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Actinide stripping by a hydrophilic BTP ligand in aqueous HNO_3 from TODGA- containing organic phase.

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¹ Institute of Nuclear Chemistry and Technology,
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Bibliography - Aromatic poly-N-dentate ligands

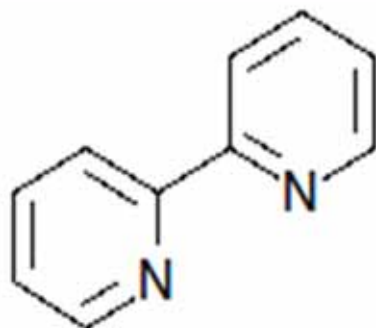
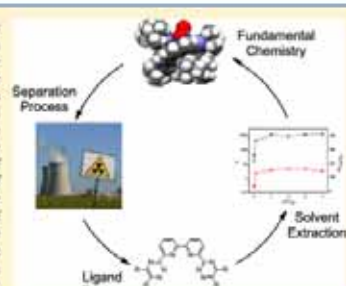
Use of Soft Heterocyclic N-Donor Ligands To Separate Actinides and Lanthanides

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Supporting Information

ABSTRACT The removal of the most long-lived radiotoxic elements from used nuclear fuel, minor actinides, is foreseen as an essential step toward increasing the public acceptance of nuclear energy as a key component of a low-carbon energy future. Once removed from the remaining used fuel, these elements can be used as fuel in their own right in fast reactors or converted into shorter-lived or stable elements by transmutation prior to geological disposal. The SANEX process is proposed to carry out this selective separation by solvent extraction. Recent efforts to develop reagents capable of separating the radioactive minor actinides from lanthanides as part of a future strategy for the management and reprocessing of used nuclear fuel are reviewed. The current strategies for the reprocessing of PUREX raffinate are summarized, and some guiding principles for the design of actinide-selective reagents are defined. The development and testing of different classes of solvent extraction reagent are then summarized, covering some of the earliest ligand designs right through to the current reagents of choice, bis(1,2,4-triazine) ligands. Finally, we summarize research aimed at developing a fundamental understanding of the underlying reasons for the excellent extraction capabilities and high actinide/lanthanide selectivities shown by this class of ligands and our recent efforts to immobilize these reagents onto solid phases.



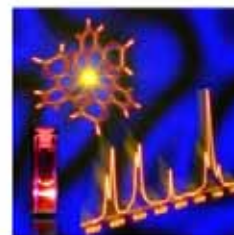
The simplest aromatic poly-N-dentate ligand is 2,2'-bipyridil

Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands

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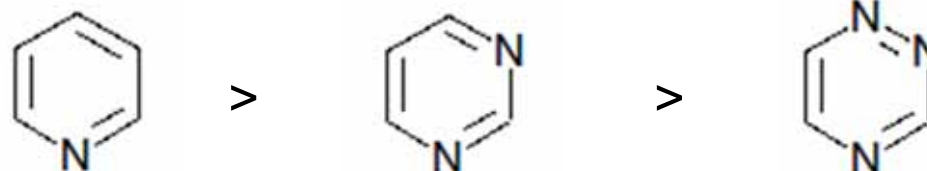
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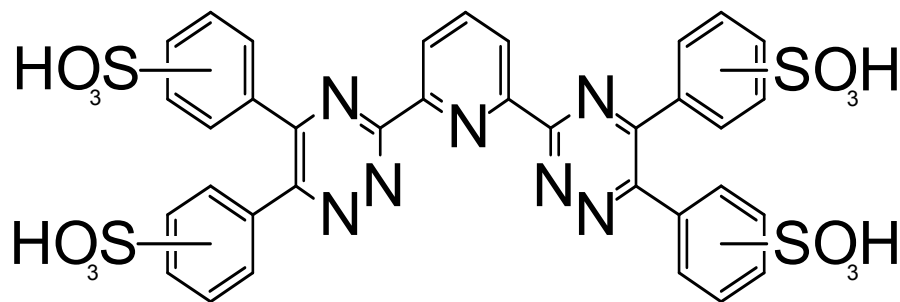
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Affinity to protonate nitrogen atoms decreases in the order:



The Choice of Selected ligand

Lipophilic poly-N-nitrogen ligands are broadly studied as selective extractants for separation of long-lived actinides from irradiated nuclear fuel. In the last years, the research was focused on the derivatives of bis-triazinyl pyridine (**BTP**) which selectively extract actinides(III) from lanthanides(III) from aqueous HNO_3 solutions to organic solvents. Moreover, selective stripping of minor actinides can be done also, using a hydrophilic ligand, e.g. **$\text{SO}_3\text{-Ph-BTP}$** delivered by Technocomm Ltd (UK).



