

*Separation of the minor actinides americium(III) and curium(III) by hydrophobic and hydrophilic BTPPhen ligands: exploiting differences in their rates of extraction and effective separations at equilibrium*

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# Separation of the Minor Actinides Americium(III) and Curium(III) Using Differences in their Rates of Extraction by Bis-(1,2,4-triazin-3-yl)phenanthrolines

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## RECEIVED DATE

Separation of Am(III) and Cm(III)

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ABSTRACT. The complexation and extraction of the adjacent minor actinides Am(III) and Cm(III) by both hydrophobic and hydrophilic pre-organized 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPPhen) ligands has been studied in detail. It has been shown that Am(III) is

extracted more rapidly than Cm(III) by the hydrophobic CyMe<sub>4</sub>-BTPhen ligand into different organic diluents under non-equilibrium extraction conditions, leading to separation factors for Am over Cm ( $SF_{Am/Cm}$ ) as high as 7.9. Furthermore, the separation of Am(III) from Cm(III) can be tuned through careful choice of the extraction conditions (organic diluent, contact time, mixing speed, ligand concentration). This ‘kinetic’ effect is attributed to the higher presumed kinetic lability of the Am(III) aqua complex towards ligand substitution. A dependence of the Am(III)/Cm(III) selectivity on the structure of the alkyl groups attached to the triazine rings is also observed, and BTPHens bearing linear alkyl groups are less able to separate Am(III) from Cm(III) than CyMe<sub>4</sub>-BTPhen. Under equilibrium extraction conditions, hydrophilic tetrasulfonated BTPhen ligands complex selectively Am(III) over Cm(III) and prevent the extraction of Am(III) from nitric acid by the hydrophobic *O*-donor ligand *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), giving separation factors for Cm(III) over Am(III) ( $SF_{Cm/Am}$ ) of up to 4.6. These results further underline the utility of the BTPhen ligands for the extremely challenging separation of the chemically similar minor actinides Am(III) and Cm(III) in future processes to close the nuclear fuel cycle.

Keywords: Americium, 1,2,4-Triazine, Curium, Separation, Kinetic Effect, BTPhen Ligand.

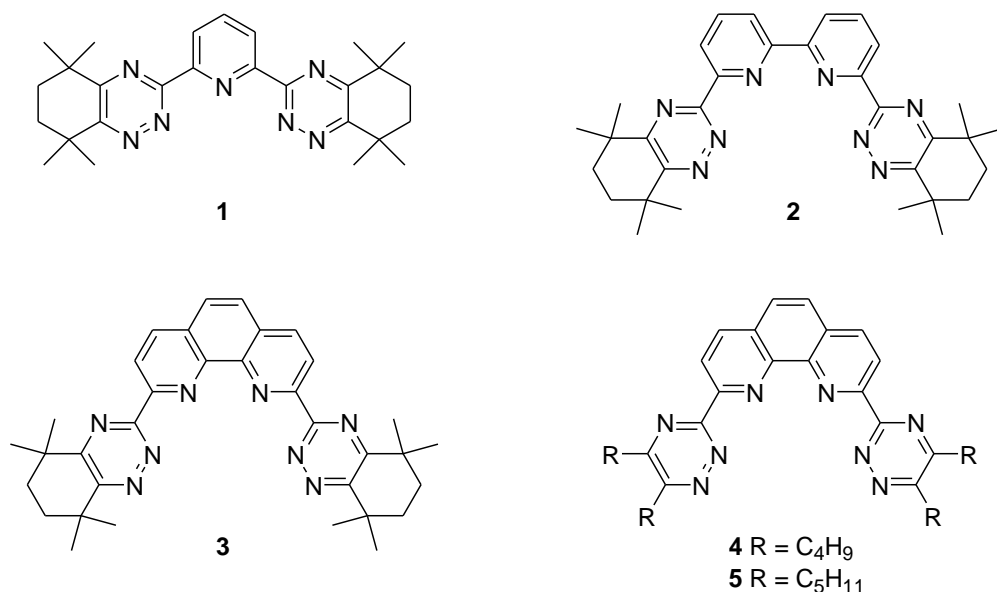
## Introduction

Spent nuclear fuel from power plants is comprised of uranium (ca. 94 %), plutonium (ca. 1 %), fission and corrosion products, including the lanthanides (ca. 5 %), and the trans-uranic minor actinides americium, curium and neptunium (ca. 0.1 %). The PUREX process has been in industrial operation since the 1950s and removes the bulk of the uranium and plutonium from spent fuel.<sup>1</sup> However, the minor actinides americium, curium and neptunium remain in the post-

PUREX raffinate and they account for much of its long-lived radiotoxicity (*ca.* 10,000 years) and heat load. Removing these elements is therefore considered a major objective in future strategies for the reprocessing of spent nuclear fuel.<sup>2</sup> As well as reducing the volume of waste that needs to be vitrified and stored in deep geological repositories, removal of the minor actinides would also greatly reduce the heat load and radiotoxicity of the remaining waste (to *ca.* 300 years to decay to the levels of natural uranium). A key strategy for spent nuclear fuel reprocessing is the ‘Partitioning and Transmutation’ (P&T) strategy.<sup>3</sup> In this strategy, the minor actinides are first separated from the lanthanides and other fission products, and then transmuted to shorter-lived radionuclides or stable non-radioactive elements by high energy neutron bombardment in advanced nuclear reactors or dedicated (accelerator-driven) transmuters. The minor actinides must first be separated from the lanthanides due to the high neutron affinity of the latter, which would preferentially absorb the neutrons, interfere with the chain-reaction in the reactor/transmuter, suppress the transmutation of the minor actinides, and generate additional radioactive waste.

In recent years, many soft *N*-heterocycles have been studied to carry out the challenging separation of the trivalent actinides from the chemically similar trivalent lanthanides in a solvent extraction process.<sup>4</sup> Despite the similar chemical properties of the trivalent actinides and lanthanides, *N*-donor ligands containing lateral 1,2,4-triazine rings (bis-(1,2,4)-triazine ligands) are able to perform this difficult separation. 2,6-Bis(1,2,4-triazin-3-yl)pyridines (BTPs), 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs) and 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthrolines (BTPhens) have emerged as the ligands of choice for this separation. The hydrophobic bis-(1,2,4)-triazine ligands CyMe<sub>4</sub>-BTP **1**, CyMe<sub>4</sub>-BTBP **2** and CyMe<sub>4</sub>-BTPhen **3** (Figure 1) have become the most promising ligands for this separation to date, and are all able to

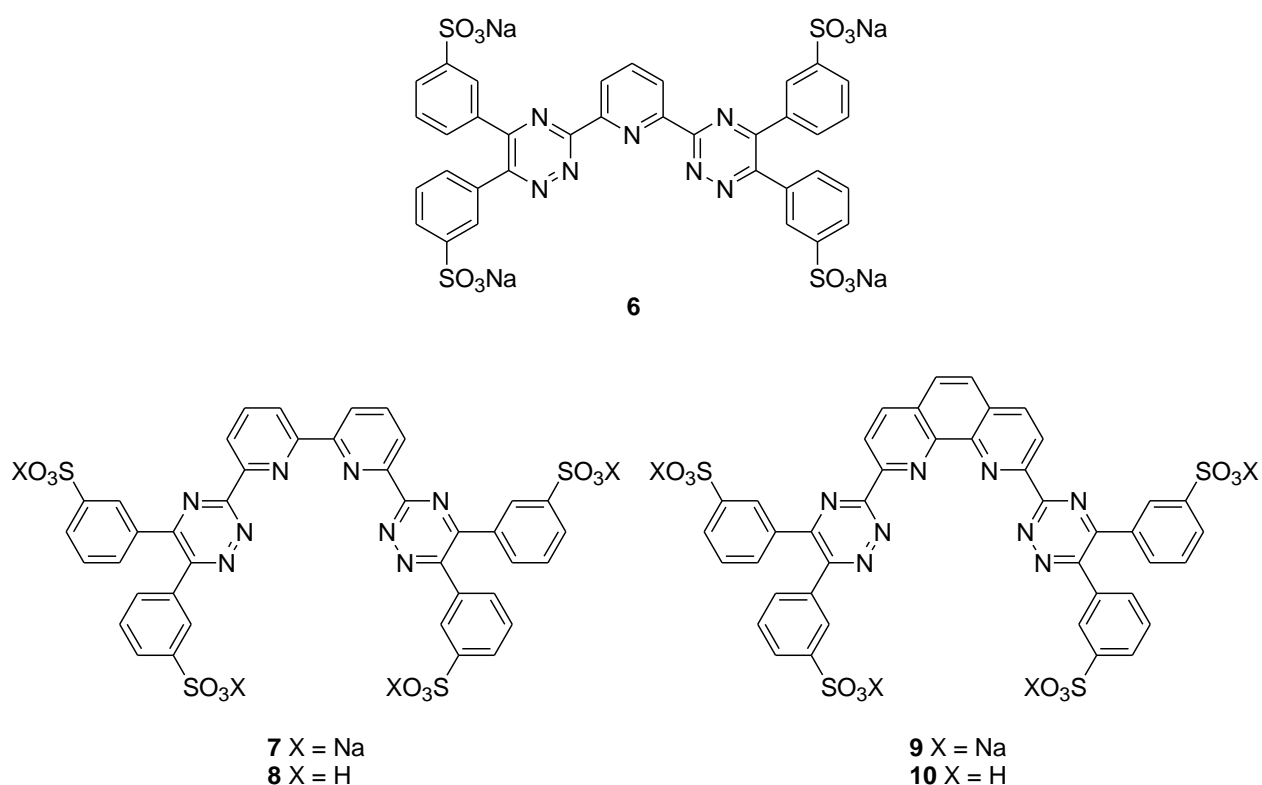
separate the minor actinides Am(III) and Cm(III) from the lanthanides via selective extraction of the actinides from aqueous nitric acid into an organic phase with very high selectivities. CyMe<sub>4</sub>-BTBP **2** has been applied successfully in a number of post-PUREX laboratory-scale selective actinide extraction (or ‘SANEX’) processes and is thus the current reference ligand for selective actinide extraction in Europe.<sup>5</sup> More recently, pre-organized BTPPhen ligands such as CyMe<sub>4</sub>-BTPPhen **3** have shown much improved extraction kinetics compared to CyMe<sub>4</sub>-BTBP **2**.<sup>6</sup>



**Figure 1.** Hydrophobic bis-1,2,4-triazine ligands **1–5** for selective actinide extraction.

An alternative approach to the separation of the minor actinides from the lanthanides via selective actinide extraction into an organic phase has been proposed. This approach is based on the ‘TALSPEAK’ process, which was developed at Oak Ridge National Laboratory in the United States in the 1960s.<sup>7</sup> In this process, the minor actinides and lanthanides are first co-extracted into an organic phase using a non-selective oxygen donor ligand, and the minor actinides are then selectively back-extracted into an aqueous phase using an actinide-selective hydrophilic ligand. In a recent improvement to this process, hydrophilic tetrasulfonated bis-(1,2,4)-triazine

ligands such as BTP **6**, BTBPs **7** and **8**, and BTPhens **9** and **10** (Figure 2) were developed as actinide-selective aqueous complexing agents.<sup>8</sup> These ligands are able to complex the trivalent minor actinides in nitric acid solutions and prevent their extraction by the non-selective hydrophobic ligand *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), resulting in highly efficient separations of Am(III) and Cm(III) from the lanthanides. Recently, tetrasulfonated BTP **6** was successfully employed in a new European laboratory-scale minor actinide separation process based on the TALSPEAK concept.<sup>9</sup>



**Figure 2.** Hydrophilic tetrasulfonated bis-1,2,4-triazine ligands **6–10** for selective actinide aqueous complexation.

