# Selective aqueous complexation of actinides with hydrophilic BTP and BTBP: Towards improved *i*-SANEX processes

Andreas Geist<sup>1</sup>, Udo Müllich<sup>1</sup>, Giuseppe Modolo<sup>2</sup>, Andreas Wilden<sup>2</sup> <sup>1</sup>Karlsruher Institut für Technologie, INE, Germany <sup>2</sup>Forschungszentrum Jülich, IEF-6, Germany

### Abstract

New hydrophilic sulphonated BTP and BTBP were synthesised and tested for their ability of selectively complexing trivalent actinides in  $HNO_3$  solutions. These compounds have good solubility in aqueous phases and complex trivalent actinides with good selectivity over lanthanides. They do not require buffering or salting out agents to be added to the actinides back extraction solution;  $HNO_3$  is used to keep the lanthanides in the organic phase. These properties make them suitable candidates for the development of improved separations processes based on the selective complexation of actinides in the aqueous phase.

## Introduction

The separation of trivalent actinides from the chemically similar lanthanides is an important task in the P&T strategy, owing to the high neutron capture cross-sections of some lanthanides. This separation has developed in Europe towards the DIAMEX/r-SANEX process: actinides(III) [Am(III) and Cm(III)] and lanthanides are co-extracted from the PUREX raffinate by the DIAMEX process, using malonamides or diglycolamides as extracting agents. Actinides(III) are then selectively extracted from the DIAMEX process.

Figure 1: *i*-SANEX scheme



The innovative SANEX (i-SANEX) process was developed at the French CEA and in the framework of the ACSEPT project [1] to simplify the DIAMEX/r-SANEX process. It is basically a DIAMEX process with selective back extraction of actinides(III) from the loaded organic phase. This concept is based on the reverse TALSPEAK process [2,3]. Actinides(III) and lanthanides(III) are co-extracted from a PUREX raffinate solution in a DIAMEX-like process, using e.g. TODGA (N,N,N',N'-tetra-*n*-octyl diglycolamide [4-7]) as extracting agent. Actinides(III) are then back extracted from the loaded organic phase using a hydrophilic complexing agent which is selective for actinides(III) over lanthanides(III). To keep the lanthanides(III) in the organic phase, a nitrate salt must be added to the selective stripping solution. Another option is adding a second extracting agent [such as HDEHP, bis(2-ethylhexyl)phosphate] to the organic phase to keep the lanthanides in the organic phase at low acidity [8].

Drawback of *i*-SANEX processes developed so far [9] is the limited acidity range ( $pH \approx 3$ ) in which the complexing agents are effective, meaning that buffering agents need to be added to the aqueous phase used for actinides back extraction. The required addition of a nitrate salt or a second extracting agent is another disadvantage considering secondary waste generation.

Alkylated 2,6-bis(1,2,4-triazin-3-yl)pyridines (BTP, Figure 2 left) [10] and alkylated 6,6'-bis (1,2,4-triazin-3-yl)-2,2'-bipyridines [11] (BTBP, Figure 2 right) are effective and highly selective lipophilic extracting agents for the *r*-SANEX process. Their performance is well studied; successful spiked and hot counter-current tests have been performed in Europe [12,13].

# Figure 2: General molecular structures of BTP (left) and BTBP (right)



Recent fundamental studies show that the selectivity of BTP and BTBP is not linked to a certain phase; their selectivity is maintained both in organic and in aqueous phase [14,15]. This means that, if hydrophilised, they should be useful as selective actinide(III) complexing agents for i-SANEX process development.

We have synthesised a hydrophilic BTP, 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl) pyridine (SO<sub>3</sub>-Ph-BTP, Figure 3 left) and the corresponding BTBP (SO<sub>3</sub>-Ph-BTBP, Figure 3 right) and tested them for their ability of selectively suppressing the extraction of actinides(III) from nitric acid solutions.

# Figure 3: SO<sub>3</sub>-Ph-BTP (left) and SO<sub>3</sub>-Ph-BTBP (right)



### **Results and discussion**

# Screening

Both SO<sub>3</sub>-Ph-BTP and SO<sub>3</sub>-Ph-BTBP have a solubility in water of not less than 0.1 mol/L. Initial screening of SO<sub>3</sub>-Ph-BTP showed that this compound efficiently lowers  $D_{Am(III)}$  even in 0.1 mol/L HNO<sub>3</sub> (+ 0.5 mol/L NH<sub>4</sub>NO<sub>3</sub> as salting out agent).

### Influence of HNO<sub>3</sub> concentration

These promising results prompted further tests with aqueous phases consisting of  $HNO_3$  (without addition of  $NH_4NO_3$ ): Am(III) and Eu(III) were extracted from  $HNO_3$  without or with 10 mmol/L SO<sub>3</sub>-Ph-BTP into (0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH).

