Ultra-Efficient Americium/Lanthanide Separation through Oxidation State Control

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ABSTRACT: Lanthanide/actinide separation is a worldwide challenge for atomic energy and nuclear waste treatment. Separation of americium (Am), a critical actinide element in the nuclear fuel cycle, from lanthanides (Ln) is highly desirable for minimizing the long-term radiotoxicity of nuclear waste, yet it is extremely challenging given the chemical similarity between trivalent Am(III) and Ln(III). Selective oxidation of Am(III) to a higher oxidation state (OS) could facilitate this separation, but so far, it is far from satisfactory for practical application as a result of the unstable nature of Am in a high OS. Herein, we find a novel strategy to generate stable pentavalent Am (Am(V)) through coordination of Am(III) with a diglycolamide ligand and oxidation with Bi(V) species in the presence of an organic solvent. This strategy leads to efficient stabilization of Am(V) and an extraordinarily high separation factor ($>10^4$) of Am from Ln through one single contact in solvent extraction, thereby opening a new avenue to study the high-OS chemistry of Am and fulfill the crucial task of Ln/Am separation in the nuclear fuel cycle. The synergistic coordination and oxidation process is found to occur in the organic solvent, and the mechanism has been well elucidated by quantum-theoretical modeling.
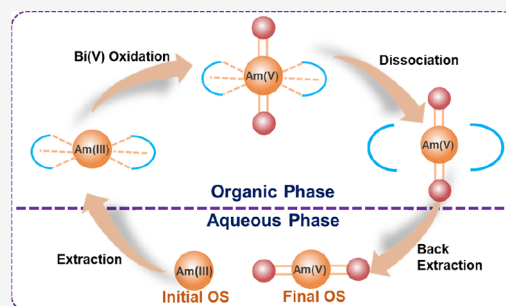
INTRODUCTION

Nuclear power plays a vital role in mitigating the fast-increasing energy demand in a low-carbon society. However, nuclear wastes generated from the utilization of nuclear energy impose a great threat to the human health and ecological environment. Treatment of nuclear waste is a worldwide grand challenge of the modern society. Developing an efficient nuclear fuel cycle that could reduce radiological hazards of nuclear wastes is crucial for the sustainable development of nuclear energy. One of the most troublesome elements in the nuclear fuel cycle is americium because its most prevalent isotope, ^{241}Am with a half-life of 432 years, dominates both the radiotoxicity and the heat load from typical spent nuclear fuel over the first several thousand years.[1,2] Therefore, the removal of Am, mainly existing in the Am(III) oxidation state, from nuclear waste is a key task in the nuclear industry and is greatly beneficial for enhancing the repository storage capacity as well as minimizing the long-term hazards of Am through trans-mutation (i.e., neutron-assisted conversion of isotopes).[3−7]

Nuclear wastes contain a mix of numerous elements, including actinides (U, Np, Pu, Am, etc.) and a large amount of fission products including lanthanides (Ln). While separation of Am from nuclear waste is critical for nuclear waste minimization and is a prerequisite for transmutation in an advanced nuclear fuel cycle, this process poses a significant challenge because Am has similar chemical properties to Ln and the coexistence of an excessive amount of Ln that

possesses high neutron cross sections can disrupt the transmutation efficiency of Am. Despite the existence of Ln(II) and Ln(IV) in the condensed phase[8−19] and Pr(V) in the gas phase,[20,21] both Am and Ln have a strong thermodynamic preference for oxidation state III and their ions are of comparable size. Accordingly, they behave with great chemical similarity under typical conditions, leaving few options for separation.[22,23] Therefore, separation of Am from Ln has become a significant challenge in advanced nuclear fuel cycles over the past decades.[24−27] One approach often exploited is to take advantage of the slightly less contracted f-orbitals in Am(III) than in Ln(III), which endows Am(III) with preference in miniscule covalent bonding with ligands bearing relatively soft donor atoms such as N and S.[25,28−34] However, this approach usually encounters drawbacks such as slow separation kinetics, instability of ligands, and narrow operational acidity, thus hampering its use in industrial applications.[25,33]