After the separation of the trivalent minor actinides from the trivalent lanthanides, one further option in the P&T strategy is to separate Am(III) from Cm(III). This separation is desirable since Am(III) makes a greater contribution to the long term radiotoxicity and heat load than does

Cm(III), and it is easier to fabricate into fuel and more easily transmuted in a reactor.<sup>10</sup> For these reasons, it is desirable to develop a process that separates Am(III) from Cm(III) by selective extraction of only Am(III) into an organic phase. However, the separation of Am(III) from Cm(III) is even more challenging than the separation of Am(III)/Cm(III) from the trivalent lanthanides, as americium and curium are neighboring elements in the actinide series. Thus the very similar chemistries of these adjacent elements render this separation one of the most challenging in the partitioning and transmutation approach.<sup>11</sup> Am(III) has the electronic configuration  $[\text{Rn}]5f^6$  whereas Cm(III) has the configuration  $[\text{Rn}]5f^7$ . Both ions have very similar ionic radii for their 9-coordinate aqua ions (1.122 Å for Am(III) *versus* 1.105 Å for Cm(III)).<sup>12</sup> Both elements exist as trivalent ions in aqueous solution and the metal-ligand bonding in both ions is essentially ionic, but with some covalent contribution to the bonding. The chemical properties of both ions are thus almost identical.

Not surprisingly, very few methods exist for separating Am(III) from Cm(III). The selective extraction of Am(III) by a mixture of a dithiophosphinic acid and a phosphate has been proposed and demonstrated, giving selectivities for Am(III) over Cm(III) of  $\sim 8$ .<sup>13</sup> However, the dithiophosphinic acid extractants are susceptible to hydrolysis and oxidation at low pH. Furthermore, the extractants contain elements other than C, H, O and N, meaning that incineration leads to corrosive products at the end of the process. Selective extraction of Am(III) from PUREX raffinate with a combination of *O*-donor diamide ligands has also been demonstrated.<sup>14</sup> Unfortunately, the process required a large number of stages to separate Am(III) from Cm(III) fully, due to the relatively low selectivity of the system [2.5 times more selective for Am(III)]. Another approach involves selective oxidation of Am(III) to higher oxidation states which have different coordination chemistries and thus different extraction properties to

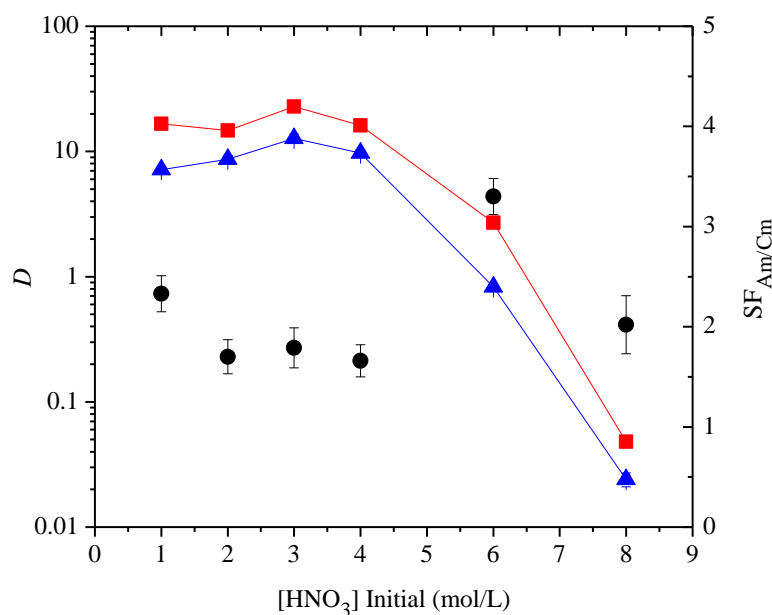


Cm(III).<sup>15</sup> In one such approach, Am(III) was selectively oxidized to Am(V) prior to its separation from Cm(III) by ion exchange chromatography.<sup>16</sup> However, it is difficult to implement this strategy on the scale required for a continuous solvent extraction process. Similarly, Am(III) has been selectively oxidized to Am(VI) prior to its separation from Cm(III) by liquid-liquid extraction.<sup>17</sup> Although the feasibility of this approach was demonstrated at laboratory-scale, the process uses sodium bismuthate as oxidant which is only sparingly soluble in nitric acid; necessitating the need for a filtration step prior to extraction of Am(VI). Recently, the selective complexation of Am(III) over Cm(III) by a crown-ether, based on the slightly larger ionic radius of Am(III) has been suggested, and a selectivity for Am(III) over Cm(III) of 4.1 (based on stability constants) has been reported.<sup>18</sup> We have previously reported that subtle electronic modulation of the BTPPhen ligands with substituents can enhance the inherent selectivity of this ligand system for Am(III) over Cm(III), giving separation factors for Am(III) over Cm(III) ( $SF_{Am/Cm}$ ) as high as 7.<sup>19</sup> We now report herein a full account of our studies on the separation of Am(III) from Cm(III) using both hydrophobic and hydrophilic bis-(1,2,4)-triazine ligands, and we demonstrate that feasible separations of Am(III) from Cm(III) can be achieved under different sets of conditions using both families of ligands, particularly when not working at equilibrium. We also discuss the likely underlying fundamental reasons for the selectivities that we observe.

## Results and Discussion

**Separation of Am(III) from Cm(III) by hydrophobic ligands in 1-octanol.** In our previous report on the separation of Am(III) from Eu(III) by CyMe<sub>4</sub>-BTPPhen **3** using 1-octanol as the diluent, we studied the co-extraction of Am(III) and Cm(III) under conditions that were designed to lower the *D* values of both metals to allow for easier back-extraction in the stripping step.<sup>XX</sup>

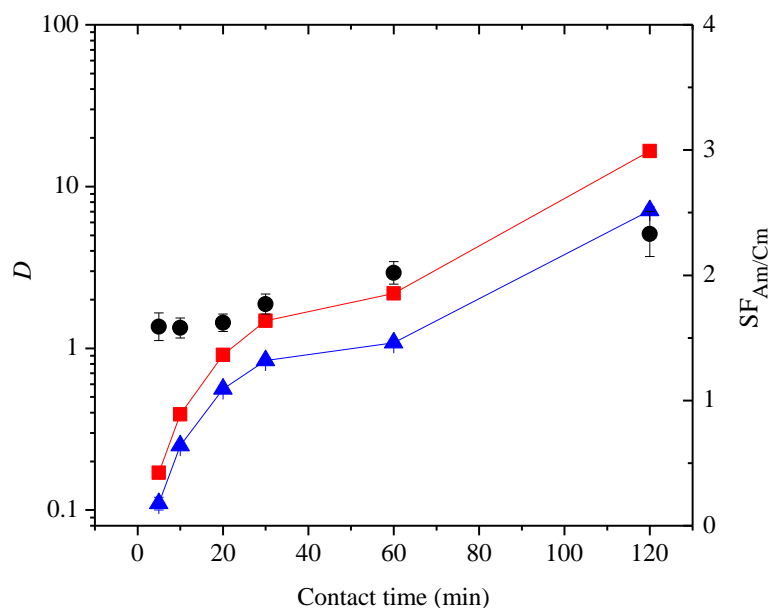
NEED A REFWe thus decided to vary the conditions systematically (nitric acid concentration, ligand concentration, diluent composition) in order to obtain a broader picture of the ability of CyMe<sub>4</sub>-BTPPhen **3** to separate Am(III) from Cm(III) under equilibrium conditions using 1-octanol as the diluent. The extraction of Am(III) and Cm(III) from nitric acid solutions into 1-octanol by CyMe<sub>4</sub>-BTPPhen **3** is presented in Figure 3. A lower ligand concentration was used here (1 mM) than that previously reported<sup>xx</sup> so that the *D* values measured would be lower and thus more precise.



**Figure 3.** Selective extraction of Am(III) over Cm(III) from nitric acid by solutions of CyMe<sub>4</sub>-BTPPhen **3** in 1-octanol (0.001 M) as a function of the initial nitric acid concentration of the aqueous phase (■ = *D*<sub>Am</sub>, ▲ = *D*<sub>Cm</sub>, ● = SF<sub>Am/Cm</sub>, contact time = 2 hours at 1800 rpm, T = 22 °C).

