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Complete List of Authors:	Bessen, Nathan ; Colorado School of Mines, Department of Chemistry and Geochemistry Yan, Qiang; University of Science and Technology of China, School of Physical Sciences; China Academy of Engineering Physics, Institute of Nuclear Physics and Chemistry Pu, Ning; Institute of Nuclear and New Energy Technology, Tsinghua University, Division of Nuclear Chemistry Technology Chen, Jing; Tsinghua University, Xu, Chao; Tsinghua University, Collaborative Innovation Center of Advanced Nuclear Energy Technology, Institute of Nuclear and New Energy Technology Shafer, Jenifer ; Colorado School of Mines, Department of Chemistry and Geochemistry

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Extraction of the Trivalent Transplutonium Actinides Americium through Einsteinium by the Sulfur Donor Cyanex 301

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Nathan Bessen,[a] Qiang Yan,[b] Ning Pu,[b] Jing Chen,[b] Chao Xu[b,*] and Jenifer Shafer[a,*]

In the extraction of lanthanides by a sulfur donor ligand, the purified Cyanex 301 (HC301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid), a transition in the coordination mode of extracted complexes has been observed between Eu and Gd. The light lanthanides La–Eu tend to be extracted as inner sphere complexes with HC301 directly coordinating the metal whereas the second half of the series Gd¬Lu have a tendency to be extracted as outer sphere complexes. Without extended actinide studies, spanning the transplutonium actinides, it was unclear if a similar change in the extraction mechanism occurs in the actinide series. To assess this, solvent extraction studies were completed examining the slope dependence of the actinides and lathanides in the presence of varied nitrate and acid concentrations. Significant variation in the slope dependences was not observed for either the actinides or the lanthanides as pC_{H+} varied, however, the nitrate dependence and neodymium spectroscopy data suggest that the formation of outer sphere complexes is suppressed by higher nitrate concentrations. This suppression of outer sphere complexes enhanced the extraction of lanthanides, but not the actinides and suggests that the actinides form inner sphere complexes. Therefore, the HC301 separations chemistry observed thus far suggest differences in the chemistry of the actinides and lanthanides continues to persist deep into the actinide series.

Introduction

One of the most challenging separations for the processing and disposal of used nuclear fuel is the separation of trivalent actinides and lanthanides due to the similar sizes, charges and chemistries of the two types of metals. Of the proposed processes for this separation, those using dithiophosphinic acids have shown some of the greatest selectivity for the actinides relative to the trivalent lanthanides[1–4]. In particular, purified Cyanex 301 (HC301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid, Figure 1), has received the most attention due to having the most significant commercial availability relative to other dithiophosphinates and reported separation factors as large as 5000 between trivalent lanthanides and actinides[4].

Despite the volume of research on HC301, a multitude of questions about its extraction characteristics remain unanswered - including how it extracts the heavier actinides. In the current literature, the heaviest actinide studied with HC301 and no other ligands was Cm by Jensen and Bond[5]. The lanthanides in this system have been more thoroughly studied and an interesting change in the extraction mechanism is observed half-way through the series[4,6,7]. The first half of the lanthanide series tend to be extracted as inner sphere complexes with distinct metal-sulfur bonds while the heavier metals from Gd to Lu are typically extracted as outer sphere complexes where water is directly solvating the metal ion[4,6,7]. This transition from inner- to outer-sphere complexes is gradual with some formation of both types of complexes occurring simultaneously[4,7,8]. Moreover, at high degrees of saponification of the HC301, metals may be extracted within reverse micelles that likely contain multiple metal ions and additional water[9,10]. In an extraction system using commercial HC301 as supplied, and the strongly coordinating ligand 3,4,3-LI(1,2-HOPO), Figure S1, in the aqueous phase, there were significant changes in the extraction of the actinides from Am to Cf, but this was attributed to changes in the stability of the aqueous complex and oxidation of Bk to the tetravalent state instead of any changes in the extraction mechanism for the different actinides[11]. Additionally, to mimic industrially anticipated conditions, the above work did not purify the commercial HC301 and much of the metal-extractant interactions under radiotracer conditions were probably controlled by the oxo-extractant impurity, Cyanex 272, Figure 1. In systems containing only purified HC301 as the extractant and no aqueous ligands, all of the actinides studied have been lighter than Bk, so it was unknown if the actinide series has the same change in extraction mechanism as the lanthanides or if they continue to be extracted as the inner sphere complexes that have been observed with the light lanthanides, Am, and Cm[3–5,12–15].