An alternative approach is to make use of the slight difference of the oxidizability of Am and Ln elements. While
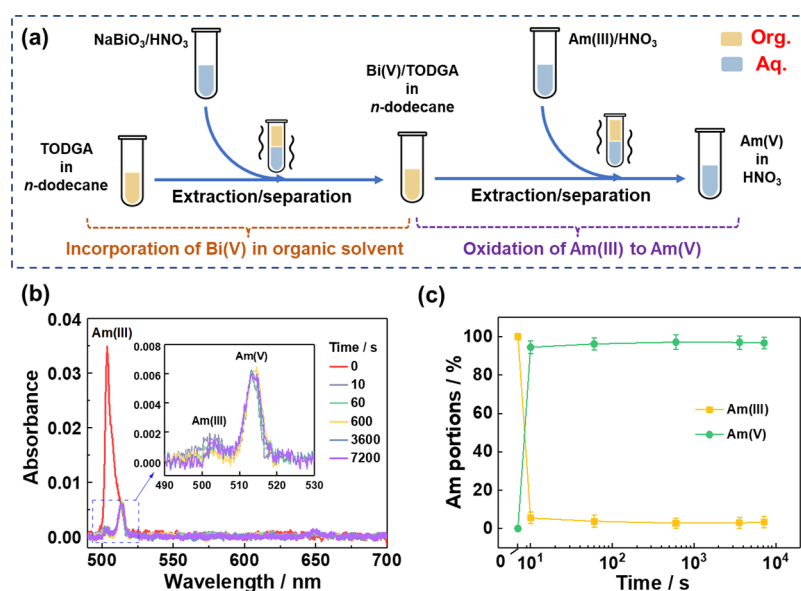
Figure 1. (a) Scheme for generation and stabilization of Am(V) in a biphasic system in the present work. (b) Variation of absorption spectra in the nitric acid aqueous solution after mixing Am(III)/HNO$_3$ solution with the Bi(V)-containing TODGA/n-dodecane organic solution. The Am(V) spectra are enlarged for visibility. (c) Time-dependent change of portions of Am in different oxidation states in the aqueous solution. The portions were estimated and calculated from the absorbance of characteristic absorption bands of Am(III) and Am(V). TODGA concentrations in the organic solution (Org.): 0.5 M. Initial ^{241}Am concentration in the aqueous solution (Aq.): 0.104 mM. The logarithmic plot is to demonstrate the fast kinetics of the oxidation process and the long-term stability of Am(V).

Am(III) can be oxidized to higher oxidation states such as Am(V)/Am(VI) under strong oxidizing conditions in aqueous solution, lanthanides in the aqueous phase are predominantly restricted to Ln(III), with a few exceptions such as Ce(IV), Pr(IV), and Tb(IV),[16,19,35,36] which enables a potential Ln/Am separation approach through oxidation state control by taking advantage of the huge difference in the coordination chemistry of Ln(III)/Ln(IV) and Am(V)/Am(VI), existing as spherical Ln^{3+}/Ln^{4+} and linear actinyl-type AmO$_2^+$/AmO$_2^{2+}$ ions, respectively. Considerable efforts have been devoted to this approach.[37,38] Am(V) or Am(VI) has been generated in aqueous solutions using strong chemical oxidants such as NaBiO$_3$, (NH$_4$)$_2$S$_2$O$_8$/AgNO$_3$, and Cu(III) periodate.[38−45] Dares and colleagues also discovered that a tin-doped indium oxide electrode surface derivatized with a terpyridine ligand is able to oxidize Am(III) to Am(V)/Am(VI), providing an additional method to access high-valent Am.[46,47] Despite the success of oxidation state control of Am in aqueous phases, its practical applications in the separation process remain rather limited because of low separation efficiency. The key problem therein is that Am(V) and Am(VI) are readily reduced by many species, especially organic solvents used in the biphasic solvent extraction process.[43,44,48] To achieve effective Ln/Am separations, high-valent Am species have to be freshly prepared[43,44] and the contact time in extraction is sometimes limited to just a few seconds.[44,49] Even under such harsh conditions, mutual Am/Ln separation factors of >100 are rarely achieved.[39−41] Therefore, developing an efficient and well-operational Am/Ln separation approach through oxidation state control remains a seminal challenge.

