Key Words

Bis-(1,2,4-triazin-3-yl) ligand

selectivity reversal

Am3+

Cm3+

solvent extraction

DFT

hydrophilic ligands

SO3PhBTP

SO3PhBTBP

SO3PhBTPhen

TODGA

Ionic liquids

complexation

Mayer's bond order

complexation energy

Objective

1. Investigate Selectivity: To study the selectivity between Am3+ and Cm3+ ions using three structurally tailored hydrophilic bis-(1,2,4-triazin-3-yl) ligands (SO3PhBTP, SO3PhBTBP, and SO3PhBTPhen).

2. Solvent Extraction Studies: To examine the extraction behavior of these ligands when used with N,N,N ,N -tetraoctyl diglycolamide (TODGA) dissolved in an ionic liquid (C4mim Tf2N).

3. DFT Calculations: To perform Density Functional Theory (DFT) calculations to understand the

coordination chemistry and bonding characteristics of the ligands with Am3+ and Cm3+.

4. Complexation Behavior: To explore the complexation abilities of the ligands and analyze the co-planarity and bond order in the complexes.

5. Comparative Analysis: To compare the experimental results with theoretical predictions and validate the findings through computational studies.

6. Practoal pplication: To develop insights that could be useful for the separation of minor actinides from nuclear waste, particularly focusing on the challenging separation of Am3+ from Cm3+.

Methodology

1. Materials:

- N,N,N ,N -tetraoctyl diglycolamide (TODGA) was synthesized and used in the study.

- Three hydrophilic 'N' donor heteropolycyclic ligands (SO3PhBTP, SO3PhBTBP, and SO3PhBTPhen) were synthesized and their purities confirmed using 1H-NMR, FT-IR, and mass spectrometry (HR-MS).

- The ionic liquid used was 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (C4mim Tf2N), procured from Iolitec, Germany.

- Actinide tracers, 241Am and 244Cm, were obtained from laboratory stock and their radiochemical purities confirmed by alpha spectrometry.

2. Distribution Measurements:

- Liquid-liquid extraction studies were conducted by equilibrating equal volumes of the RTIL phase containing 5 mmol/L of TODGA with the aqueous phase spiked with radiotracers.

- The aqueous phase contained 10 mmol/L BTP ligands at various nitric acid concentrations and either 241Am or 244Cm tracers.

- Equilibration was carried out in Pyrex glass tubes in a thermostat water bath at 25.0 0.1 C for at

least 3 hours.

- Tubes were centrifuged and aliquots from both phases were taken for radiometric assay using NaI(Tl) scintillation counter for 241Am and liquid scintillation counting for 244Cm.

- Distribution ratios of Am3+ and Cm3+ were calculated as the ratio of their radioactivities in the RTIL phase to those in the aqueous phase. Each experiment was repeated thrice, maintaining a relative standard deviation of 5%.

3. Computational Methodology:

- Geometries of free ligands and metal/ligand complexes were optimized using def-SV(P) basis sets in TURBOMOLE-7.2.

- Effective core potential (ECP) of 60 along with def-SV(P) basis sets were used for the valence electrons in Am3+ and Cm3+ complexes.

- GGA functional BP86 was used for geometrical optimization, while single point energies were calculated using the hybrid functional B3LYP with def-TZVP basis sets.

- Details of computational methodology are described in the Electronic Supplementary Information (ESI).

Key Findings

Solvent Extraction Studies:

- Extraction Behavior: The study revealed that TODGA favors the extraction of Cm3+ over Am3+ in the absence of aqueous complexants. However, the presence of hydrophilic N donor ligands significantly suppresses the extraction of both Am3+ and Cm3+ due to aqueous complexation.

- Selectivity Observations: SO3PhBTP showed marginally higher selectivity for Cm3+ over Am3+, resulting in lower extraction of Cm3+ by TODGA. SO3PhBTBP exhibited no selectivity between Am3+ and Cm3+, while SO3PhBTPhen showed better complexation ability for Am3+ over Cm3+.

- Effect of Ionic Liquid: The study highlighted that extraction patterns in the ionic liquid (RTIL) system are opposite to those in the molecular solvent, emphasizing the impact of different extraction mechanisms.

DFT Studies:

- Geometrical Structure: The DFT calculations indicated that the coordinating N atoms in BTP were more co-planar in the Cm^{3+} complex compared to the Am^{3+} complex. In contrast, BTBP and BTPhen ligands showed higher co-planarity in the Am^{3+} complexes

- Bond Distances and Co-Planarity: The bond distances and torsional angles suggested that BTP has a stronger affinity for Cm^{3+} due to higher co-planarity in its complexes. BTBP and BTPhen showed a reversal of selectivity with higher co-planarity in the Am^{3+} complexes.

- Electronic Structure: Natural population analysis and Mayer s bond order calculations demonstrated higher covalence in the M N bonds of Am^{3+} complexes compared to Cm^{3+} complexes, with significant metal ligand interactions observed in the frontier molecular orbitals of Am^{3+} complexes.

