

Key Words

lanthanides

TODGA

coordination

solvent extraction

HNO₃ (nitric acid)

n-heptane

complexation

distribution ratio

UV-Vis spectroscopy

FT-IR (Fourier Transform Infrared Spectroscopy)

Eu (europium)

Nd (neodymium)

inner-sphere

outer-sphere

Objective

1. Investigate the impact of varying HNO₃ concentrations: The study aims to explore how different concentrations of aqueous phase nitric acid (HNO₃) affect the coordination and extraction behavior of lanthanides (Ln) when using N,N,N',N'-tetraoctyldiglycolamide (TODGA) as the extractant in n-heptane.
2. Determine the coordination number of TODGA molecules: By measuring distribution ratios and using multiple spectroscopic techniques, the study seeks to evaluate the number of TODGA molecules coordinating to lanthanides at different HNO₃ levels.

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3. Examine inner-sphere and outer-sphere interactions: The research aims to understand the presence and changes in inner-sphere and outer-sphere nitrate (NO_3^-) coordination to lanthanides at varying HNO_3 concentrations.
4. Use spectroscopic techniques to study complexation: The study employs UV-Vis spectroscopy, TRLIFS (time-resolved laser-induced fluorescence spectroscopy), and FT-IR (Fourier transform infrared spectroscopy) to analyze the changes in the lanthanide coordination sphere.
5. Assess the role of NO_3^- -source in solvent extraction systems: The objective is to demonstrate how changing the NO_3^- source (e.g., using LiNO_3 instead of HNO_3) can affect the inner-sphere coordination of the lanthanide complex and, consequently, the separation efficacy.
6. Understand the implications for intralanthanide separations: By investigating these coordination behaviors, the study aims to provide insights that could enhance the separation processes for lanthanides, which are crucial for clean energy, digital technology, and medical isotopes industries.
7. Establish the relationship between acid concentration and Ln complex formation: The research seeks to clarify how increasing HNO_3 concentration influences the transition from 1:2 to 1:3 Ln complexes and the removal of coordinated NO_3^- .
8. Investigate the absence of H_2O coordination: The study examines whether water molecules coordinate to lanthanides under the tested conditions by conducting Eu lifetime analysis.
9. Provide a comprehensive understanding of Ln coordination chemistry: Combining distribution ratio measurements with multiple spectroscopic techniques aims to offer a thorough understanding of organic phase lanthanide coordination chemistry in varying acidities.
10. Improve the practical application of solvent extraction: The ultimate goal is to enhance the practical application of solvent extraction systems in industrial processes by understanding and optimizing the conditions for lanthanide extraction and separation.

Methodology

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1. Preparation of Solutions:

- Lanthanide nitrate solutions were prepared by dissolving Ln(III) nitrates in deionized water.
- The TODGA solutions in n-heptane were prepared at varying concentrations.

2. Solvent Extraction Experiments

- Solvent extraction experiments were conducted by mixing equal volumes of the aqueous lanthanide nitrate solutions and the organic TODGA solutions.
- The mixture was shaken for a specific duration to ensure equilibrium and then centrifuged to separate the phases.
- The distribution ratios (D_{Ln}) of lanthanides were determined by analyzing the metal ion concentration in the aqueous phase before and after extraction.

3. Variation of HNO₃ Concentration

- The concentration of HNO₃ in the aqueous phase was systematically varied from 0.01 to 1 M while keeping the total nitrate concentration constant at 1 M by adding LiNO₃.
- This allowed the study of the impact of HNO₃ concentration on lanthanide extraction and coordination.

4. Spectroscopic Analysis

- UV-Vis Spectroscopy: Absorption spectra of the extracted complexes were recorded to identify changes in the inner-sphere coordination environment of lanthanides, particularly using hypersensitive absorption bands.
- Fourier Transform Infrared (FT-IR) Spectroscopy: FT-IR spectra of the organic phases were recorded to investigate the coordination of nitrate ions (NO₃⁻) to lanthanides by observing vibrational shifts.
- Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIFS): Lifetime measurements of Eu(III) were conducted in both H₂O and D₂O to determine the number of coordinating water

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molecules.

5. Slope Dependence Study:

- A slope dependence study was performed by varying the concentration of TODGA in the organic phase from 0.03 to 0.2 M and analyzing the linear relationship between $\log D_{Ln}$ and $\log [TODGA]$.
- The change in slope with varying HNO_3 concentrations provided insights into the stoichiometry of the Ln complexes.

6. Data Analysis:

- The data from the distribution ratios, UV-Vis, FT-IR, and TRLIFS measurements were combined to provide a comprehensive understanding of the coordination chemistry of lanthanides under different acidities.

Key Findings

1. Effect of HNO_3 Concentration

- Increasing the concentration of HNO_3 above 0.5 M leads to a significant change in the coordination environment of lanthanides, increasing the number of coordinating TODGA molecules from a 1:2 to a 1:3 Ln complex.
- At low HNO_3 concentrations (0.01 to 0.5 M), inner-sphere nitrate coordination is prevalent, while higher HNO_3 concentrations promote outer-sphere interactions.

