The Separation of Americium(III) from Europium(III) by Two New 6,6'-Bistriazinyl-2,2'-bipyridines in Different Diluents

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The synthesis and extraction of americium(III) and europium(III) from aqueous nitric acid solutions by the new BTBP ligands 6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrofuro[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine (Cy_5-O-Me_4-BTBP) and 6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrothieno[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine (Cy_5-S-Me_4-BTBP) is described. The affinity for Am(III) and the selectivity for Am(III) over Eu(III) of Cy_5-S-Me_4-BTBP were generally higher than for Cy_5-O-Me_4-BTBP. For both ligands, the extraction of Am(III) and Eu(III) from 3 M HNO_3 into 3 mM organic solutions varied with the diluent used. The highest distribution ratios and separation factors observed were in cyclohexanone and 2-methylcyclohexanone, respectively. For Cy_5-S-Me_4-BTBP, there is a strong correlation between the distribution ratio for Am(III) and the permittivity of the diluent used. With 1-octanol as the diluent, low distribution ratios (D(Am) < 1) were observed for Cy_5-S-Me_4-BTBP although this ligand extracts Am(III) selectively ($SF_{Am/Eu}$ = 16-46 from 1-4 M HNO_3). For Cy_5-S-Me_4-BTBP, Am(III) is extracted as the disolvate. The distribution ratios for Am(III), and the separation factors for Am(III) over Eu(III) are both significantly higher for $CyMe_4$-BTBP than they are for Cy_5-O-Me_4-BTBP and Cy_5-S-Me_4-BTBP in cyclohexanone. Changing the diluent from cyclohexanone to 2-methylcyclohexanone leads to a decrease in D(Am) but an increase in $SF_{Am/Eu}$ for Cy_5-S-Me_4-BTBP.

Keywords: americium(III), europium(III), separation, nitric acid, 1-octanol, kinetics, Cy_5-O-Me_4-BTBP, SANEX process, Cy_5-S-Me_4-BTBP, cyclohexanone, 2-methylcyclohexanone, $CyMe_4$-BTBP, extraction

Introduction

The presence of long-lived radionuclides in spent nuclear fuels is responsible for the long-term radiotoxicity of the nuclear waste arising from the PUREX process. The

most important of these are the minor actinides (americium, curium and neptunium). Their conversion to shorter-lived or stable radionuclides by nuclear reactions (eg: transmutation) is considered to be a key step in the future management and geological disposal of high-level waste issuing from the reprocessing of spent nuclear fuels.[1,2] However, this transmutation can only be achieved once these radionuclides have been separated (partitioned) from the bulk of the trivalent lanthanide ions which are also present in much higher quantities than the minor actinides in PUREX raffinate.[3] Currently, a two-step strategy is foreseen to perform this separation by liquid-liquid extraction; the minor actinides and lanthanides are first co-extracted from PUREX raffinate using hard O- donor ligands (eg: TODGA, DMDOHEMA)[4,5] using the DIAMEX process[6–8] and subsequently, the minor actinides could be separated from the lanthanides using softer N- or S- donor ligands in the SANEX process.[9,10]

The separation of trivalent minor actinides from trivalent lanthanides has been a challenging problem to overcome because of the chemical similarity of the two groups of elements.[11] However, Musikas[12] and Nigond[13] discovered that soft heterocyclic N- donor ligands were able to bind selectively to trivalent actinides and subsequently, research in Europe has focused on the development of ligands capable of separating actinides from lanthanides in a SANEX process.[14–16] The 2,6-bis(1,2,4-triazin-3-yl)pyridines or BTPs **1**[17–23], (Figure 1) discovered by Kolarik,[24,25] were the first ligands to show both high affinities and high selectivities for americium(III) over europium(III) in contact with aqueous solutions of high acidity. Unfortunately, these ligands were not very resistant to radiolysis (with the exception of $BzCyMe_4$-BTP)[26], and, although actinide back-extraction (stripping) was possible with C3-BTP,[27] in the case of $CyMe_4$-BTP and $BzCyMe_4$-BTP,[26] actinide back-extraction from the loaded

organic phase could not be achieved owing to the irreversible metal binding of these annulated BTP reagents.

Subsequently, the 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridines or BTBPs **2** (Figure 1) were developed.[28–38] These ligands showed lower binding affinities towards americium(III) which allowed stripping to occur using either dilute nitric acid or glycolic acid. However, the 6,6'-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines (Cn-BTBPs, n = 1-5) were subjected to both acidic hydrolysis and radiolytic degradation by removal of their labile benzylic hydrogen atoms by free-radical species.[39] This led to the development of 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2-bipyridine ($CyMe_4$-BTBP) **3** (Figure 1) in which the benzylic hydrogens have been removed.[40] To date this ligand is the most promising for use in a future SANEX process and in a counter-current 'hot-test' using laboratory centrifugal contactors, 99.9 % of the actinides were removed from the feed solution in a 16-stage flowsheet with very high decontamination factors for Am (7,000) and Cm (1,000).[41,42]

Nevertheless, $CyMe_4$-BTBP **3** does still have some drawbacks in the context of an industrial process. Firstly, the kinetics of extraction and back-extraction are rather slow and consequently, relatively long contact times (30-60 minutes for a solution of **3** in 1-octanol/TPH) are required to reach equilibrium, necessitating the use of a phase-transfer agent (eg: diamides such as DMDOHEMA, TODGA).[4,5,40] Secondly, the use of ammonium or sodium glycolate solution of approx. pH 4 was required for the efficient stripping of the actinides from the loaded organic phase. Thus the design and assessment of new N-donor ligands which show improved kinetics and back-extraction properties is on-going. To this end we wished to know how modifying the aliphatic part of the $CyMe_4$-BTBP molecule **3** would affect the

solvent extraction properties of the resulting ligands. In this paper, we report the synthesis and selective extraction of Am(III) and Eu(III) from nitric acid solutions into organic solutions of the new BTBPs 6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrofuro[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine (Cy_5-O-Me_4-BTBP **4**, Figure 1) and 6,6'-bis(5,5,7,7-tetramethyl-5,7-dihydrothieno[3,4-*e*]-1,2,4-triazin-3-yl)-2,2'-bipyridine (Cy_5-S-Me_4-BTBP **5**, Figure 1) which are derived from heterocyclic α-diketones. A BTP derived from one of these diketones has been reported, although its properties with respect to the separation of actinides from lanthanides have not been disclosed.[43] To allow for a meaningful comparison, the solvent extraction properties of the new ligands **4** and **5** are also compared to those of $CyMe_4$-BTBP **3**.

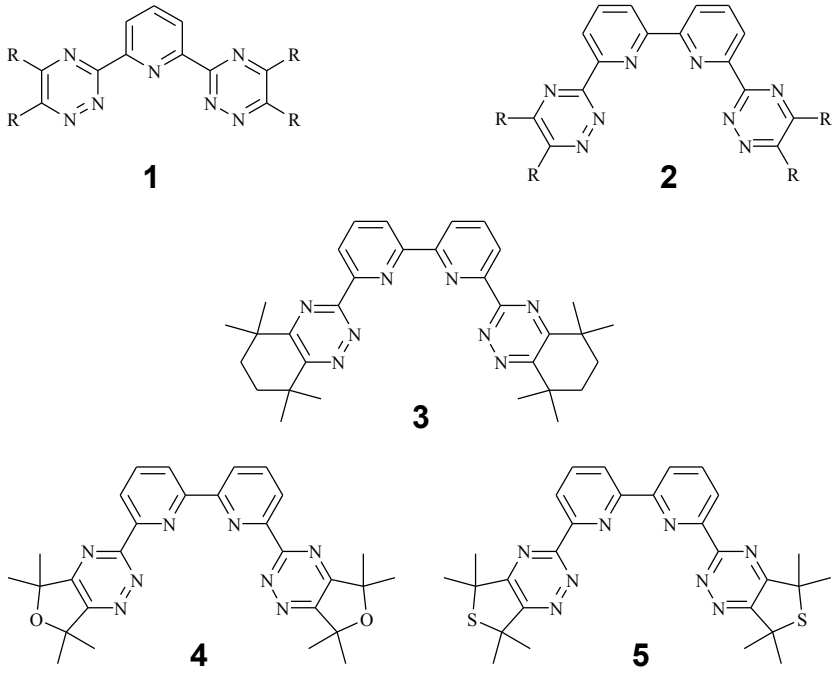


Figure 1. The structures of the BTP **1**, BTBP **2**, $CyMe_4$-BTBP **3**, Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** ligands.

