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Key Words

ynsymmetrical digylcolamide

solvent extraction

lanthanide partitioning

nuclear fuel reprocessing

ligand synthesis

Objective

1. Synthesis and Evaluation: The article aims to synthesize six novel unsymmetrical diglycolamide (UDGA) ligands and evaluate their effectiveness as solvent extraction reagents for partitioning lanthanide (Ln) ions from nitrate media.
2. Characterization of Complexes: The study characterizes the partitioning of europium between aqueous phases of varying nitric acid concentrations and a UDGA organic phase, using radiometric methods to determine stoichiometry and phase-transfer equilibrium constants.
3. Luminescence Spectroscopy: Another objective is to use luminescence spectroscopy to establish the relative stability and stoichiometry of the Eu-UDGA complexes in acetonitrile.
4. Interfacial Activity and Equilibration Time: The article aims to investigate the interfacial activity of the UDGA ligands to reduce equilibration time while maintaining high lanthanide distribution ratios.
5. Improvement of Ligand Performance: The overall goal is to design and synthesize diglycolamide extractants that improve upon previous ligand performance by adjusting the amphiphilicity of the diglycolamide moiety, introducing polar/nonpolar asymmetry to enhance phase transfer and compatibility properties.
6. Reduction of Third Phase Formation: The study also seeks to address the issue of third phase formation in TODGA systems by exploring UDGA ligands with different structural modifications to

avoid such problems and improve metal loading capacity without additional phase modifiers.

Methodology

Experimental Procedures

Materials

Chemicals and Reagents: Diglycolic anhydride (Alfa Aesar, 97%), various amines (Sigma-Aldrich, reagent grade), nitric acid (EMD Millipore OmniTrace), and organic diluents such as n-octane, 1-octanol, n-dodecane, and acetonitrile (Acros Organics, Sigma-Aldrich, Alfa Aesar, Fisher Scientific).

Radiotracer Production: Europium-152/154 was produced by neutron activation of Eu2O3 in a TRIGA nuclear reactor at the Washington State University Nuclear Science Center.

Synthesis and UDGA Extractants

1. Amidation of Diglycolic Anhydride: Adapted from previous work by Ram rez.

2. Methylation of Diglycolamic Acid: Adapted from Stodola's fundamental work.

3. Amidation of Diglycolamic Acid Methyl Ester: Adapted from a review on amide bond formation by Montalbetti and Falque.

- All synthetic steps were performed under ambient atmospheric conditions.

- Structures of synthesized ligands were confirmed using NMR and IR spectroscopy.

- Purity (>97%) was verified using 1H NMR spectroscopy integration and high-resolution mass spectrometry (HRMS).

Liquid-Liquid Solvent Extraction

1. Preparation of Organic Solutions: Ligand and diluent were prepared by mass. Mixed organic diluents (e.g., 5% or 10% v/v 1-octanol in n-dodecane) were made in large batches.

2. Aqueous Solutions: Prepared using titrated nitric acid solutions.

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3. Pre-Equilibration: Organic phase (2000 L) was pre-equilibrated with a metal-free aqueous phase (2000 L) for 30 minutes using a vortex mixer.

4. Extraction Experiments:

- Organic and aqueous phases were mixed with radiotracer europium-152/154 and contacted for at least 30 minutes.

- Samples were centrifuged to separate phases, and aliquots were taken for gamma counting.

- Distribution ratios (DEu) were calculated from the counts per minute (cpm) in each phase.

Luminescence Spectroscopy

1. Titrand Preparation: 0.5 mM Eu(NO3)3 in 0.3 mM HNO3/0.2 M H2O/99.7% MeCN.

2. Titrant Preparation: UDGA in MeCN, prepared fresh for each experiment.

3. Spectral Acquisition:

- Titrand (1000 L) was placed in a quartz fluorimeter cell.

- Titrant was added in 10.0 L aliquots, equilibrated for 1 minute before each emission spectrum was acquired.

- Excitation wavelength was 393 nm, and emission spectra were recorded in the range of 550 650 nm.

Results and Analysis

- Ligand Solubility: Solubility limits in n-octane and n-dodecane were noted, with phase incompatibility addressed using 1-octanol.

