Solvent extraction studies for the separation of trivalent actinides from lanthanides with a triazole-functionalized 1,10-phenanthroline extractant

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A new *N*-atom donor extractant 2,9-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline (EH-BTzPhen) was synthesized and used in solvent extraction studies to separate the trivalent minor actinides americium(III) and curium(III) from europium(III), representing fission product lanthanides. The extractant was found to be soluble in 1-octanol and in the Aliquat-336 nitrate ([A336][NO_3]) ionic liquid diluent, but insoluble in *n*-dodecane. The [A336][NO_3] is a fully incinerable room temperature ionic liquid, and has a higher flash point than aliphatic diluents such as 1-octanol. The EH-BTzPhen proved to be effective for selective minor actinide extraction only in combination with 2-bromohexanoic acid synergist when 1-octanol was used as a diluent ($SF_{Am/Eu} > 200$). The change of the diluent from 1-octanol to Aliquat-336 nitrate allowed selective An(III) extraction from low acidity feed solutions without the need of a synergist ($SF_{Am/Eu} \sim 70$ and $SF_{Am/Cm} \sim 1.9$-2.2). The phase transfer kinetics of the ligand-metal complexes is however very slow at 22 °C in the case of both solvents. With this newly synthesized extractant the achieved $SF_{Am/Cm}$ were comparable to the values achieved with the established $CyMe_4$BTBP and $CyMe_4$BTPhen extractants.

Keywords: Minor actinides, lanthanides, solvent extraction, Aliquat-336, ionic liquids, 1,2,3-triazole

1. Introduction

Minor actinides (neptunium, americium and curium) are responsible for the long-term heat emission and radiotoxicity of high level radioactive waste obtained after nuclear fuel reprocessing. Recycling of uranium and plutonium *via* the Plutonium Uranium Redox Extraction (PUREX) process is a mature technology applied on an industrial scale.[1] The separation of neptunium is possible with a modification of the PUREX flow sheet.[2, 3] However, trivalent americium and curium are diverted to the

highly active raffinate together with the other fission and corrosion products, because tri-*n*-butyl phosphate (TBP, the extractant used in the PUREX process), has no affinity towards the extraction of trivalent metal ions. The separate management or transmutation of americium and curium could allow for a more dense design of a deep underground final repository of conditioned high activity waste.[4, 5] However, curium would require excessive shielding and criticality control through all process stages of transmutation target fabrication due to its intensive neutron emission. Therefore, a partitioning and transmutation (P&T) scenario would largely benefit from a robust and efficient chemical separation process to separate americium from curium and the lanthanides.

Soft-donor extractants using nitrogen or sulfur-based donor groups were found to be suitable for the separation of trivalent minor actinides from lanthanides.[6-8] The tetradentate *N*-atom donor extractants 6,6'-bis(5,5,8,8- tetramethyl-5,6,7,8- tetrahydro-1,2,4- benzotriazin -3-yl)-2,2'-bipyridine ($CyMe_4BTBP$)[9, 10 11-13] and 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8- tetrahydro-1,2,4- benzotriazin -3-yl)-1,10- phenanthroline ($CyMe_4BTPhen$)[14, 15] are capable of extracting Am(III) and Cm(III) directly from highly active raffinate solutions. The metal-ligand interaction between the trivalent actinides An(III) and $CyMe_4BTBP$ or $CyMe_4BTPhen$ is possible due to the presence of four *N*-atoms each having a lone electron pair in the metal-binding cavity (Figure1). Both compounds contain the six-membered triazinyl rings, where two of the donor lone electron pairs are softer nucleophiles than the lone pair of the pyridine-type *N*-atom of the 1,10-phenanthroline or 2,2'-bipyridine moiety. The increased nucleophilicity of the *N*-atom in the 2-position in the triazinyl ring is caused by the lone pair of the adjacent non-coordinating *N*-atom at position 1 (so-called *alpha effect*).[16-19] The excellent Am/Eu separation factors ($SF_{Am/Eu}$ = 140 and $SF_{Am/Eu}$ = 200-400 for $CyMe_4BTBP$ and

CyMe$_4$BTPhen, respectively) originate from the stronger covalent character of the An(III)-N bonds compared to Ln(III)-N bonds.[7] At equilibrium, neither of these extractants show a high Am/Cm separation factor ($SF_{Am/Cm} \approx 2.5$ for CyMe$_4$BTBP and CyMe$_4$BTPhen).[11, 14] When using the ionic liquid [A336][NO_3] as diluent in combination with CyMe$_4$BTPhen as extractant similar Am/Cm separation factors were observed at equilibrium and (much higher) separation factors were observed in non-equilibrium conditions.[20] The ionic liquid [A336][NO_3] was recently also 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.[27] Moreover, TODGA was found to have a higher radiation stability in [A336][NO_3] than in aliphatic diluents.[28]

