Selective extraction of americium from curium and the lanthanides by the lipophilic ligand $CyMe_4BTPhen$ dissolved in Aliquat-336 nitrate ionic liquid

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Abstract

The feasibility of separating americium from curium and the lanthanides was studied in batch solvent extraction experiments using an organic solvent composed of 0.01 mol L^{-1} 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline ($CyMe_4BTPhen$) in the ionic liquid Aliquat-336 nitrate [A336][NO_3] from feed solutions containing *N*,*N*,*N'*,*N'*-tetraethyl diglycolamide (TEDGA), stable lanthanide ions and tracers of ^{241}Am, ^{244}Cm and ^{152}Eu. The combined use of a lipophilic and a hydrophilic ligand with opposite selectivity for Am(III) vs. Cm(III) and Ln(III) allowed the separation of Am(III) from Cm(III) and Ln(III) from moderate acidic feed solutions (1 mol L^{-1} HNO_3, $SF_{Am/Cm}$ = 3.1 - 3.9, $SF_{Am/La} > 75$, $SF_{Am/Eu} \geq 3000$).

Keywords: Ionic liquids; americium/curium separation; solvent extraction; $CyMe_4BTPhen$; TEDGA; Aliquat-336

1. Introduction

Advanced nuclear fuel cycles aim at the recovery of minor actinides (americium, curium and neptunium) from process effluents, such as highly active raffinates (HARs) originating from Plutonium-Uranium Redox Extraction (PUREX) operations.[1, 2] The separation of neptunium is feasible with a modification of the PUREX flow sheet, while americium and curium are currently routed together with the more abundant lanthanides (Ln) and other fission products into the PUREX raffinate.[3] In a fully closed nuclear fuel cycle with multiple plutonium recycling, americium would be the main contributor for the long-term heat load of the final waste form. Therefore, the separation of americium alone from the HAR and re-use in fast neutron reactors would be beneficial for a more sustainable management of the rather scarce underground high level nuclear waste repository.[4, 5] The separated americium inventory could in principle be very efficiently reduced as innovative new fuel in dedicated minor actinide burners such as Accelerator-Driven Systems.[6-8] The incentive for separate management of curium from americium relates to the high neutron emission of the curium isotopes that would render transmutation target fabrication of both Am and Cm combined in a single fuel type very difficult. Both combined separation of Am and Cm from the HAR and separate Am and Cm management strategies are studied today. [9]

Formerly elaborated methods for the Am/Cm separation can be grouped into three major categories: (1) selective oxidation of Am(III) to the tetra- or hexavalent state[10-12]; (2) separation of Am(III) and Cm(III) with the use of two ligands with opposite solubility and selectivity with respect to Am(III) and Cm(III) and (3) methods based on the size-selective separation of these two ions from each other. Category (2) and (3) are described in more detail below.

A few years ago, the so-called EXAm process was developed by the Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA) and demonstrated on genuine spent-fuel

derived highly active raffinate and on highly active concentrate (concentration factor of 3.5) in mixer-settler batteries placed in the shielded hot cell-line of the ATALANTE facility in Marcoule, France.[13-15] The process is based on the combination of lipophilic extractants: 0.45 mol L^{-1} di-2-ethylhexylphosphoric acid (HDEHP) and 0.6 mol L^{-1} *N,N'*-dimethyl-*N,N'*-dioctyl-2-hexylethoxy-malonamide (DMDOHEMA) in hydrogenated tetrapropene (TPH) and the hydrophilic complexant *N,N,N',N'*-tetraethyl diglycolamide (TEDGA, Fig. 1), with an opposite selectivity towards Am(III) vs. Cm(III) and Ln(III). The EXAm process required a careful control of pH and since the achieved Am/Cm separation factor was low ($SF_{Am/Cm}$ = 2.5), a large number of stages (68 in total for the entire flow sheet) was necessary. Speciation studies revealed that the hydrophilic ligand TEDGA in its metal-complexed form was partially extracted into the organic phase.[14]

Lange *et al*. recently reported on the selective Am(III) extraction from simulated, tracer-spiked PUREX raffinate solution *via* the joint application of the hydrophilic complexing agent TEDGA and the lipophilic extractant 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline ($CyMe_4BTPhen$, Fig. 1) in 1-octanol.[16] In these tracer-spiked batch experiments, an Am/Cm separation factor up to 4.9 was observed. Co-extraction of Cu, Ni, Mo and Cd were causing an interference with the selective Am(III) extraction process, while a good separation from the Ln(III) was obtained. This ligand combination is the only method to date which complies with the so called CHON principle (i.e that the compounds used are composed exclusively of carbon, hydrogen, oxygen and nitrogen, and are thus completely incinerable) and allows a feasible Am/Cm separation.

Wagner *et al*. chose a different combination of ligands with opposite solubility and opposite selectivity towards americium and curium for the Americium Selective extraction from a PUREX raffinate (AmSel process).[17] In that study, trivalent actinides and lanthanides were co-extracted using the lipophilic *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and Am(III)

was selectively stripped using the water-soluble sodium 3,3’,3’’,3’’’-([2,2’-bipyridine]-6,6’-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate (SO_3-Ph-BTBP). Tracer-level extractions showed a Cm/Am separation factor of 2.5 in nitric acid media. Kaufholz *et al*. studied the feasibility of a selective Am(III) stripping with 3,3′,3″,3‴-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonic acid (TS-BTPhen), from the loaded innovative SANEX solvent containing 0.2 mol L^{-1} TODGA or a Me-TODGA solvent.[18, 19] This novel sulfonated ligand allowed to obtain Cm/Am separation factors of 3.3 – 3.5 at relatively high nitric acid concentrations (0.1 – 1 mol L^{-1}) with fast kinetics, but the organic synthesis of the ligand seems less reproducible than the lipophilic version of the BTPhen molecule.[18, 20, 21] As an alternative for the hydrophilic complexant TS-BTPhen, *N,N′,N″,N‴*-tetrakis[(6- carboxypyridin-2-yl)methyl]ethylenediamine (H_4TPAEN)[22-24] in combination with TODGA offered highly similar Am/Cm separation factors (3.5 – 4.0), but with lower separation factors towards the light lanthanides. TODGA in combination with 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl)]pyridine (PyTri-diol)[25] allowed a separation factor of Cm/Am of only 1.4.

Modolo *et al.* proposed the “Lanthaniden Und Curium Americium Trennung” (LUCA) process for the continuous counter-current separation of trivalent americium from a simulated feed solution that is representative of an aqueous product obtained after an An(III)/Ln(III) separation step.[26, 27] The LUCA process is based on the synergistic application of bis(4-chlorophenyl)-dithiophosphinic acid [$(ClPh)_2PSSH$] and tris(2-ethylhexyl) phosphate (TEHP) in an (20/80) isooctane / *tert*-butyl benzene diluent mixture and was demonstrated in a spiked centrifugal contactor test to get Am/Cm separation factors between 6 and 10, under moderately acidic conditions without the use of any oxidizing reagent.

The slight difference between the ionic radii of trivalent americium and curium was exploited by Jensen *et al*, who used a solvent composed of 0.05 mol L^{-1} HDEHP in o-xylene and a

hydrophilic size-selective diaza-crown ether: 0.001 mol L^{-1} *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6 (H_2bp18c6) in 1 mol L^{-1} $NaNO_3$ and 0.05 mol L^{-1} lactate buffer at pH =3.[28] The separation reached $SF_{Cm/Am}$ = 6.5.

The tridentate lipophilic ethylhexyl diamide amine (ADAAM(EH)) extractant containing a soft *N*-donor atom and two hard *O*-donor atoms was developed recently at JAEA and tested in spiked acidic feed solutions. The extractant showed high solubility in *n*-dodecane, fast kinetics and moderate separation factors between Am(III) and Eu(III) ($SF_{Am/Eu}$ = 25).[29] The combined use of ADAAM(EH) and TEDGA showed an interesting separation of Am(III) from Cm(III). From an aqueous phase of containing 0.001 mol L^{-1} TEDGA in 1.5 mol L^{-1} HNO_3 spiked with Am(III) and Cm(III), with 0.75 mol L^{-1} ADAAM(EH) in *n*-dodecane $SF_{Am/Cm}$ = 5.7 was achieved ($D_{Am} > 1$, $D_{Cm} < 1$).[30] The feasibility of the Am(III)/Cm(III) separation was demonstrated on a counter-current mixer settler test, which allowed the recovery of 99.8 % Am(III) with only 9.6 % of Cm(III) impurity in the product.[31] The solvent composed of 0.25 mol L^{-1} ADAAM(EH) and the feed contained 1.5 mol L^{-1} HNO_3 spiked with Am(III) and Cm(III) without the use of the aqueous complexant, TEDGA.

