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CHARACTERIZING DIAMYLAMYLPHOSPHONATE (DAAP) AS AN AMERICIUM LIGAND FOR NUCLEAR FUEL-CYCLE APPLICATIONS

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Successful deployment of the currently-envisioned advanced nuclear fuel cycle requires the development of a partitioning scheme to separate Am from the lanthanides. The Am/lanthanide separation is challenging since all the metals are normally trivalent and have similar ionic radii. Oxidation of Am to higher oxidation states is one option to achieve such a separation. Hexavalent Am has now been routinely prepared in our laboratory in strongly acidic solution using sodium bismuthate as the oxidant, and then extracted into diamylamylphosphonate/dodecane solution. Here, we have characterized this phosphonate-containing solvent with regard to the extraction of Am, the lanthanides, Cm, other fission product, and/or inert constituents expected in dissolved nuclear fuel. Additionally, the effects of irradiation on dispersion numbers and the phosphonate concentration were investigated.

Keywords: *DAAP, fuel cycle, lanthanides, oxidized Am, sodium bismuthate, solvent extraction*

INTRODUCTION

Successful deployment of the currently-envisioned advanced nuclear fuel cycle requires the development of a partitioning scheme to separate Am from the lanthanides. The incorporation of Am into fast reactor fuel for its conversion into short-lived fission products is preferable to its internment in a high-level waste repository due to its decay to long-lived Np. The Am/lanthanide separation is challenging since all the metals are normally trivalent and have similar ionic radii. Methods currently being developed for this separation rely on the greater covalency due to greater exposure of the actinide *f*-electrons and the use of soft-donor ligands.[1,2] Oxidation of Am to higher oxidation states is another potential option to achieve such a separation.[3] Both pentavalent and hexavalent Am have been successfully prepared using sodium bismuthate as an oxidant in the acidic solutions used in fuel cycle separations, and separations have been demonstrated at the bench scale using tributyl phosphate (TBP), octylphenyl-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), and dibutylbutylphosphonate (DBBP) with varying degrees of success.[4,5,6]

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In a recent contribution,[7] we reported the successful partitioning of bismuthate-oxidized Am^{VI} from the bulk of lanthanides using 1 M diamylamylphosphonate (DAAP)/dodecane extraction. The compound DAAP was selected for investigation as a hexavalent Am ligand since it has been used successfully for U^{VI} extraction by Siddall,[8] Mason and Griffin,[9] and Brahmmananda Rao et al.[10] In immobilized form, DAAP has proven to be efficient for the recovery of U^{VI} from acidic media.[11] In our previous work,[4] the DAAP extraction distribution ratio for Am depended on the yield of Am^{VI}, with typical values averaging ∼4 for extraction from 6–7 M HNO_3. This resulted in a separation factor $\alpha_{Am/Eu}$ of ∼50. Since Ce was also oxidized to Ce^{IV} and very efficiently extracted with D_{Ce} ∼100–300, selective stripping was used to back extract Am with an $\alpha_{Ce/Am}$ of ∼35. The organic solvent itself acts a reducing agent for extracted Am, and thus it was stripped into an acidic aqueous phase after standing for 2 hours. Recent unpublished data suggests that waiting only a few minutes may be adequate to achieve Am stripping. These findings suggest a process wherein sodium bismuthate is used to oxidize Am to Am^{VI} in the raffinate of a post-PUREX-like extraction, followed by its extraction using 1 M DAAP/dodecane.

The actual utility of such a process depends upon the results of further characterization of the DAAP solvent. In this contribution, we continue our studies with emphasis on the behavior of other constituents of the dissolved fuel during DAAP extraction. These include nitric acid, Cm, fission products, and inert metal constituents under untreated and bismuthate-oxidized conditions, from both nitric acid and simulated first-cycle raffinate solutions. The extraction of Am and nitric acid using DAAP in Isopar L was compared to dodecane, and it was found that their behavior was substantially similar. Finally, we report the results of preliminary experiments to investigate the behavior of DAAP under γ-radiolysis.

EXPERIMENTAL

Acid Extraction

Nitric acid distribution ratios were determined by contacting aqueous nitric acid solutions with 1 M DAAP in either dodecane or Isopar L for 1 min at room temperature of 21 ± 2°C, followed by centrifugation to separate the phases. The DAAP was washed three times with 0.25 M sodium carbonate, then once with 0.1 M HNO_3 prior to use. The acid concentration in both post-contact phases was measured by titration to a phenolphthalein endpoint. The distribution ratio was calculated as the ratio of the acid concentration in the organic to the aqueous phases. Mass balance analysis averaged 105 ± 4%. Single extractions were performed, with each solution titrated in triplicate (RSD = ± 1.1%), with the mean results reported.

