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Tributylphosphate Extraction Behavior of Bismuthate-Oxidized Americium

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Higher oxidation states of americium have long been known; however, options for their preparation in acidic solution are limited. The conventional choice, silver-catalyzed peroxydisulfate, is not useful at nitric acid concentrations above about 0.3 M. We investigated the use of sodium bismuthate as an oxidant for Am^{3+} in acidic solution. Room-temperature oxidation produced AmO_2^{2+} quantitatively, whereas oxidation at 80 °C produced AmO_2^{+} quantitatively. The efficacy of the method for the production of oxidized americium was verified by fluoride precipitation and by spectroscopic absorbance measurements. We performed absorbance measurements using a conventional 1 cm cell for high americium concentrations and a 100 cm liquid waveguide capillary cell for low americium concentrations. Extinction coefficients for the absorbance of Am^{3+} at 503 nm, AmO_2^{+} at 514 nm, and AmO_2^{2+} at 666 nm in 0.1 M nitric acid are reported. We also performed solvent extraction experiments with the hexavalent americium using the common actinide extraction ligand tributyl phosphate (TBP) for comparison to the other hexavalent actinides. Contact with 30% tributyl phosphate in dodecane reduced americium; it was nevertheless extracted using short contact times. The TBP extraction of AmO_2^{2+} over a range of nitric acid concentrations is shown for the first time and was found to be analogous to that of uranyl, neptunyl, and plutonyl ions.

Introduction

Techniques for americium separation from the higher actinides and lanthanides have long been one of the important challenges in analytical radiochemistry. They are difficult due to the preference of these elements for the trivalent oxidation state, especially in the nitric acid solutions of interest in nuclear applications. A clean separation of americium from curium is necessary for the removal of isobaric interferences in curium isotopic analysis, and a facile separation of americium from trivalent fission product lanthanides would greatly simplify current designs for nuclear fuel cycle closure.[1] Higher oxidation states of americium are known and provide opportunities for separations development, but few options for their production in acidic media are available.

As the common oxidation state in acidic solution, the spectroscopic characteristics and separations chemistry of the Am^{3+} cation have been studied for many years.[1] Higher americium oxidation states have also long been known but are less well studied. Tetravalent americium has been observed in acidic aqueous solution only in the presence of very strong complexing agents.[2] Pentavalent americium was first prepared in carbonate solution by oxidation with hypochlorite at 95 °C.[3] However, in acidic solution Am^{3+} is directly oxidized to AmO_2^{2+} using strong oxidizing agents,[1] and solutions of pure AmO_2^{+} are prepared by reduction of the higher oxidation state followed by separations[4,5] or by dissolution of AmO^{2+} salts in acid. [6] The first preparation of AmO_2^{2+} was achieved using ammonium peroxydisulfate in hot 0.2 M nitric acid to produce a non-fluoride precipitable form of the element, which showed no spectroscopic absorbance for AmO_2^{+}.[7] It was later established that Am(VI) existed as the americyl cation (AmO_2^{2+}) analogously to UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}.[8] This oxidation

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(1) Morss, L. R.; Edelstein, N. M.; Fuger, J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd Ed.; Springer: Dordrecht, The Netherlands, 2006; p. 1272, 1286, 1324, 1329, 1365, 1367.

(2) Asprey, L. B.; Penneman, R. A. *Inorg. Chem.* **1962**, *1*, 134–136.

(3) Werner, L. B.; Perlman, I. *J. Am. Chem. Soc.* **1951**, *71*, 495–496.

(4) Hara, M.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1041–1045.

(5) Hara, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 89–94.

(6) Coleman, J. S. *Inorg. Chem.* **1963**, *2*, 53–57.

(7) Asprey, L. B.; Stephanou, S. E.; Penneman, R. A. *J. Am. Chem. Soc.* **1950**, *72*, 1425–1426.

(8) Asprey, L. B.; Stephanou, S. E.; Penneman, R. A. *J. Am. Chem. Soc.* **1951**, *73*, 5715–5717.

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became the basis for the separation of americium from the trivalent lanthanides and actinides in many analytical procedures, usually by fluoride precipitation of the trivalent metals.[9–12]

However, AmO_2^+ is also soluble in fluoride solution under most conditions,[13] and for many reports it is unclear whether the oxidized, soluble americium species was pentavalent, hexavalent, or a mixture of both. At higher acid concentrations, peroxydisulfate decomposes to produce hydrogen peroxide, an efficient reducing agent for AmO_2^{2+}[10] and AmO_2^+.[14] Therefore, the utility of the method is generally limited to nitric acid concentrations of less than about 0.3 M. For the tributyl phosphate (TBP) solvent-extraction separation most commonly used in nuclear applications, it is necessary to ensure production of the hexavalent species, and to do so in strongly acidic media.

