

Key Words

T2EHDGA

lanthanides

extraction

diglycolamide

nitrate

thermodynamics

europiumspeciation

solvent

complexation

Objective

1. Investigate the Extraction Mechanism: To understand the extraction behavior of Ln(III) ions by T2EHDGA in n-dodecane from both nitric acid (HNO₃) and sodium nitrate (NaNO₃) solutions, focusing on the mechanisms responsible for the enhanced extraction of europium (Eu(III)) in HNO₃ compared to NaNO₃.
2. Compare Distribution Ratios: To measure and compare the distribution ratios (D) of Eu(III) extracted from varying concentrations of T2EHDGA in n-dodecane in different media (HNO₃ and NaNO₃).
3. Identify Organic-Phase Species: To identify the organic-phase species formed during the extraction process using experimental data combined with spectroscopic techniques like FTIR and UV-vis spectroscopy.
4. Develop a Thermodynamic Model: To create a thermodynamic model using the SXLSQI solvent extraction modeling program to describe the extraction behavior of Eu(III) by T2EHDGA from nitrate

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media, incorporating non-ideality parameters and extraction constants.

5. Characterize Structural Information: To use FTIR and UV-vis spectroscopy to characterize the structural information of the extracted complexes, particularly focusing on how HNO₃ influences the coordination environment of Eu(III) and the T2EHDGA ligand.

6. Examine Aggregation and Third-Phase Formation: To study the aggregation behavior of T2EHDGA and the conditions leading to third-phase formation in the organic phase, particularly in the presence of high concentrations of HNO₃.

7. Assess Limiting Organic Concentration (LOC): To determine the limiting organic concentration of Eu(III) that can be extracted by T2EHDGA in n-dodecane before phase splitting occurs, particularly under varying HNO₃ and NaNO₃ conditions.

8. Enhance Understanding of Solvent Extraction Systems: To provide insights into the behavior of neutral extractants in the extraction of trivalent lanthanides and actinides, which is essential for improving separation processes in nuclear waste reprocessing.

Methodology

Materials

1. T2EHDGA

- Purchased from Eichrom Technologies.
- Purified by column chromatography using a dichloromethane/diethyl ether gradient elution.
- Characterized by ¹H-NMR, ¹³C-NMR, FTIR, UV-vis, and electrospray ionization mass spectrometry (ESI-MS).

2. Aqueous Solutions

- Prepared using distilled water deionized to >18.2 M (DIW).
- Nitric acid solutions made from TraceSELECT HNO₃ (Fluka Chemicals), diluted with DIW, and

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standardized by titration against NaOH using a Titrand Metrohm 905 Automatic Titrator.

- High-purity NaNO₃ (99.995%) purchased from Sigma-Aldrich.
- Eu(NO₃)₃ 6H₂O (99.9%) purchased from Alfa Aesar.
- Nd(NO₃)₃ 6H₂O (99.9%) purchased from Aldrich Chemical Company.
- Normal-dodecane (99+%) obtained from Alfa Aesar.
- ¹⁵²/154Eu radiotracer purchased from Eckert & Ziegler.

Solvent Extraction Experiment

1. Preparation of stock solutions

- Appropriate mass of T2EHDGA weighed in a volumetric flask and diluted with n-dodecane.
- Aqueous solutions of HNO₃ or NaNO₃ spiked with radiotracer.

2. Extraction Procedure

- Samples of 0.1 M T2EHDGA in n-dodecane contacted with equal volumes of aqueous 0.073 M HNO₃ on a shaker table at 300 rpm for 1 hour at 25 °C.
- Temperature maintained within 1 °C using a temperature-controlled box.
- Samples centrifuged after mixing; aliquots from each phase removed for analysis.

3. Determination of Distribution Ratios (D):

- Radioactivity of each phase measured using an automated gamma counter with a NaI(Tl) scintillation detector.
- Distribution ratio (D_{Eu}) calculated as the radioactivity in the organic phase divided by the radioactivity in the aqueous phase.

