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ABSTRACT

The separation of actinides(III) from used nuclear fuel is a key step for the recycling of used nuclear fuel in innovative fuel cycles. However, high neutron dose rates and heat load of short-lived curium isotopes complicate the production and handling of new nuclear fuel containing curium(III) and americium(III). Therefore, new processes have to be developed separating only americium(III) from PUREX (Plutonium-Uranium Recovery by Extraction) raffinate. This is achieved by coextracting An(III) and Ln(III) from PUREX raffinate using N,N,N',N'-tetraoctyl-diglycolamide (TODGA), followed by the subsequent selective stripping of Am(III) by a water-soluble bis-triazinyl-bipyridin (sodium 3,3',3'',3'''-([2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate, SO_3-Ph-BTBP). The selectivity for Am(III) over Cm(III) is $SF_{Cm(III)/Am(III)} \approx 2.5$, due to the inverse selectivity of TODGA and SO_3-Ph-BTBP. Additionally, a separation factor up to 1200 is achieved for the separation of Eu(III) from Am(III). The results demonstrate that the presented system works very well even at acidic conditions using nitric acid as the aqueous phase and does not require additional salting out agents.

Introduction

Future innovative nuclear fuel cycles are under development in many countries, aiming at the reduction of long-term radiotoxicity and heat load of nuclear waste by separating and transmuting the transuranium elements (TRU).[1-3] This leads to more compact geologic repositories and higher efficiency for the utilization of resources.[4] Therefore, many countries are developing pyrometallurgical or hydrometallurgical processes to achieve the separation of TRU from used nuclear fuel. An important benefit of hydrometallurgical separation processes is that they can easily be combined with an advanced PUREX process, in which uranium, plutonium, and neptunium are separated from used nuclear fuel.[5,6] This advanced PUREX process should be followed by the subsequent separation of americium and curium from the PUREX raffinate. This separation can be performed using the concept of DIAMEX (Diamide Extraction) and SANEX (Selective Actinide Extraction) and similar processes.[7-10] In recent years the 1c-SANEX[11] and the i-SANEX and ALSEP (Actinide-Lanthanide separation process) processes[12-18] have been developed, combining the DIAMEX and the SANEX in one compact process. i-SANEX and ALSEP are based on TALSPEAK (Trivalent Actinide Lanthanide Separation with Phosphorus-reagent Extraction from Aqueous Complexes) chemistry,[8,19,20] coextracting An(III) and Ln(III) and selectively stripping An(III) using water-soluble ligands. Furthermore, GANEX (Grouped Actinide Extraction) processes have been developed as alternative processes to co-separate all TRU.[21-26]
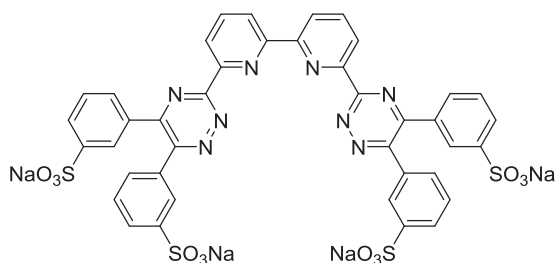
Figure 1. Structure of SO₃-Ph-BTBP.

However, short-lived curium isotopes strongly complicate the fabrication and handling of new nuclear fuel due to the high neutron dose rates and the heat load. As curium has no significant impact on the long term radiotoxicity and long-term heat load of nuclear waste, one possible solution to this problem is the separation of curium from the TRU and its disposal in the high active waste.[27] The most challenging separation in this concept is the separation of curium from americium as both are trivalent cations with similar ionic radii.[28] Different approaches for the separation have been developed and tested exploiting the oxidation of americium to higher oxidation states or the slight selectivity of some ligands and solvents.[29-34]

The americium-curium separation should be located as early in the separation process as possible in order to develop a compact separation process. Therefore, it would be beneficial to separate americium directly from the PUREX raffinate. Hence the Commissariat à l'énergie atomique et aux énergies alternatives developed and successfully tested the EXAm process.[35,36] However, there are drawbacks such as the limited pH range (pH = 2-3) and the requirement of additional ligands such as Di-(2-ethylhexyl)phosphoric acid (HEDHP) to prevent Ln(III) stripping at low ionic strength. Therefore, a more robust system would be favorable.

