

Key Words

actinide selectivity

radiochemical stability

hydrophilic ligands

nuclear fuel cycle

TODGA

Objective

1. **Develop Hydrophilic Ligands:** Synthesize a series of hydrophilic 2,6-bis-triazolyl-pyridines that can efficiently strip actinides from a diglycolamide-containing kerosene solution into an acidic aqueous phase.
2. **Evaluate Actinide Selectivity:** Demonstrate and quantify the selectivity of these ligands for actinides over lanthanides, which is crucial for effective nuclear waste treatment and recycling.
3. **Assess Chemical and Radiolytic Stability:** Investigate the chemical stability and resistance to radiolytic degradation of these ligands under harsh conditions typical of nuclear reprocessing environments.
4. **Examine Kinetics of Extraction:** Measure the extraction kinetics to ensure that the ligands can achieve equilibrium quickly, making them practical for industrial applications involving short contact times.
5. **Support a Closed Nuclear Fuel Cycle:** Contribute to the development of advanced separation processes that are fundamental for closing the nuclear fuel cycle, thereby reducing waste volume, long-term radiotoxicity, and decay heat of the final nuclear wastes.

Methodology

REFERENCE: 20038

1. Synthesis of Ligands:

- Synthesized a series of ligands based on the pyridine-2,6-bis(1H-1,2,3-triazol-4-yl) (PyTri) chelating motif.
- Used classical CuAAC (Copper-Catalyzed Azide-Alkyne Cycloaddition) conditions to prepare ligands 1 and 2 by clicking 2,6-diethynyl-pyridine with azides.
- Prepared ligand 3 through a similar cycloaddition reaction starting from tris-acetylated azide, followed by Zemplen deprotection.

2. Characterization of Ligands:

- Characterized the synthesized ligands using Nuclear Magnetic Resonance (NMR) and Electrospray Ionization Mass Spectrometry (ESI-MS) techniques.
- Evaluated the solubility of the ligands in water and diluted nitric acid solutions.

3. Extraction Experiments:

- Conducted liquid-liquid extraction tests to assess the potential of these ligands for the selective extraction of actinides.
- Measured distribution coefficients (DM values) of Eu(III), Am(III), Cm(III), and Pu(IV) using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), alpha, and gamma spectrometry.
- Compared extraction efficiency and selectivity using different ligand concentrations and in the presence of a TODGA-based organic phase.

4. Kinetics and Stability Studies:

- Evaluated the kinetics of extraction by shaking the organic and aqueous phases for different time periods and measuring the DM values to determine equilibrium times.
- Investigated the chemical stability of the ligands under acidic conditions and high temperatures.
- Assessed radiolytic stability by irradiating the ligand solutions up to 200 kGy using a ^{60}Co source and measuring the retention of extracting capability a

5. Complexation Studies:

- Studied the stoichiometry and stability of metal-ligand complexes through liquid-liquid extraction tests at different ligand concentrations and ESI-MS experiments in homogeneous solutions.
- Determined stability constants for Am(III), Pu(IV), and Eu(III) complexes with the ligands using UV-vis titrations.

6. Recycling and Recovery Tests:

- Conducted batch experiments to assess the recycling potential of the ligands and the recovery of actinides by re-extraction with fresh TODGA-based solutions.

Key Findings

1. High Actinide Selectivity:

- The hydrophilic 2,6-bis-triazolyl-pyridines ligands demonstrated high selectivity for actinides (such as Am(III), Cm(III), and Pu(IV)) over lanthanides (e.g., Eu(III)).
- Ligand 1 showed particularly high selectivity, with separation factors ($SF_{Eu/Am}$) of 144, 100 for ligand 2, and 57 for ligand 3.

2. Effective Extraction and Stripping:

- The ligands efficiently stripped actinides from a TODGA-containing kerosene solution into an acidic aqueous phase.
- In i-SANEX and GANEX processes, ligands 1 and 2 effectively coextracted actinides in different oxidation states with high efficiency and selectivity.

3. Rapid Extraction Kinetics:

- The extraction kinetics were fast, with equilibrium achieved within 5 minutes, making the ligands suitable for industrial applications involving short contact times.