The potential of the Am(III)/Am(VI) redox couple is high in acidic solution (1.68V in 1 M $HClO_4$).[1] The potentials of the Am(III)/Am(V) (1.73V) and Am(III)/Am(IV) (2.62V) couples in the same medium are even higher and may serve as barriers to the preparation of hexavalent americium. Many strong oxidizing agents including ozone do not oxidize Am^{3+} to AmO_2^{2+} under these conditions.[15,16] An ideal reagent would be a strong oxidizer that does not decompose to produce complexing or reducing agents. Among the few examples, Appelman *et al.* reported the oxidation of Am^{3+} to AmO_2^{2+} using the novel reagent silver-catalyzed cesium fluoroxysulfate.[17] Hara and Suzuki also reported oxidation of Am^{3+} to presumably AmO_2^{2+} at nitric acid concentrations as high as 2 M using sodium bismuthate.[4,18] We are not aware of subsequent reports on the use of sodium bismuthate as an oxidant for americium. The value of the Bi(III)/Bi(V) redox couple has been measured at 2.0V, which is comparable to that of the peroxydisulfate system.[19] Because it is a commercially available reagent and the potential benefits of a method for the production of AmO_2^{2+} in strongly acidic solution are considerable, we have explored its use here as an oxidant in nitric acid concentrations as high as 6 M. We used a combination of postoxidation fluoride precipitation experiments and spectroscopic analysis to demonstrate successful oxidation to the hexavalent oxidation state at these high acidities. We also investigated AmO_2^{2+} TBP solvent extraction under these conditions because the behavior of the other hexavalent actinides in TBP extraction is well characterized.

Experimental Section

The oxidation of americium was performed by adding 30−40 mg of sodium bismuthate ($NaBiO_3$) powder to 2 mL of the selected nitric acid concentration spiked with ^{243}Am from stock on hand at the Idaho National Laboratory (INL). Bismuthate was sparingly soluble in nitric acid, leaving visible amounts of undissolved solid remaining. This mixture was agitated for ≥30 min prior to use. For oxidation to AmO_2^{2+}, the use of freshly prepared acids was necessary. The same oxidation procedure using acids stored in polyethylene for days to weeks resulted in a mixture of AmO_2^+ and AmO_2^{2+}.

Spectroscopic absorbance measurements were made using a 100-cm path-length Liquid Waveguide Capillary Cell (LWCC - World Precision Instruments) coupled to a Cary 50 Bio spectrophotometer. Oxidized americium solutions were centrifuged and filtered to remove undissolved bismuthate prior to solution injection into the waveguide. All solutions were referenced to a blank solution containing the background electrolyte. Despite the wavelength range of the spectrophotometer being 200−1100 nm, data collection was restricted to 450−750 nm due to the absorbance of water and nitrate in the long path-length cell. Some spectroscopic measurements of higher americium concentrations were also made using a conventional 1 cm cell.

The behavior of bismuthate-oxidized americium with regard to precipitation as the fluoride was investigated using lanthanum fluoride coprecipitation. Untreated, and bismuthate-treated solutions of initially 8×10^3 Bq/mL-^{243}Am were spiked to 1.1 mg/mL-La^{3+} carrier with $La(NO_3)_3$, followed by two drops of concentrated hydrofluoric acid. The precipitate was allowed to digest for ten minutes, and then filtered through a 0.2-μm luer-lock syringe filter. The activity in the aqueous phase was then γ-counted to determine the fraction of americium remaining in solution. Solutions of 1×10^2 Bq/mL-$^{152}Eu^{3+}$ and 1×10^5 Bq/mL-$^{244}Cm^{3+}$ from on-hand stock were also treated for comparison. Europium and americium were determined by γ-ray counting and curium by α-liquid scintillation counting. Each measurement was performed in triplicate, and the results were reported as the mean $\pm 1\sigma$.

For solvent extraction experiments only, the americium-spiked, bismuthate-treated solutions were also spiked with 25 μL of perchloric acid ($HClO_4$) per 2 mL of each sample, resulting in 0.12 M perchloric acid. This was added to facilitate increased dissolution of bismuthate without complexing the americium. In the absence of perchloric acid partial americium reduction occurred upon contact with the organic phase, as evidenced by lower distribution ratios and spectroscopic measurements. This was true despite attempts to pretreat the solvent with bismuthate during a 2 h acid pre-equilibration step.

