DE LA RECHERCHE À L'INDUSTRIE

cea den

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

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21-24 September 2015



Content

- Introduction – Macroscopic results

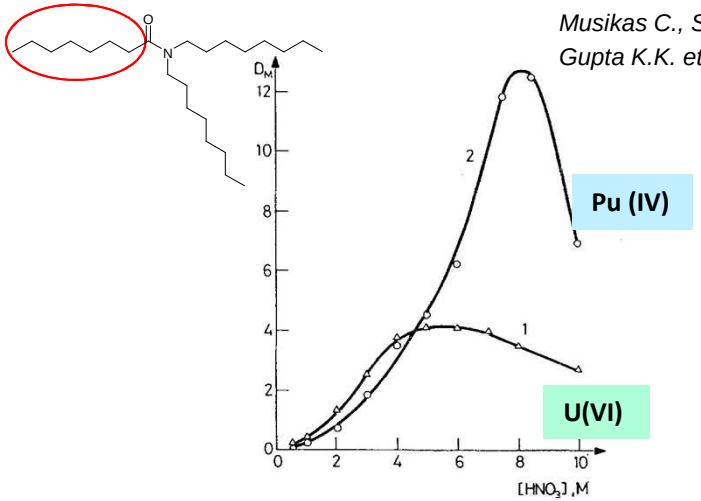
- System N,N-dialkylamide-U(VI)
  - Structure of complexes
    - Geometrical data in solid form (crystals)
    - Speciation in organic solution (ESI-MS ; FTIR ; EXAFS)
  - Extraction - Thermodynamic properties (calorimetry and Van t'Hoff)

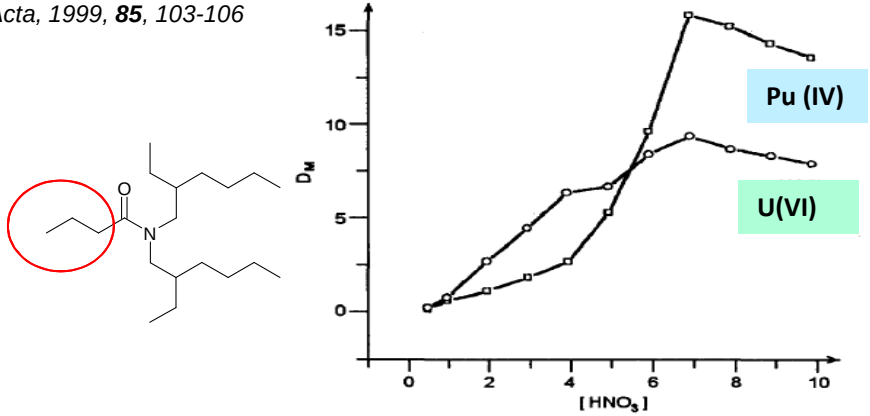
- System N,N-dialkylamide-Pu(IV)
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  - Thermodynamic properties (Van t'Hoff)

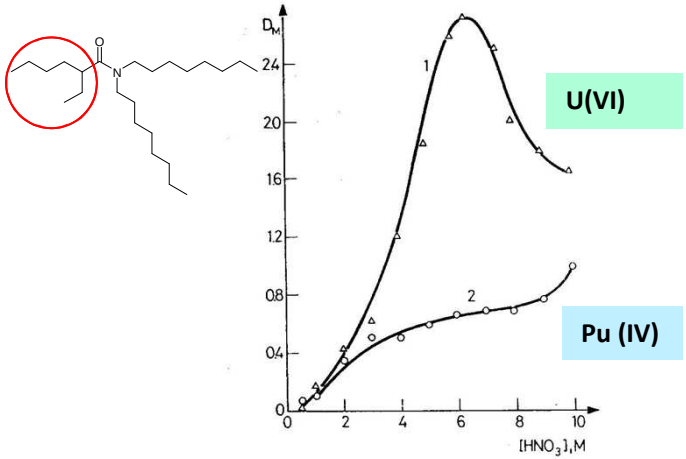
- Selectivity

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

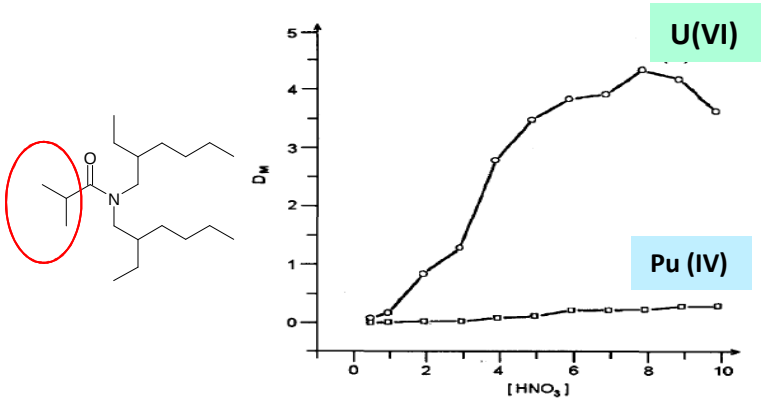
*Siddall. T.H., Journal of Physical Chemistry, 1960, **64**, 1803-1866*
*Musikas C., Separation Science and Technology, 1988., **23**, 1211-1226*
*Gupta K.K. et al;. Radiochimica Acta, 1999, **85**, 103-106*