In the present study, the feasibility of Am(III)/Cm(III) separation and Am(III)/Ln(III) separation by the joint application of the hydrophilic complexing agent TEDGA and the lipophilic extractant $CyMe_4$BTPhen dissolved in the room-temperature ionic liquid [A336][NO_3] (Fig. 1) is reported. The ionic liquid [A336][NO_3] was recently tested in combination with the hard-donor extractant TODGA for the An(III) + Ln(III) co-extraction from a simulated HAR solution and was found to be an interesting alternative to molecular diluents like *n*-dodecane.[32] Ionic liquids have a low vapor pressure and high conductivity which ensures quasi non-flammability and resistance against static charge build-up. Besides, in a recent study, the trioctylmethylammonium nitrate ([N_{1888}][NO_3]) based solvent proved to show higher radiation stability than the *n*-dodecane based solvent.[33] The high polarity of the

ionic liquids also provide good solubility for $CyMe_4BTPhen$ extractant molecule and for the extracted metal complexes, while his molecule has low solubility in the more common aliphatic diluents. Our recent radiation stability study confirmed that the radiation induced degradation of TODGA is slower in $[N_{1888}][NO_3]$ than in *n*-dodecane (results will be published elsewhere).

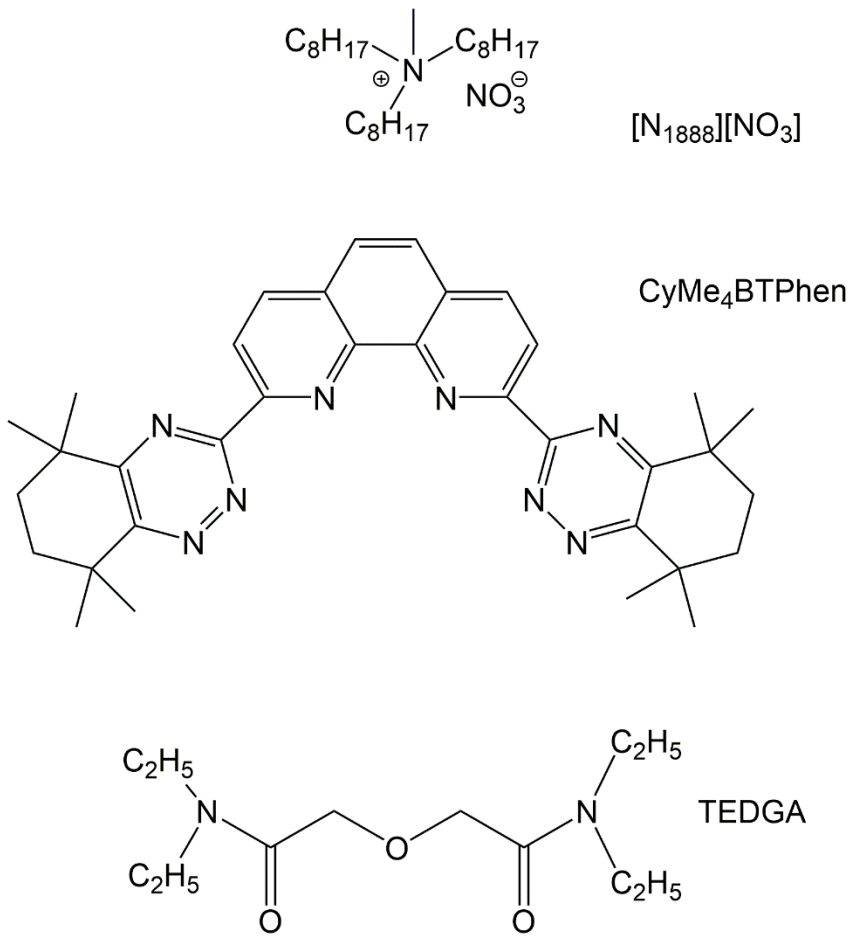


Figure 1. Chemical structures and acronyms of the organic compounds used in this study ($[A336][NO_3]$ is represented by its main component, tri-*n*-octylmethylammonium nitrate).

2. Experimental

2.1 Chemicals

Aliquat® 336 chloride ([A336][Cl], quaternary amine content: 88.2 – 90.6%) and NH_4NO_3 (purity > 99.0 %) were obtained from Sigma–Aldrich (Steinheim, Germany). 2,9-Bis(5,5,8,8-

tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline ($CyMe_4BTPhen$, purity > 98%) and *N,N,N',N'*-tetraethyl-diglycolamide (TEDGA, purity > 98%) were purchased from Technocomm Limited (Edinburgh, UK). MilliQ water was used for all dilutions (conductivity: minimum 18 MΩ cm). Potassium nitrate (purity > 97.0%), NaOH (purity: 99.0 %) were obtained from Merck KGaA (Darmstadt, Germany). $La(NO_3)_3{\cdot}6H_2O$ (purity: 99.0%) was obtained from Fluka Chemie (Buchs, Switzerland); $Ce(NO_3)_3{\cdot}6H_2O$ (purity: 99.8%), $Pr(NO_3)_3{\cdot}6H_2O$ (purity: 99.9%), $Nd(NO_3)_3{\cdot}6H_2O$ (purity: 99.9%), and $Sm(NO_3)_3{\cdot}6H_2O$ (purity: 99.9%) were obtained from Strem Chemicals (Kehl, Germany). $Eu(NO_3)_3{\cdot}6H_2O$ (purity: 99.99%) and $Gd(NO_3)_3{\cdot}6H_2O$ (purity: 99.9 %) were obtained from Alfa Aesar (Karlsruhe, Germany). $AgNO_3$ (purity: 99.9%) was obtained from Acros Organics (Geel, Belgium). ^{241}Am tracer (radiochemical purity > 99%) in 1 mol L^{-1} HNO_3 solution was available from legacy stocks of SCK•CEN. ^{244}Cm (radiochemical purity > 99.902%) and ^{152}Eu (radiochemical purity > 99%) radiotracers in 1 mol L^{-1} HNO_3 solutions were obtained from Eckert and Ziegler Nuclitec GmbH (Braunschweig, Germany). C-1S cupped stainless steel alpha planchets were obtained from GA-MA and Associates, Inc. (Florida, USA).

The [A336][Cl] ionic liquid was converted into its nitrate form [A336][NO_3] by a metathesis reaction by stirring 120 mL of [A336][Cl] with 120 mL of an aqueous solution of 2.5 mol L^{-1} KNO_3 for 4 hours, followed by phase separation in a 1 L separation funnel. The equilibration and separation steps were repeated seven times until no AgCl precipitation was observed upon addition of a few drops of a $AgNO_3$ solution to the aqueous phase. After the metathesis reaction, the organic phase was washed three times with an equal volume of MilliQ water. The density of [A336][NO_3] was determined with a density meter (Anton Paar DMA 4500 M).

2.2 Batch solvent extraction and analytical procedures

Batch extraction studies were performed using 4 mL glass vials that fit into the boreholes of an in-house fabricated metal block used as an adapter for a TMS-200 Thermoshaker (Nemus Life, Sweden). The temperature was controlled by the use of a cooling loop connected to a MC250 Microcool chiller (Lauda-Brinkmann, Germany). Spiked feed solutions were prepared in a way, that 1 mL of the initial aqueous feed solution contained 3 kBq of each of the tracers ^{241}Am, ^{152}Eu and ^{244}Cm. All tracer-spiked aqueous feed solutions were prepared in advance and mixed thoroughly before adding to the known amount of organic phase.

A stock solution for the lanthanide-nitrate containing aqueous phase was prepared by dissolving the calculated amounts of trivalent nitrate salts of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Yb and Y in 0.1 mol L^{-1} HNO_3 to obtain a 10^{-3} mol L^{-1} initial concentration of each Ln. From this mother solution 1 mL was taken for dilution to 100 mL in the desired final nitric acid concentration to obtain a final lanthanide concentration of 10^{-5} mol L^{-1} each. The exact nitric acid concentration of the stock solutions was determined by titration using an autotitrator (716 MPT Titrino, Metrohm, Switzerland). The total nitrate concentration was adjusted using NH_4NO_3.

In a typical extraction experiment, 1 mL of the aqueous phase was mixed with an equal volume of pre-equilibrated organic phase and shaken at 22 °C at 2060 rpm in a 4 mL vial. The organic phase was pre-equilibrated with an acid solution of the same acid concentration as used for the feed solution of the extraction step, in order to minimize volume changes of the organic phase during extraction. The added aliquots of the organic phase were weighed on an analytical balance. After the equilibration, the phase disengagement was enhanced by centrifugation of the vials for 5 min at 4000 rpm using a ThermoFischer Scientific centrifuge (for the inactive experiments) or a Heraeus Labofuge 200 centrifuge (for the tracer-spiked experiments). After phase separation, 300 µL aliquots of the aqueous and organic phases were collected for analysis.

