

## **Key Words**

selective separation

Am(III)

Eu(III)

QL-DAPhenLigand

high acidity

extraction

spectroscopy

theoretical calculations

separation factor (SF<sub>Am/Eu</sub>)

coordination chemistry

## **Objective**

1. Development of a New Ligand: The primary objective is to synthesize a novel tetradentate amide ligand, 2,9-diacyl-bis((3,4-dihydroquinoline-1(2H)-yl)-1),10-phenanthroline (QL-DAPhen), which can be used to selectively extract trivalent actinides (Am(III)) from lanthanides (Eu(III)) under high acid conditions.
2. Improvement of Extraction Efficiency: The study aims to enhance the extraction efficiency and selectivity of the QL-DAPhen ligand for Am(III) over Eu(III) in high acidity environments (HNO<sub>3</sub> solution).
3. Spectroscopic and Theoretical Analysis: To investigate the coordination chemistry and extraction mechanism of the QL-DAPhen ligand with Eu(III) through various spectroscopic techniques (NMR titration, UV-vis titration, FT-IR spectroscopy, and ESI-MS) and theoretical calculations (DFT).
4. Thermodynamic Stability: To determine the stability constants and thermodynamic advantages of

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the 1:1 and 1:2 complex species formed between the ligand and Eu(III).

5. Bond Characteristics: To analyze the covalent nature of the Am-N bonds compared to Eu-N bonds, which explains the preferential bonding with Am(III).

6. Application Potential: To lay a theoretical foundation for the potential application of phenanthroline-based ligands in the separation of actinides from practical systems, thereby contributing to the development of advanced nuclear fuel cycle systems and reducing radioactive toxicity.

## Methodology

1. Preparation of Aqueous Phase: Trace amounts of  $^{241}\text{Am(III)}$  or  $\text{Eu(III)}$  were added to  $\text{NaNO}_3$  (1 M) solutions with different nitric acid concentrations (0.5–4 M).

2. Preparation of Organic Phase: The organic phase was prepared by dissolving a certain concentration of QL-DAPhen in 3-nitrobenzotrifluoride.

3. Extraction Process: An equal amount (usually 1.0 mL) of aqueous solution and organic phase was mixed and shaken vigorously at  $25 \pm 1^\circ\text{C}$  for 30 minutes in a constant-temperature oscillator to reach extraction equilibrium.

4. Measurement of Am(III): The  $\alpha$ -ray activity of  $^{241}\text{Am(III)}$  in the aqueous solution before and after extraction was determined by a low-background  $\alpha$ -scintillation detector. The distribution ratio ( $D$ ) was calculated by the ratio of the radioactive counts of the organic phase to the aqueous phase after extraction.

5. Measurement of Eu(III): The concentration of  $\text{Eu(III)}$  was determined by ICP-OES, and the distribution ratio ( $D$ ) was calculated by the ratio of the concentration in the organic phase to the aqueous phase. The separation factor ( $\text{SF}_{\text{Am/Eu}}$ ) was calculated by the distribution ratio of  $^{241}\text{Am(III)}$  to  $\text{Eu(III)}$ .

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6. ESI-MS Study: The species changes of the complexes formed by QL-DAPhen and Eu(III) at different concentration ratios were studied by MS titration using the positive ion mode on ESI-MS.
7. UV-Vis Spectroscopy Study: The coordination behavior of QL-DAPhen with Eu(III) in a methanol/water solution was determined by UV-vis spectrophotometry, and the absorbance was measured at 240 500 nm. The data were processed and fitted using the HypSpec program.
8.  $^1\text{H}$  NMR Spectroscopy Titration: Titration solutions were prepared by dissolving QL-DAPhen ligand and lanthanum nitrate in  $\text{CD}_3\text{CN}/\text{CDCl}_3$ . The spectra were recorded on a Bruker Avance III model 500 MHz instrument after ultrasonication for 2 minutes to ensure complexation balance.
9. Computational Studies: The complexation behaviors of Am(III) and Eu(III) with QL-DAPhen were optimized using density functional theory (DFT) with BP86 functional and RECPs for Am and Eu atoms. Harmonic vibrational frequencies were calculated to confirm the optimized structures as local minima. Solvation energies in aqueous and 3-nitrotrifluorotoluene solutions were calculated using the COSMO model.
10. Solvent Extraction Studies: The effect of nitric acid concentration on the extraction of Am(III) and Eu(III) was investigated, and the distribution ratios and separation factors were determined under different conditions, such as solution acidity, contact time, concentration of  $\text{NaNO}_3$ , and concentration of the ligand.