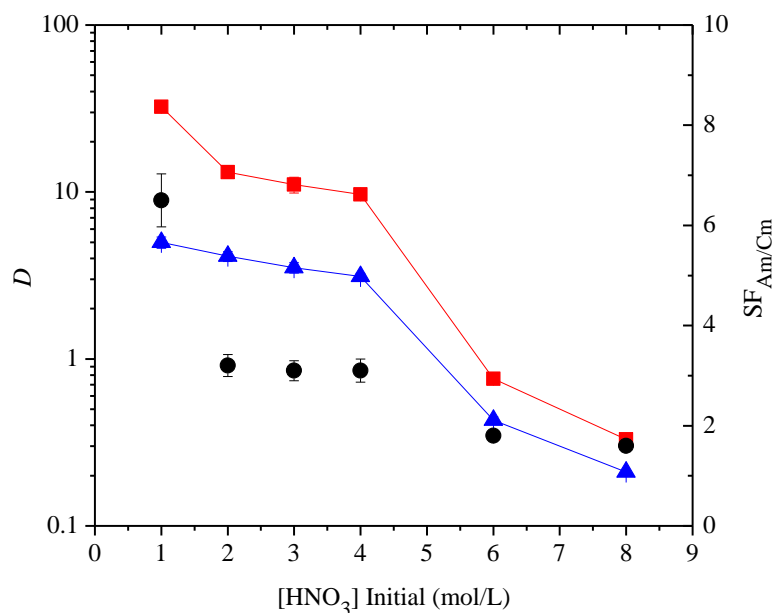
As shown, the *D* values for Am(III) are slightly larger than those for Cm(III), but there is no significant selectivity for Am(III) over Cm(III) under these conditions. The maximum separation factor for Am(III) over Cm(III) (SF<sub>Am/Cm</sub>) is found to be 3.3 in 6 M HNO<sub>3</sub>. However, even with

this modest selectivity, a feasible separation of Am(III) and Cm(III) could be achieved by liquid-liquid extraction under these conditions as  $D_{Am} > 1$  and  $D_{Cm} < 1$  HMMMM – ONLY JUST – PROBABLY STRESS THE TOLERANCE IS TOO CLOSE – MAKES THE KINETIC RESULTS LOOK BETTER. We also examined the separation of Am(III) from Eu(III) under these conditions and found that the maximum separation factor for Am(III) over Eu(III) was also found at this acidity ( $SF_{Am/Eu} = 338$  in 6 M  $HNO_3$ , see Supporting Information). We also studied the extraction of Am(III) and Cm(III) from 1 M  $HNO_3$  by CyMe<sub>4</sub>-BTPhen **3** as a function of contact time, and found that equilibrium was achieved within 2 hours of phase mixing using a Heidolph Multi Reax shaker at 1,800 rpm. The variation in  $SF_{Am/Cm}$  with contact time is shown in Figure 4.



**Figure 4.** Selective extraction of Am(III) over Cm(III) from 1 M nitric acid by solutions of CyMe<sub>4</sub>-BTPhen **3** in 1-octanol (0.001 M) as a function of contact time (■ =  $D_{Am}$ , ▲ =  $D_{Cm}$ , ● =  $SF_{Am/Cm}$ , mixing at 1800 rpm, T = 22 °C).

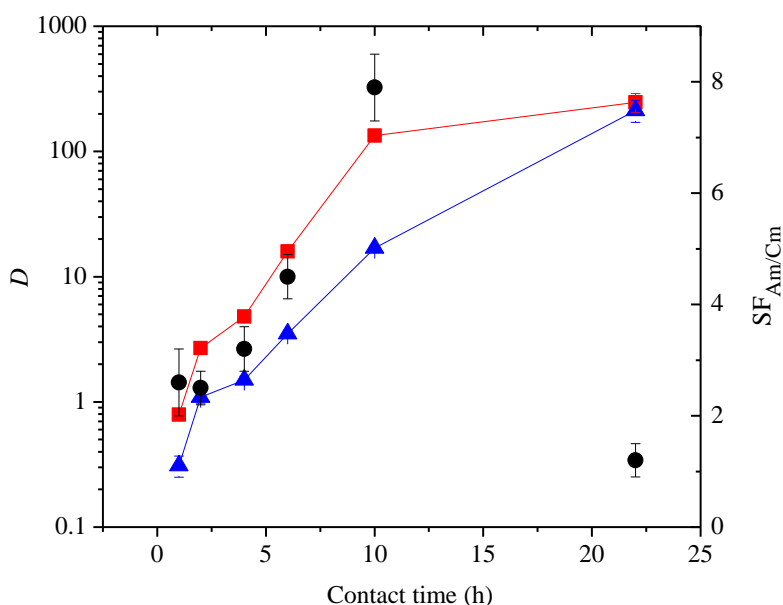
In our previous work on CyMe<sub>4</sub>-BTPPhen **3**, we studied 1-octanol/toluene mixtures as the organic phase and found a significant selectivity for Am(III) over Cm(III) under certain conditions ( $SF_{Am/Cm} = 4.0$ . Organic phase: 0.01 M CyMe<sub>4</sub>-BTPPhen **3** in 1-octanol/toluene (40:60); Aqueous phase: 4.0 M HNO<sub>3</sub>).<sup>XX</sup> We therefore decided to probe the separation of Am(III) from Cm(III) in this solvent system more deeply in order to see if this selectivity could be replicated. The extraction of Am(III) and Cm(III) into 1-octanol/toluene (40:60) as a function of [HNO<sub>3</sub>] is shown in Figure 5. Although these conditions are not identical to those reported in our previous work (longer contact time, slower orbital shaker), a significantly high selectivity for Am(III) over Cm(III) was again observed; this time in the extraction from 1 M HNO<sub>3</sub> ( $SF_{Am/Cm} = 6.5$ ). The selectivity for Am(III) over Cm(III) found at 4 M HNO<sub>3</sub> ( $SF_{Am/Cm} = 3.1$ ) is slightly lower than that reported previously.<sup>XX</sup> The selectivity observed at 1 M HNO<sub>3</sub> would be more than sufficient for a feasible separation of Am(III) from Cm(III) provided that  $D_{Am} > 1$  and  $D_{Cm} < 1$ . We also briefly looked at the separation of Am(III) from Eu(III) under these conditions and found that an efficient separation of Am(III) from Eu(III) could be achieved in 1 M HNO<sub>3</sub> (see Supporting Information). Unfortunately, when the concentration of CyMe<sub>4</sub>-BTPPhen **3** was lowered to 0.001 M (ie: to bring the  $D$  values down), the selectivity for Am(III) over Cm(III) at 1 M HNO<sub>3</sub> decreased to 2.7 (see Supporting Information).



**Figure 5.** Selective extraction of Am(III) over Cm(III) from nitric acid by 0.01 M solutions of CyMe<sub>4</sub>-BTPhen **3** in 1-octanol/toluene (40:60) as a function of the initial nitric acid concentration of the aqueous phase ( $\blacksquare = D_{Am}$ ,  $\blacktriangle = D_{Cm}$ ,  $\bullet = SF_{Am/Cm}$ , contact time = 6 hours at 250 rpm, T = 22 °C).

We then measured the variation in the extraction of Am(III) and Cm(III) with contact time to check if the extraction system was at equilibrium. The extraction of Am(III) and Cm(III) from 2.4 M HNO<sub>3</sub> by CyMe<sub>4</sub>-BTPhen **3** in octanol/toluene (40:60) at different contact times is presented in Figure 6. It can be seen that the  $D$  values were still increasing after 6 hours of contact, and thus equilibrium had not been reached. Equilibrium extraction of Am(III) and Cm(III) was not achieved even after 22 hours of phase mixing under these conditions. This is partially due to the slow shaking speed used in the extraction experiments (250 rpm). Thus it became apparent that the selectivity observed above in Figure 5 was thus not one that exists at equilibrium, but one that is due to the faster rates of extraction of Am(III) by CyMe<sub>4</sub>-BTPhen **3**

than Cm(III) and is therefore a kinetic effect. Nevertheless, a very promising separation factor for Am(III) over Cm(III) of 7.9 was observed after 10 hours of phase contact (Figure 6).

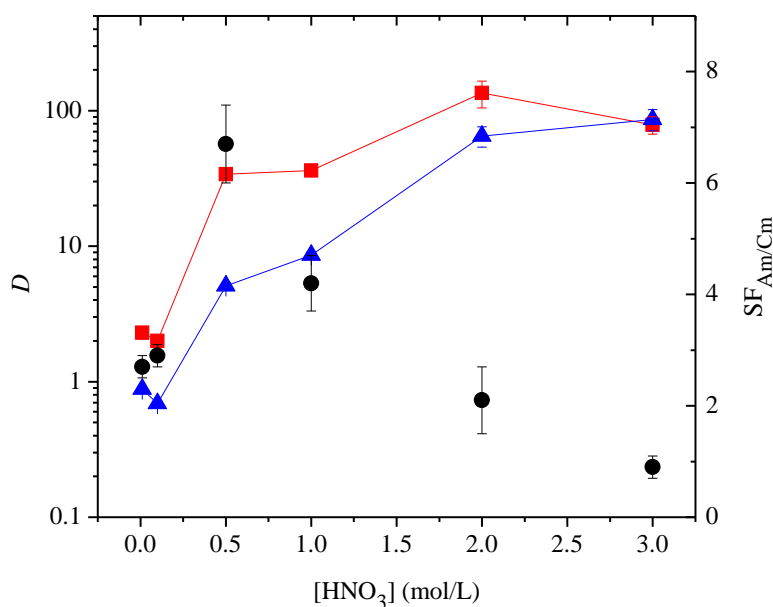


**Figure 6.** Selective extraction of Am(III) over Cm(III) from 2.4 M nitric acid by 0.005 M solutions of CyMe<sub>4</sub>-BTPhen **3** in 1-octanol/toluene (40:60) as a function of contact time (■ =  $D_{Am}$ , ▲ =  $D_{Cm}$ , ● =  $SF_{Am/Cm}$ , mixing at 250 rpm, T = 22 °C).