In this work, we design a novel strategy to generate and stabilize Am(V) in the presence of an organic solvent. Different from previous reports that apply oxidants in the aqueous solution, herein, we incorporate Bi(V) species into an organic solvent, creating a unique redox environment that can efficiently convert Am(III) coordinated by diglycolamide

ligands to Am(V). Furthermore, when an aqueous Am/Ln solution is in contact with the Bi(V)-containing organic solution, Ln ions are well extracted into the organic phase, while the generated Am(V) ions stay exclusively in the aqueous phase and are efficiently stabilized through a mechanism of in situ extraction/oxidation of its reducing product Am(III). This strategy leads to exceptionally high Ln/Am separation factors (>10^4) over a broad range of experimental conditions in biphasic extraction.

■ RESULTS AND DISCUSSION

Generation and Stabilization of Am(V) in Acidic Aqueous Solutions. Considering the large redox potential of Am(V)/Am(III) and Am(VI)/Am(III) couples (1.73 and 1.68 V *vs* SCE, respectively),[38] usually strong oxidants must be used to obtain Am(V) and Am(VI). So far, high-valent Am ions were generated in acidic solutions in only a few occasions.[38−47] Modifying the coordination modes of Am(III) can alter its oxidation potential to open new routes to generate high-valent Am. As mentioned before, a tin-doped indium oxide electrode surface derivatized with a terpyridine ligand that could coordinate with Am(III) verified this idea and both Am(V) and Am(VI) were generated successfully in acidic aqueous solutions.[46,47] However, subsequent Am/Ln separation efforts encounter a significant challenge due to the rapid reduction of these high-valent Am ions when contacting with organic reagents for separation.[50] To overcome this fast reduction challenge, we design a scheme (Figure 1a) to generate and stabilize high-valent Am in a biphasic system with deliberate control of the coordination chemistry of Am and proper selection of the oxidant that could be loaded in the organic solvent. In this scheme, highly oxidative Bi(V) (bismuthic acid) species were loaded into the organic solvent of n-dodecane in the presence of a tridentate ligand TODGA (N,N,N',N'-tetraoctyl diglycolamide; Figures S1−S3 in the Supporting Information) through a simple extraction mecha-

nism: when the nitric acid solution with BiO_3^- ions contacts with the TODGA/*n*-dodecane solvent, the hydrophobic BiO_3^- ions can be extracted into the organic solvent by forming BiO_3^--H^+ ionic pairs or bismuthic acid $HBiO_3$ (Figures S4–S6; experimental details are provided in the Supporting Information). The Bi(V)-containing organic solvent was then contacted with the Am(III)/HNO_3 aqueous solution to generate Am(V). In the *n*-dodecane organic solvent, the ion–ion and ion–dipole Coulombic interactions have been enhanced by almost 40 times as the dielectric constants of *n*-dodecane and water at 20 °C are 2.02 and 80.4, respectively, which can adjust the redox properties and significantly help stabilize the Am(V) ion in an organic solution.

The UV–Vis absorption spectra were collected to monitor the conversion of Am(III) to Am(V) as Am ions with different oxidation states can be well discriminated by virtue of their characteristic absorption bands.[43,46,47] In nitric acid solutions, Am(III) usually exhibits a sharp and strong absorption peak at ~503 nm with high molar absorptivities (mostly >300 cm^{-1}·M^{-1}), while Am(V) shows a sharp but relatively weak absorption peak at ~513 nm with much smaller molar absorptivities (~50 cm^{-1}·M^{-1}). The exact peak position and molar absorptivity depend on the concentration of HNO_3 (Figure S7) and temperature.[51,52] As shown in Figure 1b, upon mixing Am(III) aqueous solution (3.0 M HNO_3) directly with the Bi(V)-containing TODGA/*n*-dodecane solvent, the absorption band of Am(III) at 503.6 nm decreased rapidly and, concurrently, the characteristic absorption bands of Am(V) at 513.8 nm appeared in the aqueous solution. More than 94% of Am(III) was converted to Am(V) in 10 s after mixing the two phases, and >96% of Am remained in the Am(V) state in the aqueous phase for at least 2 h (Figure 1c). There are no observable absorptions of Am in the organic phase (Figure S8), and the fraction of Am in this phase was estimated to be less than 1% of total Am. It is worth noting that previous quantitative preparation of free Am(V) in highly acidic aqueous solution was only achieved at a high temperature of 80 °C and using $NaBiO_3$ as the oxidant.[38,43] Such a high temperature condition could potentially cast safety issues in radioactive operations. The present work is the first report to directly generate quantitative and stable Am(V) in highly acidic solution under ambient conditions.