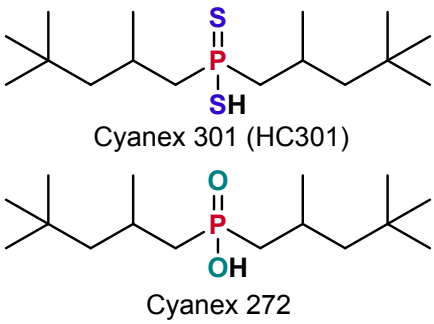

Figure 1. Structure of Top: HC301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid, Cyanex 301) and Bottom: Cyanex 272.

[a.] Colorado School of Mines, 1500 Illinois St, Golden, CO 80401
[b.] Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

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In this work, the extraction of the trivalent actinides Am–Es and most of the lanthanides from an aqueous, sodium nitrate media by purified HC301 was examined to determine if the extracted complexes of actinides with HC301 undergo a change from inner sphere to outer sphere complexes with the heavier members of the series as is observed within the lanthanide series. Based on slope analysis of the previous extraction results, the impact of nitrate anions in the aqueous phase on the extraction was also tested for these metals.

Experimental

Reagents

Sodium nitrate (ACS grade), anhydrous dodecane (≥99%), anhydrous hexanes (≥99%), and 50% sodium hydroxide solution were obtained from Sigma-Aldrich and used as supplied. Ethanol (200 proof, ≥99%) was purchased from Pharmco by Greenfield Global. Concentrated nitric acid (ACS grade) was purchased from Mallinckrodt Chemicals and hydrochloric acid (ACS grade) were supplied from Macron Fine Chemicals. Sodium sulfate (ACS grade) and ammonium sulfate (ACS grade) were obtained from Fisher Chemical. Lanthanum oxide (99.99%), neodymium oxide (99.995%), samarium oxide (99.99%), europium oxide (99.99%), gadolinium oxide (99.99%), dysprosium oxide (99.9%), erbium oxide (99.995%), ytterbium oxide (99.995%), and lutetium oxide (99.95%) was purchased from Treibacher Industrie AG. Praseodymium oxide (99.9%), holmium oxide (99.99%), and thulium oxide (99.99%) was purchased from Yick-Vic Chemicals and Pharmaceuticals. All lanthanide oxides were converted to the nitrate by dissolution in nitric acid.

Cyanex® 301 GN extractant (HC301) was obtained from Solvay and purified as follows[16]. The crude HC301 was dissolved in hexanes and converted to the ammonium salt by bubbling with dry ammonia gas generated from the reaction between ammonium sulfate and sodium hydroxide. The solid NH_4C301 salt was filtered, washed, dissolved in a 6.8% solution of ethanol in water, and adjusted to pH 10 by addition of sodium hydroxide. To this, hexane and 0.005 equivalents of neodymium nitrate were added and shaken for two minutes. After the phases disengaged, the hexane phase was removed, and this process was repeated 14 more times. The remaining aqueous phase was acidified with hydrochloric acid and the regenerated HC301 was extracted with hexane. This hexane phase was removed and dried over anhydrous sodium sulfate before evaporation of the hexane to recover the purified HC301 (18.9% yield). The resulting purity was found to exceed 99.9% by ^{31}P NMR after 2048 scans of a sample containing almost entirely purified HC301 in a minimal amount of $CDCl_3$.

Radiotracer Distribution Studies

Caution! The europium-152/154, americium, curium, berkelium, californium, and einsteinium solutions used in this work were radioactive. Appropriate precautions must be made when handling these samples.