Energetics of the Am^{3+} and Cm^{3+} Complexation

- Complexation Energies: The complexation energies indicated that all ligands showed more favorable complexation with Cm^{3+} over Am^{3+}. However, BTP exhibited the highest selectivity for Cm^{3+} over Am^{3+}, while BTPhen showed a preference for Am^{3+}.

- Comparison with TODGA: The study concluded that BTP remains selective towards Cm^{3+} over Am^{3+} even when considering the competitive complexation with TODGA. In contrast, BTPhen favored Am^{3+} over Cm^{3+} due to its higher degree of covalence.

Conclusion

1. Selective Extraction: The study concluded that SO3PhBTP demonstrated selectivity for Am^{3+}

over Cm3+ with an SF (Am/Cm) value of 2.5. Conversely, SO3PhBTPhen exhibited selectivity for Cm3+ over Am3+ with an SF (Am/Cm) value of less than 0.5. SO3PhBTBP showed no selectivity between Am3+ and Cm3+.

2. Ligand Interaction and Covalence: DFT studies revealed that the metal-ligand interactions in the complexes of BTP, BTBP, and BTPhen derivatives were primarily governed by ionic interactions. However, a higher degree of covalence in the M N bonds was observed in the Am3+ complexes compared to the Cm3+ complexes.

3. Reversal of Selectivity: The reversal of selectivity between BTP, BTBP, and BTPhen ligands for Am3+ and Cm3+ was rationalized through DFT calculations, which considered the competitive complexation with the diglycolamide ligand.

4. Implications for Nuclear Fuel Cycle: The findings provide valuable insights for the design of ligands for the selective separation of minor actinides, which is crucial for the efficient management of nuclear waste.

Relevance to Study

Selective Separation of Actinides: The article provides insights into the selective separation of Am3+ and Cm3+, which is a critical step in managing minor actinides in the nuclear fuel cycle.

Hydrophillic Ligands: The study focuses on hydrophilic bis-(1,2,4-triazin-3-yl) ligands (SO3PhBTP, SO3PhBTBP, and SO3PhBTPhen), evaluating their effectiveness in selectively complexing Am3+ and Cm3+ ions.

Solvent Extraction: The research explores solvent extraction using TODGA in an ionic liquid medium, highlighting the different behaviors of Am3+ and Cm3+ in the presence of various ligands, which is relevant for developing efficient extraction processes in nuclear chemistry.

Density Functional Theory (DFT) Calculations: DFT studies provide a theoretical basis for

understanding the selectivity and binding characteristics of the ligands, aiding in the rational design of new ligands for improved actinide separation.

Ligand Design: The findings emphasize the importance of ligand structure on selectivity, suggesting that tailored ligand design can enhance the separation of specific actinides, which is crucial for the nuclear fuel cycle.

Impact on PUREX Process: Insights from this study can be applied to optimize the PUREX (Plutonium Uranium Redox Extraction) process by improving the selective separation of minor actinides from lanthanides and other elements.

Radiochemical Separation: The research contributes to the development of advanced strategies for the radiochemical separation of minor actinides, reducing radiotoxicity and improving waste management in nuclear chemistry.

Practical Application: The study's findings on ligand selectivity and extraction efficiency are directly applicable to the practical challenges faced in the nuclear fuel cycle, aiding in the development of more effective separation processes.

Critical Parameters Identified

High Importance

Chemical Stability: The study evaluates the stability of hydrophilic ligands (SO3PhBTP, SO3PhBTBP, SO3PhBTPhen) in the presence of nitric acid, an essential condition in nuclear fuel reprocessing.

Radiolysis Resistance: Although the study does not directly address radiolysis resistance, the evaluation of ligands in a radioactive environment with 241Am and 244Cm tracers indirectly supports the consideration of radiolysis resistance.

Thermodynamics: Thermodynamic data, including complexation energies and Mayer s bond order

calculations, provide insights into the selectivity and binding strength of the ligands toward Am3+ and Cm3+ ions, determining the feasibility of separation processes.

Medium Importance

Kinetics: The study mentions the equilibration time for extraction experiments, which impacts the kinetics of the separation process, though detailed kinetic studies are not a primary focus.

Loading Capacity: The extraction studies indirectly address loading capacity by examining the distribution ratios of Am3+ and Cm3+ in the presence of different ligand concentrations.

Operational Condition Range: The research explores solvent extraction under varying nitric acid concentrations and different ligands, highlighting the ligands' ability to function under a range of operational conditions.

Low Importance

Solubility: The solubility of ligands in the ionic liquid (C4mim Tf2N) and their compatibility with the solvent system are considered but are not the primary focus.

Dispersion Numbers: Dispersion numbers are not explicitly discussed, as the study primarily focuses on the chemical interactions and selectivity of ligands.

Phase Disengagment: Phase disengagement is implicitly addressed through the description of liquid-liquid extraction methods, but specific parameters and efficiency of phase disengagement are not detailed.