AmSel, a New System for Extracting Only Americium from PUREX Raffinate

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Abstract

AmSel, a new system for the hydrometallurgical separation of only americium from HAR is presented. A water soluble BTBP (bis-triazinyl-pyridine), SO_3-Ph-BTBP, is used to selectively strip Am(III) from a TODGA solvent loaded with Am(III), Cm(III) and Ln(III). First results from liquid-liquid extraction experiments prove the feasibility; the separation factor between Am(III) and Cm(III) is 2.5, independent of HNO_3 and SO_3-Ph-BTBP concentrations. Monophasic complexation studies show that SO_3-Ph-BTBP forms 1:2 complexes both with An(III) and Ln(III). Differences in stability constants of the Cm(III) and Eu(III) 1:2 complexes explain the selectivity observed in extraction experiments. A tentative flow sheet is presented

Introduction

The concept of recycling transuranium elements (TRU) in advanced nuclear fuel cycles could lead to better resource efficiency and more compact geologic repositories for high active wastes. The required chemical processes — both pyrometallurgical and hydrometallurgical — for separating TRU from irradiated nuclear fuels are under development in many countries. Hydrometallurgical processes could be implemented as an extension to the PUREX process, separating uranium, neptunium and plutonium in an advanced PUREX process,[1] followed by the separation of americium and curium from the PUREX raffinate. In Europe, DIAMEX and SANEX processes have been developed for this task.[2] More recently, processes integrating DIAMEX and SANEX have been developed,[3,4,5,6] such as 1c-SANEX and i-SANEX. Alternatively, GANEX processes have been developed for co-separating TRU in one process.[7,8,9,10,11,12,13]

However, the recycling of transuranium elements as nuclear fuel is complicated by the presence of curium. Its short term high decay heat and neutron emission requires remotely handled fuel fabrication under continuous cooling in neutron shielded hot cells. Since curium does not contribute significantly to long term heat load and radiotoxicity it could be routed with the fission products for final disposal after decay storage. Thus processes for separating americium from curium have been developed. Some of these rely on the oxidation of americium to higher oxidation states,[14] making it extractable by e.g. TBP. Other processes exploit the more or less pronounced selectivity of some solvents for Am(III) over Cm(III).[15,16]

The americium-curium separation would be placed downstream of the SANEX process. Preferably, this separation should be located early on in the process sequence. Hence, the

French EXAm process was developed and successfully tested,[17] separating only americium from the PUREX or COEX™ raffinate. EXAm combines a malonamide extracting agent and a hydrophilic diglycolamide to co-extract Am(III) and the light Ln(III), followed by selective Am(III) stripping using a polyaminocarboxylate.

Alternative processes are being developed in the framework of the European SACSESS project. Starting from the i-SANEX system[4,5,6] using TODGA to co-extract Am(III), Cm(III) and lanthanides and SO_3-Ph-BTP[18] to selectively strip Am(III) + Cm(III), the AmSel (americium selective separation) system was developed. Replacing SO_3-Ph-BTP with SO_3-Ph-BTBP (6,6'-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine,[19] Figure 1), AmSel makes use of reverse Am(III)/Cm(III) selectivity (TODGA prefers Cm(III),[18] BTBP prefers Am(III)[20]).
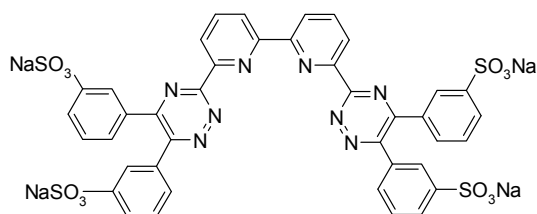

Figure 1. SO_3-Ph-BTBP.

The AmSel system — first results

It is expected that combining TODGA and a water soluble BTBP, namely SO_3-Ph-BTBP, would result in a system able to separate Am(III) + Cm(III) from Ln(III) but also able to separate Am(III) from Cm(III) + Ln(III) with a selectivity for Cm(III) over Am(III) of $SF_{Cm(III)/Am(III)} \approx 2.6$ (the product of TODGA's and BTBP's selectivity, being $SF_{Cm(III)/Am(III)} = 1.6$[18] and $SF_{Am(III)/Cm(III)} = 1.6$,[20] respectively).