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

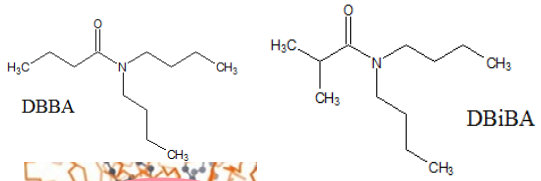


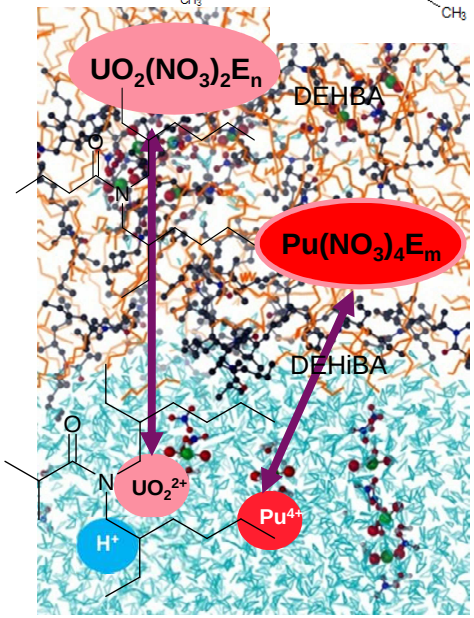
J.N. Mathur. J.N, Radiochim. Acta, 1996 and Prabhu, D.R. J. Inorg. Nucl. Chem., 1997

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

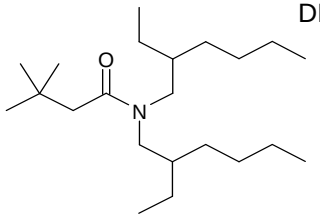
New investigations on the selectivity

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





DEHDMBA



1/ Speciation and structural information

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

$M(NO_3)_bE_n$

2/ Thermodynamic properties related to the extraction

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

$$M^{m+} + b\,NO_3^- + n\,\overline{E} \leftrightarrows \overline{M(NO_3)_bE_n} \qquad K°_{ext}$$

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

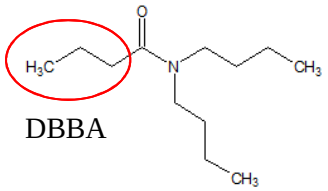
Ligand	DEHBA	DEHDMBA	DEHiBA
D_U	4.2	3.3	1.5
D_{Pu}	3.1	0.90	0.07
$SF_{U/Pu}$	0.7	3.6	20.7

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

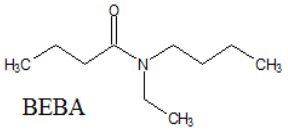
Stability constant

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

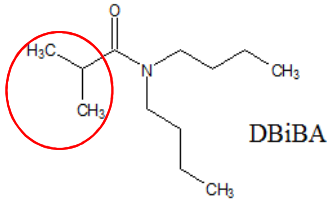
Structure of U(VI)-amides complexes (crystals X-ray diffraction)



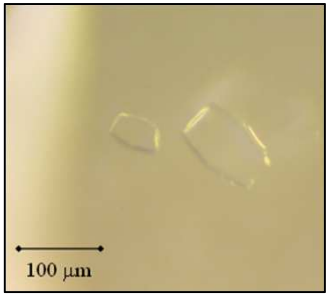
DBBA



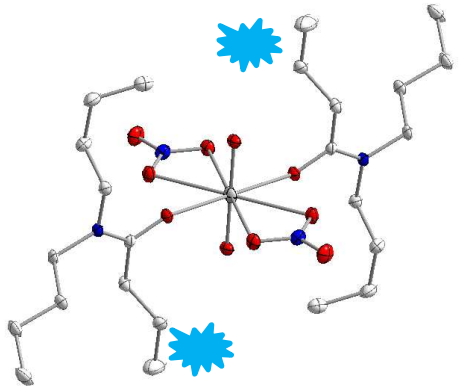
BEBA



DBiBA



- 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 Å d_{C-N} = 1.32 - 1.34 Å

- Influence of ramified alkyl chains

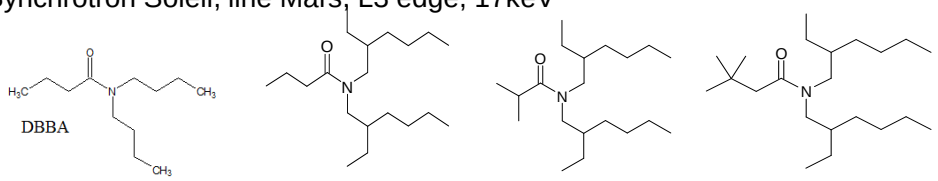
DBiBA: isopropyl group turns towards the cation – significant steric constrains and distorsion (torsion angle) ⇒ Less favorable configuration

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

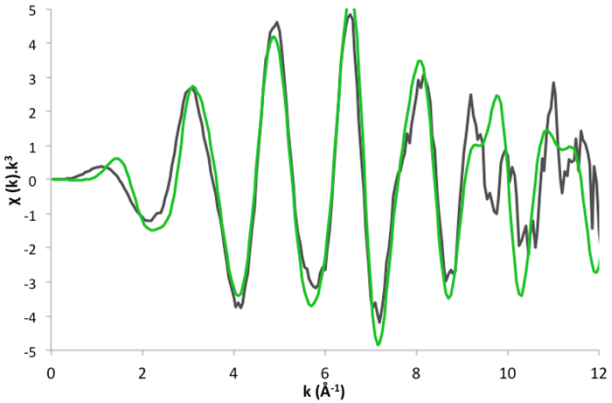
Nature of U(VI)-amides complexes in solution (1)

