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Speciation and Thermodynamics Data to better describe the Efficiency of Actinides Separation by N,N-dialkylamides

M.-C. Charbonnel, L. Berthon-Nigond, N. Boubals, T. Dumas, D.
Guillaumont, C. Tamain

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21-24 September 2015

Speciation and Thermodynamics Data to Better Describe the Efficiency of Actinides Separation by N,N-dialkylamides

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Département radiochimie et procédés
Service modélisation et chimie des procédés de séparation



- Introduction – Macroscopic results

- System N,N-dialkylamide-U(VI)
 - ❑ Structure of complexes
 - ❖ Geometrical data in solid form (crystals)
 - ❖ Speciation in organic solution (ESI-MS ; FTIR ; EXAFS)
 - ❑ Extraction - Thermodynamic properties (calorimetry and Van t'Hoff)

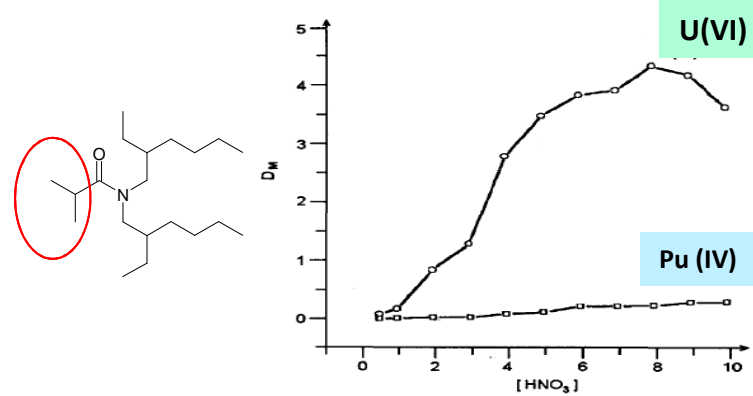
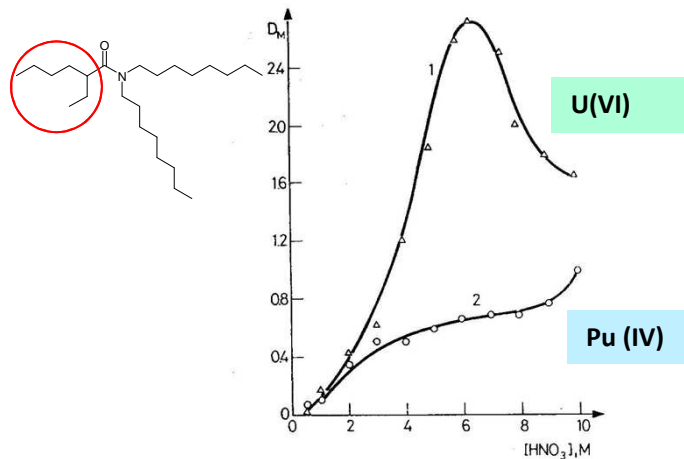
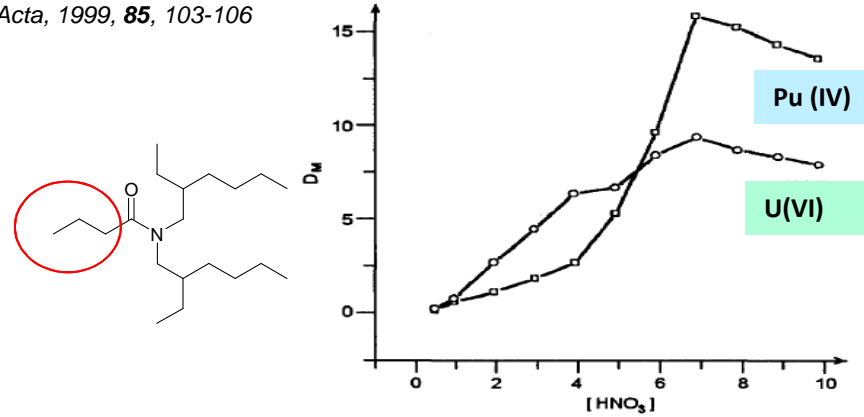
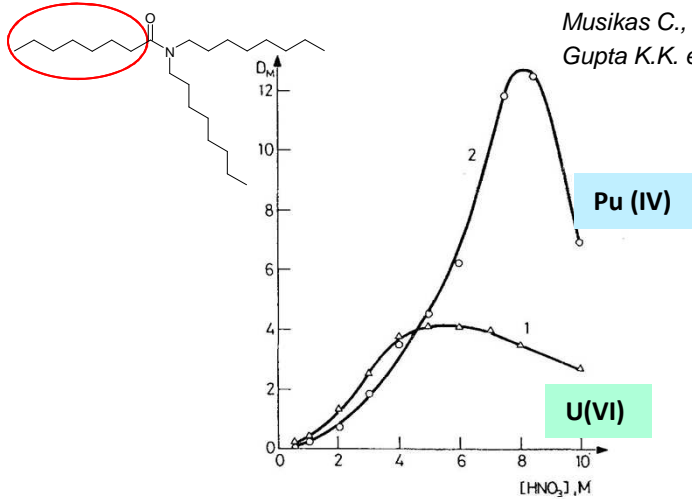
- System N,N-dialkylamide-Pu(IV)
 - ❑ Structure of complexes
 - ❖ Geometrical data in solid form (crystals)
 - ❖ Speciation in organic solution (ESI-MS ; FTIR ; EXAFS)
 - ❑ Thermodynamic properties (Van t'Hoff)

