**REFERENCE: 20041**


**Key Words**

diglycolamides

molecular scaffolds

actinide/lanthanide separation

multipodal ligands


**Objective**

1. Review Compilation: Compile the complexation and separation behaviors of trivalent actinides and lanthanides with various multiple diglycolamide (DGA) group-containing ligands.
2. Scaffold Evaluation: Evaluate different molecular scaffolds (e.g., C- and N-pivot tripodal backbones, benzene-centered tripodal backbones, calix[4]arene, pillar[5]arene, and azamacrocycle scaffolds) and dendrimers with DGA arms for their extraction and complexation efficiency.
3. Extraction Efficiency and Selectivity: Analyze the enhanced extraction efficiency and improved selectivity of grouped DGA units on single backbones/scaffolds, with a particular focus on the separation of UO2  ions.
4. Experimental and Theoretical Studies: Use combined experimental methods, luminescence studies, and Density Functional Theory (DFT) studies to understand the extraction and separation behavior of these DGA-based ligands.
5. Practical Applications: Assess the implications of these findings for the development of suitable ligands for the extraction and separation of actinide and lanthanide ions in nuclear waste management and potential societal benefits (e.g., use of 241Am in smoke detectors and thermoelectric devices).

**Methodology**

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N/A - review article

**Key Findings**

1. Enhanced Extraction Efficiency: Multiple diglycolamide (DGA) ligands significantly improve the extraction efficiency of trivalent lanthanide and actinide ions compared to single DGA units. This enhancement is attributed to the preorganization of multiple DGA arms on molecular scaffolds.

2. Selectivity Improvement: Grouping DGA units on a single scaffold often improves selectivity for certain ions, particularly UO2 . This is critical for the separation of trivalent actinides and lanthanides in nuclear waste management.

3. Effect of Scaffold Type:

- Tripodal Backbones: Both C- and N-pivot tripodal DGA ligands show varied extraction efficiencies depending on the medium. N-pivot tripodal ligands exhibit higher extraction in room temperature ionic liquids (RTILs) compared to molecular solvents.

- Benzene-Centered Backbones: Benzene-centered tris-DGA ligands show high extraction efficiencies with varying trends depending on the preorganization of the ligand structure.

- Aza-Crown Ethers: Aza-crown ethers with attached DGA arms show high selectivity for Eu over Am due to the involvement of nitrogen atoms in metal binding.

- Calix[4]arenes and Pillar[5]arenes: These scaffolds demonstrate substantial extraction capabilities, particularly when DGA arms are attached at specific positions, with calix[4]arenes showing higher extraction when DGA arms are at the lower rim.

4. Impact of Spacer Length and Substitution: Spacer length and the nature of substituents (e.g., alkyl groups) on the DGA arms significantly affect extraction behavior. Longer spacers and bulkier substituents generally enhance extraction by increasing the ligand's flexibility and lipophilicity.

5. Luminescence and DFT Studies: Time-resolved luminescence spectroscopy and Density

Functional Theory (DFT) studies provide insights into the coordination environment and stability of metal-ligand complexes, supporting the experimental extraction data.

6. DGA-Based Dendrimers: Higher generation dendrimers (with more DGA arms) show significantly higher extraction efficiencies for trivalent metal ions compared to lower generations. This is due to the increased number of binding sites and higher lipophilicity.

7. Room Temperature Ionic Liquids (RTILs): Extraction studies in RTILs reveal different trends compared to molecular solvents, often showing enhanced extraction for certain metal ions due to the unique solvation and complexation environment provided by RTILs.

8. Thermodynamic and Entropic Contributions: The extraction processes are often entropy-driven, with preorganization of DGA arms on scaffolds leading to favorable entropy changes and higher metal ion selectivities.

9. Application Potential: The findings highlight the potential for developing efficient and selective ligands for the extraction and separation of trivalent lanthanides and actinides, crucial for nuclear waste management and other applications.

Conclusion

1. Enhanced Extraction Efficiency:

- DGA ligands anchored in multiple numbers on different scaffolds show significantly enhanced extraction efficiency due to preorganized ligand structures and higher hydrophobicity from long alkyl chains on DGA arms.

- Trends in Am and Eu extraction with different benzene-substituted DGA derivatives align with DFT study explanations.

2. Role of Room Temperature Ionic Liquids (RTILs):

- Significant enhancement in the extraction of trivalent actinide and lanthanide ions in RTILs compared to molecular diluents is likely due to different operative extraction mechanisms in these media.

3. Comparison of DGA Ligands:

- Generally, higher extraction for Eu  compared to Am  with DGA-based ligands, except for TREN-DGA where Am  extraction is superior in RTIL medium.