EXAFS

Synchrotron Soleil, line Mars, L3 edge, 17keV

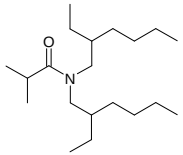


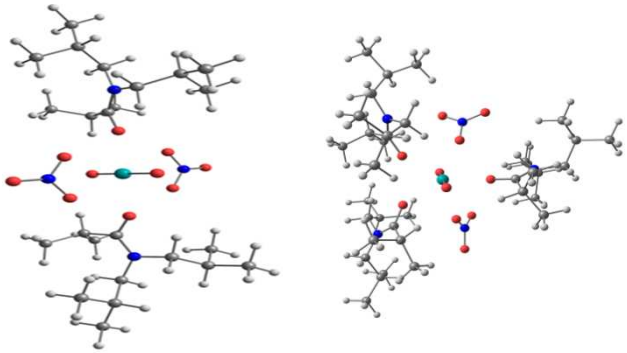
M-O$_{amide}$	DBBA toluene	DEHBA dodecane	DEHiBA dodecane	DEHDMBA dodecane
U(VI)	2.35(1)	2.40(2)	2.38(2)	2.40(2)

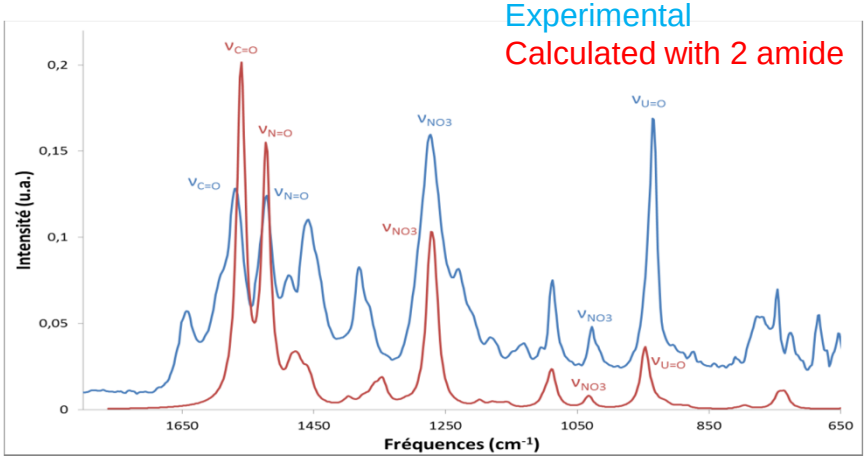


- Model from solid compounds suitable with organic samples: 2 amides and 2 bidentate and symetrical nitrate
- No modification with ramification of alkyl chain

FTIR (experimental + DFT calculations)



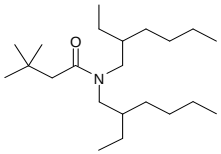




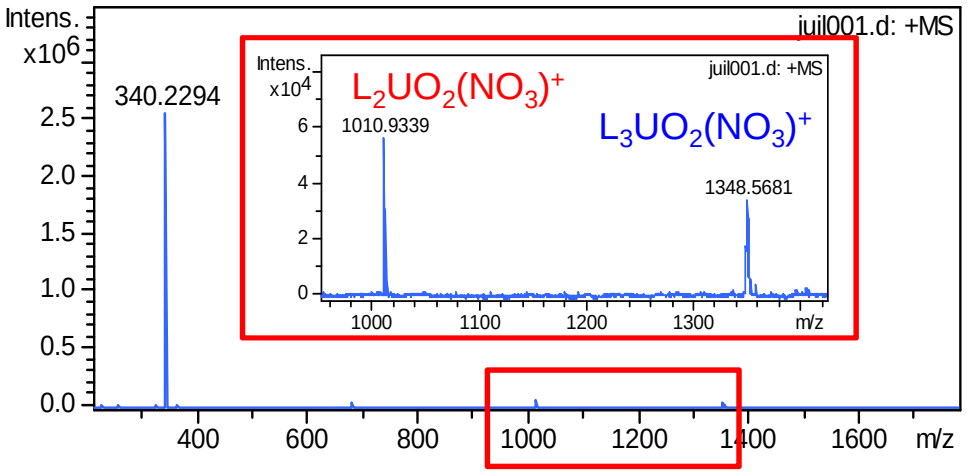
- Same stoechiometry 1:2 with the 3 amides

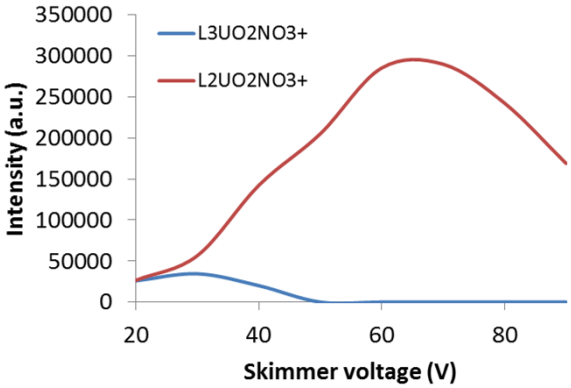
Nature of U(VI)-amides complexes in solution (2)