Metals Extraction

Stable lanthanides and other stable metal ions expected as fuel dissolution constituents were extracted from either nitric acid or first-cycle raffinate simulant using 1 M DAAP/dodecane. The DAAP was washed three times with 0.25 M sodium carbonate, then once with 0.1 M HNO_3 prior to use. The organic phase was pre-equilibrated with the appropriate acid concentration prior to contact. All contacts were 15 sec in duration at room temperature of 21 ± 2°C, followed by centrifugation to separate the phases. The raffinate composition is shown in Table 1, where the constituent concentrations shown are

Table 1 Simulated first-cycle raffinate constituent concentrations (mM) following the dilution caused by acidity adjustment

Rb	0.23	Ce	1.15
Y	0.28	Nd	1.88
Zr	1.86	Sm	1.25
Cs	1.10	Eu	0.04
Ba	0.96	Gd	0.07
La	0.59		

half those used in previous work[12] due to the dilution caused when adjusting the acidity of the simulant across a wide range of concentrations.

Those metals not already in the simulant were added at 1–10 mM in concentration, as indicated in the text. The post-extraction aqueous and organic phases were analyzed by ICP-MS. Samples were diluted to an appropriate concentration range in a 1% nitric acid containing an internal standard. For organic samples, a minimum dilution factor of 1000 was required to prevent fouling of the cones in the mass spectrometer. The distribution ratios were calculated as the ratio of the analytical concentration of the metal in the organic phase divided by that in the aqueous phase. They were measured both in untreated and bismuthate-oxidized raffinate simulant and in nonsimulant nitric acid solution for comparison. Oxidized solutions were treated by the addition of 30–40 mg $NaBiO_3$ powder to 2 mL, using 1 h contacts on a shaker plate, as has previously been reported for Am oxidation.[7] Similarly, the organic phase was pre-equilibrated with bismuthate powder in the appropriate acid concentration for 1 h. The solvent extraction contact was then performed as described above. Mass-balance analysis for the two phases was within $98 \pm 5\%$, except for the least acidic bismuthate-treated solutions, which had mass balance as low as 40% for some metals for solutions < 3 M in HNO_3.

In the case of radiotracers, the activities in the post-contact aqueous and organic phases were determined by standard radiometric counting techniques. The initial tracer concentrations are given in the text. For the radio-lanthanides, Cs, and Am both the aqueous and organic phases were analyzed by γ-ray counting, while Cm and Tc were measured by liquid scintillation counting. In all cases, the distribution ratios were calculated as the ratio of the activity in the organic to the aqueous phase. The average mass balance for radiometrically determined metals was $99 \pm 4\%$.

DAAP Analysis

The determination of DAAP concentrations was conducted with a liquid chromatographic procedure adapted from Elias et al.[13] coupled with mass spectrometric detection. A Dionex (Sunnyvale, CA) ultraperformance liquid chromatograph (UPLC) with an Ultimate 3000 RS pump, autosampler, column compartment, and Diode Array Detector (DAD), and a Bruker (Billerica, MA) electrospray-quadrupole time-of-flight mass spectrometer (ESI-QTOF-MS) with Hystar 3.2 software were used. The LC was performed isocratically with 60:40 mixture of 0.1% formic acid in water at pH ~2.6 and 3.6% 1-octanol in 2-propanol on a C_8 column (Zorbax, 150×2.1 mm, 3.5 μm) at a flow rate of 0.2 mL min^{-1} at 50°C. The capillary voltage of the ESI was 4.5 kV for positive ion mode. The temperature of the ESI chamber was set at 220°C; the nebulizer and drying gases were both N_2, and the drying gas flow rate was 9 L min^{-1}. The nebulizer pressure was 0.4 bar.

The DAAP concentration was based on the area of the peak that eluted at 6.5 min, with an extracted ion chromatogram for the protonated species at m/z 293.

Dispersion Number Measurements

The rate of phase disengagement for irradiated DAAP solutions and non-irradiated control solutions was compared by measuring their dispersion numbers (N_{Di}). The dispersion number was defined by Leonard as: [14]

$$N_{Di} = (1/t_b)\,(\Delta Z/g)^{1/2} \tag{1}$$

where t_b is the time for the dispersion to break, ΔZ is the initial thickness of the dispersion band (height of liquid in the cylinder), and g is the gravitational constant (9.81 m s^{-2}). The time for the band to break was measured with a stop watch, following mixing of the phases at an equal volume phase ratio by hand in a stoppered graduate cylinder at a rate of about 2 cycles per second. Care was taken to shake each contact as consistently as possible. Cylinder contents were mixed for 20 s, placed in an upright position for 10 s, and then mixed another 20 s. After the second mix, the cylinder was returned to the upright position and t_b was measured. The dispersion was considered to be broken when the last droplet broke, and the solution temperature of $23.3 \pm 0.3°C$ was then also measured. Each measurement was performed in triplicate, with the result reported as the mean ± 1 σ.