As shown in Figure 4, addition of 10 mmol/L SO<sub>3</sub>-Ph-BTP to the aqueous phase significantly suppresses Am(III) extraction whereas it has only small influence on Eu(III) extraction. For 0.1 mol/L < [HNO<sub>3</sub>] < 0.6 mol/L,  $D_{Am(III)} < 1$  and  $D_{Eu(III)} > 1$ . The separation factor SF<sub>Eu(III)/Am(III)</sub> is in the range of 500-1 000, as compared to SF<sub>Eu(III)/Am(III)</sub>  $\approx$  7 without SO<sub>3</sub>-Ph-BTP (being the selectivity of TODGA).

Figure 4 implies that  $SO_3$ -Ph-BTP's efficiency decreases with increasing HNO<sub>3</sub> concentration: The slopes of  $logD_{M(III)}$  vs.  $log[HNO_3]$  are steeper with  $SO_3$ -Ph-BTP than without. A qualitative explanation for this finding may be the possible protonation of  $SO_3$ -Ph-BTP. With increasing HNO<sub>3</sub> concentration the free  $SO_3$ -Ph-BTP concentration available for the complexation of Am(III) [or Eu(III)] is decreased. Further measurements and calculations are required to quantify this behaviour.

In a more "realistic" experiment, Am(III) + Eu(III) were extracted from a spiked PUREX raffinate surrogate (4.2 mol/L HNO<sub>3</sub>, 0.2 mol/L oxalic acid, 0.02 mol/L HEDTA) into (0.2 mol/L TODGA + 5 vol.% 1-octanol in kerosene). The loaded phase was stripped into:

- $H_2O$ , resulting in  $D_{Am(III)} = 23$ ,  $D_{Eu(III)} = 180$ ,  $SF_{Eu(III)/Am(III)} = 7.5$ ;
- 10 mmol/L SO<sub>3</sub>-Ph-BTP in H<sub>2</sub>O, resulting in  $D_{Am(III)} = 0.059$ ,  $D_{Eu(III)} = 49$ ,  $SF_{Eu(III)/Am(III)} = 830$ .

Clearly, SO<sub>3</sub>-Ph-BTP is also very effective under process-like conditions.

Also, initial tests showed that different batches of SO<sub>3</sub>-Ph-BTP give similar results.

Results on the influence of  $SO_3$ -Ph-BTBP on the extraction of Am(III) and Eu(III) are found in Table 1. Whereas both Am(III) and Eu(III) are extracted from 0.5 mol/L HNO<sub>3</sub>, addition of 10 mmol/L  $SO_3$ -Ph-BTBP suppresses Am(III) extraction. Eu(III) extraction is only slightly lowered. These results are similar to those found with  $SO_3$ -Ph-BTP.

### Figure 4: Effect of SO<sub>3</sub>-Ph-BTP on the extraction of Am(III) and Eu(III) into TODGA

Organic phase - 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH

Aqueous phase – <sup>241</sup>Am(III) + <sup>152</sup>Eu(III) (1 kBq/mL each) in HNO<sub>3</sub>, with (filled symbols, solid lines) or without (open symbols, dashed lines) 10 mmol/L SO<sub>3</sub>-Ph-BTP



Table 1: Extraction of Am(III) and Eu(III) into TODGA, influence of SO<sub>3</sub>-Ph-BTBP

Organic phase - 0.2 mol/L TODGA + 5 vol.% 1-octanol in kerosene

Aqueous phase - <sup>241</sup>Am(III) + <sup>152</sup>Eu(III) in 0.5 mol/L HNO<sub>3</sub> without or with 10 mmol/L SO<sub>3</sub>-Ph-BTBP

[SO₃-Ph-BTBP]	D <sub>Am(III)</sub>	D <sub>Eu(III)</sub>	SF <sub>Eu(III)/Am(III)</sub>
0	120	900	7.5
10 mmol/L	0.33	150	450

# Influence of SO<sub>3</sub>-Ph-BTP concentration

Figure 5 shows the extraction of Am(III) and Eu(III) from 0.5 mol/L HNO<sub>3</sub> with varied concentration of SO<sub>3</sub>-Ph-BTP into a solution of (0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH). The horizontal dashed lines represent distribution ratios ( $D_{Eu(III)} = 950$ ,  $D_{Am(III)} = 120$ ) in the absence of SO<sub>3</sub>-Ph-BTP. Adding increasing concentrations of SO<sub>3</sub>-Ph-BTP increasingly suppresses the extraction of Am(III); the extraction of Eu(III) is less affected.

The slope of logD<sub>Am(III)</sub> vs. log[SO<sub>3</sub>-Ph-BTP] is -1.9; the slope of logD<sub>Eu(III)</sub> vs. log[SO<sub>3</sub>-Ph-BTP] seems to approach a similar value. The separation factor  $SF_{Eu(III)/Am(III)}$  has a value of 900 for 20 mmol/L SO<sub>3</sub>-Ph-BTP; with increasing SO<sub>3</sub>-Ph-BTP concentration it approaches a value of approximately 1 200. This separation factor,  $SF_{Eu(III)/Am(III)} \approx 1200$ , may be understood as the product of TODGA's selectivity ( $SF_{Eu(III)/Am(III)} \approx 8$ ) and the selectivity of a BTP, which is in the range of 150 [10].

