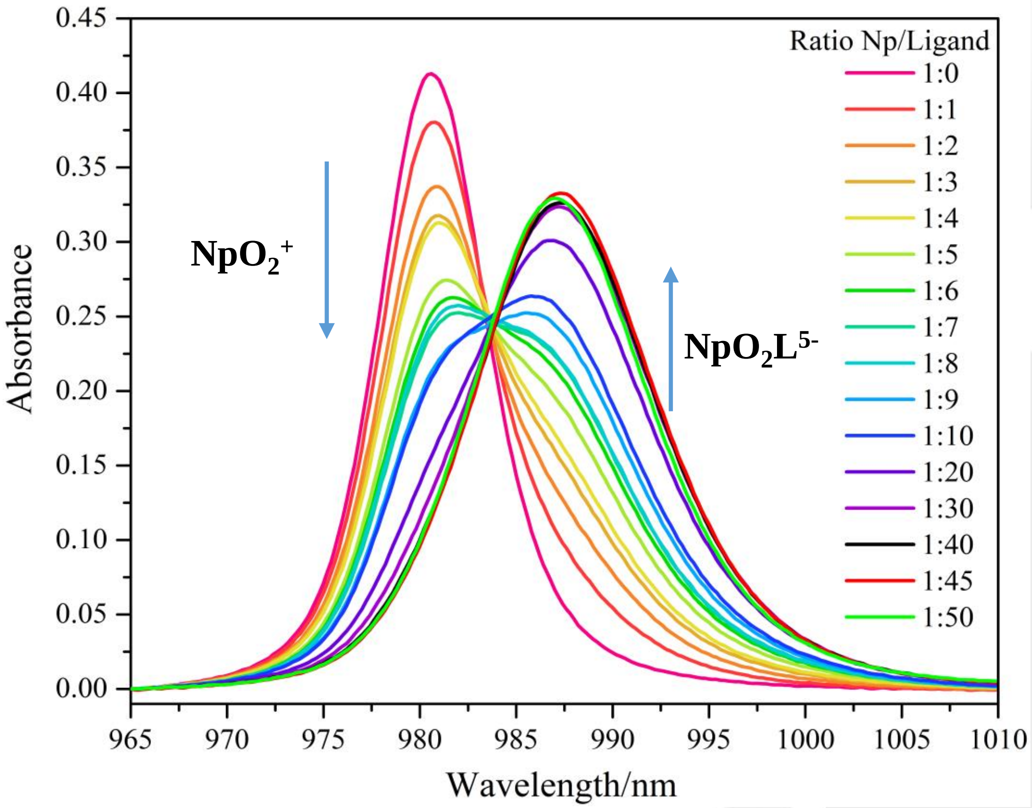




UV-Vis-NIR spectrophotometry

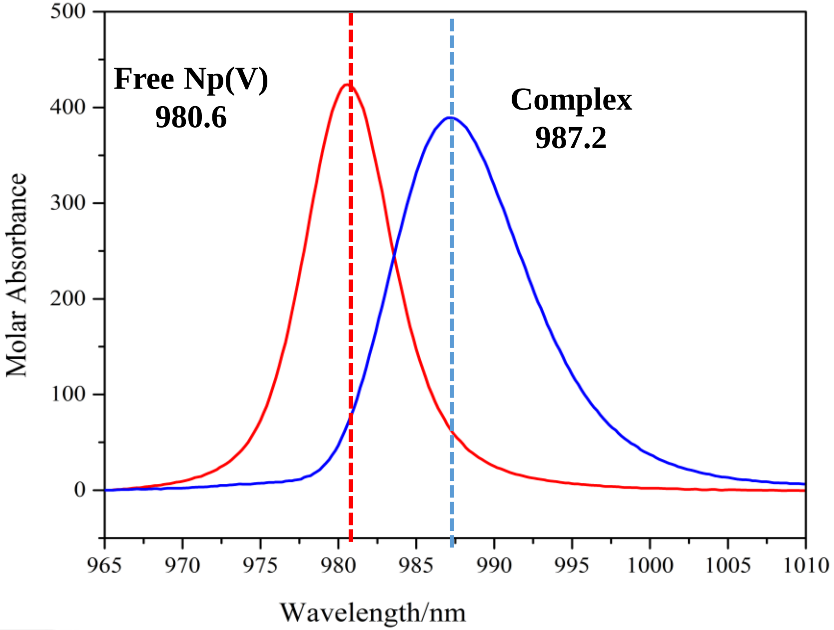
Complexation of Np(V) with aromatic carboxylic acid

