

## **Key Words**

Diglycolamides

Lanthanide separations

Spectroscopy

Small-angle scattering

## **Objective**

1. To review the current state of knowledge regarding the application of diglycolamides (DGAs) in hydrometallurgical-based f-element separations, with a particular focus on lanthanides.
2. To assess the impact of DGA molecular structure on intra-lanthanide partitioning patterns, aiming to design more efficient lanthanide separation systems.
3. To investigate the effects of varied diluents, inclusion and variation of phase modifiers, and DGA derivatization on system characteristics using spectroscopic and scattering techniques.
4. To provide new insights into the speciation of lanthanide-DGA complexes in the organic phase, which is crucial for improving the efficiency of hydrometallurgical lanthanide processing.
5. To understand the role of co-extracted anions (e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) and cations (e.g., H<sup>+</sup>, Na<sup>+</sup>) in influencing the aggregate size, morphology, and distribution coefficients of lanthanide-DGA complexes.

## **Methodology**

### **1. Solvent Extraction Studies:**

- Solvent extraction was employed to study the transfer of lanthanides (Ln<sup>3+</sup>) from the aqueous phase to the organic phase using diglycolamide (DGA) extractants.
- Distribution coefficients (D values) were determined for different lanthanides to assess the

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extraction efficiency and separation factors.

### 2. Spectroscopic Techniques:

- Fourier-Transform Infrared Spectroscopy (FT-IR): FT-IR was used to evaluate changes in the vibrational stretches of DGAs after acid and metal extraction, focusing on C=O, C-O-C, and N-O vibrational modes.
- Ultraviolet-Visible (UV-Vis) Spectroscopy: UV-Vis spectroscopy detected changes in the inner coordination sphere of select lanthanides through hypersensitive and non-hypersensitive absorbance bands.
- Fluorescence Spectroscopy: Used specifically for Eu<sup>3+</sup> containing samples to determine the number of coordinating water molecules.

### 3. Scattering Techniques:

- Extended X-ray Absorption Fine Structure (EXAFS): Provided element-specific structural information about the inner coordination spheres of lanthanide ions in both solution and solid states.
- Small-Angle Neutron Scattering (SANS): Used to investigate the aggregation behavior of DGAs in the presence of phase modifiers and to calculate aggregate sizes and the number of extractant molecules per complex.

### 4. Titration Methods:

- Karl Fischer Titration: Measured the concentration of water in the organic phase.
- Potentiometric Titration: Determined the concentration of H<sup>+</sup> ions in the organic phase.

5. Molecular Dynamics Simulations: Simulations were used to validate the experimental results and provide insights into the molecular interactions and structural changes of the lanthanide-DGA complexes.

6. Slope Analysis Speciation: Slope analysis was employed to determine the number of DGA molecules per lanthanide ion and to study the speciation of lanthanide-DGA complexes in the

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organic phase.

7. Evaluation of Acidic and Alkaline Effects: The effects of different acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ ) on the extraction behavior and speciation of lanthanide-DGA complexes were studied to understand their impact on the aggregation and distribution coefficients.

### Key Findings

#### 1. Aggregation Behavior:

- Evidence of morphology changes with increasing  $\text{Nd}^{3+}$  loading was observed for TODGA/n-heptane systems in contact with 3 M  $\text{LiNO}_3$  and 0.01 M  $\text{HNO}_3$ . The addition of 5 vol% 1-octanol reduced the number of TODGA molecules participating in the Nd-DGA extracted complex to 2.4.
- Molecular dynamics simulations suggest polymetallic complexes bridged by nitrates with TODGA molecules surrounded by phase modifiers, indicating a microstructure for both malonamides and DGAs

#### 2. Solvent Effects:

- The presence of phase modifiers like 1-octanol and DMDOHEMA significantly influences the aggregation behavior of DGA systems. 1-octanol decreased the power-law X-ray scattering at low q-values, indicating either polydisperse reverse micellar-like aggregates or aggregates independent of  $\text{Nd}^{3+}$  concentration. In contrast, DMDOHEMA resulted in mixed aggregates and increased polydispersity of solutes.
- The dielectric constant of the diluent plays a crucial role in the extraction mechanism and the nature of the (DGA) ( $\text{HNO}_3$ ) adducts

#### 3. Spectroscopic Analysis:

- FT-IR spectroscopy revealed changes in the  $\text{C}=\text{O}$  vibrational stretches upon contact with different

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lanthanides, indicating changes in the extracted Ln-DGA complexes. For example, a red shift in the C=O stretch was observed for La<sup>3+</sup> to Nd<sup>3+</sup>, suggesting a change in Ln-TODGA interactions.