ESI-MS



DEHDMBA





[U(VI)]= 5.10^{-4}M ; [L]= 5.10^{-4}M ; [HNO_3]= 0.03 M in CH_3CN-H_2O *Skimmer 30 V*

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

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

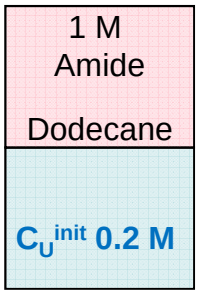
N. Condamines and C. Musikas. SEIE. **10** (1). 69-100 (1992)
V. K. Manchanda et al. Nucl. Technol. **134** (3). 231-240 (2001).
P. N. Pathak et al.. Radiochimica Acta **89** (7). 447-452 (2001)

stoechiometry 1:2

$$UO_2^{2+} + 2\,NO_3^- + 2\,\overline{L} \rightarrow \overline{UO_2(NO_3)_2(L)_2}$$

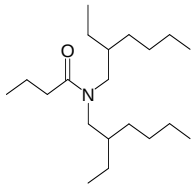
Extraction U(VI) - Thermodynamic properties (1)

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

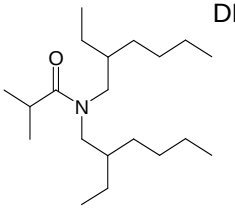


aqueous medium
3M HNO_3
And {1M HNO_3 + 2M $LiNO_3$}

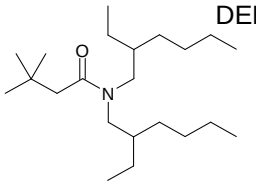
DEHBA



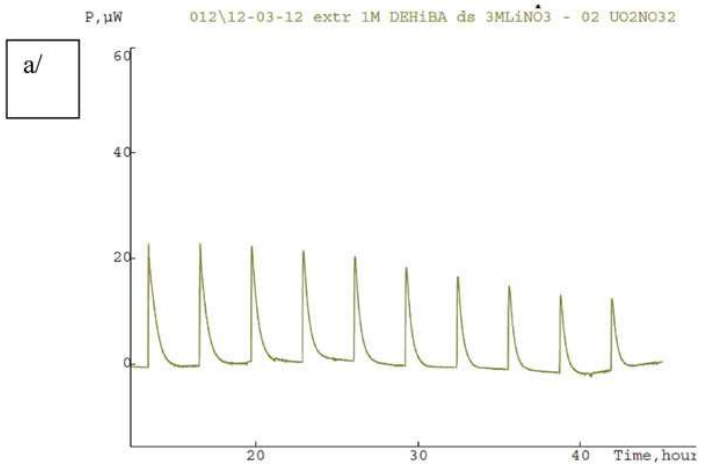
DEHiBA

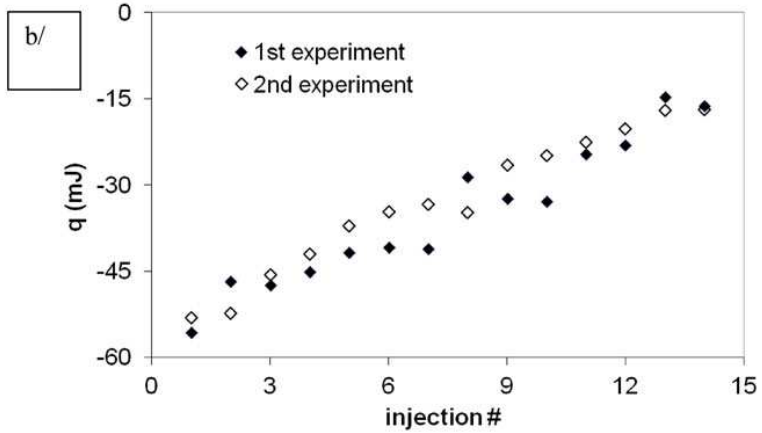


DEHDMBA



➢ Calorimetry





DEH*i*BA.
initial aqueous phase:
500 μL $C_{UO2(NO3)2}$ = 0.07 mol L^{-1} and C_{LiNO3} = 3 mol L^{-1}
initial organic phase:
300 μL C_{DEHiBA} = 1 mol L^{-1} in *n*-dodecane

25.000 ◦C – stirring 120 tr min^{-1} –
15 × 15 μL organic phase with a speed of 0.5 μL s^{-1}

$\Delta_{ext}H$ = -27.9 ± 0.3 kJ/mol

F. Rodrigues et al.
2012. Procedia Chemistry (7). 59-65
2014. Molecular Physics. (112) 9-10.1362-1374

Extraction U(VI) - Thermodynamic properties (2)

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

$$K_U^{'} = \frac{[\overline{UO_2(NO_3)_2(L)_2}]}{a_{UO_2(NO_3)_2}\,[\overline{L}]^2_{libre}} \quad \Rightarrow \quad \ln K_U^{'} = \left(\frac{-\Delta_{ext}H}{R}\right) \times \frac{1}{T} + \left(\frac{\Delta_{ext}S}{R}\right)$$

Methodology

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

FX measurements

Mikulin relation
Simple solutions theory

Concentrations in molality scale (mol/kg)

