REFERENCE: 20020

Key Words

selective separation

AM(III)

Cm(III)

Ln(III)

hydrophillic ligands

TODGA

extraction

complexation

coordination

DFT calculations

aqueous phase

organic phase

N-donors

separation factors

competitive extraction

Objective

1. Design and Synthesize Hydrophilic Ligands: To create four novel hydrophilic ligands with hard-soft hybrid donors derived from pyridine and phenanthroline skeletons for selective complexation of An(III) in the aqueous phase.

2. Evaluate TODGA as a Lipophilic Extractant: To use TODGA as the lipophilic extractant in the organic phase for the extraction of Ln(III).

3. Develop a Competitive Extraction Strategy: To develop a new strategy for the competitive

extraction of An(III) and Ln(III) based on TODGA and hydrophilic ligands.

4. Assess Selectivity of 2OH-DAPhen: To determine the selectivity of 2OH-DAPhen for Am(III) over Ln(III) at different HNO_3 concentrations.

5. Investigate Coordination Mode and Bonding Properties: To use 1H NMR titration, UV-vis spectrophotometric titration, luminescence titration, FT-IR, ESI-HRMS analysis, and DFT calculations to investigate the coordination mode and bonding properties of 2OH-DAPhen with Ln(III).

6. Determine Separation Factors: To measure the separation factors for Eu/Am, Eu/Cm, and La/Am.

7. Improve Extraction Efficiency with Salting-Out Agent: To enhance extraction efficiency and separation factors by introducing $NaNO_3$ as a salting-out agent.

8. Optimize Conditions for Selective Binding: To identify the optimal conditions for the selective binding of Am(III) and Cm(III) over Ln(III).

9. Evaluate Stability Constants: To determine the stability constants of Ln(III) complexes with DAPhen in nitric acid medium.

10. Analyze Complex Formation Mechanism: To gain insight into the mechanism of complex formation between DAPhen ligands and metal ions through various analytical techniques.

11. Compare Ligand Affinity: To compare the affinity of different hydrophilic ligands (2OH-DAPy, 2OH-DAPhen, 4OH-DAPhen, and 6OH-DAPhen) for Am(III) and Ln(III).

12. Explore Hydrophilic Ligands' Solubility: To assess the solubility of hydrophilic ligands in neutral to acidic aqueous solutions.

13. Investigate Extraction Performance of TODGA: To evaluate the extraction performance of TODGA for trivalent metal ions under various conditions.

14. Examine Structural and Electronic Properties: To use DFT calculations to examine the structural and electronic properties of the formed complexes.

REFERENCE: 20020

15. Provide a Feasible Alternative Method: To develop a feasible alternative method for the selective separation of trivalent actinides from lanthanides using competitive extraction.

Methodology

1. Design and Synthesis of Hydrophilic Ligands: Four novel hydrophilic ligands were synthesized using primary amines and carboxylic acid esters, specifically focusing on creating ligands with hard-soft hybrid donors derived from pyridine and phenanthroline skeletons.

2. Preparation of the Organic Phase: The organic phase was prepared by dissolving TODGA, a lipophilic extractant, in a kerosene/1-octanol (95/5, v/v) mixture to extract Ln(III) ions.

3. Extraction Experiemnts:

- Simulating PUREX Raffinate: Traces of 241Am(III) and 244Cm(III), along with 0.01 mM of La(III) and Eu(III), were spiked into HNO_3 solutions to simulate trivalent f-element cations in PUREX raffinate.

- Competitive Extraction: An equal volume of the aqueous phase (containing hydrophilic ligands in HNO_3 solution) and the organic phase was placed in a glass vial and shaken for 30 minutes at room temperature to reach extraction equilibrium. Post-separation, the phases were analyzed to determine the distribution ratios of the metal ions.

4. Salting-Out Agent: The effect of $NaNO_3$ as a salting-out agent was evaluated to enhance extraction efficiency and separation factors, determining the optimal concentration for improving separation factors.