Tributylphosphate was dissolved to 30% by volume in dodecane and was pre-equilibrated and preoxidized for 2 h by shaking with the appropriate acid concentration also containing sodium bismuthate powder. The solvent extraction contacts were performed at equal volume and room temperature (20 ± 2 °C) and were of 15-s duration, except for the time-dependence studies discussed in the text. The phases were separated by centrifugation for 1 min, and aliquots of each were γ-counted to determine the Am distribution ratio (D_{Am}). The distribution ratio is a measure of the efficiency with which TBP-complexed americium is transferred to the organic phase, and is measured as the ratio of the specific americium activity in the organic phase divided by that in the aqueous phase ($D_{Am} = [Am]_o/[Am]_{aq}$). Solvent extraction experiments were also performed using ^{237}Np, ^{239}Pu and natural uranium, from on-hand stock solutions, under the same conditions used to oxidize americium to

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(9) Ward, M.; Welch, G. A. *J. Chem. Soc.* **1954**, 4038.

(10) Moore, F. L. *Anal. Chem.* **1963**, *35*, 715–719.

(11) Holcomb, H. P. *Anal. Chem.* **1964**, *36*, 2329–2332.

(12) Hinman, F. D. *Anal. Chem.* **1986**, *58*, 1238–1241.

(13) Penneman, R. A.; Keenan, T. K. *The Radiochemistry of Americium and Curium Rept. NAS-NS-3006* **1960**, 7.

(14) Hara, M.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 635–638.

(15) Tsushima, S.; Nagasaki, S.; Suzuki, A. *Sep. Sci. Technol.* **1996**, *31*, 2443–2453.

(16) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*. Chapman and Hall: New York, USA, 1986; Vol. *II*, p 913.

(17) Appelman, E. H.; Diamond, H.; Horwitz, E. P.; Sullivan, J. C. *Radiochim. Acta* **1991**, *55*, 61–64.

(18) Hara, M.; Suzuki, S. *J. Radioanal. Chem.* **1977**, *36*, 95–104.

(19) Ford-Smith, M. H.; Habeeb, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 461–464.

Table 1. Effect of Bismuthate Treatment on Fluoride Precipitation of Eu, Am, and Cm from 1M-HNO_3[a]

species	% recovered in solution
Am- untreated	0.07 ± 0.02
Am-bismuthate-treated	102 ± 1
Cm-untreated	0.50 ± 0.03
Cm-bismuthate-treated	1.2 ± 1.0
Eu-untreated	0.5 ± 0.3
Eu-bismuthate-treated	0.7 ± 0.3

[a] Each value is the mean and standard deviation for triplicate precipitations.

AmO_2^{2+}. Neptunium was determined by γ-counting, plutonium by liquid scintillation counting, and uranium by ICP-mass spectrometry. Mass balance analysis was performed to verify the measured distribution ratios by comparing the sum of activity in the phases with the initial activity in the pre-extraction samples, except for uranium. Recoveries averaged 100 ± 5%. Because organic-phase uranium could not be measured by ICP-MS, it was calculated by mass balance. All extractions were performed in triplicate, and the results plotted were the means, except for uranium, which was run only once.

Results and Discussion

Fluoride-Precipitation of Trivalent Metals. One attribute of oxidized americium species is that they are soluble in aqueous solution in the presence of excess fluoride ion. This is in contrast to the behavior of Am^{3+}, which forms the insoluble AmF_3 complex and precipitates out of solution under similar conditions.[20] Hence, the introduction of fluoride ions can be used as a test for the presence of oxidized americium species. Contact with sodium bismuthate in our experiments produced americium species that did not coprecipitate as the fluoride when lanthanum fluoride carrier was precipitated from solution. This was presumed by Hara and Suzuki to be AmO_2^{2+} when they conducted similar experiments.[4,18] It can be seen in Table 1 that americium was quantitatively converted to a nonprecipitable form in 1 M nitric acid and that all of the activity remained in the aqueous phase following fluoride precipitation. This indicates that the bismuthate oxidation method is useful for the preparation of oxidized americium in strongly acidic solution, something not previously possible with the conventional peroxydisulfate system. In contrast, untreated americium was quantitatively precipitated from the aqueous phase, as expected for Am^{3+}. Also shown in Table 1 are results for treated and untreated europium and curium. Both precipitated as the fluoride, whether bismuthate-treated or not. Because Eu^{3+} and Cm^{3+} were not expected to be oxidized, this indicated that oxidation of americium was indeed the mechanism preventing its precipitation as the fluoride.