In a further set of kinetics experiments, we reduced the concentration of CyMe<sub>4</sub>-BTPhen **3** to 0.001 M in order to reduce the  $D$  values observed in Figure 6, and changed the shaking speed to 1,800 rpm (Heidolph Multi Reax orbital shaker) to achieve more intensive phase mixing. Under these conditions, equilibrium extraction of Am(III) and Cm(III) was reached after 6 hours of shaking, and a maximum selectivity for Am(III) over Cm(III) was observed after 20 minutes of contact ( $SF_{Am/Cm} = 4.0$ , see Supporting Information). As above, a trend of first increasing  $SF_{Am/Cm}$  values, then decreasing  $SF_{Am/Cm}$  values with contact time was found, supporting the proposal that the selectivity of CyMe<sub>4</sub>-BTPhen **3** for Am(III) over Cm(III) arises due to the

faster rates of extraction of Am(III) by the ligand. We also measured the separation of Am(III) from Eu(III) by CyMe<sub>4</sub>-BTPhen **3** under these conditions and found that a highly effective separation of Am(III) from Eu(III) was achieved at the lower ligand concentration of 0.001 M, in agreement with our previous work.<sup>xx</sup> Under these conditions,  $D_{Am} > 1$ ,  $D_{Eu} < 1$  and  $SF_{Am/Eu}$  of up to 228 was found (see Supporting Information). Confirmation that Eu(III) was being extracted as a 1:2 M:L complex was obtained by measuring the dependence of  $\log D_{Eu}$  on  $\log [CyMe_4-BTPhen \text{ 3}]$ , which gave a straight line with a slope of 1.9 ( $R^2 = 0.9998$ , see Supporting Information), in agreement with our previous results.<sup>xx</sup> REF NEEDED

**Separation of Am(III) from Cm(III) by hydrophobic ligands in cyclohexanone.** Having studied the separation of Am(III) from Cm(III) by CyMe<sub>4</sub>-BTPhen **3** in 1-octanol and 1-octanol/toluene mixtures, we next elected to study the extraction of Am(III) and Cm(III) by CyMe<sub>4</sub>-BTPhen **3** using cyclohexanone as the diluent. This diluent has been suggested for processing spent nuclear fuels and has the advantage that extraction equilibrium is achieved much more rapidly than with 1-octanol.<sup>20</sup> The extraction of Am(III) and Cm(III) by CyMe<sub>4</sub>-BTPhen **3** in cyclohexanone as a function of the nitric acid concentration of the aqueous phase is presented in Figure 7.



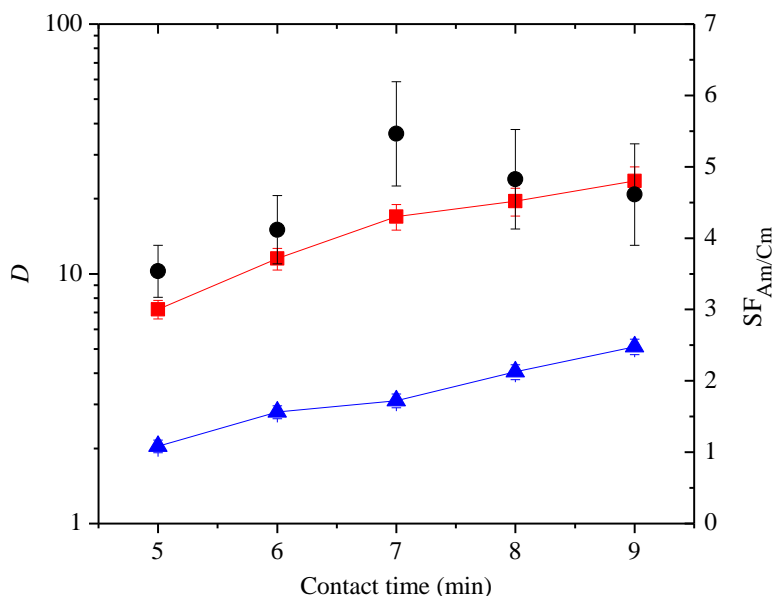
**Figure 7.** Selective extraction of Am(III) over Cm(III) from nitric acid by solutions of CyMe<sub>4</sub>-BTPPhen **3** in cyclohexanone (0.005 M) as a function of the initial nitric acid concentration of the aqueous phase ( $\blacksquare = D_{Am}$ ,  $\blacktriangle = D_{Cm}$ ,  $\bullet = SF_{Am/Cm}$ , contact time = 7 minutes at 250 rpm, T = 22 °C).

As shown, Am(III) is preferentially extracted over Cm(III) across a range of nitric acid concentrations. The highest selectivities for Am(III) over Cm(III) were observed in 0.5 M HNO<sub>3</sub> and in 1.0 M HNO<sub>3</sub>, with separation factors for Am(III) over Cm(III) of 6.7 and 4.2, respectively. These selectivities are comparable to those previously observed with a 5-bromo-substituted BTPPhen ligand in 1-octanol,<sup>Reference 24 in rejected Am/Cm separation paper (ACS Version)</sup> and underline the potential utility of the BTPPhen ligands for the difficult separation of Am(III) from Cm(III).

Having identified the optimum nitric acid concentrations of the aqueous phase, we then examined the influence of contact time on the separation of Am(III) and Cm(III) by CyMe<sub>4</sub>-



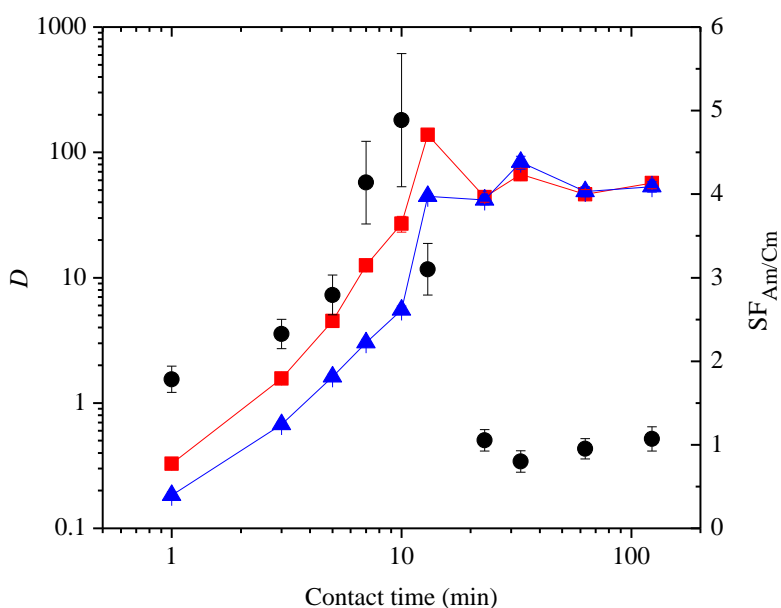
BTPhen **3**. The extraction of Am(III) and Cm(III) from 0.5 M HNO<sub>3</sub> by solutions of **3** in cyclohexanone (0.005 M) as a function of contact time is presented in Figure 8. The distribution ratio for Am(III) rises more rapidly than that of Cm(III) with contact time, resulting in a further enhancement of the separation factor for Am(III) over Cm(III) in the initial stages of extraction. This indicates that Am(III) is extracted more rapidly than Cm(III). A maximum selectivity for Am(III) over Cm(III) was observed after 7 minutes of contact ( $SF_{Am/Cm} = 5.5$ ) and the selectivity for Am(III) over Cm(III) decreased thereafter. Lower selectivities for Am(III) over Cm(III) were observed when the concentration of **3** was 0.001 M ( $SF_{Am/Cm} \leq 2.5$ , see Supporting Information).



**Figure 8.** Selective extraction of Am(III) over Cm(III) from 0.5 M nitric acid by solutions of CyMe<sub>4</sub>-BTPhen **3** in cyclohexanone (0.005 M) as a function of contact time (■ =  $D_{Am}$ , ▲ =  $D_{Cm}$ , ● =  $SF_{Am/Cm}$ , mixing at 250 rpm, T = 22 °C).

We then explored the extraction of Am(III) and Cm(III) from 1 M HNO<sub>3</sub> by solutions of CyMe<sub>4</sub>-BTPhen **3** at longer contact times. The results are shown in Figure 9. Again, Am(III) was more rapidly extracted than Cm(III), and the separation factor for Am(III) over Cm(III) rose to a

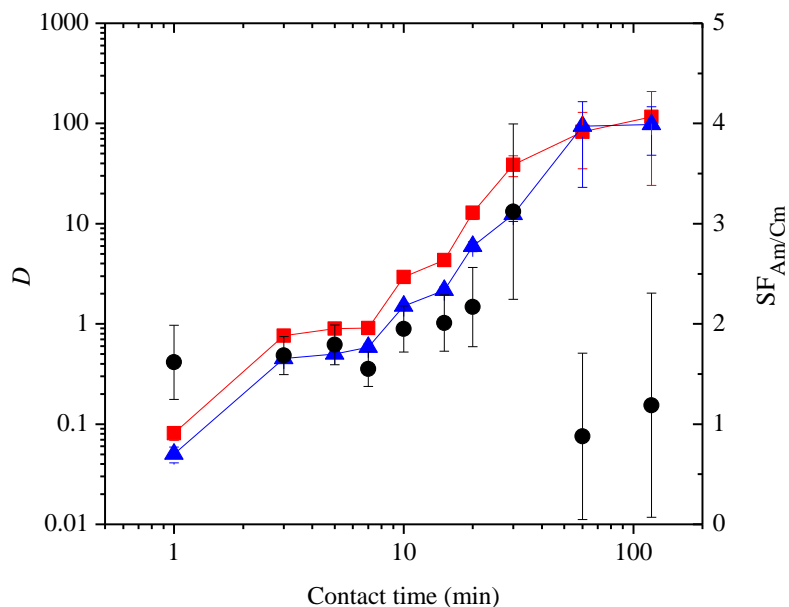
maximum of 4.8 after 10 minutes of contact before decreasing again to 1.0 after 120 minutes of contact (presumably at equilibrium). The initial increase in  $SF_{Am/Cm}$  with contact time was even more pronounced in 1 M  $HNO_3$  than in 0.5 M  $HNO_3$  (Figure 8). Thus the separation of Am(III) from Cm(III) observed here in cyclohexanone appears to be due to a kinetic effect that is emphasised at short contact times. To our knowledge, this is the first time that such a kinetic effect has been demonstrated in the separation of two metal ions by bis-(1,2,4)-triazine ligands.



**Figure 9.** Selective extraction of Am(III) over Cm(III) from 1 M nitric acid by solutions of CyMe<sub>4</sub>-BTPPhen **3** in cyclohexanone (0.005 M) as a function of contact time ( $\blacksquare = D_{Am}$ ,  $\blacktriangle = D_{Cm}$ ,  $\bullet = SF_{Am/Cm}$ , mixing at 250 rpm,  $T = 20 \pm 1$  °C).