5. Spectroscopic and Analytical Techniques:

- 1H NMR Titration: Used to study the coordination mode and bonding properties of the ligands with Ln(III).

- UV-Vis Spectrophotometric Titration: Employed to investigate the complexing behavior between

2OH-DAPhen and trivalent metal ions.

- Luminescence Titration and Lifetime Decay Curves: Recorded to understand the hydration number and coordination environment of the metal-ligand complexes.

- FT-IR and ESI-HRMS Analysis: Conducted to confirm the participation of nitrate anions in the inner coordination sphere of the complexes.

- DFT Calculations: Performed to provide insight into the electronic properties and stability of the metal-ligand complexes.

6. Determination of Separation Factors: Calculated for Eu/Am, Eu/Cm, and La/Am to assess the selectivity and efficiency of the extraction process.

7. Evaluation of Ligand Solubility: The solubility of the hydrophilic ligands in neutral to acidic aqueous solutions was assessed to determine their practicality in extraction processes.

8. Optimization of Extraction Conditions: Various parameters, including ligand concentration and HNO3 concentration, were optimized to achieve the best separation performance.

Key Findings

Enhanced Selectivity of 2OH-DAPhen:

- The ligand 2OH-DAPhen displayed exceptional selectivity towards Am(III) over Ln(III) across a range of HNO3 concentrations (0.05 to 3.0 M).

- Maximum separation factors were 1365 for Eu/Am, 417.66 for Eu/Cm, and 42.38 for La/Am

Effectiveness of Competitve Extraction:

- The competitive extraction strategy using TODGA and 2OH-DAPhen significantly enhanced the extraction efficiency and separation factors of Ln(III) to Am(III).

- The addition of NaNO3 as a salting-out agent improved the separation factors, with the optimal concentration being 1.0 M NaNO3

REFERENCE: 20020

Coordination and Bonding Properties:

- Spectroscopic and analytical techniques (1H NMR titration, UV-vis spectrophotometric titration, luminescence titration, FT-IR, ESI-HRMS) revealed that the predominant species formed was a 1:1 ligand/metal complex.
- DFT calculations confirmed the higher affinity of 2OH-DAPhen for Am(III) compared to Eu(III)

Improved Extraction Performance

- The introduction of hydrophilic ligands into the aqueous phase significantly suppressed the extraction efficiency of TODGA to Am(III), leading to higher separation factors.
- 2OH-DAPhen showed the best solubility and selectivity among the synthesized ligands (2OH-DAPy, 2OH-DAPhen, 4OH-DAPhen, 6OH-DAPhen)

Formation of Complexes

- 2OH-DAPhen showed the best solubility and selectivity among the synthesized ligands (2OH-DAPy, 2OH-DAPhen, 4OH-DAPhen, 6OH-DAPhen)
- FT-IR and ESI-HRMS analyses showed the participation of nitrate anions in the inner coordination sphere of the complexes

Comparative Analysis of Ligands

- Among the ligands tested, 2OH-DAPhen exhibited the highest selectivity for Am(III) over Ln(III), making it the most suitable candidate for further studies and applications

Conclusion

- High Selectivity of 2OH-DAPhen: The hydrophilic ligand 2OH-DAPhen exhibited outstanding selectivity for Am(III) over Ln(III) across a wide range of nitric acid concentrations (0.05 to 3.0 M). This selectivity was achieved through the formation of a stable 1:1 complex with Am(III).
- Effective Competitive Extraction Strategy: The study developed an effective competitive extraction

strategy using TODGA as a lipophilic extractant and 2OH-DAPhen as a hydrophilic masking agent. This strategy significantly improved the separation factors of Am(III) from Eu(III) and La(III).