Distribution data were determined for the extraction of Am(III), Cm(III), and Ln(III) from aqueous solutions containing SO_3-Ph-BTBP in HNO_3 into organic solutions of 0.2 mol/L TODGA + 5 % vol. 1-octanol in TPH. So far, not all data from alpha spectrometry and ICP-MS are available; in these cases only Am(III) and Eu(III) distribution ratios determined by gamma spectrometry are given.

The dependence of Am(III), Cm(III), and Ln(III) distribution ratios on HNO_3 concentration is shown in Figure 2 (with an earlier and less pure batch of SO_3-Ph-BTBP, batch #1) and Figure 3 (with a purer batch, batch #2). Under the experimental conditions applied, $D_{Am(III)}$ < 1 and $D_{Cm(III)}$ > 1 for 0.7–0.8 mol/L HNO_3, with $SF_{Cm(III)/Am(III)} \approx 2.5$, which is in good agreement with our expectations. Distribution ratios for Eu(III) are much higher than those for Am(III) and Cm(III); $SF_{Eu(III)/Am(III)} \approx 200$ for 0.7–0.8 mol/L HNO_3. $SF_{Eu(III)/Am(III)}$ decreases with increasing HNO_3 concentration, as already observed with SO_3-Ph-BTP.[18] Generally, Am(III) can be separated from Cm(III) + Ln(III) in 0.7–0.8 mol/L HNO_3.