HSO_3PhBTP

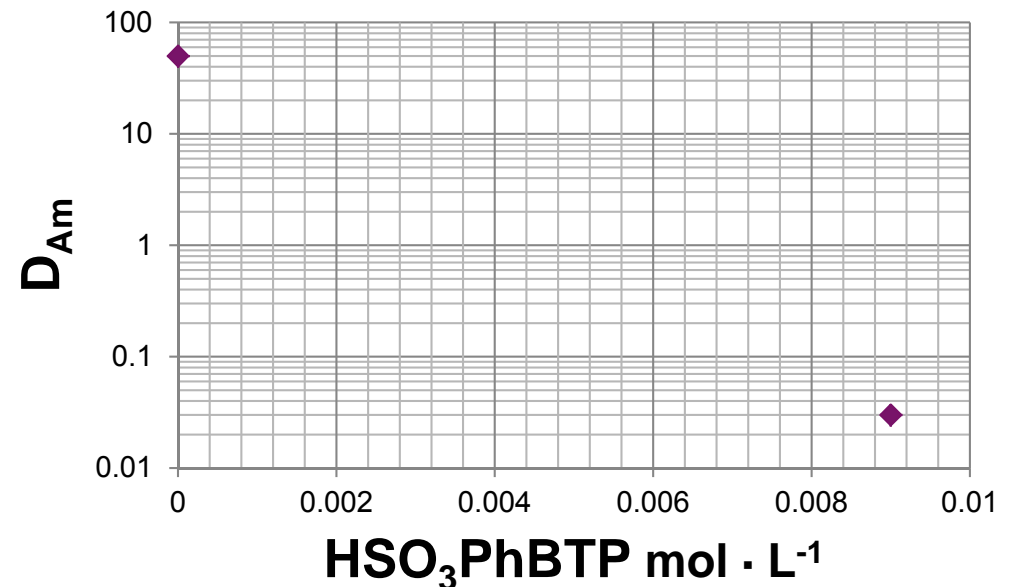
Bibliography Complexes of An(III), Ln(III) with HSO₃PhBTP

Stability constant of An with SO₃-Ph-BTP ligand ← **TRLFS**, An³⁺ forms more stable complexes than Ln³⁺. Complexes (1:1), (1:2) and (1:3) were observed

Stability constants of Cm and Eu with SO₃-Ph-BTP ligand; at **pH 3** (TRLFS)

| β | Cm | Eu |
|-----------|------|------|
| β_1 | 5,4 | 5,2 |
| β_2 | 9,3 | 8 |
| β_3 | 12,2 | 10,2 |

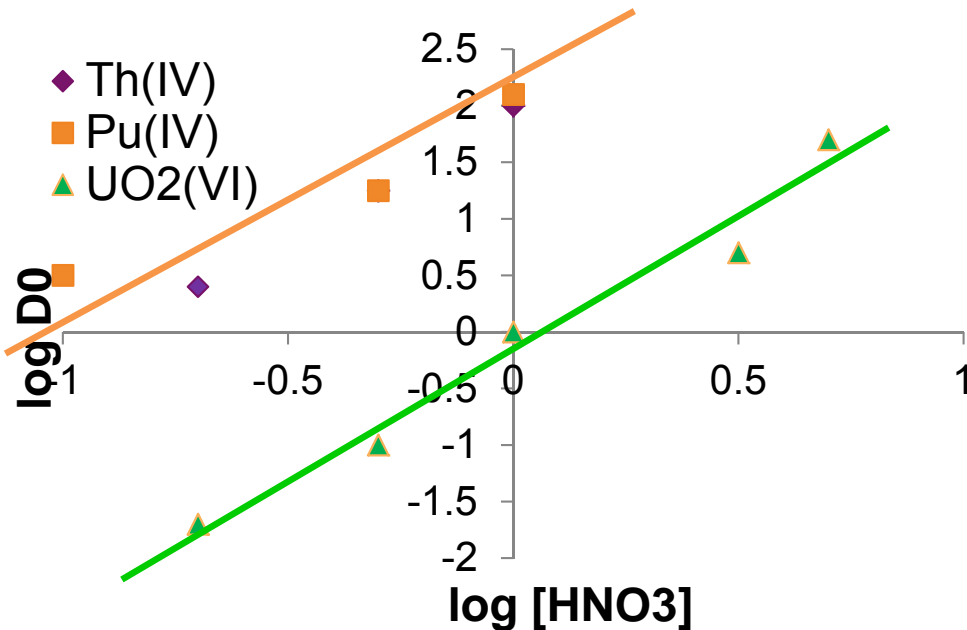
Ch.M. Ruff, U. Müllich, A. Geist, P. J. Panak, Dalton Trans., 2012, 41, 14594