Gamma spectrometric analysis of ^{241}Am (using the 59.5 keV γ-peak) and ^{152}Eu (using the 121.8 keV, 344 keV, 778.9 keV, 964 keV, 1112 keV and 1408 keV γ-peaks) was performed using a HPGe detector (Canberra Semiconductors N. V., Olen, Belgium) with Genie2000 software. The α-particle emitting radionuclide activities were determined for each separated phase using α spectroscopy. Weighed masses of the organic or aqueous phases were pipetted on a cupped steel planchet, heated under an infrared lamp (Theratherm 150 W, Osram, Germany) and subsequently burned in using a gas torch. The ^{241}Am (E_α = 5.485 MeV) and ^{244}Cm (E_α = 5.805 MeV) α peaks were measured using an α spectrometer (Alpha Analyst, Canberra) equipped with Passivated Implanted Planar Silicon (PIPS) alpha detectors (Canberra Olen N.V., Olen, Belgium). The spectra were analyzed using Apex Alpha software.

The concentration of stable elements was determined by ICP-MS method using a X2Series II ICP-MS instrument (ThermoFischer Scientific, Bremen, Germany). The distribution ratios of the lanthanides were determined from the initial and the equilibrated aqueous phase concentrations, by preparing a 1:100 dilution of the separated aqueous phase (e.g. diluting 100 μL of the sample to 10 mL carrier solution).

All ICP-MS samples, calibration standards, and quality control standards were made using a carrier solution prepared from 20 mL 67 – 69 wt.% HNO_3 diluted to 1 L. Calibration of the instrument was performed using a multi-element calibration standard (M1 Cläritas, SpexCertiprep Ltd., UK) covering the expected concentration range in the final dilutions (0 – 20 μg L^{-1}). As internal standards, In and Tl (Spex Certiprep Ltd, UK) were used. Nd (CPI International, California, USA) was used as the analyte for the quality control standard at a 10 μg L^{-1} concentration.

The *distribution ratio* (*D*) of a given analyte was calculated as the ratio of the concentration or radioactivity of the analyte present in the organic phase over the concentration or radioactivity

present in the aqueous phase. In the case of α- or γ-spectroscopic methods equation (1) was used, while in the case of ICP-MS measurements, the distribution ratio of the stable elements was determined on the basis of the initial and final aqueous concentrations as given in equation (2). The method of distribution ratio calculation according to Equation 2 was previously validated against the method based on Equation 1 using ICP-MS measurements for stable Eu(III) and γ-measurement for ^{152}Eu tracer.[32] The distribution ratio of stable lanthanide ions could be determined by the ICP-MS method with +/- 10 % combined uncertainty at 2 σ confidence level.

$$D_M = \frac{[M^{3+}]_{org.\ eq.}}{[M^{3+}]_{aq.\ eq.}}$$

(1)

$$D_M = \frac{[M^{3+}]_{aq.\ ini.} - [M^{3+}]_{aq.\ eq.}}{[M^{3+}]_{aq.\ eq.}} \qquad (2)$$

The highest and lowest distribution ratio limits for ^{241}Am and ^{244}Cm determined by the detection limits in the aqueous or organic phases were 1000 and 0.001, respectively, with α spectrometry. Gamma spectrometry allowed the determination of distribution ratios for ^{241}Am and ^{152}Eu between 200 and 0.005.

The *separation factor* (*SF*) of two elements in two phases was calculated from the distribution ratios of the respective elements in accordance with equation (3):

$$SF = \frac{D_{Mx}}{D_{My}} \qquad (3)$$

The acidity of the aqueous phases was determined by either titration using an autotitrator (716 MPT Titrino, Metrohm Switzerland) filled with 0.1 mol L^{-1} or 0.01 mol L^{-1} NaOH stock

solution (Titrisol, Merck) or by measurement with a pH meter (691 pH meter, Metrohm, Switzerland). The NaOH concentration was verified by titration using oxalic acid stock solution prepared from anhydrous oxalic acid. The total number of protons determined via titration was used as a parameter in the x-axis for acid dependency studies.

The nitric acid concentration in the loaded organic phase was determined by directly titrating a weighed aliquot of the organic phase loaded previously with a chosen aqueous solution of nitric acid. To the ionic liquid, approximately 60 mL of MilliQ water was added and the mixture was stirred for 15 min prior to the start of the titration. From kinetic experiments it is known that 15 min is needed for reaching equilibrium in the acid extraction (or back-extraction of the acid in the present case).

3. Results and discussion

The combined use of $CyMe_4BTPhen$ in [A336][NO_3] and TEDGA is studied for the separation of Am(III) from Cm(III) and Ln(III) as a function of contact time, aqueous phase composition (complexing agent and nitric acid concentrations), as well as temperature.

Extraction and back-extraction kinetics

Batch liquid-liquid extraction experiments were performed with an organic solvent composed of 0.01 mol L^{-1} $CyMe_4BTPhen$ in the ionic liquid [A336][NO_3] from a feed solution freshly prepared with 0.01 mol L^{-1} TEDGA. Solutions were prepared freshly before the start of each experiment, as TEDGA has shown to undergo hydrolytic degradation in nitric acid.[34] Figure 2-5 displays the distribution ratios of Am(III), Cm(III) and Eu(III) as a function of mixing time for different situations: (Figure 2) extraction with $CyMe_4BTPhen$ in [A336][NO_3] (without TEDGA), (Figure 3) [A336][NO_3] only in the presence of TEDGA (without $CyMe_4BTPhen$), (Figure 4) using equimolar concentrations of $CyMe_4BTPhen$ and TEDGA, and (Figure 5) in back-extraction mode from a pre-loaded solvent phase in the presence of an

excess of TEDGA. In the case of samples containing TEDGA (Figure 3-5), the acidity of the feed solution was kept low (pH = 3) to minimize hydrolytic degradation of TEDGA. NH_4NO_3 was added to provide appropriate nitrate concentration. In the presence of only the lipophilic extractant, equilibrium for the three metal ions was achieved between 2 and 4 h of contact time (Figure 2), showing very high distribution ratios around 1000 for Am(III) and Cm(III) and 8.7 ± 0.1 for Eu(III). The distribution ratios of Am(III) increased at a higher rate than in the case of Cm(III) and Eu(III), resulting in very high (non-equilibrium) separation factors of $SF_{Am/Cm}$ = 18 ± 2 and $SF_{Am/Eu}$ = 1193 ± 200 at 1 h contact time. Under equilibrium conditions the $SF_{Am/Cm}$ and $SF_{Am/Eu}$ decreased to 1.6 – 2.5, and 143-164, respectively. The observed distribution ratios and separation factors at equilibrium are comparable to those reported on 0.01 mol L^{-1} $CyMe_4BTPhen$ in 1-octanol.[35] Under these conditions however, the separation of Am(III) from Cm(III) or Eu(III) is not feasible, since these ions are also co-extracted to the organic phase. Such kinetic effects were formerly observed when using $CyMe_4BTPhen$ in cyclohexanone. However, the time window available for an efficient separation of Am from Cm was narrower (10 to 20 min).[36] The underlying reason for the kinetic effect was explained by the higher kinetic lability (or water exchange rates) of the Am(III) aqua-complexes towards substitution by a ligand compared to the aqua-complexes of Cm(III) and Eu(III) ions.[37, 38]

The extraction of ^{241}Am, ^{244}Cm and ^{152}Eu by [A336][NO_3] (without $CyMe_4BTPhen$) was followed in the presence of TEDGA (Figure 3). It was found in previous studies that [A336][NO_3] slightly extracts trivalent metal ions itself.[32] Masking of metal ions by TEDGA resulted in a factor of three lower distribution ratios for Am(III) and Cm(III), and in a factor of 14 lower distribution ratios for Eu(III), compared to extraction by [A336][NO_3].[32] Former speciation studies related to the EXAm process[14] showed the presence of heteroleptic metal complexes with the lipophilic extractant DMDOHEMA and TEDGA in the organic phase. In

the present study, the distribution ratios of all the three metal ions remained low for contact times as long as 25 h, suggesting, that the trivalent metal-TEDGA complexes are quantitatively retained in the aqueous phase.