RESULTS AND DISCUSSION

Am Extraction in Dodecane and Isopar L

The solvent extraction distribution ratios for the extraction of bismuthate-oxidized Am and Ce from nitric acid over the concentration range 0.5–6.0 M are shown in Fig. 1.
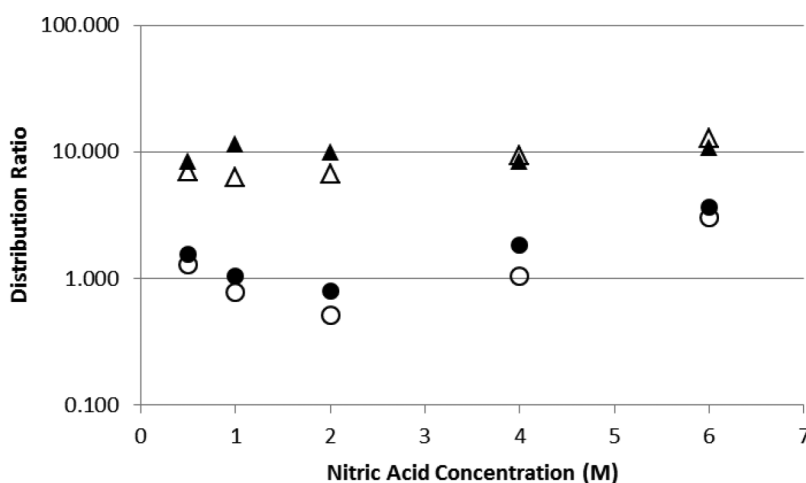

Figure 1 The extraction of Am (circles) and Ce (triangles) from bismuthate-oxidized nitric acid solution by 1 M DAAP/dodecane (open symbols) or Isopar L (closed symbols).

The organic phase was 1 M DAAP in either dodecane or Isopar L. At the highest acidity used of 6 M HNO_3, the D_{Am} was ~3.5. Maximum Am distribution ratios have been achieved at slightly higher acidities of about 6–7 M HNO_3 and are typically ≥ 4. Thus, the substitution of Isopar L for dodecane had no significant effect on the extraction of either metal, and the behavior of each was similar to that previously reported.[7] Although the D_{Am} values reported here represent nominally hexavalent Am, it must be acknowledged that the presence of residual Am^{III} will depress these measured distribution ratios. Typical bismuthate oxidation yields have been reported to lie between 80–94%, with higher yields at higher Am concentrations.[7] Further, increased duration of contact with the organic phase will decrease the measured D_{Am} in exponential fashion, presumably by reduction of hexavalent Am.[4,7] The measured values may be corrected for these effects to calculate an ideal D_{AmVI}. Assuming a measured D_{Am} of ~4, a yield of 90% Am^{VI}, and a D_{AmIII} of 0.1, all from 6.5 M HNO_3,[7] it may be calculated that the ideal D_{AmVI} is ~4.4 for a 10 s contact. Using the exponential relationship between contact time and D_{Am} reported in reference [7] this may be extrapolated to an ideal D_{AmVI} of 5.6 at zero contact time. The efficiency of the extraction depends on the successful creation and maintenance of the hexavalent oxidation state, which in this case resulted in a decrease from an ideal 85% Am extracted to a measured amount of 80%, for one contact.

It can also be seen in Fig. 1 that at acidities < 2 M HNO_3, the D_{Am} decreases with nitric acid concentration, indicating that Am is trivalent in this range. Similar previous data showed that Am and Eu extraction were nearly identical in this acid concentration range,[7] and the same trend of decreasing extraction with increasing acidity is also found for Cm and the trivalent lanthanides as reported later here. This lack of americium oxidation under low acid conditions is attributed to the very sparing solubility of the bismuthate oxidant under those conditions. As the acid concentration increases, the D_{Am} also begins to increase, indicating the oxidative production of Am^{VI} as sufficient amounts of the oxidizing agent are dissolved.

Acid Extraction in Dodecane and Isopar L

The extraction of acidity by basic neutral organophosphorus ligands results in competition for the active phosphoryl group, and may limit metal extraction efficiency, especially at higher acid concentrations.[15] The acid is extracted in undissociated form, and its complexes with other neutral organophosphorus ligands have been observed by mass spectrometry.[13] Understanding the extent of HNO_3 extraction is necessary to the modeling of any process based on DAAP. Therefore, we measured the distribution ratio for HNO_3 from acidic solution using 1 M DAAP in both dodecane and Isopar L. These results are shown in Fig. 2. The nitric acid extracted is shown as a function of the equilibrium aqueous nitric acid concentration in Fig. 3. Although D_{HNO3} decreased with increasing nitric acid concentration, the amount of acid extracted from the highest initial aqueous acid concentrations approach 1 M HNO_3; equal in concentration to the DAAP. This did not prevent metal extraction, as was shown in Fig. 1.