- Trends in extraction of Am  and Eu  by different calix[4]arenes with DGA units were confirmed by single-phase complexation studies and DFT-based calculations.

4. High Separation Factors

- The highest separation factor for Eu  over Am  was achieved with a DGA-substituted pillar[5]arene (P5DGA) in 1-octanol.

- Rationally designed ligands with multiple DGA moieties on suitable supramolecular scaffolds have significant potential for recognizing and separating trivalent actinides and lanthanides.

5. Application in Sensor Development

- Ligands showing high affinity for trivalent actinides and lanthanides could be used to develop sensors for detecting and estimating these radiotoxic elements in environmental samples with high sensitivity.

- Potential application in separating radiotoxic elements from nuclear waste solutions using membrane-based techniques, which require very small ligand inventories.

**Relevance to Study**

Enhanced Extraction Efficiency: Multiple DGA ligands significantly enhance the extraction efficiency of trivalent actinides and lanthanides due to the preorganization of ligating sites and increased hydrophobicity from long alkyl chains on the DGA arms .

Selectivity Improvement: Grouping DGA units on a single scaffold improves selectivity for certain

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ions, especially UO2 , which is critical for developing suitable ligands for nuclear waste management .

Scaffold Variety: Different scaffolds (e.g., C- and N-pivot tripodal backbones, benzene-centered tripodal backbones, calix[4]arene, pillar[5]arene, and azamacrocycle scaffolds) and dendrimers with DGA arms were evaluated for their efficiency in extracting trivalent actinides and lanthanides .

Room Temperature Ionic Liquids (RTILs): The use of RTILs significantly enhances the extraction of trivalent actinides and lanthanides compared to molecular diluents due to different extraction mechanisms .

High Separation Factors: The highest separation factor for Eu  over Am  was achieved with a DGA-substituted pillar[5]arene (P5DGA) in 1-octanol. This demonstrates the potential for designing ligands with multiple DGA moieties for effective recognition and separation of trivalent actinides and lanthanides .

Sensor Development: Ligands with high affinity for trivalent actinides and lanthanides can be used to develop sensors for detecting and estimating these radiotoxic elements in environmental samples with high sensitivity .

Membrane-Based Techniques: Some extractants may be applied in membrane-based techniques to separate radiotoxic elements from nuclear waste solutions, achieving separation with very small ligand inventories .

**Critical Parameters Identified**

High Importance

1. Chemical Stability

- Preorganization of Ligands: The preorganization of multiple DGA arms on molecular scaffolds enhances the chemical stability of the ligands, ensuring they remain functional under the chemical

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conditions present in nuclear fuel reprocessing.

- Scaffold Types: Different scaffolds (e.g., C- and N-pivot tripodal backbones, benzene-centered tripodal backbones, calix[4]arene, pillar[5]arene, azamacrocycle scaffolds) were evaluated for their chemical stability in extracting trivalent actinides and lanthanides.

2. Radiolysis Resistance

- RTILs Stability: The use of room temperature ionic liquids (RTILs) provides a medium that is radiolytically more stable than molecular solvents, enhancing the resistance of the ligands to radiation-induced degradation.

3. Thermodynamics

- Entropy-Driven Processes: The extraction processes are highly entropy-driven, with preorganization of DGA arms on scaffolds leading to favorable entropy changes and higher metal ion selectivities.

- DFT Studies: Density Functional Theory (DFT) studies provide insights into the stability and binding strength of metal-ligand complexes, supporting the experimental extraction data.

Medium Importance

1. Kinetics

- Extraction Kinetics: The study does not directly focus on the kinetic aspects, but the enhanced extraction efficiency implies favorable kinetics for the separation process.

2. Loading Capacity

- Higher Generation DGA-Dens: DGA-functionalized poly(propylene imine) diaminobutane dendrimers of higher generations show significantly higher extraction efficiencies due to the increased number of binding sites, indicating high loading capacity.

3. Operational Condition Rnage

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- RTILs vs. Molecular Solvents: Different extraction behaviors were observed in RTILs compared to molecular solvents, suggesting that these ligands can operate under a broad range of conditions.
- Varying Spacer Lengths and Substituents: Spacer lengths and the nature of substituents on DGA arms affect the extraction efficiency, indicating the ligands' adaptability to various operational conditions.

Low Importance

1. Solubility

- RTILs and Solubility: The enhanced extraction in RTILs suggests that solubility can be managed through the selection of appropriate solvents.

2. Dispersion Numbers

- Not Specifically Addressed: The study does not specifically address dispersion numbers, as it focuses more on the extraction efficiency and selectivity of the ligands.

3. Phase Disengagement

- Membrane-Based Techniques: Potential application in membrane-based techniques for separating radiotoxic elements suggests that phase disengagement is considered but not a primary focus of the study.