The kinetics in the presence of equimolar concentrations of $CyMe_4BTPhen$ and TEDGA showed that equilibrium is reached after 12 h contact time (Figure 4), significantly longer than for extraction with $CyMe_4BTPhen$ only. Addition of TEDGA caused a decrease in distribution ratios of Am(III) and Cm(III) by approximately one order of magnitude while the distribution ratios of Eu(III) decreased by two orders of magnitude. The effect of the latter contributes to a steady increase of the Am/Eu separation factor as a function of extraction time (from $SF_{Am/Eu} \sim 150$ to $SF_{Am/Eu} \geq 3000$), until equilibrium was reached. The $SF_{Am/Cm}$ in this case also reached higher than equilibrium values (4.8 – 10.1) for contact times shorter than 10 h, while decreased to equilibrium values of 2.9 – 3.4 after 12 h, comparable to the case when $CyMe_4BTPhen$ was used alone.

The kinetics of stripping (and thus reversibility of the extraction) was studied from a loaded organic phase containing 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3] (Figure 5). As the [A336][NO_3] solvent extracts considerable quantities of nitric acid[32] which would hinder the back-extraction without a previous acid scrubbing step, the solvent was loaded from an aqueous phase containing 3 mol L^{-1} NH_4NO_3 at pH = 3 and the desired metal ions. The loaded solvent was separated and contacted with a fresh stripping solution that had an identical 3 mol L^{-1} NH_4NO_3 concentration and pH = 3 as the loading step, and an excess of TEDGA (added at 0.2 mol L^{-1} concentration to counteract the effect of $CyMe_4BTPhen$) (Figure 5). The distribution ratios of Am(III) and Cm(III) both decreased with time. The distribution ratios of Am(III) and Cm(III) both decreased with time. However, no equilibrium was reached after 8 hours contact time ($D_{Am} = 0.79 \pm 0.1$, $D_{Cm} = 0.26 \pm 0.04$, the activity of ^{152}Eu was below minimum detectable activity in the organic phase). Contrary to the extraction kinetic

experiments (Figure 4 and 5); the Am/Cm separation factors for short contact times in back-extraction kinetic experiments were significantly lower ($SF_{Am/Cm}$ = 0.9 – 1.9) and slowly increased with the back-extraction time ($SF_{Am/Cm}$ = 2.9). The opposite trend for the Am/Cm separation factors in the forward and back-extraction steps further support the assumption that higher than equilibrium Am/Cm separation factors are linked to differences in the aqueous chemistry of Am(III) and Cm(III) ions.

Quantitative removal of the tracers from the same loaded organic phase was also tested with a low nitrate concentration stripping solution at pH = 2. A stripping solution composed of 0.01 mol L^{-1} HNO_3 and 0.2 mol L^{-1} TEDGA allowed quantitative back extraction within 4 h contact time (D_{Am} = 0.018±0.003, D_{Cm} = 0.0034±0.0007, D_{Eu} < 0.001).

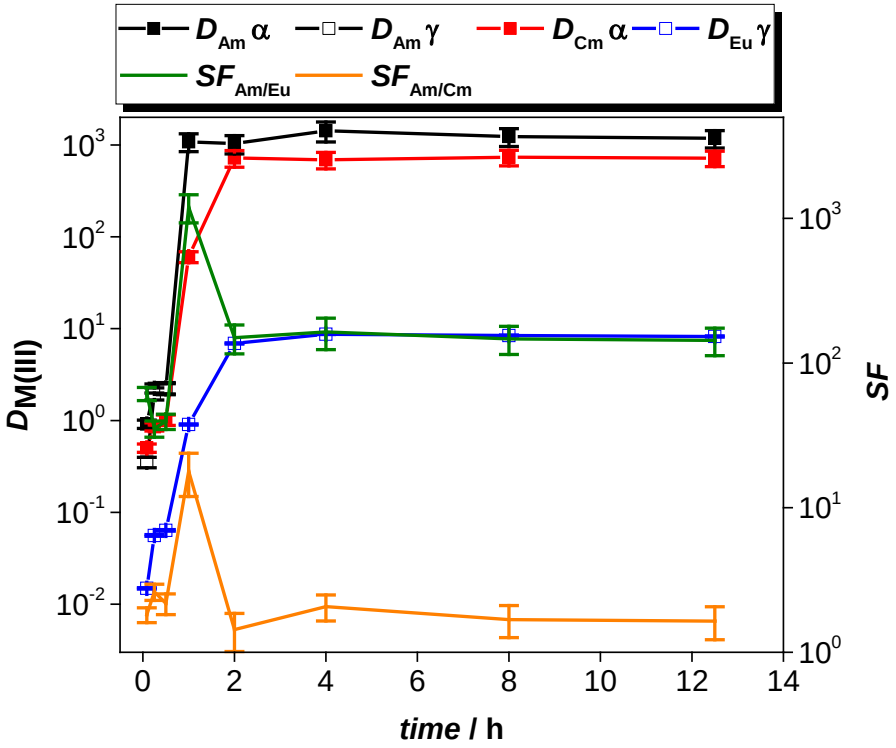


Figure 2. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of equilibration time. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 1 mol L^{-1} HNO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu; T = (22±1) °C, 2060 rpm.

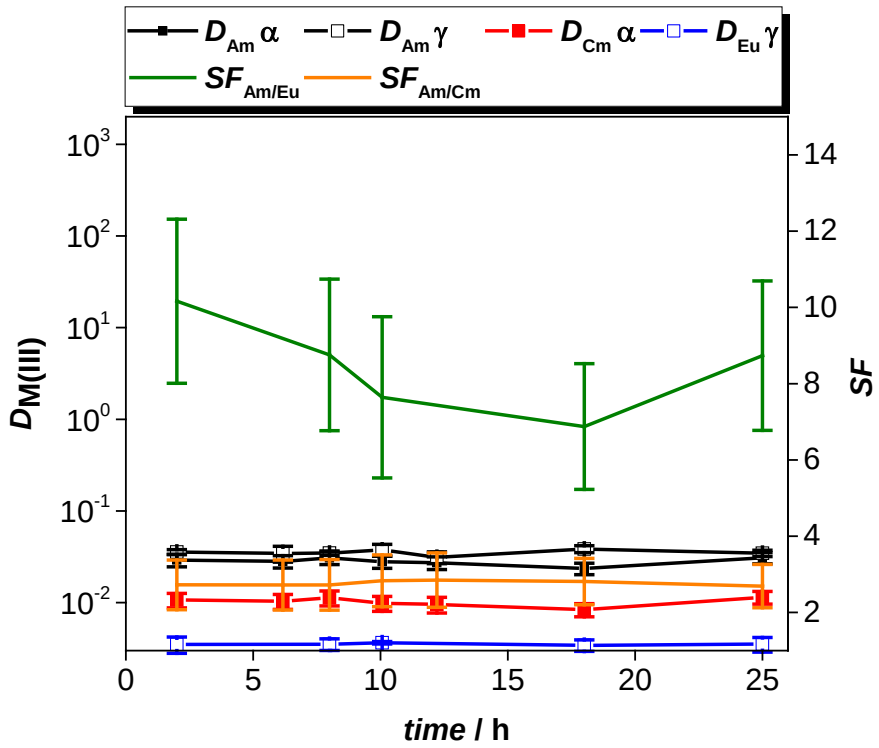


Figure 3. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of equilibration time. Org.: [A336][NO_3], Aq.: 0.010 mol L^{-1} TEDGA, 3 mol L^{-1} NH_4NO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3; T = (22±1) °C, 2060 rpm.

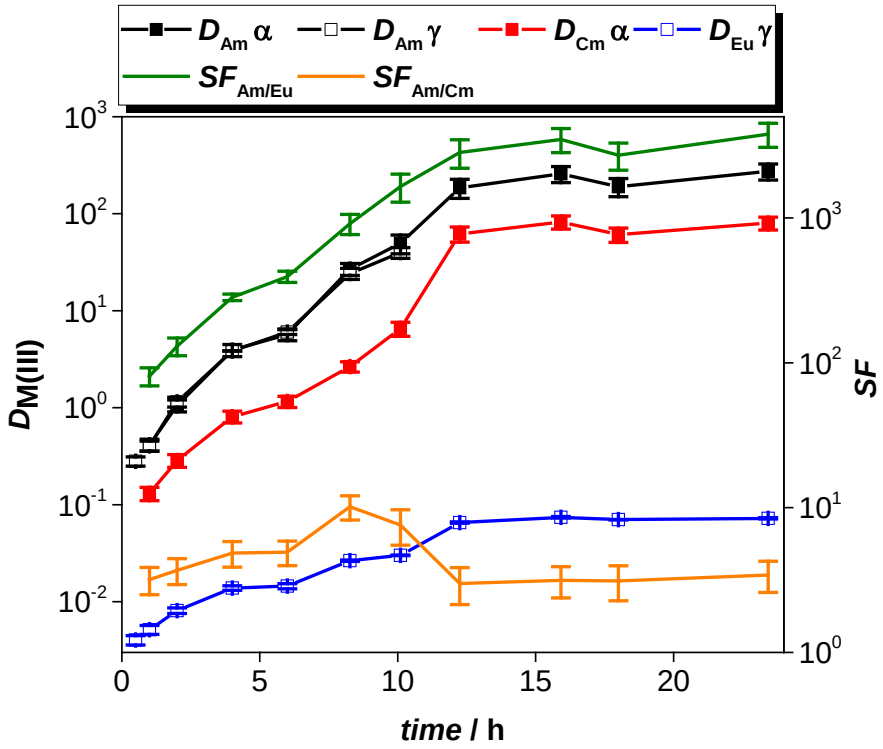


Figure 4. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of equilibration time. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 0.010 mol L^{-1} TEDGA, 3 mol L^{-1} NH_4NO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3, T = (22±1) °C, 2060 rpm.