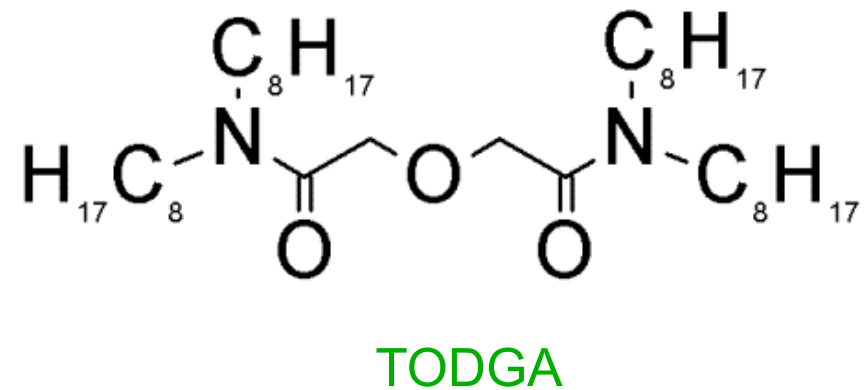
Distribution ratio of Am (0.5 M NH₄NO₃ + HNO₃ (**pH 1**)/**0.2 M TODGA** in kerosene
A. Geist et al., Solv. Extr. Ion Exch., 30: 433–444, 2012

Liquid-liquid Extraction of Actinides with TODGA

In certain separation schemes under study (innovative-SANEX) the f-block elements are extracted together from acidic PUREX raffinate to the organic phase using e.g. lipophilic tri-O-dentate ligand, TODGA.



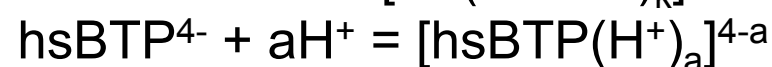
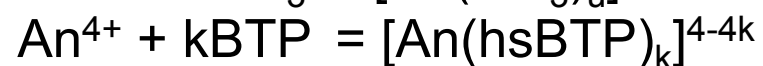
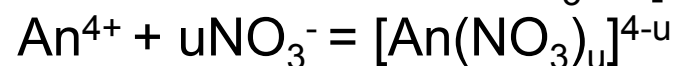
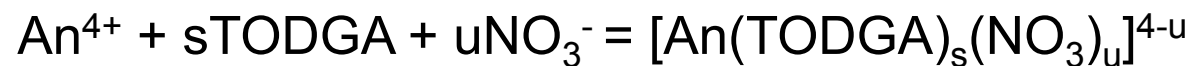
0.2 M TODGA



Yuji Sasaki*, Yasuhiro Tsubataa, Yoshihiro Kitatsujia, Yumi, Solvent Extraction and Ion Exchange Volume 31, Issue 4, 2013 401-415

Principle of the LLE Method

| | |
|-------------------|-----------------------------------|
| TODGA(org) | |
| M^{n+} | SO ₃ -Ph-BTP (aq) |
| H^+ | NO ₃ ⁻ (aq) |



where hsBTP = SO₃PhBTP

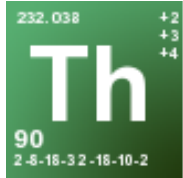
$$D_0 = \frac{[An(TODGA)_l(NO_3)_u]}{[An] + \sum_1^u [An(NO_3)_u]^{4-u}}$$

$$K_{ex} = \frac{[An(TODGA)_s(NO_3)_u]}{[An][TODGA]^s[NO_3]^u}$$

$$D = \frac{D_0}{1 + \sum_{i=1}^u K_{nitrate,u} [NO_3^-]^u + \sum_{i=1}^k K_{BTPk} [hsBTP]^k}$$

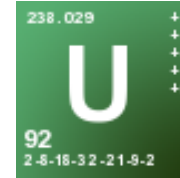
$$\frac{D_0}{D} - 1 = \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n$$