- Optimal Conditions for Separation: The optimal separation conditions were identified, including the use of 1.0 M $NaNO_3$ as a salting-out agent, which enhanced the extraction efficiency and selectivity.
- Application of Spectroscopic Techniques: Various spectroscopic and analytical techniques (^1H NMR, UV-Vis, FT-IR, ESI-HRMS) were successfully applied to investigate the coordination mode and bonding properties of the metal-ligand complexes, confirming the formation of a 1:1 complex.
- DFT Calculations: DFT calculations provided valuable insights into the electronic properties and stability of the complexes, showing that 2OH-DAPhen has a higher affinity for Am(III) compared to Eu(III), which was consistent with experimental findings.
- Industrial Applicability: The simple structure and facile synthesis of the hydrophilic DAPhen ligands, combined with their high selectivity and affinity for Am(III), indicate their potential for industrial applications in the separation of actinides from lanthanides.

Relevance to Study

Selective Complexation: The study identifies ligands (e.g., 2OH-DAPhen) that show high selectivity for actinides (Am(III), Cm(III)) over lanthanides, which is crucial for efficient separation processes in nuclear fuel reprocessing.

Hydrophilic Ligand Development: The synthesized hydrophilic ligands, particularly with hard-soft hybrid donors, are designed to bind selectively with actinides in aqueous solutions, enhancing separation efficiency.

Competitive Extraction Strategy: The developed competitive extraction strategy using TODGA and hydrophilic ligands provides a method to selectively extract actinides from lanthanides, aiding in the recycling and disposal of nuclear waste.

REFERENCE: 20020

Spectroscopic Analysis: The use of various spectroscopic techniques to confirm the formation and stability of metal-ligand complexes supports the development of reliable ligands for nuclear fuel cycle applications.

Optimized Conditions: The identification of optimal conditions (e.g., HNO3 concentrations, salting-out agents) for selective separation informs best practices in nuclear fuel reprocessing.

DFT Calculations: Theoretical insights from DFT calculations help in understanding the electronic properties and binding affinities of the ligands, guiding the selection of effective ligands for actinide separation.

Critical Parameters Identified

High Importance

Chemical Stability:

Finding: The synthesized hydrophilic ligands (e.g., 2OH-DAPhen) demonstrated stability in a range of HNO3 concentrations (0.05 to 3.0 M).

Relevance: Ensures ligands remain functional over the required duration of the separation process and under the chemical conditions present in nuclear fuel reprocessing

Radiolysis Resistance:

Finding: While not explicitly tested for radiolysis resistance, the ligands are intended for use in highly radioactive environments, implying a need for resistance to radiation-induced degradation.

Relevance: Crucial for maintaining separation efficiency under radiation

Thermodynamics:

Finding: DFT calculations confirmed the higher affinity of 2OH-DAPhen for Am(III) compared to

REFERENCE: 20020

Eu(III), indicating favorable thermodynamics for selective binding.

Relevance: Influences selectivity and binding strength of ligands towards specific metal ions, making the separation process feasible at a fundamental level

Medium Importance

Kinetics:

Findings: The extraction experiments showed efficient binding and separation kinetics, with equilibrium reached within 30 minutes.

Relevance: Affects the speed and efficiency of the separation process, ensuring practical time frames for separation

Loading Capacity:

Finding: The study optimized the ligand concentration and HNO_3 levels to maximize the separation factors, indicating attention to loading capacity.

Relevance: Determines how much material can be processed before ligand saturation, impacting process efficiency

Operational Condition Range:

Finding: The ligands operated effectively across a broad range of HNO_3 concentrations (0.05 to 3.0 M).

Relevance: Flexibility in operating under various conditions increases the applicability of the separation process

Low Importance

REFERENCE: 20020

Solubility:

Finding: 2OH-DAPhen exhibited good solubility in neutral to acidic aqueous solutions.

Relevance: While important for practical use, solubility can be managed through solvent selection or adjustments in conditions

Dispersion Number (for applied systems with conditional values):

Finding: Not specifically addressed in the study.

Relevance: Influences mass transfer efficiency but is less critical compared to other factors

Phase Disengagement (for applied systems with conditional values):

Finding: Not specifically addressed, but efficient phase separation was implied in the methodology.

Relevance: Important for practical separation of phases but highly dependent on system design and operation parameters.