Behavior of Ln Fission Products and Cm Extracted from Nitric Acid Solution

Previously we showed the distribution ratios measured for 1 mM La and Sm extracted from a range of nitric acid concentrations using 1 M DAAP/dodecane.[7] Samarium was
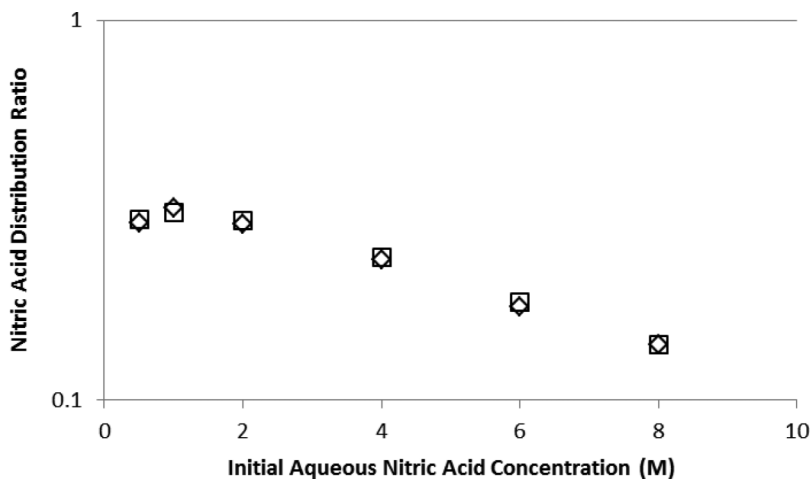
Figure 2 The extraction of HNO_3 by 1 M DAAP in dodecane (diamonds) or Isopar L (boxes).
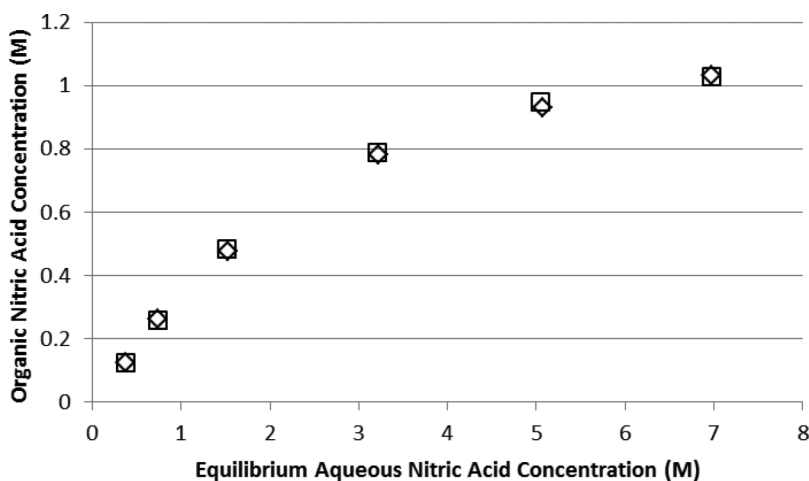

Figure 3 The extraction of nitric acid by 1 M DAAP in dodecane (diamonds) or Isopar L (boxes).

extracted more than twice as efficiently as La, with the highest distribution ratios measured at 2.0 M HNO_3 being 0.531 and 0.186, respectively. The distribution ratios for both metals decreased with increasing nitric acid concentrations, until at the 6.5 M acid concentration proposed for Am extraction they were 0.086 and 0.007, respectively. As expected for non-oxidizable lanthanides, these extraction efficiencies were unchanged after bismuthate treatment. [7]

Here, we have continued the investigation of lanthanide behavior during DAAP extraction. The distribution ratios for tracer concentrations of ^{98}Y (1×10^{-10} M), ^{153}Gd (2×10^{-10} M), and ^{166m}Ho (5.4×10^{-8} M) are shown in Fig. 4, for extraction over a range of nitric acid concentrations. It can be seen that the distribution ratios are low, that they decrease with increasing acid concentration, and that they are unchanged by bismuthate
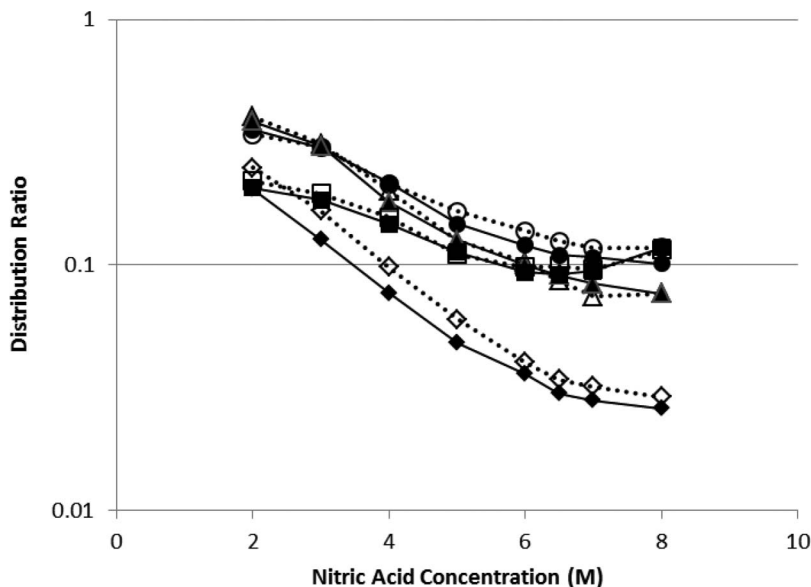
Figure 4 The distribution ratios for tracer Gd (triangles), Y (boxes), Ho (circles), and Cm (diamonds) versus nitric acid concentration for untreated (open symbols/dotted lines) and bismuthate-treated (closed symbols/solid lines) nitric acid solution using 1 M DAAP/dodecane.

oxidative treatment. These results are as expected, based on the behavior of La and Sm, above.

The behavior of Cm was similar to the lanthanides, although with overall lower distribution ratios, shown for the extraction of 6×10^{-8} M ^{244}Cm from nitric acid solution in Fig. 4. Also, as expected, Cm was not oxidized by bismuthate treatment.