Extraction U(VI)/Pu(IV) by N,N-dialkylamides

Siddall, T.H., *Journal of Physical Chemistry*, 1960, **64**, 1803-1866

Musikas C., *Separation Science and Technology*, 1988., **23**, 1211-1226

Gupta K.K. et al.; *Radiochimica Acta*, 1999, **85**, 103-106

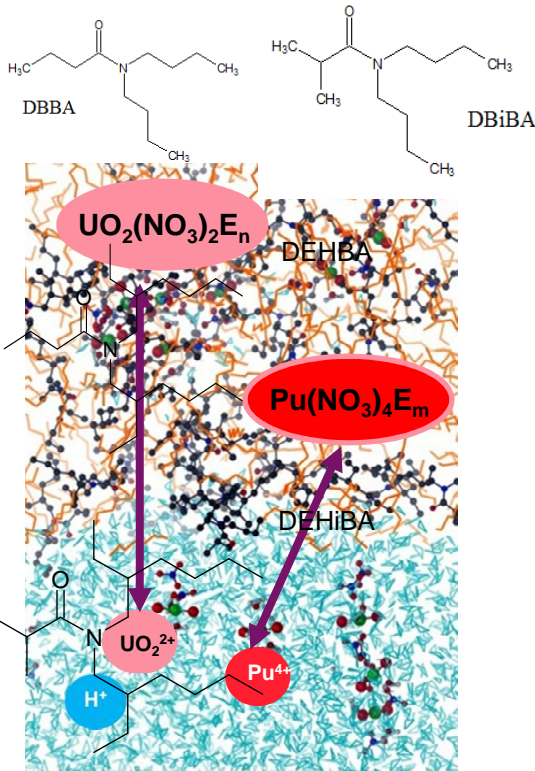


G.M. Nair et al., *J. Radioanal. Nuc. Chem.*, 1995, 191. 323.

J.N. Mathur. *J.N, Radiochim. Acta*, 1996 and Prabhu, D.R. *J. Inorg. Nucl. Chem.*, 1997

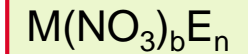
How explain the important effect of the alkyl chains on the selectivity U(VI)/Pu(IV)?

Objective: Better knowledge about the influence of the ramification of alkyl chains



1/ Speciation and structural information

- Geometry around the cation
 - Crystals (XRD)
 - In solution (EXAFS)
- Stoichiometry of complexes (ESI-MS, slope analysis)



2/ Thermodynamic properties related to the extraction

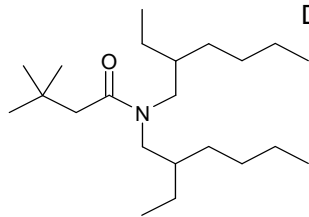
Describe **the distribution** of a solute as a single net equilibrium and application of classical mass balance



$$D_M = \frac{c_M^{org}}{c_M^{aq}}$$

Stability constant

$$\Delta_{extr} X (G-H-S)$$

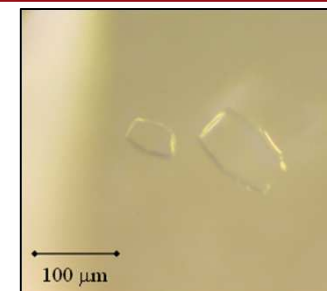
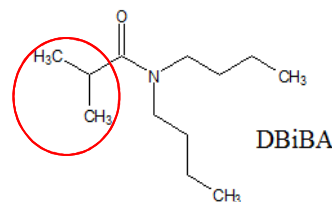
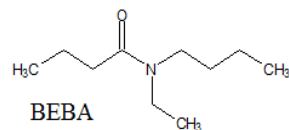
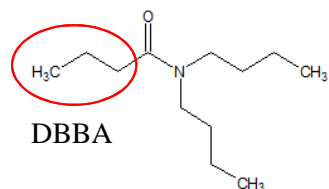


DEHDMBA

Ligand	DEHBA	DEHDMBA	DEHiBA
D_U	4.2	3.3	1.5
D_{Pu}	3.1	0.90	0.07
$SF_{U/Pu}$	0.7	3.6	20.7

$C_L = 1 \text{ mol.l}^{-1}$ in dodecane- $[HNO_3] = 3 \text{ mol.l}^{-1}$

Structure of U(VI)-amides complexes (crystals X-ray diffraction)

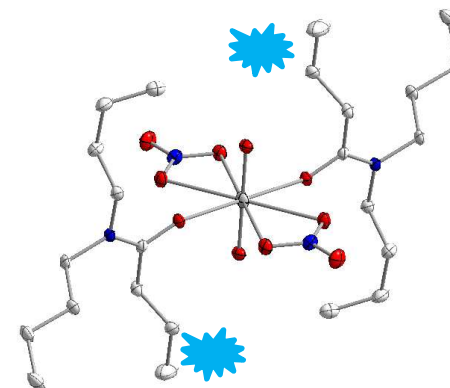


- **Identical coordination sphere for all complexes**
 - Stoichiometry 1:2 (2 monoamides and 2 bidentate nitrates)
 - CN = 6
 - Hexagonal bi-pyramide

➤ Similar distances

	DBBA	BEBA	DBiBA
U-O _{ligand}	2.343(1)	2.325(1)	2.344(1)
C=O (Å)	1.247(1)	1.256(1)	1.251(1)
C-N (Å)	1.295(1)	1.165(1)*	1.323(1)
U-O-C-N (°)	163.6(1)	155.4(1)	89.9(1)/96.4(1)

free amide : $d_{C=O} = 1.23 - 1.24 \text{ \AA}$ $d_{C-N} = 1.32 - 1.34 \text{ \AA}$



➤ Influence of ramified alkyl chains

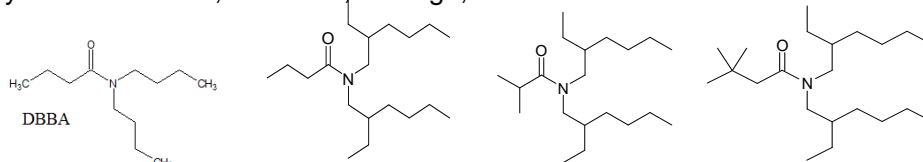
DBiBA: isopropyl group turns towards the cation –
significant steric constraints and distortion (torsion angle)