We present a new system for the separation of americium from curium based on the *i*-SANEX process,[12,13] called the AmSel (Americium Selective Extraction) process. Analogously to the *i*-SANEX process, the trivalent lanthanides and actinides are coextracted using TODGA. In the AmSel process this coextraction is followed by a selective stripping of Am(III) using a water-soluble BTBP (sodium 3,3',3'',3'''-([2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate, SO₃-Ph-BTBP) (Fig. 1).[37-39] The separation of Am(III) from Cm(III) and the trivalent lanthanides is performed utilizing the inverse selectivity of BTBP ligands (having a selectivity for Am(III) over Cm(III) of $SF_{Am(III)/Cm(III)} \approx 1.6$, i.e., preferring Am(III))[40] and TODGA (having a selectivity for Cm(III) over Am(III) of $SF_{Cm(III)/Am(III)} \approx 1.6$, i.e., preferring Cm(III)).[41]

Experimental

Extraction experiments

The aqueous phase consisted of ²⁴¹Am(III), ²⁴⁴Cm(III), ¹⁵²Eu(III) (1 kBq/mL each) and 6 mg/L of each Y(III) and La(III) – Lu(III) in either 20 mmol/L SO₃-Ph-BTBP in nitric acid (varied concentrations) or in 0.5 mol/L nitric acid with varied SO₃-Ph-BTBP concentrations. The organic phase consisted of 0.2 mol/L TODGA + 5 vol.% 1-octanol in Exxsol D80 (a kerosene diluent). Octan-1-ol was added to the organic phase to avoid third phase formation.[42]

The experiments were carried out by shaking a mixture of 500 μL aqueous and 500 μL organic phase on a vortex shaker (40 Hz) for 30 min and separating phases after centrifugation. ²⁴¹Am and ¹⁵²Eu activities were measured using a gamma counter. Alpha activities of ²⁴¹Am and ²⁴⁴Cm were determined by alpha spectroscopy. Organic samples for alpha spectroscopy were stripped into 0.5 mol/L ammonium glycolate (pH = 4) (A:O = 10), aqueous samples diluted by a factor of 10 using 0.5

mol/L ammonium glycolate (pH = 4) before measurement. Y(III), La(III), and Ce(III) – Lu(III) were determined by ICP-MS. For ICP-MS the ammonium glycolate solutions were diluted by a factor of 100 with 2% HNO_3 (suprapure).

To investigate stripping kinetics the organic phase was loaded with [241]Am(III) and [152]Eu(III) (1 kBq/mL each) by extraction from 3 mol/L nitric acid. 500 μL of this loaded organic phase was contacted with an aqueous phase consisting of 20 mmol/L SO_3-Ph-BTBP in 0.29 mol/L HNO_3. Due to a release of coextracted nitric acid, this procedure resulted in a nitric acid concentration of approximately 0.5 mol/L after stripping.[13] Two different shakers (40 Hz and 5 Hz) were used; contacting times were varied.

Chemicals

SO_3-Ph-BTBP was synthesized as described by Müllich et al.[38] Other chemicals (e.g., lanthanide nitrates) were purchased by Alfa Aesar or Sigma Aldrich and used as received. The Cm(III) stock solution used for "Time Resolved Laser Fluorescence Spectroscopy" (TRLFS) studies contained $3.34 \cdot 10^{-6}$ mol/L Cm(III) in 15.7 mmol/L $HClO_4$. For Eu(III) TRLFS studies a stock solution of 1.1 mmol/L $Eu(ClO_4)_3$ in 10 mmol/L $HClO_4$ was used. The radionuclides were taken from laboratory stock. All solutions were prepared with ultrapure water (Millipore, Billerica, USA; 18.2 MΩcm).