The effect of replacing 2 (1,2,4-) triazine moieties by 2 (1,2,3-) triazole moieties in the case of the BTP complexants for An(III) and Ln(III) separation was demonstrated in the hydrophilic, tridentate complexant 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl)]pyridine (PyTri-Diol).[21, 22] It proved to be a viable CHON-compliant alternative for the previously suggested SO_3-Ph-BTP molecule in the i-SANEX process.[23, 24] Similarly, a hydrophilic tetradentate 2,9-bis-(1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline complexant (BTrzPhen) was developed and tested with the purpose of Am(III)/(Cm(III)+Ln(III)) separation in an i-SANEX type process.[25] The compound allowed a $SF_{Cm/Am}$ of 2.5 from a loaded *N*,*N*,*N'*,*N'*-tetra-*n*-octyl diglycolamide (TODGA) containing solvent. The achieved Eu(III)/Am(III) separation factors were lower by a factor of two than those achieved with PyTri-Diol. With both BTrzPhen and PyTri-Diol molecules, the increase of aqueous nitric acid concentration resulted in a loss of stripping efficiency, presumably be due to protonation of the extractants.

Recently the synthesis and solvent extraction of the lipophilic, tetradentate 6,6'-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-2,2'-bipyridine (EH-BTzBP) was reported.[26] It was found that the extractant shows promising Am/Eu separation factors when used in combination with 2-bromohexanoic acid. The extraction properties of the novel extractant with respect to Cm(III) were not investigated.

For the present study, the unprecedented lipophilic 2,9-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline (EH-BTzPhen) was synthesized (Figure 1). The extraction of An(III) and Ln(III) was studied using 1-octanol and Aliquat-336 nitrate ([A336][NO_3]) diluents. The purpose of this investigation was to study the extraction kinetics and selectivity of the extractant regarding Am(III), Cm(III), and Eu(III). The selectivity in solvent extraction is compared to the extractants with six-membered heterocycles.

2. Experimental

2.1 Materials used for solvent extraction

Aliquat® 336 chloride ([A336][Cl], quaternary amine content: 88.2 – 90.6 %) of which the main component is tri-*n*-octylmethylammonium chloride ([N_{1888}][Cl]), 1-octanol (purity > 99 %), citric acid (purity > 99 %), 2-bromohexanoic acid (purity 97 %), silver(I) nitrate (purity: 99.9 %), ammonium nitrate (purity > 99 %), $Dy(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %) and $Yb(NO_3)_3 \cdot 5H_2O$ (purity: 99.9 %) were obtained from Sigma-Aldrich (Steinheim, Germany). Potassium nitrate (purity > 97.0 %), sodium nitrate (purity > 97.0 %) and sodium hydroxide (Titrisol) were obtained from Merck KGaA (Darmstadt, Germany). $Gd(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %) and $Eu(NO_3)_3 \cdot 6H_2O$ (purity: 99.99 %) were obtained from Alfa Aesar GmbH (Karlsruhe, Germany).

$La(NO_3)_3 \cdot 6H_2O$ (purity: 99.0 %) was obtained from Fluka Chemica (Seelze, Germany). $Pr(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %), $Nd(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %), $Sm(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %), $Y(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %) and $Ce(NO_3)_3 \cdot 6H_2O$ (purity: 99.9 %) were obtained from Strem Chemicals (Kehl, Germany). Trace metal grade nitric acid was obtained from Fischer Scientific Ltd. (Loughborough, UK). MilliQ water was used for all dilutions (resistivity: minimum 18.2 MΩ cm). ^{241}Am tracer in 1 mol L^{-1} HNO_3 solution (radiochemical purity > 99 %) 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).

The [A336][Cl] ionic liquid was converted into its nitrate form 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 drops of $AgNO_3$ 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), while the density of nitric acid solutions and nitrate solutions were taken from density tables.