BTP are known to extract An(III) and Ln(III) 1:3 complexes [10,15-18]. We expect SO<sub>3</sub>-Ph-BTP to behave similarly, and an ongoing TRLFS study actually proves this. However, the observed slope of  $\log D_{Am(III)}$  vs.  $\log[SO_3-Ph-BTP]$  is not in agreement with the formation of a 1:3 complex; a slope of -3 is expected. It remains to be answered whether this is explained by the postulated protonation of SO<sub>3</sub>-Ph-BTP (see above).



Figure 5: Extraction of Am(III) and Eu(III) into TODGA, influence of [SO<sub>3</sub>-Ph-BTP]

Figure 6: Am(III) and Eu(III) back extraction kinetics with SO<sub>3</sub>-Ph-BTP

Organic phase – 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH, loaded with  $^{241}\rm{Am}(III)$  +  $^{152}\rm{Eu}(III)$  (1 kBq/mL each) from 3 mol/L HNO\_3

Aqueous phase – 20 mmol/L SO\_3-Ph-BTP in 0.29 mol/L HNO\_3  $\,$ 



#### Back extraction kinetics

The kinetics of back extraction was also tested. (0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH) was loaded with  $^{241}$ Am(III) +  $^{152}$ Eu(III) from 3 mol/L HNO<sub>3</sub>. The loaded solvent was contacted with a solution of SO<sub>3</sub>-Ph-BTP in 0.29 mol/L HNO<sub>3</sub>.

The influence of contacting time on Am(III) and Eu(III) distribution ratios is shown in Figure 6. Although the mechanical shaking device used for this experiment is not very efficient (oscillating at approximately 5 Hz), equilibrium was attained after 10 min. Even after only 3 min the distribution ratios were close to equilibrium. This indicates that the selective An(III) back extraction with  $SO_3$ -Ph-BTP is not impeded by slow kinetics.

#### An(III) + Ln(III) extraction

Figure 7 shows distribution ratios for the extraction of An(III) and Ln(III) from  $HNO_3$  into (0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH). Although all Ln(III) except Pm(III) were measured, only data up to Dy(III) are shown; the heavier Ln(III) not being present LWR fuel. Am(III) and Cm(III) are extracted into TODGA with distribution ratios similar to those of the lighter lanthanides(III).

#### Figure 7: Extraction of An(III) and Ln(III) into TODGA

Organic phase – 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH Aqueous phase – <sup>241</sup>Am(III) + <sup>244</sup>Cm(III) (1 kBq/mL each) + (Y(III) + Ln(III), 20 mg/L each) in HNO<sub>3</sub>  $A/O = 1, T = (293\pm0.5)$  K



Distribution ratios for the extraction of An(III) and Ln(III) from  $HNO_3$  containing 20 mmol/L  $SO_3$ -Ph-BTP into (0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH) are shown in Figure 8. The extraction of Am(III) and Cm(III) is strongly suppressed. The extraction of the lightest lanthanides is virtually unchanged; the extraction of heavier lanthanides is increasingly suppressed but not to an extent as to interfere with An(III) extraction.

Clearly, an efficient separation of Am(III) + Cm(III) from all lanthanides is viable, the lowest selectivity [Cm(III) over La(III)] still having a separation factor of approximately 50 in the relevant acidity range ( $\leq 0.5 \text{ mol/L HNO}_3$ ). Cm(III) and Am(III) show similar distribution ratios. Obviously, the better extractability of Cm(III) by TODGA (SF<sub>Cm(III)/Am(III)</sub> = 1.6) is compensated by BTP's better affinity for Cm(III) by [e.g. SF<sub>Cm(III)/Am(III)</sub> = 1.6 for the extraction of An(III) from HNO<sub>3</sub> by *n*-Pr-BTP].

### Figure 8: Effect of SO<sub>3</sub>-Ph-BTP on the extraction of An(III) and Ln(III) into TODGA

Organic phase - 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH

Aqueous phase - 20 mmol/L SO<sub>3</sub>-Ph-BTP + <sup>241</sup>Am(III) + <sup>244</sup>Cm(III) (1 kBq/mL each) + (Y(III) + Ln(III), 20 mg/L each) in HNO<sub>3</sub>



# Conclusions

Two new hydrophilic complexing agents for actinides,  $SO_3$ -Ph-BTP and  $SO_3$ -Ph-BTBP, were synthesised and tested. These are highly efficient compounds for the selective stripping of An(III) from e.g. a loaded TODGA phase. Since they remain efficient in  $HNO_3$ ,  $HNO_3$  can be used as salting out agent for the lanthanides in the selective stripping section; no salts or buffering agents are required. The equilibrium and shaking tube kinetic data available indicate that a flow sheet for a selective An(III) stripping section should not require many stages.

### Acknowledgements

Financial support from the Commission of the European Community (project ACSEPT, FP7-CP-2007-211 267) is acknowledged.

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