Superb Ln/Am Separation Performance. The aforementioned scheme of generation and stabilization of Am(V) in the biphasic system provides a novel strategy for an ultra-efficient Ln/Am separation. Utilizing this strategy, one can treat a Ln/Am feed solution in the same recycling procedure to generate and stabilize Am(V) exclusively in the aqueous phase; in contrast, the lanthanides (Ln = La, Ce, Pr, Nd, Eu, etc.) will remain mostly in the Ln(III) oxidation states (except for Ce, which can be oxidized to Ce(IV) under the experimental condition; Figure S9) and be readily extracted into the organic phase due to the high extractability of TODGA toward Ln(III). We successfully demonstrate this separation strategy through a series of solvent extraction experiments (Figure 2) as described below.

At first, the separation of a trace amount of ^{241}Am from ^{152,154}Eu, a representative lanthanide ion, was examined. As shown in Figure 2, the extraction of Eu is very effective, with a distribution ratio $D_{Eu} > 100$ mostly, while the extraction of ^{241}Am remains at comfortable low levels ($D_{Am} < 0.01$), resulting in extraordinarily high Eu/Am separation factors ($SF_{Eu/Am} > 10^4$) after phase separation. More importantly, such
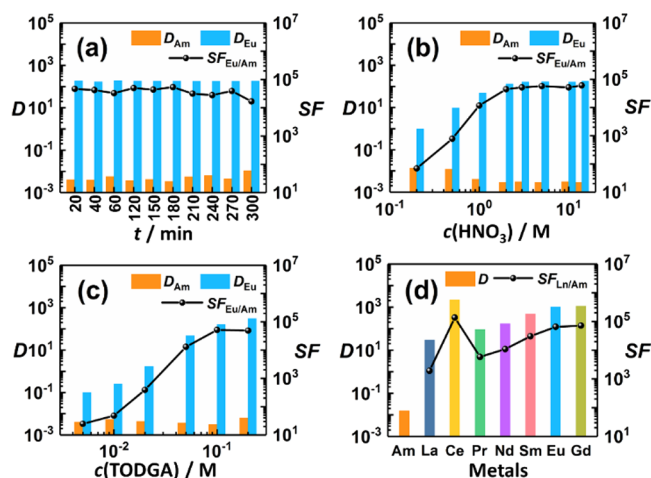

Figure 2. Separation results of ^{241}Am and Ln(III) with the oxidation state control strategy developed in this work. (a) Effect of contact time. (b) Effect of HNO_3 concentration. (c) Effect of TODGA concentration. (d) Separation of simulated feed solution. Initial aqueous phase: (a, c) trace amount of ^{241}Am (~10^{-8} M) and ^{152,154}Eu (~10^{-9} M) in 3.0 M HNO_3; (b) trace amount of ^{241}Am (~10^{-8} M) and ^{152,154}Eu (~10^{-9} M) in HNO_3 of different concentrations; (d) simulated Am/Ln waste solution containing 0.1 mM ^{241}Am and approximate mM level of Ln (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) in 3.0 M HNO_3 (see Table S1 for detailed composition). Initial organic phase: (a, b) 0.1 M TODGA in Bi(V)-containing *n*-dodecane; (c) different concentrations of TODGA in Bi(V)-containing *n*-dodecane; (d) 0.5 M TODGA in Bi(V)-containing *n*-dodecane. The contact time for panels (b)–(d) is 1 min.

high $SF_{Eu/Am}$ values persist at least for 5 h (Figure 2a), which is in accordance with the high stability of Am(V) as indicated by spectral analysis (Figure 1c) and underscores the advantages of this strategy over previous schemes using the oxidation approach.[39–41,49,53,54] The long-term persistence of the efficient Ln/Am separation is sufficient to allow practical operation using separation equipment such as centrifugal contactors or mixer-settlers. Moreover, the experiments show that our scheme is able to achieve high $SF_{Eu/Am}$ values (>10^4) in a remarkable wide range of aqueous acidities from at least 1.0 to 14.0 M HNO_3 (Figure 2b), thus avoiding the difficulty of acidity adjustment usually involved in practical radioactive waste treatment.