Spectroscopy of Bismuthate-Oxidized Americium. Bismuthate treatment at room temperature produced AmO_2^{2+} quantitatively when prepared with new acid solutions, whereas treatment at 80 °C produced AmO_2^{+} quantitatively as evidenced by spectroscopic measurements. These results are shown in Figures 1 and 2 respectively for americium in 0.1 M nitric acid. This represents the direct production of AmO_2^{2+} and AmO_2^{+} in acidic solution. However, when oxidation was performed at room temperature with acids aged in polyethylene bottles, a mixture of the two higher oxidations states resulted, possibly due to the presence of trace reducing contaminants leached from the containers, or to HNO_2 production in the HNO_3. Upon initial preparation, a broad absorbance between 450−600 nm was seen due to Bi(V).[21] This broad peak decreased in intensity over the course of about 40 min as Bi(V) was reduced. Following the disappearance of Bi(V), a decrease in intensity of the AmO_2^{2+} peak began, accompanied by an increase in AmO_2^{+}. This is shown in Figure 3. This is an indication that the solubilized Bi(V) acts as a holding oxidant for AmO_2^{2+} and that as expected, the product of AmO_2^{2+} reduction is AmO_2^{+}. These results also indicate that both oxidation states were not precipitated as the fluoride under the conditions described above.

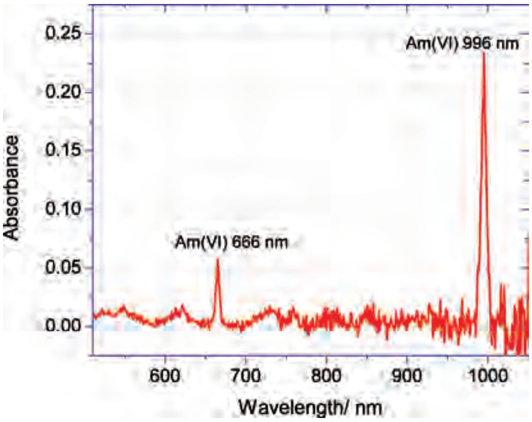

Figure 1. UV−vis absorbance spectrum of AmO_2^{2+} in 0.1 M nitric acid. The spectrum was collected using 1 mM americium in a conventional 1 cm cell.

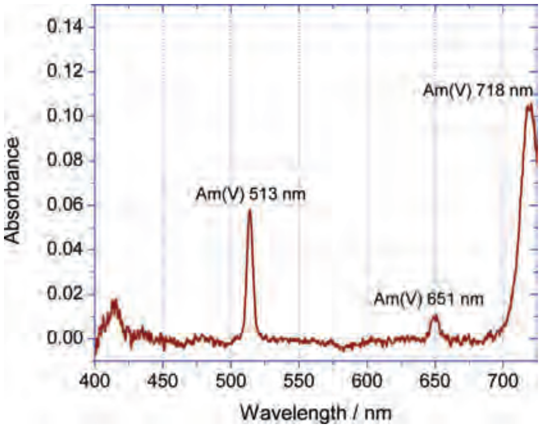

Figure 2. UV−vis absorbance spectrum of AmO_2^{+} in 0.1 M nitric acid. The spectrum was collected using 1 mM americium in a conventional 1 cm cell.

The extinction coefficients for these peaks were determined in 0.1 M HNO_3. The result for Am^{3+} at 503 nm was 386.7 ± 19.3 L/mol·cm, for AmO_2^{+} at 513 nm 72.5 ± 3.6 L/mol·cm, and for AmO_2^{2+} at 666 nm 27.9 ± 1.4 L/mol·cm. This was accomplished by measuring americium peak heights using known concentrations as determined by γ-ray spectroscopy (Figure 4.) The corresponding values in 1 M $HClO_4$ from the literature are similar at 410, 60 and 30.5 L/mol·cm, respectively.[1,22]

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(20) Nash, K. L.; Cleveland, J. M. *Radiochim. Acta* **1984**, *37*, 19–24.

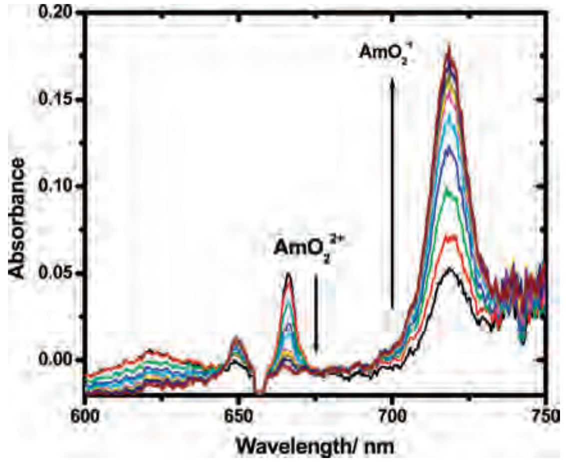

Figure 3. UV−vis absorbance spectra illustrating the decay of the AmO_2^{2+} peak, and in-growth of AmO_2^+ with time, following the disappearance of bismuthate absorbance. The spectrum was collected using 0.01 mM americium in a 100 cm liquid waveguide capillary cell.