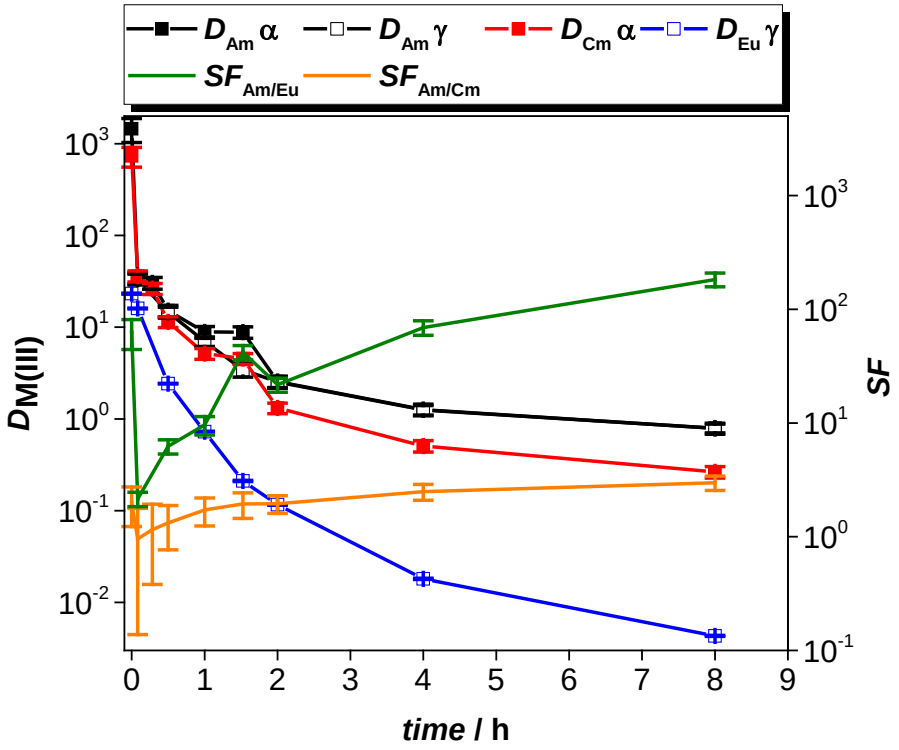
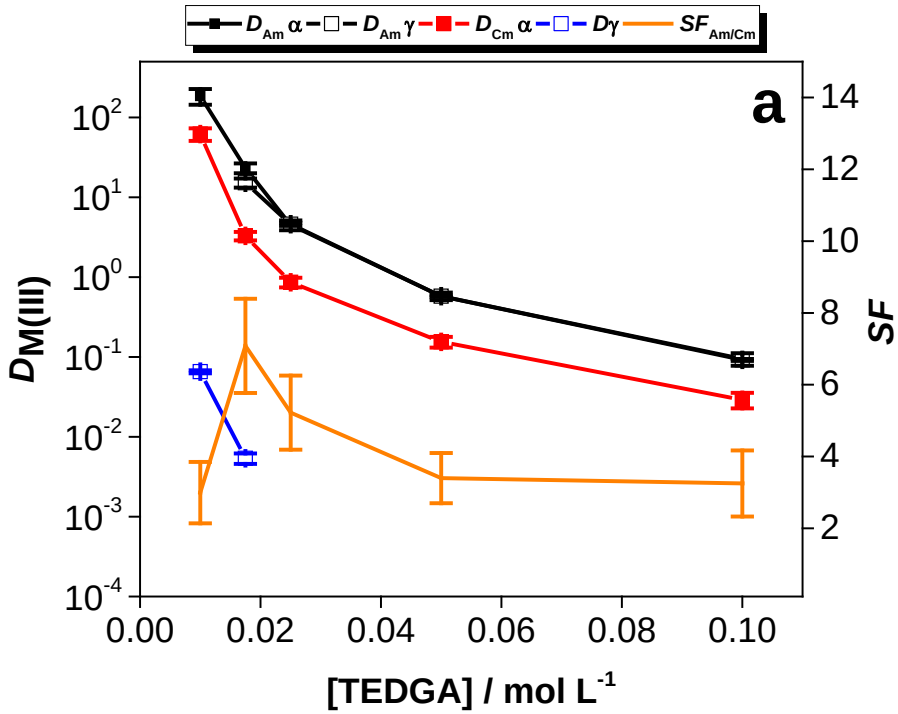


Figure 5. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of equilibration time. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], loaded from an aqueous phase containing 3 mol L^{-1} NH_4NO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3, Aq.: 0.2 mol L^{-1} TEDGA, 3 mol L^{-1} NH_4NO_3. Mixing performed at T = (22 ± 1) °C, 2060 rpm.

Influence of TEDGA concentration on distribution ratios

The effect of the TEDGA concentration on the equilibrium D values of Am(III), Cm(III) and Eu(III) was investigated for variable concentrations of TEDGA (5 – 100 mmol L^{-1}) in 3 mol L^{-1} NH_4NO_3 solution at pH = 3 (Figure 6 a). The low acidity in the feed solution was chosen in order to minimize the degradation of TEDGA due to acid-induced hydrolysis and still avoid hydrolysis of the trivalent minor actinides and lanthanides.[34] With the increase of TEDGA concentration in the aqueous phase a decrease of distribution ratios of all metal ions

was observed. The radioactivity of ^{152}Eu in the organic phase was below the detection limit for TEDGA concentrations higher than 0.0175 mol L^{-1}. At lower TEDGA concentrations the $SF_{Am/Eu}$ exceeded 2800. The $SF_{Am/Cm}$ increases to a maximum of 7.1 at 0.0175 mol L^{-1} after which it decreases to 3.2 at higher TEDGA concentrations.



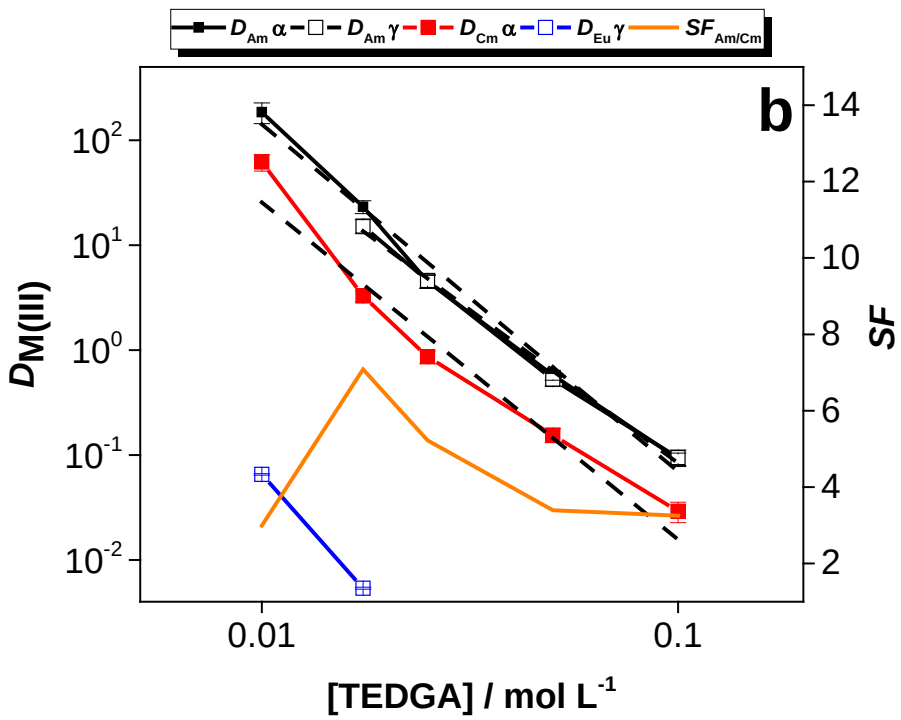


Figure 6. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of the TEDGA concentration. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 3 mol L^{-1} NH_4NO_3, 0.005 – 0.1 mol L^{-1} TEDGA, [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3, T = (22±1) °C, 2060 rpm, t = 12 h.