Distribution measurements were made with $^{152/154}$Eu, ^{241}Am, ^{244}Cm, ^{249}Bk, ^{249}Cf, and $^{253/254}$Es radiotracers using an organic phase of 0.50 M HC301 dissolved in dodecane that had been pre-equilibrated with the appropriate aqueous phase prior to the introduction of metal. The aqueous phase contained 5 mM Lu(III) as the carrier metal and the appropriate concentration of sodium nitrate. The desired pC_{H+} was obtained by addition of nitric acid or sodium hydroxide. Equal volumes (0.750 mL) of the aqueous phase and pre-equilibrated organic phase were combined in a glass vial and the appropriate volume (4–8 µL) of the desired lanthanide or actinide (Eu, Am–Es, dissolved in 0.001 M nitric acid) was added to achieve an activity of approximately 30,000 CPM. Samples were shaken for 30 min at a room temperature of 21-23°C and subsequently centrifuged for 2 min. This was sufficient for the extraction of metal to obtain equilibrium. The activity (***A***) of a 0.300 mL sample of each phase was counted on a HIDEX 300 SL liquid scintillation counter. Ultima Gold AB scintillation cocktail was used for experiments that require discrimination between two radioisotopes (one α emitter and one β^- emitter). When α/β discrimination was not needed, Ecoscint A scintillation cocktail was used. The pC_{H+} (which is $-\log_{10}[H^+]$ on the molar concentration scale) of the remaining, equilibrated aqueous phase was measured with an Orion 8103BNUWP Ross Ultra pH probe. The distribution ratio (*D*) for a given radioisotope was calculated by $D = A_{org}/A_{aq}$. To quantify the separation between an actinide and Eu, the separation factor (*SF*) was calculated by the formula: $SF_{An/Eu} = D_{An}/D_{Eu}$.

Lanthanide Distribution Studies

The distribution ratios of the non-radioactive lanthanides were collected from a system much like that used for the radiotracer experiment, except for the aqueous phase which contained a set of four or five lanthanides (either La, Pr, Nd, Sm, and Lu, or Eu, Gd, Dy, and Lu, or Ho, Er, Tm, Yb, and Lu) at a concentration 5 mM of each metal, the appropriate amount of sodium nitrate, and the equilibrium pC_{H+} was adjusted to 4.46 ± 0.05. An aliquot of the aqueous phase was taken and diluted in 3% nitric acid for analysis in a Varian Liberty Series II inductively coupled plasma-atomic emission spectrometer (ICP-OES). The emission wavelengths used for each metal are shown in Table S1. The concentration of metal in the aqueous phase (C_{aq}) was measured directly and metal concentration in the organic phase (C_{org}) was measured by back extraction of the metal into a 0.5 M HNO_3 aqueous solution. The distribution ratio (*D*) for a given lanthanide was calculated by $D = C_{org}/C_{aq}$.

UV-vis Spectrophotometry

Organic phase samples were prepared by extracting Nd with a 0.50 M HC301 organic phase from a 0.5 M $Nd(NO_3)_3$ aqueous phase with up to 6.5 M $NaNO_3$ added. The UV-vis spectra was collected using a portion of the resulting Nd-loaded organic phase. UV-vis spectra were collected with a Cary 6000i spectrophotometer using quartz cuvettes with a 1 cm pathlength. Spectra were collected using a bandwidth of 0.5 nm and an integration time of 0.100 seconds. The reference cell was loaded with the organic phase that had not been contacted with any aqueous phase.

Computational Studies

Geometry optimizations and frequency calculations of $M(C301)_3$ and $M(C301)_2(NO_3)$ complexes were done using density functional theory (DFT) using a PBE functional with scalar relativity[17–19] and triple-ζ plus one polarization function (TZP) with a small frozen core approximation[20] in ADF 2019.104[21]. The 2,4,4-trimethylpentyl groups of HC301 were truncated to methyl groups to reduce the computational time. The calculations used COSMO solvation with hexane and the atomic radii were set to the Allinger radii divided by 1.2[22]. Coordinates of the optimized structures can be found in the SI.

Results and Discussion

Carrier Metals

Although ^{31}P NMR results suggest the purity of the purified HC301 exceeds 99.9%, appreciable extraction of trace amount of $^{152/154}$Eu was still found at pH 3.5 with the purified reagent, indicating there were still impurities that exhibit strong affinity to Eu(III) and causing much lower and more variable separation factors. Therefore, carrier metals had to be used to mask the impurities. Both Eu and Lu was considered for this purpose. As shown in Figure 2, the distribution ratio of Eu at a constant pC_{H+} of 4.66 was found to be dependent upon the concentration of Eu and Lu in the aqueous phase. At higher concentrations of Eu and Lu, the distribution ratio of Eu decreased.