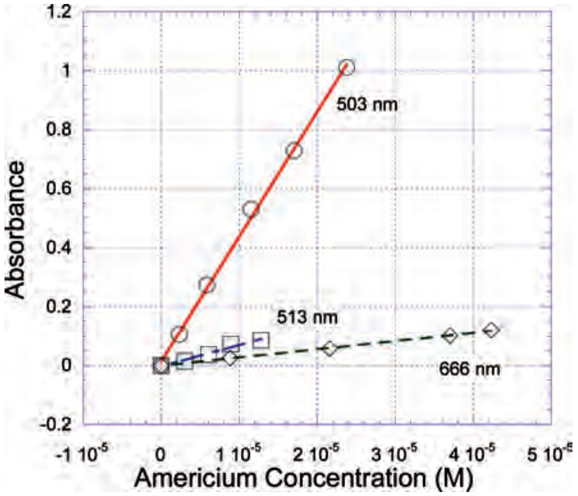

Figure 4. Extinction coefficient determinations for Am^{3+} at 503 nm (386.7 L/mol·cm), AmO_2^+ at 513 nm (72.5 L/mol·cm), and AmO_2^{2+} at 666 nm (27.9 L/mol·cm), in 0.1 M HNO_3.

Table 2. Distribution Ratios for the Solvent Extraction of NpO_2^{+2} Oxidized with Bismuthate in the Presence and Absence of 0.12 M Perchloric Acid[a]

$[HNO_3]$(M)	Np	Np−$HClO_4$	Np−$NaBrO_3$
0.5	1.84	1.69	
1.0	4.01	4.27	3.40
2.0	9.61	8.29	9.53
3.0	13.7	11.8	13.5
4.0	17.0	15.4	15.2
6.0	18.9	14.7	15.8

[a] Results are for a single extraction only, and are also shown for a trial using sodium bromate as an alternate oxidizing agent.

30% Tributyl Phosphate Extraction. The solvent-extraction behavior of UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} with 30% TBP in alkane diluents is well-known.[23] It was therefore deemed of interest to compare the extraction of AmO_2^{2+} to the better-known actinyl ions with the bismuthate oxidation method to prepare oxidized americium in acidic solution. These actinyl oxocations are extracted as neutral TBP adducts, with increasing distribution ratios as acidity increases due to coextraction of the nitrate ion, required for charge balance. Their extraction efficiency reaches a maximum at about 3 M nitric acid, after which it levels out or begins to decrease. This is usually attributed to competition for TBP by nitric acid, which also is complexed. The analogous behavior of the actinides in their common oxidation states is the basis for much separations chemistry and has been exploited on the process scale. Generally, the stability of actinide complexes increases with *Z* number due to the increase in metal ion charge density along the actinide contraction. However, the efficiency of hexavalent actinide extraction with TBP decreases with *Z* number.[23] Because the hexavalent actinides occur as dioxocations, charge density on the metal center is quenched by drawing electron density from the axial oxygens.[24] This has been shown to result in an overall lower metal charge density along the hexavalent actinide series.[25] This results in a weaker metal bond with the TBP oxygen along the series. On the basis of this behavior, it was expected that AmO_2^{2+} would continue the trend exhibited by uranium, neptunium, and plutonium, with extraction efficiency somewhat lower than PuO_2^{2+}. Actinides in the trivalent and pentavalent oxidation states are essentially inextractable.

During initial TBP extraction experiments using the oxidation methods described above, it was found that contact with the organic phase rapidly reduced americium, resulting in lower than expected D_{Am}. The reducing tendency of TBP toward metals in higher oxidation states has been previously reported. Harrington et al. presented spectroscopic evidence of reduction of CrO_4^{2-} after extraction into 60% TBP.[26] To counteract the reducing tendency of the solvent here, a small amount of perchloric acid was added to the aqueous phase. This resulted in much higher D_{Am} values. We believe that this is due to increased dissolution of the solid sodium bismuthate in perchloric acid treated solutions and not to the Hofmeister series effect that would predict increased distribution ratios for metal perchlorate salts over that of metal nitrate salts.[27] To verify this, we performed solvent extraction experiments with solutions of NpO_2^{2+} with and without perchloric acid. These data are shown in Table 2, along with that for the more conventional neptunium oxidation reagent sodium bromate, for comparison. There was no increase in solvent extraction efficiency due to the mere presence of perchloric acid. Additionally, we prepared saturated solutions of sodium bismuthate in 2 M HNO_3 in triplicate, in the presence and absence of 0.12 M perchloric acid. These were filtered and analyzed for bismuth concentration by ICP-OES. The concentration for pure 2 M HNO_3 was 69.2 ± 1.7 ug/mL and for perchloric acid-spiked 2 M

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(21) El-Shahawi, M. S.; Aldhaheri, S. M. *Fresenius J. Anal. Chem.* **1996**, *354*, 200–203.