- Equilibration Time: Monitored the distribution ratio with varying equilibration times.

- Nitric Acid Dependence: Evaluated the extraction efficiency at different nitric acid concentrations.

- Metal Ligand Complex Stoichiometry: Determined using radiometric slope analysis, confirmed with luminescence spectroscopy data.

- Luminescence Titrations: Analyzed changes in emission spectra to determine conditional stability constants (MHL).

Key Findings

Liquid-Liquid Solvent Extraction

Ligand Solubility

- High Solubility: The synthesized ligands were highly soluble in n-octane and n-dodecane.
- Phase Compatability Issue: Upon contact with aqueous nitric acid and Eu(III), some ligands formed a third phase, which was mitigated by adding 1-octanol as a phase modifier.

Equilibration Time

- Rapid Equilibration: The new unsymmetrical diglycolamide (UDGA) ligands, particularly N,N-dihexyl-N'-pyrrolidinyldiglycolamide (DHpyrDGA), reached equilibrium within 2 minutes, which is faster compared to TODGA (15 20 minutes).

Nitric Acid Dependence

- Distribution Ratios (DEu): Dioctyl derivatives exhibited high distribution ratios (DEu > 1000 at 3.0 M HNO3) and did not form a third phase at high nitric acid concentrations.
- Nitric Acid Dependence: Different UDGA ligands showed varying slopes in nitric acid dependence, indicating changes in extraction efficiency with varying acid concentrations.

Metal-Ligand Complex Stoichiometry

Stoichiometry: Solvent extraction experiments indicated a 3:1 ligand-to-metal ratio for the Eu-UDGA complexes in the organic phase.

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Conditional Extraction Equilibrium COnstants (log Kex): The log Kex values suggested that UDGA ligands were stronger extractants than TODGA, with the pyrrolidinyl derivatives showing the highest extraction strength.

Luminescence Spectroscopy

Complex Formation

- Eu)III) Complexes: Luminescence spectroscopy titrations showed the formation of 1:1 through 1:4 metal ligand complexes in acetonitrile.

-Peak Splitting: Significant spectral changes, including peak splitting around 615 nm, indicated complex speciation during titrations.

Conditional Stability Constants

- Log MHL Values: MHL Values: The conditional stability constants for the UDGA ligands were determined, showing that the Eu-UDGA complexes were 10 1000 times stronger than Eu-TODGA complexes.

- Step-Wise Stability Constants (log KMHL): The steady decrease in step-wise stability constants with increasing ligand coordination suggested steric crowding around the metal center

Overall Analysis

- Enhanced Performance: The UDGA ligands demonstrated improved extraction performance compared to TODGA, with faster equilibration times, higher distribution ratios, and stronger complex formation.

- Potential for Future Research: The study identified dioctyl derivatives as the most promising ligands for further investigation, suggesting the potential for further optimization by exploring longer

or more branched alkyl chains

Conclusion

1. Successful Synthesis: Six new unsymmetrical diglycolamide (UDGA) ligands were synthesized using a three-step organic synthesis procedure.

2. Extraction Behavior: The trivalent lanthanide metal extraction behavior of the new ligands was studied using radiotracer 152,154Eu(III). The ligands DHpyrDGA and DOpyrDGA reached equilibrium within less than 2 minutes, demonstrating rapid extraction kinetics.

3. Equilibrium Constants: The conditional metal extraction equilibrium constants (log Kex) were determined using ligand dependence slope analysis, indicating that the UDGA ligands were comparable to or stronger than the symmetrical diglycolamide, TODGA.

4. Complex Stoichiometry: The metal ligand complex stoichiometry was found to be approximately 1:3 for both UDGA ligands and TODGA.

5. Nitric Acid Dependence: The extraction efficiency varied with the concentration of nitric acid. The dihexyl derivatives showed strong extraction but also tended to form a third phase at higher nitric acid concentrations, which is undesirable for a biphasic system.

6. Optimal Extractants: The dioctyl derivatives were identified as the most promising extractants due to their ability to avoid third phase formation while maintaining high distribution ratios.

7. Strength of Complexes: Luminescence spectroscopy titrations revealed that the UDGA ligands formed 1:1 through 1:4 metal ligand complexes that were significantly stronger (10 1000 times) than those formed by TODGA.