2.2 Synthesis of EH-BTzPhen

All chemicals used for the synthesis of EH-BTzPhen were purchased from Acros Organics, Sigma Aldrich, Alfa Aesar and TCI Europe and used as received. For column chromatography, 70-230 mesh silica 60 (Acros) was used as the stationary phase. NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer and chemical

143 shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H), or
144 the internal (NMR) solvent signal (^{13}C). The high-resolution mass spectrum was
145 acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer
146 (Synapt G2 HDMS, Waters, Milford, MA). The sample was infused at 3 µl/min and the
147 spectrum was obtained in positive ionization mode with a resolution of 15000 (FWHM)
148 using leucine enkephalin as lock mass. The melting point was determined on a Mettler-
149 Toledo DSC 1 instrument, using a heating rate of 4 °C min^{-1} and under a helium
150 atmosphere.

151 The 2,9-diethynyl-1,10-phenanthroline was prepared in two steps from neocuproine, as
152 described in the literature.[25, 29] EH-BTzPhen was synthesized according to a modified
153 literature procedure using a copper-catalyzed azide-alkyne cycloaddition reaction
154 (click-reaction) between the 2,9-diethynyl-1,10-phenanthroline and racemic 3-
155 (azidomethyl)heptane, dissolved in DCM (Scheme 1).[30] 2,9-Diethynyl-1,10-
156 phenanthroline (600 mg, 2.63 mmol) and racemic 3-(azidomethyl)heptane (939 mg,
157 6.05 mmol) were added to a 250 mL round-bottom flask and dissolved in 53 mL of
158 dichloromethane (DCM). A solution of sodium ascorbate (1.042 g, 5.26 mmol) in
159 47 mL of water was added as a second phase. While stirring, a solution of $CuSO_4 \cdot 5H_2O$
160 (13 mg, 0.053 mmol) and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)
161 (28 mg, 0.053 mmol) in 10.5 mL of H_2O:DMSO (1:1) was added slowly, followed by
162 the addition of *N,N*-di-isopropylethylamine (DIPEA) (1.869 g, 14.46 mmol). The
163 resulting mixture was stirred vigorously at room temperature for two days after which it
164 was diluted with chloroform and washed with water (3x) and brine (1x). The organic
165 layer was dried over Na_2SO_4 and concentrated. Next, the crude product was dissolved in
166 diethyl ether and filtered. The filtrate was then concentrated and further purified via
167 column chromatography on silica ($CHCl_3$:*i*PrOH with gradient (1:0 to 19:1)) to yield

the pure product as an off-white solid (75 % yield, 1.066 g, mixture of stereoisomers). M_p = 147 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.56 (br s, 2H), 8.65 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 8.4 Hz, 2H), 7.92 (s, 2H), 3.39 – 2.80 (m, 4H), 1.26 – 1.10 (m, 2H), 1.05 – 0.88 (m, 4H), 0.83 – 0.29 (m, 24H) (Figure S1). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 151.69, 147.92, 145.51, 137.24, 128.58, 126.36, 125.34, 120.67, 53.67, 39.23, 29.57, 27.93, 22.97, 22.81, 13.98, 9.98 (Figure S2).

HRMS (ESI-Q-TOF): *m/z* $[M + H]^+$ calculated for $C_{32}H_{42}N_8$: 539.3605; found: 539.3601.

2.3 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 mounted on 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).

A stock solution for the lanthanide-nitrate containing aqueous phases 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(III). From this stock 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) 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). Spiked feed solutions were

prepared by adding 3 kBq (in 10 µL volume) of each of the tracers ^{241}Am, ^{152}Eu and ^{244}Cm to 1 mL of the initial aqueous feed solution. All tracer-spiked aqueous feed solutions were prepared in advance and mixed thoroughly before contacting with the organic phase.

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 vial. The organic phase was pre-equilibrated with a nitric acid solution of the same acid concentration as used for the feed solution of the extraction step. After the equilibration, the phase disengagement was enhanced by centrifugation of the vials for 5 min at 4000 rpm using a Heraeus Labofuge 200 centrifuge. After phase separation, 300 µL aliquots of the aqueous and organic phases were collected for gamma activity measurements.

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 activities of α-particle emitting radionuclides in each separated phase were determined using α spectroscopy. Weighed amounts 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) alpha peaks were measured using an α spectrometer (Alpha Analyst, Canberra) equipped with Passivated Implanted Planar Silicon (PIPS) α detectors (Canberra Olen N.V., Olen, Belgium). The spectra were analyzed using Apex Alpha software.