The dependence of Am(III) and Eu(III) distribution ratios on SO_3-Ph-BTBP concentration is shown in Figure 4. The slope for log $D_{Am(III)}$ vs. log *[SO$_3$-Ph-BTBP]* is −1.3, the slope for log $D_{Eu(III)}$ vs. log *[SO$_3$-Ph-BTBP]* is > −1 (actually showing a curvature). The flatter slope of $D_{Eu(III)}$ vs. log *[SO$_3$-Ph-BTBP]* is explained by $D_{Eu(III)}$ approaching the value for the TODGA system without SO_3-Ph-BTBP for lower SO_3-Ph-BTBP concentrations, as also observed with SO_3-Ph-BTP.[18]
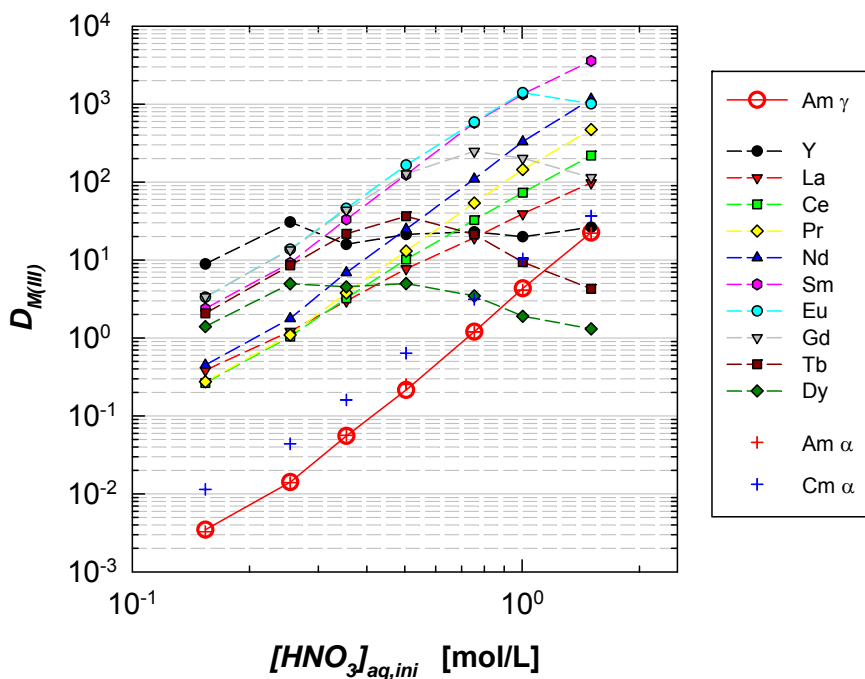
Figure 2. Extraction of Am(III), Cm(III), and Ln(III), influence of HNO$_3$ concentration. Organic phase, 0.2 mol/L TODGA + 5% vol. 1-octanol in TPH. Aqueous phase, ^{241}Am(III) + ^{244}Cm(III) + ^{152}Eu(III) (2 kBq/mL each) + Ln(III) (10 mg/L each) + 20 mmol/L SO$_3$-Ph-BTBP (batch #1) in HNO$_3$. A/O = 1, T = (293 ± 0.5) K.
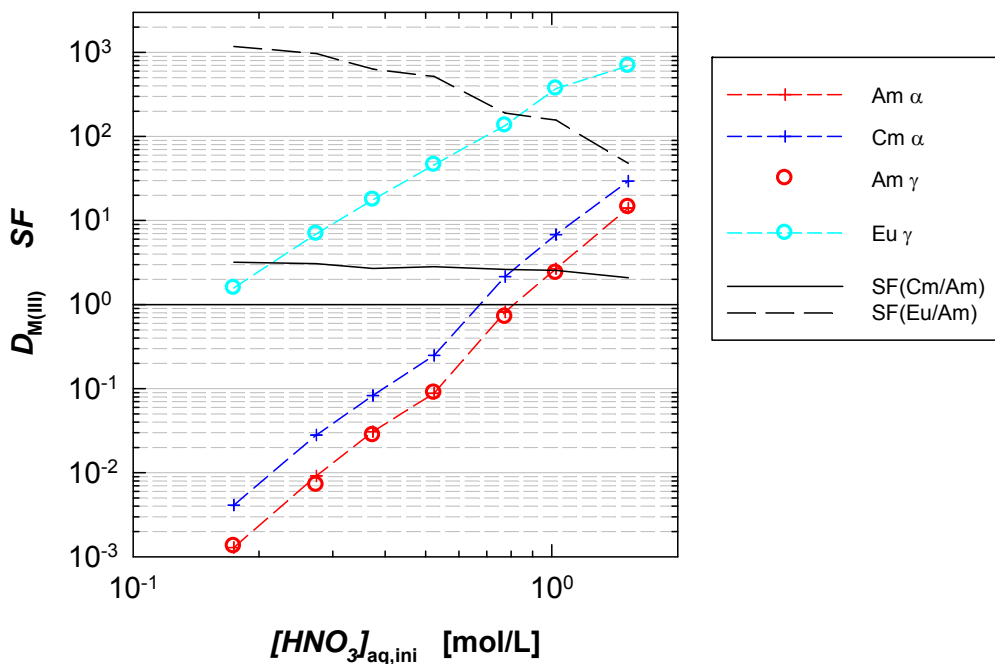