TRLFS setup

TRLFS studies were performed using a Nd:YAG laser-pumped (Continuum Surelite Laser) dye laser system (NARROWscan D-R Dye Laser) with a repetition rate of 10 Hz. A wavelength of 396.6 nm was used for the excitation of Cm(III), a wavelength of 394 nm was used for Eu(III). After spectral decomposition by a spectrograph (Shamrock 303i) with 1199 lines mm^{-1} grating the spectra were recorded by an ICCD camera (iStar Gen III, ANDOR) with an integrated delay controller. The fluorescence signal was detected after a delay time of 1 μs to discriminate short-lived fluorescence of organic compounds.

Preparation of TRLFS samples

The preparation of the TRLFS samples was performed analogously to those of the batch extraction experiments. The aqueous phase consisted of 20 mmol/L SO_3-Ph-BTBP and $1 \cdot 10^{-7}$ mol/L Cm(III) or $5 \cdot 10^{-6}$ mol/L Eu(III) in 0.5 mol/L HNO_3. The organic phase consisted of 0.2 mol/L TODGA + 5 vol.% 1-octanol in Exxsol D80. Aliquots (500 μL) of each phase were contacted for 30 min and separated after centrifugation. Subsequently, the aqueous and the organic phases were investigated separately by TRLFS.

Precipitation test

To investigate whether a precipitate forms at back extraction conditions, an organic phase consisting of 0.2 mol/l TODGA + 5 vol.% 1-octanol in Exxsol D80 was contacted with an aqueous phase containing 110 mg/L Y(III), 315 mg/L La(III), 610 mg/L Ce(III), 290 mg/L Pr(III), 1035 mg/L Nd(III), 210 mg/L Sm(III), 50 mg/L Eu(III), 40 mg/L Gd(III), and 10 mg/L of each Er(III) – Lu(III) in 0.5 mol/L HNO_3. The loaded organic phase was contacted with an aqueous phase containing 20 mmol/L SO_3-Ph-BTBP in 0.5 mol/L HNO_3. The M(III) concentrations used were similar to concentrations reported for PUREX raffinate.[43]

Results and discussion

Stripping kinetics

The stripping kinetics of the TODGA/SO$_3$-Ph-BTBP system was investigated by contacting an organic phase loaded with [241]Am(III) and [152]Eu(III) with an aqueous phase containing 20 mmol/L SO$_3$-Ph-BTBP. Two different shakers with 40 Hz and 5 Hz were used. When applying the fast shaker, equilibrium is reached after less than 7 min, which is when the first sample is taken.

Therefore, a slower device was applied to investigate whether stripping kinetics is observed at slower shaking rate. Even at the lower shaking rate, equilibrium is reached after 15 min (Fig. 2). The distribution ratio of Am(III) is close to equilibrium already after 2 min, proving that stripping of Am (III) by SO$_3$-Ph-BTBP is not affected by slow kinetics. In order to assure equilibrium was reached, the fast device (40 Hz) was applied in subsequent experiments.

Influence of nitric acid concentration

Extraction experiments investigating the influence of nitric acid concentration on the An(III) and Ln(III) distribution ratios were performed. Batch experiments were carried out containing Am(III), Cm(III), and Eu(III) in the aqueous phase at different nitric acid concentrations. The distribution ratios are shown in Fig. 3.

Generally, the distribution ratios of Am(III), Cm(III), and Eu(III) increase with increasing nitric acid concentration. This effect is caused by the increasing nitrate concentration, which results in an increased formation of the $[M(TODGA)_3](NO_3)_3$ complex, thus increasing extraction of An(III) or Ln(III) into the organic phase. The extraction of An(III) into the organic phase is strongly suppressed by SO$_3$-Ph-BTBP, resulting in large separation factors between Ln(III) and An(III) (at 0.5 mol/L HNO$_3$ $SF_{Eu(III)/Am(III)}$ = 600). This value is in good agreement with values reported in the literature.[37] In addition to the Ln(III)/An(III) separation factor, a separation factor of 2.4–3.6 is observed for the separation of Am(III) from Cm(III) (Fig. 3). This separation factor is the product of TODGA's slight preference for the extraction of Cm(III) over Am(III), $SF_{Cm(III)/Am(III)} \approx 1.6$,[13] and SO$_3$-Ph-BTBP's inverse selectivity, $SF_{Am(III)/Cm(III)} \approx 1.6$, as previously observed for lipophilic BTBPs.[40]