- UV-Vis spectroscopy showed that phase modifiers like 1-octanol do not alter the inner coordination sphere of Nd<sup>3+</sup>, but influence the outer-sphere coordination

### 4. Complex Formation:

- Slope analysis and molecular dynamics simulations indicate the formation of 1:2 or 1:3 Ln complexes depending on the system conditions. The presence of phase modifiers and the type of diluent can alter the number of DGA molecules per Ln complex.

- Homoleptic Ln(DGA)<sub>3</sub> complexes were prevalent in systems without coordinating water or nitrate molecules in the inner-coordination sphere, as supported by EXAFS and TRLS data

### 5. Polydispersity and Aggregate Size:

- Dynamic Light Scattering (DLS) revealed that the average diameter of aggregates varied significantly depending on the alkyl chain length of the DGA derivatives, with shorter alkyl chains resulting in larger aggregate sizes. The trend in aggregate sizes followed THDGA > TODGA > TDDGA > TDdDGA.

- The concentration of HNO<sub>3</sub> influenced the size distribution of aggregates, with higher HNO<sub>3</sub> concentrations resulting in a broader size distribution

## Conclusion

1. Morphology Changes with Lanthanide Loading: Increasing Nd<sup>3+</sup> loading results in morphology changes in TODGA/n-heptane systems, particularly when in contact with 3 M LiNO<sub>3</sub> and 0.01 M HNO<sub>3</sub>. The addition of 5 vol% 1-octanol reduces the number of TODGA molecules participating in the overall Nd-DGA extracted complex to 2.4.

2. Aggregation Behavior and Phase Modifiers: Phase modifiers like 1-octanol and DMDOHEMA

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significantly influence the aggregation behavior of DGA systems. 1-octanol reduces the number of TODGA molecules per complex, while DMDOHEMA results in mixed aggregates, increasing polydispersity.

3. Coordination and Spectroscopic Analysis: FT-IR and UV-Vis spectroscopy indicate that the addition of phase modifiers does not change the inner coordination sphere of  $\text{Nd}^{3+}$  but influences the outer-sphere coordination. Molecular dynamics simulations suggest polymetallic complexes bridged by nitrates, with TODGA molecules surrounded by phase modifiers.

4. Speciation and Complex Formation: The prevalent complexes are 1:3  $[\text{Ln}(\text{DGA})_3]^{3+}$  or 1:2  $[\text{Ln}(\text{DGA})_2(\text{NO}_3)_x(\text{H}_2\text{O})_y]^{3-x}$  with outer-sphere anions for charge neutrality. Slope analysis and molecular dynamics simulations support these findings, indicating the formation of 1:2 or 1:3 Ln complexes depending on the system conditions.

5. Impact of  $\text{HNO}_3$  Concentration: Increasing  $\text{HNO}_3$  concentration increases the number of aggregates and their size, particularly for shorter alkyl chain DGA derivatives. This suggests a correlation between aggregate size and the molecular structure of the extracted Ln species.

6. Effect of Different Acids:

- Different strong acids ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HCl}$ ) influence aggregate sizes and  $\text{Ln}^{3+}$  extraction. Larger aggregates form in the presence of  $\text{HClO}_4$ , while  $\text{HCl}$  results in the smallest aggregates.

7. Third Phase Formation (TPF): High loading of acid or Ln in the organic phase can cause TPF, leading to adverse effects on industrial processes. Phase modifiers can prevent TPF by disrupting the polymer chains in the organic phase.