Our scheme is applicable to the separation with both the trace amount of ^{241}Am and macro amount of ^{241}Am as well, as indicated by the generation and stabilization of high-concentration Am(V) in the previous section (Figure 1). The separation of high-concentration ^{241}Am from Ln can be demonstrated by directly treating simulated Am/Ln waste feed solution (Table S1) consisting of various Ln and 0.1 mM ^{241}Am.[55,56] As shown in Figure 2d, excellent separation of ^{241}Am from all selected Ln ions (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd), with an average $SF_{Ln/Am}$ value of 46,000, has been achieved through only one single contact. In particular, extremely high SF values of 65,000, 72,000, and 137,000 are obtained for Eu/Am, Gd/Am, and Ce/Am systems, respectively. These are among the highest mutual Ln/Am separation factors that have ever been reported and outperform previous results using the oxidation state control approach, where mutual Ln/Am separation factors of >100 were rarely achieved (Table S2).[39–41,49,53,54] With such record-high separation factors, quantitative separation of Am from Ln
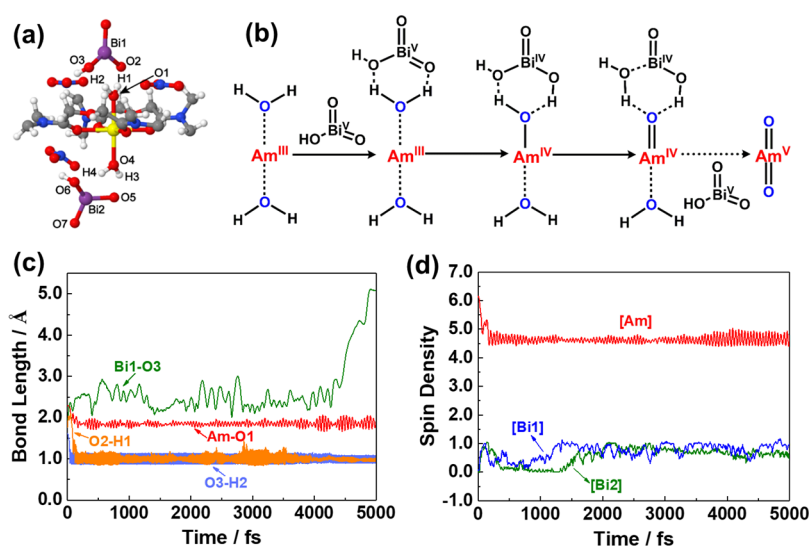
Figure 3. QM/MM MD simulations for the oxidation of Am(III) (species **A**) by bismuthic acid in an organic solution in the presence of TODGA. (a) Starting geometry of species **A** with atoms numbered. (b) Illustration of the oxidation process. The coordinated TODGA ligands around Am are omitted for clarity. (c) Bond distance fluctuation for representative bonds during the simulations. (d) Spin density population fluctuation on Am and Bi centers during the simulations, which becomes steady after 1500 ps simulation time.

can be easily realized through simple contacting operations. The much higher Ce/Am separation factors shown in Figure 2d are attributed to the oxidation of Ce(III) to Ce(IV) by Bi(V) species.[42] As Ce(IV) is more extractable than Ce(III) and other Ln(III) by TODGA due to its higher charge than Ln(III), it thus can be better separated from Am(V) in our separation system (Figure S9). Such an extremely high $SF_{Ce/Am}$ value also overcomes a major drawback in previous Am oxidation/separation approaches, where poor Am/Ce separations were usually encountered.[49,57]

Unique Oxidation and Separation Mechanism. Given the superb Ln/Am separation performance of our scheme, it is vital to understand the in-depth mechanism underlying the efficient generation and stabilization of Am(V) in the biphasic system. One of the particular questions to be answered is how the oxidation of Am(III) to Am(V) occurred during the biphasic extraction process. Since the oxidant Bi(V) species were incorporated in the TODGA/n-dodecane organic solvent (Figure S4) prior to the extraction and Am(III) can be well extracted into the organic solvent by TODGA, it is reasonable to hypothesize that Am(III) is oxidized to Am(V) in the organic solvent and then the generated Am(V) transferred back into the aqueous solution. To verify this hypothesis, additional oxidation experiments were performed in the absence of aqueous solutions. Am(III) ions and Bi(V) species were loaded into two equal aliquots of TODGA/n-dodecane solution, respectively, through extraction (see the Supporting Information for details). As shown in Figure S10, when the Am(III)/TODGA/n-dodecane solution was mixed with the Bi(V)/TODGA/n-dodecane solution, the sharp and intense absorption band of Am(III) at 505.2 nm decreased rapidly and, concurrently, characteristic absorption bands of Am(V) at 514.4 nm appeared and intensified in the newly formed homogeneous organic solution. More than 90% of Am(III) was converted to Am(V) in 30 s after mixing the two organic solutions (Figure S10). More importantly, >95% of Am was found in the Am(V) state after 20 min and >90% of Am remained as Am(V) even after 2 h (Figure S10). These results thus verify our hypothesis that the oxidation occurs in the

