

Key Words

uranium

thorium

extraction

ligandsphenanthroline

carboxamide

complexation

nitrate

solvent

separation

efficiency

stability

constants

coordination

acid

Objective

1. Design and Synthesis of Ligands: Develop and synthesize new unsymmetrical acidic phenanthroline carboxamide ligands (DEAPA and DOAPA) based on the hard-soft combination strategy to improve the selective extraction of uranium(VI) over thorium(IV).
2. Extraction Efficiency: Investigate the extraction efficiency, selectivity, kinetics, and stripping performance of these ligands in nitric acid solutions to evaluate their practical application potential.
3. Complexation Mechanism: Systematically study the complexation mechanism of DEAPA and DOAPA with uranium(VI) and thorium(IV) using various techniques such as slope analysis, NMR

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spectrometric titration, UV-vis spectrophotometric titration, and single-crystal X-ray diffraction.

4. Coordination Behavior: Analyze the coordination behavior of these ligands with uranium(VI) and thorium(IV) to understand the structure-activity relationship and the reasons for their selective extraction capabilities.

5. Practical Application: Provide insights into the design of new ligands for the efficient separation of uranium(VI) from thorium(IV), which can improve the utilization efficiency of nuclear fuel and promote the safety of thorium-based fuel cycles

Methodology

Chemicals: Uranyl(VI) nitrate, thorium(IV) nitrate, 1,10-phenanthroline-2,9-dicarboxylic acid, tetraethylammonium nitrate (Et₄NNO₃), and other chemical reagents were purchased with analytical purity (AR) and used without further purification.

Synthesis

1. 2,9-(Dimethoxycarbonyl)-1,10-phenanthroline: React 1,10-phenanthroline-2,9-dicarboxylic acid with thionyl chloride in methanol, heat, reflux, and purify.
2. 9-(Methoxycarbonyl)-1,10-phenanthroline-2-carboxylic Acid: React the product from step 1 with KOH in methanol, stir, acidify, filter, and dry.
3. 9-(N,N-Dioctylcarbamoyl)-1,10-phenanthroline-2-methoxycarbonyl: React the product from step 2 with thionyl chloride, then with di-n-octylamine and triethylamine, chromatograph, and dry.
4. DOAPA: React the product from step 3 with KOH in methanol, acidify, filter, and dry.
5. DEAPA: Substitute di-n-octylamine with diethylamine in step 3.

Solvent Extraction: Perform liquid liquid extraction experiments at 298 ± 1 K using DEAPA/DOAPA in n-octanol and uranyl(VI) nitrate/thorium(IV) nitrate solutions. Determine metal ion concentrations

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using ICP OES/ICP MS.

Stripping Experiments: Use 1 M H_2SO_4 , Na_2CO_3 , HCl , and HNO_3 for stripping. Contact U(VI)/Th(IV)-loaded phase with stripping agents in three stages to investigate efficiency.

^1H NMR Spectrometric Titration: Prepare DOAPA, uranyl(VI) nitrate, and thorium(IV) nitrate stock solutions in CD_3OD /DMSO- d_6 . Add stock solutions to NMR tubes with varying M/L ratios and record spectra.

UV-Vis Spectrophotometric Titration: Determine pK_a and stability constants of U(VI) and Th(IV) complexes with DOAPA and DEAPA. Record absorption spectra and obtain stability constants using HyperSpec.

Single-Crystal X-ray Diffraction Measurements: Obtain single crystals of DEAPA with U(VI) and Th(IV) complexes by solvent diffusion and analyze with X-ray diffraction to determine complex mechanisms.

Key Findings

1. Solvent Extraction:

Efficiency and Selectivity: DEAPA and DOAPA demonstrated high efficiency in extracting uranium(VI) from thorium(IV). DOAPA showed a significantly higher distribution ratio ($D_{\text{U(VI)}} = 1566$) at 4 M HNO_3 compared to DEAPA ($D_{\text{U(VI)}} = 4$).

Acidity Influence: The extraction efficiency increased with higher nitric acid concentrations, particularly for DOAPA.

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Extraction Kinetics: Equilibrium was achieved rapidly, within 1 minute for DEAPA and 4-6 minutes for DOAPA.

Selective Extraction: The separation factor ($S_{FU(VI)/Th(IV)}$) was very high for DOAPA (1582), indicating excellent selectivity for uranium over thorium.

2. Stripping Experiments:

Stripping Agents: Th(IV) was more easily stripped compared to U(VI) using 1 M H_2SO_4 , Na_2CO_3 , HCl, and HNO_3 .

Selective Stripping: 1 M HNO_3 was particularly effective in selectively stripping Th(IV), leaving most U(VI) in the organic phase.