☐ **Np(V)-Mellitic acid (I=1.0M NaCl, room temperature)**



Absorption spectra of Np(V)-mellitic acid species

Hypspec

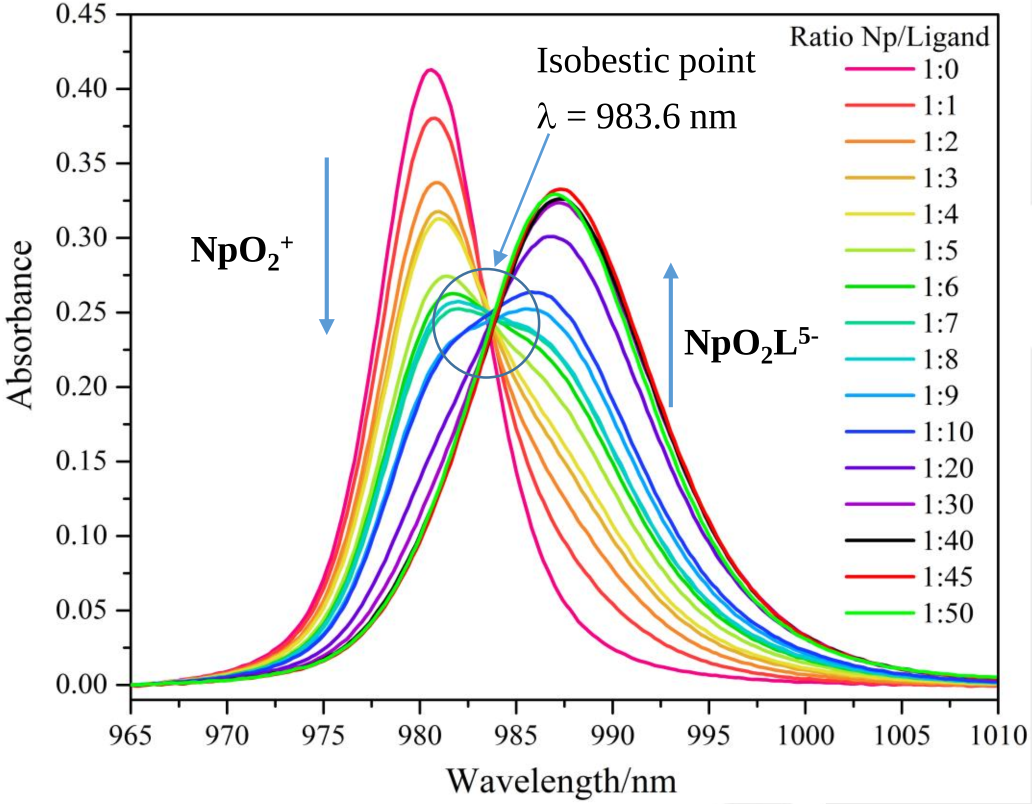


Equilibrium	log β^{app}	media	Ref.
$NpO_2^+ + L^{6-} \leftrightarrow NpO_2L^{5-}$	**2.35 ± 0.02**	I=1.0M NaCl pH=6	Current work
	2.34 ± 0.01	I=1.0M $NaClO_4$	Choppin et al.

[7] Choppin G R, et al,. Journal of alloys and compounds, 1998, 271: 774-777.