## Key Findings

### Solvent Extraction Studies

#### 1. Effect of Nitric Acid Concentration:

- The distribution ratios of Am(III) and Eu(III) increased with nitric acid concentration up to 3 M, where maximum values were observed ( $D_{\text{Am}} = 17$  and  $D_{\text{Eu}} = 0.37$ ). This indicates good acid adaptability of the ligand QL-DAPhen.

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- The separation factor ( $SF_{Am/Eu}$ ) exceeded 30 across a wide range of acidity, showing high selectivity for Am(III) over Eu(III) .

### 2. Extraction Kinetics:

- The extraction equilibrium for both Am(III) and Eu(III) was reached in about 5 minutes, which is faster compared to other phenanthroline-based ligands that typically reach equilibrium in 20 minutes.

- This rapid equilibrium may be attributed to the large quinoline group enhancing the ligand's preorganization capabilities .

### 3. Effect of Nitrate Ion Concentration:

- The distribution ratio of Am(III) increased with nitrate ion concentration up to 0.8 M, indicating involvement of nitrate ions in the extraction process.

- Beyond 1 M  $NaNO_3$ , the distribution ratio stabilized, possibly due to the competitive effect of  $Na^+$  ions offsetting the nitrate ions' promotion effect .

## Spectroscopy Studies

### 1. FT-IR Spectroscopy

- The FT-IR spectra of QL-DAPhen and its complex with Eu(III) showed distinct peaks, confirming complex formation. Key peaks for the amide group were identified, providing insights into the ligand's structure .

### 2. ESI-MS Study

- Mass spectrometry identified the formation of 1:1 and 1:2 complexes between QL-DAPhen and Eu(III), supporting the presence of these species in the organic phase during extraction .

### 3. UV-Vis Spectroscopy Study:

- UV-Vis titration confirmed the formation of 1:1 and 1:2 complexes between QL-DAPhen and

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Eu(III). Stability constants were calculated ( $\log [EuL] = 5.2$  and  $\log [EuL_2] = 9.4$ ), indicating that the 1:1 species is more stable .

### 4. NMR Titration Spectroscopy Analysis:

- NMR titration using La(III) as a diamagnetic substitute for Eu(III) demonstrated the formation of LaL<sub>2</sub> and LaL complexes, corroborating the UV-Vis and MS findings .

## Theoretical Calculations

### 1. DFT Calculations

- Density Functional Theory (DFT) calculations revealed that Am-N bonds in the complexes have more covalent characteristics compared to Eu-N bonds, explaining the ligand s preferential binding with Am(III) .

- Gibbs free energy changes for the reactions indicated that the 1:1 metal/ligand complex ML(NO<sub>3</sub>)<sub>3</sub> is the predominant species in the extracted organic phase. The calculated G values aligned well with experimental results .

## Conclusion

1. Synthesis and Efficiency: The novel tetradentate amide ligand QL-DAPhen was synthesized successfully. It demonstrated high efficiency and selectivity in separating trivalent actinides from lanthanides under high acidity conditions .

2. Complex Formation: Slope analysis, NMR titration, UV-Vis spectrophotometric titration, and ESI-MS studies confirmed the coexistence of 1:1 and 1:2 complex species in the organic phase. The formation of the 1:1 complex is thermodynamically more favorable under the extraction conditions .