⇒ Less favorable configuration

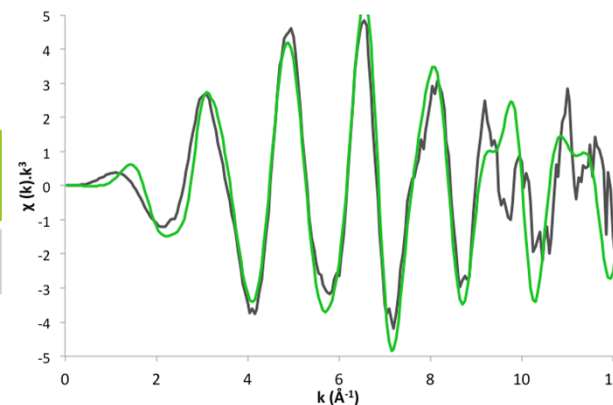
C. Tamain et al, 9th international conference on f-elements, Oxford, 6-9 Sept 2015

EXAFS

Synchrotron Soleil, line Mars, L3 edge, 17keV

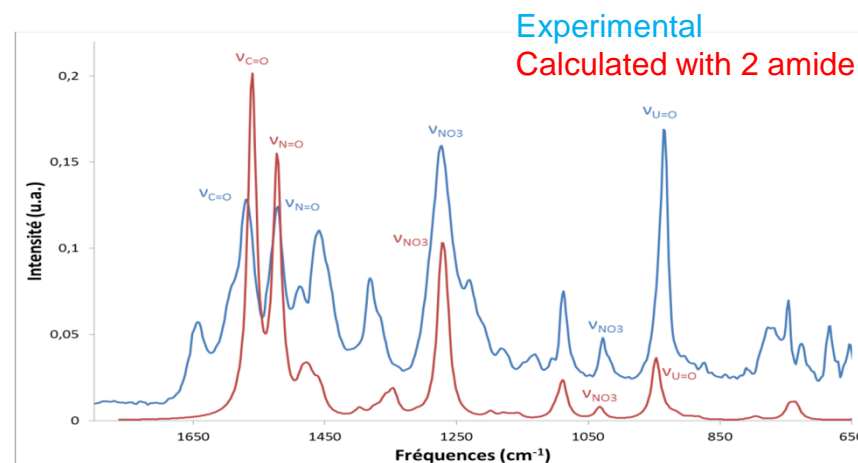
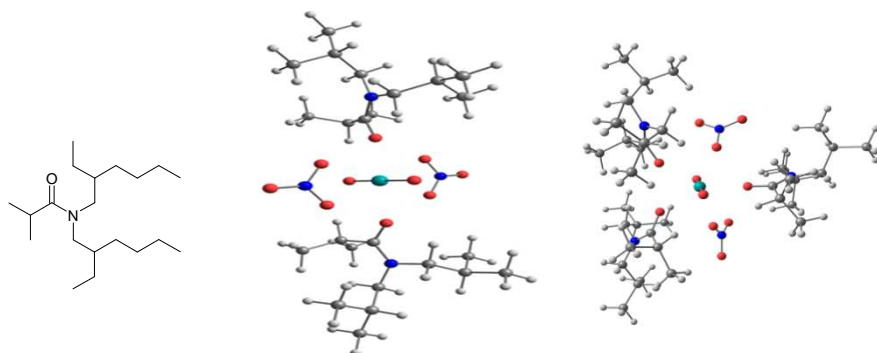


M-O _{amide}	DBBA toluene	DEHBA dodecane	DEHiBA dodecane	DEHDMBA dodecane
U(VI)	2.35(1)	2.40(2)	2.38(2)	2.40(2)



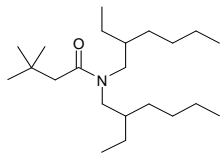
- Model from solid compounds suitable with organic samples: 2 amides and 2 bidentate and symmetrical nitrate
- No modification with ramification of alkyl chain

FTIR (experimental + DFT calculations)

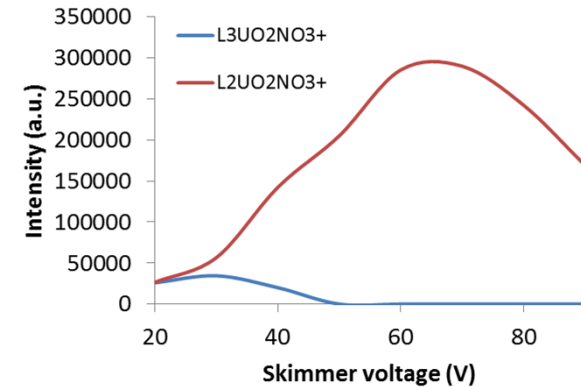
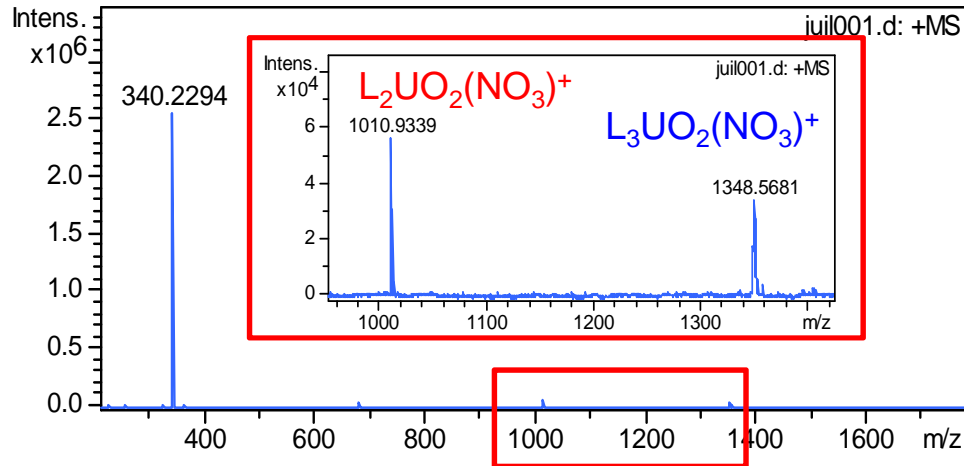