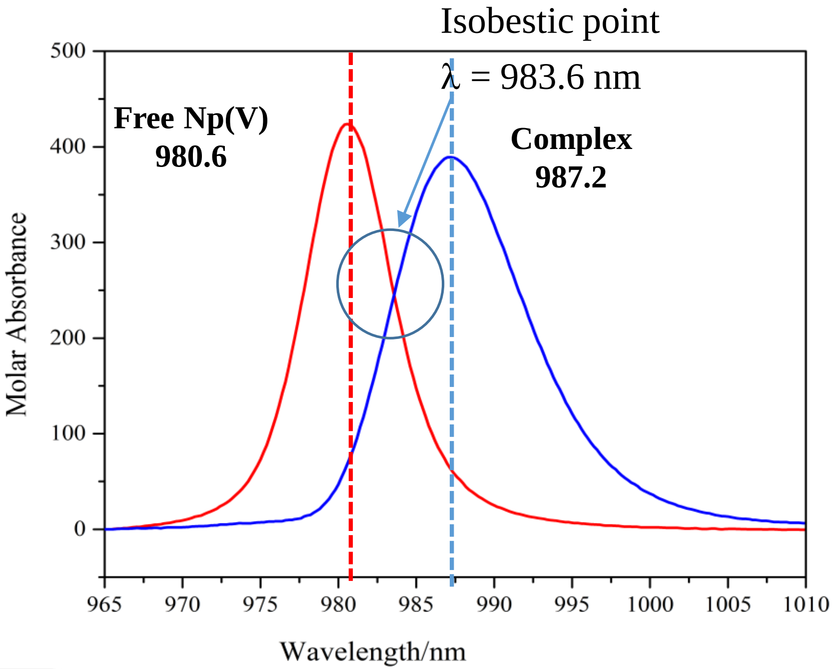
Complexation of Np(V) with aromatic carboxylic acid

☐ Np(V)-Mellitic acid (I=1.0M NaCl, room temperature)



Absorption spectra of Np(V)-mellitic acid species

Hypspec

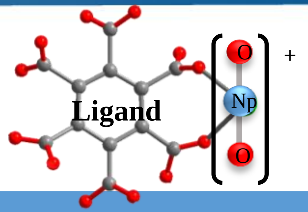


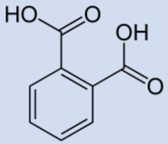
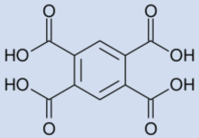
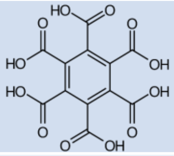
Equilibrium	log β^{app}	media	Ref.
$NpO_2^+ + L^{6-} \leftrightarrow NpO_2L^{5-}$	**2.35 ± 0.02**	I=1.0M NaCl pH=6	Current work
	2.34 ± 0.01	I=1.0M $NaClO_4$	Choppin et al.

[7] Choppin G R, et al,. Journal of alloys and compounds, 1998, 271: 774-777.

Complexation of Np(V) with aromatic carboxylic acid

Stoichiometry of Np(V) with aromatic carboxylic acid 1:1



	Phthalic acid	Pyromellitic acid	Mellitic acid
structure			
Equilibrium	$NpO_2^+ + L^{2-} \leftrightarrow NpO_2L^-$	$NpO_2^+ + L^{4-} \leftrightarrow NpO_2L^{3-}$	$NpO_2^+ + L^{6-} \leftrightarrow NpO_2L^{5-}$
$\log \beta^{app}$ Current work	**1.37 ± 0.02** I=1.0M NaCl pH=6	**1.64 ± 0.02** I=1.0M $LiClO_4$ pH=6	**2.35 ± 0.02** I=1.0M NaCl pH=6
$\log \beta^{app}$ Ref.	1.62 ± 0.02 I=1.0M $NaClO_4$	1.80 ± 0.01 I=1.0M $NaClO_4$	2.34 ± 0.01 I=1.0M $NaClO_4$
n	1	2	6
$\log \beta^c$ Current work	**1.37**	**1.34**	**1.57**

n:Number of chelating binding sites **$\log \beta^c$** :statistically corrected stability constants

[7] Choppin G R, et al,. Journal of alloys and compounds, 1998, 271: 774-777.

Complexation of Pa(V) with aromatic carboxylic acid

Methodology

^{233}Pa

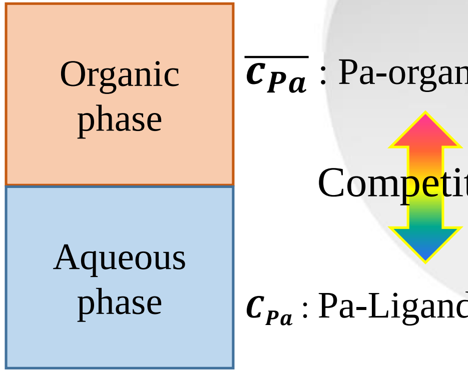
- **Stock solutions (cPa=10^{-8} M)**

  Purification from ^{237}Np : ion exchange chromatography

  In 3M $HClO_4$

- **Complexation of Pa(V) with mellitic acid by liquid-liquid extraction at ultra-trace level at pH=1**