Figure 3. Extraction of Am(III), Cm(III), and Eu(III), influence of HNO$_3$ concentration. Organic phase, 0.2 mol/L TODGA + 5% vol. 1-octanol in TPH. Aqueous phase, ^{241}Am(III) + ^{244}Cm(III) + ^{152}Eu(III) (2 kBq/mL each) + Ln(III) (10 mg/L each) + 20 mmol/L SO$_3$-Ph-BTBP (batch #2) in HNO$_3$. A/O = 1, T = (293 ± 0.5) K.
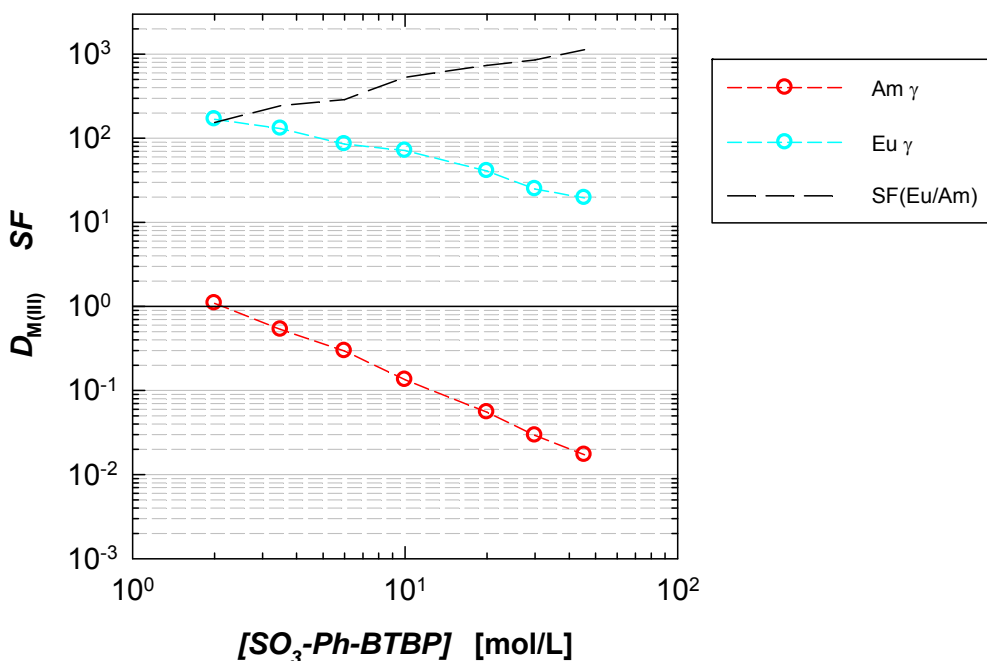
Figure 4. Extraction of Am(III) and Eu(III), influence of SO$_3$-Ph-BTBP concentration. Organic phase, 0.2 mol/L TODGA + 5% vol. 1-octanol in TPH. Aqueous phase, [241]Am(III) + [244]Cm(III) + [152]Eu(III) (2 kBq/mL each) + Ln(III) (10 mg/L each) + SO$_3$-Ph-BTBP (batch #2) in 0.5 mol/L HNO$_3$. A/O = 1, T = (293 ± 0.5) K.