We evaluated a number of non-lanthanide fission products and other fuel dissolution constituents for their extraction behavior with the 1 M DAAP solvent. These include 2 mM Rh, 4 mM Cd, 2 mM Pd, and 5 mM Ag. Only Pd showed any measurable extraction, with the highest distribution ratio measured of D_{Pd} being 0.263 at 2 M HNO_3. The D_{Pd} dropped rapidly at higher acidity, being ≤ 0.001 by 6 M HNO_3. Previously we reported Mo and Ru results that indicated Mo was somewhat extracted across the entire acid concentration range with $D_{Mo} = \sim0.1$ for untreated and bismuthate-treated solution, and with normally inextractable Ru oxidized and extracted with a D_{Ru} of 5.42 at 6.5 M HNO_3 from bismuthate-treated solution.[7] The mass balances for Rh, Cd, and Ag were poor at the lowest nitric acid concentration for Bi-treated solutions, and the mass balance for Pd was poor at the two lowest nitric acid concentrations. This is probably due to co-precipitation of these metals on the solid oxidant, as has been seen for some other metals.[7]

The high-yield fission products ^{137}Cs and ^{99}Tc were also investigated with regard to 1 M DAAP/dodecane extraction from nitric acid. The concentration in the initial aqueous phase was 1×10^{-7} M for both metals. The results, shown in Fig. 5, indicate that Cs and Tc are not well extracted at any acidity and that Cs behavior was not affected by the oxidation. The distribution ratios for Cs were very low, with only < 5 Bq mL^{-1} detected in the organic phase, resulting in $D_{Cs} < 0.0001$. Technetium was somewhat better extracted in the presence of bismuthate, although this can hardly be attributed to oxidation. This was especially true at higher nitric acid concentrations, although the D_{Tc} values were still low.
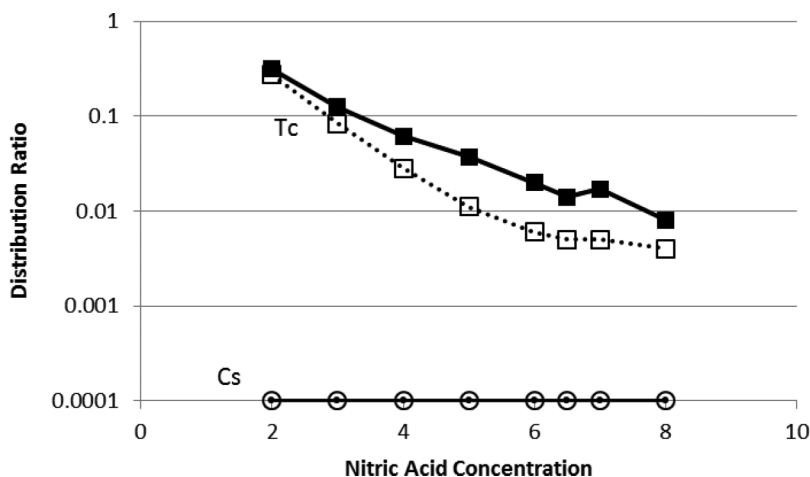
Figure 5 The distribution ratios for Bi-treated Tc (closed boxes), untreated Tc (open boxes), Bi treated Cs (points), and untreated Cs (open circles) from nitric acid solution using 1 M DAAP/dodecane.

Table 2 Solvent extraction distribution ratios for selected lanthanide fission products using 1 M DAAP/dodecane before and after bismuthate treatment of first-cycle raffinate simulant adjusted to varying nitric acid concentrations

	Nitric Acid Concentration (M)							
Constituent	2.0	3.0	4.0	5.0	6.0	6.5	7.0	8.0
Y	0.187	0.184	0.146	0.110	0.096	0.091	0.091	0.099
Y-Bi	0.191	0.182	0.149	0.122	0.096	0.095	0.090	0.096
La	0.140	0.062	0.027	0.013	0.008	0.005	0.004	0.003
La-Bi	0.149	0.062	0.028	0.012	0.007	0.006	0.004	0.003
Ce	0.189	0.107	0.054	0.026	0.017	0.012	0.010	0.008
Ce-Bi	41.3	119	148	399	1130	884	779	540
Nd	0.271	0.186	0.112	0.063	0.044	0.033	0.028	0.024
Nd-Bi	0.289	0.180	0.115	0.068	0.042	0.037	0.028	0.024
Sm	0.435	0.365	0.203	0.121	0.091	0.071	0.064	0.062
Sm-Bi	0.458	0.338	0.198	0.133	0.089	0.081	0.063	0.059
Eu	0.423	0.347	0.211	0.145	0.114	0.090	0.076	0.071
Eu-Bi	0.444	0.351	0.241	0.153	0.098	0.094	0.078	0.072
Gd	0.359	0.285	0.186	0.121	0.094	0.079	0.069	0.072
Gd-Bi	0.441	0.392	0.277	0.207	0.187	0.179	0.152	0.149