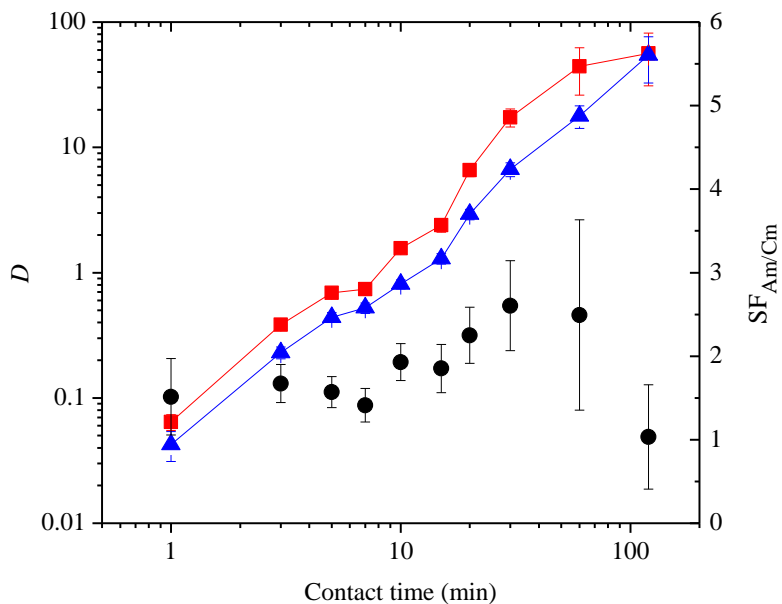
We next studied the previously reported BTPPhen ligands C4-BTPPhen **4**<sup>21</sup> and C5-BTPPhen **5**<sup>Reference 28 in rejected Am/Cm separation paper (ACS Version),<sup>22</sup></sup> to see if this kinetic separation effect was also observed in other BTPPhen ligands. The extraction of Am(III) and Cm(III) from 0.5 M  $HNO_3$  by solutions of C4-BTPPhen **4** in cyclohexanone as a function of contact time is shown in Figure 10.

BTPhen ligand **4** did not show the same kinetic effect at short contact times as CyMe<sub>4</sub>-BTPhen **3**, and was generally not as selective for Am(III) over Cm(III) as **3** ( $SF_{Am/Cm} \leq 3.1$ ).



**Figure 10.** Selective extraction of Am(III) over Cm(III) from 0.5 M nitric acid by solutions of C4-BTPhen **4** in cyclohexanone (0.005 M) as a function of contact time ( $\blacksquare = D_{Am}$ ,  $\blacktriangle = D_{Cm}$ ,  $\bullet = SF_{Am/Cm}$ , mixing at 250 rpm,  $T = 22\text{ }^{\circ}\text{C}$ ).

Similar results were observed with the C5-BTPhen ligand **5** (Figure 11). The separation factor for Am(III) over Cm(III) increased slightly with contact time and reached a maximum value of 2.6 after 30 minutes of phase contact. Thus the initial increase in the separation selectivity for Am(III) over Cm(III) with contact time appears to be dependent on the structure of the alkyl side groups appended to the triazine rings in BTPhen ligands.



**Figure 11.** Selective extraction of Am(III) over Cm(III) from 0.5 M nitric acid by solutions of C5-BTPhen **5** in cyclohexanone (0.005 M) as a function of contact time ( $\blacksquare = D_{Am}$ ,  $\blacktriangle = D_{Cm}$ ,  $\bullet = SF_{Am/Cm}$ , mixing at 250 rpm,  $T = 22\text{ }^{\circ}\text{C}$ ).

The high selectivities for Am(III) over Cm(III) observed above under non-equilibrium conditions with CyMe<sub>4</sub>-BTPhen **3** in 1-octanol or 1-octanol/toluene mixtures at long contact times, or in cyclohexanone at short contact times, could form the basis of an improved process for separating Am(III) from Cm(III) in future spent nuclear fuel reprocessing. Notably, such kinetic separations have been proposed previously for separating similar metal ions, or even isotopes of the same metal ion. The kinetic separation of <sup>235</sup>U(VI) from <sup>238</sup>U(VI) during liquid-liquid extraction, or its sorption onto cation exchangers, has been previously reported,<sup>23</sup> and separation factors for <sup>235</sup>U(VI) over <sup>238</sup>U(VI) of up to 1.01 were achieved. Even with this modest selectivity, the industrial applicability of the isotope separation was demonstrated to be both technologically and economically feasible.<sup>24</sup> The kinetic separation of Co(II) from Ni(II) using

cation exchangers has also been reported, giving separation factors of up to 1.1.<sup>25</sup> A prominent example of the utility of kinetic effects in metal separations is the use of 8-hydroxyquinolines such as the commercially available Kelex 100<sup>®</sup> in hydrometallurgy. These reagents efficiently separate Cu(II) from Fe(III) at short mixing times due to the significantly faster rates of extraction of Cu(II) into organic diluents.<sup>26</sup> The separation selectivities for Am(III) over Cm(III) observed above for CyMe<sub>4</sub>-BTPPhen **3** in both diluent systems (1-octanol and 1-octanol/toluene, and cyclohexanone) are significantly larger than the above values, and compare favorably to those reported previously in other methods proposed for separating Am(III) from Cm(III).<sup>xx-xx</sup>

The exact origin of the above separation of Am(III) from Cm(III) under kinetic conditions is not fully understood at this point. It is well known that the structures and metal:ligand stoichiometries of the Am(III) and Cm(III) complexes formed with a given bis-(1,2,4)-triazine ligand under extraction relevant conditions are identical. The metal–ligand bonding in these complexes is believed to have a significant covalent contribution,<sup>27</sup> and recent experimental evidence from <sup>15</sup>N NMR and TRLFS measurements support this hypothesis.<sup>28</sup> Hydrophobic BTPs form 1:3 metal:ligand complexes with both Am(III) and Cm(III) as revealed by both EXAFS and TRLFS studies, respectively.<sup>29</sup> The average M–N bond lengths in these Am(III) and Cm(III) 1:3 BTP complexes are nearly identical (the slightly higher M–N bond length in the Cm(III) complex is attributed to its slightly smaller ionic radius). Furthermore, differences in extraction selectivity between Cm(III) and Eu(III) are based on the different thermodynamic stabilities of their 1:3 complexes with BTPs, and not on structural differences between their respective complexes.<sup>36,37</sup> The same holds true for the tetradentate bis-(1,2,4)-triazine ligands. Both hydrophobic and hydrophilic BTBPs form 1:2 metal:ligand complexes with Cm(III) and Eu(III) as shown by TRLFS studies.<sup>30</sup> In addition, CyMe<sub>4</sub>-BTPPhen **3** and CyMe<sub>4</sub>-BTBP **2** both

form identical 1:2 complexes with Cm(III) as shown by TRLFS studies,<sup>31</sup> while CyMe<sub>4</sub>-BTBP **2** forms a 1:2 complex with Am(III) as shown by EXAFS studies.<sup>32</sup> A single bidentate nitrate ion completes the inner coordination sphere in the Am(III) and Cm(III) 1:2 complexes of both ligands **2** and **3**, which is in agreement with the solution and solid state structures of the corresponding lanthanide(III) complexes of **2** and **3**.<sup>33</sup> It thus seems likely that in the present study, CyMe<sub>4</sub>-BTPPhen **3** forms structurally identical 1:2 complexes with both Am(III) and Cm(III), and that the kinetic effect observed above is not due to differences in the structures of the extracted complexes. However, it is unclear at this point if the diluent is playing any role in this kinetic effect, for instance through preferential formation of ternary complexes.

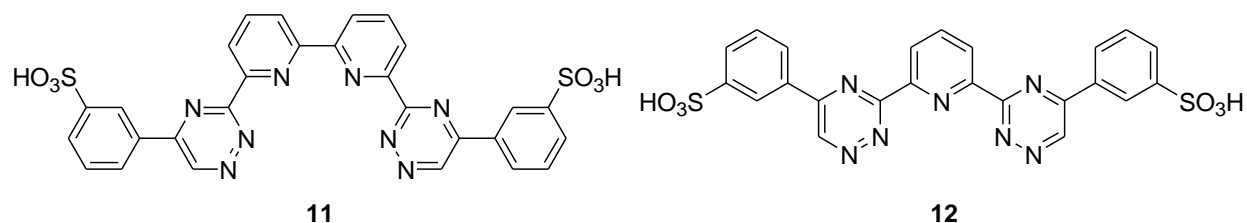
A more likely explanation for the observed kinetic effect is based on differences in the kinetic labilities of the Am(III) and Cm(III) aqua complexes toward ligand substitution. It is well known that the water exchange rate constants of the trivalent lanthanide aqua complexes decrease on going from left to right [from Gd(III) to Yb(III)] across the lanthanide series, in accordance with the decreasing ionic radius of the later lanthanides (the lanthanide contraction).<sup>34</sup> The aqua ions at the beginning of the series are thus more kinetically labile towards substitution than those at the end. However, equivalent data for actinide aqua complexes are very scarce, and limited only to studies on U(VI) and Th(IV).<sup>35</sup> To the best of our knowledge, no data exist on the rates of water exchange of Am(III) and Cm(III) aqua complexes. However, assuming a linear correlation with the lanthanides based on cation radius, the second order water exchange rates for Am(III)–Cf(III) are estimated to range from  $1 \times 10^9$  to  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>36</sup> Since the ionic radius of Cm(III) is slightly lower than that of Am(III) (1.105 Å versus 1.122 Å, respectively),<sup>12</sup> it seems reasonable to assume that the same trend in water exchange rates observed in the lanthanide series will hold true for the trivalent actinides, and that the Am(III) aqua complex will thus be

more kinetically labile than the Cm(III) aqua complex. This would mean that the Am(III) aqua complex will undergo ligand substitution with CyMe<sub>4</sub>-BTPPhen **3** at the interface more rapidly than the Cm(III) aqua complex under kinetic conditions, resulting in a more rapid extraction of Am(III) than Cm(III) as observed above. It is also notable that the relative rates of oxidation of unstable Am(II) and Cm(II) in aqueous solution to the corresponding trivalent ions follow this same trend, with Am(II) reacting more rapidly than Cm(II) ( $9.7 \times 10^4 \text{ s}^{-1}$  versus  $6 \times 10^4 \text{ s}^{-1}$ , respectively).<sup>37</sup>