organic solution where the Coulombic interaction is drastically enlarged due to the much higher dielectric constant of n-dodecane than water. Moreover, the unprecedented generation of stable Am(V) in an organic solvent opens a new route to explore Am chemistry in atypical oxidation states in an organic medium. Notably, the same Bi(V) oxidant in aqueous solution will only oxidize Am(III) to Am(VI) rather than Am(V) under ambient conditions (Figure S11),[42–44,49] thus revealing the distinct oxidation mechanism and unique redox environment in the organic solution than in the aqueous solution.

To further elucidate the oxidation mechanism of Am(III) by the Bi(V) oxidant in the organic solution, large-scale quantum mechanics/molecular mechanics (QM/MM) molecular dynamics (MD) simulations were performed using our recently developed pseudopotentials for lanthanide and actinide series.[58,59] Two selected Am(III) species adopted for the QM/MM MD simulations are $Am(TODGA)_2(H_2O)_2(NO_3)_3$ (**A**) and $Am(TODGA)_2(NO_3)_3$ (**B**) (Figures S12–S14), which were deduced experimentally as two plausible species in this work (Figure S15) as well as in previous reports.[60–62] As shown in Figure 3 and Figure S16, the MD results indeed show that the Bi(V) (bismuthic acid) species help generate Am(V) from **A** and **B**, respectively.

The MD-derived pathways for the oxidation processes are provided as supplementary videos, and additional results for the MD simulations are included in the Supporting Information (Figures S17–S22). Taking species **A** as an example (Figure 3a,b), at the beginning of the simulations, the two $HBiO_3$ species approach quickly to the coordination shell of the Am(III) center and abstract H and/or H+ sequentially from the two H_2O molecules by forming the reduction and dehydrate products $(HO)Bi^{IV}(O)^+$ and H_2O. The two Am(V)=O bonds formed are shortened to 1.82–1.84 Å at 200 fs (Figure 3c and Figure S20), which are much shorter than the original $H_2O \rightarrow Am(III)$ dative bond (~2.40 Å) in **A**. Such a ligated $[OAmO]^+$ geometry is maintained up to 5000 fs, which proves the high stability of the newly formed americyl ion in the organic solution. The calculated Mulliken spin density population of Am center decreases from ~6.5 to ~4.5,

and that of the bismuth center increases from ~0.0 to ~1.0 (Figure 3d), suggesting that the Am(III, f^6) center is oxidized by the bismuth center to Am(V, f^4) rather than Am(VI, f^3). One can see from Figure 3d that the spin density population of Bi fluctuates sharply back and forth between ~0.0 and ~1.0 at the very beginning (<500 fs) of the simulation, but it finally becomes steady as ~1.0 after ~1500 fs. Such fluctuations at the beginning are ascribed to the large number of samplings required for QM/MM MD simulations. For the similar process starting with species **B**, the QM/MM MD simulations also indicate the instant formation of Am(V) species $[OAmO]^+$ in the organic solution through the direct interaction of the central Am atom with the O ion from $(HO)Bi^V(O)_2$ species (Figure S16). However, the spin density population of Bi fluctuates even more significantly at the very beginning of the simulations and becomes steady only after ~2000 fs in this case, suggesting that water molecules in species **A** may help promote the oxidation of Am(III) to Am(V) in the organic phase. Nevertheless, all these computational results agree with the foregoing experimental observation of the fast generation and stabilization of Am(V) in the organic solution. Moreover, one can speculate that the intermediate Bi(IV) species can be converted to more stable Bi(III) ones eventually.