For Am(III) the slope of decrease of distribution ratios in a log D_{Am} vs. log [TEDGA] plot is approximately –3, while the curium data clearly show a non-linear relationship (Figure 6 b) indicating that the aqueous speciation of Cm(III) might be different from that of Am(III) and includes multiple species. More reliable speciation methods, such as time-resolved laser fluorescence spectroscopy should be used to verify if there is indeed a difference in the aqueous speciation of Am(III) and Cm(III) in aqueous solutions containing TEDGA complexant.

Influence of nitric acid concentration on the distribution ratios

Under the most plausible partitioning scenarios, the feed solution for an Am/Cm separation process would contain high concentrations of nitric acid. Therefore the influence of the nitric

acid concentration (0.01 – 6 mol L^{-1}) was tested (Figure 7). During these experiments the TEDGA (0.0175 mol L^{-1}) and $CyMe_4BTPhen$ concentrations (0.01 mol L^{-1}) were kept constant. The TEDGA concentration was chosen on the basis of the TEDGA concentration dependency experiment (Figure 6 a): with 0.0175 mol L^{-1} TEDGA, D_{Am} ~ 20 1, D_{Cm} ~ 3, D_{Eu} << 1, but ^{152}Eu(III) is still above the minimum detectable activity in the organic phase after extraction. With this ligand concentration, the distribution ratios of the trivalent actinides and lanthanides can be modulated easily by changing the aqueous feed acidity, i.e. to find conditions where $D_{Am} > 1$, $D_{Cm} < 1$ and $D_{Eu} << 1$. With the increase of aqueous feed acidity the distribution ratios of Am(III), Cm(III) and Eu(III) increased. A similar increase in distribution ratios with the nitric acid concentration (0.001 – 3 mol L^{-1}) in the presence of 0.01 mol L^{-1} TEDGA was observed by Lange *et al*. for extraction with 0.01 mol L^{-1} $CyMe_4BTPhen$ in 1-octanol.[16] The Am/Cm separation factor was insensitive to the aqueous feed acidity within uncertainty (values ranging from 3.0 to 4.2 in the investigated acidity range). The radioactivity of ^{152}Eu in the organic phase was below detection limits for feed solutions < 2 mol L^{-1} HNO_3. The behavior of other lanthanides in case of extraction from 1 mol L^{-1} HNO_3 was determined by ICP-MS (Table 1 and Figure 8). The highest distribution ratio obtained was that of lanthanum (D = 0.046 ± 0.005) resulting in the lowest Am/Ln separation factor for the Am/La pair of 75.

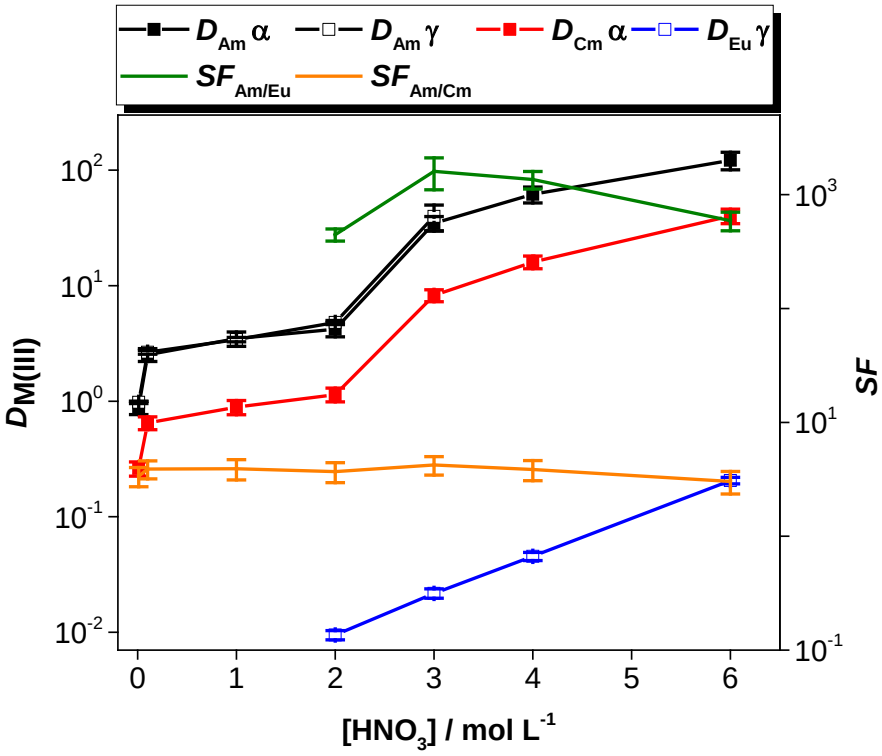


Figure 7. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in $[A336][NO_3]$, Aq.: 0.01 – 6 mol L^{-1} HNO_3, 0.0175 mol L^{-1} TEDGA, [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu, 2060 rpm, T = (22±1) °C, t = 12 h.

Table 1. Metal ion distribution ratios for extraction with 0.01 mol L^{-1} $CyMe_4BTPhen$ in $[A336][NO_3]$ from 0.0175 mol L^{-1} TEDGA in 1 mol L^{-1} HNO_3

Ion	D_M	$SF_{Am/Ln}$
Y	< 0.001	> 3000
La	0.046 ± 0.005	75 ± 13
Ce	0.018 ± 0.002	190 ± 35
Pr	0.012 ± 0.001	290 ± 50
Nd	0.011 ± 0.001	315 ± 50
Sm	0.005 ± 0.0005	690 ± 120
Eu	< 0.001	> 3000

Gd	0.0015 ± 0.0002	2300 ± 450
Dy	< 0.001	> 3000
Yb	< 0.001	> 3000
Am α	3.48 ± 0.49	
Am γ	3.42 ± 0.56	
Cm α	0.89 ± 0.13	
Eu γ	< 0.001	> 3000

Extraction conditions: see Figure 7.

The distribution ratios of the trivalent lanthanides decrease with the decrease of ionic radius along the lanthanide series (Figure 8). This trend was not expected, as the distribution ratios of Ln(III) with $CyMe_4BTPhen$ alone showed increase from La(III) to Sm(III) and decrease from Sm(III) to Lu(III) and Y(III).[35] TEDGA, when used in combination with the EXAm solvent, showed an increasing selectivity towards the heavier Ln(III).[39] The selectivities of the lipophilic extractant and the hydrophilic complexant towards the heavier lanthanides (when used in combination) resulted in a decrease of the distribution ratios along the lanthanide series, indicating that TEDGA has a dominant effect on the Ln(III) distribution ratios. The low distribution ratios of Ln(III) indicate that TEDGA forms more stable complexes with these metal ions in the aqueous phase than $CyMe_4BTPhen$ in the ionic liquid [A336][NO_3]. Although both the trivalent lanthanides and actinides are considered as hard acids according to Pearson's HSAB theory[40], there is a markedly stronger interaction between the trivalent actinide ions (5*f* series) and the soft donor ligand $CyMe_4BTPhen$, compared to the interaction with Ln(III).[35]

The increased Am/Cm separation observed for the combination of $CyMe_4BTPhen$ and TEDGA is a product of two factors. On the one hand, the slightly higher affinity of TEDGA for Cm(III) over Am(III) to form $M(TEDGA)_3$ complexes in the aqueous phase (in line with the actinide contraction of trivalent ion ionic radii along the actinide series). On the other

hand, it is also due to the slightly higher affinity of the soft-donor extractant $CyMe_4BTPhen$ for Am(III) over Cm(III) to form $M(CyMe_4BTPhen)_2$ complexes in the organic phase. This is probably related to the differences in electronic orbital structures of these ions or due to a size effect (better fit of the cation in the coordination cavity). Such a size effect was previously observed with Hbp18c6 complexant by Jensen *et al*.[28]

During the kinetic studies, the faster initial extraction of Am(III) over Cm(III) has been observed both in the presence and absence of TEDGA (Figures 2, 4, 11 and S1). The exact origin of the difference between the extraction kinetics was formerly proposed to be related to the slightly higher average number of water molecules surrounding the Cm(III) ions in their aqua complexes, as compared to the Am(III) ions.[36] In fact, the uncertainty in the coordination numbers of hydrated Am(III) or Cm(III) ions does not allow one to firmly state that there is a difference in the coordination numbers. An EXAFS study on the hydrated trivalent actinides, however, did show a tendency of shortening of the average M(III) – O distances along the actinide series, perfectly in line with the actinide contraction.[41] The average Cm(III)-O distance (2.455(8) Å) in the aqua-complexes was found to be shorter than the average Am(III)-O distance (2.472(8) Å), indicating a slightly stronger electrostatic interaction between the Cm(III) ion and the surrounding, polarized water molecules. A similar trend in the An(III) – O_{water} distances was observed in dilute, moderate and highly acidic nitrate solutions of Cm(III) and Am(III).[42] In the case of the hydrated trivalent lanthanide ions, an 18-fold decrease in the lability (or exchange rate constant of a water molecule) was observed along the series: $[Gd(H_2O)_8]^{3+}$ - $[Yb(H_2O)_8]^{3+}$.[43] One could expect a similar decrease in the lability trend in the $[An(H_2O)_8]^{3+}$ series. Apart from the first coordination sphere, very little is known about the structure of the second coordination sphere of the hydrated actinide ions or about the role it (and the hydrogen-bond network) might play in the kinetics of complexation.

