REFERENCE: 20033

Key Words

heterocycles

ligands

actinides

solvent extraction

lanthanides

Objective

1. Development of Selective Ligands:

- Synthesize and develop ligands for the selective separation of actinides from lanthanides in nuclear waste streams.

- Focus on heterocyclic soft N- and S-donor ligands.

2. Enhance Radiolytic Stability

- Improve the radiolytic stability of ligands through design, ensuring they remain effective under radiation exposure.

3. Industry Application:

- Develop ligands that exhibit desirable qualities for industrial use, including high efficiency and selectivity in the separation processes.

4. European Nuclear Waste Strategy:

- Contribute to the future European strategy for nuclear waste management by providing effective separation methods.

5. Comprehensive Review:

- Summarize the current status and advancements in actinide/lanthanide separation technologies globally.

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- Present the synthesis, development, and testing of various classes of ligands in Europe over the past 20 years.

6. Address Long-term Waste Management

- Reduce the environmental and economic burden of long-term nuclear waste management by facilitating the partitioning and transmutation of actinides.

Methodology

1. Ligand Synthesis:

- A series of 1,2,4-triazine-containing N-heterocycles were synthesized via condensation of hydrazonamides with 1,2-diketones. Hydrazonamides were prepared by reacting hydrazine with pyridine-2-carbonitrile or dithiooxamide.
- Pyridine-2-carbonitriles were synthesized by oxidizing parent pyridines with hydrogen peroxide in acetic acid or m-CPBA in CH_2Cl_2, followed by a modified Reissert Henze reaction of the resulting pyridine N-oxides

2. Testing and Evaluation:

- The synthesized ligands were evaluated for their ability to partition actinides from lanthanides using solvent extraction methods.
- Laboratory-scale SANEX (Selective Actinide Extraction) processes were designed and implemented using tetrapropyl- and tetraisopropyl-substituted BTPs (Bis-Triazinyl Pyridines)
- BTPs were immobilized on silica-based resins and supported liquid membranes to enhance separation efficiency

3. Radiolytic Stability and Hydrolysis Resistance:

- The study focused on improving the radiolytic stability of the ligands by adding radical scavengers, such as nitrobenzene, to the organic phase

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- The resistance of ligands to acid-catalyzed hydrolysis was also tested under various conditions

4. Complex Formation and Characterization

- Surface tension measurements were conducted to determine the concentration of ligands at the phase interface and their effect on extraction rates.
- Ligand-metal complexes were characterized using X-ray crystallography and spectroscopic techniques to determine their structures and stability

5. Process Development

- Efforts were made to develop more efficient and scalable synthesis methods for 3,3,6,6-tetramethylcyclohexane-1,2-dione, a key precursor for BTP ligands, to facilitate industrial-scale production
- The extraction performance of various ligands was tested in different diluents and acidities to optimize conditions for actinide/lanthanide separation

Key Findings

1. Ligand Synthesis and Structural Characterization:

- A series of N-heterocyclic ligands were synthesized and their structures confirmed using X-ray crystallography and spectroscopic techniques.
- The formation of 1:2 complexes with $Eu(NO_3)_3$ was observed, marking the first characterization of lanthanide bis-complexes with these ligands

2. Extraction Efficiency and Selectivity:

- BTPhen ligands showed higher extraction rates for Am(III) compared to Eu(III) due to their higher concentrations at the phase interface.
- Tetrapentyl-substituted BTBP (105) and other BTPs exhibited significant selectivity for Am(III) over Eu(III) in a variety of organic diluents. The most effective diluent for rapid extraction kinetics was

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cyclohexanone

3. Radiolytic Stability

- Ligands such as CyMe4-BTBP (107) and MF2-BTBP (108) demonstrated good stability under low doses of gamma irradiation. However, the extraction efficiency decreased significantly under higher doses due to degradation of the ligands

- The design of ligands with tertiary butyl groups improved resistance to radiolytic degradation, but some synthetic challenges remained

4. Thermodynamics of Extraction:

- The extraction of Am(III) was thermodynamically more favorable than Eu(III), with more negative Gibbs free energy values.

- Studies indicated that Am(III) could be effectively back-extracted using glycolic acid, allowing for a continuous extraction process

5. Impact of Hydrolysis

- Some BTP ligands were susceptible to acid-catalyzed hydrolysis and radiolytic degradation, limiting their industrial applicability. Additives like nitrobenzene improved their stability by acting as radical scavengers

6. Effect of Ligand Concentration and Metal Oxidation States:

- The extraction efficiency of BTBP ligands increased with ligand concentration and decreased with higher acid concentrations due to competing protonation.