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

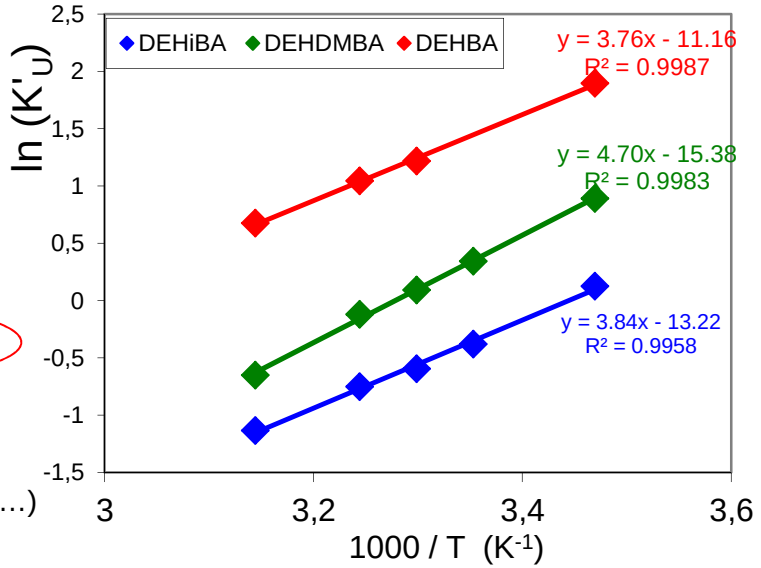
$$j\,HNO_3 + i\,\overline{L} \xleftarrow{K_{HNO_3}} \overline{L_i(HNO_3)_j}$$

$$m_{\overline{U}} = \frac{1000 C_{\overline{U}}}{1000\rho - C_{\overline{U}} M_U - C_{\overline{HNO_3}} M_{HNO_3} - C_{\overline{H_2O}} M_{H_2O} - C^{tot}_{L,éq} M_L}$$

Measured

Published data (Condamines. Ferru….)

HNO_3 3M

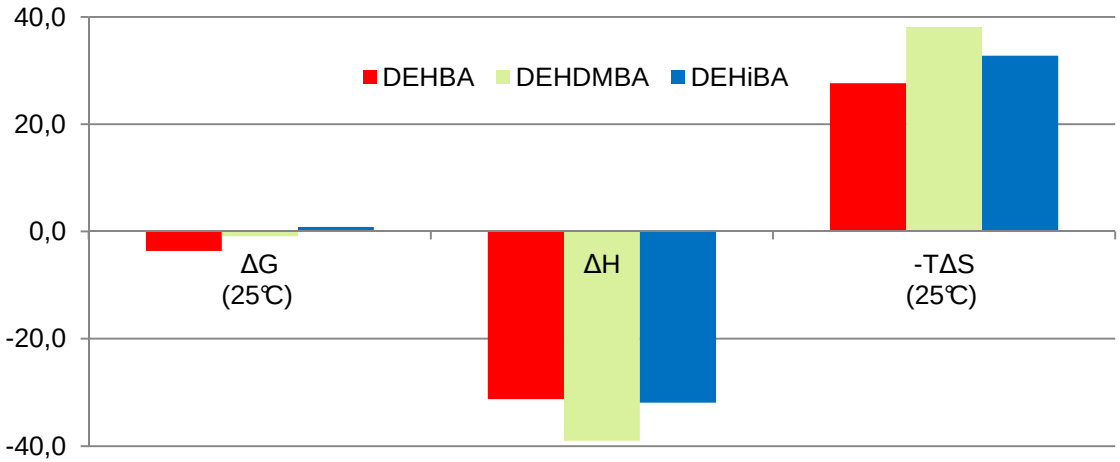


		DEHBA	DEHDMBA	DEHiBA
$\Delta_{ext}H$ (kJ/mol)	$LiNO_3$-HNO_3 2-1M	-31.3	-35	-27.9
	HNO_3 3M	-27.9	-39	-32 – (-23.6)
	HNO_3 2M	-29.2		
	HNO_3 4M			-17
$T\Delta_{ext}S$ (kJ/mol)	$LiNO_3$-HNO_3 2-1M	-24.4	-34.4	-28.7
	HNO_3 3M	-27.6	-38	-32.8

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

Extraction of U(VI) - conclusions

$$UO_2^{2+} + 2\,NO_3^- + 2\,\overline{L} \rightarrow \overline{UO_2(NO_3)_2(L)_2}$$



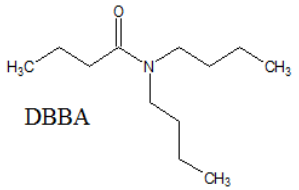
HNO_3 3M

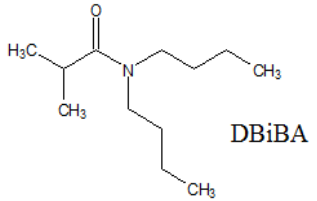
Similar complexes 1:2 with the 3 amides

Similar thermodynamic properties with the 3 amides: compensation between ΔH and TΔS

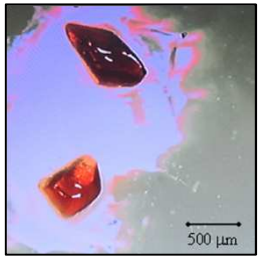
No influence of the steric hindrance of the radical