### 3. Theoretical Support:

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- DFT calculations supported that the Am-L bonds exhibit more covalent properties than the Eu-L bonds, providing a theoretical foundation for the ligand s preferential complexation with Am(III) .
- The study illustrates the impact of tailoring ligand frameworks on species distribution during extraction, offering valuable insights for designing effective actinide extractants .

### Relevance to Study

**High Selectivity for Actinides:** The study demonstrates that the QL-DAPhen ligand exhibits high selectivity for Am(III) over Eu(III) in nitric acid solutions, which is crucial for effective separation processes in nuclear fuel reprocessing

**Acid Stability:** The ligand shows excellent stability in high acidity environments (up to 3 M HNO<sub>3</sub>), which is important for handling the highly acidic conditions typically found in nuclear waste solutions

**Rapid Extraction Kinetics:** The extraction equilibrium for both Am(III) and Eu(III) is reached within 5 minutes, which is significantly faster than other phenanthroline-based ligands. This can improve the efficiency of the separation process in industrial applications

**Complex Formation:** The QL-DAPhen ligand forms stable 1:1 and 1:2 complexes with Eu(III), as confirmed by various spectroscopic techniques and theoretical calculations. This stability is beneficial for maintaining the integrity of the ligand during the extraction process

**Thermodynamic Advantages:** Thermodynamic analysis indicates that the formation of the 1:1 complex is more favorable under the extraction conditions, providing insights into optimizing the ligand design for better performance

**Covalent Bond Characteristics:** Density Functional Theory (DFT) calculations reveal that the Am-N bonds in the complexes have more covalent characteristics compared to Eu-N bonds, explaining the preferential binding with Am(III). This understanding can guide the development of new ligands with enhanced selectivity

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Tailoring Ligand Frameworks: The study illustrates that modifying the ligand framework, such as incorporating a quinoline group, can significantly impact species distribution and extraction efficiency. This information is valuable for designing more effective ligands for nuclear fuel cycle applications.

### Critical Parameters Identified

#### High Importance

**Chemical Stability:** The QL-DAPhen ligand shows excellent stability in high acidity environments, maintaining its functionality in up to 3 M HNO<sub>3</sub>, which is essential for nuclear fuel reprocessing.

**Radiolysis Resistance:** The study does not explicitly address radiolysis resistance, which is crucial for ligands used in radioactive environments. However, the stability in high acidity suggests a robust chemical structure that might withstand radiolysis, but this would need specific evaluation.

#### Thermodynamics:

- Thermodynamic analysis indicates that the 1:1 complex formation is more favorable under extraction conditions, suggesting strong and selective binding to Am(III) over Eu(III).
- Gibbs free energy changes for the reactions confirm the feasibility and efficiency of the separation process, supporting the ligand's high selectivity and binding strength.

#### Medium Importance

**Kinetics:** The extraction equilibrium for both Am(III) and Eu(III) is reached within 5 minutes, indicating rapid and efficient kinetics, which is beneficial for practical separation processes.

**Loading Capacity:** The study does not directly address the loading capacity, but the ability to form stable complexes with both 1:1 and 1:2 stoichiometries suggests good capacity for metal ion binding.

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Operational Condition Range: The ligand operates effectively in a broad range of nitric acid concentrations (0.5-4 M), demonstrating flexibility and applicability in various reprocessing conditions

### Low Importance

Solubility: The QL-DAPhen ligand is soluble in 3-nitrobenzotrifluoride, and the solubility can be managed by selecting appropriate solvents and conditions

Dispersion Numbers: The study does not provide specific information on dispersion numbers, which would be relevant for mass transfer efficiency in specific system setups.

Phase Disengagement: While the study does not explicitly discuss phase disengagement, the clear separation of organic and aqueous phases during extraction experiments implies effective phase disengagement under the studied conditions