Experimental

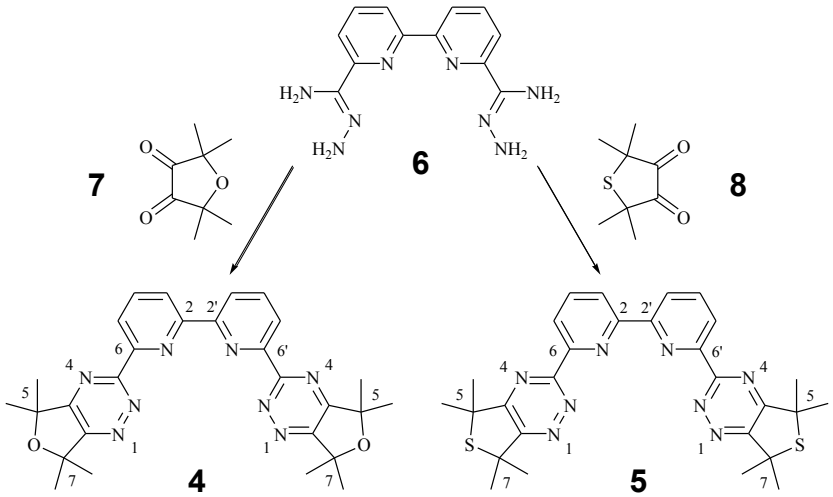
Synthesis

General

Melting points (Mp) were obtained on a Stuart SMP10 instrument and are uncorrected. IR spectra were recorded as Nujol® mulls on a Perkin Elmer RX1 FT-IR instrument. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded using either a Bruker AMX400 or an Avance XXX400 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Coupling constants (*J*) are quoted in Hertz. Assignments were verified with ^{1}H-^{1}H and ^{1}H-^{13}C COSY experiments as appropriate. Quaternary carbons are indicated by the abbreviation 'quat'. Mass spectra were obtained under electrospray conditions on a Thermo Scientific LTQ Orbitrap XL instrument. Elemental microanalyses were carried out by Medac Ltd., Brunel Science Centre, Surrey (UK). All organic reagents were obtained from either Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich and used as received.

2,2'-Bipyridine-6,6'-dicarbohydrazonamide **6**[32,44,45] was obtained in 87 % yield by the reaction of 2,2'-bipyridine-6,6'-dicarbonitrile[46,47] with excess hydrazine hydrate in ethanol for 14 days.[48] 2,2'-Bipyridine-6,6'-dicarbonitrile was obtained in 79 % overall yield by the oxidation of 2,2'-bipyridine with hydrogen peroxide in acetic acid,[49–51] followed by a Reissert-Henze reaction of the bis-*N*-oxide with trimethylsilyl cyanide (3 eq) and benzoyl chloride (3 eq) in DCM at reflux for 24 hours.[47,52–55] **WARNING:** *trimethylsilyl cyanide is a volatile hydrogen cyanide equivalent*. The heterocyclic α-diketones **7** and **8** were prepared according to literature procedures. 2,2,5,5-Tetramethylfuran-3,4(2*H*,5*H*)-dione **7**[56,57] was synthesized in 45 % overall yield by the mercuric acetate-catalyzed cyclization of 2,5-dimethyl-3-hexyne-2,5-diol in dilute aqueous sulfuric acid,[58–60] followed by oxidation of the resulting dihydrofuranone with selenium dioxide in dioxane.[61,62] 2,2,5,5-Tetramethylthiophene-3,4(2*H*,5*H*)-dione **8**[63] was obtained in 80 % yield by the

reaction of 2,5-dibromo-2,5-dimethylhexane-3,4-dione with sodium sulfide in methanol.[64] 2,5-Dibromo-2,5-dimethylhexane-3,4-dione[63,64] was synthesized in 22 % overall yield by the intermolecular acyloin reaction of ethyl isobutyrate with sodium and chlorotrimethylsilane in toluene,[65] followed by oxidation with excess bromine in chloroform.[64,66] 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2'-bipyridine **3** ($CyMe_4$-BTBP) was synthesized in 56 % yield as previously described[40] with the modification that the condensation reaction with 3,3,6,6-tetramethylcyclohexane-1,2-dione[67,68] was performed in dioxane at reflux for 24 hours. The syntheses of Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** are shown in Scheme 1. The new ligands Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** were synthesized by condensation of the dicarbohydrazonamide **6** with each of the diketones **7** and **8**, respectively. The crude products obtained contained several additional impurities and extensive purification by chromatography and trituration was required to obtain pure samples of both ligands **4** and **5**. In contrast, the synthesis of $CyMe_4$-BTBP **3** produced no additional impurities other than some unreacted diketone which was easily removed by trituration with EtOH.



Scheme 1. The synthesis of Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5**.

*Synthesis of Cy_5-O-Me_4-BTBP **4***

2,2'-Bipyridine-6,6'-dicarbohydrazonamide **6** (1.77 g, 6.58 mmol) was suspended in THF (100 mL) and 2,2,5,5-tetramethylfuran-3,4(2*H*,5*H*)-dione **7** (2.26 g, 14.48 mmol, 2.2 eq) was added. Triethylamine (10 mL) was added and the suspension was heated under reflux for 26 hours. The solution was allowed to cool to room temperature and the solvent was removed *in vacuo*. The solid product was purified by chromatography, eluting with MeOH/DCM/Et_3N (2.5 %:96.5 %:1 %) to afford the crude product as a yellow solid (0.82 g). This solid was again purified by chromatography, eluting with MeOH/DCM/Et_3N (1 %:98 %:1 %) to afford the crude product as a yellow solid. This solid was further purified by trituration with hot MeOH (30 mL). The insoluble solid was filtered and washed with MeOH (20 mL) and ether (20 mL) and allowed to dry in air to afford the pure product **4** as a yellow solid (0.35 g, 10 %). Mp: above 300 ^{o}C (MeOH). Found: C, 65.46 %; H, 5.97 %; N, 21.96 %; $C_{28}H_{30}O_2N_8$ requires C, 65.87 %; H, 5.92 %; N, 21.94 %. IR ν_{max} (Nujol) 2923, 1586, 1574, 1542, 1458, 1376, 1267, 1247, 1208, 1178, 1150, 1123, 1079, 983, 914, 804, 741, 718, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12H, 4 × Me), 1.74 (s, 12H, 4 × Me), 8.11 (t, *J* 7.8, 2H, 4-H and 4'-H), 8.60 (dd, *J* 7.8 and 1.0, 2H, 5-H and 5'-H), 8.93 (dd, *J* 7.8 and 1.0, 2H, 3-H and 3'-H) ppm. ^{13}C NMR ($CDCl_3$): δ 28.4 (4 × Me), 29.0 (4 × Me), 81.0 (2 × quat), 81.1 (2 × quat), 123.4 (C-3 and C-3'), 124.6 (C-5 and C-5'), 138.1 (C-4 and C-4'), 152.4 (2 × quat), 156.1 (2 × quat), 162.9 (2 × quat), 163.3 (2 × quat), 166.2 (2 × quat) ppm. HRMS (CI) *m/z* 511.2553: *calculated for* $[C_{28}H_{30}O_2N_8 + H]^+$ 511.2564.