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

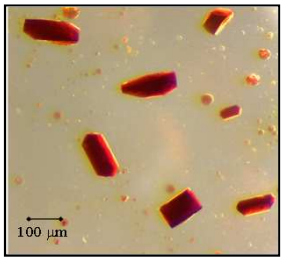




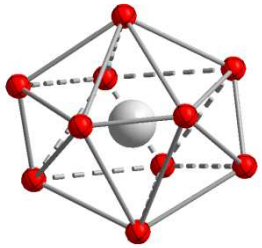
Pu(IV)



Ce(IV)



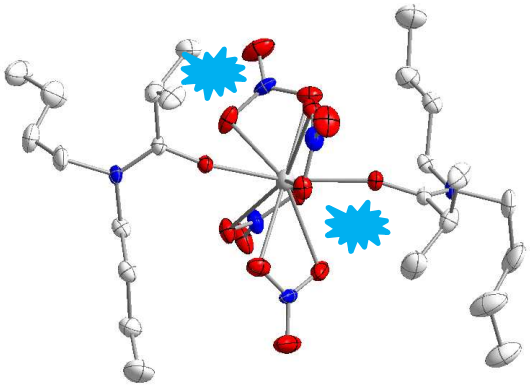
Ce(IV)



Identical coordination sphere for all complexes

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

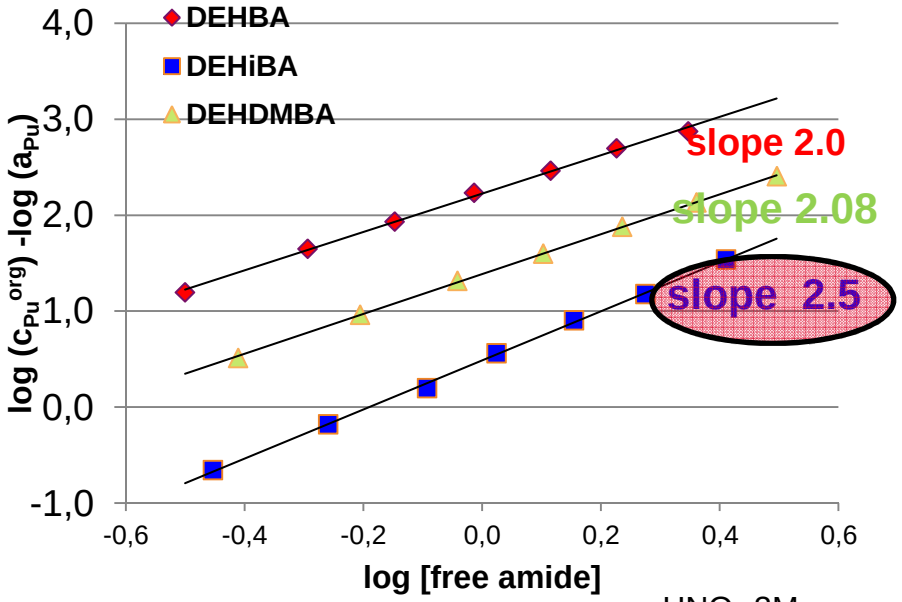
	Ce(IV) DBBA	Ce(IV) DBiBA	Pu(IV) DBBA
M-O $_{amide}$ (Å)	2.250(1)	2.251(1)	2.26(1)
C-N (Å)	1.238(1)	1.326(1)	1.26(1)
U-O-C-N (°)	136.3(9)	104.2(8)	136.1(5)
M-O $_{nitrate}$ (Å)	2.457(2)	2.472(2)	2.43(1)



Nature of Pu(IV)-amides complexes in solution (1)

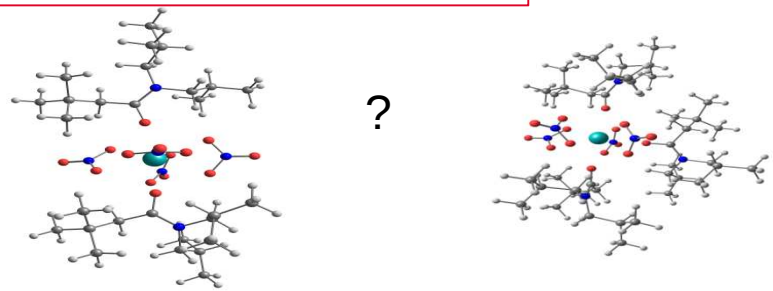
Slope analysis

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



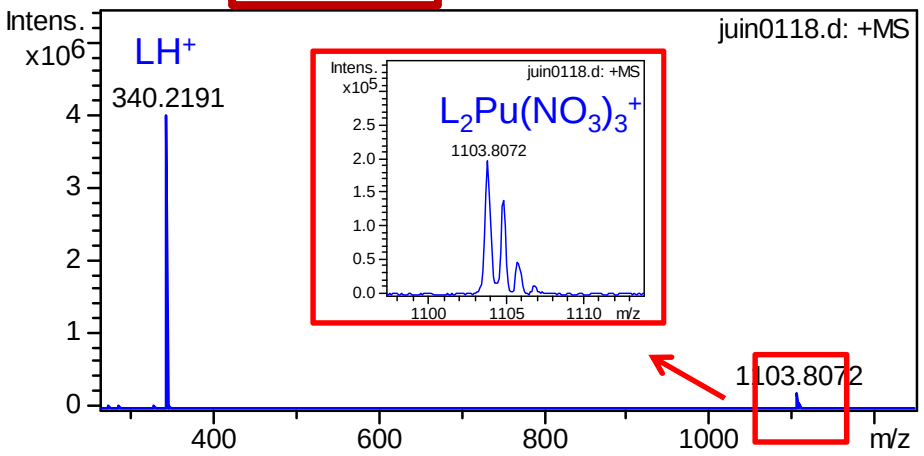
HNO_3 3M

Behavior of DEHiBA different



?

