REFERENCE: 20047

Key Words

complexation

thermodynamics

diglycolamide

solvent extraction

DFT

Objective

1. Comparative Extraction Study: To study the comparative extraction behavior of trivalent lanthanide and actinide ions (La , Eu , Lu , Am , and Cm) using tetra-n-octyl diglycolamide (TODGA).

2. Structural Analysis: To analyze the structure, bonding, energetic, and thermodynamic parameters of the trivalent lanthanide and actinide ions with a tridentate ligand, tetra-methyl diglycolamide (TMDGA), in both gas and solvent phases.

3. Computational Calculations: To perform calculations using density functional theory (DFT) with the BP86 and B3LYP functionals and SVP and TZVPP basis sets to understand the complexation and extraction behavior.

4. Free Energy of Extraction: To calculate the free energy of extraction using the Born Haber thermodynamic cycle and the COSMO solvation model for lanthanide and actinide ions in an aqueous dodecane biphasic system.

5. Bonding Analysis: To investigate the electrostatic and covalent nature of interactions between the ligands and the metal ions through different bonding analyses.

6. Optimization of Experimental and Theoretical Methods: To compare the experimental solvent extraction data with the trends predicted by free energy changes in the gas phase calculations and

to optimize the computational methods for accuracy in structural prediction.

Methodology

Solvetn Extraction Studies

Reagents and Chemicals

- TODGA Synthesis: Tetra-n-octyl diglycolamide (TODGA) was synthesized and characterized by elemental analysis, melting point, and NMR (1H and 13C) spectral analysis.
- Radiochemical Purity: Laboratory stock solutions of 241Am and 244Cm were used after checking their radiochemical purity by alpha-spectrometry.
- Tracer Solutions: 152Eu and 154Eu were procured and their radiochemical purity was ascertained by gamma-ray spectrometry. 140La and 177Lu were prepared by irradiating their respective natural isotopes in a Dhruva reactor.
- Preparation: Suprapur nitric acid (Merck) and MilliQ water (Millipore) were used for preparing the tracer solutions.

Distribution Studies

- Procedure: Distribution studies were conducted with 241Am, 244Cm, 140La, 177Lu, and 152,154Eu as tracers spiked in aqueous solutions containing 1 M nitric acid.
- Organic Phases: Prepared by dissolving varying concentrations of TODGA in n-dodecane.
- Equal Volumes: Equal volumes (1 mL) of the organic and aqueous phases were taken in stoppered tubes, agitated in a thermostated water bath at 25 0.1 C for 2 hours, and centrifuged.
- Aliquots: Suitable aliquots (0.1 mL) were taken from both phases followed by radiometric assay by gamma-ray counting using a well-type NaI(Tl) scintillation detector coupled to a multi-channel analyzer.

- Distribution Ratio (D): Calculated as the ratio of counts per minute of the radiotracer per unit volume in the organic phase to that in the aqueous phase. The material balance was within 5%.

Computational Studies

Computational Protocols

- Software and Functional: The minimum energy structures of TMDGA and TiBDGA and their complexes with trivalent lanthanides (La , Eu , Lu) and actinides (Am , Cm) were calculated using the GGA-based BP86 functional and the B3LYP hybrid functional with the SVP and TZVPP basis sets.
- Relativistic Effects: For La, Eu, Lu, Am, and Cm, an ECP core potential was used where 46, 28, 46, 60, and 60 electrons were kept in the core, respectively.
- Geometry Optimization: Performed at the BP86/SVP level, with total energies calculated using the B3LYP functional with the TZVPP basis set.
- Solvation Models: The COSMO solvation scheme was used to account for solvent effects, with default COSMO radii used for all elements except La , Eu , Lu , Am , and Cm , for which specific values were used.
- Free Energy Calculations: The free energy of extraction was calculated using the Born Haber thermodynamic cycle and the COSMO solvation model.

Structural Analysis

- X-ray Data Comparison: The optimized structures were compared with X-ray data for validation.
- Bond Distances: Structural parameters such as CQO, C O (ether), and C N bond distances were analyzed.

REFERENCE: 20047

Bonding and Therdynamic Analysis

- Natural Population Analysis (NPA): Performed to compute the charge on the metal ion and atomic orbital population.

- Atom in Molecule (AIM) Topological Parameters: Calculated using the AIM theory to describe bonding nature.

- Second Order Stabilization Energy: Evaluated to predict the selectivity of metal ions towards ligands.

- Stepwise Binding Energy: Calculated to study the complexation behavior of Ln/An ions with TMDGA.

- Free Energy of Extraction: Evaluated for the transfer of metal ions from the aqueous to the dodecane phase using different solvation models and thermodynamic cycles.

Key Findings

1. Extraction Order

- The solvent extraction experiment showed that the order of extraction of the studied ions was: Lu > Eu > Cm > Am > La .

- This order was in line with the trends predicted based on free energy changes in gas phase calculations.

2. Structure and Bonding:

- The calculations revealed that the structure obtained at the BP86/SVP level of optimization was in close agreement with X-ray data and also with the structure obtained at the B3LYP/TZVP level of theory.

- The bonding analyses indicated that the interactions between the ligands and metal ions were primarily electrostatic with less covalent character.

REFERENCE: 20047

3. Free Energy of Extraction

- The free energy of extraction for the metal ions was found to follow the order: Lu > Eu > La after dispersion correction.

- The COSMO and DCOSMO-RS models predicted the same metal ion selectivity trend.

4. Solvation effects

- The solvation energy of the metal ions played a decisive role in the free energy of extraction.

- Explicit solvation using monomer and cluster water models was employed to account for solvation effects, revealing that solvation significantly influenced the thermodynamic selectivity.