Extraction of Ln Fission Products and Cm from Simulated First-Cycle Raffinate

Continued investigation of the extraction of the lanthanides was conducted from simulated first-cycle raffinate, adjusted across a range of acid concentrations (constituents given in Table 1). The results are shown in Table 2, where it can be seen that similar behavior was found as from nitric acid solution, excepting that the distribution ratios are slightly lower than from nitric acid. This is attributed to loading of the ligand by the higher concentration of total metals in the simulant. In all cases, the distribution ratio of the metal decreased with increasing acidity. Only Ce was oxidized and extracted.
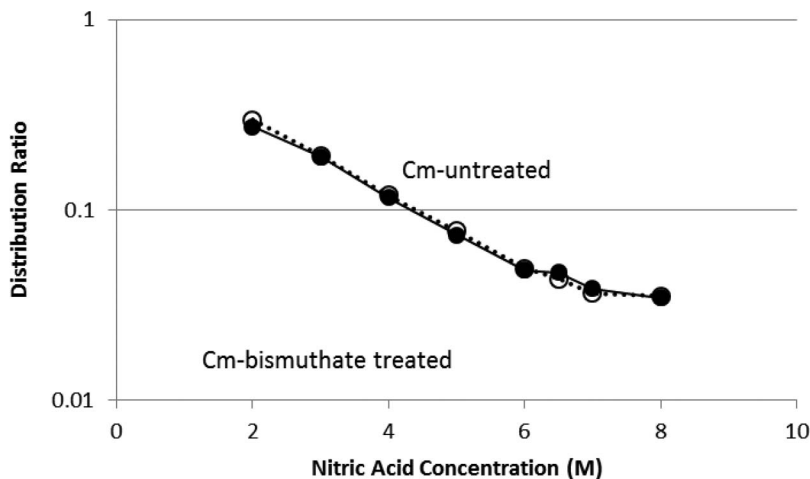
Figure 6 The distribution ratios for tracer Cm versus nitric acid concentration for untreated (open circles) and bismuthate-treated (closed circles) raffinate simulant solution using 1 M DAAP/dodecane.
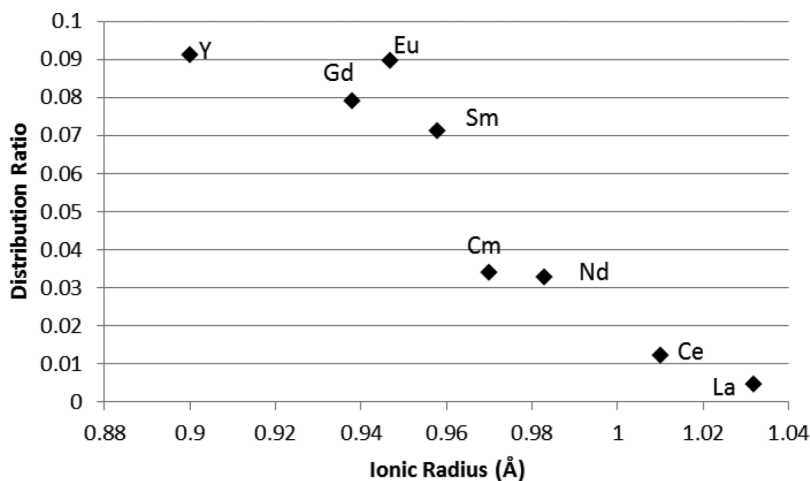

Figure 7 The distribution ratios for DAAP extraction of the lanthanides, Y, and Cm from untreated first-cycle raffinate simulant adjusted to 6.5 M in HNO_3. Radii are those of Shannon[16] for six-coordinate trivalent ions.

     Curium was also evaluated for its extraction from simulated raffinate, as shown in Fig. 6. Its behavior was similar to that from nitric acid solution in Fig. 4, similar to that of the lanthanides in Table 2, and it was not oxidized by bismuthate treatment of the raffinate simulant.

     The distribution ratios of the lanthanides, Y, and Cm from untreated, first-cycle raffinate simulant, adjusted to 6.5 M in HNO_3, are plotted versus their six-coordinate trivalent ionic in Fig. 7. There it can be seen that the lower radii, higher charge-density ions were better complexed by DAAP. Both Cm and Y fit the curve reasonably well, and the usual discontinuity at Gd can be seen.

Since Eu has one of the highest Ln distribution ratios measured, the separation factor for Am extraction from the remaining trivalent metals are higher than the value of ∼50 for $\alpha_{Am/Eu}$ previously reported. We report here, for example, a value of ∼133 for $\alpha_{Am/Cm}$, assuming a D_{Am} of 4.[7]

Other Fission Products and Fuel Dissolution Constituents

The extraction of a number of non-lanthanide metals of interest were also investigated by 1 M DAAP/dodecane extraction from first-cycle raffinate simulant adjusted over a range of nitric acid concentrations. Of Rb, Zr, Cs, Ba, Rh, Cd, Pd, and Ag only Pd and Zr showed measurable extraction, with both Bi-treated and untreated Pd having negligible extraction at higher acidity, similarly to that reported in pure nitric acid solution. Zirconium, however, was extracted in measurable amounts, and its distribution ratios were about a factor of 2 higher in oxidized solution. Thus DAAP has the same disadvantage as other fuel-cycle ligands in regard to Zr extraction. The D_{Zr} values measured are shown as a function of nitric acid concentration for extraction from raffinate simulant in Fig. 8.