Method of the determination of the Distribution coefficient



spectrophotometry

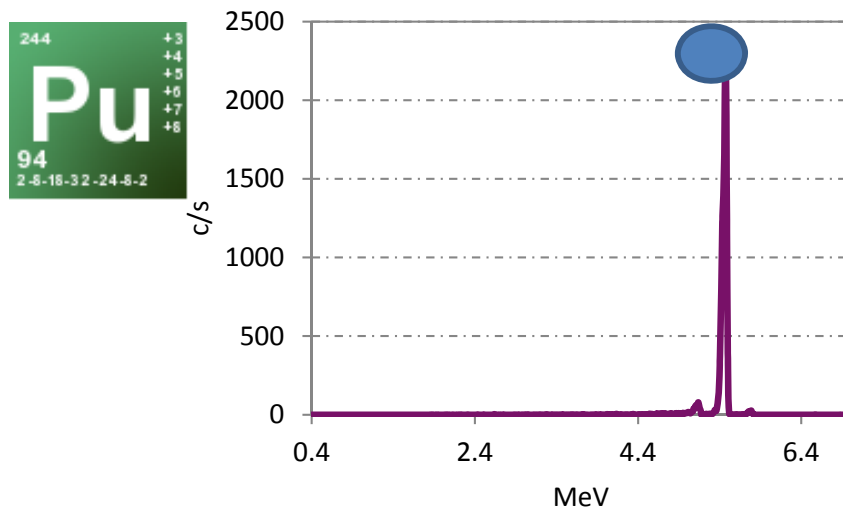
Complex Arsenazo(III)-Th 660 nm



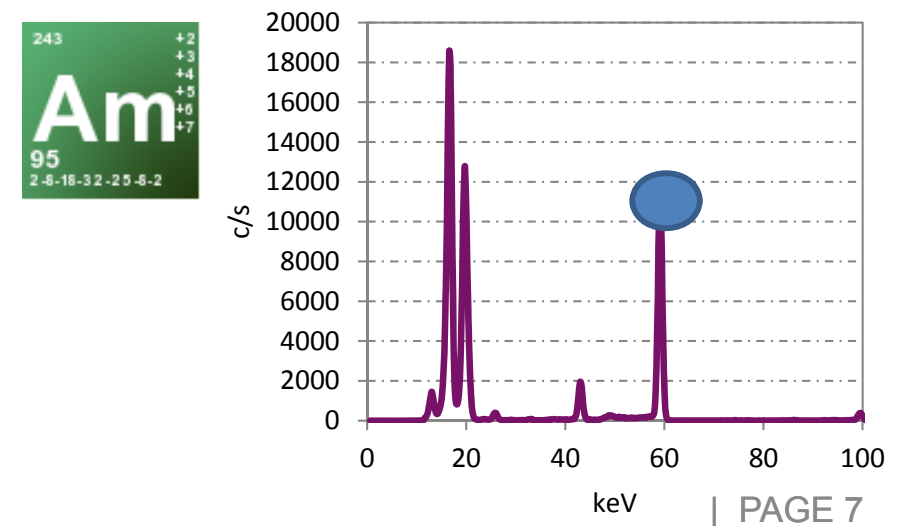
spectrophotometry

Complex Arsenazo(III)- $UO_2(2+)$ 655 nm

alpha spectrometry

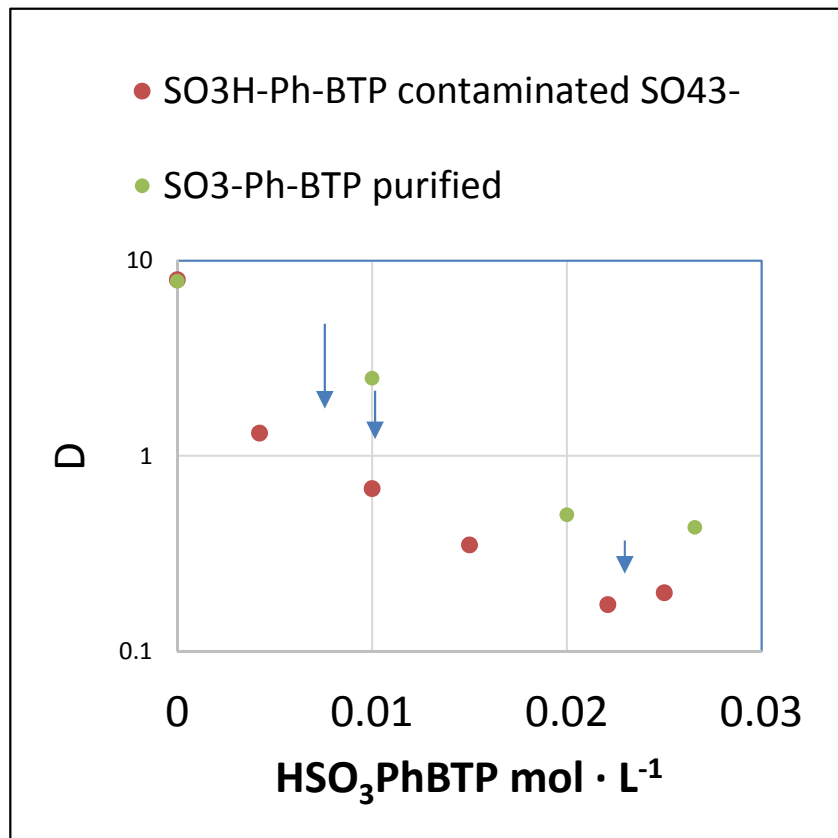


gamma spectrometry



Purification of ligand

Ligand has to be additional purify in case of the presence sulphate which form relatively strong complexes with An(IV)