5. Optimization and Validation:

- The optimized structures of TMDGA and TiBDGA ligands and their complexes with trivalent lanthanides and actinides showed good agreement with experimental data, validating the computational methods used.

- The structural parameters calculated using the BP/SVP level of theory were found to be very close to those predicted using the B3LYP/TZVP level of theory, justifying the use of BP86/SVP for geometry optimization.

6. Hydrated Metal Ion-Nitrate Complexes:

- The study of hydrated metal ion nitrate complexes indicated that nitrate ions strongly coordinate with metal ions, influencing the extraction process.

- The free energy calculations showed that hydrated nitrate ion pairs are more stable than metal hydrates alone, suggesting the importance of nitrate ions in the extraction process.

Conclusion

1. Extraction Efficiency:

- The study concluded that tetra-n-octyl diglycolamide (TODGA) is an efficient extractant for

separating trivalent lanthanide and actinide ions.

- The experimental extraction order was found to be Lu > Eu > Cm > Am > La , which matched the predicted free energy changes in the gas phase calculations.

2. Computational Validation:

- The density functional theory (DFT) calculations at the BP86/SVP and B3LYP/TZVP levels showed good agreement with experimental data, validating the computational approach for predicting structural and energetic parameters.

3. Free Energy Calculations:

- The free energy of extraction calculations indicated that the process is exergonic (spontaneous) for all studied metal ions in the presence of TODGA.

- The Born Haber thermodynamic cycle and COSMO solvation model successfully predicted the metal ion selectivity trend, with dispersion correction further improving the accuracy.

4. Role of Nitrate Ions:

- The presence of nitrate ions was found to significantly influence the extraction process, with hydrated nitrate ion pairs being more stable than isolated hydrated metal ions.

- This underscores the importance of considering the nitrate ions in both experimental and theoretical studies of metal ion extraction.

5. Thermodynamics and Bonding INsights:

- The bonding analyses indicated that the interactions between TODGA and metal ions were primarily electrostatic, with some covalent character.

- The study provided detailed insights into the thermodynamics and structural parameters of the metal ion ligand complexes, enhancing the understanding of their complexation behavior.

6. Importance of Solvation Models:

- The study highlighted the critical role of solvation in determining the free energy of extraction.

REFERENCE: 20047

- Both explicit solvation models (monomer and cluster water) were used to account for solvent effects, showing that solvation significantly impacts the thermodynamic selectivity.

Relevance to Study

Ligand Efficiency: Demonstrates the effectiveness of tetra-n-octyl diglycolamide (TODGA) in extracting trivalent lanthanides and actinides, which is crucial for the separation processes in the nuclear fuel cycle.

Extraction Trends: Provides data on the extraction order of metal ions (Lu > Eu > Cm > Am > La), aiding in the selection of ligands based on desired extraction selectivity.

Computational Validation: Validates computational methods (DFT) for predicting ligand behavior, which can be used to screen and design new ligands for nuclear fuel reprocessing.

Thermodynamic Insights: Offers detailed thermodynamic parameters and bonding analyses, helping in the understanding of ligand-metal interactions and their stability under nuclear fuel cycle conditions.

Nitrate Ion Influence: Highlights the significant role of nitrate ions in the extraction process, informing ligand design that considers complexation with nitrates present in nuclear waste.

Solvation Effects: Emphasizes the importance of solvation models in predicting extraction efficiency, guiding the selection of ligands that perform well under aqueous and organic phase conditions encountered in the nuclear fuel cycle.

Radiolysis Resistance: Although not directly covered, the structural stability and bonding insights can contribute to understanding ligand stability under radiolytic conditions prevalent in nuclear reprocessing environments.

Critical Parameters Identified

High Importance

REFERENCE: 20047

1. Chemical Stability:

- The article does not explicitly address the chemical stability of TODGA under various conditions, but the successful extraction of lanthanides and actinides indicates that TODGA remains functional under the experimental conditions.

- The structural analysis and bonding studies suggest that TODGA forms stable complexes with metal ions, implying good chemical stability.

2. Radiolysis Resistance:

- The study does not directly address radiolysis resistance. However, understanding the thermodynamics and stability of TODGA complexes can provide insights into its potential resistance to radiolytic degradation, which is crucial for applications in nuclear fuel reprocessing.

3. Thermodynamics:

- The thermodynamic data, including free energy of extraction and binding energies, are extensively analyzed. The findings indicate that TODGA has favorable thermodynamic properties for extracting lanthanides and actinides, which influences its selectivity and binding strength towards specific metal ions.

Medium Importance

1. Kinetics:

- The study focuses on the thermodynamic aspects rather than the kinetics of the extraction process. However, the efficient extraction observed in the experiments suggests that TODGA likely has favorable kinetic properties for practical applications.

2. Loading Capacity:

- The article does not specifically address the loading capacity of TODGA. The focus is more on the extraction efficiency and selectivity rather than the maximum amount of material that can be

processed.

3. Operational Condition Range:

- The experiments were conducted under specific conditions (e.g., 1 M HNO3, 25 C), but the study does not explore a broad range of operational conditions. However, the ability of TODGA to extract multiple metal ions suggests a degree of flexibility in its operational range.

Low Improtance

1. Solubility:

- The study uses TODGA dissolved in n-dodecane, indicating it has sufficient solubility in the chosen organic solvent. The solubility aspect is not a major focus, as it is generally managed through solvent selection.

2. Dispersion NUmbers:

- The article does not discuss dispersion numbers. The focus is on the thermodynamics and extraction efficiency rather than mass transfer efficiency.

3. Phase Disengagement:

- The study briefly mentions the use of centrifugation to separate phases after extraction. However, phase disengagement specifics are not a primary focus and are highly dependent on the system design and operational parameters.