REFERENCE: 20035

Key Words

selective

ligand

actinides

lanthanides

DFT

Objective

1. Experimental Verification of Theoretical Predictions: The primary objective was to experimentally verify the predictions made through Density Functional Theory (DFT) simulations. The simulations suggested that tridentate O,N,O-donor cyclic dilactams, which belong to the family of pyridine-2,6-dicarboxamides, are highly selective and efficient for separating lanthanides and actinides due to their higher degree of "ligand preorganization."

2. Synthesis of New Ligands: The study aimed to synthesize three new ligands of the cyclic dilactam type and evaluate their performance in extraction experiments. This was to establish whether these ligands indeed have higher selectivity and efficiency compared to open-structure pyridine-2,6-dicarboxamides.

3. Comparison of Extraction Efficiency:Comparison of Extraction Efficiency: An objective was to compare the extraction efficiency and selectivity of the newly synthesized cyclic dilactams with the previously studied open-structure pyridine-2,6-dicarboxamides. The comparison focused on their ability to separate americium (Am) from europium (Eu).

4. Solvate Number Determination: Another objective was to determine the solvate numbers (SNs) for Eu and Am cations by slope analysis. This involved studying the stoichiometry of the complexes in which these ions pass from the aqueous phase into the organic phase during the extraction

process, and how this depends on the polarity of the organic solvent.

5. Evaluation of Solvent Effects: The study aimed to evaluate how the polarity of different organic solvents affects the extraction process. Specifically, it sought to understand the formation of different complex stoichiometries (1:1 and 2:1) in solvents with varying dielectric constants.

Methodology

1. DFT Simulations: Density Functional Theory (DFT) simulations were performed to predict the selectivity and efficiency of tridentate O,N,O-donor cyclic dilactams for separating lanthanides and actinides. The simulations focused on the conformational rigidity of the ligands and their preorganization to enhance selectivity.

2. Synthesis of Ligands: Three new ligands of the cyclic dilactam type were synthesized. The synthetic protocols involved using commercially available reagent-grade materials and dry solvents. Specific procedures were followed to attach substituents and prepare the cyclic dilactams.

3. Characterization of Ligands: The synthesized ligands were characterized using various analytical techniques:

- NMR Spectroscopy: To determine the structure and purity of the ligands.

- FT-IR Spectroscopy: To identify functional groups.

- Mass Spectrometry (ESI-HRMS and MALDI-TOF): For molecular weight determination.

- X-ray Diffraction: To confirm the crystal structure of the ligands and their complexes.

4. Extraction Experiments:

- The extraction experiments were conducted at 25 C using m-nitro(trifluoromethyl)benzene (F-3), chloroform, and 1,2-dichloroethane as organic diluents.

- The organic and aqueous phases, each 1 mL, were placed in polypropylene vials. The organic phase was pre-equilibrated with a solution of nitric acid of the desired concentration.

- The aqueous phase contained nitric acid, europium nitrate, and was spiked with ^{241}Am or ^{152}Eu.

- The samples were agitated for 3 minutes and separated by centrifugation for 5-10 minutes. Aliquots were taken for analysis.

5. Determination of Distribution Ratios and Solvate Numbers:

- The distribution ratios (D) of Am and Eu were determined radiometrically using a scintillation -spectrometer.

- The solvate numbers (SNs) for Eu and Am were determined by slope analysis, plotting the logarithm of the distribution ratios against the ligand concentration.

6. Comparison of Extraction Capacities:

- The extraction capacities of the cyclic dilactams were compared to those of open-structure pyridine-2,6-dicarboxamides by evaluating the distribution ratios (D) and separation factors (SFAm/Eu) under varying nitric acid concentrations.

- The effect of different organic solvents on the composition of extractable complexes was analyzed by determining the solvate numbers in solvents of different polarities.

7. Quantum Chemical Calculations:

- Geometrical parameters, dipole moments, and formation energies of the metal-ligand complexes were calculated using DFT. The calculations included the optimization of ligand and complex structures and the estimation of Gibbs free energies for the formation of these complexes.

8. Validation of Theoretical Predictions:

- The experimental results were compared with the theoretical predictions to validate the effectiveness and selectivity of the synthesized ligands for separating americium and europium. The agreement between the experimental data and the theoretical models was evaluated.

Key Findings

Quantum Chemical Simulation

1. Structural Predictions:

- The DFT simulations predicted that cyclic dilactams (IV) and their complexes (IX) and (X) with Eu and Am exhibit shorter interatomic M O and M N distances compared to their open-structure counterparts, indicating stronger coordination bonds.

- Am N and Am O coordination bonds were found to be significantly stronger than Eu N and Eu O bonds.

2. Dipole Moments and STability:

- The dipole moments of the europium complexes were higher, suggesting more ionic metal-to-ligand bonds in europium complexes compared to americium complexes.

- The Gibbs formation energies for the cyclic dilactam complexes were higher, indicating more stable complexation compared to open-structure ligands.

3. Coordination Numbers:

- The calculated structures showed that the coordination numbers for americium and europium in the 2:1 complexes (XIII) and (XIV) were 12, which is higher than the typical coordination numbers for lanthanide and actinide complexes with bulky ligands.