- Same stoichiometry 1:2 with the 3 amides

ESI-MS



DEHDMBA



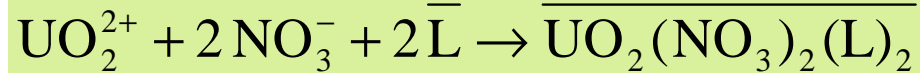
[U(VI)] = 5.10^{-4} M ; [L] = 5.10^{-4} M ; [HNO₃] = 0.03 M in CH₃CN-H₂O Skimmer 30 V

➤ Same stoichiometry 1:2 (predominant) and 1:3 with the 3 amides

Slope method ($\log D_U = f(\log c_{\text{free amide}})$)

N. Condamines and C. Musikas. SEIE. **10** (1). 69-100 (1992)
V. K. Manchanda et al. Nucl. Technol. **134** (3). 231-240 (2001).
P. N. Pathak et al.. Radiochimica Acta **89** (7). 447-452 (2001)

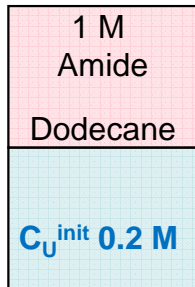
stoichiometry 1:2



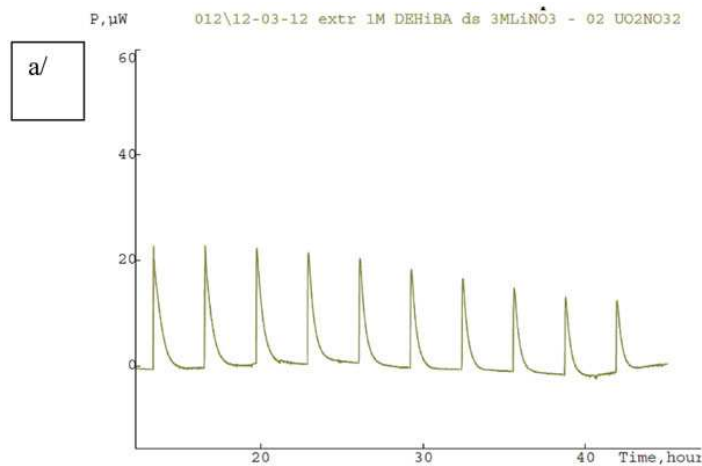
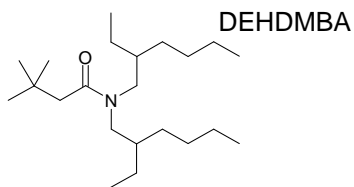
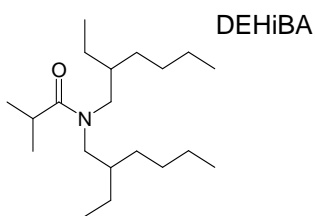
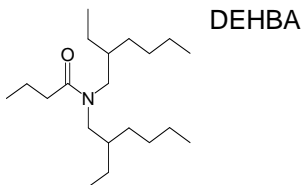
Extraction U(VI) - Thermodynamic properties (1)

Some data published: studies with U(VI) as traces (Prabhu97, Pathak01,...)

➤ Calorimetry



aqueous medium
3M HNO₃
And {1M HNO₃ + 2M LiNO₃}

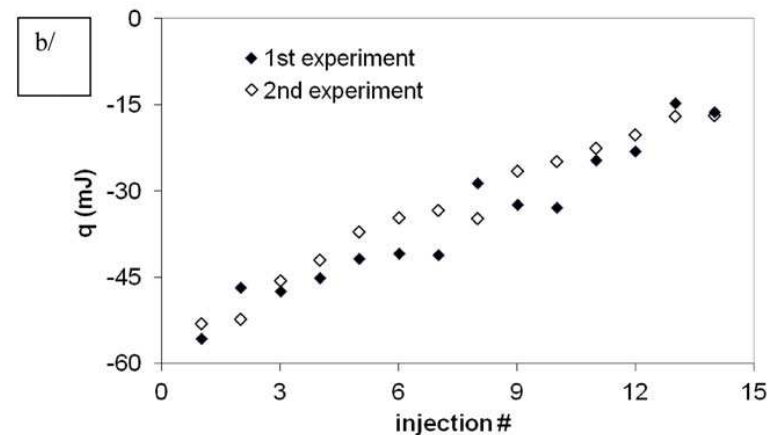


DEHBA.

initial aqueous phase:

500 µL $C_{UO_2(NO_3)_2} = 0.07 \text{ mol L}^{-1}$ and $C_{LiNO_3} = 3 \text{ mol L}^{-1}$

initial organic phase:

300 µL $C_{DEHBA} = 1 \text{ mol L}^{-1}$ in *n*-dodecane25.000 °C – stirring 120 tr min⁻¹ –15 × 15 µL organic phase with a speed of 0.5 µL s⁻¹

$$\Delta_{\text{ext}}H = -27.9 \pm 0.3 \text{ kJ/mol}$$

F. Rodrigues et al.

2012. Procedia Chemistry (7). 59-65

2014. Molecular Physics. (112) 9-10.1362-1374

➤ **Van't Hoff method ($K'_{ext U} = f(T)$)**

$$K'_U = \frac{[\overline{UO_2(NO_3)_2(L)_2}]}{a_{UO_2(NO_3)_2} [\bar{L}]_{libre}^2}$$



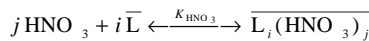
$$\ln K'_U = \left(\frac{-\Delta_{ext}H}{R} \right) \times \frac{1}{T} + \left(\frac{\Delta_{ext}S}{R} \right)$$

Methodology

$$K'_U = \frac{[\overline{UO_2(NO_3)_2(L)_2}]}{a_{UO_2(NO_3)_2} [\bar{L}]_{libre}^2} \rightarrow \text{FX measurements}$$

Mikulin relation
Simple solutions theory
Concentrations in molality scale (mol/kg)