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This is consistent with the findings of Zhu et al. who found that higher concentrations of lanthanides increase separation factors by decreasing the extraction of lanthanides[23]. It is expected that Lu would be more effective at masking the impurities than Eu as Lu is the most readily extracted lanthanide by both Cyanex 272 and Cyanex 302,[24,25] which are common extracting impurities and degradation products found in HC301[26–30]. Indeed, Lu was found to be more effective than Eu in this regard as it suppressed the extraction of Eu at lower concentrations than Eu (Figure 2). For these reasons, all subsequent experiments were conducted with an aqueous phase containing 5 mM $Lu(NO_3)_3$ to ensure that the strongly extracting impurities were fully masked.

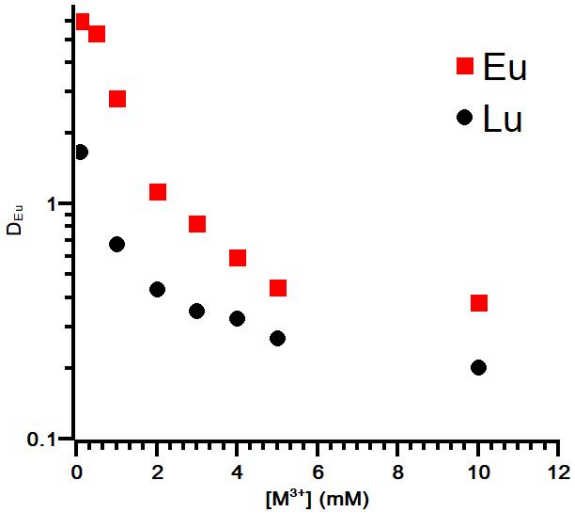

Figure 2. The distribution ratio of Eu with varying aqueous concentrations of Eu (red squares) or Lu (black circles). The organic phase consisted of 0.5 M HC301 in *n*-dodecane and the aqueous phase is 1 M $NaNO_3$ adjusted to pC_{H+} 4.66

Transplutonium Actinide Extraction

The distribution ratios of Eu and the actinides Am through Es at varying equilibrium pC_{H+} are shown in Figure 3 (top). The distribution ratios of the actinides are closely grouped with slopes ranging from 2.4 ± 0.1 (Bk) to 2.57 ± 0.07 (Am). Europium is more weakly extracted compared to any of the actinides tested and has a lower slope of 1.13 ± 0.08. These slopes present with less of a proton dependence than those observed by both Zhu et al.[3] and Jensen and Bond[5], particularly for Eu. The seemingly decreased proton dependence may be due to examining a wider range of pC_{H+} here and the presence of the 5 mM Lu carrier. As Lu competes with Eu for extraction[8], the addition of Lu suppresses the extraction of Eu by trace impurities. The greater extraction of the actinides, particularly at higher pC_{H+} gives rise to a separation factor that increases with pC_{H+} (Table 1). Separation factors at pC_{H+} 4 range from 700 for Es to 6300 for Am. The separation factor for Am is comparable to the value of 5900 seen by Zhu et al[3]. and 6000 seen by Hill et al[31].