8. Recommendations for Future Research: The study highlights the need for additional spectroscopic and scattering investigations across the Ln series, particularly for light Ln. Future research should employ techniques like EXAFS, FT-IR, UV-Vis, and small-angle scattering to systematically study Ln-DGA complexes and their interactions.

## **Relevance to Study**

**Hydrogen Bond Networks:** DGAs form extensive hydrogen-bonding networks that are crucial for the selective extraction of lanthanides ( $\text{Ln}^{3+}$ ). This is essential for designing ligands that can efficiently separate lanthanides in nuclear fuel reprocessing

**Phase Modifiers:** The use of phase modifiers, such as 1-octanol and DMDOHEMA, significantly impacts the aggregation behavior and extraction efficiency of DGAs. Phase modifiers prevent third phase formation (TPF), a common issue in nuclear fuel reprocessing, by disrupting hydrogen-bond networks and promoting better solubility and stability of the extractants

**Speciation and Complex Formation:** DGAs can form various complexes with lanthanides, such as 1:2 or 1:3  $\text{Ln}$

complexes, depending on the conditions. Understanding these complexation behaviors helps in selecting appropriate DGAs for specific lanthanide separations in the nuclear fuel cycle

**Effect of Diluents:** The choice of diluent affects the extraction efficiency and aggregation behavior of DGA systems. Aliphatic diluents combined with phase modifiers are shown to enhance the performance of DGAs, making them suitable for industrial applications in nuclear fuel reprocessing

**Radiation Stability:** The stability of DGAs under radiolytic conditions is a critical factor for their application in nuclear fuel reprocessing. The document discusses the radiolytic stability of various DGA derivatives, which is crucial for ensuring long-term functionality in radioactive environments

**Thermodynamic Insights:** Thermodynamic data from spectroscopic and scattering techniques provide insights into the speciation and stability of lanthanide-DGA complexes. This information is vital for selecting ligands with optimal extraction efficiencies and selectivities for different lanthanides

## **Critical Parameters Identified**

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### High Importance

#### 1. Chemical Stability:

- The study discusses the impact of acid concentration (e.g.,  $\text{HNO}_3$ ) on the stability and aggregation behavior of DGAs. It highlights how different DGAs and their derivatives perform under varying acid conditions, ensuring their functionality in separation processes
- The interaction of DGAs with different diluents and phase modifiers, which can influence the chemical stability of the extractants under operational conditions, is also examined

#### 2. Radiolysis Resistance:

- The stability of DGAs under radiolytic conditions is addressed, indicating their potential longevity and resistance to degradation in radioactive environments, which is crucial for nuclear fuel reprocessing applications

#### 3. Thermodynamics:

- Thermodynamic data from spectroscopic and scattering techniques provide insights into the stability and speciation of lanthanide-DGA complexes. These findings influence the selectivity and binding strength of ligands towards specific metal ions, critical for the feasibility of separation processes

### Medium Importance

#### 1. Kinetics:

- The study touches on the aggregation behavior and dynamic changes of DGAs in the presence of lanthanides and acids, which can affect the speed and equilibrium of the separation process

#### 2. Loading Capacity:

- Findings regarding the number of TODGA molecules participating in the Nd-DGA extracted complex and the impact of phase modifiers on aggregate size suggest how much material can be

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processed before saturation

### 3. Operational Condition Range:

- The study examines the performance of DGAs under different acid concentrations and in the presence of various phase modifiers, indicating their ability to operate under a broad range of conditions, which increases their flexibility and applicability

## Low Importance

### 1. Solubility

- The impact of different diluents on the solubility and aggregation behavior of DGAs is discussed. The choice of diluent affects the extraction efficiency and solubility of the extractants

### 2. Dispersion nUmbers:

- The study does not specifically address dispersion numbers, but the discussion on aggregate sizes and their distribution indirectly touches upon mass transfer efficiency

### 3. Phase Disengagement:

- The phenomenon of third phase formation (TPF) and the role of phase modifiers in preventing TPF are discussed, which is critical for the practical separation of phases after the extraction process in industrial applications