The ligand substitution mechanism in metal complexation was described by Langford and Gray as either being an associative or a dissociative type.[44] In the case of an associative activation mechanism, the reaction coordinate passes through a transition state, where one additional ligand (which can be a solvent molecule) enters into the first coordination sphere of the metal ion. In the case of the dissociative mechanism, the reaction coordinate goes through a transition state where the first coordination sphere is not completely filled as one ligand is separated from the first coordination shell. Water exchange in the square antiprismatic eight-coordinate first coordination shell of trivalent Ln(III) aqua complexes is known to occur via an associative mechanism (with an intermediate nine-coordinate trigonal antiprismatic structure).[45]

In moderately acidic nitrate solution (relevant for the kinetic experiments of the present study Figure 4) the first coordination sphere of Am(III) and Cm(III) ions is filled by water molecules.[42] In the case of 1 mol L^{-1} HNO_3 (relevant for the kinetic experiments in present study Figure 2), the inner coordination sphere of Cm(III) and Eu(III) contains one nitrate ion on average.[46] During the extraction from an acidic aqueous solution of MA(III), the complexation by the first (bulky, tetradentate) $CyMe_4BTPhen$ ligand implies substitution of four of the coordinated water molecules. The most plausible way it can occur is the nearly simultaneous dissociation of four water molecules (or three water molecules and one nitrate ion) at the aqueous/organic interphase. The shorter Cm(III) – O distances suggest that this dissociative ligand substitution step for the Cm(III) aqua complexes requires a higher activation energy than in the case of Am(III) aqua complexes.

When the extraction is performed from a TEDGA containing Ln(III) + An(III) feed solution, the aqueous phase speciation is further complicated by the presence of a dynamic equilibrium between heteroleptic TEDGA and water complexes of the metal ions. $[LnTEDGA]^{3+}$ and $[Ln(TEDGA)_2]^{3+}$ complexes are predominant for the light lanthanides, whereas

$[Ln(TEDGA)_3]^{3+}$ is the predominant species for the heavier lanthanides.[39] In the case of An(III), the prevalent (but not exclusive) species are of $[An(TEDGA)_3]^{3+}$ composition. The ligand substitution in the case of these complexes can only proceed via a dissociative mechanism due to steric hindering. However, it is not known whether a TEDGA molecule or multiple water molecules are the preferred leaving groups. When metal ion is in a heteroleptic complex (e.g. the first coordination shell contains more than one type of species), the water exchange rates can be faster or slower, compared to homoleptic metal aqua ions.[47] The observed differences in the highest non-equilibrium values of $SF_{Am/Cm}$ achieved from TEDGA complexed feed solutions compared to non-complexed acidic solutions (Figure 4 vs. 2), do not allow to ascertain the identity of the leaving group due to the complexity of the aqueous phase speciation.

Apart from a supposedly higher activation energy barrier for the dissociation of a coordinated water molecule in the first coordination sphere of Cm(III), another factor, namely differences in the diffusion coefficients, might contribute to the differences in the extraction kinetics between Am(III) and Cm(III). The change in the charge density along the Ln(III) series as well as along the An(III) series results in a progressive decrease of their limiting diffusion coefficient in water.[48] Calculations suggest lower limiting diffusion coefficient for Cm(III) than for Am(III) in water (5.87×10^{-10} m^2s^{-1} and 5.91×10^{-10} m^2s^{-1}, respectively).[48] The combined effect of differences in microscopic properties (e.g. differences in water exchange rate and in the limiting diffusion coefficients) of the metal aqua ions of Am(III) and Cm(III) can be responsible for the observed macroscopic differences in the extraction kinetics.

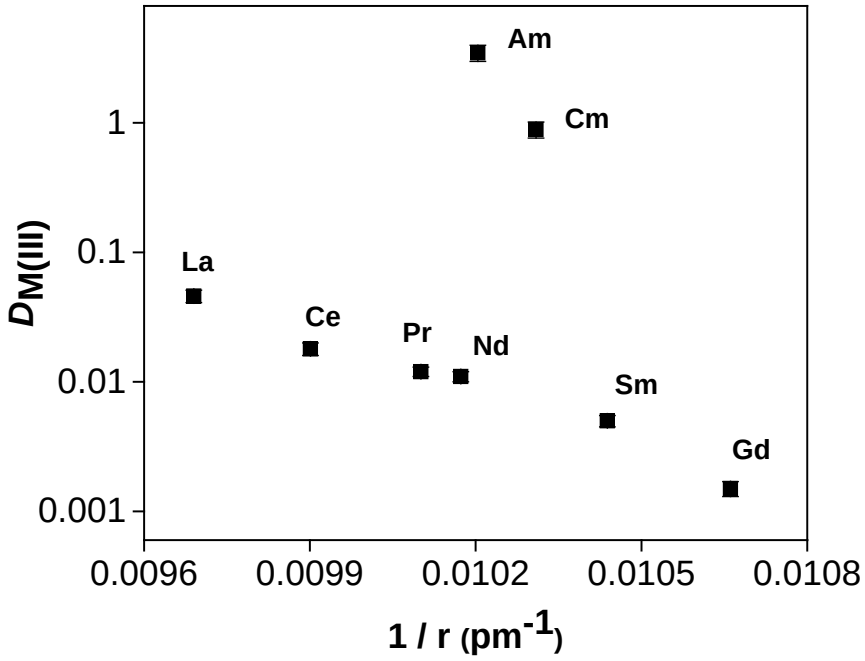


Figure 8. Org.: 0.01 mol L^{-1} CyMe$_4$BTPhen in [A336][NO$_3$], Aq.: 1 mol L^{-1} HNO$_3$, 0.0175 mol L^{-1} TEDGA, [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu, 2060 rpm, T = (22±1) °C, t = 12 h.

Exploiting the differences in extraction kinetics for the separation of chemically similar Co(II) from Ni(II) has been already used in solvent extraction ("kinetic separation").[49] The reproducibility of higher than equilibrium separation factors (Figure 4) was therefore investigated as a function of nitrate ion concentration at a constant pH = 3 (Figure 9). The rectangular field in Figure 9 indicates a concentration range, where the Am/Cm separation is feasible (e.g. between 0.5 – 6 mol L^{-1}), since in one step more than 50 % of the Am(III) ions are extracted to the organic phase, while more than 50 % of Cm(III) remains in the aqueous phase. The distribution ratios of Am(III) and Cm(III) rise with an increase in the nitrate ion concentration up to 2 mol L^{-1}, after which a slight decrease is observed. In the case of Eu(III)

a slight increase with nitrate concentration was found. The Am/Cm separation factors vary between 3.7 and 6.6 and the Am/Eu separation factors vary between 122 and 980.

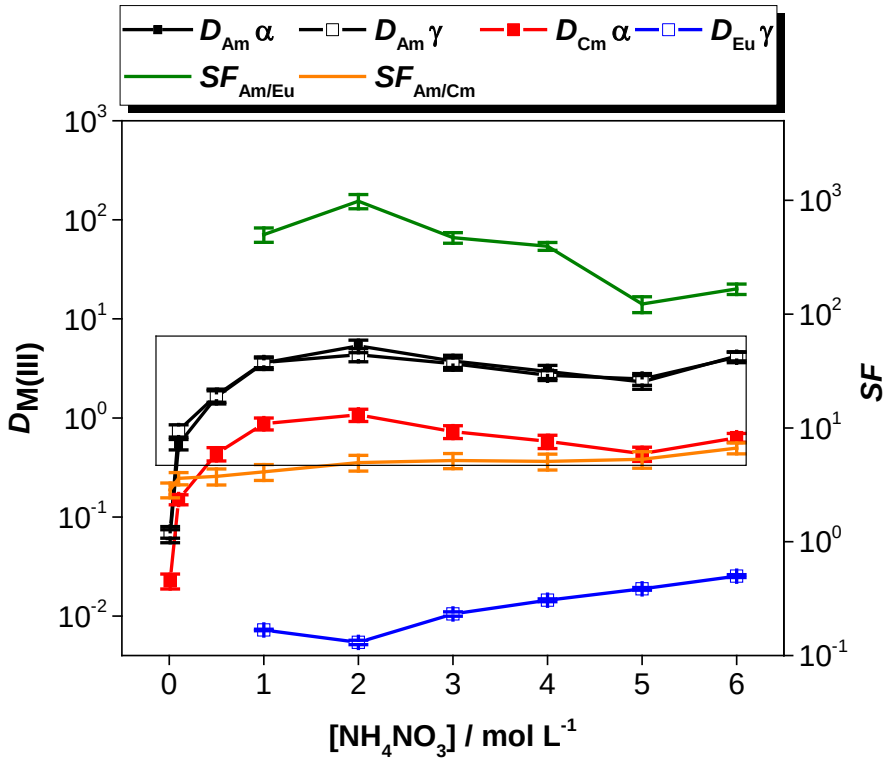


Figure 9. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of the NH_4NO_3 concentration. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 0.01 mol L^{-1} TEDGA, 0.01 – 6 mol L^{-1} NH_4NO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3, T = (22 ± 1)°C, 2060 rpm, t = 4 h.