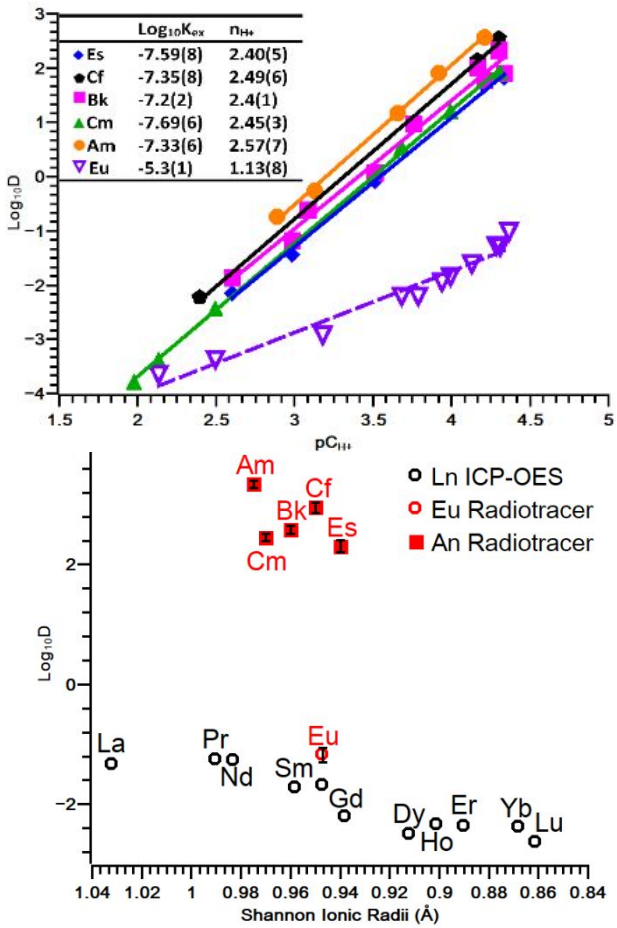

Figure 3. Top: The distribution ratios of radiotracer Eu, Am, Cm, Bk, Cf, and Es as a function of pC_{H+} with 0.50 M HC301 in dodecane at an ionic strength of 1 M $NaNO_3$. Bottom: The distribution ratios for the extraction of the actinides Am, Cm, Bk, Cf, and Es and the lanthanides at pC_{H+} 4.50 as a function of ionic radii with 0.50 M HC301 in dodecane at an ionic strength of 1 M $NaNO_3$. Distribution ratios for the radiotracers were extrapolated from the graph on the top. Error bars are shown at 3σ uncertainty.

Table 1. The separation factors of Am, Cm, Bk, Cf, and Es from radiotracer Eu with 0.50 M HC301 in dodecane at an ionic strength of 1 M and pC_{H+} = 4.00.

Metal	SF
Am	6300
Cm	930
Bk	1400
Cf	2800
Es	700

The distribution ratios at pC_{H+} 4.50 are shown in Figure 3 (bottom). The distribution ratios for the actinides and lanthanide tested each form their own group with actinides being more strongly extracted and the lanthanides more weakly. The distribution ratio for Eu measured by the radiotracer is slightly higher than for the ICP-OES method which could arise from the extrapolation of the radiotracer distribution ratios to pC_{H+} 4.50. Across the lanthanide series, it can be seen that the distribution ratio for the lanthanides initially decreases slightly, then remains relatively consistent for the heavier lanthanides even though they are extracted as outer sphere complexes under these conditions[4,6,7]. Also, an emulsion is observed

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at the interface between the aqueous and organic phases for the heavier lanthanides at higher pC_{H+} but not for the lighter lanthanides. All radiotracer studies had mass balances within 100 ± 3%. This trend in the distribution ratios of the lanthanides is also consistent with the distribution ratios observed by He et al[6].

The similarity of the distribution ratios within both the lanthanide and actinide series suggests that the potential change from inner sphere to outer sphere coordination within a series interestingly does not have a large impact on the quantity of metal extracted and therefore the consistency of distribution ratios for the actinides is not necessarily indicative of changing coordination modes within that series. This also suggests that electronic structure differences between the actinides and lanthanides are perhaps the most significant contributor driving their group separation since inner sphere lanthanide and actinide complexes show significant differences in separation factor. This would be consistent with observations from Jensen[5] and Kaneko[32–34].

The similar distribution ratios and slopes among the actinides shown in Figure 3 do not conclusively suggest either a consistent extraction mechanism across the series or a change from inner- to outer-sphere complexes. This is different from the behavior within the lanthanide series where there is a change in the mechanism across the series[4,6,7]. The first half of lanthanide series tend to be extracted as inner sphere complexes with bonds between the metal and HC301, while the heavier lanthanides tend to form outer sphere complexes[4,6,7]. Due to the presence of the Lu carrier and the co-extraction of water within its outer sphere complexes, there is some possibility that this could impact the speciation of the actinides. At higher pC_{H+} values than tested here, saponification of the HC301 will be more extensive and may cause the actinides to be extracted within reverse micelles as has been observed with the lanthanides[9,10].

Nitrate Dependency

As the slopes shown in Figure 3 for the distribution ratio as a function of pC_{H+} are less than the value of three that would be expected to maintain a neutral extracted complex, the dependence of partitioning on nitrate anion (as sodium nitrate) in the aqueous phase was tested. Figure 4 shows the normalized UV-vis spectra of Nd^{3+} in the organic phase after extraction from an aqueous phase containing between 1.50 and 6.50 M nitrate at a pC_{H+} of 4.32 ± 0.05. The organic phase spectra are different from the aqueous spectrum and they continue to change with changing nitrate concentrations. This is especially clear in the hypersensitive transitions from 560 to 610 nm. These changes in the organic Nd^{3+} spectra indicate that the coordination environment of Nd^{3+} is changing with the aqueous nitrate concentration. The spectral changes can be further interpreted via the nephelauxetic effect[35]. Coordination of nitrate causes a redshift[36,37] and coordination of water causes a blueshift approaching the spectra of the hydrated Nd ion[9]. The small red shift suggests nitrate complexation may be relevant for this system.