4. Chemical and Radiolytic Stability

REFERENCE: 20038

- The ligands exhibited high chemical stability under acidic conditions and high temperatures, essential for nuclear reprocessing environments.
- Radiolytic stability tests showed that ligand 1 remained effective even after being irradiated up to 200 kGy, with minimal degradation and retention of extracting capability.

5. High Loading Capacity and Recycling

- The ligands displayed high loading capacity for actinides, crucial for efficient separation processes.
- The recycling potential of the ligands was demonstrated, with successful recovery of actinides by re-extraction using fresh TODGA-based solutions.

6. Complexation and Selectivity Mechanism:

- The higher stoichiometry observed for Am-ligand complexes compared to Eu-ligand complexes contributed to the high selectivity.
- Stability constants for Am(III), Pu(IV), and Eu(III) complexes indicated a stronger affinity of the ligands for actinides over lanthanides.

7. Practical Implications for Nuclear Fuel Cycle:

- The study suggests that the competitive TODGA-PyTri system, leveraging the lower affinity of TODGA for actinides and higher affinity of the triazole derivatives for Am(III) and Pu(IV), could lead to significant advancements in nuclear waste treatment and the closure of the nuclear fuel cycle.

Relevance to Study

High Selectivity for Actinides: Demonstrates ligands' ability to selectively bind actinides (Am, Cm, Pu) over lanthanides, which is crucial for effective separation processes in nuclear waste treatment.

Chemical and Radiolytic Stability: Highlights ligands' stability under acidic conditions and high radiation doses, ensuring long-term functionality in harsh nuclear reprocessing environments.

Fast Kinetics: Shows that the ligands achieve equilibrium quickly, making them suitable for industrial

REFERENCE: 20038

applications with short residence times in separation devices.

Water Solubility: Ensures that the ligands can operate effectively in aqueous phases, which is essential for their application in liquid-liquid extraction processes.

Practical Application in Separation Processes: Supports the implementation of advanced separation processes such as i-SANEX and GANEX, aimed at improving the efficiency and sustainability of the nuclear fuel cycle.

Critical Parameters Identified

High Importance

- 1. Chemical Stability:** The study demonstrates that the hydrophilic 2,6-bis-triazolyl-pyridines ligands maintain chemical stability under acidic conditions and high temperatures, which are typical in nuclear fuel reprocessing environments.
- 2. Radiolysis Resistance:** The ligands showed high radiolytic stability, with ligand 1 remaining effective even after exposure to radiation doses up to 200 kGy. This ensures that the ligands can resist degradation under the radioactive conditions present during nuclear waste processing.
- 3. Thermodynamics:** The thermodynamic properties, including stability constants for Am(III), Pu(IV), and Eu(III) complexes, were investigated. The ligands exhibited a higher affinity for actinides compared to lanthanides, demonstrating favorable thermodynamics for selective actinide extraction.

Medium Importance

- 1. Kinetics:** The extraction kinetics were rapid, achieving equilibrium within 5 minutes. This quick equilibrium is essential for practical applications, ensuring efficient separation within the short residence times in industrial devices.
- 2. Loading Capacity:** The ligands displayed a high loading capacity for actinides, crucial for

REFERENCE: 20038

processing significant amounts of nuclear waste before the ligands become saturated. This efficiency is essential for large-scale applications.

3. Operational Condition Range: The ligands were effective under a range of conditions, including different nitric acid concentrations and radiation doses. This flexibility enhances their applicability in various nuclear fuel reprocessing scenarios.

Low Importance:

1. Solubility: The ligands were hydrophilic and soluble in water and diluted nitric acid solutions, ensuring their applicability in aqueous phases. While important, solubility can be managed through solvent selection.

1. Dispersion Numbers: This study does not specifically address dispersion numbers, which are more relevant to system-specific mass transfer efficiencies.

3. Phase Disengagement: Phase disengagement was not a primary focus of this study. The ligands' ability to operate effectively in liquid-liquid extraction processes suggests satisfactory phase disengagement, but detailed evaluations would depend on specific system designs and operation parameters.