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

in the aqueous phase in accordance with Equation (1).

$$D_M = \frac{[M_{org.eq.}]}{[M_{aq.eq.}]} \quad (1)$$

The highest and lowest distribution ratio limits for ^{241}Am and ^{244}Cm determined by the α spectrometry detection limits in the aqueous or organic phases were 1000 and 0.001, respectively. γ spectrometry allowed the determination of distribution ratios for ^{241}Am between 200 and 0.05 and between 1000 and 0.001 for ^{152}Eu.

The *separation factor* (*SF*) of two elements was calculated from the distribution ratios of the respective elements in accordance with Equation (2):

$$SF = \frac{D_{Mx}}{D_{My}} \quad (2)$$

3. Results and discussion

Solubility tests were conducted on the freshly synthesized extractant. The solubility of the extractant was lower than 0.01 mol L^{-1} in *n*-dodecane, resulting in a slurry with most of the compound left undissolved. It also shows to be insoluble in pentane, hexane and heptane. The π-π stacking of the planar phenanthroline groups of EH-BTzPhen molecules might be a reason for the preferred crystallization over solubilisation in aliphatic diluents. The extractant proved to be soluble in various polar diluents; 1-octanol (up to 0.2 mol L^{-1}) and the ionic liquid [A336][NO_3] (up to 0.2 mol L^{-1}). The compound showed a high solubility (during the synthesis and purification steps) in dichloromethane, chloroform and diethylether. In contrast to our EH-BTzPhen, the tridentate 2,6-Bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl]pyridine (PTEH), carrying identical moieties was highly soluble both in apolar kerosene as well as polar DCM and 1-octanol.[31] For solvent extraction studies, 0.01 mol L^{-1} solutions of the EH-BTZPhen

237 in both 1-octanol and in Aliquat-336 nitrate ionic liquid were used. Scoping studies
238 were performed to test the compatibility of the extractant in these two diluents with an
239 acidic aqueous phase. 1 mol L^{-1}, 0.75 mol L^{-1} and 0.5 mol L^{-1} HNO_3 resulted in the
240 formation of a white precipitate in the case of both solvents, which did not dissolve after
241 several weeks. With 0.1 mol L^{-1} HNO_3 the organic phase remained clear, however a
242 small amount of opaque layer was formed at the interphase. Protonation of the nitrogen
243 atoms in the second or third position of triazole rings and subsequent inter-molecular *H*-
244 bond formation can be a plausible reason for the observed precipitation. The
245 unsubstituted 1*H*-1,2,3-triazole is a stronger base ($pK_a = 1.17$)[32] than the 1,2,4 triazine
246 ($pK_a < 0$). In comparison to EH-BTzPhen, neither $CyMe_4$BTBP, nor $CyMe_4$BTPhen
247 (both containing triazines) show acid-induced precipitation when their organic solutions
248 are contacted with acidic aqueous phases. The acid-induced precipitation of EH-
249 BTzPhen is a marked contrast with the result of the acid stability test using 1 mol L^{-1}
250 HNO_3 performed by Muller and Nash on EH-BTzBP in toluene.[26] The structural
251 difference between the two compounds is the *cis*-locked conformation of the 1,10-
252 phenanthroline moiety compared to the 2,2'-bipyridine unit. Contact of organic
253 solutions of EH-BTzPhen with aqueous phases at lower acidities (pH 2-3) did not result
254 in the formation of precipitates. Solvent extraction studies were conducted only at these
255 pH values to prevent precipitation.
256
257 Since the structurally similar EH-BTzBP molecule was previously tested in a molecular
258 diluent, we also tested our new cis-locked EH-BTzPhen in 1-octanol.[26] This scoping
259 solvent extraction study did not result in extraction of ^{241}Am(III), ^{244}Cm(III) and
260 ^{152}Eu(III) from 1 mol L^{-1} NH_4NO_3 aqueous feed solution with 0.01 mol L^{-1} EH-
261 BTzPhen in 1-octanol: $D_{Am} = (0.25 \pm 0.04)$, $D_{Eu} = (0.094 \pm 0.001)$. It is known that

some soft *N*-atom donor extractants are able to extract the metal nitrates directly from acidic feed solutions without the need for a synergist. The formerly mentioned $CyMe_4BTBP$ and $CyMe_4BTPhen$ are examples of such tetradentate extractants. The tridentate 2,6-bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4yl]pyridine (PTEH) (in a solution of 0.2 mol L^{-1} in kerosene/1-octanol mixture) was able to extract Am(III) selectively ($SF_{Am/Eu}$ ~ 80) without the addition of a synergist.[31]