The Fourier-transform infrared (FTIR) spectra of the organic phase did not show the presence of water or nitrate in the organic phase for any of the nitrate concentrations. This lack of FTIR observable water and nitrate in the organic phase was also seen when Lu was extracted even though greater amounts of water are thought to be extracted with Lu. The lack of observable water and nitrate features is most likely related to the system conditions and the anticipated limit of detection for the experimental approach used. The limit of detection for nitrate can be estimated to be approximately 200 mM based on calculations from previous, similar systems[38]. Similar estimates for water were not available, but water is below the detection limit when water concentrations are as high as 170 mM in similarly analysed organic phase systems containing tributyl phosphate (Figure S3).

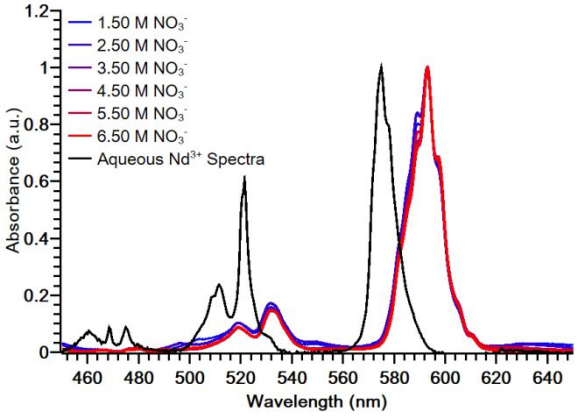

Figure 4. The UV-vis spectra of the organic phase resulting from the extraction of Nd^{3+} by 0.50 M HC301 in dodecane from an aqueous phase containing 0.5 M Nd^{3+} and varying concentrations of NO_3^- (from 1.50 to 6.50 M NO_3^-) at a pC_{H+} of 4.32 ± 0.05. The aqueous Nd^{3+} is also shown. Spectra are normalized to have an absorbance of 1 at 593 nm.

As the coordination of Nd^{3+} changes with nitrate concentration, the spectra alone provides limited information about how the distribution ratios of Nd or other metals are affected. To look more closely at this, distribution ratios were measured for most lanthanides and the actinides Am, Cm, Bk, and Es at different nitrate concentrations and activities[39]. The results for the actinides and lanthanides are shown in Figures 5 and S1. Distribution ratios were corrected for the formation of aqueous nitrate complexes using the formula given by Harrigton et al[40]. and formation constants determined by Tian and Shuh[41] and Peppard et al[42]. Formation constants for Cm, Bk, and Es with nitrate were assumed to be the same as for Am. A higher pC_{H+} was used for the lanthanides to give measurably high distribution ratios. The actinides were minimally affected by the changing nitrate activity as they have a flat or slightly negative slope. However, the lanthanides have increased extraction at higher nitrate activities and this trend becomes somewhat more pronounced along the lanthanide series.

As the slope of the distribution ratio plotted against the nitrate activity is approximately zero or slightly negative, nitrate does not appear to have an effect on the extraction of these actinides. As the actinides Am and Cm have previously been observed to form inner sphere complexes with no coordinating water molecules[5,12], the lack of nitrate dependence for Am is consistent with previous observation because the higher nitrate concentration can alter the amount of water in the organic phase through the salting out effect. The lack of nitrate dependence for Bk and Es in the presence of HC301 suggests these actinides also form inner sphere complexes at the pC_{H+} tested. The lanthanides show a much greater dependence on nitrate activity where higher nitrate activities promote extraction, especially for the heavier lanthanides. A possible explanation is the co-extraction of nitrate in heteroleptic complexes of the form $Ln(C301)_2(NO_3)$. Bhattacharya observed Eu complexes of this form at lower concentrations (<0.3 M) of HC301 than used here[43] and computationally observed that the formation of $M(C301)_2(NO_3)$ and $M(C301)_3$ complexes with Am, La, Eu, and Lu were close to the same reaction energy[44]. Therefore, it is plausible that these heteroleptic