With increasing nitric acid concentration the separation factors decline. The decreasing selectivity of SO$_3$-Ph-BTBP can be explained by the protonation of coordinating nitrogen atoms. As a result,
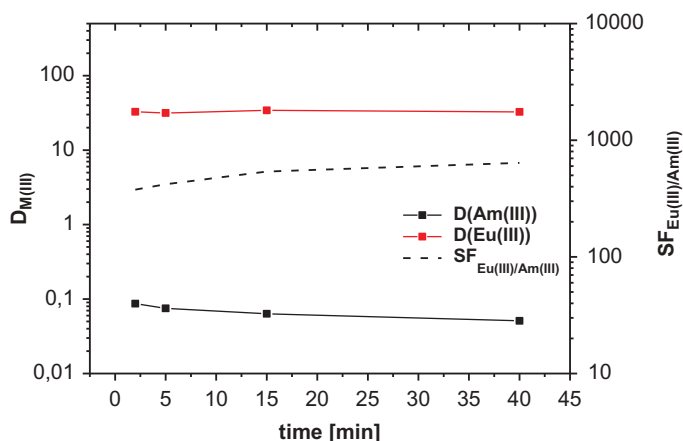

Figure 2. Am(III) and Eu(III) stripping kinetics with SO$_3$-Ph-BTBP applying a 5 Hz shaker. Organic phase consisting of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80, loaded with [241]Am(III), [152]Eu(III) and 0.21 mol/L HNO$_3$ by extracting from 3 mol/L HNO$_3$. Aqueous phase containing 20 mmol/L SO$_3$-Ph-BTBP in 0.29 mmol/L HNO$_3$. A/O = 1, T = 293 ± 1 K.
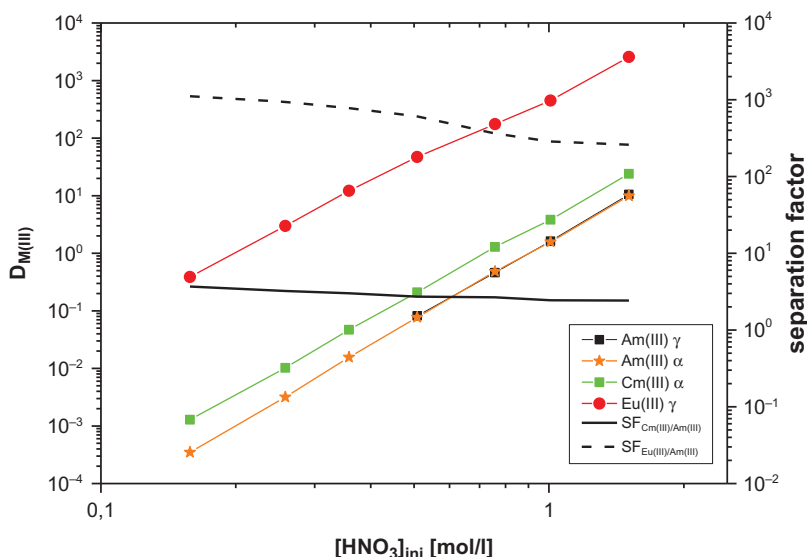
Figure 3. Extraction of Am(III), Cm(III), and Eu(III) into the organic phase with the aqueous phase containing 20 mmol/L SO$_3$-Ph-BTBP. Organic phase consisting of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80. Aqueous phase containing [241]Am(III), [244]Cm(III), and [152]Eu(III) (1 kBq/mL each) + Y(III), La(III), and Ln(III) (6 mg/L each) and 20 mmol/L SO$_3$-Ph-BTBP with various nitric acid concentrations. A/O = 1, T = 293 ± 1 K.