However, some other *N*-atom donor extractants, like the tetradentate EH-BTzBP are not able to stabilize the metal nitrates in an aliphatic organic phase, but extraction is possible with the use of a lipophilic anion source.[26] Therefore, the addition of 2-bromohexanoic acid as a lipophilic anion source was tested with the present EH-BTzPhen extractant (Figure 2). Speciation studies of Eu(III) complexes with EH-BTzBP using time-resolved laser-fluorescence spectroscopy (TRLFS) did not show the presence of bromohexanoate anions in the first coordination sphere.[35] Therefore, it is assumed that bromohexanoate anions act as outer-sphere anions for charge compensation in the organic phase. Figure 2 shows that the extraction kinetics of 0.01 mol L^{-1} EH-BTzPhen + 1 mol L^{-1} 2-bromohexanoic acid in 1-octanol is slow. The equilibrium distribution ratios were reached in 24 h for ^{241}Am(III) and ^{244}Cm(III) and within 12 h for ^{152}Eu(III). Equilibrium distribution ratios were (400 ± 100) for ^{241}Am(III), (190 ± 50) for ^{244}Cm(III) and (1.7 ± 0.2) for ^{152}Eu(III).

The solvent extraction mechanism for the EH-BTzBP/bromohexanoic acid/toluene solvent was suggested to be best described as a cation exchange between the acidic protons of 2-bromohexanoic acid and the trivalent metal ions and we assume a similar mechanism for the EH-BTzPhen analogue (Equation (3)).[26]

$$M^{3+}_{(aq.)} + 2\ \text{EH-BTzPhen}_{(org.)} + 3\ (HA)_{2,(org.)} \rightleftharpoons$$

$$M(EH\text{-}BTzPhen)_2A_3\,(HA)_{3(org.)} + 3\,H^+_{(aq.)} \quad (3)$$

Where HA represents 2-bromohexanoic acid.

The use of 2-bromohexanoic acid would be difficult in nuclear fuel cycle applications as the introduction of high concentrations of bromine in the organic solvent is a disadvantage from the point of view of secondary waste treatment. Furthermore, radiation induced degradation would most probably liberate highly corrosive bromine from such a solvent.

Figure 3 shows the distribution ratios of ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) for batch liquid-liquid extraction experiments using feed solutions with [Ln(III)] = 10^{-5} mol L^{-1}, pH = 3 and 1 mol L^{-1} NH_4NO_3 and an organic phase composed of 0.01 mol L^{-1} EH-BTzPhen in [A336][NO_3] as a function of equilibration time. Kinetic experiments were conducted until 110 h, after which the Am(III) distribution values reached equilibrium, while distribution ratios of ^{244}Cm(III) and ^{152}Eu(III) still slightly increased. Such an extremely slow extraction is not advantageous in a continuous solvent extraction process, as it would require the design of a plant with large footprint and cost. The solvent radiolysis and equipment wear would also be more important in case of very long contact times. However, it is shown in our recent study using the $CyMe_4BTPhen$ complexant in [A336][NO_3] that the slow kinetics can be significantly improved by increasing the temperature.[20] The time needed to reach the equilibrium is more dependent on factors affecting diffusion of species to and from the interphase. By comparing the kinetics of $CyMe_4BTPhen$ in [A336][NO_3] under comparable conditions as used in this study, we hypothesize that the high viscosity of the ionic liquid cannot be alone the reason.

We assume the reason for significantly slower kinetics of An(III) extraction by EH-BTzPhen as compared to $CyMe_4BTPhen$ is linked to the higher basicity of the 1,2,3-triazole rings compared to 1,2,4 triazines. Even when the acid concentration in the organic phase is not sufficient to cause a complete aggregation of the protonated EH-BTzPhen molecules (manifesting in visible precipitation) there might be a lower degree of association/supramolecular organization caused by an intermolecular *H*-bond network. In that case, not the single EH-BTzPhen molecules are the diffusing entities, but larger number of them, held together by a *H*-bond network. In liquids, according to the Stokes-Einstein equation the radius of the diffusing entity is inversely proportional to the diffusion coefficient. Thus the increase of diffusion coefficient of the extractant, caused by association via *H*-bonds can be the reason for the observed slow extraction kinetics.