*Synthesis of Cy$_5$-S-Me$_4$-BTBP **5***

2,2'-Bipyridine-6,6'-dicarbohydrazonamide **6** (1.50 g, 5.55 mmol) was suspended in THF (100 mL) and 2,2,5,5-tetramethylthiophene-3,4(2*H*,5*H*)-dione **8** (2.10 g, 12.22 mmol, 2.2 eq) was added. Triethylamine (10 mL) was added and the suspension was

heated under reflux for 24 hours. The solution was allowed to cool to room temperature and the solvent was removed *in vacuo*. The solid product was purified by chromatography, eluting with MeOH/DCM/Et_3N (5 %:94 %:1 %) to afford the crude product as a yellow solid (2.24 g). This solid was again purified by chromatography, eluting with MeOH/DCM/Et_3N (2.5 %:96.5 %:1 %) to afford the crude product as a yellow solid. This solid was further purified by trituration with hot MeOH (50 mL). The insoluble solid was filtered and washed with MeOH (50 mL) and ether (50 mL) and allowed to dry in air to afford the pure product **5** as a yellow solid (0.64 g, 21 %). Mp: 284 ^oC (MeOH). Found: C, 61.71 %; H, 5.53 %; N, 20.92 %; S, 11.58 %; $C_{28}H_{30}N_8S_2$ requires C, 61.97 %; H, 5.57 %; N, 20.64 %; S, 11.81 %. IR ν_{max} (Nujol) 2918, 1583, 1516, 1461, 1375, 1253, 1185, 1154, 1118, 1082, 1025, 993, 801, 740, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.87 (s, 12H, 4 × Me), 1.92 (s, 12H, 4 × Me), 8.09 (t, *J* 7.8, 2H, 4-H and 4'-H), 8.60 (dd, *J* 7.8 and 1.0, 2H, 5-H and 5'-H), 8.96 (dd, *J* 7.8 and 1.0, 2H, 3-H and 3'-H) ppm. ^{13}C NMR ($CDCl_3$): δ 31.7 (4 × Me), 32.4 (4 × Me), 52.0 (2 × quat), 52.4 (2 × quat), 123.3 (C-3 and C-3'), 124.5 (C-5 and C-5'), 138.1 (C-4 and C-4'), 152.3 (2 × quat), 156.1 (2 × quat), 162.3 (2 × quat), 164.3 (2 × quat), 167.0 (2 × quat) ppm. HRMS (CI) *m/z* 543.2097: *calculated for* $[C_{28}H_{30}N_8S_2 + H]^+$ 543.2108.

Solvent Extraction and Solubility Determination

Solvent extraction studies were performed at the Czech Technical University in Prague, Břehová 7, 115 19 Prague 1 (Czech Republic). The aqueous solutions were prepared by spiking nitric acid solutions (0.001-4 mol dm^{-3}) with stock solutions of ^{241}Am and ^{152}Eu tracers in nitric acid. The stock solution of ^{241}Am in 0.5M HNO_3 was prepared by dissolving americium oxide in 5M HNO_3 and subsequent dilution with water. The stock solution of $^{152+154}Eu$ (~1.5 MBq/mL) was prepared by appropriate

dilution of a commercial preparation (REu-2) supplied by Polatom (Poland). Solutions of each of the ligands **4** and **5** (0.005 mol dm^{-3}) were prepared by dissolving in the appropriate diluent without an additional phase modifier. Prior to labelling, the aqueous phases were pre-equilibrated with the neat diluents by shaking them for 6 hours at 250 min^{-1} and volume ratio of 1:1. Prior to contacting with the labelled aqueous phases, the organic phases were pre-equilibrated with the respective non-labelled aqueous phases by shaking them for 6 hours at 250 min^{-1} and volume ratio of 1:1. In each case, 1.2 mL of labelled aqueous phases were prepared from which 200 µL standards were taken (to allow for mass balance calculations) prior to the contacts of the aqueous phases with the organic phases. Each organic phase (1 mL) was shaken separately with each of the aqueous phases for 6 hours at ambient temperature (ca. 25 ^{o}C, non-thermostatted) using an GFL 3005 Orbital Shaker (250 min^{-1}). The contact time of 6 hours was sufficient to attain the distribution equilibrium. After phase separation by centrifugation, two parallel 200 µL aliquots of each phase were withdrawn for the analysis. The same procedure was used to investigate the kinetics of ^{241}Am extraction. In these experiments, the contact time of the phases was varied as required and the separation of the phases performed as fast as possible.

Activity measurements of ^{241}Am and ^{152}Eu were performed with a γ-ray spectrometer EG&G Ortec (USA) with a PGT (USA) HPGe detector. The γ-lines at 59.5 keV, and 121.8 keV were examined for ^{241}Am, and ^{152}Eu, respectively. From the measured count rates of the organic, A_{org}, and aqueous, A_{aq}, phases, the distribution ratios, D, were calculated as:

$$D = \frac{A_{org}}{A_{aq}}$$

The errors given in the figures and/or throughout the text are 1σ and are based on counting statistics, only. Preliminary experiments have shown that the contribution of

chemical operations to the combined uncertainty of the results is about 5 %. The minimum detectable values of distribution ratios, D_{min}, were calculated as:

$$D_{\min} = \frac{2.71 \cdot t_{vz} + 2.326 \cdot \sqrt{(M-2) \cdot T / (t_{vz} \cdot t_{bg})}}{A_{st}}$$

where A_{st} is the count rate of the initial standard sample, M is the number of channels in the evaluated peak (in the Region Of Interest), T is the gross area of a ROI set at the position of the respective peak in the background spectrum measured for the time t_{bg}, and t_{vz} is the time of measurement of the sample. This formula has been derived for 90% probability of the right decision. For each sample, a recovery (mass balance) R for each of the radionuclides was calculated as:

$$R = 100 \cdot \frac{A_{aq} + A_{org}}{A_{st}} \ [\%]$$

Only results with R ∈ <90; 110> % were considered internally consistent and were further processed. The approximate solubilities of **4** and **5** were determined by stepwise dissolution of a known mass of the ligand in the appropriate solvent. The solvent was then added incrementally in 200 µL aliquots followed by ultrasound after each addition until a clear solution was obtained. The resulting solutions were used in the liquid-liquid extraction tests. The approximate solubilities of **4** and **5** are shown in Table 1. Ligand **5** was generally more soluble than ligand **4** in almost all diluents examined. This may be a consequence of the larger hydrophobic sulfur atom present in **5**. The best diluent for both ligands **4** and **5** was tetrachloroethane although this diluent would be unsuitable in a separation process. The maximum solubilities of the ligands **4** and **5** in 1-octanol, which is the preferred solvent for a SANEX process, were < 3 and 5 – 10 mmol dm^{-3}, respectively. This compares with a solubility of $CyMe_4$-BTBP **3** of 10 mM dm^{-3} in the same diluent.[40]

Table 1. The approximate solubilities of the ligands **4** and **5** in various diluents.