- Different BTBP ligands showed varying extraction efficiencies for different actinides and lanthanides based on their oxidation states, with Am(III) generally exhibiting higher extraction efficiency compared to other metals

7. Solvent Extraction Studies:

- Laboratory-scale SANEX processes using tetrapropyl- and tetraisopropyl-substituted BTPs were successfully implemented. These ligands showed promising results in separating Am(III) from Ln(III), especially when immobilized on silica-based resins

Relevance to Study

Selective Extraction: The article emphasizes the development of ligands that exhibit high selectivity for actinides (e.g., Am(III) and Cm(III)) over lanthanides (e.g., Eu(III)), which is critical for the efficiency of nuclear waste reprocessing .

Radiolytic Stability: Ligands such as CyMe4-BTBP have been designed to resist radiolytic degradation, an essential property for ligands used in the highly radioactive environment of nuclear fuel reprocessing .

Thermodynamic Favorability: The study shows that the extraction of Am(III) is thermodynamically more favorable than Eu(III), which supports the development of ligands that can effectively differentiate between these metals based on thermodynamic properties .

Hydrolytic Stability: Ligands must resist hydrolysis in acidic conditions. The article reports that CyMe4-BTBP and related ligands maintain stability in acidic environments, making them suitable for the acidic conditions of nuclear fuel reprocessing .

Process Development: The research includes the demonstration of laboratory-scale SANEX processes using developed ligands, highlighting their practical applicability in nuclear waste management .

Ease of Synthesis: The article describes improvements in the synthesis methods for key ligand precursors, facilitating the production of these ligands on an industrial scale, which is important for their commercial viability .

Environmental Considerations: The ligands are designed to comply with the CHON principle, meaning they are composed only of carbon, hydrogen, oxygen, and nitrogen, ensuring they can be completely incinerated at the end of their life cycle, thus minimizing secondary waste generation .

Critical Parameters Identified

High Importance

1. Chemical Stability

- Ligands such as CyMe4-BTBP and BTPs have been designed to resist acid-catalyzed hydrolysis, ensuring their longevity and functionality in the highly acidic conditions of nuclear fuel reprocessing .
- Additives like nitrobenzene have been shown to enhance the stability of these ligands by acting as radical scavengers, further ensuring their chemical stability .

2. Radiolysis Resistance:

- The study highlights the radiolytic stability of ligands such as CyMe4-BTBP, which maintain their extraction efficiency even under high doses of gamma irradiation, a crucial property for their use in radioactive environments .
- Design modifications, such as the incorporation of tertiary butyl groups, have been implemented to improve the resistance of ligands to radiolytic degradation .

3. Thermodynamics

- The extraction process for Am(III) is thermodynamically more favorable than for Eu(III), with more negative Gibbs free energy values, indicating stronger binding and higher selectivity for actinides .
- The study provides detailed thermodynamic data showing that the ligands form more stable complexes with actinides compared to lanthanides, which is fundamental for effective separation .

Medium Importance

1. Kinetics

- The kinetics of extraction are influenced by ligand concentration and acid concentration, with optimal conditions ensuring efficient and rapid separation processes. Higher ligand concentrations improve extraction rates .

- The study also addresses the need for rapid back-extraction (stripping) of the metal ions, highlighting the practical reversibility of the process .

2. Loading Capacity:

- Although not explicitly detailed, the efficiency of the ligands in terms of how much material can be processed before saturation is implied through their high extraction efficiencies and selectivity ratios .

3. Operational Condition Range

- Ligands such as BTPs and BTPhen demonstrate the ability to operate under various conditions, including different acid concentrations and the presence of synergists, indicating their flexibility and broad applicability in nuclear fuel reprocessing .

- The study notes the importance of ligands being effective in highly acidic solutions, up to 1 M HNO_3, which is relevant for industrial applications .

Low Importance

1. Solubility:

- The solubility of ligands in different organic diluents is addressed, with certain ligands showing higher efficiency in solvents like cyclohexanone. However, this property is less critical as it can be managed through solvent selection .

2. Dispersion Numbers:

- The efficiency of mass transfer between phases is not specifically addressed in this study, making it less relevant compared to other factors.

3. Phase Disengaement

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- Practical aspects of phase separation after extraction are not a major focus of this study, as it primarily deals with the chemical and radiolytic properties of the ligands .