Influence of temperature

The effect of temperature on the solvent extraction system and especially on the Am/Cm separation factor was studied at 22 °C, 30 °C and 40 °C (Figure 10). The distribution ratios of Am(III) and Cm(III) only vary slightly with the increase of temperature from 22 °C to 40 °C

and the $SF_{Am/Cm}$ decreases from 3.9 to 2.7. The distribution ratios of ^{152}Eu remained below the detection limit at 22 °C and 30 °C. This system seems relatively insensitive towards change in extraction temperature within the investigated range.

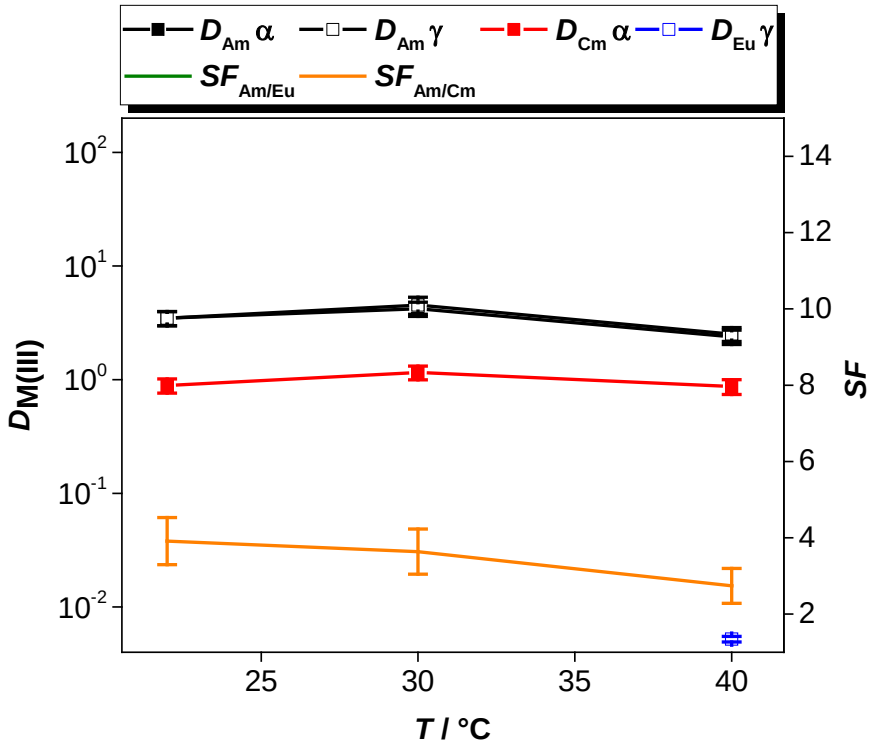


Figure 10. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of temperature. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 0.01 mol L^{-1} TEDGA, 3 mol L^{-1} NH_4NO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at pH = 3, 2060 rpm, t = 12 h.

Since the kinetics of extraction was investigated at a higher temperature (40 ± 1) °C (Figure 11) in order to see, if at higher temperatures could allow a faster extraction, compared to the experiments performed at (22 ± 1) °C. At this higher temperature, the equilibrium was achieved for all metal ions; Am(III), Cm(III) and Eu(III) within 1 h mixing time. In this case,

the difference in extraction kinetics and consequently higher than equilibrium separation factors were not observed $SF_{Am/Eu}$ = 900-1300 or $SF_{Am/Cm}$ = 3.2 – 3.9.

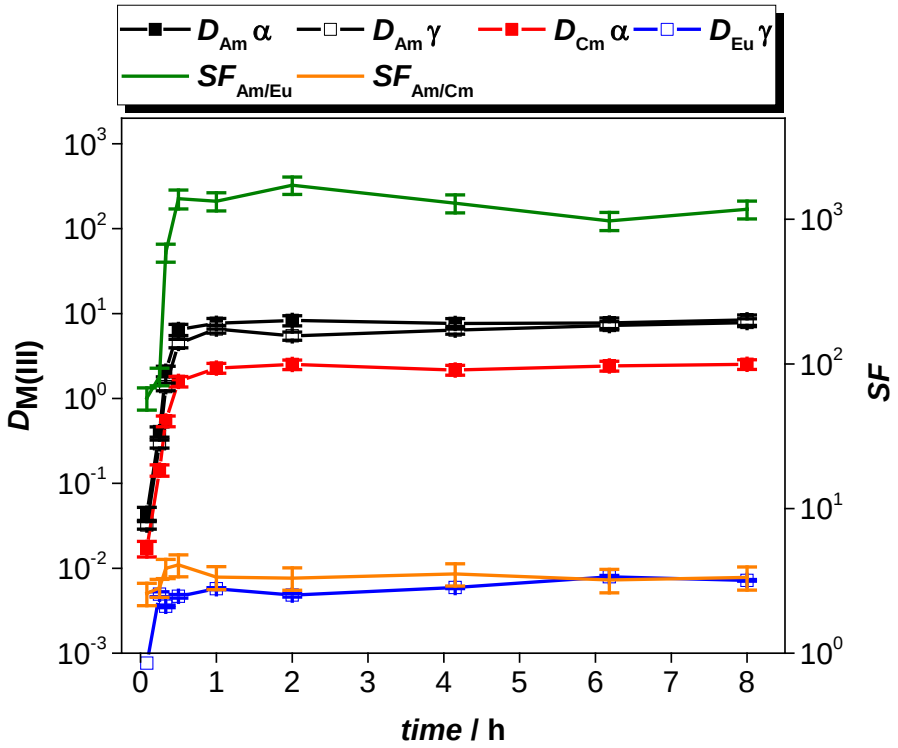


Figure 11. Distribution ratios of Am(III), Cm(III) and Eu(III) as a function of equilibration time. Org.: 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3], Aq.: 0.0175 mol L^{-1} TEDGA, 1 mol L^{-1} HNO_3 [Ln(III)] (La-Dy, Yb, Y) = 10^{-5} mol L^{-1} each; spiked with tracers of ^{241}Am, ^{244}Cm and ^{152}Eu at 2060 rpm.

4. Conclusions

The present paper describes a separation method that complies with the CHON principle and allows the simultaneous separation of Am(III) from Cm(III) and the Ln(III) from a moderately acidic feed solution. It was found that the desired separation is most selective when using an aqueous feed containing 1 mol L^{-1} HNO_3 and 0.0175 mol L^{-1} TEDGA and an

organic phase composed of 0.01 mol L^{-1} $CyMe_4BTPhen$ in [A336][NO_3] ($SF_{Am/Cm}$ = 3.1 - 3.9, $SF_{Am/La}$ > 75, $SF_{Am/Eu} \geq 3000$). The method is robust towards relatively large changes in the HNO_3 concentration of the feed, or in temperature, but sensitive for changes in TEDGA concentration. Am/Cm separation factors at lower temperatures were higher under non-equilibrium conditions, both in the presence and absence of the hydrophilic complexing agent TEDGA with separation factors up to $SF_{Am/Cm} \approx 17$. A test in a continuous set-up is desirable to demonstrate if non-equilibrium separations are feasible. Otherwise, if equilibrium conditions are required, the extraction can be performed at elevated temperatures since slow kinetics at lower temperatures require modulation of the diluent composition and/or engineering efforts. For a better understanding of the reason for the higher than equilibrium separation factors, further research would be needed involving phase transfer rate experiments (aqueous to organic phase and vice-versa), comparisons of diffusion speed of the complexed metal ions and speciation studies using TRLFS method on TEDGA complexes of both Am(III) and Cm(III).

5. Acknowledgement

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