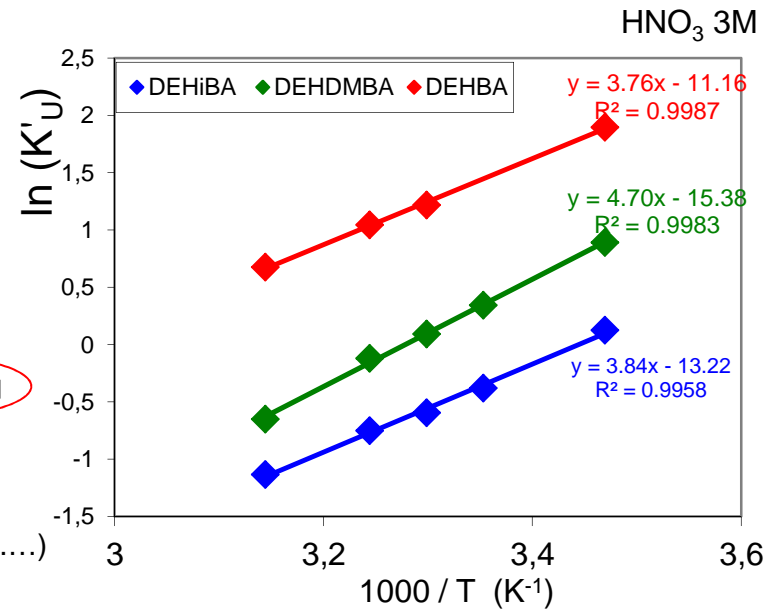
$$[\bar{L}]_{libre} = C_L^{tot} - \sum i [L_i \cdot (HNO_3)_j] - 2[\overline{UO_2(NO_3)_2(L)_2}]$$



Published data (Condamines, Ferru...)

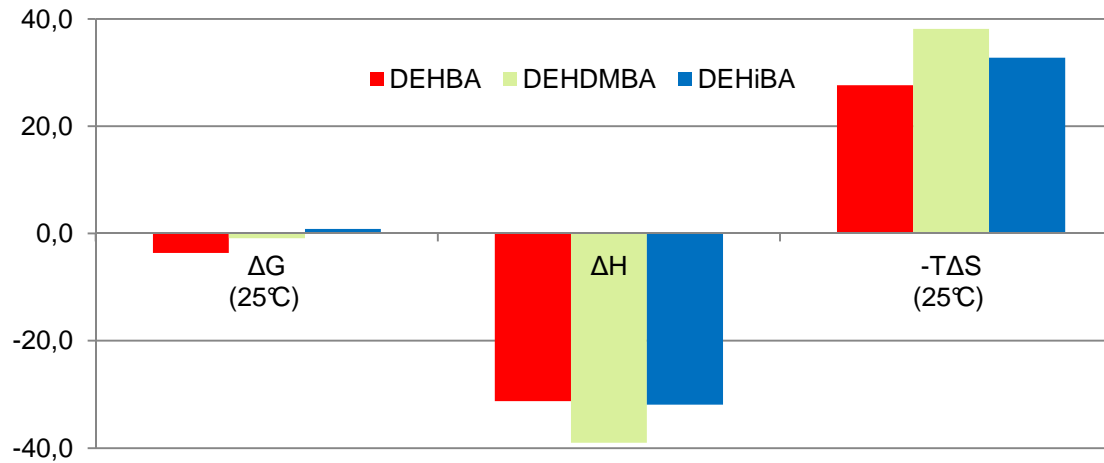
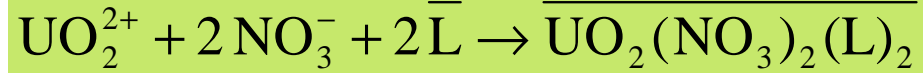
$$m_U = \frac{1000 C_U}{1000 \rho - C_U M_U - C_{HNO_3} M_{HNO_3} - C_{H_2O} M_{H_2O} - C_{L, \text{éq}}^{tot} M_L}$$

Measured



		DEHBA	DEHDMBA	DEHiBA
$\Delta_{ext}H$ (kJ/mol)	LiNO ₃ -HNO ₃ 2-1M	-31.3	-35	-27.9
	HNO ₃ 3M	-27.9	-39	-32 - (-23.6)
	HNO ₃ 2M	-29.2		
	HNO ₃ 4M			-17
$T\Delta_{ext}S$ (kJ/mol)	LiNO ₃ -HNO ₃ 2-1M	-24.4	-34.4	-28.7
	HNO ₃ 3M	-27.6	-38	-32.8

Pathak et al., 2001
Manchanda et al., 2001
Prabhu et al. 1997



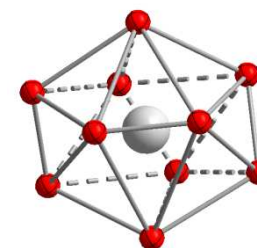
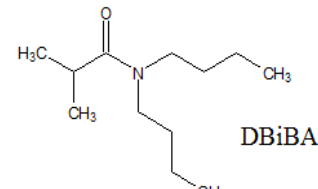
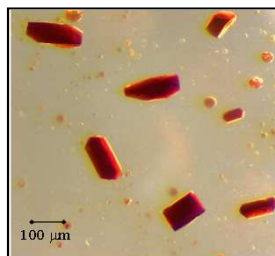
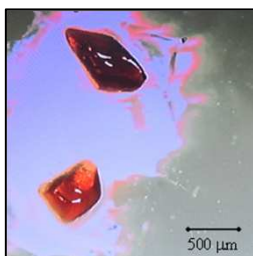
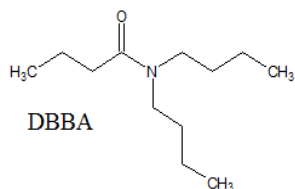
HNO₃ 3M

Similar complexes 1:2 with the 3 amides

Similar thermodynamic properties with the 3 amides: compensation between ΔH and $T\Delta S$

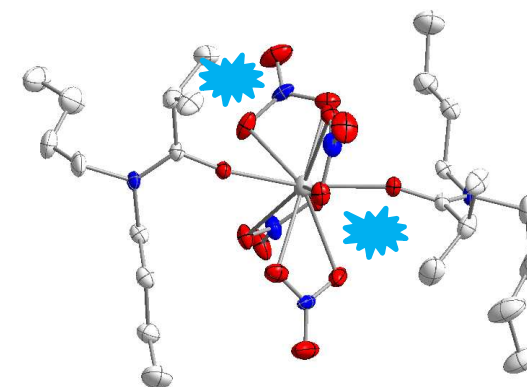
No influence of the steric hindrance of the radical