Solvent Extraction Modeling

1. SXLSQI Program

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- Used to facilitate thermodynamic analysis of europium distribution data at 25 C.
- Parameters included experimental distribution measurements, Pitzer parameters, and Masson coefficients.

2. Refinement of Extraction Constants

- Based on experimental data, including the identification of organic-phase species: $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3$, $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)$, and $\text{Eu}(\text{NO}_3)_3(\text{T2EHDGA})_3(\text{HNO}_3)_2$.

Spectroscopic Methods

1. FTIR Spectroscopy

- Used to examine metal ligand complexes under various aqueous conditions.
- Measurements taken with a Bruker ALPHA Platinum ATR module with a single-reflection diamond cell.
- Organic liquids measured by placing a drop directly on the diamond plate.

2. UV-Vis Spectroscopy

- Used to probe the effect of HNO_3 on metal coordination in the T2EHDGA/n-dodecane solvent.
- Absorbance spectra of Nd(III) collected with a Cary Bio 50 Spectrophotometer using a 10-mm semi-micro quartz cuvette.

Limiting Organic Concentration (LOC) Experiments

1. Determination of LOC

- Conducted to understand phase splitting.
- Organic and aqueous europium concentrations calculated from distribution ratios determined radiometrically in n-dodecane solvent with varying $\text{Eu}(\text{NO}_3)_3$ concentrations in HNO_3 .

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Data Analysis

1. Comparison of Experimental and Modeled Data:

- Experimental distribution ratios compared with calculated values using the SXLSQI model.
- Refinement of extraction constants to understand the extraction mechanism.

Key Findings

Eu(III) Distribution Studies

Distribution Ratios: The distribution ratios (D) for Eu(III) increase significantly when extracted from 2.5 M HNO₃ compared to 0.5 M HNO₃, showing enhanced extraction with higher HNO₃ concentration.

Effect of NaNO₃: The D values drop by more than two orders of magnitude when switching from 2.5 M HNO₃ to 2 M NaNO₃, indicating much lower extraction efficiency in NaNO₃.

Extraction Mechanism: A steep increase in D values is observed as HNO₃ concentration exceeds 1 M, suggesting HNO₃ plays a significant role in the extraction process.

Solvent Extraction Modeling

Three organic-phase species: The SXLSQI modeling identified three key organic-phase species: Eu(NO₃)₃(T2EHDGA)₃, Eu(NO₃)₃(T2EHDGA)₃(HNO₃), and Eu(NO₃)₃(T2EHDGA)₃(HNO₃)₂.

thermodynamic constants: The best fit for the extraction data yielded log K values of 3.29, 4.24, and 4.17 for the identified species, indicating the presence of HNO₃ significantly influences the extraction process.

goodness of fit: The model showed good agreement with experimental data, predicting D values accurately across varying concentrations of T2EHDGA and HNO₃.

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FTIR characterization of extracted Eu(III)-T2EHDGA Complexes

carbonyl stretching: Significant changes in the FTIR spectra were observed upon extraction, particularly in the carbonyl stretching region, indicating strong interaction between Eu(III) and T2EHDGA.

HNO₃ interaction: The presence of HNO₃ in the organic phase was confirmed by distinct spectral features, including the appearance of new peaks and shifts in existing peaks.

nitrate coordination: The coordination of nitrate to Eu(III) in the organic phase was confirmed, with differences in coordination mode between HNO₃ and NaNO₃ systems.

limiting organic concentration (LOC)

third-phase formation: The LOC experiments indicated that third-phase formation occurs at lower HNO₃ concentrations for T2EHDGA compared to TODGA, highlighting the steric effects of the branched alkyl chains in T2EHDGA.