Test with BaCl₂ can generate large amount of white powder

Neutralization with NaOH until pH = 7

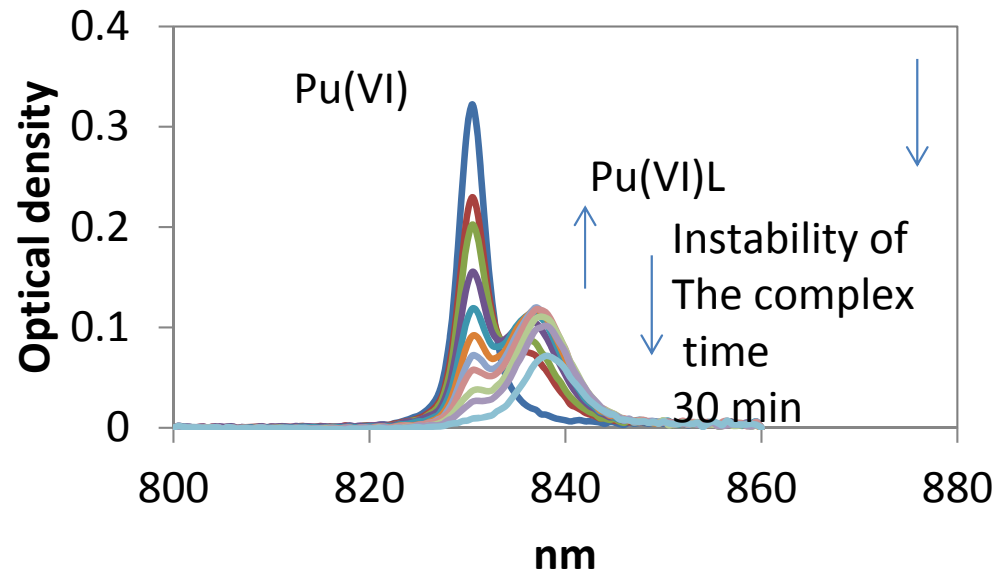
Solubilization in MeOH at least three times

Evaporation or precipitation with acetone

Preliminary experiments

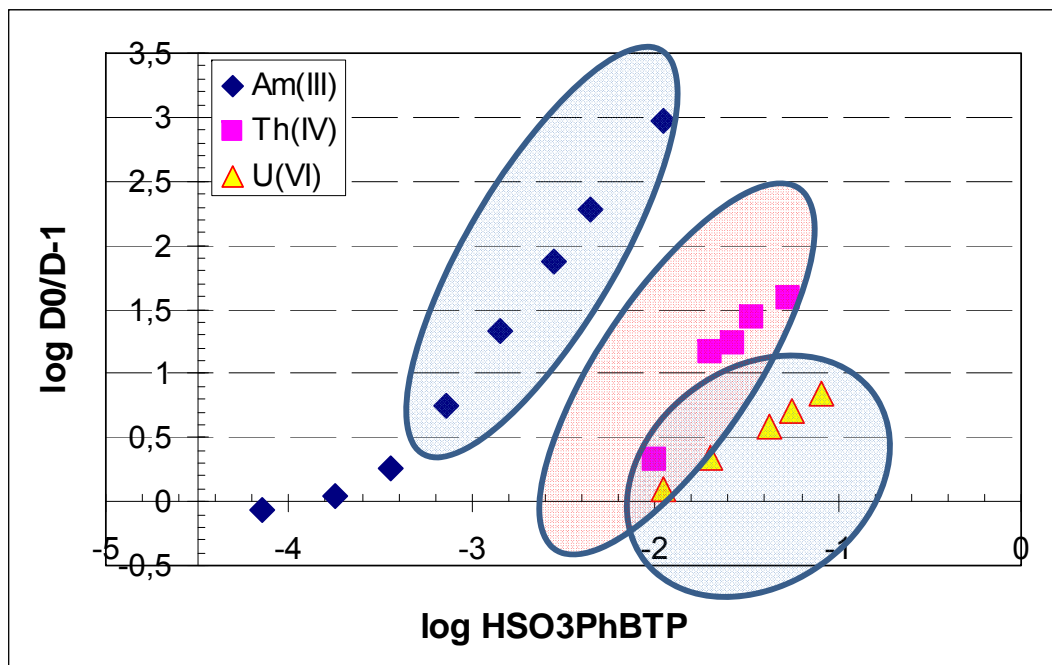
Experiments with Th(IV), Pu(IV)
 UO_2^{2+} , PuO_2^{2+} , NpO_2^{2+}
reduction