Extraction Experiments

4. Extraction Capacities:

- The cyclic dilactams exhibited significantly higher extraction capacities for Am and Eu compared to open-structure pyridine-2,6-dicarboxamides. Specifically, the distribution ratios for the cyclic dilactams were more than three orders of magnitude higher.

5. Selectivity:

- The cyclic dilactams showed 5 6-fold higher selectivity for the separation of the Am /Eu pair,

aligning with the theoretical predictions.

6. Effect of Organic Solvents:

- The polarity of the organic solvent significantly influenced the composition of the extracted complexes. Highly polar solvents favored the formation of 1:1 complexes (LM(NO3)3), while low-polarity solvents favored the formation of 2:1 complexes (L2M(NO3)3).

Solvate Number Determination

7. Complex Stoichiometry:

- Slope analysis revealed that the stoichiometry of the extracted complexes depends on the solvent's polarity. Strongly polar solvents (> 20) mainly extract 1:1 complexes, while low-polarity solvents (10) mainly extract 2:1 complexes.

Comparison of Etraction Capacities

8. Efficiency of Different Ligands:

- Cyclic dilactams (VI) and (VII) demonstrated higher distribution coefficients (D) for Am and Eu compared to the open-structure ligand (II).
- The length of the alkyl substituents in cyclic dilactams influenced the distribution coefficients but did not significantly change the separation factors (SFAm/Eu).

Solvent Effect on Composition of Extractable Complexes

9. Solvent Polarity Influence:

- The extraction efficiency and the type of complexes formed were significantly influenced by the polarity of the solvent. Solvents with higher polarity led to the formation of more polar complexes.

Conclusion

10. Theoretical and Experimental Agreement:

- The experimental results confirmed the theoretical predictions, demonstrating that cyclic dilactams are more effective and selective for the separation of americium and europium compared to open-structure ligands.

- The high degree of ligand preorganization in cyclic dilactams contributed to their superior performance.

Relevance to Study

High Selectivity and Efficiency: Demonstrates that cyclic dilactams have significantly higher selectivity and efficiency for separating actinides (Am) from lanthanides (Eu) compared to open-structure pyridine-2,6-dicarboxamides.

Experimental Verification: Provides experimental evidence supporting DFT predictions that cyclic dilactams exhibit superior performance due to their preorganized structure.

Enhanced Chemical Stability: Shows that cyclic dilactams form stronger coordination bonds with metal ions, suggesting higher chemical stability which is crucial in the harsh conditions of nuclear fuel reprocessing.

Impact of Solvent Polarity: Highlights the importance of solvent polarity on the extraction process, indicating that the choice of solvent can significantly influence ligand performance and complex stoichiometry.

Improved Separation Factors: Reports that the separation factors (SFAm/Eu) for cyclic dilactams are 5 6 times higher than those for open-structure ligands, which is critical for efficient separation processes in the nuclear fuel cycle.

Thermodynamic Favorability: Confirms that cyclic dilactams have higher Gibbs formation energies,

indicating thermodynamically favorable complexation with actinides and lanthanides.

Adaptability of Different Conditions: Demonstrates that the cyclic dilactams can function effectively across a range of acid concentrations and solvents, showcasing their versatility and robustness in various operational conditions.

Critical Parameters Identified

High Importance

1. Chemical Stability: Cyclic dilactams exhibit stronger coordination bonds (shorter M O and M N distances) compared to open-structure ligands, suggesting enhanced chemical stability essential for the harsh conditions of nuclear fuel reprocessing.

2. Radiolysis Resistance: The study does not explicitly address radiolysis resistance, but the enhanced stability and stronger coordination bonds of cyclic dilactams suggest they may be more resistant to degradation under radiation.

3. Thermodynamics:

- Higher Gibbs formation energies of cyclic dilactams indicate thermodynamically favorable complexation with actinides and lanthanides.

- Improved separation factors (SFAm/Eu) and distribution ratios (D) demonstrate the high thermodynamic efficiency of cyclic dilactams in selective metal ion binding.

Medium Importance

1. Kinetics: The study primarily focuses on the thermodynamic aspects and does not provide detailed kinetic data. However, the efficiency observed in extraction experiments suggests favorable kinetics.

2. Loading Capacity: Higher distribution ratios (D) for cyclic dilactams indicate a potentially higher

loading capacity, allowing more material to be processed before the ligand becomes saturated.

3. Operational Condition Range: The study shows that cyclic dilactams can operate effectively across a range of nitric acid concentrations and in various solvents, highlighting their versatility and broad operational condition range.

Low Importance

1. Solubility: The solubility of cyclic dilactams in different solvents is reported, with higher solubility observed for ligands with longer alkyl chains. This can be managed by selecting appropriate solvents or modifying ligand structure.

2. Dispersion Numbers: The study does not explicitly address dispersion numbers.

3. Phase Disengagement: The study does not explicitly address phase disengagement. However, efficient extraction and clear phase separation in experiments suggest that cyclic dilactams perform well in this regard under the tested conditions.