ESI-MS



[Pu(IV)]= 5.10^{-4}M ; [L]= 5.10^{-4}M ; [HNO_3]= 0.04 M dans CH3CN-H2O

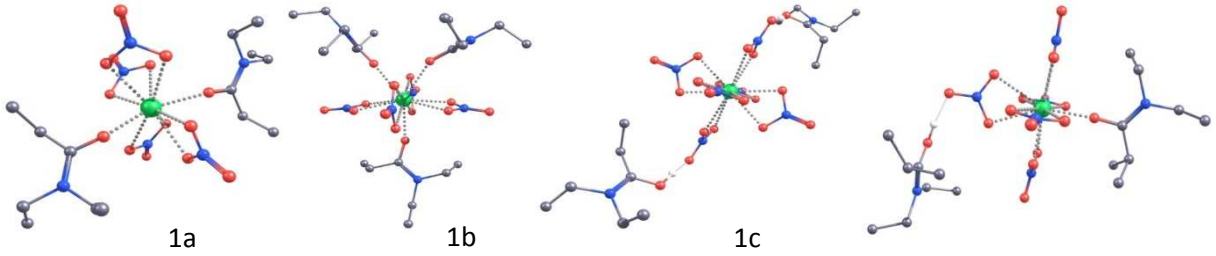
L = DEHDMBA

Same stoechiometry 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

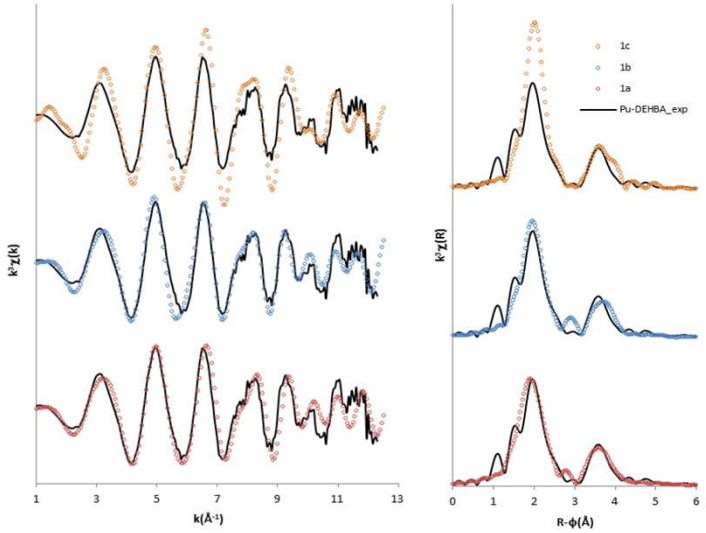


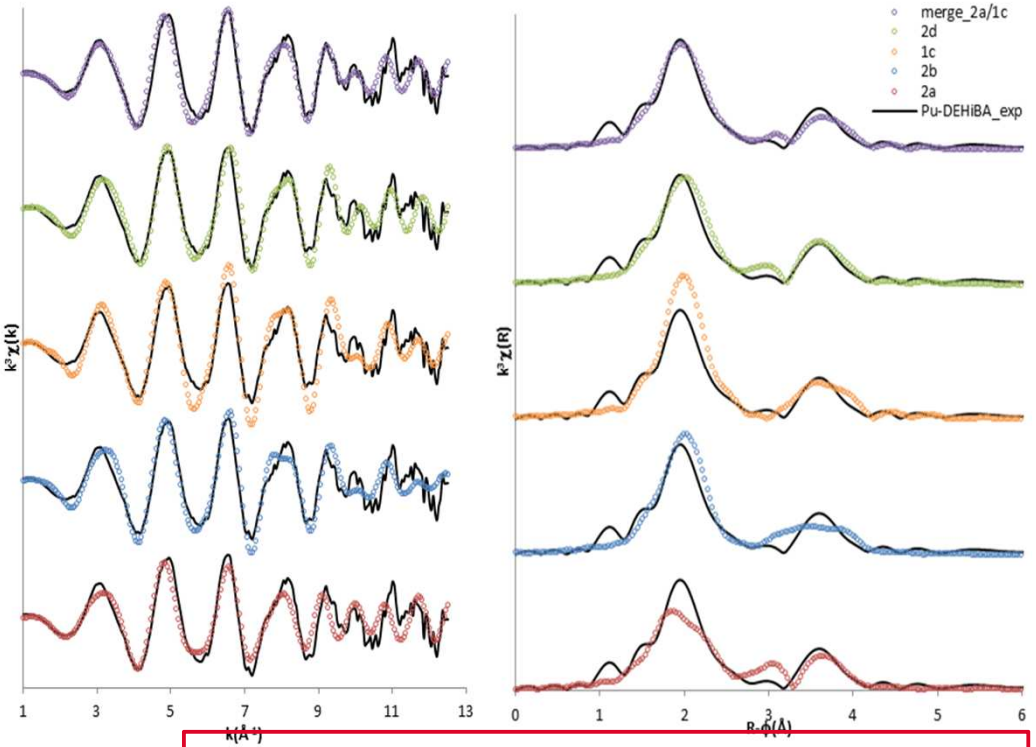
1a 1b 1c

DEHiBA

$Pu(NO_3)_4L_2$ $Pu(NO_3)_4L_3$ $Pu(NO_3)_4(HNO_3)_2,L_2$ $Pu(NO_3)_4(HNO_3)_2L$, L

DEHBA





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

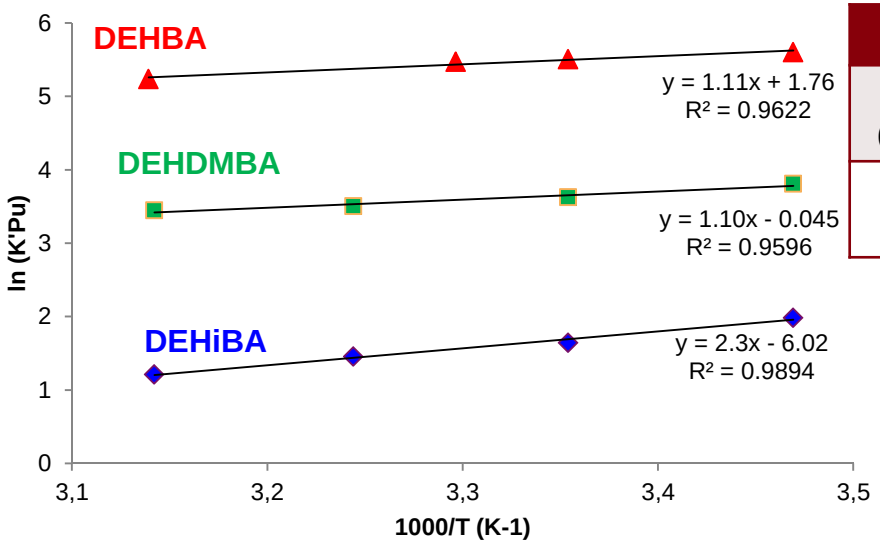
Best fit: $Pu(NO_3)_4L_2$

Best fit: mixture of $Pu(NO_3)_4L_2$ and $Pu(NO_3)_4(HNO_3)_2,L_2$ or $Pu(NO_3)_4(HNO_3)_2L$, L

Extraction Pu(IV) - Thermodynamic properties (1)

$$Pu^{4+} + 4\,NO_3^- + 2\,\overline{L} \rightarrow \overline{Pu(NO_3)_4(L)_2}$$

$$\ln K_{ext}' = \left(\frac{-\Delta H^{app}}{R}\right) \times \frac{1}{T} + \left(\frac{\Delta S^{app}}{R}\right)$$

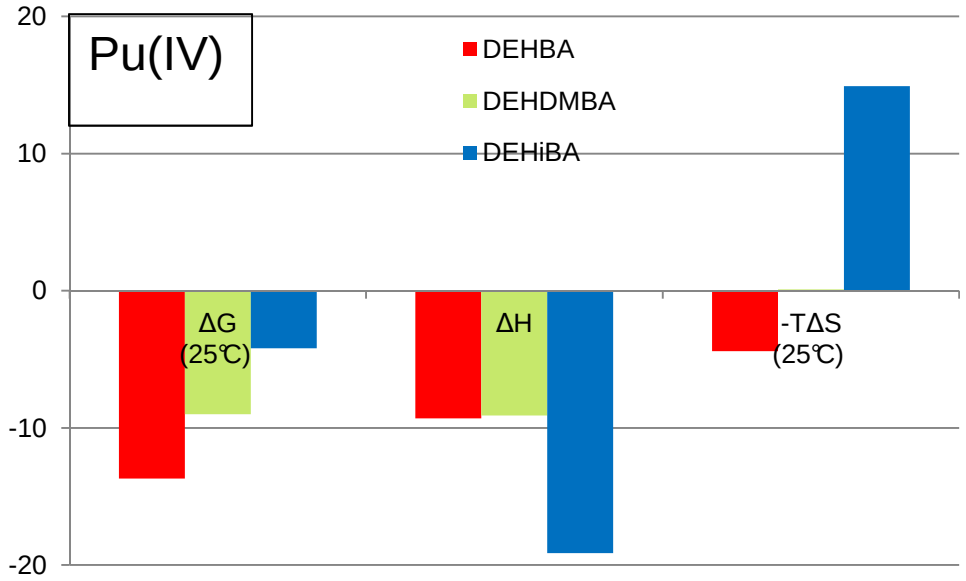


HNO_3 3M

		DEHBA	DEHDMBA	DEHiBA
$\Delta_{ext}H$ (kJ/mol)	$LiNO_3$ 2M-HNO_3 1M HNO_3 3M	- -9.3	-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

Extraction Pu(IV) - Thermodynamic properties (2)

$$Pu^{4+} + 4\,NO_3^- + n\,\overline{L} \rightarrow \overline{Pu(NO_3)_4(L)_n}$$



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/ $\Delta\,(\Delta_{ext}G°)_{L2/L1} = \Delta(\Delta_{dehydration}G°)_{L2/L1} + \Delta(\Delta_{coordination}G°)_{L2/L1} + \Delta(\Delta_{solvation}G°)_{L2/L1}$

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

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

Conclusion

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): furthet studies will focuse 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

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XRD C. Tamain
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Thank you for your attention

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