the free concentration of SO$_3$-Ph-BTBP is lower at high nitric concentrations, resulting in a drop of selectivity. This effect has also been described for hydrophilic BTP extracting agents.[13]

Influence of SO$_3$-Ph-BTBP concentration

The extraction of Am(III) and Cm(III) from 0.5 mol/L HNO$_3$ with various SO$_3$-Ph-BTBP concentrations into 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80 is shown in Fig. 4. Increasing concentration of SO$_3$-Ph-BTBP leads to a decrease of distribution ratios. The separation factor $SF_{Cm(III)/Am(III)}$ exhibits

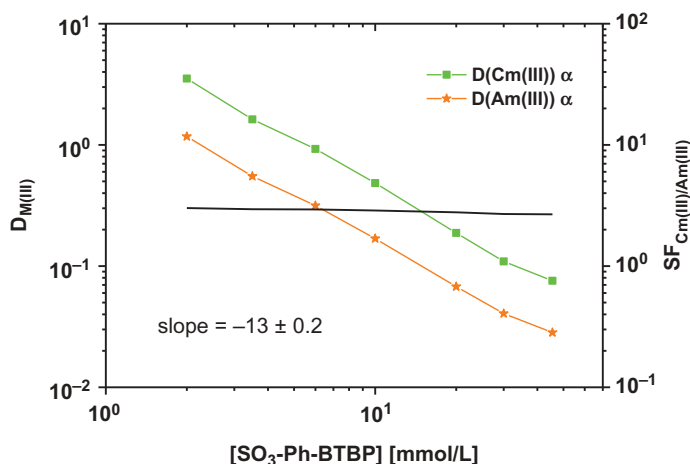**Figure 4.** Influence of the SO$_3$-Ph-BTBP concentration on the extraction of Am(III) and Cm(III) into the organic phase. Organic phase consisting of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80. Aqueous phase containing [241]Am(III) and [244]Cm(III) (1 kBq/mL each) and various SO$_3$-Ph-BTBP concentrations in 0.5 mol/L HNO$_3$. A/O = 1, T = 293 ± 1 K.

values in the range of 2.5–3 at the applied conditions. These separation factors are a product of the inverse selectivity of SO$_3$-Ph-BTBP (SF$_{Am(III)/Cm(III)}$ ≈ 1.6)[40] and TODGA (SF$_{Cm(III)/Am(III)}$ ≈ 1.6).[41]

Plotting logD$_{Am(III)}$ and logD$_{Cm(III)}$ vs log[SO$_3$-Ph-BTBP] yields a slope of -1.3 (R^2 = 0.9979). This value implies the formation of a 1:1 complex in the aqueous phase during the extraction process. However, this is unlikely as BTBP-ligands are known to form 1:2 complexes.[40,44-46] Therefore, Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is applied to the aqueous and the organic phases of the extraction experiments to investigate this issue.

TRLFS experiments

To clarify the composition of the complexes formed during the extraction process, batch extraction experiments were carried out containing Cm(III) or Eu(III) in concentrations suitable for TRLFS ([Cm] = 10^{-7} mol/L, Eu(III) = 5·10^{-6} mol/L). The aqueous and organic phases of these extraction experiments were investigated separately and the obtained fluorescence spectra are shown in Fig. 5 in comparison to the spectra of the 1:2 complexes for the SO$_3$-Ph-BTBP[39] and the 1:3 complexes for TODGA.[47]