Structure of M(IV)-amides complexes (crystals X-ray diffraction)



Identical coordination sphere for all complexes

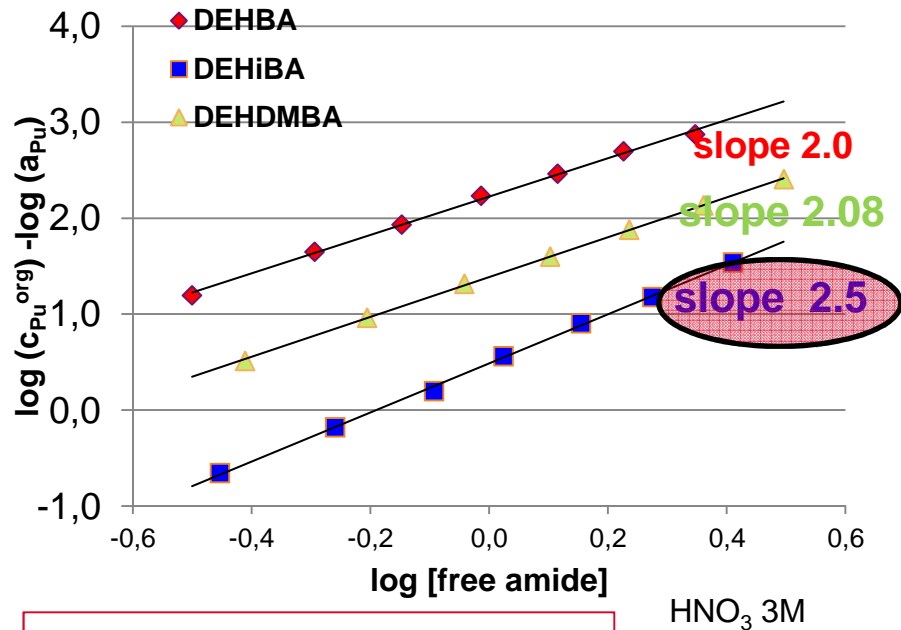
- **Stoichiometry 1:2** (2 monoamides and 4 bidentate nitrates)
- CN = 10
- Distorted bi-capped dodecahedron



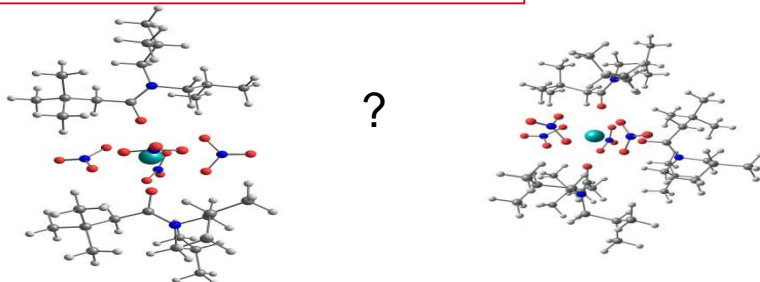
	Ce(IV)	Pu(IV)
	DBBA	DBiBA
M-O amide (Å)	2.250(1)	2.251(1)
C-N (Å)	1.238(1)	1.326(1)
U-O-C-N (°)	136.3(9)	104.2(8)
M-O nitrate (Å)	2.457(2)	2.472(2)

Slope analysis

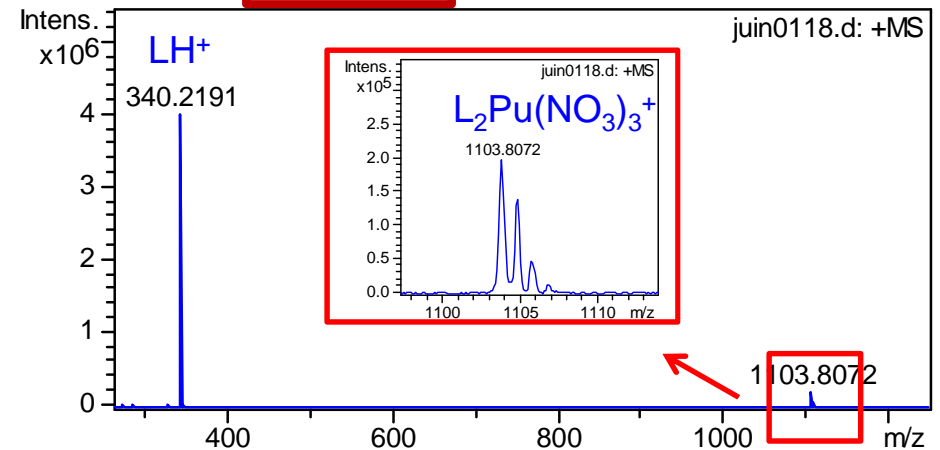
Few previous studies with different stoichiometries
3.6 DEHBA - 2.4 DEHiBA - Prabhu et al, 1997
2.9 DEHBA - 3.8 DEHiBA - Pathak et al., 2001)



Behavior of DEHiBA different



ESI-MS



[Pu(IV)] = 5.10⁻⁴M ; [L] = 5.10⁻⁴M ; [HNO₃] = 0.04 M dans CH₃CN-H₂O

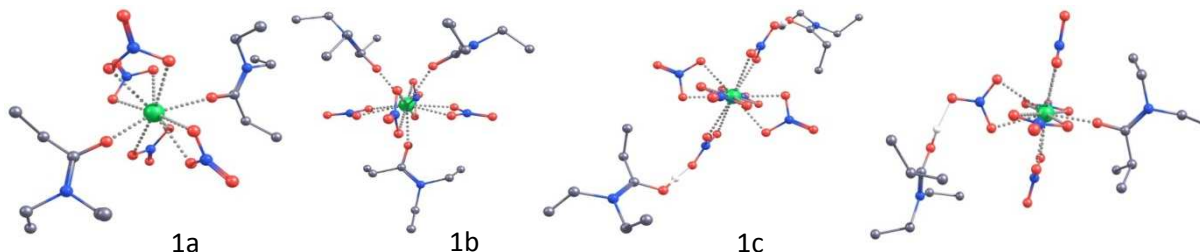
L = DEHDMBA

Same stoichiometry 1:2 (predominant) and 1:3 with the 3 amides

Nature of Pu(IV)-amides complexes in solution (2)