At pH 1 we observed the formation of the complex with Pu(VI) and reduction



0.001 M Pu(VI), HSO_3PhBTP 0-0.15 M, pH 1

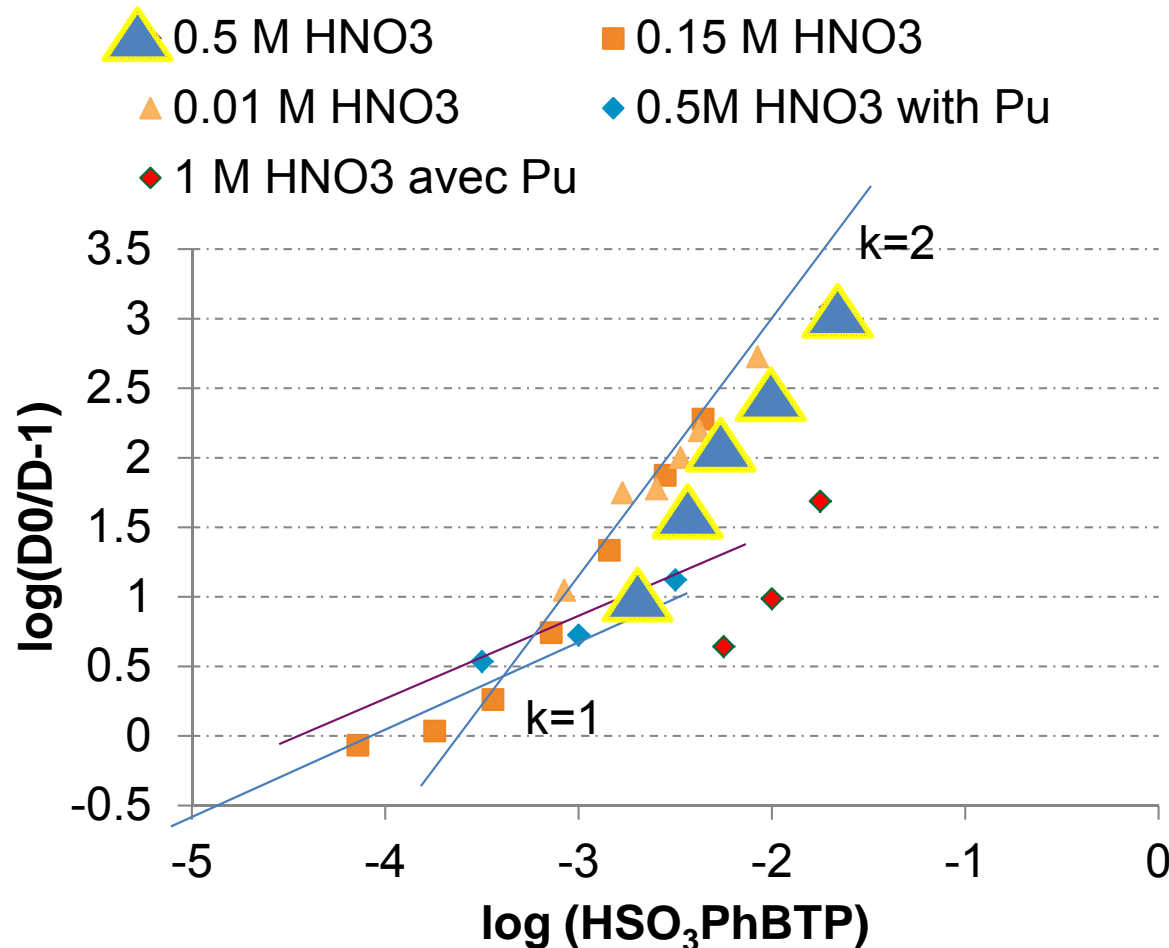
Extraction of An as a function of ligand



Extraction of Th(IV), Am(III) and UO_2^{2+} by TODGA in 5% octanol-kerosene from acidic aqueous solution. Temperature of extraction 25 °C , time 30 min, O/A =1

| | UO_2^{2+} | Th | Am |
|------------------------------|-------------|----------------|-----------------|
| C An mol/L | 0.0002 | 0.0001 | trace |
| C NO_3^- | 1 | 1 | 1 |
| Phase aqueous | 0.15 M | 0.15 M HNO_3 | 0.015 M HNO_3 |
| Phase organic | 0.6 M TODGA | 0.06 M TODGA | 0.1 M TODGA |