(22) Stephanou, S. E.; Nigon, J. P.; Penneman, R. A. *J. Chem. Phys.* **1953**, *21*, 42–45.

(23) Schulz, W. W.; Navratil, J. D. *Science and Technology of Tributyl Phosphate*; CRC Publishers: Boca Raton, USA, 1984; Vol. *III*, p 153; Vol. *I*, p 3100

(24) Sarsfield, M. J.; Helliwell, M. *J. Am. Chem. Soc.* **2004**, *126*, 1036–1037.

(25) Choppin, G. R.; Rao, L. F. *Radiochim. Acta* **1984**, *37*, 143–146.

(26) Harrington, R. C.; Martin, L. R.; Nash, K. L. *Sep. Sci. Technol.* **2006**, *41*, 2283–2298.

(27) Hofmeister, F. *Arch. Exp. Pathol. Pharmakol.* **1888**, 247–260.

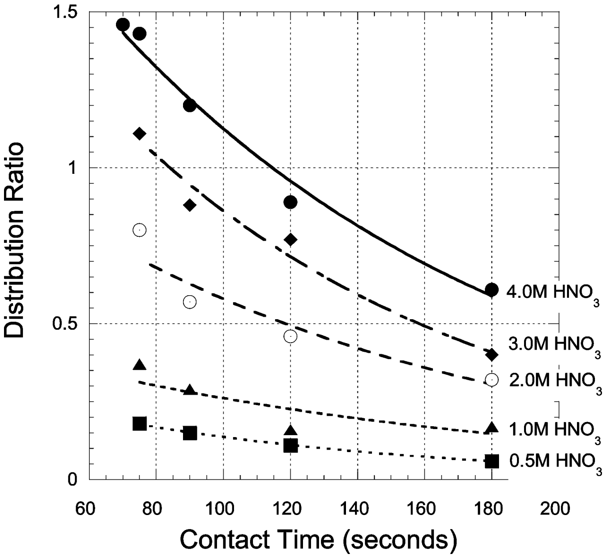

Figure 5. Dependence of the AmO_2^{2+} distribution ratios on contact time for 30% TBP extractions over a range of nitric acid concentrations. Contact time includes both solvent extraction contact and centrifugation. All points are the means of triplicate extractions.

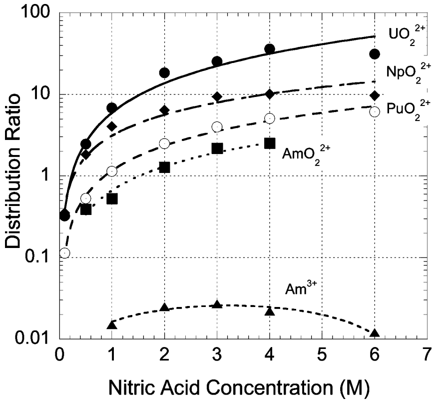

Figure 6. Extraction of the hexavalent actinides U, Np, Pu, and Am, all treated by sodium bismuthate oxidation. The extraction of untreated Am^{3+} is also shown. The AmO_2^{2+} distribution ratios were extrapolated to zero contact time based on the measured values in Figure 5.

HNO_3 was 20% higher at 87.2 ± 1.7 ug/mL. Therefore, we concluded that the increased dissolution of bismuthate to produce dissolved Bi(V) in the presence of perchloric acid acts as a holding oxidant to mitigate americium reduction by TBP. As was previously shown (Figure 3), Bi(V) acts as a holding oxidant for AmO_2^{2+}.

Further evidence of americium reduction during TBP extraction is found in contact-time experiments. The decrease in D_{Am} with contact time is shown in Figure 5 over a range of nitric acid concentrations. Because the TBP concentration is $\sim 10^5$ times the americium concentration, the reduction of americium by TBP may be assumed to proceed with pseudo-first-order kinetics. Therefore, the data in Figure 5 were fitted to exponential decay kinetics, and maximum distribution ratios were calculated for contact times of zero minutes. A maximum D_{Am} of ~2.5 was predicted from 4 M nitric acid. The maximum D_{Am} found from the plots in Figure 5 were plotted over the range of acid concentrations and are shown in Figure 6. Also plotted in Figure 6 are our results for uranium, neptunium, and plutonium extracted following bismuthate oxidation. The UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} solvent extraction behavior found here is in agreement with previous work using other oxidants.[23] The americium curve falls aspredicted for the AmO_2^{2+} ion. Previous attempts to measure hexavalent americium extraction with TBP using the peroxydisulfate system have failed due to the ineffectiveness of americium oxidation in acidic solution and the generation of sulfate, which complexes americium and suppresses D_{Am}.[28] Also shown in Figure 5 are our data for untreated Am^{3+}, for comparison to the AnO_2^{2+} ions. It should be noted that whereas TBP apparently reduces oxidized americium, the effect on TBP concentration is vanishingly small given the very large TBP concentration, and Figure 6 shows that americium extraction was nonetheless possible using short contact times.