The fluorescence spectra obtained from the aqueous phase match very well with the spectra of the 1:2 complexes [M(SO$_3$-Ph-BTBP)$_2$] (M = Cm(III)/Eu(III)). This proves that during the extraction process the same 1:2 M(III)-BTBP complexes are formed in the aqueous phase; the 1:1 M(III)-BTBP complex is not present at a significant concentration. Furthermore, the organic phase spectra display the exclusive formation of the [M(TODGA)$_3$](NO$_3$)$_3$ complexes. So far it is not understood why the slope analyses in the extraction experiments do not yield the expected values. However, this effect has already been observed for SO$_3$-Ph-BTP at the same conditions.[13]
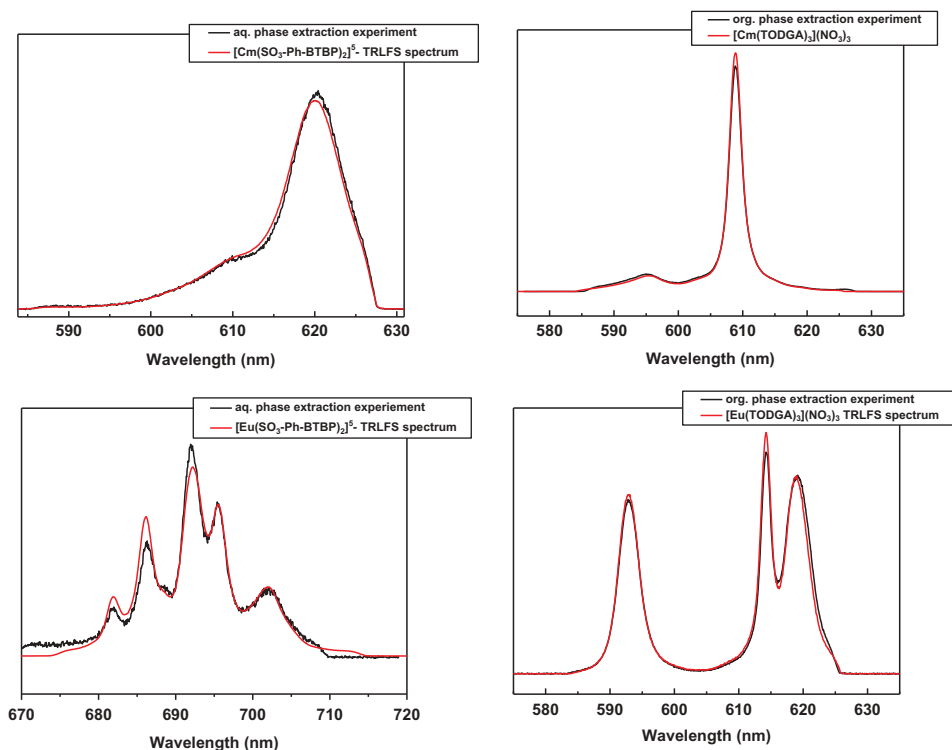

Figure 5. Cm(III) (top) and Eu(III) (bottom) (Eu(III) spectra: left $^5D_0 \rightarrow {}^7F_4$ transition, right $^5D_0 \rightarrow {}^7F_1$ and $^7F_2$ transition) emission spectra of the aqueous phase (left) and the organic phase (right) of the extraction experiments in comparison to the [M(SO$_3$-Ph-BTBP)$_2$] (aqueous phase) and [M(TODGA)$_3$](NO$_3$)$_3$ emission spectra (M = Cm(III), Eu(III)).

Ln(III) behavior

Extraction batch experiments containing all stable Ln(III), La(III), Y(III), Am(III), and Cm(III) were carried out to investigate the extraction properties of light and heavy lanthanides. The distribution ratios as a function of nitric acid concentration are shown in Fig. 6.