Complexation of Cm(III) and Eu(III) with SO$_3$-Ph-BTBP — TRLFS study

The complexation of Cm(III) and Eu(III) with SO$_3$-Ph-BTBP in H$_2$O (pH = 3, adjusted with HClO$_4$) and in 0.5 mol/L HNO$_3$ was studied by TRLFS: Increasing concentrations of SO$_3$-Ph-BTBP were added to solutions of [248]Cm(ClO$_4$)$_3$ (initially $1 \cdot 10^{-7}$ mol/L) or Eu(ClO$_4$)$_3$ (initially $5 \cdot 10^{-7}$ mol/L), and the emission spectra were recorded 15 min after each addition. The species distribution as a function of SO$_3$-Ph-BTBP is determined, and stability constants are derived. For details, see.[21]

Complexation of Cm(III) and Eu(III) with SO$_3$-Ph-BTBP in H$_2$O (pH = 3)

The evolution of the Cm(III) emission spectra with increasing concentrations of SO$_3$-Ph-BTBP is shown in Figure 5. The Cm(III) aquo ion (emission band at 593.9 nm) is transformed into a new species 1 (emission band at 607.1 nm) and finally into a new species 2 (emission band at 619.0 nm). These are attributed to the Cm(III)-BTBP 1:1 and 1:2 complexes,[22] as confirmed by slope analysis (not shown). The respective Cm(III) species distribution is shown in Figure 6. The 1:2 complex is the dominating species for SO$_3$-Ph-BTBP concentrations > 10^{-5} mol/L.
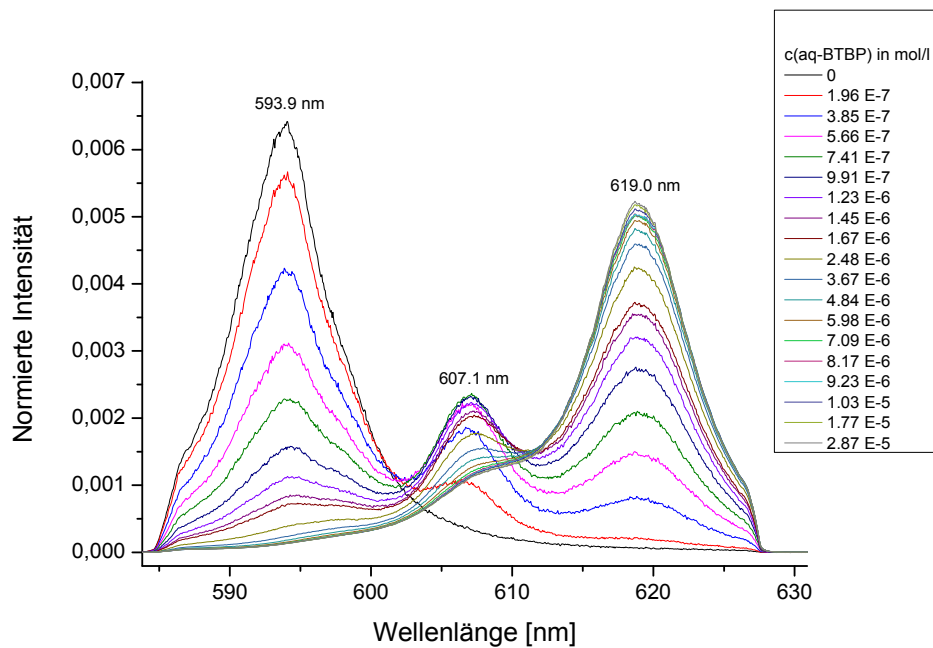
Figure 5. Normalised Cm(III) fluorescence spectra with increasing concentrations of SO_3-Ph-BTBP in H_2O (pH = 3), $[Cm(III)]_{ini}$ = $1 \cdot 10^{-7}$ mol/L, $[SO_3$-Ph-BTBP] = 0 – $2.9 \cdot 10^{-5}$ mol/L.
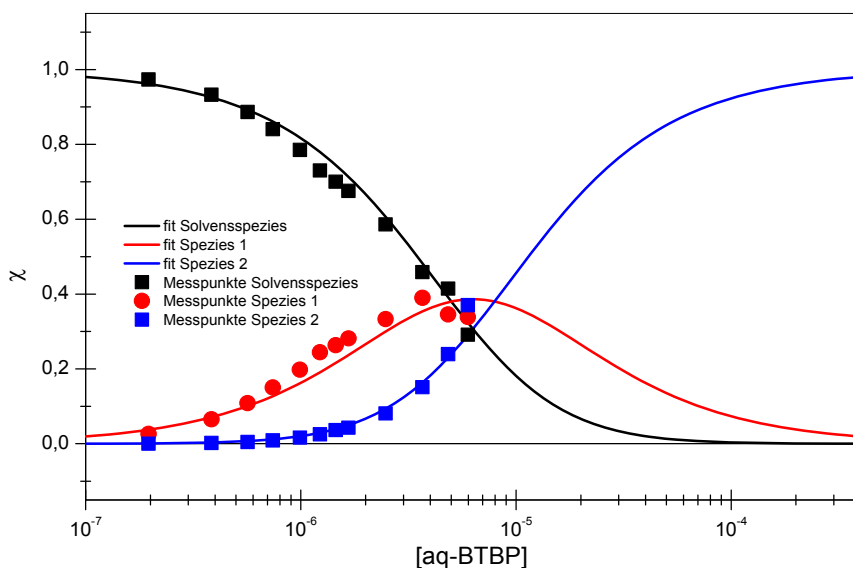

Figure 6. Species distribution of Cm(III) with SO_3-Ph-BTBP in H_2O
(pH = 3). Lines calculated with log β_{01} = 5.3 and log β_{02} = 10.4.

The species distribution from the respective experiment with Eu(III) is shown in Figure 7. The Eu(III) 1:2 complex is the dominating species for SO_3-Ph-BTBP concentrations > $3 \cdot 10^{-4}$ mol/L.