Slope Analysis. The assumption that neutral complexes are extracted into the alkane phase necessitates charge balance of the TBP−metal complex.[23] Thus, a stoichiometry of one NO_3^- is expected for extraction of the AmO_2^+ complex and of two NO_3^- for the extraction of the AmO_2^{2+}complex. Slope analysis is a common method used for verification of these expectations. The extraction of the neutral AmO_2^{2+} complex is shown in eq 1, and results in the equilibrium expression shown in eq 2:

$$AmO_2^{2+} + 2NO_3^- + n\mathrm{TBP} \rightarrow \mathit{AmO_2(NO_3)_2}\cdot n\mathrm{TBP} \quad (1)$$

$$K_{ex} = [\mathit{AmO_2(NO_3)_2 \cdot nTBP}]/[AmO_2^{2+}][NO_3^-]^2[\mathrm{TBP}]^n \quad (2)$$

The italics indicate organic phase species. Because the organic-phase americium concentration over the aqueous phase americium concentration is D_{Am}, eq 2 may be rewritten in the form of the equation for a line, where the slope of a plot of the logarithm of the D_{Am} versus the logarithm of the nitrate concentration is the nitrate extraction stoichiometry, assuming that the TBP concentration is held constant:[29]

$$\log D_{Am} = 2\log[NO_3^-] + (\log K_{ex} + n\log[\mathrm{TBP}]) \quad (3)$$

However, nitric acid is known to partition into TBP in competition with metal extraction to form a 1:1 adduct of $TBP \cdot HNO_3$.[23] To minimize this competition for the ligand, solvent extraction experiments to measure the nitrate dependence of americium extraction were carried out in 0.1 M HNO_3 and were salted to appropriate nitrate concentrations using $NaNO_3$. A rigorous analysis would require the use chemical activities rather than concentrations. However, the determination of activity coefficients in this multielectrolyte, biphasic system is complicated and was not attempted here.[30] Attempts to perform slope analysis at constant ionic strength have also been criticized.[31] Therefore, a treatment based on chemical concentrations is in keeping with common practice and was performed here.[26,29,32]

Slope analysis was performed for AmO_2^+ extraction, resulting in a slope of 0.96 ± 0.12, in agreement with the charge balance requirement for the extraction of the AmO_2^+

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(28) Kamoshida, M.; Fukusawa, T. *J. Nucl. Sci. Technol.* **1996**, *33*, 403–408.

(29) Nash, K. L.; Lavallette, C.; Borkowski, M.; Paine, R. T.; Gan, X. *Inorg. Chem.* **2002**, *41*, 5849–5858.

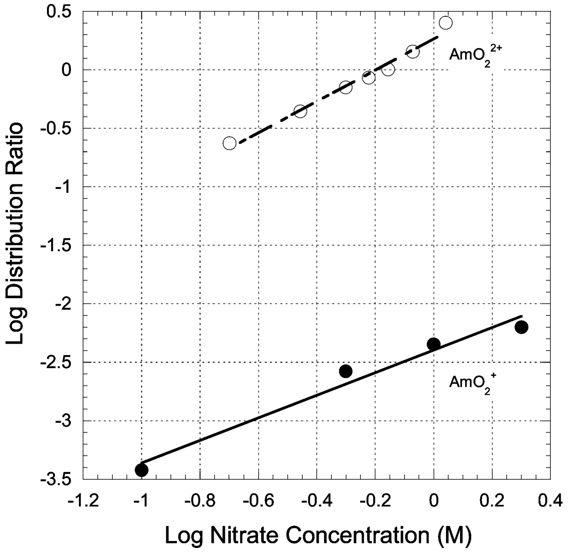

Figure 7. Slope analysis plots of log D_{Am} versus log activity-corrected nitrate concentration for the extraction of $\mathrm{AmO_2}^+$ ($m = 0.96$) and $\mathrm{AmO_2}^{2+}$ ($m = 1.3$) by 30% TBP in dodecane, over a range of sodium nitrate concentrations.

ion as a neutral complex. These data are shown in Figure 7. No correction for nitrato-complexation of $\mathrm{AmO_2}^+$ was necessary, and was not expected based upon analogy with $\mathrm{NpO_2}^+$, for which spectroscopic studies have failed to detect nitrato-complex formation.[31]