The light Ln(III) show a linear increase of the distribution ratios with increasing nitric acid concentration. At conditions suitable for separating Am(III) from Cm(III) and Ln(III) (approximately 0.5 mol/L HNO_3) all Ln(III) present in the PUREX raffinate (Y(III), La(III), Ce(III) – Dy(III))
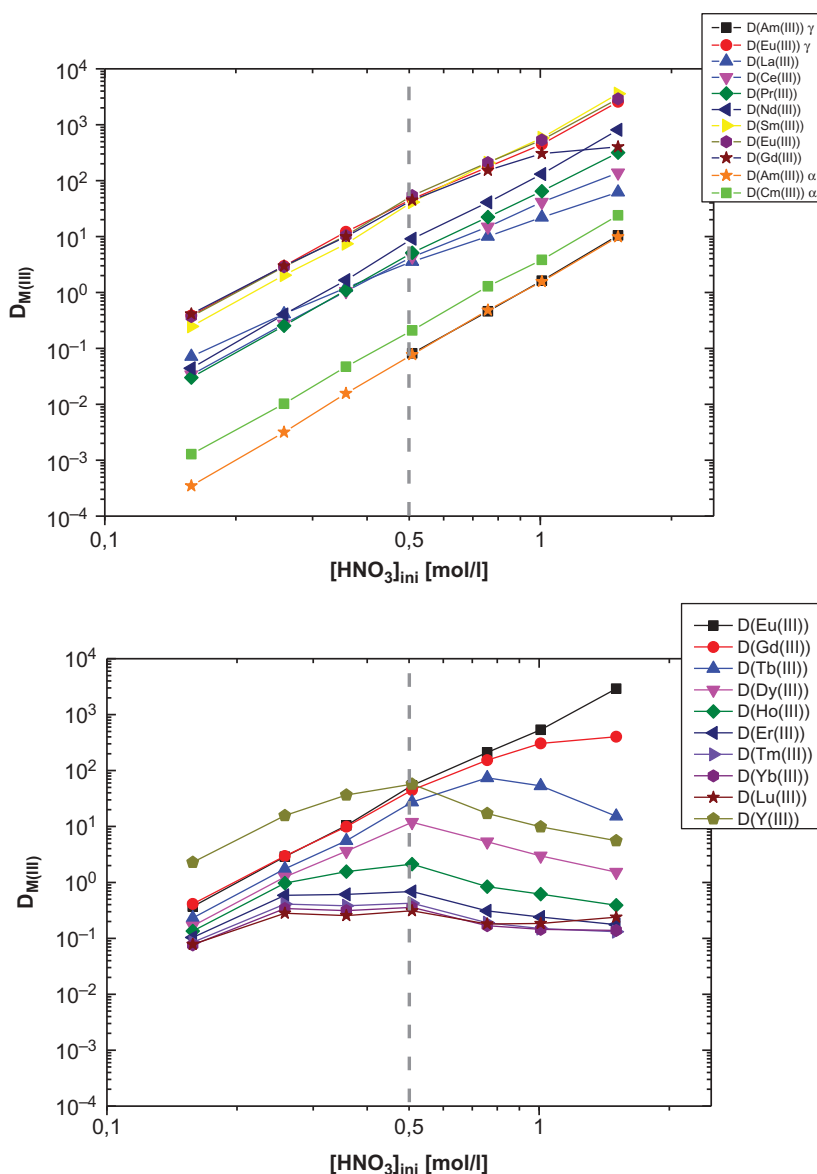
Figure 6. Distribution ratios of Am(III), Cm(III), La(III), and light Ln(III) (Ce - Gd) (top) and heavy Ln(III) (Eu – Lu) and Y(III) (bottom) as a function of nitric acid concentration. Organic phase consisting of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80. Aqueous phase containing [241]Am(III), [244]Cm(III), and [152]Eu(III) (1 kBq/mL each) + Y(III), La(III), and Ln(III) (6 mg/L each) and 20 mmol/L SO_3-Ph-BTBP with various nitric acid concentration. A/O = 1, T = 293 ± 1 K.