EXAFS spectra
+ simulation with FEFF and
DFT (atomic positions)

Synchrotron SOLEIL, Saclay, Mars
Synchrotron ESRF, Grenoble, ROBL



$\text{Pu}(\text{NO}_3)_4\text{L}_2$

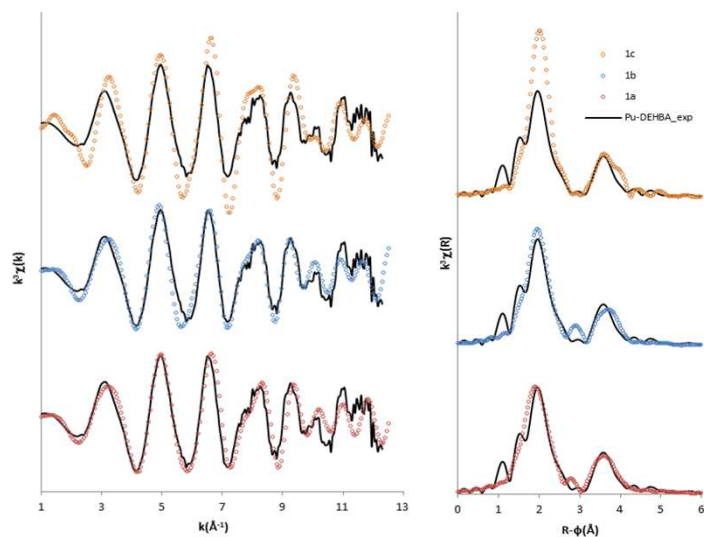
$\text{Pu}(\text{NO}_3)_4\text{L}_3$

$\text{Pu}(\text{NO}_3)_4(\text{HNO}_3)_2\text{L}_2$

$\text{Pu}(\text{NO}_3)_4(\text{HNO}_3)_2\text{L, L}$

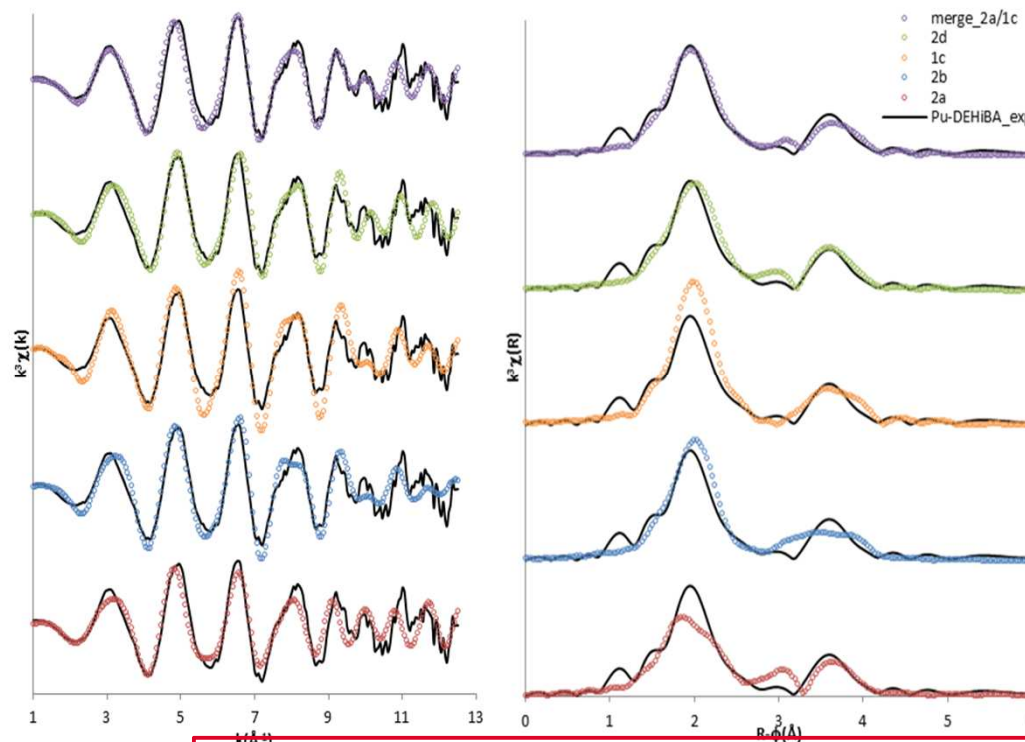
DEHiBA

DEHBA

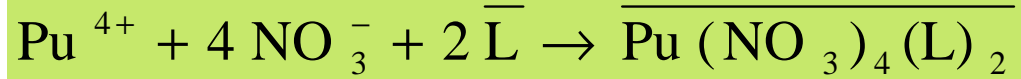


Experimental (Pu(IV) extracted from HNO_3
3M by amide 0.5M-dodecane)

