REFERENCE: 20011

Key Words

separation

Am3+

Cm3+

branched diglycolamides (DGA)

hydrophilic polyaza-heterocycles

SO3PhBTPhen

TiBDGA

ligand-based separation

radiotoxic elements

minor actindies

trivalent lanthanides

computational studies

organic diluent

aqueous complexant

selectivity

Objective

1. To achieve improved separation behavior of Am3+ and Cm3+ using a cooperative effect of branched diglycolamides (DGA) and hydrophilic N-donor heterocycles.
2. To understand the effect of the position of branching in the alkyl chains of DGA derivatives on the separation behavior of Am3+ and Cm3+.
3. To explore the highest reported separation factor (S.F.) value for Cm3+ over Am3+ using TiBDGA and SO3PhBTPhen without involving oxidation or reduction steps.

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4. To investigate the effect of various organic diluents on the extraction behavior of metal ions.

5. To study the role of aqueous phase acidity on the extraction efficiency and selectivity of Am3+ and Cm3+ using DGA derivatives.

6. To conduct computational studies to explain the high selectivity favoring Cm3+ ion extraction using DGA derivatives.

7. To compare the separation behavior of different DGA derivatives in conjunction with hydrophilic N-donor heterocycles.

8. To systematically study different lipophilic DGA derivatives along with hydrophilic aqueous complexants for the separation of Am3+ and Cm3+.

9. To identify the most promising aqueous complexant among SO3PhBTP, SO3PhBTBP, and SO3PhBTPhen for the separation of Am3+ and Cm3+.

10. To evaluate the potential of improving the selectivity for Cm3+ over Am3+ by choosing suitable organic diluents and adjusting the concentration of DGA and SO3PhBTPhen.

11. To achieve a high separation factor by using TiBDGA with branching at the -carbon atom with respect to the amidic N atom.

12. To extend the separation studies using n-pentyl and iso-pentyl derivatives of DGA.

13. To explore the possibility of improving the extraction efficiency without losing selectivity by playing with the concentration of DGA and SO3PhBTPhen.

14. To provide a detailed understanding of the mutual selectivity phenomenon for designing ligands for further improvement in Am3+ and Cm3+ separation.

15. To report an impressive separation behavior of Am3+ and Cm3+ using a cooperative effect of opposite selectivity of two classes of ligands taken in two different phases.

Methodology

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1. Reagents and Chemicals:

- Preparation of ligands (TBDGA, TiBDGA, TsBDGA, TPDGA, TiPDGA, TODGA, T2EHDGA) and confirmation of their purities via 1H NMR, FT-IR, and HR-MS.

- Actinide tracers (241Am and 244Cm) used from laboratory stock solutions with confirmed radiochemical purities.

- Other reagents used were of analytical reagent grade.

2. Liquid-Liquid Extraction StudiesL

- Equal volumes (0.5 mL) of the aqueous phase containing 241Am and 244Cm in varying concentrations of HNO3 and the organic phase containing DGAs in different organic diluents were equilibrated for approximately an hour at 25 0.1 C.

- Tubes were centrifuged for 2 minutes, followed by a radiometric assay of the separated aliquots to calculate the distribution ratio (D) value of the metal ions and the separation factor (S.F.) values.

3. Efect of Organic Diluent:

- Various organic diluents of differing polarity were chosen to study Am3+ and Cm3+ separation from a 0.2 M HNO3 medium containing 1 mM SO3PhBTPhen.

- n-Octanol was chosen as the organic diluent due to its higher solvating capacity and extraction efficiency for both metal ions without losing mutual selectivity.

4. Effect of Aqueous Phase Acidity:

- Extraction efficiency of metal ions by lipophilic DGA derivatives increases with increasing HNO3 concentration.

- SO3PhBTPhen chosen as the representative aqueous complexant for HNO3 concentration variation studies.

- Optimal HNO3 concentration found to be 0.2 M for maximizing S.F. values.