A similar analysis for $\mathrm{AmO_2}^{2+}$ was attempted. Assuming quantitative oxidation of americium to $\mathrm{AmO_2}^{2+}$, a slope of 1.3 ± 0.1 was obtained, rather than the expected value of 2. This may be an indication of the existence of the $[\mathrm{AmO_2(NO_3)}]^+$ ion. It is well-known that $\mathrm{UO_2}^{2+}$, $\mathrm{NpO_2}^{2+}$, and $\mathrm{PuO_2}^{2+}$ form mononitrato species of the general formula $[\mathrm{AnO_2(NO_3)}]^+$. This being the case, the experimentally determined distribution ratios are no longer the simple ratios of the americium activity in the organic and aqueous phases but must include the sum of the aqueous americium species:[26,29]

$$D_{\mathrm{Am}} = \frac{[\mathrm{Am}]_{(org)}}{[\mathrm{AmO}_2^{2+}]_{(aq)} + [\mathrm{AmO}_2(\mathrm{NO}_3)^{+}]_{(aq)}} \tag{4}$$

A corrected term D_{AmVI} is the hypothetical distribution ratio of the bare $\mathrm{AmO_2}^{2+}$ ion into the TBP phase. So the above equation can be rewritten as:

$$D_{\mathrm{Am}} = \frac{D_{\mathrm{Am(VI)}}}{(1 + \beta[\mathrm{NO}_3^-])} \tag{5}$$

The log β for the uranyl complex $[\mathrm{UO_2(NO_3)}^+]$ is well characterized at 0.3.[33] However, there is much debate over the formation constants for the analogous neptunium and plutonium species. The reported values for neptunium range from −0.9 to −0.3, and those for plutonium from −0.6 to 1.86, and the uranium value of 0.3 has been recommended in calculations for the other species.[31]When this value was applied to our data using eq 5, the slope of the nitrate dependency plot increased to 1.8 ± 0.1. A log β value of 0.7 yields a slope of 2.0 ± 0.1. However, because americium is reduced during the solvent extraction contact and small amounts of $\mathrm{AmO_2}^+$ will depress the value of D_{Am}, and because the existence of polynitrato species cannot be ruled out, a better estimate of the log β for $[\mathrm{AmO_2(NO_3)}]^+$ cannot be provided at this time.

Conclusions

Sodium bismuthate was found to quantitatively oxidize Am^{3+} to $\mathrm{AmO_2}^{2+}$ at room temperature and to $\mathrm{AmO_2}^+$ at 80 °C, even in strongly acidic solution. A facile and reliable method for the preparation of these oxidation states in acidic solution has not been previously available and is of benefit to the development of new separations schemes for americium from the other trivalent actinides and lanthanides. However, $\mathrm{AmO_2}^{2+}$ was found to be readily reduced by trace contaminates and required careful reagent preparation. The extinction coefficients in 0.1 M $\mathrm{HNO_3}$ for the visible absorbance peaks at selected wavelengths were measured and are given here. Spectroscopic interrogation revealed that $\mathrm{AmO_2}^{2+}$ was stable in acidic solution until the Bi(V) concentration was depleted, at which point it began to reduce to $\mathrm{AmO_2}^+$. When solvent extraction experiments using the solvent system 30% TBP in dodecane were performed, contact with the TBP-containing phase reduced $\mathrm{AmO_2}^{2+}$. However, if contacts were conducted in the presence of a small amount of perchloric acid, the solvent extraction of $\mathrm{AmO_2}^{2+}$ was possible up to the maximum investigated nitric acid concentration of 6 M. The use of perchloric acid increased the dissolution of bismuthate, and increased the concentration of Bi(V) oxidant in solution, mitigating reduction of americium by the organic extractant. The TBP extraction behavior of $\mathrm{AmO_2}^{2+}$ was analogous to that of uranyl, neptunyl, and plutonyl ions and continued the known trend of decreasing extraction efficiency with Z number. The result is a relatively low maximum D_{Am} of ~2.5; however, this may be high enough to develop a TBP-based solvent extraction system for americium if future work can develop methods to better stabilize the oxidation state in the presence of trace reducing agents.

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(30) During the review of a previous draft of this manuscript, the reviewers were unable to agree on the most appropriate way of performing activity corrections in this multielectrolyte, multiphase system.

(31) OECD Nuclear Energy Agency, Ed. *Chemical Thermodynamics of Neptunium and Plutonium*; Elsevier: Amsterdam, The Netherlands, 2001; p 194, 412, 414, 799.

(32) Hannel, T. S.; Out, E. O.; Jensen, M. P. *Solv. Extr. Ion Exch.* **2007**, *25*, 241–256.

(33) Grenthe, I.; Fuger, J.; Konings, R.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; North Holland: Amsterdam, 1992.