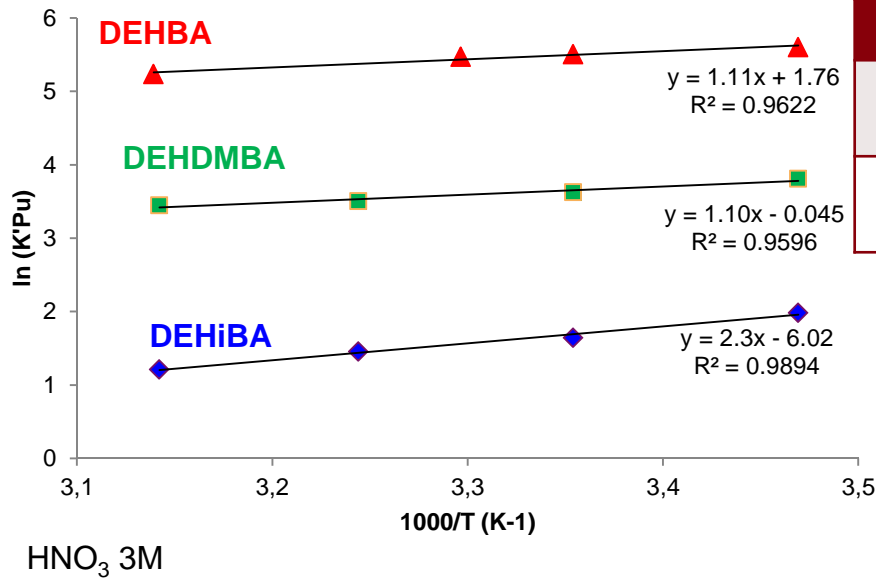
Best fit: $\text{Pu}(\text{NO}_3)_4\text{L}_2$



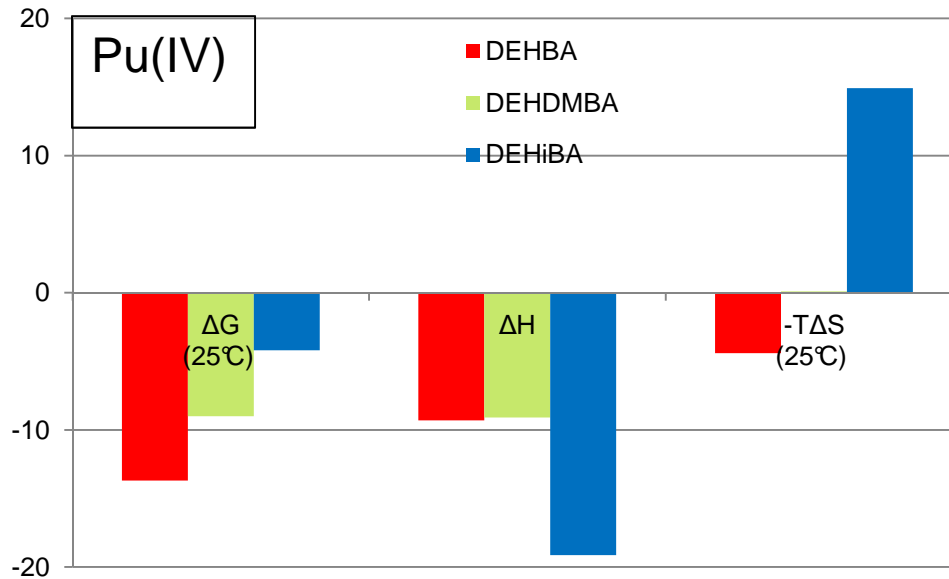
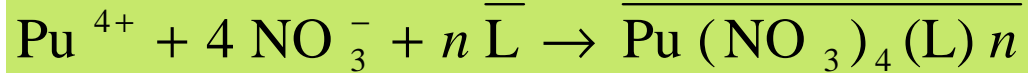
Best fit: mixture of $\text{Pu}(\text{NO}_3)_4\text{L}_2$ and $\text{Pu}(\text{NO}_3)_4(\text{HNO}_3)_2\text{L}_2$
or $\text{Pu}(\text{NO}_3)_4(\text{HNO}_3)_2\text{L, L}$



$$\ln K_{ext} = \left(\frac{-\Delta H^{app}}{R} \right) \times \frac{1}{T} + \left(\frac{\Delta S^{app}}{R} \right)$$



		DEHBA	DEHDMBA	DEHiBA
$\Delta_{ext}H$ (kJ/mol)	LiNO ₃ 2M-HNO ₃ 1M HNO ₃ 3M	-	-8.9 -9.1	-7.9 -19
$T\Delta_{ext}S$ (kJ/mol)	LiNO ₃ 2M-HNO ₃ 1M HNO ₃ 3M	-4.4	0.9 0.1	-4 -15



ΔH increases with steric hindrance

Entropic term favorable when steric hindrance decreases

Presence of complexes with outer sphere amide

Detailed analysis to identify the driving force

$$1/ \Delta(\Delta_{\text{ext}} G^\circ)_{\text{L2/L1}} = \Delta(\Delta_{\text{dehydration}} G^\circ)_{\text{L2/L1}} + \Delta(\Delta_{\text{coordination}} G^\circ)_{\text{L2/L1}} + \Delta(\Delta_{\text{solvation}} G^\circ)_{\text{L2/L1}}$$

$$2/ \Delta(\Delta_{\text{ext}} G^\circ)_{\text{Pu/U}} = \Delta(\Delta_{\text{ext}} H^\circ)_{\text{Pu/U}} - T \Delta(\Delta_{\text{ext}} S^\circ)_{\text{Pu/U}}$$

Further analysis:

- check the nature of complexes with other amides and in less acidic conditions, if necessary, addition of equilibria (with related thermodynamic properties)

Selectivity U(VI)/Pu(IV) by dialkylamide extractants

- extraction of U(VI): no (small) influence of ramified alkyl chain on structure and on thermodynamic properties

- extraction of Pu(IV): influence of ramified alkyl chain on C=O
 - no influence in solid phase (first amide-Pu crystal!)
 - amides are partially present in the outer sphere
 - thermodynamic properties (enthalpy and entropy) modified

The selectivity U(VI)/Pu(IV) comes from the behaviour of Pu(IV): further studies will focus on this cation

Interest of multi techniques approach for such complex systems.

Importance of speciation insight to complete the thermodynamic approach

Calorimetry

N. Boubals
F. Rodrigues (PhD)

ESI-MS

L. Berthon
N. Zorz
N. Martin (student)

EXAFS

T. Dumas

DFT calculations

D. Guillaumont
G. Javierre (student)
E. Acher (PhD)

XRD

C. Tamain
Y. Hacene Cherkaski (student)

Thank you for your attention

Commissariat à l'énergie atomique et aux énergies alternatives
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Direction de l'énergie nucléaire
Département de radiochimie des procédés
Service de modélisation et chimie des procédés de séparation

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