This leaves the question of why the above kinetic separation of Am(III) from Cm(III) using cyclohexanone as the diluent is only observed with CyMe<sub>4</sub>-BTPPhen **3** and not BTPPhens **4** and **5**. Clearly, the structure of the alkyl side-chains appended to the outer 1,2,4-triazine rings is having an effect on the selectivity of the extraction. It was previously observed in studies on BTPs that branching at the benzylic positions of the alkyl groups leads to a higher selectivity in the extraction of Am(III) over Eu(III).<sup>38</sup> This effect was attributed to reduced coordination of water molecules to the metal in the 1:3 BTP complexes containing bulky branched alkyl groups compared to those containing non-bulky linear alkyl groups, which leads to an extractable 1:3 complex with a more hydrophobic exterior, and a lower likelihood of substitution of the coordinated BTP ligands by aqua ligands. This effect is maximised in the highly branched CyMe<sub>4</sub>-BTP **1**, which has one of the highest Am(III)/Eu(III) selectivities for any BTP ligand reported to date ( $SF_{\text{Am/Eu}} = 5000$ ). It is thus likely that the same effect is observed above with CyMe<sub>4</sub>-BTPPhen **3**. Thus we propose that **3** forms a more hydrophobic 1:2 complex with Am(III) more rapidly than Cm(III), resulting in the rapid and selective Am(III) extraction observed above. In contrast, BTPPhens **4** and **5** bearing linear alkyl groups form Am(III) and Cm(III) 1:2 complexes with a less hydrophobic exterior than that formed by **3**, and thus the opportunity for a

more rapid extraction of Am(III) than Cm(III) is lost, leading to a lower separation factor for Am(III) over Cm(III) with these ligands.

**Separation of Am(III) from Cm(III) by hydrophilic ligands in nitric acid.** We previously showed that hydrophilic tetrasulfonated bis-(1,2,4)-triazine ligands **7–10** (Figure 2) were capable of separating Am(III) from Eu(III) via selective Am(III) complex formation in aqueous nitric acid, leading to highly efficient separations of Am(III) from Eu(III) when the *O*-donor ligand *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) was used as the hydrophobic extractant in the organic phase.<sup>xx</sup> TODGA is the preferred European ligand for the non-selective co-extraction of actinides and lanthanides from PUREX raffinate.<sup>39</sup> We now report our results on the ability of these ligands, together with the disulfonated BTBP and BTP ligands **11** and **12** shown in Figure 12, to separate Am(III) from Cm(III) in this two-ligand system.

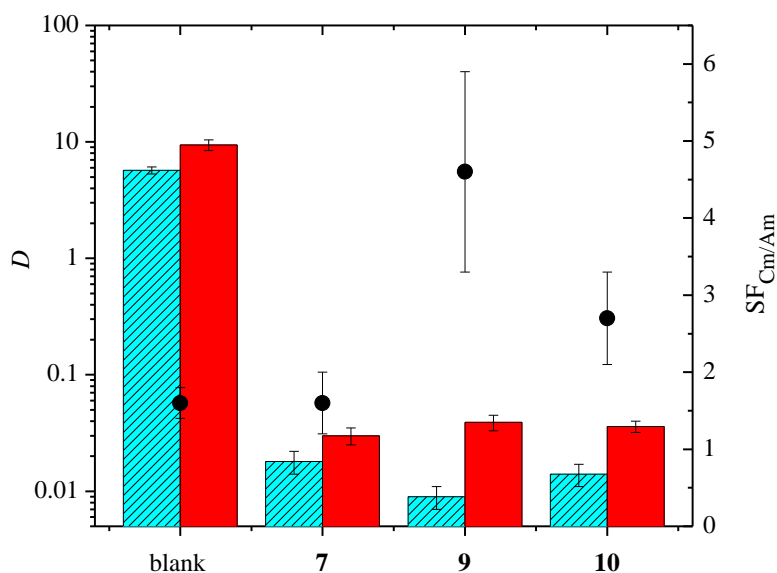


**Figure 12.** Hydrophilic disulfonated BTBP ligand **11** and BTP ligand **12** for selective actinide aqueous complexation in nitric acid.

The sulfonated ligands **7–12** were evaluated for their ability to suppress selectively (mask) the extraction of Am(III) and Cm(III) from nitric acid solutions by TODGA. Each of the sulfonated ligands (0.01 M) was added to HNO<sub>3</sub> solutions of different concentrations which were spiked with Am(III) and Cm(III) tracers, and the distribution ratios and separation factors were measured after contacting these aqueous phases with organic solutions containing TODGA (0.2 M) in kerosene/octanol (volume ratio 95:5). These results were compared to that of a blank



experiment, which did not contain any sulfonated ligand in the aqueous phase. Due to the rapid extraction kinetics of TODGA, the results reported here are necessarily under equilibrium conditions. The results for sulfonated ligands **7**, **9** and **10** in 0.28 M HNO<sub>3</sub> are shown in Figure 13.

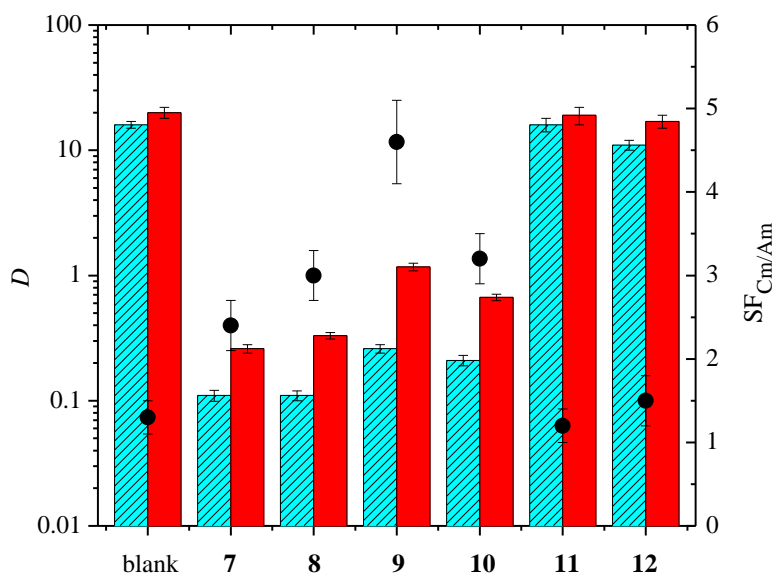


**Figure 13.** Extraction of Am(III) and Cm(III) from 0.28 M nitric acid by solutions of TODGA (0.2 M) in 1-octanol/kerosene (5:95) in the absence and presence of hydrophilic sulfonated bis-(1,2,4)-triazine ligands **7–10** (0.01 M) in the aqueous phase (dashed blue bar =  $D_{Am}$ , clear red bar =  $D_{Cm}$ , • =  $SF_{Cm/Am}$ , contact time = 6 hours at 250 rpm, T = 22 °C).

As expected, the extraction of Am(III) and Cm(III) into the organic phase by TODGA was suppressed by each of the tetrasulfonated ligands **7**, **9** and **10**, and the  $D$  values for Am(III) and Cm(III) subsequently decreased to below 0.1 compared to that of the blank sample. This is in agreement with our previous studies on Am(III)/Eu(III) separation by the tetrasulfonated ligands **7–10**.<sup>XX</sup> Compared to the blank sample, the separation factors for Cm(III) over Am(III) increased

slightly in the case of tetrasulfonated BTPhen ligands **9** and **10**, which differ only in the counterion used ( $\text{Na}^+$  v  $\text{H}^+$ ). With tetrasulfonated BTPhen **9**, a significantly high separation factor for Cm(III) over Am(III) of 4.6 was observed.

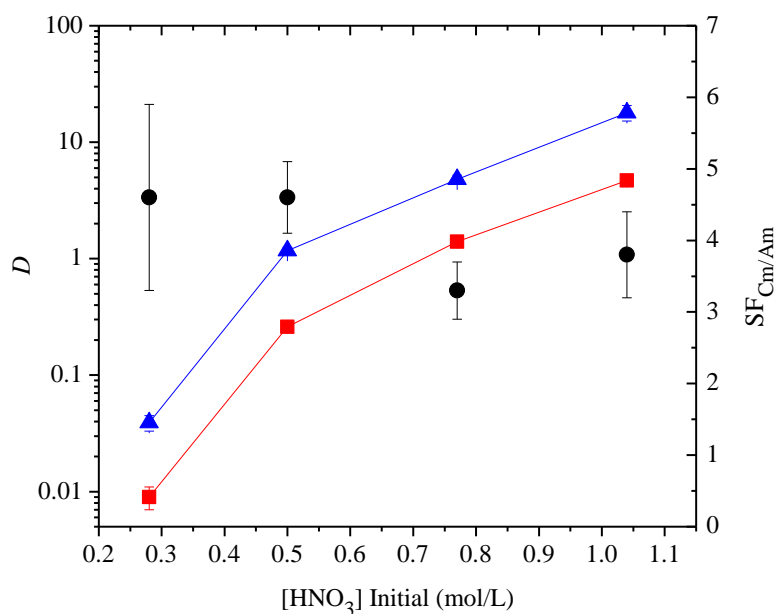
The results for the extraction of Am(III) and Cm(III) from 0.5 M  $\text{HNO}_3$  by TODGA in the absence and presence of sulfonated ligands **7–12** in the aqueous phase are presented in Figure 14. The tetrasulfonated ligands **7–10** all suppress the extraction of Am(III) and Cm(III) by TODGA, giving lower  $D$  values compared to those observed in the blank sample. In contrast, the disulfonated ligands **11** and **12** were unable to suppress the extraction of either metal, and the  $D$  values and separation factors were virtually identical to those of the blank experiment. This agrees with our earlier work on Am(III)/Eu(III) separation with these ligands, where we found the same marked difference in selective complexation performance between tetrasulfonated ligands and their disulfonated counterparts.<sup>xx</sup> For the tetrasulfonated ligands **7–10**, the separation factors for Cm(III) over Am(III) all increased compared to that in the blank experiment, indicating that they complex Am(III) more strongly than Cm(III) in the aqueous phase, and Cm(III) is more easily extracted. The selectivity is highest for the tetrasulfonated BTPHens **9** and **10** ( $\text{SF}_{\text{Cm/Am}} = 4.6$  for **9**,  $\text{SF}_{\text{Cm/Am}} = 3.2$  for **10**). With ligand **9**, a feasible separation could be achieved as  $D_{\text{Cm}} > 1$  and  $D_{\text{Am}} < 1$  (Figure 14).