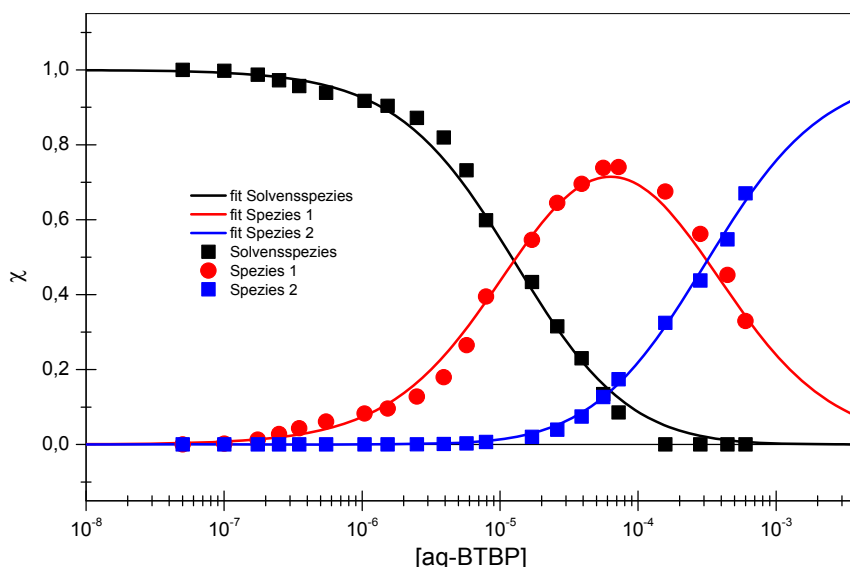Figure 7. Species distribution of Eu(III) with SO_3-Ph-BTBP in H_2O (pH = 3). Lines calculated with log β_{01} = 4.9 and log β_{02} = 8.4.

Conditional stability constants for the Cm(III) and Eu(III) 1:1 and 1:2 complexes in H_2O (pH = 3) are derived from the speciation data, see Table 1. The difference between the Cm(III) and Eu(III) log β_{02} values corresponds to a separation factor of 100. This is in good agreement with with e.g. CyMe$_4$-BTBP's selectivity for Cm(III) over Eu(III) determined in liquid-liquid extraction experiments.[20]

Table 1. SO_3-Ph-BTBP, conditional stability constants for the Cm(III) and Eu(III) 1:1 and 1:2 complexes in H_2O (pH = 3).

	Cm(III)	Eu(III)	Δ
log β_{01}	5.3	4.9	0.4
log β_{02}	10.4	8.4	2

Complexation of Cm(III) and Eu(III) with SO_3-Ph-BTBP in 0.5 mol/L HNO_3

The selective back-extraction of Am(III) in a SO_3-Ph-BTBP/TODGA Am-only extraction process would be performed at a HNO_3 concentration of 0.5–0.8 mol/L, depending on the SO_3-Ph-BTBP concentration (see above). Thus, the complexation of Cm(III) and Eu(III) with SO_3-Ph-BTBP was studied in 0.5 mol/L HNO_3.

Other than is the case in H_2O, direct formation of the Cm(III) or Eu(III) 1:2 complex species is observed in 0.5 mol/L HNO_3; formation of the 1:1 complex species is suppressed. The Cm(III) species distribution is shown in Figure 8, the Eu(III) species distribution in Figure 9. With Cm(III), the 1:2 complex is the dominating species for SO_3-Ph-BTBP concentrations > $2.5 \cdot 10^{-4}$ mol/L. The Eu(III) 1:2 complex is the dominating species for SO_3-Ph-BTBP concentrations > $2 \cdot 10^{-3}$ mol/L. The stability constants of the 1:2 Cm(III) and Eu(III) complexes are given in Table 2.

The conditional stability constant of the Cm(III) 1:2 complex is approx. two orders of magnitude higher than that of the Eu(III) 1:2 complex, as is the case in H_2O (pH = 3). However, the absolute log β_{02} values in 0.5 mol/L HNO_3 are approx. three orders of magnitude lower than the respective values in H_2O (pH 3). This is explained by (a) the competition between protons and metal ions for SO_3-Ph-BTBP and (b) the complexation of