Solvent	BTBP solubility (mM) at 25 °C	
	Cy_5-O-Me_4-BTBP **4**	Cy_5-S-Me_4-BTBP **5**
1-octanol	< 3	5 – 10
Cyclohexanone	5	14
Tetrachloroethane	> 32	> 32
Dichloroethane	6 – 7	> 32
Toluene	2 – 3	16 – 32
Nitrobenzene	2 – 3	> 32
Cyclohexanol	< 3	< 3
Dipentyl ether	< 3	< 3
Chlorobenzene	< 3	7 – 8

Results and Discussion

The distribution ratios and separation factors for the extraction of Am(III) and Eu(III) from 3 M nitric acid solutions into 3 mM organic solutions of each of the ligands **4** and **5** are shown in Figure 2. For Cy_5-O-Me_4-BTBP **4**, the highest distribution ratio observed was 0.043 in cyclohexanone and the highest separation factor observed was more than 8 in 2-methylcyclohexanone. To our knowledge, this is the first time that 2-methylcyclohexanone has been studied as a potential diluent for the separation of An(III) from Ln(III). When compared with the extraction of Am or Eu by neat cyclohexanone in the absence of any ligand (Figure 2) it must be concluded that the diluent itself is responsible for much of the extraction observed in this diluent. With Cy_5-S-Me_4-BTBP **5**, the extraction was found to depend more strongly on the diluent used and slightly higher distribution ratios and separation factors were observed than was the case with Cy_5-O-Me_4-BTBP **4**. As with ligand **4**, the highest distribution ratio observed was in cyclohexanone (0.247) and the highest separation factor observed was in 2-methylcyclohexanone (44.0). Clearly, the extraction of Am(III) and Eu(III) by cyclohexanone itself is significant and proceeds with little selectivity. This may explain the higher D values and the lower separation factors observed compared to the other diluents.

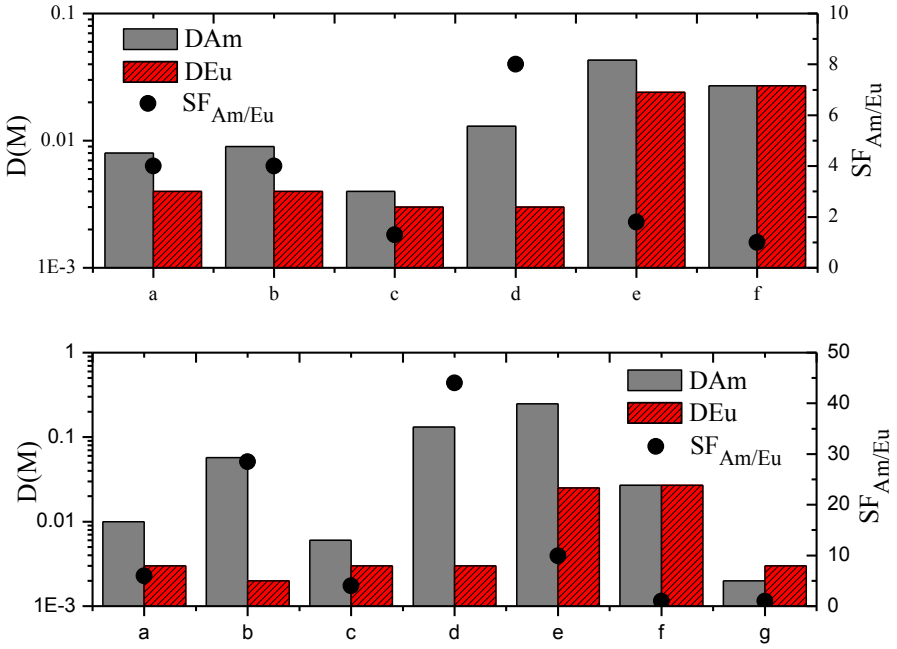


Figure 2. Extraction of Am(III) and Eu(III) from 3 M HNO_3 by 3mM Cy_5-O-Me_4-BTBP **4** (top) and 3mM Cy_5-S-Me_4-BTBP **5** (bottom) in various diluents (a = tetrachloroethane, b = dichloroethane, c = nitrobenzene, d = 2-methylcyclohexanone, e = cyclohexanone, f = cyclohexanone without ligand **4** or **5**, g = toluene).

We attempted to rationalise these results by looking for a correlation between the distribution ratio for Am(III) and the basic characteristics of the diluents used. The properties considered were permittivity, dipole moment and solubility parameter.

The equation:

$$r = \frac{n \cdot \sum x \cdot y - (\sum x) \cdot (\sum y)}{\sqrt{\left[n \sum x^2 - (\sum x)^2\right] \cdot \left[n \sum y^2 - (\sum y)^2\right]}}$$

where *r* is the correlation coefficient, *n* is the number of data points correlated, and x, y are variables (the value of the property and the distribution ratio, respectively), was used to evaluate the correlation.

The only confirmed correlation observed was that between D(Am) and the permittivity[69] of the diluent (Figure 3). For non-aromatic diluents (when nitrobenzene was omitted from the data), a high correlation coefficient of 0.93 was observed. One interpretation of this correlation is that the lipophilic ion pair

$[Am(BTBP)_2(NO_3)_3]$ is more soluble in polar diluents and thus more easily extracted into diluents of high permittivity.

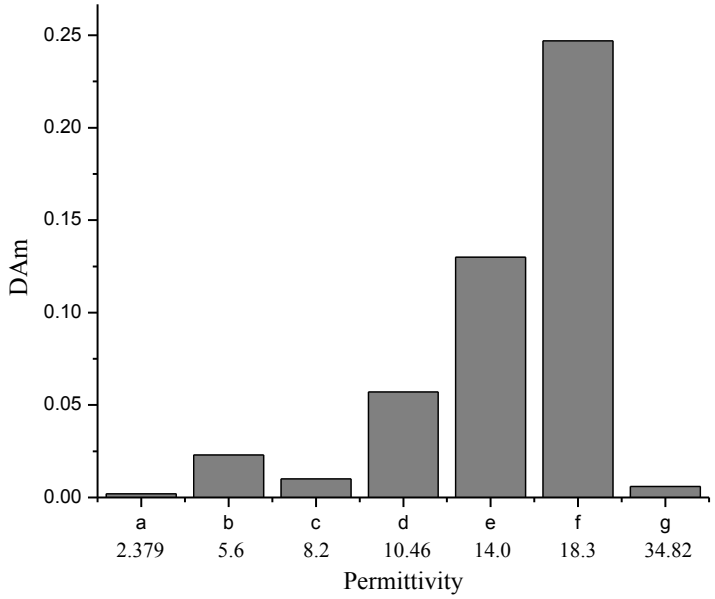


Figure 3. Correlation of the distribution ratio for Am(III) for Cy_5-S-Me_4-BTBP **5** with the permittivity of the diluent (x axis). (a = toluene, b = chlorobenzene, c = tetrachloroethane, d = dichloroethane, e = 2-methylcyclohexanone, f = cyclohexanone, g = nitrobenzene). Correlation coefficient = 0.93 (without nitrobenzene).

We then carried out a detailed examination of the extraction of Am(III) and Eu(III) by the ligand **5** in 1-octanol which is the preferred diluent for a SANEX process. As the solubility of Cy_5-O-Me_4-BTBP **4** in 1-octanol was less than 5 mM (cf. Table 1), its extraction properties in this diluent were not studied. The distribution ratios and separation factors for Cy_5-S-Me_4-BTBP **5** as a function of the initial nitric acid concentration are presented in Figure 4. Distribution ratios for Am(III) were larger than those for Eu(III) at nitric acid concentrations of 1-4 M and the highest separation factor observed was 46 from 2 M HNO_3. It is also apparent that the distribution ratio increases with increasing $[HNO_3]$ and this trend is also observed with $CyMe_4$-BTBP **3**[40] and the other BTBPs.[28–38] The maximum D value observed was 0.46 from 4 M HNO_3.