  Determination of the distribution coefficient D by γ spectrometry (311.9 keV)



Organic phase

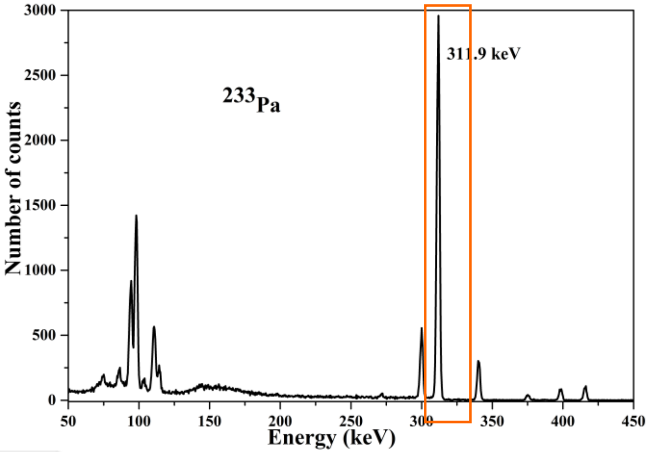
Aqueous phase

$\overline{C_{Pa}}$: Pa-organic extractant/Toluene

Competition

C_{Pa} : Pa-Ligand /(H,Na)ClO_4

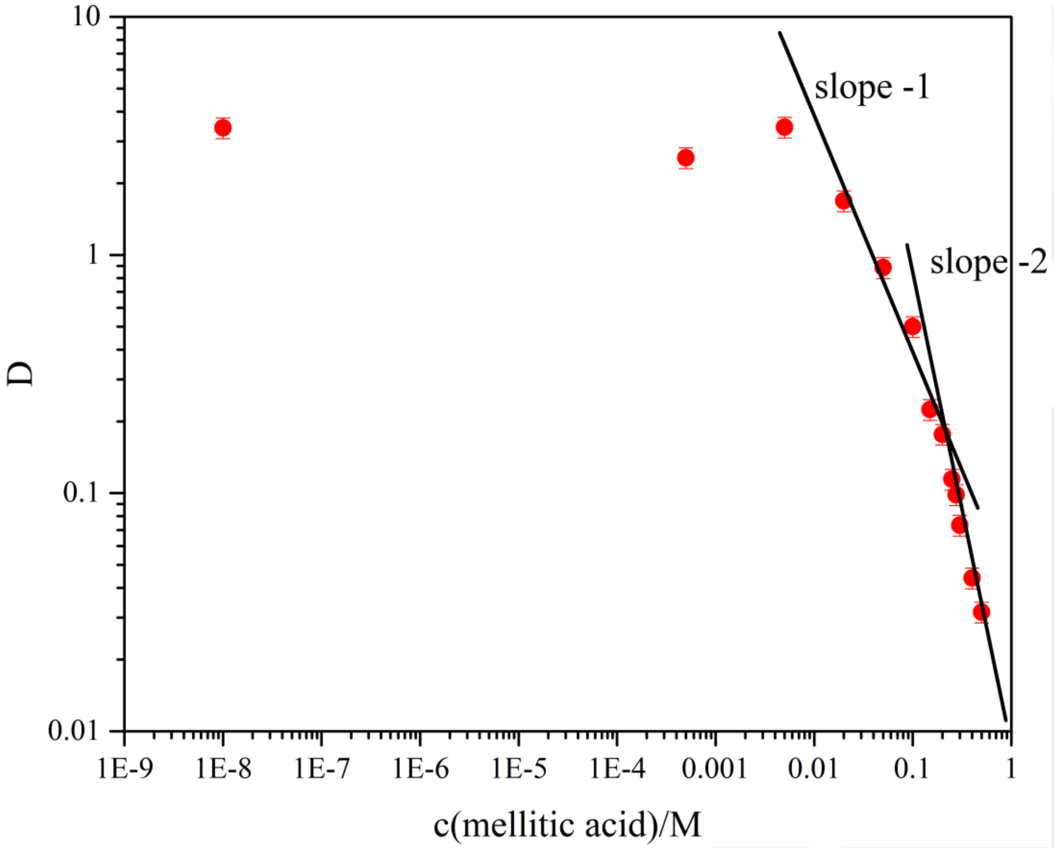
$$D = \frac{\overline{C_{Pa}}}{C_{Pa}} = \frac{\overline{A_{Pa}}}{A_{Pa}}$$