Efficiency: Three-stage stripping with 1 M HNO_3 resulted in over 98% of Th(IV) remaining in the aqueous phase while retaining 95% of U(VI) in the organic phase.

3. 1H NMR Spectrometric Titration

Complex Formation: DOAPA formed a 1:1 complex with U(VI) and both 1:1 and 1:2 complexes with Th(IV). This was evident from the NMR spectra where new peaks indicated the formation of these complexes.

Complex Stability: The intensity of the ligand peaks decreased with the addition of metal ions, confirming the strong complexation ability of DOAPA, especially with U(VI).

4. UV-Vis Spectrophotometric Titration

Stability Constants: The stability constants ($\log K$) indicated a stronger affinity of the ligands for U(VI) over Th(IV). For example, DOAPA showed a $\log K$ of 6.91 for U(VI) compared to 6.19 for Th(IV).

Complex Species: The titration data fit models indicating the presence of multiple species, with the

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isosbestic points suggesting equilibrium between different complexes.

5. Single-Crystal X-ray Diffraction Measurements

Coordination Geometry: U(VI) formed an eight-coordinated complex with DEAPA, while Th(IV) formed complexes with coordination numbers of 10 and 12.

Structural Analysis: The X-ray diffraction data provided detailed insights into the coordination environment, showing that the carboxylic acid group played a significant role in the strong complexation with U(VI).

Complex Stability: The bond lengths in the complexes confirmed that the interaction between the ligands and U(VI) was stronger than with Th(IV), explaining the higher extraction efficiency for U(VI).

Relevance to Study

Improved Efficiency and Selectivity: The study demonstrates that the newly synthesized ligands (DEAPA and DOAPA) provide high efficiency and selectivity in the extraction of uranium(VI) from thorium(IV). This is crucial for optimizing the nuclear fuel cycle, particularly in thorium-based fuels where separation processes are essential.

Structural Insights: Detailed structural analysis using single-crystal X-ray diffraction reveals the coordination behavior of these ligands with uranium and thorium. Understanding these interactions helps in designing ligands with better performance characteristics for nuclear applications.

Stability and Complexation: The findings on the stability constants and complexation behavior of the ligands with U(VI) and Th(IV) support the selection of ligands that form stable complexes, enhancing the safety and efficiency of the nuclear fuel cycle.

Application in Thorex Process: The research supports the application of these ligands in the Thorex (thorium-uranium extraction) process, which is pivotal for the reprocessing of thorium-based nuclear

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fuel. Efficient separation of uranium from thorium helps in recycling and reducing nuclear waste.

Environmental and Safety Considerations: The study emphasizes the use of ligands that avoid the secondary pollution associated with organophosphorus extractants, aligning with environmental and safety goals in nuclear chemistry.

Insight into Functional Group Effects: By systematically studying the effect of different functional groups on ligand performance, the research provides a foundation for selecting and designing ligands that can meet the specific requirements of the nuclear fuel cycle.

Critical Parameters Identified

High Importance

Chemical Stability: The ligands (DEAPA and DOAPA) exhibit excellent stability under high acidity conditions (up to 4 M HNO₃). This chemical stability ensures that the ligands remain functional over the required duration of the separation process and under the chemical conditions present in nuclear fuel reprocessing.

Radiolysis Resistance: Although not directly studied, the implication is that the synthesized ligands' strong binding and structural properties might confer some resistance to radiolysis, crucial for processing radioactive materials. Future studies could confirm this aspect.

Thermodynamics: The thermodynamic parameters, including stability constants ($\log K$), indicate strong and selective binding of U(VI) over Th(IV). This high selectivity and strong binding are fundamental for the feasibility of the separation processes.

Medium Importance

Kinetics: The study found that the extraction equilibrium for DEAPA is achieved in 1 minute and for DOAPA in 4-6 minutes. Efficient kinetics ensure that the separation process occurs within practical

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time frames.

Loading Capacity: The high distribution ratios ($DU(VI) = 1566$ for DOAPA) suggest a high loading capacity, meaning the ligands can process significant amounts of uranium before becoming saturated.

Operational Condition Range: The ligands are effective across a broad range of nitric acid concentrations (0.1 to 4 M HNO_3). This flexibility in operating conditions increases the applicability of the separation process.

Low Importance

Solubility: While solubility issues were noted (e.g., DEAPA's limited solubility in water), they were manageable within the experimental setup using appropriate solvents.

Dispersion Numbers: The study did not specifically address dispersion numbers. This parameter is more system-specific and was not a primary focus in evaluating ligand performance.

Phase Disengagement: Similar to dispersion numbers, phase disengagement was not a primary focus of this study. The practical separation of phases was implied but not detailed.