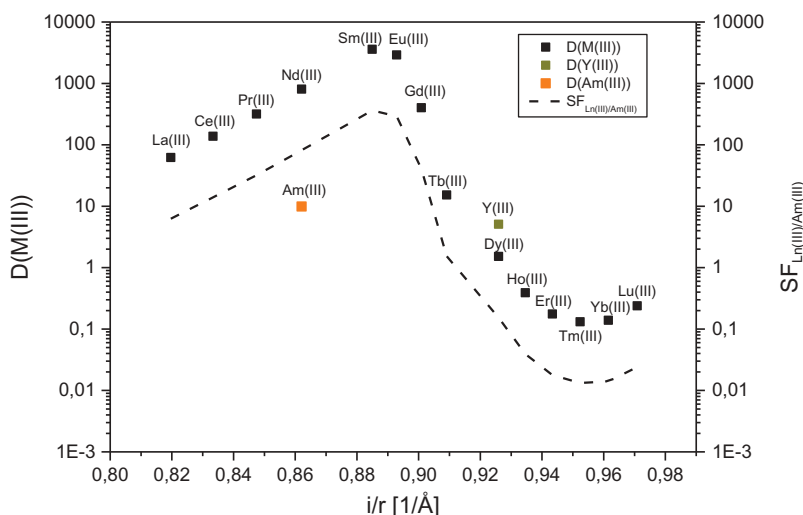**Figure 7.** Distribution ratios and separation factors $SF_{M(III)/Am(III)}$ of Y(III), La(III), and Ln(III) vs. the inverse ionic radii in 1.5 mol/L nitric acid. Organic phase consisting of 0.2 mol/L TODGA + 5% vol. 1-octanol in Exxsol D80. Aqueous phase containing [241]Am(III), [244]Cm(III), and [152]Eu(III) (1 kBq/mL each) + Y(III), La(III), and Ln(III) (6 mg/L each) and 20 mmol/L SO$_3$-Ph-BTBP in 1.5 mol/L HNO$_3$.

show distribution ratios above 1. Therefore, they will not be stripped from a loaded organic phase at process conditions.

However, some heavy lanthanides and Y(III) do not show a linear trend at increasing nitric acid concentration. After an initial linear increase the distribution ratios of the heavy lanthanides (Tb(III)–Lu(III)) drop with increasing nitric acid concentration. Tm(III), Yb(III), and Lu(III) do not show a linear increase of the distribution ratios at all. At 1.5 mol/L nitric acid concentration the distribution ratios of Ho(III) - Lu(III) are below 1.

This effect has not been observed for SO$_3$-Ph-BTP.[13] The reason for the decrease of selectivity between the heavy Ln(III) and Am(III) is not yet understood. One possible reason for this unexpected result is the formation of complexes with a composition different from [Ln(SO$_3$-Ph-BTBP)$_2$] in the aqueous phase. Further spectroscopic investigations on this topic are on their way to elucidate this issue.

Ln(III) precipitation

First extraction experiments contained approximately 400 mg/L of M(III) (24 mg/L of each Ln(III), Y(III), and La(III)) in the aqueous phase. Upon addition of SO$_3$-Ph-BTBP to a solution containing the M(III) dissolved in 0.17 mol/L–0.38 mol/L nitric acid a precipitate formed. The precipitate did not dissolve after 7 days. Since the precipitate formed without addition of the organic phase or [241]Am(III)/[244]Cm(III) tracer, the Ln(III) complexes of SO$_3$-Ph-BTBP show low solubility at the applied conditions. To investigate whether this low solubility of Ln(III) complexes might impede a process, the stripping of a loaded organic phase containing Y(III), La(III), and Ln(III) concentrations similar to those of a PUREX raffinate[43] ([Ln]$_{tot}$ = 2.72 g/L, composition see experimental section) was investigated at process conditions. Here no precipitation was observed, even after contacting the phases for 30 days. This is due to the low Ln(III) concentrations in the aqueous phase which are a result of the high distribution ratios of the lanthanides contained in PUREX raffinate in the SO$_3$-Ph-BTBP/TODGA system (Fig. 6). Hence, precipitation is not expected to impede the AmSel Process.

Conclusions

SO$_3$-Ph-BTBP was tested as a hydrophilic stripping agent for the selective stripping of Am(III) from a TODGA organic phase containing Am(III), Cm(III), and Ln(III). The inverse selectivties of SO$_3$-Ph-BTBP and TODGA multiply resulting in a separation factor $SF_{Cm(III)/Am(III)} \approx 2.5$. The separation factors between Am(III) and each Ln(III) present in the PUREX raffinate are higher than $SF_{Cm(III)/Am(III)}$. Therefore, the AmSel process will not be limited by An(III)/Ln(III) selectivity. As SO$_3$-Ph-BTBP in nitric acid is used as an aqueous phase, no additional ligands, buffers or salting out agents are required. These properties make the AmSel process a promising alternative to the separation system used in the EXAm process for Am(III)-only separation.

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