The use of sodium bismuthate as the aqueous-phase oxidant introduces dissolved Bi^V to solution, which is reduced to Bi^{III}. Therefore, the distribution ratios for Bi^{III} were also measured from [207]Bi-traced nitric acid, traced raffinate simulant, and from traced simulant that was oxidatively treated with sodium bismuthate. As shown in Fig. 9, the behavior of Bi^{III} during DAAP extraction is similar to that of the trivalent lanthanides, although with higher distribution ratios at low acid concentrations. However, at the acid concentrations proposed for process application, the extraction of Bi^{III} is low, which is an advantage for this ligand over what we previously reported for CMPO.[5]

Behavior of Irradiated DAAP

The utility of any solvent extraction ligand for application to the nuclear fuel cycle will be potentially limited by its radiation stability. The decay of fission product and actinide
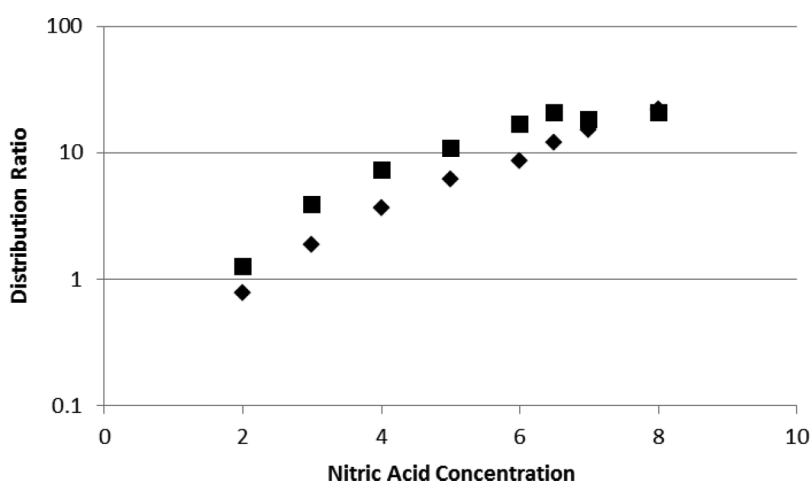

Figure 8 The extraction of Zr from first-cycle raffinate simulant versus nitric acid concentration for bismuthate treated (squares) and untreated (diamonds) solution using 1 M DAAP/dodecane.
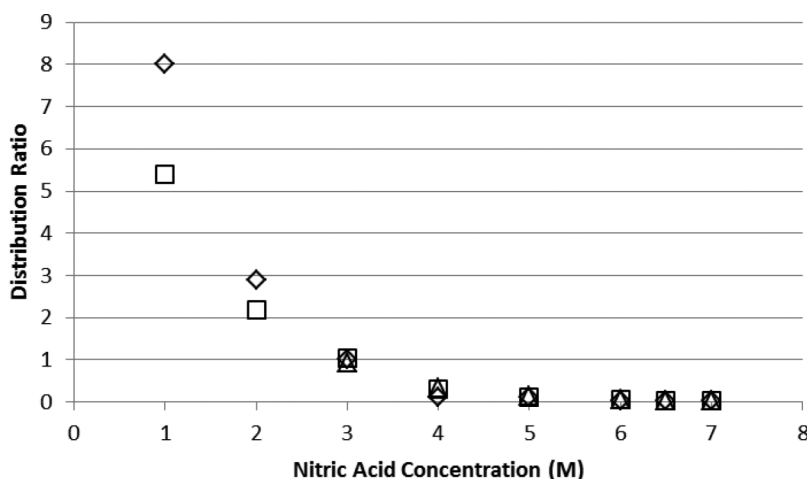
Figure 9 The extraction of Bi[III] from [207]Bi-traced nitric acid solution (diamonds), traced raffinate simulant (boxes), and from traced simulant oxidatively treated with sodium bismuthate (triangles) using 1 M DAAP/dodecane.

metals in the fuel dissolution produce highly energetic α and β/γ radiation, the main part of which deposits its energy in the organic and aqueous diluents used in solvent extraction. The diluents are either ionized to produce electrons and their parent radical cations or they are excited following which they may decay to neutral radicals. These transient reactive species then diffuse into the solution to react with ligands such as DAAP. The important reactive species and their common reactions were summarized by Mincher and Mezyk.[17] The effects of β/γ irradiation on 1 M DAAP/dodecane solutions are reported here.

Dispersion Numbers

The dimensionless dispersion numbers (N_{Di})[14] for solutions of 1.0 M DAAP/dodecane were measured before and after irradiation to a series of absorbed doses. The samples were irradiated in contact with raffinate simulant adjusted to 6.5 M in HNO_3 (Table 1), and with constant air-sparging to best simulate process conditions. The sample "t_0 initial" was the initial, unirradiated blank solution, while "t_0 final" was sparged in contact with 6.5 M HNO_3 without irradiation for the same duration during which the remaining samples were irradiated. As can be seen in Table 3 the dispersion numbers were essentially unchanged by irradiation to an absorbed dose as high as 130 kGy, indicating that irradiation did not change the excellent phase-separation characteristics of this solvent, at least for absorbed doses of this magnitude.