γ spectrum of Pa(V) at ultra-trace level

Complexation of Pa(V) with aromatic carboxylic acid

☐ Pa(V)-Mellitic acid (pH=1, I=1.0M NaClO$_4$, 25°C)



Variations of D as function of mellitic acid concentration
(C$_{TBP}$ = 3 M, I = 1.0 M (Na, HClO$_4$), T = 25 °C, pH = 1)

- Determination of the maximum stoichiometry of the complexes
- Determination of conditional constants by adjusting (D$_0$/D -1) with a polynomial of order.

$$Pa(V) + i \cdot mell \leftrightarrow Pa(V) - (mell)_i \quad \beta_i^{\text{cond}} = \frac{[Pa(V)-(mell)_i]}{[Pa(V)]\,[mell]^i} \quad (i{=}1{,}2)$$

$$\frac{D_0}{D} - 1 = \boxed{\frac{[H^+]}{[H^+]+K2}}\left(\beta_1^{cond}[melli] + \beta_2^{cond}[melli]^2\right)$$

$$PaO(OH)^{2+} + H_2O \leftrightarrow PaO(OH)_2^{+}$$

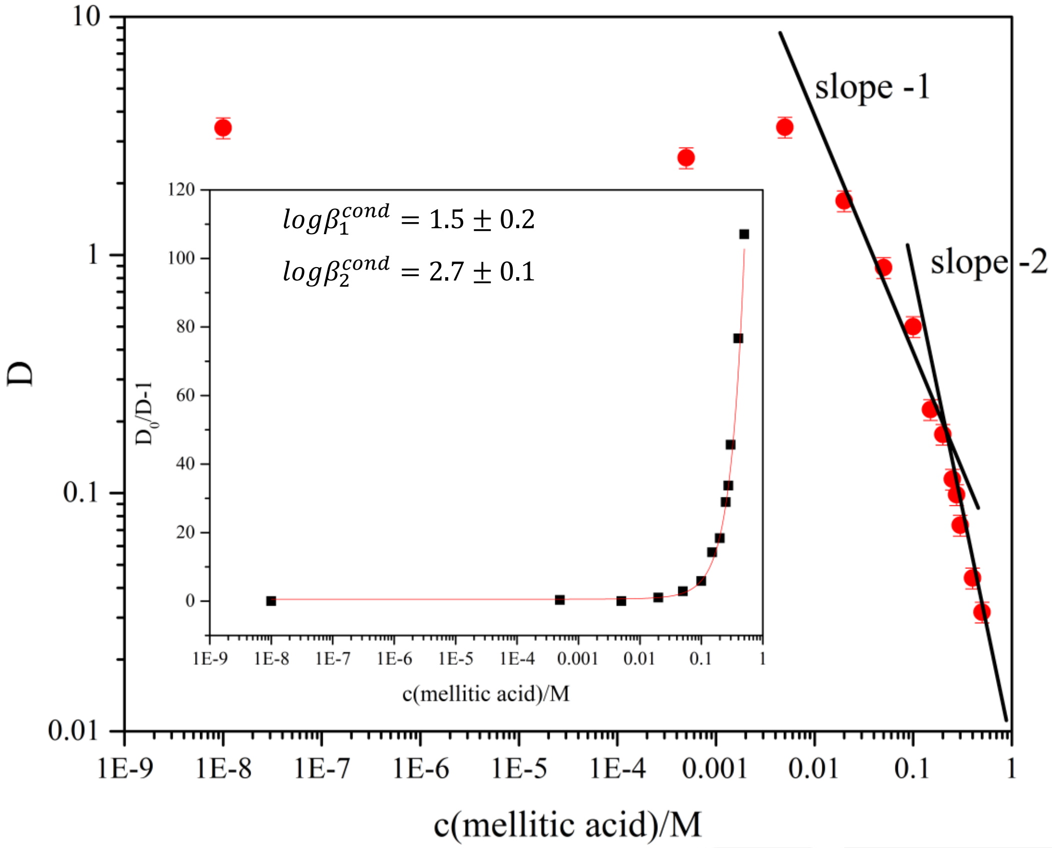
$$\beta_1^{\text{app}} = \alpha_{L6-} \times \beta_1^{cond} \quad \beta_2^{\text{app}} = \alpha_{L6-}^2 \times \beta_2^{cond} \quad \alpha_{6-} = \frac{[melli]_{total}}{[L^{6-}]}$$