**Figure 14.** Extraction of Am(III) and Cm(III) from 0.5 M nitric acid by solutions of TODGA (0.2 M) in 1-octanol/kerosene (5:95) in the absence and presence of hydrophilic sulfonated bis-(1,2,4)-triazine ligands **7–12** (0.01 M) in the aqueous phase (dashed blue bar =  $D_{Am}$ , clear red bar =  $D_{Cm}$ , • =  $SF_{Cm/Am}$ , contact time = 6 hours at 250 rpm,  $T = 22\text{ }^{\circ}\text{C}$ ).

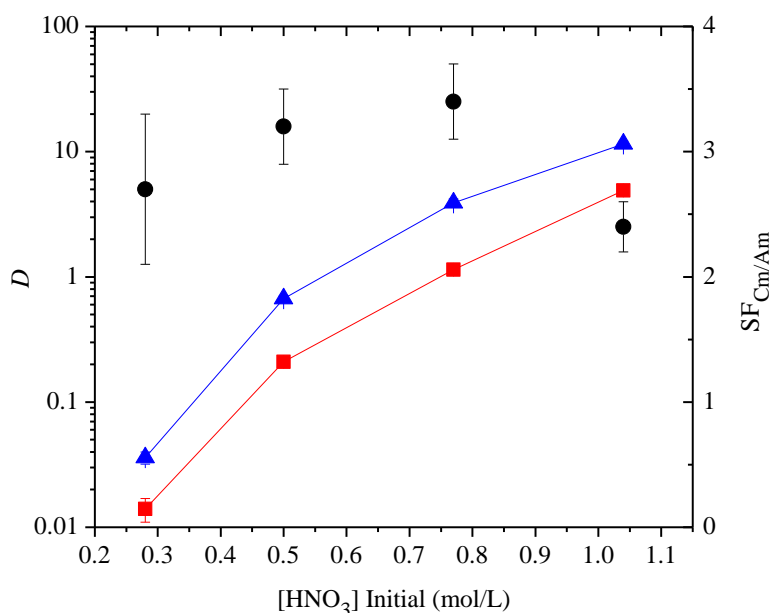
We also studied the extraction of Am(III) and Cm(III) by TODGA from nitric acid solutions of higher acidity in the absence and presence of sulfonated ligands **7–12**. In the extraction from 0.77 M  $\text{HNO}_3$ , the tetrasulfonated ligands **7–10** all showed higher separation factors for Cm(III) over Am(III) compared to the blank experiment. Once again, the BTPPhen ligands **9** and **10** showed the higher separation factors compared to the BTBPs ( $SF_{Cm/Am} = 3.3$  for **9**,  $SF_{Cm/Am} = 3.4$  for **10**, see Supporting Information). Similar results were observed in the extraction from 1.04 M  $\text{HNO}_3$ , although the  $D$  values for both metals exceeded 1 making a practical separation less feasible at this acidity. Under these conditions, BTPPhen **9** showed the highest selectivity ( $SF_{Cm/Am} = 3.8$ , see Supporting Information).

We and others have previously observed that the ability of hydrophilic sulfonated bis-(1,2,4)-triazine ligands to suppress Am(III) by TODGA decreases as the nitric acid concentration of the aqueous phase increases, with optimum results being found when  $[\text{HNO}_3] \leq 0.5 \text{ M}$ .<sup>XX</sup> Having identified the tetrasulfonated BTPhen ligands **9** and **10** as the best candidates for Am(III)/Cm(III) separation by hydrophilic ligands under thermodynamic conditions, we next studied the variation in the separation factor for Cm(III) over Am(III) with the nitric acid concentration of the aqueous phase. The results for BTPhen ligand **9** are shown in Figure 15 and the results for BTPhen ligand **10** are shown in Figure 16.



**Figure 15.** Extraction of Am(III) and Cm(III) from nitric acid solutions by solutions of TODGA (0.2 M) in 1-octanol/kerosene (5:95) in the presence of hydrophilic tetrasulfonated BTPhen ligand **9** (0.01 M) in the aqueous phase (■ =  $D_{\text{Am}}$ , ▲ =  $D_{\text{Cm}}$ , ● =  $\text{SF}_{\text{Cm/Am}}$ , contact time = 6 hours at 250 rpm,  $T = 22 \text{ }^\circ\text{C}$ ).

As expected, the  $D$  values for both Am(III) and Cm(III) increased with increasing  $[\text{HNO}_3]$  in both cases, in agreement with previous results.<sup>xx</sup> This could be because the extraction of metal ions by TODGA becomes more thermodynamically favoured as  $[\text{HNO}_3]$  increases due to the removal of nitrate ions from the aqueous phase. The separation factors for Cm(III) over Am(III) generally decrease as  $[\text{HNO}_3]$  increases, apart from BTPPhen **10** where the selectivity increases up to  $[\text{HNO}_3] = 0.77 \text{ M}$  (Figure 16). The highest separation factors are found in  $0.28 \text{ M HNO}_3$  and in  $0.5 \text{ M HNO}_3$  for BTPPhen **9** (Figure 15), and in  $0.28 \text{ M HNO}_3$ ,  $0.5 \text{ M HNO}_3$  and  $0.77 \text{ M HNO}_3$  for BTPPhen **10** (Figure 16). We also studied the variation in  $\text{SF}_{\text{Cm/Am}}$  with  $[\text{HNO}_3]$  for tetrasulfonated BTBPs **7** and **8**, and disulfonated ligands **11** and **12**. Tetrasulfonated BTBPs **7** and **8** showed similar trends as the corresponding BTPPhens **9** and **10**, although the selectivities were generally lower ( $\text{SF}_{\text{Cm/Am}} \leq 3$ , see Supporting Information). The disulfonated ligands **11** and **12** did not show any significant selectivity for Cm(III) over Am(III).



**Figure 16.** Extraction of Am(III) and Cm(III) from nitric acid solutions by solutions of TODGA (0.2 M) in 1-octanol/kerosene (5:95) in the presence of hydrophilic tetrasulfonated BTPPhen ligand **10** (0.01 M) in the aqueous phase (■ =  $D_{Am}$ , ▲ =  $D_{Cm}$ , ● =  $SF_{Cm/Am}$ , contact time = 6 hours at 250 rpm, T = 22 °C).

Thus, hydrophilic tetrasulfonated BTPPhen ligands **9** and **10** also have the ability to separate Am(III) from Cm(III) via selective Am(III) complex formation in nitric acid, in agreement with previously reported results on BTPPhen ligand **9**.<sup>XX</sup> The higher selectivity of these pre-organized ligands for Am(III) over Cm(III) is in agreement with the results reported above for CyMe<sub>4</sub>-BTPPhen **3** and other hydrophobic bis-(1,2,4)-triazine ligands.<sup>XX</sup> REF Tetrasulfonated BTP **6**<sup>XX</sup> is one of a number of hydrophilic ligands currently being developed as an actinide-selective stripping agent for use in a new minor actinide partitioning process in Europe.<sup>40</sup> Since the tetrasulfonated BTPPhens **9** and **10** show higher separation factors for Cm(III) over Am(III) than **6**, these ligands could represent a further refinement of this process by allowing for the simultaneous separation of Am(III) from Cm(III), as well as the separation of Am(III) and Cm(III) from the lanthanides.

**Table 1.** Summary of the separation factors for Am(III) over Cm(III) ( $SF_{Am/Cm}$ , for hydrophobic ligands) and Cm(III) over Am(III) ( $SF_{Cm/Am}$ , for hydrophilic ligands) observed with BTPPhen ligands.

Ligand	Hydrophobic or hydrophilic?	$SF_{Am/Cm}$	$SF_{Cm/Am}$	Organic phase	Aqueous phase	Contact time	Reference
<b>3</b>	hydrophobic	3.3	–	1 mM L in octanol	6 M HNO <sub>3</sub>	2 h	this work
<b>3</b>	hydrophobic	4.0	–	10 mM L in octanol:toluene (40:60)	4 M HNO <sub>3</sub>	1 h	6a

3	hydrophobic	3.1	–	10 mM L in octanol:toluene (40:60)	4 M HNO <sub>3</sub>	6 h	this work
3	hydrophobic	6.5	–	10 mM L in octanol:toluene (40:60)	1 M HNO <sub>3</sub>	6 h	this work
3	hydrophobic	7.9	–	5 mM L in octanol:toluene (40:60)	2.4 M HNO <sub>3</sub>	10 h	this work
3	hydrophobic	4.0	–	1 mM L in octanol:toluene (40:60)	4 M HNO <sub>3</sub>	20 min	this work
<b>5-Br CyMe<sub>4</sub>- BTPhen</b>	hydrophobic	7.0	–	30 mM in octanol	0.1 M HNO <sub>3</sub>	?	17
<b>5-(HO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) CyMe<sub>4</sub>- BTPhen</b>	hydrophobic	5.0	–	30 mM in octanol	1 M HNO <sub>3</sub>	?	17
3	hydrophobic	6.7	–	5 mM L in cyclohexanone	0.5 M HNO <sub>3</sub>	7 min	this work
3	hydrophobic	4.2	–	5 mM L in cyclohexanone	1 M HNO <sub>3</sub>	7 min	this work
3	hydrophobic	5.5	–	5 mM L in cyclohexanone	0.5 M HNO <sub>3</sub>	7 min	this work
3	hydrophobic	4.8	–	5 mM L in cyclohexanone	1 M HNO <sub>3</sub>	10 min	this work
4	hydrophobic	3.1	–	5 mM L in cyclohexanone	0.5 M HNO <sub>3</sub>	30 min	this work
5	hydrophobic	2.6	–	5 mM L in cyclohexanone	0.5 M HNO <sub>3</sub>	30 min	this work
9	hydrophilic	–	4.6	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 0.28 M HNO <sub>3</sub>	6 h	this work
9	hydrophilic	–	4.6	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 0.5 M HNO <sub>3</sub>	6 h	this work
10	hydrophilic	–	3.2	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 0.5 M HNO <sub>3</sub>	6 h	this work
9	hydrophilic	–	3.3	0.2 M TODGA in octanol:kerosene	10 mM L in 0.77 M	6 h	this work