Results - Extraction of Americium from acidic solution HSO_3PhBTP and NaNO_3



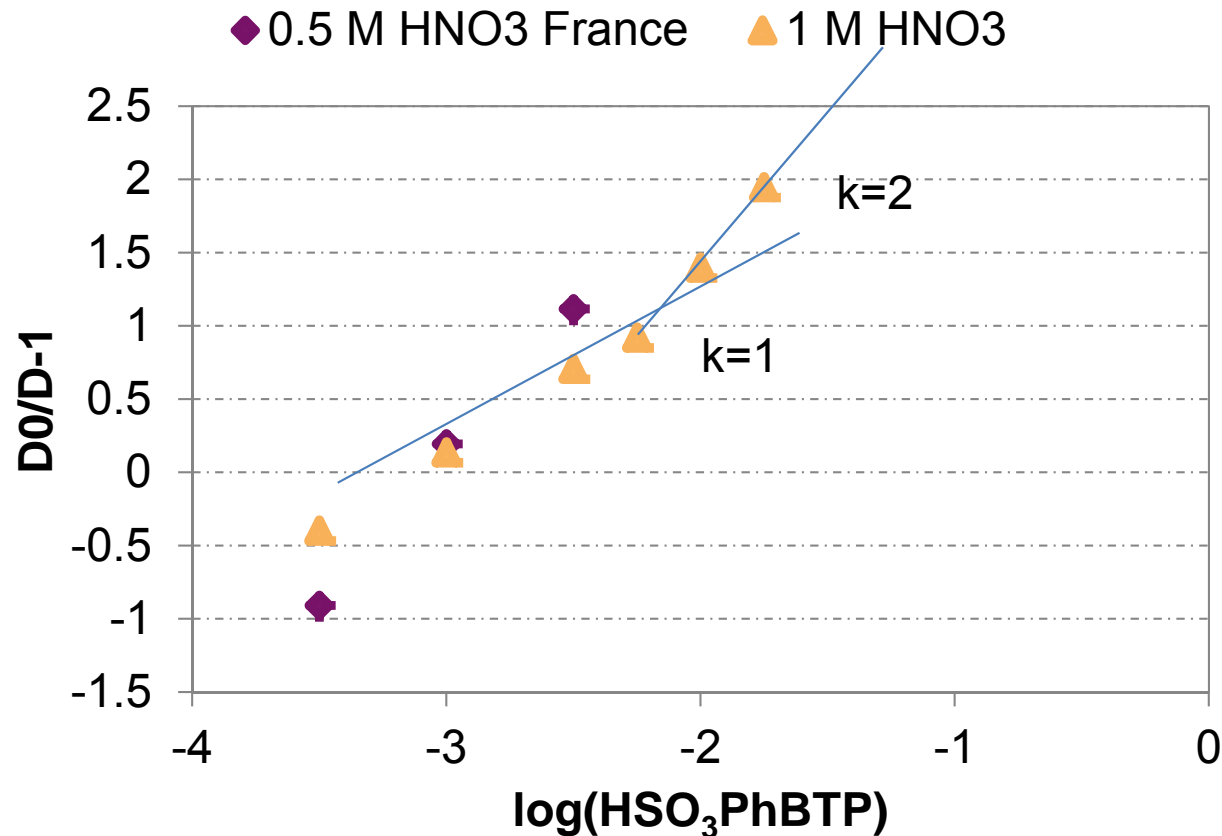
Phase organic: 0.1 M TODGA and 0.06 M TODGA when Am was measured with Pu

| acidity | $\log \beta_1$ | $\log \beta_2$ |
|---------|-----------------|-----------------|
| 0.02 | 5.27 ± 0.54 | 8.24 ± 1.01 |
| 0.15 | 4.76 ± 0.45 | 8.73 ± 1.03 |
| 0.5 | 4.70 ± 0.51 | 8.48 ± 1.04 |
| 1.0 | 5.21 ± 1.01 | 9.74 ± 2.01 |
| 3.0 | In progress | In progress |

| β | Cm | Eu |
|-----------|------|------|
| β_1 | 5,4 | 5,2 |
| β_2 | 9,3 | 8 |
| β_3 | 12,2 | 10,2 |



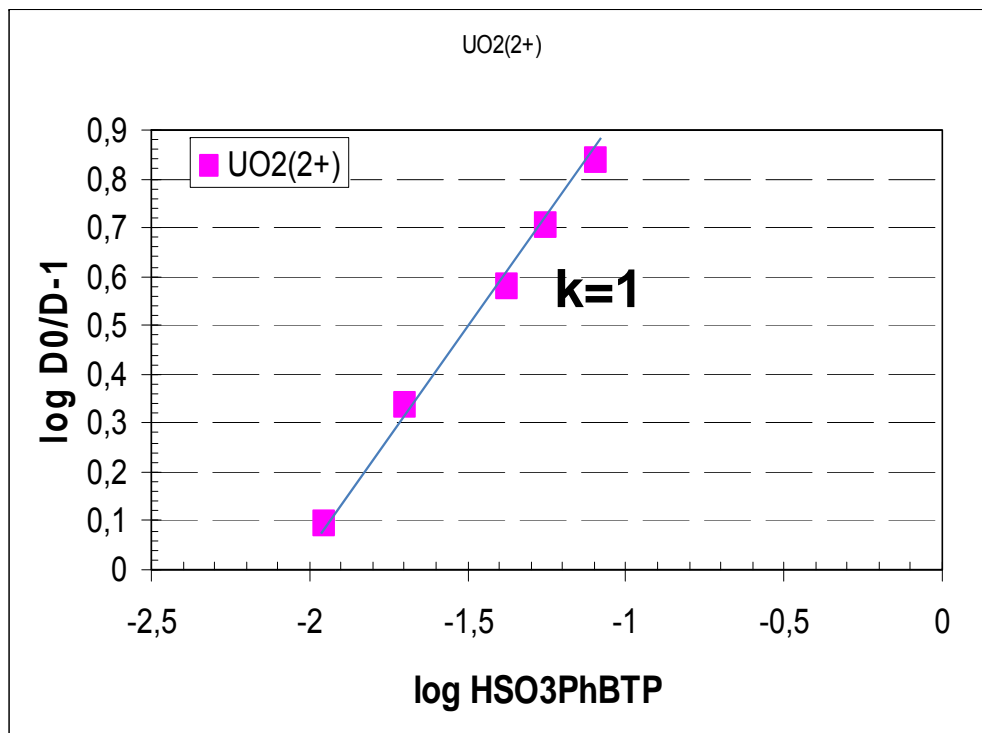
Results - Extraction of Plutonium from acidic solution HSO₃PhBTP and NaNO₃