In addition to the QM/MM MD simulations, DFT calculations were also applied to further comprehend the preference for Am(V) generation in this organic medium in comparison with Am(VI) (Figure S23). The calculated reduction potential of 2.91 V for the couple $[Am^{VI}O_2L_2]^{2+}/[Am^VO_2L_2]^+$ (L = diglycolamide ligand) in the organic solution is apparently much larger than that of $[Am^{VI}O_2(H_2O)_5]^{2+}/[Am^VO_2(H_2O)_5]^+$ in the aqueous solution (1.99 V), suggesting that Am(V) is much more difficult to be further oxidized to Am(VI) in this organic medium than in the aqueous phase. These results are consistent with the enhanced Coulombic interaction and the experimental observation that Am(V) instead of Am(VI) is formed in the organic solution by using the Bi(V) oxidant.

Obviously, the unique redox environment of the Bi(V)-containing organic solvent plays a vital role in the generation and stabilization of Am(V) from Am(III). However, the superior stabilization of Am(V) and its separation from Ln(III) in the biphasic system are not merely resulted from this unique redox environment of the organic solvent but also benefit from the intrinsic valence selectivity of the TODGA ligand and an in situ Am(III) extraction/oxidation mechanism (Scheme 1a). The generated $Am^VO_2^+$ in the organic solvent has a very low tendency to coordinate with TODGA and thus will be back-extracted into the aqueous solution, and $Am^VO_2^+$ in the aqueous solution tends to be gradually reduced to Am(III) again (Figure S24). However, as shown in Scheme 1a, the reduced Am(III) will be extracted readily and quantitatively by TODGA into the organic solvent, which can be once again oxidized to Am(V) in the organic solvent through the mechanism we proposed (Figure 3b and Figure S16b) and then moves back into the aqueous phase. This Am(III)/Am(V) recycling procedure creates a unique opportunity to quantitatively retain Am(V) in the acidic aqueous part of the biphasic system for practical separation. In contrast, as aforementioned, the lanthanides will remain mostly in Ln(III) (except Ce(IV) in the experimental condition), and both Ce(IV) and Ln(III) will stay in the organic solution after extraction (Scheme 1b). Therefore, the exceptionally high Ln/Am separation factors in the present work are a result of both

Scheme 1. (a) Dynamic Am^{III}/Am^V Recycle for the Generation and Stabilization of Am(V) in the Biphasic System with the Bi(V)-Containing Organic Phase and (b) Reactions of Ln in the Same System[a]
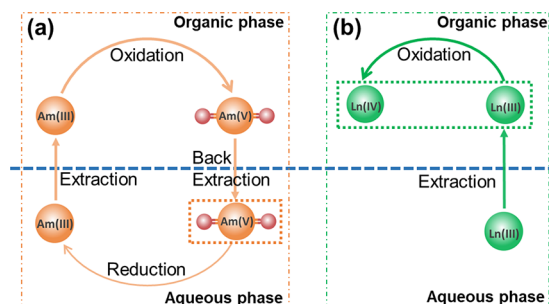
[a]Note that only Ce could be oxidized from III to IV in this system. The species in thick dashed frames represent the final species in the system after equilibrium.

the unique redox environment of the organic solvent and the distinctive recycling procedure of the biphasic solvent extraction system.

■ CONCLUSIONS

We have demonstrated in this work that the incorporation of the oxidative Bi(V) species into an organic solvent can effectively induce the formation of Am(V) from Am(III) in the organic phase. In a biphasic extraction system, a combination of the unique redox environment of the organic phase and the intrinsic valence selectivity of the functional ligand such as TODGA offers an appealing mechanism to generate Am(V) in the organic phase and back-extract it exclusively into the acidic aqueous phase while extracting Ln(III, IV) into the organic phase, which leads to exceptionally high Ln/Am separation factors. This work thus provides a promising strategy to fulfill the seminal challenge of Am/Ln separation in a scenario that combines the extreme conditions of strong radiation, high acidity, and large excess amount of lanthanides. This system also offers opportunity to explore and enrich the limited knowledge of high-valent americium chemistry in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c00594.

> Experimental details, materials, methods, and additional data including supplementary figures and tables for Am/Ln separation, Bi(V) incorporation, and computational results (PDF)
> Oxidation of Am by H_2O and $HBiO_3$ (MP4)
> Oxidation of Am by $HBiO_3$ (MP4)

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Notes

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