Supporting Information

Redox Stabilization of Am(V) in a Biphasic Extraction System Boosts Americium/Lanthanides Separation Efficiency

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1. Experimental Section

1.1 Chemicals and Materials

Milligram level of $^{241}Am_2O_3$ supplied by Institute of Nuclear and New Energy Technology (INET) was dissolved in concentrated HNO_3, giving the stock solution of ^{241}Am. $^{152,154}Eu$ was provided by China Institute of Atomic Energy (CIAE). The analytical-grade hydrated nitrate of Ln (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) and hydrated $NaBiO_3$ were purchased from Aladdin Reagent Company. TODGA was obtained from Qingdao Beitwall Technology Co., Ltd. Ultrapure water with a resistivity of 18.2 MΩ·cm was applied for all the experiments. Unless specifically noted, all the other reagents in this work were of AR grade or higher quality and utilized as received. ***CAUTION:*** *Considering the high radioactivity of* ^{241}Am *and* $^{152,154}Eu$ *isotopes, all the relevant experiments must be performed in customized fume hood or glove box with negative pressure and ventilation system to reduce the potential irradiation hazard to operators.*

1.2 Measurements

The quantitative analysis for trace and macro amount of radioactive isotopes are different. For the trace amount of radionuclides, the counting rate of ^{241}Am and $^{152,154}Eu$ was directly determined by an ultra-low background Liquid Scintillation Counter (LSC, Quantulus 1220, PerkinElmer). For macro amount of ^{241}Am used for spectra analysis, an appropriate volume of the solution should be accurately sampled and diluted by 10000 folds with 0.1 M HNO_3 solution before radioactivity measurement. Subsequently, the mole or mass concentration of ^{241}Am in the solution was calculated based on the counting rates of ^{241}Am from the liquid scintillation measurement and the specific activity of ^{241}Am (3.43 Ci/g, half-life of ^{241}Am is 432.6 y). Specifically, 100 μL of each sample was injected into a 20 mL plastic capped vial and mixed with 10 mL scintillation cocktail (Hisafe 3) by hand shaking. The content of non-radioactive metal ions was measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Thermo Elemental, Inc.). All the absorption spectra of ^{241}Am were collected on Cary 6000i UV-Vis-NIR spectrophotometer (Agilent, Inc.) by transferring 2.0 mL solution into a 10 mm cuvette with screwed caps and measured at room temperature (25.0 ± 0.1 °C). The reference solution was HNO_3 or TODGA/*n*-dodecane with corresponding concentration for aqueous or organic samples, respectively.

1.3 Oxidation of ^{241}Am(III)

The oxidation of ^{241}Am(III) was performed by adding 15 mg of $NaBiO_3$ solid powder to 1.0 mL HNO_3 solution containing ^{241}Am(III), and then mixed vigorously for 2 h. Afterwards, solid residues of undissolved $NaBiO_3$ was removed by centrifugation and filtration through 0.22-μm polyether sulfone (PES) filters (Millipore) before spectrometric characterization or solvent extraction.

1.4 Incorporation of Bi(V) into the organic solvent

The incorporation of Bi(V) into the organic phase was carried out by mixing the TODGA/*n*-dodecane solution with isovolumic 3.0 M HNO_3 solution containing 15 mg/mL $NaBiO_3$ for 2 h. After sufficient agitation, the organic phase was separated by centrifugation.