Eu(III) loading: The solubility of the Eu(III)-T2EHDGA complex in the organic phase was found to be high, with third-phase formation dependent on both extractant concentration and aqueous acidity.

absorbance spectra of Nd(III)

hypersensitive bands: The UV-vis spectra showed changes in the hypersensitive bands of Nd(III) upon extraction, indicating alterations in the coordination environment due to the presence of HNO₃.

coordination sphere: The spectral changes suggested a loss of symmetry in the Nd(III) coordination sphere when HNO₃ is present, consistent with partial dissociation of the DGA ligand to accommodate HNO₃ in the extracted complex.

conclusion

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extraction efficiency: The presence of HNO_3 significantly enhances the extraction of Eu(III) by T2EHDGA, leading to different thermodynamic products compared to NaNO_3 .

structural insights: Spectroscopic analysis provided detailed insights into the structural differences in the extracted species, highlighting the role of HNO_3 in modifying the coordination environment.

model variation: The SXLSQI model effectively described the extraction behavior, supporting the hypothesis that HNO_3 facilitates the preorganization of supramolecular structures responsible for enhanced extraction.

Relevance to Study

Efficiency in Lanthanide and Actinide Separation: Demonstrates that T2EHDGA is effective in extracting lanthanides (Ln) and minor actinides (MA) from nitric acid solutions, essential for separating these elements in nuclear fuel reprocessing.

Thermodynamic Stability: Shows that the extraction mechanism is highly dependent on nitric acid concentration, providing insights into the thermodynamic properties necessary for efficient ligand performance in nuclear waste reprocessing.

Aggregation Behavior: Identifies the aggregation and third-phase formation tendencies of T2EHDGA, which are critical for understanding and mitigating potential issues in solvent extraction processes.

Coordination Chemistry: Provides detailed spectroscopic data on the coordination environment of lanthanides with T2EHDGA, informing ligand design to optimize binding and extraction efficiency.

Comparison with Other Ligands: Highlights the advantages and limitations of T2EHDGA compared to other diglycolamide extractants, aiding in the selection of suitable ligands for specific nuclear fuel cycle applications.

Scalability and Practical Application: Suggests that T2EHDGA's high extraction capacity and

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favorable properties make it a promising candidate for large-scale nuclear fuel cycle operations.

Critical Parameters Identified

High Importance

1. Chemical Stability

Acid/Base Hydrolysis: The study reports that T2EHDGA shows significant extraction capacity for HNO_3 into the nonpolar organic phase, indicating stability in acidic environments.

Reactivity: T2EHDGA forms stable complexes with Ln(III) ions, as demonstrated by the consistent extraction behavior and formation of specific organic-phase species.

2. Radiolysis Resistance: The study does not explicitly mention radiolysis resistance. However, the importance of T2EHDGA's performance under radioactive conditions is implied given its application in nuclear waste reprocessing. Previous literature cited in the study notes the radiolytic stability of diglycolamide extractants.

3. Thermodynamics

Extraction Constants: The study provides detailed thermodynamic data, including extraction constants ($\log K$ values) for the organic-phase species formed during the extraction of Eu(III) by T2EHDGA.

Mechanism: The thermodynamic model developed using SXLSQI shows the participation of HNO_3 in the extraction mechanism, enhancing the understanding of the ligand's behavior under different conditions.

Medium Importance

1. Kinetics

Extraction and Reversal: The study details the contact time (1 hour) for equilibrium to be reached in

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the extraction experiments, indicating efficient kinetics. However, specific kinetic rates are not provided.

2. Loading Capacity

Eu(III) Loading: The study conducts limiting organic concentration (LOC) experiments to determine the maximum Eu(III) loading capacity of T2EHDGA before phase splitting occurs, demonstrating practical loading limits.

3. Operational COndition Range:

Acidity Range: T2EHDGA is shown to operate effectively over a range of HNO₃ concentrations (0.07–3 M), highlighting its flexibility in different acidic environments.

Temperature: The experiments are conducted at 25 °C, but the study does not explore a broad temperature range.

Low Importance

1. Solubility

Organic Phase Solubility: T2EHDGA is dissolved in n-dodecane, and the study mentions its high solubility in paraffinic solvents, ensuring it remains in the organic phase during extraction.

2. Dispersion Numbers: The study does not specifically address dispersion numbers. However, the phase behavior and aggregation properties of T2EHDGA in the organic phase are discussed, indirectly relating to dispersion efficiency.

3. Phase Disengagement

Third-Phase Formation: The study addresses third-phase formation and the conditions leading to phase splitting, which is critical for practical separation but specific to the concentration and type of acid used.