2. Distribution Ratio Measurements:

- The distribution ratios of lanthanides increase with increasing HNO_3 concentration, indicating a higher extraction efficiency and a change in complex stoichiometry.

3. Spectroscopic Analysis:

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- UV-Vis Spectroscopy: Hypersensitive absorption bands of Nd(III) showed distinct changes with varying HNO₃ concentrations, reflecting changes in the inner-sphere coordination environment.
- FT-IR Spectroscopy: The spectra revealed shifts in the TODGA C=O vibrational stretch and the presence of monodentate and bidentate nitrate coordination, which varied with HNO₃ concentration.
- TRLIFS: Lifetime measurements of Eu(III) indicated that no water molecules coordinated to Eu under the tested conditions, even with varying HNO₃ concentrations.

4. Complex Formation:

- The study confirmed the formation of the well-established cationic, trischelate homoleptic [Ln(TODGA)₃]³⁺ complex at higher HNO₃ concentrations.
- At lower HNO₃ concentrations, a 1:2 Ln complex is more prevalent, with inner-sphere nitrate coordination.

5. Role of NO₃⁻ Source:

- Changing the NO₃⁻ source from HNO₃ to LiNO₃ significantly impacts the inner-sphere coordination of lanthanides, which in turn affects the extraction and separation efficacy.
- The study highlighted the importance of considering the nitrate source in solvent extraction systems, particularly for systems with a propensity for outer-sphere interactions.

6. Importance of Analytical Techniques:

- Combining distribution ratio measurements with multiple spectroscopic techniques provided a comprehensive understanding of the coordination chemistry of lanthanides in organic phases.
- This approach allowed for detailed insights into how lanthanide complexes evolve in response to changes in aqueous phase acidity.

7. Implications for Lanthanide Separations:

- The findings have practical implications for improving intralanthanide separations, which are crucial for various industries including clean energy, digital technology, and medical isotopes.

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- Understanding the coordination behavior under different extraction conditions can lead to optimized processes for high-purity lanthanide separations.

Relevance to Study

Impact of Aqueous Phase Acidity: Understanding how varying HNO_3 concentrations affect lanthanide coordination is crucial for optimizing solvent extraction processes in nuclear fuel cycle chemistry.

Coordination Behavior: The study highlights the transition from 1:2 to 1:3 Ln complexes with increasing HNO_3 , informing ligand selection based on coordination preferences under different acidity conditions.

Role of Nitrate Ions: Findings on the influence of nitrate ion sources (HNO_3 vs. LiNO_3) on inner- and outer-sphere coordination provide insights into selecting appropriate ligands for efficient separation.

Spectroscopic Techniques: Utilizing UV-Vis, FT-IR, and TRLIFS to analyze coordination environments aids in selecting ligands that form stable complexes with desired optical and spectroscopic properties.

Hydration Effects: The study's demonstration that no water molecules coordinate to Eu(III) under varying HNO_3 concentrations is relevant for choosing ligands that minimize hydration, enhancing extraction efficiency.

Distribution Ratios: Measuring distribution ratios across different TODGA concentrations and HNO_3 levels helps in selecting ligands that achieve optimal metal ion partitioning between phases.

Complex Stability: Insights into the stability of 1:3 Ln complexes in high acid concentrations inform ligand design to ensure stable complex formation under operational conditions.

Implications for Intralanthide Separations: The research provides a basis for improving

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intralanthanide separations, crucial for the purity required in nuclear fuel cycles.

Critical Parameters Identified

High Importance

Chemical Stability

- The study emphasizes the stability of Ln

complexes under varying HNO₃ concentrations, highlighting how chemical stability influences the effectiveness of the extraction process.

- The presence of inner-sphere and outer-sphere interactions with nitrate ions affects the stability of the complexes formed.

Radiolysis Resistance

- Although not directly addressed, the study's focus on stable coordination environments under high acidity conditions suggests that the ligand's resistance to harsh chemical conditions may correlate with radiolysis resistance.

Thermodynamics:

- The findings on the distribution ratios and transition from 1:2 to 1:3 Ln complexes with increasing HNO₃ concentrations provide insights into the thermodynamic stability of these complexes.
- The study demonstrates how HNO₃ concentration influences the binding strength and selectivity of TODGA towards lanthanides.

Medium Importance

Kinetics (forwards and reverse):

- The study's slope dependence analysis between log D_{Ln} and log [TODGA] suggests kinetic

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aspects of ligand coordination, although it is not the primary focus.

Loading Capacity:

- By determining the number of TODGA molecules coordinating to lanthanides (1:2 vs. 1:3 complexes), the study indirectly informs the loading capacity of the ligand, indicating how much material can be processed.

Operational Condition Range:

- The research examines ligand performance across a range of HNO₃ concentrations, showcasing its operational versatility under different acidic conditions.

Low Importance

Solubility

- The solubility of TODGA in n-heptane is implied but not explicitly addressed, indicating its suitability for the solvent system used.

Dispersion Numbers:

- The study does not focus on dispersion numbers, which are more specific to applied systems with conditional values and mass transfer efficiency.

Phase Disengagement:

- Phase disengagement is not a primary focus of the study; however, the successful separation of organic and aqueous phases after extraction is implicitly achieved, supporting the practicality of the solvent extraction process.