8. Future Research Directions: Future work will focus on synthesizing ligands with longer alkyl chains (e.g., didecyl or didodecyl) or increased branching (e.g., di-2-ethylhexyl or 3,7-dimethyloctyl) to enhance solubility in the organic phase while maintaining high extraction efficiency

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Relevance to Study

Synthesis and Characterization: The article presents the synthesis and thorough characterization of six new unsymmetrical diglycolamide (UDGA) ligands, which are potential candidates for the separation processes required in nuclear fuel reprocessing.

Extraction Efficiency: The synthesized UDGA ligands were found to be strong extractants for Eu(III), demonstrating comparable or superior extraction efficiencies to the well-known symmetrical diglycolamide ligand, TODGA. This is crucial for efficient lanthanide/actinide separation in nuclear fuel reprocessing.

Rapid Equilibration: Ligands such as DHpyrDGA and DOpyrDGA reached equilibrium within 2 minutes, significantly faster than TODGA, which is beneficial for industrial applications where time efficiency is critical.

Third Phase Formation: The article addresses the issue of third phase formation, which is a common problem in solvent extraction systems. The dioctyl derivatives (4 6) did not form a third phase at high nitric acid concentrations, making them more suitable for practical applications in the nuclear fuel cycle.

Conditional Extraction Equilibrium Constants: The study provides detailed data on the conditional extraction equilibrium constants (log Kex), which helps in understanding the strength and stability of the metal-ligand complexes under various conditions.

Stoichiometry of Metal-Ligand Complexes: The stoichiometry of approximately 3:1 (ligand to metal) for the Eu-UDGA complexes is reported, which is consistent with the requirements for efficient extraction processes in nuclear chemistry.

Luminescence Spectroscopy: The use of luminescence spectroscopy to determine the stability and stoichiometry of Eu-UDGA complexes in acetonitrile provides insights into the strength of these ligands compared to traditional ligands like TODGA.

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Future Research Directions: The article suggests future work to focus on synthesizing ligands with longer or more branched alkyl chains to enhance solubility and maintain high extraction efficiency, indicating ongoing development towards optimizing these ligands for nuclear applications.

Critical Parameters Identified

High Importance

Chemical Stability

-Phase Compatibility: The study notes that some UDGA ligands formed a third phase when in contact with nitric acid and Eu(III), indicating potential stability issues. However, the use of 1-octanol as a phase modifier resolved this issue.

-Solvent Extraction Equilibrium: The conditional extraction equilibrium constants (log Kex) were determined, suggesting the ligands are stable enough to form strong complexes with Eu(III) under the tested conditions.

Radiolysis Resistance: The study does not directly address radiolysis resistance. Further testing would be required to determine how these ligands withstand radiation.

Thermodynamics:

- Equilbrium Constants: The conditional extraction equilibrium constants (log Kex) provided in the study offer insights into the thermodynamic feasibility of the separation process. These constants help determine the selectivity and binding strength of the ligands towards specific metal ions.

Medium Importance

Kinetics

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Equilibration Time: The study highlights that ligands such as DHpyrDGA and DOpyrDGA reached equilibrium within 2 minutes, which is significantly faster than TODGA. This rapid equilibration is crucial for efficient processing.

Loading Capacity:

High Extraction Efficiency: The dioctyl derivatives showed high distribution ratios (DEu > 1000 at 3.0 M HNO3), indicating a strong capacity to load and extract metal ions.

Operational Condition Range

Nitric Acid Dependence: The ligands were tested across various nitric acid concentrations. The dioctyl derivatives maintained high extraction efficiency without forming a third phase even at high acid concentrations, demonstrating a broad operational range.

Low Importance

Solubility

Ligand Solubility: The synthesized ligands were highly soluble in n-octane and n-dodecane. Solubility was managed by using 1-octanol to prevent third phase formation, indicating that solubility issues can be addressed with appropriate solvents.

Dispersion Numbers: Not directly addressed in the study. This would be specific to the system setup and was not a focus of this research.

Phase Disengagement

Third Phase Formation: The study observed third phase formation with some ligands, but this was resolved by adding 1-octanol, ensuring clean phase disengagement. While critical, it was specific to

the system and managed effectively.