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the metal ions by nitrate anions. Further experiments and calculations to quantify these effects are under way.
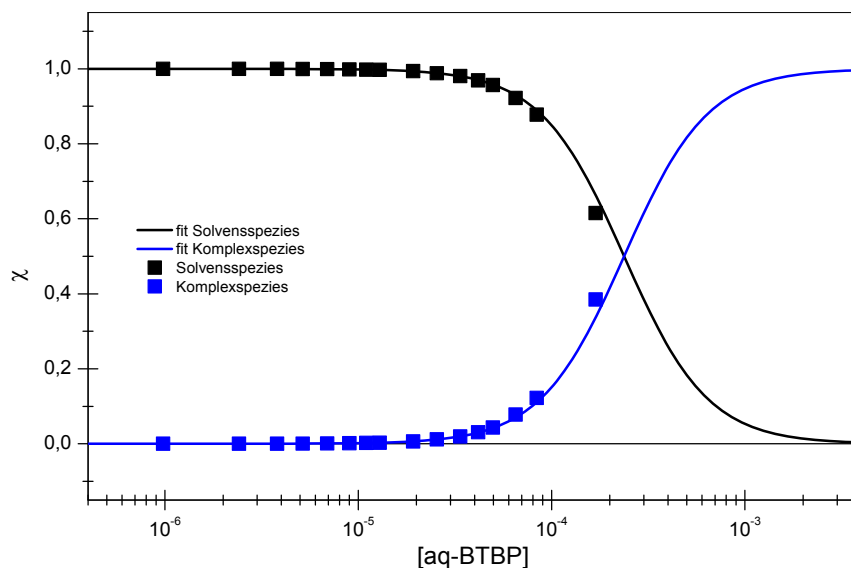

Figure 8. Species distribution of Cm(III) with SO_3-Ph-BTBP in 0.5 mol/L HNO_3. Lines calculated with $\log \beta_{02} = 7.25$.
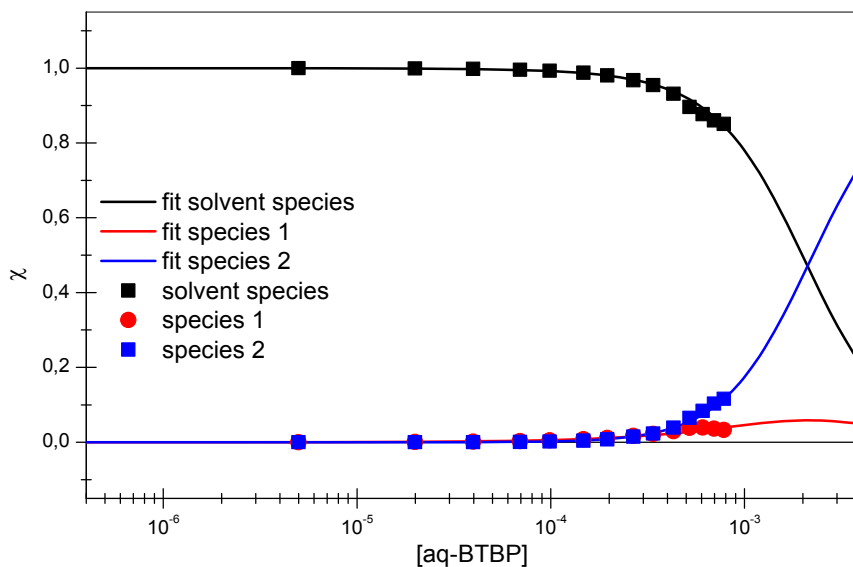

Figure 9. Species distribution of Eu(III) with SO_3-Ph-BTBP in 0.5 mol/L HNO_3. Lines calculated with $\log \beta_{01} = 1.77$ and $\log \beta_{02} = 5.35$.

Table 2. SO_3-Ph-BTBP, conditional stability constants for the Cm(III) and Eu(III) 1:2 complexes in 0.5 mol/L HNO_3.

	Cm(III)	Eu(III)	Δ
$\log \beta_{02}$	7.25	5.35	1.9

Biphasic vs. monophasic experiments

The monophasic complexation experiments clearly show that the final complexes formed with Cm(III) or Eu(III) and SO_3-Ph-BTBP are 1:2 complexes. This is in agreement with

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extraction and complexation studies performed with lipophilic BTBP extracting agents (see[23] and references therein).

The results from the biphasic extraction experiments seem to contradict; the slope for log $D_{Am(III)}$ vs. log *[SO$_3$-Ph-BTBP]* is −1.3, see Figure 4. A similar discrepancy was observed with SO$_3$-Ph-BTP[18] (slope for log $D_{Am(III)}$ vs. log *[SO$_3$-Ph-BTP]* being −1.9 with a slope of −3 expected based on the formation of 1:3 complexes[21]). So far we do not have a valid explanation for these findings. Further studies will address this issue.