Radiolytic Change in DAAP Concentration

The concentration of DAAP in nominally 1 M DAAP/dodecane solutions irradiated to absorbed doses as high as 500 kGy were measured in post-irradiation samples. In these experiments, samples were irradiated as the neat organic phase, the organic phase in contact with an equal volume of 6.5 M HNO_3, or the organic phase in contact with raffinate simulant adjusted to 6.5 M in nitric acid and with continuous air-sparging. The rate of decrease

Table 3 The effect of irradiation upon the dispersion numbers for 1 M DAAP/dodecane solutions irradiated in contact with raffinate simulant adjusted to 6.5 in M HNO_3. The samples were continuously air-sparged during irradiation

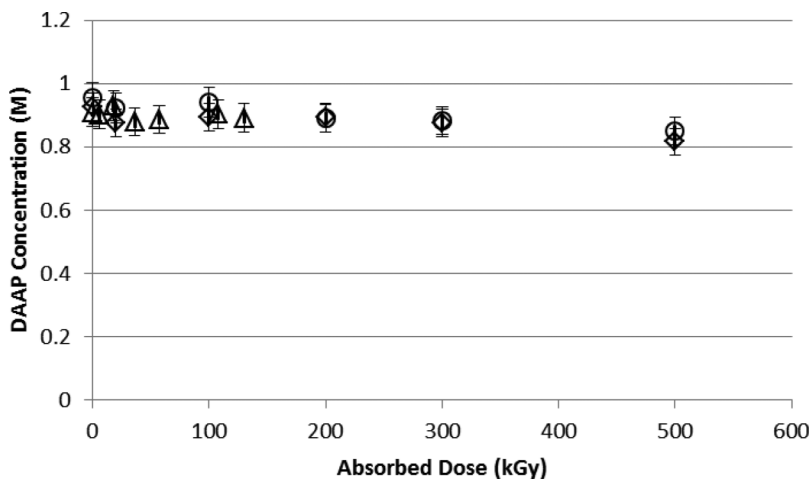| Absorbed Dose (kGy)	N_{Di}
$t_{0initial}$	$1.64 \times 10^{-3} \pm 4.6 \times 10^{-5}$
t_{0final}	$1.97 \times 10^{-3} \pm 2.4 \times 10^{-5}$
18.1	$1.99 \times 10^{-3} \pm 4.3 \times 10^{-5}$
36.2	$1.81 \times 10^{-3} \pm 5.5 \times 10^{-5}$
57.4	$2.21 \times 10^{-3} \pm 3.1 \times 10^{-5}$
108	$1.81 \times 10^{-3} \pm 7.3 \times 10^{-5}$
130	$1.97 \times 10^{-3} \pm 2.4 \times 10^{-5}$

Figure 10 The radiolytic change in DAAP concentration for nominally 1.0 M DAAP/dodecane, irradiated with ^{60}Co γ-rays in the absence of the aqueous phase (circles), in contact with an equal volume of 6.5 M HNO_3 (diamonds), or in contact with raffinate stimulant adjusted to 6.5 M HNO_3 with continuous air sparging (triangles). Error bars are $\pm 5\%$ based on triplicate determinations.

in DAAP concentration was similar and minimal in all cases. This is shown in Fig. 10. Based on this metric the radiolysis of DAAP/dodecane solution does not adversely affect the use of DAAP as a fuel-cycle ligand.

CONCLUSIONS

Diamylamylphosphonate is a selective reagent for the extraction of tetra-, and hexavalent metals from nitric acid solution. The extraction of Am was reliable from bismuthate-oxidized solution, with only Ce also oxidized and extracted among the lanthanides. The remaining trivalent lanthanides were not significantly extracted from either nitric acid or simulated raffinate, with or without oxidative treatment. Their distribution ratios increased with decreasing ionic radius, resulting in the lowest distribution ratios for the more abundant lanthanides. Curium behaved similarly to the trivalent lanthanides, most resembling Nd. Curium was not oxidized by bismuthate treatment. Thus, the method provides a solvent extraction-based separation of Am from both the lanthanides and Cm,

with an $\alpha_{Am/Cm}$ value of $\sim$133 from first-cycle raffinate simulant solution. Among non-lanthanide metals found in fuel dissolution only Ru and Zr showed significant extraction, especially under oxidizing conditions. The undesirable extraction of Zr is common among fuel-cycle ligands. The other normally problematic metals include Mo, Pd, and Tc; however, these were not significantly extracted by 1 M DAAP/dodecane, especially at the nitric acid concentrations of interest in Am partitioning.

The irradiation of DAAP solutions did not result in a significant decrease in DAAP concentration under aerated or deaerated conditions, or in the presence or absence of the aqueous phase, even at the high absorbed dose of 500 kGy. Dispersion numbers were also unchanged by irradiation. Thus, based on the work presented here there are no adverse findings to disqualify the use of DAAP as an Am^{VI} ligand for fuel-cycle applications.

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