The distribution ratios for $^{241}Am(III)$ and $^{244}Cm(III)$ reached values up to $D_{Am} = (20\pm3)$, $D_{Cm} = (8\pm1)$, respectively, while $^{152}Eu(III)$ distribution ratios reached values up to $D_{Eu} = (0.307\pm0.003)$. This is a factor of about 20 lower for An(III) and a factor of 6 lower for $^{152}Eu(III)$ compared to the 1-octanol diluent. In addition, the $^{241}Am(III)/^{152}Eu(III)$ separation factors were lower in the case of the ionic liquid based solvent ($SF_{Am/Eu} \sim 70$ compared to $SF_{Am/Eu} \sim 200$ in 1-octanol). These separation factors are similar to the one reported by Muller and Nash using EH-BTzBP in combination with 2-bromohexanoic acid in toluene.[26]

The equilibrium $^{241}Am(III)/^{152}Eu(III)$ separation factor of $SF_{Am/Eu} \approx (70 \pm 20)$ reached promising values for a minor actinide separation process. These distribution ratios are significantly lower, compared to those obtained with 0.01 mol L^{-1} $CyMe_4BTPhen$ in

[A336][NO_3]: D_{Am} (1000±250), D_{Cm} ~ (670±160), D_{Eu} = (9.9±0.2), while the Am/Eu separation factor is similar: $SF_{Am/Eu}$ = (100±30). The lower distribution ratios in general might be an advantage for back-extraction of the An(III) from the loaded organic phase.

The ^{241}Am(III)/^{244}Cm(III) separation factor was between 2.1 – 3.5 throughout the investigated contact time (Figure 3), thus slightly higher than in the case of the first solvent (0.01 mol L^{-1} EH-BTzPhen and 1 mol L^{-1} 2-bromohexanoic acid in 1-octanol). The change of the triazinyl rings to 1,2,3-triazolyl rings thus lead to a slight increase of Am(III)/Cm(III) separation factors compared to $CyMe_4$BTPhen extractant in [A336][NO_3] which typically shows a $SF_{Am/Cm}$ 1.4 – 1.8 at equilibrium and higher values under non-equilibrium conditions. In the case of EH-BTzPhen, it seems no such difference exists between the $SF_{Am/Cm}$ at shorter or longer extraction times. From this it is hypothesized, that the higher $SF_{Am/Cm}$ are related to the slightly stronger interaction between the triazole donating *N*-atoms and Am(III) as compared to the interaction with Cm(III).

The effect of NH_4NO_3 concentration on the distribution ratios of ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) was tested at 110 h equilibration time (Figure 4). The distribution ratios increased with increasing NH_4NO_3 concentration. In general, the ^{241}Am(III)/(III) and Am(III)/Cm(III) selectivity remained constant over the range of NH_4NO_3 concentration (disregarding some fluctuations that are presumably caused by measurement uncertainties). The increase of distribution ratios as a function of the nitrate concentration suggests that nitrate ions are serving as counter ions in the extracted complex. The exact extraction mechanism cannot be determined solely on the basis of solvent extraction experiments.

In our efforts to develop a new, more performant tetradentate *N*-donor extractant molecule, the EH-BTzPhen was synthesized and subject to basic solvent extraction screening. During these screening studies the molecule displayed unfortunately important disadvantages, such as incompatibility with higher nitric acid concentrations and very slow extraction kinetics, indicating that its application in continuous processes will not be feasible using the investigated solvent composition and extraction parameters. Therefore, more advanced extractions studies (e.g. effect of acidity, temperature, ligand concentration) were not relevant and thus not performed. Notwithstanding these disadvantages, the interesting Am/Cm and Am/Eu separation factors supports further work on triazole-modified phenanthrolines to overcome the current issues.

4. Conclusions

As conclusion, the newly synthesized lipophilic tetradentate, CHON-compliant soft-donor extractant EH-BTzPhen was found to provide interesting selectivity for An(III) over Eu(III) at low acidities. The compound is soluble in both 1-octanol and [A336][NO_3]. The extraction of Am(III) and Cm(III) was possible in 1-octanol with the combined use of 2-bromohexanoic acid synergist. When [A336][NO_3] is used as diluent, extraction of An(III) is feasible without the presence of synergist, although with slow extraction kinetics at 22 °C. The extractant formed a precipitate in contact with highly acidic feed solutions. The modulation of the electron density on two of the nitrogen atoms in the complexing cavity (e.g. by replacing 1,2,4-triazinyl with 1,2,3-triazol moieties) of $CyMe_4$BTPhen retained the Am/Cm and Am/Eu selectivities, but at lower distribution ratios (beneficial for back-extraction), which might be exploited in further work involving modified 5-membered heterocycle moieties crafted on bipyridine or phenanthroline backbone. The use of CHON-compatible, non-flammable

[A336][NO_3] as a diluent for the EH-BTzPhen allowed the extraction of An(III) ions without the addition of a synergist. This latter finding might be of interest for further research on complexants that proved to be effective only in the presence of 2-bromohexanoic acid or similar synergists.