Ligand	Equilibrium	β^{app}
Mellitic acid	$Pa(V) + L^{6-} \leftrightarrow Pa(V) - (L^{6-})$	14.7 ± 0.3
	$Pa(V) + 2L^{6-} \leftrightarrow Pa(V) - (L^{6-})_2$	29.0 ± 0.4

Complexation of Pa(V) with aromatic carboxylic acid

☐ Pa(V)-Mellitic acid (pH=1, I=1.0M NaClO$_4$, 25°C)

- Determination of the maximum stoichiometry of the complexes
- Determination of conditional constants by adjusting (D$_0$/D -1) with a polynomial of order.



Variations of D as function of mellitic acid concentration
(C$_{TBP}$ = 3 M, I = 1.0 M (Na, HClO$_4$), T = 25 °C, pH = 1)

$$Pa(V) + i \cdot mell \leftrightarrow Pa(V) - (mell)_i \quad \beta_i^{\text{cond}} = \frac{[Pa(V)-(mell)_i]}{[Pa(V)]\,[mell]^i} \quad (i=1,2)$$

$$\frac{D_0}{D} - 1 = \boxed{\frac{[H^+]}{[H^+]+K2}}(\beta_1^{cond}[melli] + \beta_2^{cond}[melli]^2)$$

$$PaO(OH)^{2+} + H_2O \leftrightarrow PaO(OH)_2^{+}$$

$$\beta_1^{\text{app}} = \alpha_{\text{L6}-} \times \beta_1^{cond} \quad \beta_2^{\text{app}} = \alpha_{\text{L6}-}^2 \times \beta_2^{cond} \quad \alpha_{6-} = \frac{[melli]_{total}}{[L^{6-}]}$$

Ligand	Equilibrium	β^{app}
Mellitic acid	$Pa(V) + L^{6-} \leftrightarrow Pa(V) - (L^{6-})$	14.7 ± 0.3
	$Pa(V) + 2L^{6-} \leftrightarrow Pa(V) - (L^{6-})_2$	29.0 ± 0.4

Summary and perspective

Thermodynamic study

Stoichiometry of Np(V) with aromatic carboxylate
1:1

NpO_2^+

Stability constants of

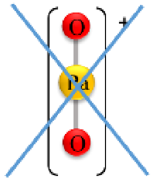
Np(V)-aromatic carboxylic acid(10^{-4}~10^{-3}M)

UV-Vis spectrophotometry

Ligand	Equilibrium	β^{app}
Phthalic acid	$NpO_2^+ + L^{2-} \leftrightarrow NpO_2L^-$	1.37 ± 0.02
Pyromellitic acid	$NpO_2^+ + L^{4-} \leftrightarrow NpO_2L^{3-}$	1.64 ± 0.02
Mellitic acid	$NpO_2^+ + L^{6-} \leftrightarrow NpO_2L^{5-}$	2.35 ± 0.02
Anthranilic acid	$NpO_2^+ + L^- \leftrightarrow NpO_2L$	1.85 ± 0.04

Stoichiometry of Pa(V) with mellitic acid
1:1 and 1:2

$PaO(OH)^{2+}$



Stability constants of

Pa(V)-aromatic carboxylic acid(~10^{-10}M)

Liquid-liquid extraction

Equilibrium	β^{app}
$Pa(V) + L^{6-} \leftrightarrow Pa(V) - (L^{6-})$	14.7 ± 0.3
$Pa(V) + 2L^{6-} \leftrightarrow Pa(V) - (L^{6-})_2$	29.0 ± 0.4

Summary and perspective

Structural study

ATR-FTIR spectroscopy

X-ray absorption spectroscopy (EXAFS)

Theoretical calculations at PhLAM laboratory (Lille)

→

Coordination geometry

Interatomic distances

Electronic structure

Sorption study

Influence of organic ligands on the sorption of An(V) by phosphate-based minerals in solution

- Thermodynamic study
- Kinetic study

Acknowledgement

IJCLab–Pôle Énergie et Environnement/RAPHYNEE
X. Doligez
D. Escalante
Y. Pei
E. Abou-Chacra (M1)

Lille/PhLAM
V. Vallet
F. Réal

Fundings

NEEDS project-CASA

Thanks for your attention