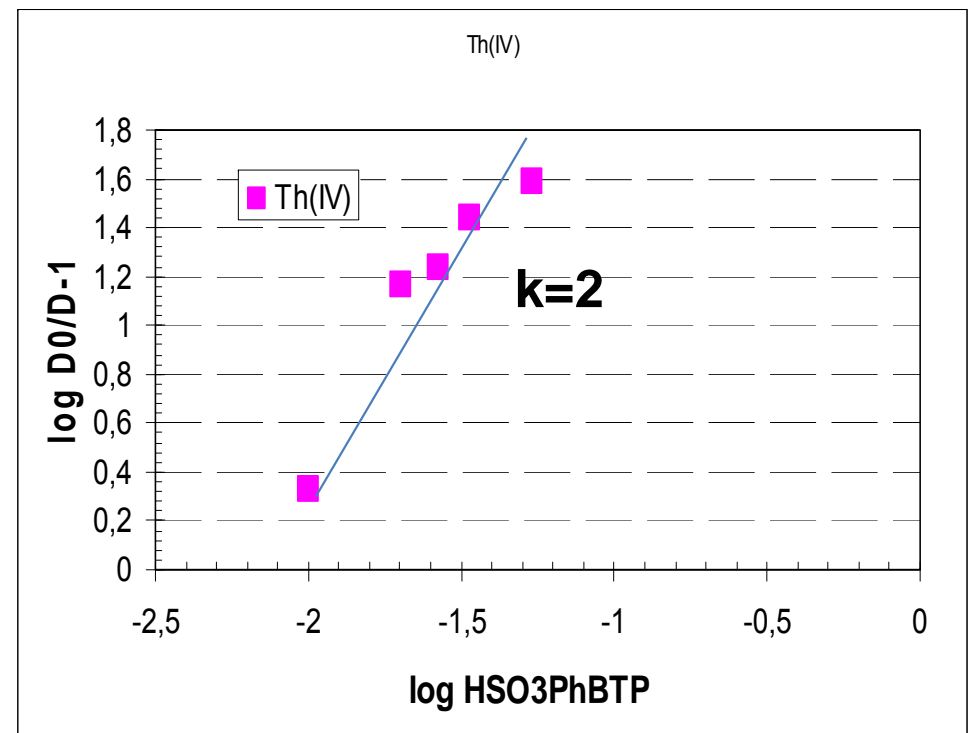
| acidity | log β ₁ | log β ₂ |
|---------|--------------------|--------------------|
| 0.5 | 5.01 ± (0.51) | 8.98 ± (1.01) |
| 1.0 | 4.34 ± (0.51) | 8.80 ± (1.02) |
| 3.0 | In progress | In progress |

C_{Pu(VI)} = 0.1 mM, 1.0 M (H, Na)NO₃
 TODGA = 0.06 M in kerosene/5% octanol

Results - Extraction of Uranium(VI) and Thorium(IV) from acidic solution HSO_3PhBTP and NaNO_3



$\log K_1 = 2.66$
0.15 M HNO_3
TODGA 0.6 M



preliminary results
 $\log K_1 = 3.63$
 $\log K_2 = 6,00$
0.15 M HNO_3
TODGA 0.06 M

Conclusion

- Am^{3+} , Th^{4+} , Pu^{4+} forms complexes 1:1, 1:2 and UO_2^{2+} , 1:1 under the conditions of experiments.
- No evidence of the complexes 1:3 under the conditions of experiments.
- The results for Am^{3+} are in accordance with the data existed for Cm(III) and Eu(III).
- The order of the conditional stability constants for the complexes 1:1 is $\text{Pu}^{4+} \sim \text{Am}^{3+} > \text{Th}^{4+} > \text{UO}_2^{2+}$.

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