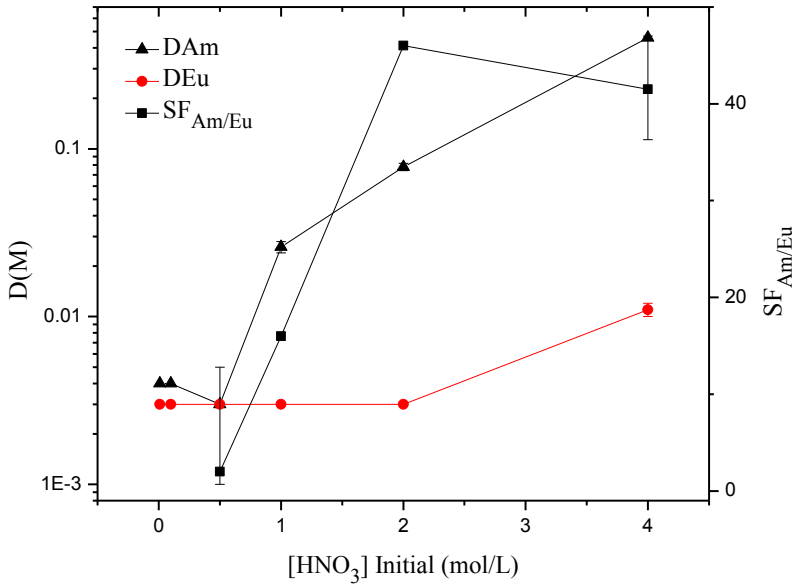


Figure 4. Extraction of Am(III) and Eu(III) by Cy_5-S-Me_4-BTBP **5** in 1-octanol (5 mM) as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

The dependence of D(Am) with time for Cy_5-S-Me_4-BTBP **5** in 1-octanol is shown in Figure 5. It is evident that the kinetics of extraction is rather slow and the equilibrium distribution ratio was only reached after approx. 6 hours of contact. No attempt to evaluate the effect of phase-modifiers (eg: TODGA, DMDOHEMA)[4,5] on the kinetics of extraction was carried out in this study. The equilibrium distribution ratio remained largely constant over 168 hours of contact, indicating that Cy_5-S-Me_4-BTBP **5** is stable and does not suffer from hydrolytic degradation.

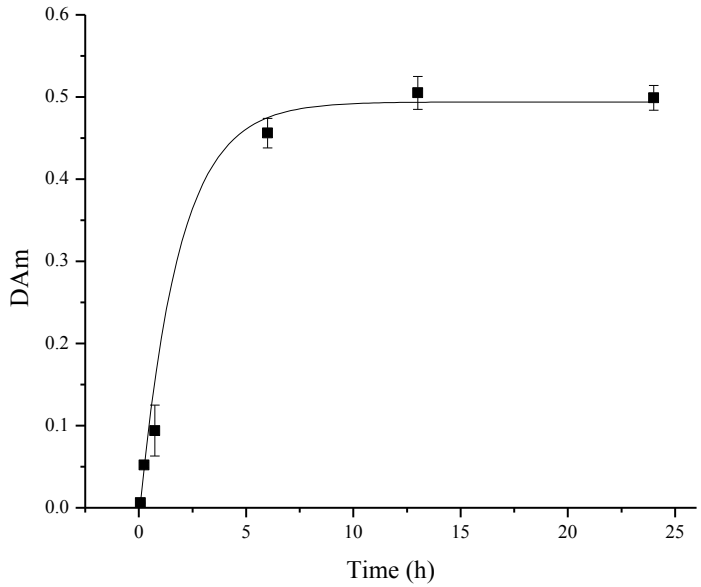


Figure 5. Extraction of Am(III) from 4 M HNO_3 as a function of time for Cy_5-S-Me_4-BTBP **5** in 1-octanol (5 mM).

Since cyclohexanone gave the most promising results for both ligands (cf. Figure 2), a detailed study of the extracting properties of ligands **4** and **5** was then carried out using this diluent. The D values and $SF_{Am/Eu}$ for Cy_5-O-Me_4-BTBP **4** as a function of the initial nitric acid concentration are presented in Figure 6. In 1-4 M HNO_3, D(Am) > D(Eu) and the highest separation factor observed was 5.8 in 2 M HNO_3. Some loss of the diluent to the aqueous phase had occurred after contact as the volume of the organic phase had decreased and the volume of the aqueous phase had increased.

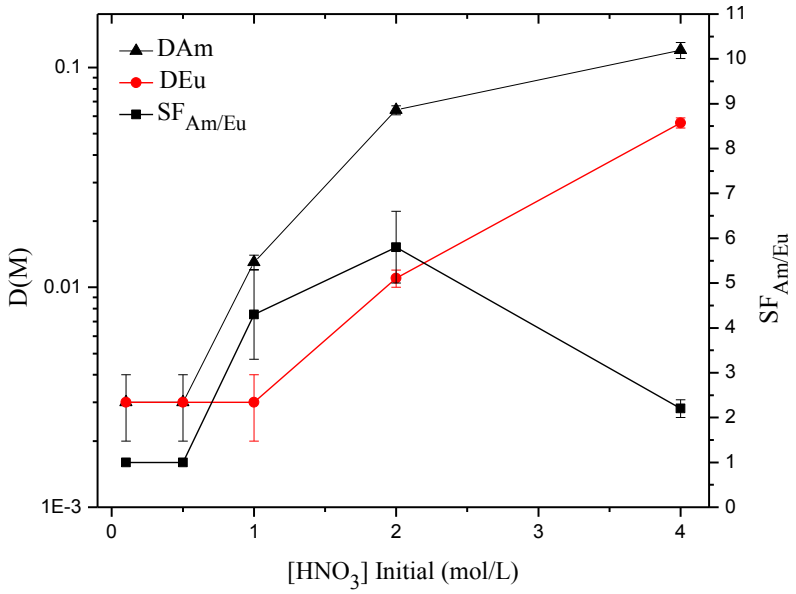


Figure 6. Extraction of Am(III) and Eu(III) by Cy_5-O-Me_4-BTBP **4** in cyclohexanone (5 mM) as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

Slightly better results were obtained with Cy_5-S-Me_4-BTBP **5** in cyclohexanone (Figure 7). In this case the highest distribution ratio for Am(III) was 0.7 at 4 M HNO_3 and the highest separation factor observed was 22 at 2 M HNO_3. Thus a higher distribution ratio and a lower separation factor were observed for this ligand in cyclohexanone than in 1-octanol (Figure 4). Once again, a decrease in the volume of the organic phase and an increase in the volume of the aqueous phase were observed after phase contact. These observations could be explained by the co-extraction of Am(III) and Eu(III) by the diluent itself (cf. Figure 2) and by the partial miscibility of cyclohexanone and water, respectively.