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Supplemental online material

Supplementary data [^{1}H and ^{13}C-NMR spectra of the EH-BTzPhen] are available online.

Figure 1. Chemical structures of the copounds used in this study. [A336][NO_3] is represented by its main component, tri-n-octylmethylammonium nitrate ([N_{1888}][NO_3]). Two additional soft donor extractants, $CyMe_4BTPhen$ and $CyMe_4BTBP$ are represented

to facilitate comparison of the structures. The numbering of nitrogen atoms in the triazynil rings are indicated for the sake of ease.

Figure 2. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm separation factors as a function of equilibration time. Extraction conditions: T = 22 ± 1 °C; 2060 rpm; a/o = 1/1; organic phase 0.01 mol L^{-1} EH-BTzPhen + 1 mol L^{-1} 2-bromohexanoic acid in 1-octanol, Aqueous phase: pH = 3; 1 mol L^{-1} NH_4NO_3, [Ln(III)] = 10^{-5} mol L^{-1} each.

Figure 3. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm separation factors as a function of equilibration time**.** Extraction conditions: *T* = 22 ± 1 °C; 2060 rpm; a/o = 1/1; organic phase 0.01 mol L^{-1} EH-BTzPhen in [A336][NO_3], Aqueous phase: pH = 3; 1 mol L^{-1} NH_4NO_3, [Ln(III)] = 10^{-5} mol L^{-1} each.

Figure 4. Distribution ratios of Am(III), Cm(III) and Eu(III) and Am/Eu and Am/Cm separation factors as a function of nitrate ion concentration. Extraction conditions: *T* = 22 ± 1 °C; 2060 rpm; *t* = 110 h; a/o = 1/1; organic phase 0.01 mol L^{-1} EH-BTzPhen in [A336][NO_3], Aqueous phase: pH = 3; various concentration of NH_4NO_3, [Ln(III)] = 10^{-5} mol L^{-1} each.

Scheme 1. Synthetic pathway towards EH-BTzPhen.

References

1. H. H. Anderson and L. B. Asprey, US Pat. 2,924,506, **1960**.
2. R. J. Taylor, C. R. Gregson, M. J. Carrott, C. Mason and M. J. Sarsfield, *Solv. Extr. Ion Exch.*, 2013, **31**, 442-462.
3. H. Chen, R. J. Taylor, M. Jobson, D. A. Woodhead, C. Boxall, A. J. Masters and S. Edwards, *Solv. Extr. Ion Exch.*, 2017, **35**, 1-18.
4. C. Poinssot, S. Bourg, S. Grandjean and B. Boullis, *Procedia Chem.*, 2016, **21**, 536-544.
5. D. Greneche, B. Quiniou, L. Boucher, M. Delpech, E. Gonzalez, F. Alvarez, M. A. Cuñado, G. Serrano, J. L. Cormenzana, W. Kuckshinrichs, R. Odoj, W. von Lensa, J. Wallenius, D. Westlén, C. Zimmermann and J. Marivoet, *RED-IMPACT Impact of Partitioning, Transmutation and Waste Reduction Technologies on the Final Nuclear Waste Disposal*, Forschungszentrum Jülich GmbH Institut für Energieforschung (IEF) Sicherheitsforschung und Reaktortechnik (IEF-6), Jülich, Germany, 2008.
6. P. J. Panak and A. Geist, *Chem. Rev.*, 2013, **113**, 1199-1236.
7. F. W. Lewis, M. J. Hudson and L. M. Harwood, *Synlett*, 2011, **18**, 2609-2632.