Tentative AmSel flow sheet

A tentative AmSel flow sheet similar to the SO$_3$-Ph-BTP i-SANEX process flow sheet[3,6] is shown in Figure 10.

1) "Extraction/scrubbing" section: TODGA (with 1-octanol as modifier) in kerosene is used to co-extract Am(III), Cm(III) + Ln(III). Masking agents are added to the feed to prevent co-extraction of Zr, Mo and Pd.[24,25]
2) "Am(III) stripping" section: The loaded organic phase is contacted with SO$_3$-Ph-BTBP in HNO$_3$ of appropriate concentration to selectively strip Am(III); partially co-stripped Cm(III) + Ln(III) are re-extracted in the left part of the section.
3) "Cm(III) + Ln(III) stripping" section: Cm(III) + Ln(III) are stripped from the organic phase using e.g. a glycolate solution.

Due to the rather low Am(III)/Cm(III) selectivity (as compared to the An(III)/Ln(III) selectivity of the SO$_3$-Ph-BTP i-SANEX system), significantly more stages are expected to be required in the "Am(III) stripping" section.
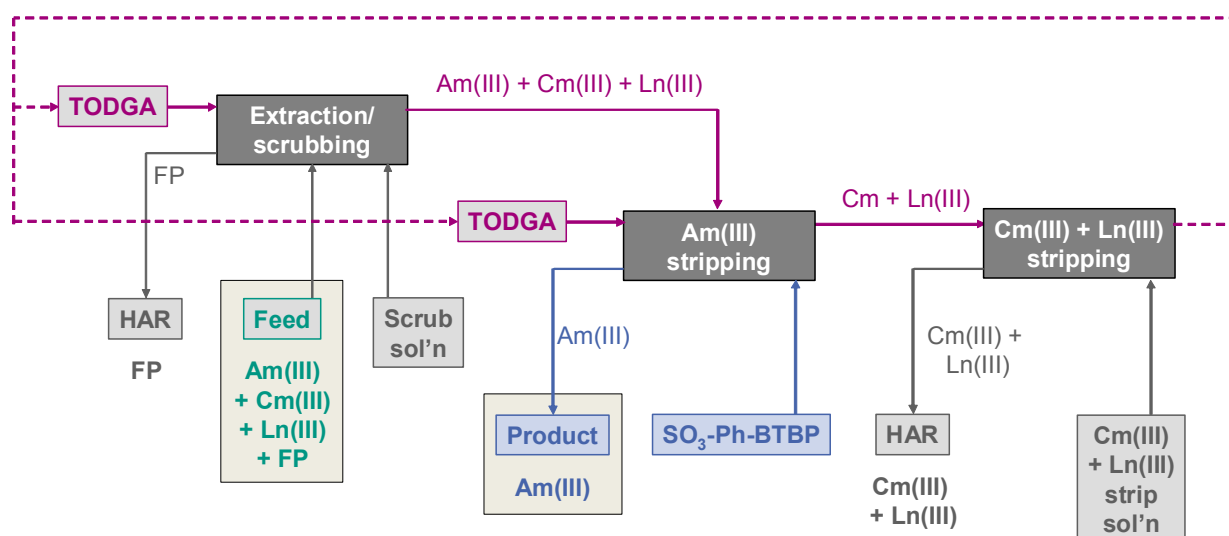

Figure 10. Tentative AmSel flow sheet.

Conclusions

A new solvent extraction system for separating only Am(III) from HAR is introduced, based on reverse selectivity in the organic and in the aqueous phase. TODGA is used to co-extract Am(III), Cm(III) and Ln(III); SO$_3$-Ph-BTBP is used to selectively strip Am(III). Although the Am(III)/Cm(III) selectivity is low *(SF$_{Cm(III)/Am(III)}$ ≈ 2.5)*, sufficient selectivity is expected in a multi-stage process. The fact that HNO$_3$ of suitable concentration is used to keep Cm(III) + Ln(III) in the organic phase during Am(III) stripping is advantageous; no auxiliary chemicals are required for this purpose. Work towards the demonstration of the AmSel process is being carried out in the SACSESS project.

Acknowledgement

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