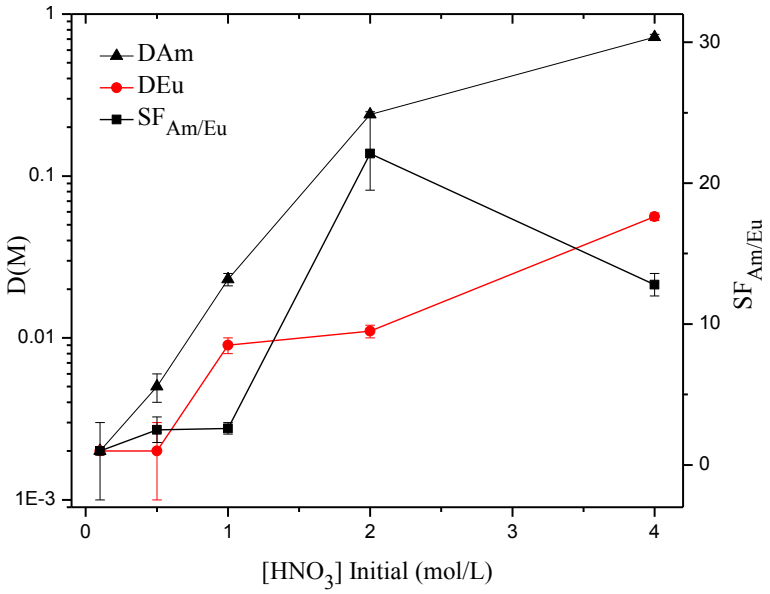


Figure 7. Extraction of Am(III) and Eu(III) by Cy_5-S-Me_4-BTBP **5** in cyclohexanone (5 mM) as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

In order to verify this, the extraction of Am(III) and Eu(III) by cyclohexanone itself without the ligands **4** or **5** was then studied. The results are shown in Figure 8. Clearly the extraction of Am(III) and Eu(III), although small, is significant and increases as [HNO_3] increases. When comparing the data in Figure 8 with those in Figures 6 and 7, it can be clearly seen that no net extraction of Eu(III) by either of the ligands was observed at any HNO_3 concentration – the D(Eu) values are practically identical in the presence and in absence of the ligands. However, both ligands extract Am(III) at HNO_3 concentrations higher than 1 M.

The diluent itself is also mildly selective for Eu(III) over Am(III) as separation factors of Am(III) over Eu(III) of less than 1 are obtained except in 4 M HNO_3. Extraction of Eu(III) and Am(III) by the diluent may hence contribute to the lower separation factors obtained for Cy_5-S-Me_4-BTBP **5** in cyclohexanone than in 1-octanol. The mechanism of the extraction of both trivalent metal ions by cyclohexanone is unclear at this moment. This property of cyclohexanone causes this diluent to behave as a phase transfer agent for the M(III) ions, a phenomenon that was forecasted earlier by

Narbutt.[37] Hence, the kinetics of extraction with this diluent should be much faster than with 1-octanol.

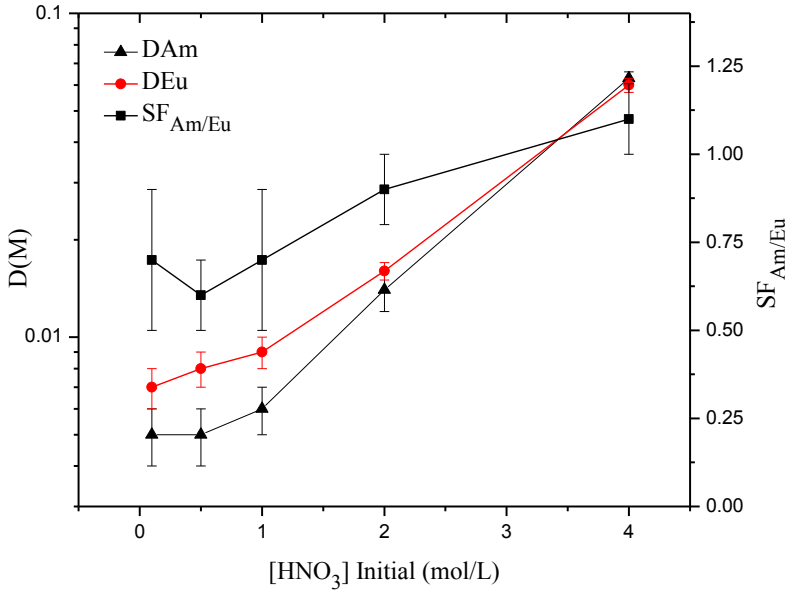


Figure 8. Extraction of Am(III) and Eu(III) by cyclohexanone itself as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

To verify this assumption, the kinetics of the extraction of Am(III) by Cy_5-S-Me_4-BTBP **5** in cyclohexanone were then studied. The extraction of Am(III) from 4 M HNO_3 as a function of time is shown in Figure 9. The equilibrium D value was achieved after only 30 minutes of contact; a rate of extraction that is comparable to, but not as fast as that obtained with C5-BTBP in cyclohexanone.[30,31] This rate of extraction is fast enough for an efficient separation process. In contrast, the same ligand **5** requires 6 hours of contact to reach equilibrium in 1-octanol (Figure 5). The faster kinetics observed in cyclohexanone can be attributed to the phase-transfer properties of this diluent which also gives faster kinetics with C5-BTBP.[30,31] In comparison, $CyMe_4$-BTBP **3** requires a phase-transfer agent (eg: TODGA, DMDOHEMA) to achieve comparable kinetics in 1-octanol.[40] This result confirms the suggestion of Narbutt and Krejzler who concluded that "this quite well water-soluble ketone should not be considered an inert solvent (diluent), but a reagent which

solvates the M(III) ions in the aqueous phase and acts as phase transfer reagent for An and Ln ions, greatly improving the kinetics of their solvent extraction using BTBP ligands".[37]

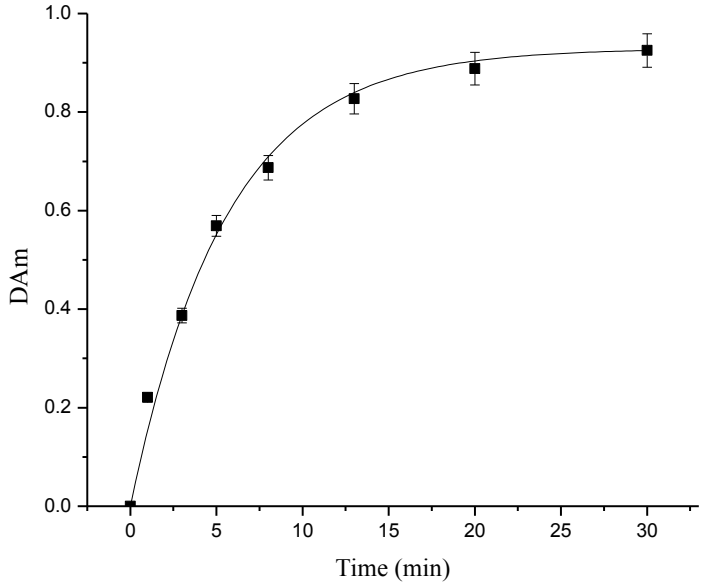


Figure 9. Extraction of Am(III) from 4 M HNO_3 as a function of time for Cy_5-S-Me_4-BTBP **5** in cyclohexanone (5 mM).

The relationship between the distribution ratio for Am(III) and the concentration of Cy_5-S-Me_4-BTBP **5** in cyclohexanone was then studied to establish the metal:ligand stoichiometry of the extracted species. It is known that the BTBPs can extract Am(III) into 1-octanol as both 1:1 and 1:2 species with the 1:2 species being more favoured.[28–38] A plot of –log (D(Am)) v –log [Cy_5-S-Me_4-BTBP] gave a straight line with a slope of 1.83. However, this does not take into account the extraction of Am(III) by cyclohexanone itself. When the values of D(Am) are corrected for the extraction by the diluent itself (D – Do), a slope of 1.94 is obtained (Figure 10). This indicates that Am(III) is extracted as the 1:2 complex. From these results, the extraction of Am(III) by **5** proceeds by a solvating mechanism:

$$Am^{3+}_{aq} + 3NO_3^-{}_{aq} + 2BTBP_{org} \rightarrow [Am(BTBP)_2(NO_3)_3]_{org}$$

These results suggest that the formation of less-hydrophobic 1:1 complexes is not responsible for the lower extraction efficiency of Cy_5-S-Me_4-BTBP **5** compared to $CyMe_4$-BTBP **3**.

