Key Words

americium (Am)

lanthanides (Ln)

oxidation state control

diglycolamide ligand

Bi(V) species

Pentavalent Am (Am(V))

solvent extraction

nuclear fuel cycle

radiotoxicity

coordination chemistry

hifh-valent americium chemistry

biphasic system

high separation factor

organic solvent

quantim-theoretical modeling

Objective

1. Develop a novel strategy to stabilize pentavalent americium (Am(V)): This involves the coordination of Am(III) with a diglycolamide ligand and oxidation using Bi(V) species in the presence of an organic solvent .

2. Achieve high separation factors for americium from lanthanides: The study aims to achieve an extraordinarily high separation factor (>10^4) of Am from Ln through a single contact in solvent extraction .

3. Elucidate the mechanism of synergistic coordination and oxidation: The research seeks to understand the mechanism behind the efficient generation and stabilization of Am(V) in the biphasic system using quantum-theoretical modeling

4. Enhance the nuclear fuel cycle: By effectively separating Am from Ln, the strategy aims to minimize the long-term radiotoxicity of nuclear waste, thus contributing to the sustainability of nuclear energy .

5. Investigate the redox environment and chemical behavior of high-valent americium: The study explores the distinct oxidation mechanism and unique redox environment in the organic solvent compared to the aqueous solution .

6. Provide practical applications for nuclear waste treatment: The research aims to offer a practical and efficient approach for the separation of Am from Ln in the context of nuclear waste management .

7. Generate stable Am(V) under ambient conditions: The study demonstrates the generation of stable Am(V) in highly acidic solutions under ambient conditions, which contrasts with previous methods requiring high temperatures .

8. Evaluate the extraction kinetics and stability of Am(V): The research includes experiments to monitor the conversion of Am(III) to Am(V) and the stability of Am(V) in the organic phase .

9. Demonstrate the scalability of the separation process: The study tests the separation process with both trace and macro amounts of 241Am, demonstrating its scalability and effectiveness in treating simulated Am/Ln waste feed solutions .

10. Understand the interactions within the biphasic system: The research seeks to understand how the organic solvent's properties, such as dielectric constant and Coulombic interactions, contribute to the stabilization and separation of Am(V) .

11. Explore the broader implications of high-valent actinide chemistry: The study opens new

avenues for exploring the chemistry of high-valent actinides in organic media .

12. Optimize ligand and solvent systems for enhanced separation: The research investigates the role of the TODGA ligand and Bi(V)-containing organic solvents in achieving high separation factors .

13. Address challenges in advanced nuclear fuel cycles: By providing a robust separation method, the study aims to overcome the challenges associated with the chemical similarity of Am and Ln in advanced nuclear fuel cycles .

14. Evaluate the environmental and operational safety of the separation process: The study assesses the safety and practicality of generating and stabilizing Am(V) at ambient conditions, which is critical for industrial applications .

15. Contribute to the sustainable development of nuclear energy: The research supports the goal of developing an efficient nuclear fuel cycle that reduces radiological hazards and enhances the repository storage capacity for nuclear waste .

Methodology

1. Solvent Preparation: The Bi(V)-containing organic solvent was prepared by incorporating Bi(V) species into an organic solvent (n-dodecane) with a tridentate ligand TODGA (N,N,N ,N -tetraoctyl diglycolamide) through a simple extraction mechanism

2. Oxidation and Extraction Process: Am(III) ions were oxidized to Am(V) in the Bi(V)-containing TODGA/n-dodecane organic solvent. The generated Am(V) ions were then transferred back into the aqueous phase, whereas the lanthanides (Ln) were extracted into the organic phase

3. Spectroscopic Monitoring: UV-Vis absorption spectra were collected to monitor the conversion of Am(III) to Am(V), with characteristic absorption bands used to discriminate between different oxidation states of Am ions

4. Separation Experiments: Solvent extraction experiments were conducted to separate Am from Ln. This involved contacting an aqueous solution containing Am(III) with the Bi(V)-containing organic solution, which resulted in high separation factors for Am from Ln through a single contact

5. Mechanistic Studies: Quantum-theoretical modeling (DFT and QM/MM MD simulations) was used to understand the mechanism of Am(III) oxidation to Am(V) in the organic phase and the role of the Bi(V) species in this process

6. Parameter Variation: The effects of various parameters such as contact time, HNO3 concentration, and TODGA concentration on the separation efficiency were systematically studied to optimize the separation process

7. Long-term Stability Tests: The long-term stability of Am(V) in the biphasic system was assessed to ensure the practicality of the separation method for industrial applications

8. Redox Environment Analysis: The unique redox environment created by the Bi(V)-containing organic solvent was analyzed, highlighting its role in stabilizing Am(V) and enhancing the separation performance

9. Experimental Validation: The separation strategy was validated using both trace and macro amounts of 241Am, demonstrating the scalability and effectiveness of the method for treating simulated Am/Ln waste feed solutions

10. Comparison with Previous Methods: The study compared the new separation approach with previous Am/Ln separation methods, highlighting the superior separation factors and stability achieved with the Bi(V)-containing organic solvent system

Key Findings

Generation and Stabilization of Am(V) in Acidic Aqeous Solutions

Oxidation Process: Am(III) was successfully oxidized to Am(V) using a Bi(V)-containing organic

solvent in acidic aqueous solutions. The oxidation was rapid, with more than 94% of Am(III) converting to Am(V) within 10 seconds.