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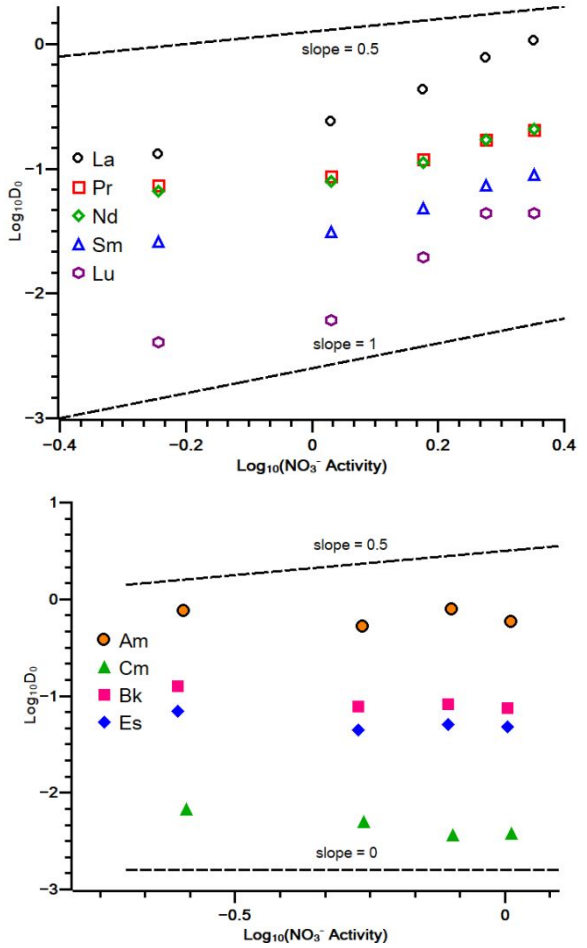

Figure 5. Top: The distribution ratio for the actinides Am (pC_{H+} 3.23), Cm (pC_{H+} 2.51), Bk (pC_{H+} 2.93), and Es (pC_{H+} 2.93) with 0.50 M HC301 in n-dodecane and Bottom: The distribution ratio for the lanthanides La, Pr, Nd, Sm, and Lu at pC_{H+} 4.45 with 0.50 M HC301 in *n*-dodecane. Activities were calculated from the activity coefficients from ref. [39]. Distribution ratios were corrected for the formation of aqueous nitrate complexes using the formula given by Harrigton et al[40]. and formation constants determined by Tian and Shuh[41] and Peppard et al[42].

complexes have favorable or nearly equal reaction energies for all the lanthanides and a mixture of the $M(C301)_3$ and $M(C301)_2(NO_3)$ are extracted.

To test this hypothesis, the substitution of a simplified C301 anion for a nitrate anion, Equation 3, was modelled using DFT calculations and the resulting thermodynamic parameters are shown in Figure 6 and Table S2. Examples of the complexes modelled are shown in Figure 7. The uncertainty of the calculated Gibbs free energy (ΔG) is estimated to be approximately 4-8 kJ/mol[45,46]. Although this is the approach used by Bhattacharya, the metal centers are undercoordinated with a coordination number of six and all complexes are assumed to be inner sphere. These simplifications may limit the application of this modelling to this system, especially for the heavier lanthanides that form outer sphere complexes and highlight the utility of more realistic calculations. The calculated ΔG of this reaction is endergonic for all the metal studied which indicates that this substitution is unfavorable, but it is less endergonic for the lanthanides, particularly the heavier lanthanides. Interestingly, this follows a similar trend in the propensity of the metals to form outer sphere complexes and indicates that the direct coordination of the heavy lanthanides by HC301 is less favorable. Several of the metals examined have values of ΔG that are slightly higher or lower than would be expected given the ΔG of neighboring metals and the general trend observed, but these variances are well within the estimated uncertainty of these calculations of 4-8 kJ/mol[45,46]. Overall, this trend suggests that if the heteroleptic complex does form, it will do so most readily with the lanthanides, particularly the heaviest lanthanides. For all the transplutonium actinides tested, it is even more unfavorable for the formation of the heteroleptic com of plex, which is consistent with the observed weak influence of nitrate on the extraction of these metals.