5. Computational Studies:

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- Structures of free ligands and their complexes with Am3+ and Cm3+ optimized using def-SV(P) basis sets and TURBOMOLE-7.2.1.
- Geometry optimizations performed using BP86 functional, with single point energies calculated using B3LYP and def-TZVP basis sets.
- Calculations carried out in the gas phase to study structural parameters and relative trends in complexation ability

Key Findings

1. Effect of Organic Diluent:

- Various organic diluents were tested, and n-octanol was found to provide the highest extraction efficiency for both Am3+ and Cm3+ while maintaining selectivity.
- The highest extraction efficiencies were observed in n-octanol, n-dodecane, and Solvesso-100, with n-octanol chosen for further studies due to its solvating capacity and mutual selectivity for metal ions

2. Effect of Aqueous Phase Acidity:

- The extraction efficiency of both Am3+ and Cm3+ increased with increasing HNO3 concentration, but the highest selectivity (S.F. values) was observed at 0.2 M HNO3.
- Lower concentrations of HNO3 resulted in too low extraction efficiencies to measure, while higher concentrations reduced selectivity

3. Comparison of Different DGA Derivatives:

- A range of DGA derivatives was compared for their selectivity between Am3+ and Cm3+.
- The study showed that the position of branching in the alkyl chains of DGA derivatives significantly affects selectivity.
- TiBDGA showed the highest selectivity for Cm3+ over Am3+, with an S.F. value of up to 10 when

combined with SO3PhBTPhen

4. Computational Studies:

- DFT calculations indicated that TiBDGA forms weaker complexes with both Am3+ and Cm3+ compared to TBDGA, which was attributed to higher preorganization energy requirements.

- The study showed that the complexation energy for Cm3+ was higher than that for Am3+ for all DGA derivatives studied, aligning with the experimental selectivity observed

5. Extraction Studies of Metal Ions by Different DGA Derivatives:

- Different DGA derivatives, including pentyl and iso-pentyl derivatives, were evaluated for their extraction capabilities.

- TiPDGA formed stronger complexes than TPDGA for both metal ions, resulting in higher extraction efficiency

Relevance to Study

Separation of Minor Actinides: The study focuses on separating Am3+ and Cm3+, which are minor actinides with long-term radiotoxicity. This is crucial for reducing radiotoxicity in nuclear waste management

Selective Ligand Design: The article demonstrates the effectiveness of branched diglycolamides (DGA) and hydrophilic N-donor heterocycles, particularly SO3PhBTPhen, in achieving high selectivity for Cm3+ over Am3+. This highlights the importance of ligand design in enhancing selectivity for specific actinides

Effect of Organic Diluents: The study identifies n-octanol as an effective organic diluent for maintaining high extraction efficiency and selectivity, emphasizing the role of solvent choice in ligand performance

Impact of Aqueous Phase Acidity: The research shows that adjusting the acidity of the aqueous

phase can significantly affect extraction efficiency and selectivity, which is critical for optimizing separation processes in nuclear fuel reprocessing

Computational Validation: Computational studies support the experimental findings, providing a deeper understanding of the complexation mechanisms and helping in the rational design of more effective ligands

Exploration of DGA Derivatives: The study compares various DGA derivatives, illustrating how structural modifications (e.g., branching in alkyl chains) can influence selectivity and efficiency. This knowledge aids in the selection and development of optimized ligands for nuclear applications

Critical Parameters Identified

High Importance

Chemical Stability: The study mentions the stability of ligands, particularly the branched diglycolamides (DGA) and hydrophilic N-donor heterocycles, under the experimental conditions used for separation of Am3+ and Cm3+

Radiolysis Resistance: Although the study does not explicitly test radiolysis resistance, the ligands performance in handling highly radiotoxic elements like Am3+ and Cm3+ implies a need for stability under radiation, which can be inferred as part of the chemical stability and overall ligand performance in nuclear applications

Thermodynamics: The study extensively discusses the selectivity and binding strength of various DGA derivatives towards Am3+ and Cm3+, with computational studies supporting these findings. This directly relates to the thermodynamic feasibility of the separation process

Medium Importance

Kinetics: The study includes equilibrium studies, which indirectly address the kinetics of the

extraction process. The attainment of equilibrium within an hour indicates favorable kinetics for practical application

Loading Capacity: The study does not explicitly discuss loading capacity, but the use of different concentrations of DGA derivatives and the resulting extraction efficiencies provide some insight into the ligands' capacity to process materials before becoming saturated

Operational Condition Range: The study evaluates the effects of varying organic diluents and aqueous phase acidity, demonstrating the ligands' performance under different conditions. This highlights the ligands' operational flexibility

Low Importance

Solubility: Solubility of the ligands is mentioned, particularly the higher solubility of TODGA and T2EHDGA in various organic diluents, which is essential for their practical application but considered of lower importance compared to other factors

Dispersion Numbers: Not specifically addressed in the study. The focus is more on extraction efficiency and selectivity rather than mass transfer efficiency between phases.

Phase Disengagement: The study mentions the centrifugation step to separate phases after extraction, implying practical considerations for phase disengagement, but this is a minor focus compared to chemical stability and selectivity