				(5:95)	HNO <sub>3</sub>		
10	hydrophilic	–	3.4	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 0.77 M HNO <sub>3</sub>	6 h	this work
9	hydrophilic	–	3.8	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 1.04 M HNO <sub>3</sub>	6 h	this work
9	hydrophilic	–	3.3	0.2 M TODGA in octanol:TPH (5:95)	10 mM L in 0.6 M HNO <sub>3</sub>	1 min	8d
9	hydrophilic	–	3.6	0.2 M TODGA in octanol:TPH (5:95)	10 mM L in 0.65 M HNO <sub>3</sub>	5 min	8f
7	hydrophilic	–	2.4	0.2 M TODGA in octanol:kerosene (5:95)	10 mM L in 0.5 M HNO <sub>3</sub>	6 h	this work
7	hydrophilic	–	~2.5	0.2 M TODGA in octanol:Exxsol D80 (5:95)	10 mM L in 0.5 M HNO <sub>3</sub>	30 min	8e

## Conclusions

We have studied the complexation and extraction of the similar adjacent trivalent minor actinides Am(III) and Cm(III) by hydrophobic and hydrophilic 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPPhen) ligands. A kinetic effect was observed in the extraction of Am(III) and



Cm(III) by hydrophobic ligand CyMe<sub>4</sub>-BTPPhen **3** into three different diluents (octanol, octanol:toluene 40:60, cyclohexanone), leading to a more rapid extraction of Am(III) than Cm(III). Separation factor for Am(III) over Cm(III) ( $SF_{Am/Cm}$ ) as high as 7.9 are observed under these non-equilibrium (kinetic) extraction conditions. This kinetic effect can be tuned through careful choice of the extraction variables (organic diluent, contact time, shaking speed, ligand concentration) and could thus potentially be exploited to carry out the challenging but necessary separation of Am(III) from Cm(III) in a future closed nuclear fuel cycle. In contrast, no such kinetic effect is observed with BTPPhen ligands **4** and **5** containing linear alkyl groups, and these ligands do not separate Am(III) from Cm(III) as effectively as **3**.

We attribute this kinetic separation to the slightly higher kinetic lability of the Am(III) aqua complex towards ligand substitution compared to the Cm(III) aqua complex, in analogy with the known trend in kinetic labilities of the corresponding trivalent lanthanide aqua complexes. Finally we have shown that, under equilibrium conditions, hydrophilic tetrasulfonated BTPPhen ligands **9** and **10** can complex selectively Am(III) over Cm(III) in nitric acid and suppress its extraction by TODGA, leading to effective separations of Am(III) from Cm(III) ( $SF_{Cm/Am}$  up to 4.6 observed). Taken together with the separation factors reported previously in the literature (summarized collectively in Table 1), these results underline both hydrophobic and hydrophilic pre-organized 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPPhen) ligands as promising candidates for the difficult separation of Am(III) from Cm(III) in used nuclear fuel reprocessing, either under kinetic or thermodynamic (ie: equilibrium) extraction conditions.

## Experimental Section

**Materials and Methods.** The hydrophobic ligands CyMe<sub>4</sub>-BTPPhen **3**,<sup>6a</sup> C4-BTPPhen **4**<sup>19</sup> and C5-BTPPhen **5**<sup>19,20</sup> were synthesized at the University of Reading as reported previously. The

hydrophilic sulfonated ligands **7–12** were also synthesized at the University of Reading as described previously.<sup>8c</sup> The stock solution of <sup>241</sup>Am in HNO<sub>3</sub> was prepared by dissolving americium oxide in 5 M HNO<sub>3</sub> and subsequent dilution with water. The stock solution of <sup>152</sup>Eu was prepared by appropriate dilution of a commercial preparation (REu-2) supplied by Polatom (Poland). The stock solution of <sup>244</sup>Cm was prepared by dissolving moist curium nitrate (37 MBq, reference date 16th February 2007, TENEX Russia) in 2 mL of 0.01 M HNO<sub>3</sub> by appropriate dilution with water. The working solutions of all radionuclides were prepared from the respective radionuclide stock solutions by appropriate dilution. Solvent extraction measurements were performed at the Czech Technical University in Prague (Czech Republic).

**Solvent Extraction Measurements with Hydrophobic Ligands.** The aqueous solutions were prepared by spiking nitric acid solutions (0.01–4 mol dm<sup>-3</sup>) with working solutions of <sup>241</sup>Am, <sup>244</sup>Cm and <sup>152</sup>Eu tracers in diluted nitric acid. Solutions of the hydrophobic ligands **3–5** were prepared by dissolving in the appropriate diluent. Prior to labelling, the aqueous phases were pre-equilibrated with the neat diluents by shaking them for 4 h at 400 min<sup>-1</sup> and volume ratio of 4:1. The organic phases were pre-equilibrated with the respective non-labelled aqueous phases by shaking them for 4 h at 400 min<sup>-1</sup> and volume ratio of 1:1. In each case, 1.22 mL of labelled aqueous phases were prepared from which one 200 μL and two 10 μL standards were taken (to allow for mass balance calculations) prior to contacting the aqueous phases with the organic phases. Each organic phase (1 mL) was shaken separately with each of the aqueous phases for a given time at a thermostatted temperature using an GFL 3005 Orbital Shaker (250 min<sup>-1</sup>), or a Heidolph Multi Reax Shaker (1800 min<sup>-1</sup>). After phase separation by centrifugation, two parallel 200 μL and two 10 μL aliquots of each phase were withdrawn for gamma or alpha measurements, respectively.

For alpha measurements, the aliquots were deposited on stainless steel planchets, evaporated to dryness under an infra-red lamp, and heated in a burner flame until the sample glowed with a dull red colour.<sup>41</sup> The same procedure was used to investigate the kinetics of <sup>241</sup>Am and <sup>244</sup>Cm extraction. Alpha activity measurements of <sup>241</sup>Am and <sup>244</sup>Cm were performed with ORTEC® OCTETE Plus Integrated Alpha-Spectroscopy System equipped with ion-implanted-silicon ULTRA Alpha Detector Model BU-020-450-AS. The double peaks at 5443 + 5486 keV and 5763 + 5805 keV in the alpha spectra were evaluated for <sup>241</sup>Am and <sup>244</sup>Cm, respectively, by AlphaVision-32 Alpha Analysis Software (ORTEC, Advanced Measurement Technology, Inc., USA).

For gamma measurements, the aliquots were pipetted into glass ampoules, their walls were washed with 1 mL of distilled water or the diluent used and the ampoules were covered with a piece of parafilm. Gamma activity measurements of <sup>241</sup>Am and <sup>152</sup>Eu were performed with a  $\gamma$ -ray spectrometer EG&G Ortec (USA) with a PGT (USA) HPGe detector. The  $\gamma$ -lines at 59.5 keV, and 121.8 keV were examined for <sup>241</sup>Am, and <sup>152</sup>Eu, respectively.

The errors given in the figures are  $2\sigma$  propagated errors based on counting statistics, sample preparation, and sampling errors. *Caution! <sup>241</sup>Am, <sup>244</sup>Cm and <sup>152</sup>Eu are highly radioactive isotopes. All radiotracer experiments were carried out in radiochemical laboratories equipped and granted with permission for handling these isotopes.*

**Solvent Extraction Measurements with Hydrophilic Ligands.** The aqueous solutions were prepared by spiking 1.19 mL of nitric acid solutions (0.28 – 1.04 mol L<sup>-1</sup>) with or without the hydrophilic sulfonated ligand **7–12** (10 mmol L<sup>-1</sup>) with 10  $\mu$ L of working solutions of <sup>241</sup>Am, <sup>244</sup>Cm, and <sup>152</sup>Eu radiotracers. The organic phase solutions consisted of 0.2 mol L<sup>-1</sup> TODGA dissolved in 5 % vol. 1-octanol in kerosene. In each case before contacting with the organic

phase, an aliquot of 200  $\mu\text{L}$  was taken from the labeled aqueous phases to measure the gamma activity of europium, and two 10  $\mu\text{L}$  aliquots to measure the alpha activity of americium and curium, to allow for activity balance calculations. Each organic phase (1 mL) was shaken with each of the aqueous phases (1 mL) for a given time at a thermostatted temperature, using a horizontal GFL 3005 Orbital Shaker ( $250 \text{ min}^{-1}$ ). After phase separation by centrifugation (1 minute, 6000 rot/min), two parallel 200  $\mu\text{L}$  aliquots of each phase were withdrawn into glass ampules for the gamma measurements. The walls of the glass ampules were washed with 1 mL of distilled water or 5 vol. % 1-octanol in kerosene and ampules were covered with a piece of parafilm. For the alpha spectrometry, two parallel 10  $\mu\text{L}$  aliquots of each phase were withdrawn and samples prepared as described above. Sample preparation for the alpha measurements, and the measurement of both the alpha and gamma activities, were performed as described above.

ASSOCIATED CONTENT. Tables and graphs of solvent extraction data for hydrophobic ligands **3–5** and hydrophilic ligands **7–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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<sup>3</sup> Reference 2 in rejected Am/Cm separation paper (ACS Version)

<sup>4</sup> References 3-6 in rejected Am/Cm separation paper (ACS Version), 2016 Russ. Chem. Rev. review

<sup>5</sup> References 7-9 in rejected Am/Cm separation paper (ACS Version)

<sup>6</sup> References 10-12 in rejected Am/Cm separation paper (ACS Version)

<sup>7</sup> Reference 19 in our 2015 Sulfonates paper

<sup>8</sup> References 24a and 24b in our 2015 Sulfonates paper, our 2015 Sulfonates paper

<sup>9</sup> References 24c and 24d in our 2015 Sulfonates paper

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- <sup>35</sup> 24, 26
- <sup>36</sup> The Chemistry of the Actinide and Trans-actinide Elements, 4<sup>th</sup> Ed, Springer, 2011.
- <sup>37</sup> 25
- <sup>38</sup> 18, 19, 20

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<sup>39</sup> Ref 30 in our 2015 Sulfonates paper

<sup>40</sup> For a recent example, see: 21

<sup>41</sup> Reference 36 in rejected Am/Cm separation paper (ACS Version)