As the DFT calculations suggest that the heteroleptic complex is unlikely to form with the actinides and the distribution ratios being independent of nitrate concentration suggest an inner sphere complex, a possible structure of the extracted actinide complex can be hypothesized. Figure 8 shows a trivalent actinide coordinated by three C301 anions to achieve charge neutrality in an inner sphere, homoleptic complex. It should be noted that this gives the actinide a coordination number of six rather than the eight or nine typically encountered in trivalent actinide complexes. For this reason, it is likely that an additional ligand, likely water or neutral HC301, also coordinate to the metal center.

$$M(C301)_3 + NO_3^- \rightleftharpoons M(C301)_2(NO_3) + C301^- \quad (3)$$

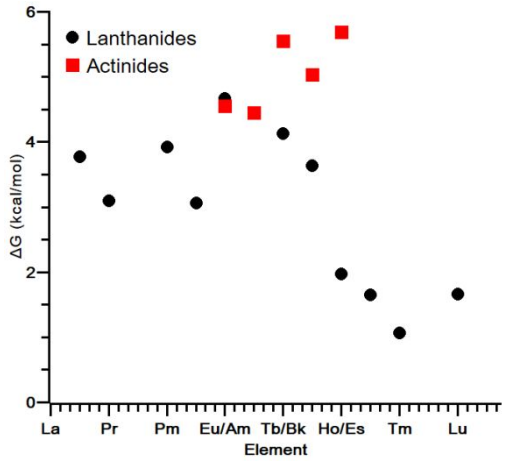

Figure 6. Calculated Gibbs free energy for lanthanides and actinides in the reaction $M(C301)_3 + NO_3^- \rightleftharpoons M(C301)_2(NO_3) + C301^-$. ΔG is calculated at a temperature of 298.15 K.

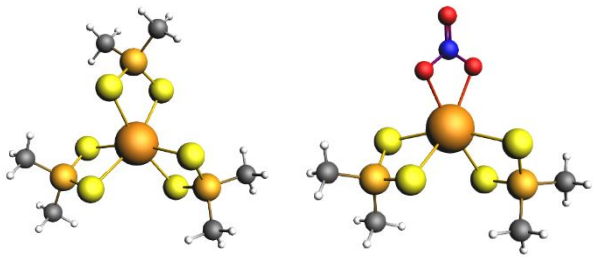

Figure 7. Left: The structure of the $Am(C301)_3$ complex. Right: The structure of the $Am(C301)_2(NO_3)$ complex. The alkyl groups have been truncated for clarity and to simplify DFT calculations.

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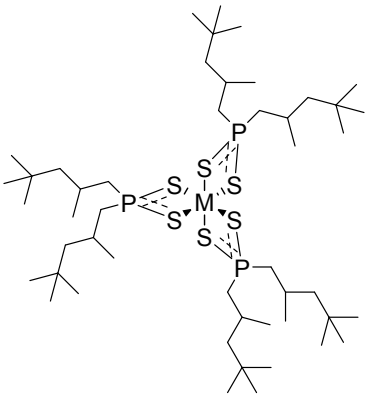

Figure 8. Possible structure of $M(C301)_3$ complexes where M = Am, Cm, Bk, Cf, or Es.

Conclusions

The extraction of Ln and the trivalent actinides Am through Es with HC301 has been investigated. The distribution ratios and pC_{H+} dependency of the actinides is similar from Am to Es. This alone cannot fully justify a claim of either consistent inner sphere or a change from inner- to outer-sphere coordination within the actinide series occurs as it does with the lanthanide series.

The aqueous nitrate activity dependency was also probed, and the extraction of the actinides was found to be less dependent on the nitrate activity than the lanthanides, particularly the later members of the series. This suggests that the actinides tested are extracted as inner sphere complexes while the lanthanides, especially the heavier lanthanides, are more prone to outer sphere complex formation. A similar trend was observed in the calculated ΔG values for the formation of heteroleptic $M(C301)_2(NO_3)$ complexes.

More work remains to be done to more completely understand this behavior. Additional experimental studies, such as EXAFS, would further support the idea that actinides continue to be extracted as inner sphere complexes across the series. Experimental students with macroscopic amounts of transcurium actinides is a fascinating area for further research but limited by material availability. Computational studies could also assist in understanding this difference in extraction method between the lanthanide and actinide series and why it occurs.

Conflicts of interest

There are no conflicts to declare.

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