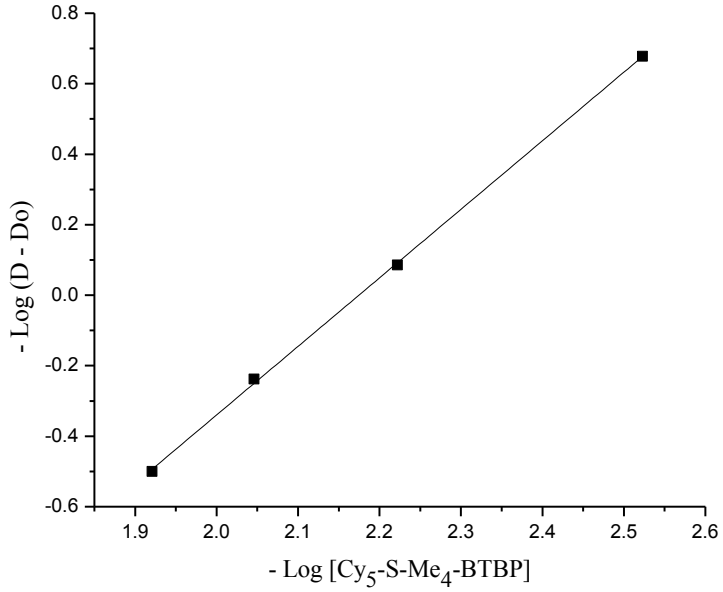


Figure 10. Dependence of D(Am), corrected on the extraction by cyclohexanone itself (y axis), on the concentration of Cy_5-S-Me_4-BTBP **5** (x axis) in cyclohexanone (from 3 M HNO_3). $y = 1.94x - 4.23$, $R^2 = 0.99$.

In order to allow for a detailed comparison of the ligands **4** and **5** with $CyMe_4$-BTBP **3**, the extraction of Am(III) and Eu(III) by Cy_5-O-Me_4-BTBP **4**, Cy_5-S-Me_4-BTBP **5** and $CyMe_4$-BTBP **3** in cyclohexanone was carried out. The extraction properties of the related ligand C5-BTBP in cyclohexanone have been studied previously.[30,31] We thus studied the dependence of D(Am) and D(Eu) on [HNO_3] for $CyMe_4$-BTBP **3** under the same conditions that were used for Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** (Figures 6 and 7). The dependence of D(Am) on the initial nitric acid concentration for the three ligands **3**, **4** and **5** in cyclohexanone is presented in Figure 11. It is clear that the extraction of Am(III) by $CyMe_4$-BTBP **3** is greater than by Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** in cyclohexanone. The highest distribution ratio observed for **3** was 12.2 from 2 M HNO_3. This compares with the maximum D values observed for ligands **4** and **5** of 0.12 and 0.72, respectively. The distribution

ratios also increase with increasing nitric acid concentration for all three ligands except for $CyMe_4$-BTBP **3** where the maximum value is already reached at 2 M HNO_3.

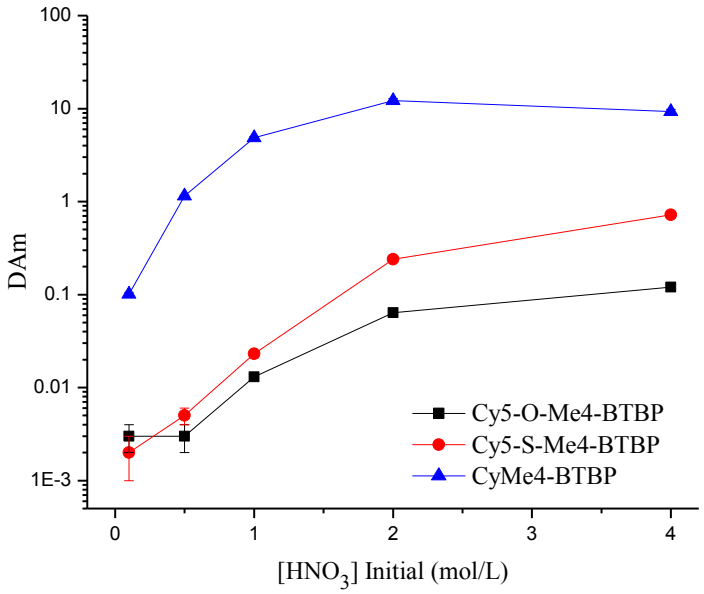


Figure 11. Comparison of the dependencies of the distribution ratios for americium(III) on initial nitric acid concentrations for Cy_5-O-Me_4-BTBP **4** (■), Cy_5-S-Me_4-BTBP **5** (●) and $CyMe_4$-BTBP **3** (▲) in cyclohexanone (5 mM for all ligands).

The dependence of the separation factors of Am(III) over Eu(III) on the initial nitric acid concentration for the three ligands **3**, **4** and **5** in cyclohexanone is shown in Figure 12. Once again $CyMe_4$-BTBP **3** proved superior to both Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5**. The separation factors for **3** were uniformly larger than those of ligands **4** and **5** over the range 0.1 – 4 M HNO_3. For all three ligands, the separation factors first increase, then start to decrease as the nitric acid concentration increases. This effect can be attributed to the non-selective extraction of both Am(III) and Eu(III) by the diluent itself that increases with increasing nitric acid concentration. It should be noted that the separation factors discussed here describe the separation properties of the combinations ligand – cyclohexanone, not the separation properties of the ligands themselves. Since no net extraction of Eu(III) by either of the ligands **4** or **5** was observed at any HNO_3 concentration after the

correction for the Eu extraction by the neat cyclohexanone, the only conclusion that can be made here is that it cannot be excluded that the ligands yield high separation factors.

It is clear that both the affinity for Am(III) and the selectivity for Am(III) over Eu(III) of both of the ligands **4** and **5** are lower than those for $CyMe_4$-BTBP **3**. One possible reason for this could be that the reduction in the ring size of the aliphatic part of the $CyMe_4$-BTBP molecule **3**, combined with the replacement of a CH_2- group with a heteroatom (O- in **4** and S- in **5**) produces a complex which is somewhat less hydrophobic than $CyMe_4$-BTBP **3**. Another explanation could be that the electron-withdrawing inductive effect of the O- or S- heteroatom in **4** or **5** reduces the electron density in the triazine rings and weakens the coordinating ability of the 2-N donor atom.

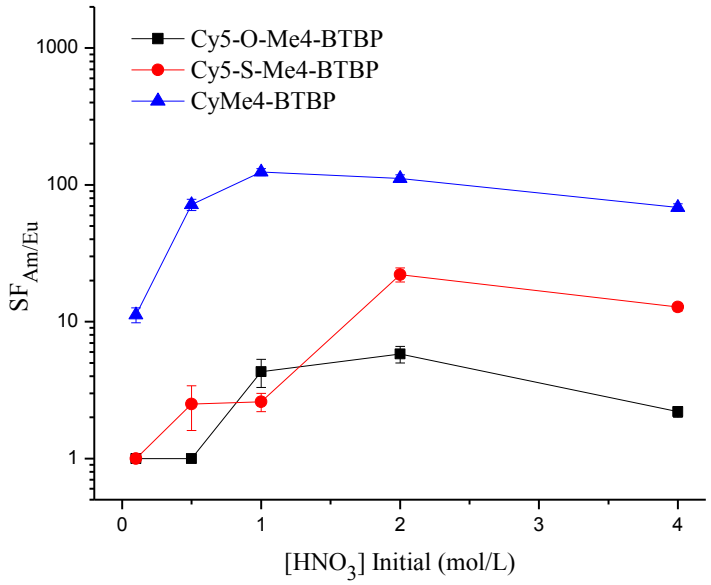


Figure 12. Comparison of the dependencies of the separation factors for Am(III) over Eu(III) on initial nitric acid concentrations for Cy_5-O-Me_4-BTBP **4** (■), Cy_5-S-Me_4-BTBP **5** (●) and $CyMe_4$-BTBP **3** (▲) in cyclohexanone (5 mM for all ligands).