Stability: Over 96% of Am remained in the Am(V) state for at least 2 hours under ambient conditions, demonstrating the stability of Am(V) in the biphasic system

Superb Ln/Am Separation Performance

High Separation Factors: The separation of 241Am from various lanthanides (Ln) showed exceptional separation factors (SFLn/Am), with values as high as 137,000 for Ce/Am, 72,000 for Gd/Am, and 65,000 for Eu/Am.

Long-Term Stability: The high separation factors persisted for at least 5 hours, which is sufficient for practical applications using separation equipment like centrifugal contactors or mixer-settlers

Unique Oxidation and Separation Mechanism

Mechanism: Am(III) is oxidized to Am(V) in the organic solvent and then transferred back into the aqueous phase. The enhanced Coulombic interactions in the organic solvent (n-dodecane) help stabilize the Am(V) ion

Back Extraction: The generated Am(V) in the organic phase has a low tendency to coordinate with TODGA, leading to its back-extraction into the aqueous phase while lanthanides are extracted into the organic phase

Spectroscopic and Computational Analysis

UV-Vis Absorption Spectra: UV-Vis spectra confirmed the fast conversion and long-term stability of Am(V) in the biphasic system. The characteristic absorption bands of Am(V) were identified and used to monitor the process

Quantum-Theoretical Modeling: QM/MM MD simulations provided insights into the oxidation mechanism of Am(III) to Am(V) by the Bi(V) species, highlighting the role of Coulombic interactions and the unique redox environment of the organic solvent

Relevance to Study

High Separation Factors: Demonstrates the ability to achieve exceptionally high separation factors of $>10^4$ for Am/Ln separation using the diglycolamide ligand (TODGA) in conjunction with Bi(V) species, which is crucial for efficient separation in the nuclear fuel cycle

Stabilization of Pentavalent Americium: Highlights a novel strategy for stabilizing pentavalent americium (Am(V)) in acidic aqueous solutions through coordination with TODGA and oxidation with Bi(V) species, providing insights into ligand design for effective oxidation state control

Synergistic Coordination and Oxidation Process: Elucidates the mechanism of synergistic coordination and oxidation in an organic solvent, emphasizing the role of ligands like TODGA in enhancing the efficiency of the separation process

Quantum-Theoretical Modeling: Utilizes quantum-theoretical modeling to understand the coordination chemistry and redox behavior of americium, which is essential for designing ligands with optimal properties for actinide separation

Robustness and Scalability: Validates the separation process with both trace and macro amounts of 241Am, demonstrating the robustness and scalability of the ligand-based separation method for practical applications in the nuclear fuel cycle

Enhanced Extraction Kinetics and Stability: Shows that the use of TODGA ligand and Bi(V)-containing organic solvents significantly improves the extraction kinetics and stability of high-valent americium, which is crucial for industrial applications

Critical Parameters Identified

High Importance

Chemical Stability: The study demonstrates that the Bi(V)-containing organic solvent with the TODGA ligand effectively stabilizes pentavalent americium (Am(V)) in acidic solutions, maintaining over 96% of Am in the Am(V) state for at least 2 hours under ambient conditions

Radiolysis Resistance: The study mentions the need for ligands to withstand the radioactive environment in nuclear waste treatment. While specific radiolysis resistance data isn't provided, the stability of the TODGA ligand under these conditions can be inferred from the successful separation performance

Thermodynamics: The feasibility of separating Am from Ln through oxidation state control is confirmed, with exceptionally high separation factors (>10^4). Quantum-theoretical modeling supports the understanding of the thermodynamic properties of the system

Medium Importance

Kinetics (forwards and reverse): The study shows rapid conversion of Am(III) to Am(V) within 10 seconds, indicating favorable kinetics for the forward reaction. The long-term stability of Am(V) further suggests favorable kinetics for maintaining the separation

Loading Capacity: Although specific loading capacities are not detailed, the study validates the separation process with both trace and macro amounts of 241Am, indicating that the system can handle varying loads effectively

Operational Condition Range: The system operates effectively over a broad range of HNO3 concentrations (1.0 to 14.0 M), demonstrating flexibility in operational conditions

Low Importance

Solubility: Solubility issues are managed by using n-dodecane as the organic solvent, ensuring that

the Bi(V) species and TODGA ligand remain effective

Dispersion Numbers: While dispersion numbers are not explicitly discussed, the efficiency of mass transfer between the phases can be inferred from the high separation factors achieved in the biphasic system

Phase Disengagement: The study mentions the use of equipment like centrifugal contactors or mixer-settlers, indicating that phase disengagement considerations have been addressed for practical applications