8. Z. Kolarik, *Chem. Rev*, 2008, **108**, 4208-4252.
9. M. G. B. Drew, M. R. S. J. Foreman, A. Geist, M. J. Hudson, F. Marken, V. Norman and M. Weigl, *Polyhedron*, 2006, **25**, 888-900.
10. A. Geist, C. Hill, G. Modolo, M. R. S. J. Foreman, M. Weigl, K. Gompper and M. J. Hudson, *Solv. Extr. Ion Exch.*, 2006, **24**, 463-483.
11. A. Wilden, C. Schreinemachers, M. Sypula and G. Modolo, *Solv. Extr. Ion Exch.*, 2011, **29**, 190-212.
12. D. Magnusson, B. Christiansen, M. R. S. Foreman, A. Geist, J. P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy and C. Sorel, *Solv. Extr. Ion Exch.*, 2009, **27**, 97-106.
13. M. G. B. Drew, M. R. S. J. Foreman, C. Hill, M. J. Hudson and C. Madic, *Inorg. Chem. Commun.*, 2005, **8**, 239-241.
14. F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T. H. Vu and J. P. Simonin, *J. Am. Chem. Soc.*, 2011, **133**, 13093-13102.
15. S. Lange, A. Wilden, G. Modolo, F. Sadowski, M. Gerdes and D. Bosbach, *Solv. Extr. Ion Exch.*, 2017, **35**, 161-173.
16. E. Buncel and I.-H. Um, *Tetrahedron*, 2004, **60**, 7801-7825.
17. G. Klopman, *Tetrahedron*, 1970, **26**, 4549-4554.
18. J. Clayden, N. Greeves and S. Warren, *Organic chemistry*, Oxford : Oxford University Press, 2nd edn., 2012.
19. M. J. Hudson, L. M. Harwood, D. M. Laventine and F. W. Lewis, *Inorg. Chem.*, 2013, **52**, 3414-3428.
20. P. Zsabka, K. Van Hecke, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans and T. Cardinaels, *Solv. Extr. Ion Exch.*, 2020, **38**, 194-211.
21. E. Mossini, E. Macerata, A. Wilden, P. Kaufholz, G. Modolo, N. Iotti, A. Casnati, A. Geist and M. Mariani, *Solv. Extr. Ion Exch.*, 2018, **36**, 373-386.
22. E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.-C. Charbonnel, F. Sansone, A. Arduini and A. Casnati, *J. Am. Chem. Soc.*, 2016, **138**, 7232-7235.
23. Z. Kolarik, U. Müllich and F. Gassner, *Solv. Extr. Ion Exch.*, 1999, **17**, 23-32.
24. A. Geist, U. Müllich, D. Magnusson, P. Kaden, G. Modolo, A. Wilden and T. Zevaco, *Solv. Extr. Ion Exch.*, 2012, **30**, 433-444.
25. A. C. Edwards, P. Mocilac, A. Geist, L. M. Harwood, C. A. Sharrad, N. A. Burton, R. C. Whitehead and M. A. Denecke, *Chem. Commun.*, 2017, **53**, 5001-5004.
26. J. M. Muller and K. L. Nash, *Solv. Extr. Ion Exch.*, 2016, **34**, 322-333.
27. P. Zsabka, K. Van Hecke, L. Adriaensen, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans and T. Cardinaels, *Solv. Extr. Ion Exch.*, 2018, **36**, 519-541.
28. P. Zsabka, K. Van Hecke, A. Wilden, G. Modolo, M. Hupert, V. Jespers, S. Voorspoels, M. Verwerft, K. Binnemans and T. Cardinaels, *Solv. Extr. Ion Exch.*, 2020, **38**, 212-235.
29. N. T. Coogan, M. A. Chimes, J. Raftery, P. Mocilac and M. A. Denecke, *J. Org. Chem.*, 2015, **80**, 8684-8693.
30. M. C. Nielsen, A. F. Larsen, F. H. Abdikadir and T. Ulven, *Eur. J. Med. Chem.*, 2014, **72**, 119-126.
31. A. Ossola, E. Macerata, E. Mossini, M. Giola, M. C. Gullo, A. Arduini, A. Casnati and M. Mariani, *J. Radioanal. Nucl. Chem.*, 2018, **318**, 2013-2022.

32. J.-L. M. Abboud, C. Foces-Foces, R. Notario, R. E. Trifonov, A. P. Volovodenko, V. A. Ostrovskii, I. Alkorta and J. Elguero, *Eur. J. Org. Chem.*, 2001, **16**, 3013-3024.
33. V. Ji Ram, A. Sethi, M. Nath and R. Pratap, in *The Chemistry of Heterocycles*, eds. V. Ji Ram, A. Sethi, M. Nath and R. Pratap, Elsevier, 2019, DOI: https://doi.org/10.1016/B978-0-08-101033-4.00005-X, pp. 149-478.
34. A. R. Katritzkyt and A. F. Pozharskii, *Handbook of Heterocyclic Chemistry*, Pergamon Press, Oxford, Second edn., 2000.
35. J. M. Muller, S. S. Galley, T. E. Albrecht-Schmitt and K. L. Nash, *Inorg. Chem.*, 2016, **55**, 11454-11461.