With respect to the extraction of Am(III) and Eu(III) by Cy_5-S-Me_4-BTBP **5** in 2-methylcyclohexanone, the separation factors in this diluent were greater than in cyclohexanone (cf. Figure 2). The dependence of the distribution ratios and separation

factors of Cy_5-S-Me_4-BTBP **5** on the initial nitric acid concentration in 2-methylcyclohexanone is shown in Figure 13. The highest D value for Am(III) observed was 0.43 (from 4 M HNO_3) and the highest $SF_{Am/Eu}$ observed was 31 (from 4 M HNO_3). These values are comparable to those obtained with ligand **5** in 1-octanol (cf. Figure 4). Thus there is a lower affinity of ligand **5** for Am(III) but a higher selectivity for Am(III) over Eu(III) in 2-methylcyclohexanone than in cyclohexanone (cf. Figure 7). At low acidities (0.1-0.5 M HNO_3), there appeared to be an unexpected selectivity for Eu(III) over Am(III) (even though the error bars for D(Am) and D(Eu) practically overlap). This reversal in selectivity was not observed with ligand **5** in cyclohexanone.

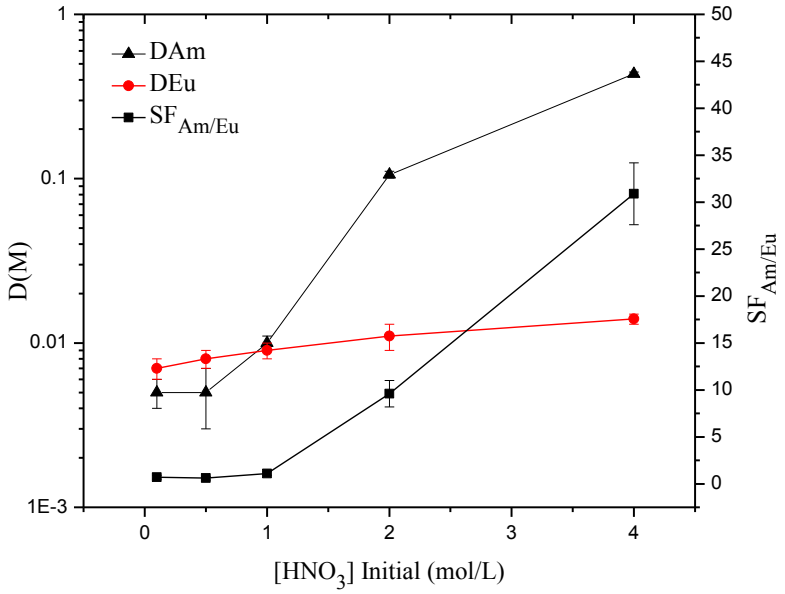


Figure 13. Extraction of Am(III) and Eu(III) by Cy_5-S-Me_4-BTBP **5** in 2-methylcyclohexanone (5 mM) as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

Accordingly, we then studied the extraction of Am(III) and Eu(III) by 2-methylcyclohexanone itself as a function of the initial nitric acid concentration. These results are shown in Figure 14. Generally, the distribution ratios for Am(III) and Eu(III) are lower than those observed in cyclohexanone (cf. Figure 8) and the highest values observed were D(Am) = 0.005 and D(Eu) = 0.007. For HNO_3 concentrations

higher than 1 M, the data measured enable calculation of Am/Eu separation factors corrected for the contribution of 2-methylcyclohexanone to the extraction of metal ions. The corrected values, that characterise the separation properties of the ligand **5** itself, are $SF_{Am/Eu}$ = 17 for 2M HNO_3 and $SF_{Am/Eu}$ = 43 for 4M HNO_3.

The most notable difference between the extraction of Am(III) and Eu(III) by cyclohexanone itself and 2-methylcyclohexanone itself is that, for 2-methylcyclohexanone, these values do not increase at higher acidities as was observed with cyclohexanone. There is also a slight selectivity for Eu(III) over Am(III) from 0.1-2 M HNO_3 as was the case with cyclohexanone. In addition, no observable mixing of the two phases had occurred and we observed no changes in the volumes of the aqueous and organic phases after 6 hours of contact with 4 M HNO_3. Thus two of the principal disadvantages of cyclohexanone as a potential diluent have been eliminated by using 2-methylcyclohexanone. The extraction of both Am(III) and Eu(III) at higher acidities has been suppressed and no loss of the diluent to the aqueous phase has occurred. Further work is underway on the use of $CyMe_4$-BTBP **3** with this diluent and various 2-, 3- and 4-alkylcyclohexanones in an effort to identify potential new diluents suitable for a separation process.

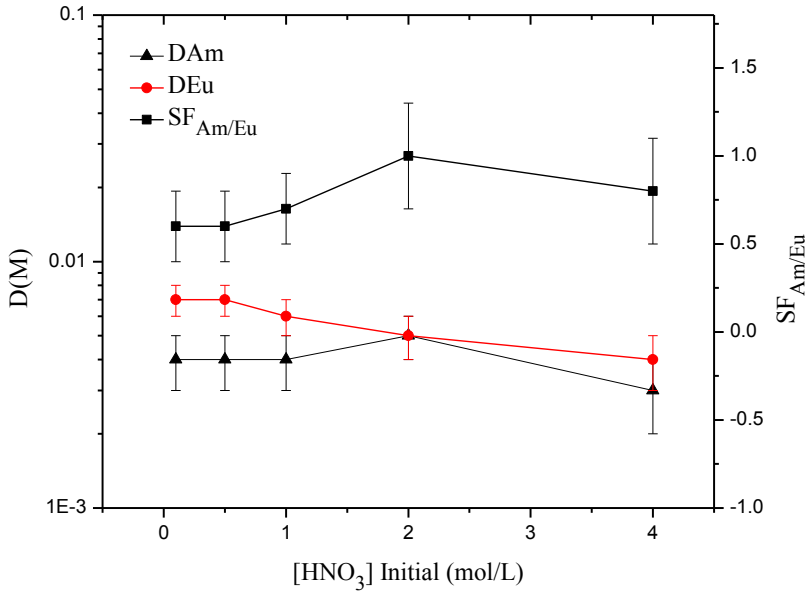


Figure 14. Extraction of Am(III) and Eu(III) by 2-methylcyclohexanone itself as a function of initial nitric acid concentration (▲ = D(Am), ● = D(Eu), ■ = $SF_{Am/Eu}$).

Conclusions

It has been shown that the affinities for Am(III) and the selectivities for Am(III) over Eu(III) of both of the ligands Cy_5-O-Me_4-BTBP **4** and Cy_5-S-Me_4-BTBP **5** are lower than those of $CyMe_4$-BTBP,[40] indicating that the design of the aliphatic part of the BTBP molecule is very important in the context of the development of future ligands for the partitioning of actinides from lanthanides. The kinetics of extraction of Am(III) and Eu(III) by ligand **5** were faster in cyclohexanone than in 1-octanol due to the phase-transfer effect of cyclohexanone. In addition, 2-methylcyclohexanone has been introduced as a potential new diluent that has some desirable properties compared to cyclohexanone.

Acknowledgments

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