1.5 Solvent Extraction

TODGA/*n*-dodecane was used as the organic phase and HNO_3 solution containing ^{241}Am and Ln (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) was the aqueous phase. The distributions of cations in each phase were measured through LSC or ICP-AES. For the batch extraction, the aqueous solutions were spiked with trace amount of ^{241}Am and ^{152,154}Eu. Equal volume (1.0 mL) of the organic phase and the aqueous phase were agitated in a stoppered glass tube at 25.0 ± 0.1 °C. Subsequently, the mixed liquid was centrifuged for phase separation and an aliquot (100 μL) of sample was taken from each phase for radioactive analysis. The counting rates of ^{241}Am and ^{152,154}Eu were determined simultaneously with LSC. For separation test with simulated feed solution, two comparative experiments were conducted simultaneously. One was performed with 1.0 mM ^{241}Am mixed with macro amount of Ln and analyzed by LSC to determine the distribution of radioactive ^{241}Am, while the other one was carried out without ^{241}Am to facilitate the measurement of non-radioactive Ln ions. Concentration of Ln in the aqueous phase was diluted to appropriate levels and then determined by ICP-AES, and that in the organic phase was calculated through mass balances by the difference of the concentrations in the aqueous solution before/after extraction. The distribution ratio (D) of ^{241}Am and Ln was defined as the ratio of metal ion concentration in the organic phase ($[M]_{org.}$) to that in the aqueous phase ($[M]_{aq.}$), $D_M = [M]_{org.} / [M]_{aq.}$. The separation factor $SF_{Ln/Am}$ value was expressed as $SF_{Ln/Am} = D_{Ln} / D_{Am}$. At least duplicate experiments were carried out to ensure the reproducibility of the extraction data.

2. Supplementary Figure

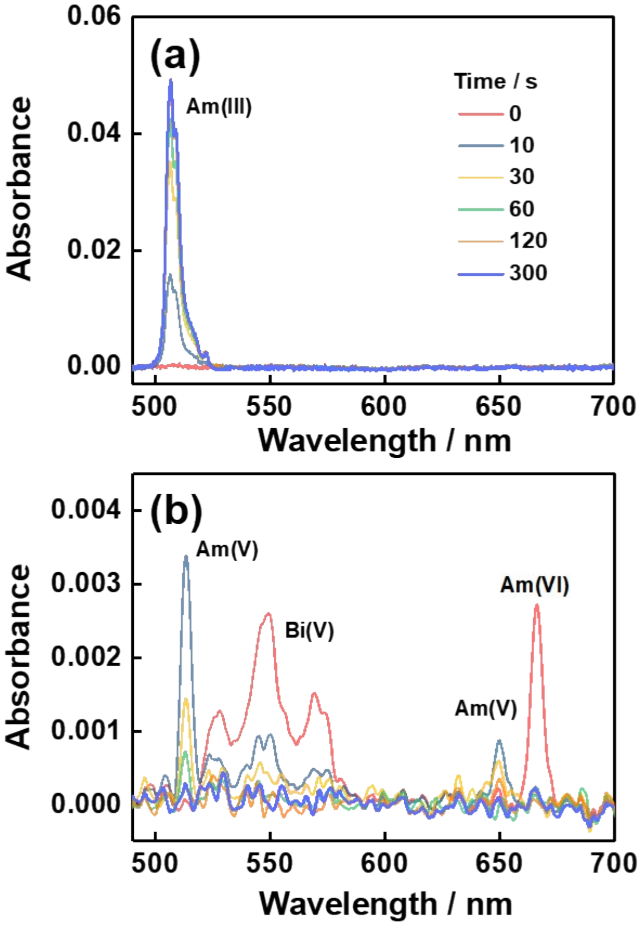

Figure S1. Variation in absorption spectra of Am in the case of Am(VI)/HNO_3 solution mixing with TODGA without Bi(V)-incorporated *n*-dodecane: (a) organic phase; (b) aqueous phase. (Org.): 0.1 M TODGA/*n*-dodecane; (Aq.): 0.1 mM ^{241}Am(VI) in 3.0 M HNO_3. The spectra were collected using 0.1 mM Am in a 10 mm cuvette.

3. Supplementary Table

Table S1. Composition of simulated feed solution.

Element	^{241}Am	La	Ce	Pr
Concentration (g/L)	0.241	0.240	0.468	0.224
Element	Nd	Sm	Eu	Gd
Concentration (g/L)	0.801	0.148	0.027	0.038
[HNO_3] = 3 M				