

## **Key Words**

actinide partitionng

PyTri-Ethyl-Hexyl-PTEH

electrospray ionization mass spectrometry (ESI-MS)

time-resolved laser fluorescence spetroscopy (TRLFS)

selective actinide extraction (SANEX)-like processes

## **Objective**

1. Investigate the Complexation Behavior of PyTri-Ethyl-Hexyl\_PTEH Ligand
2. Explore the Ligand's selectivity towards actinides over lanthanides
3. employ advanced analytical techniques for ligand investigation
4. assess the potential for large-scale implementation

## **Methodology**

1. Chemicals
2. ESI-MS Sample Preparation (monophasic solutions, extraction samples)
3. ESI-MS Measurements
4. TRLFS Sample Preparation (titrations, extraction tests)
5. TRLSF Measurments
6. NMR Sample Preparation
7. NMR Measurements

## **Key Findings**

1. ESI-MS: Investigations of La(III) and Eu(III) Speciation with PTEH

## REFERENCE: 20037

- Identification of complex species: ESI-MS spectra showed the formation of several complex species between La(III) or Eu(III) and the PTEH ligand. Notably a dominant species was the mono charged  $1:2[\text{ML}_2(\text{NO}_3)_2]^+$  complex for both La(III) and Eu(III), where M represents the metal ion
- Stoichiometry of complexes: the analyses identified different stoichiometries of metal-ligand complexes, including 1:1, 1:2, and 1:3 M/L ratios. The  $1:2[\text{ML}_2(\text{NO}_3)_2]^+$  species was particularly highlighted for its intensity and presumed stability
- influence of acidity: experiments conducted w/o  $\text{HNO}_3$  demonstrated that the acidity of the solution had a negligible effect on the complexation mechanism, confirming that the observed species formed independently of the nitric acid presence
- variation with  $[\text{L}]:[\text{M}]$  ratios: changing the ligand-to-metal ( $[\text{L}]:[\text{M}]$ ) ratio from 1 to 10 did not show a significant alteration in the speciation spectrum, although there was a noticeable decrease in the stability of lower stoichiometry complexes and a variation in the relative intensity of detected species
- Eu(III) Complexation Similarities and Differences: similar to La(III), Eu(III) formed a dominant  $1:2[\text{EuL}_2(\text{NO}_3)_2]^+$  complex, w/ minor species indicating the potential for Eu(II) complexes. Highlighted the formation of a more pronounced  $1:3[\text{EuL}_3(\text{NO}_3)]^{2+}$  complex for Eu(III) compared to La(III)
- complex formation in different media: explored the formation of La(III) and Eu(III) complexes w/ PTEH in both monophasic soln containing 3M  $\text{HNO}_3$  and in the absence of  $\text{HNO}_3$ , confirming the formation of similar complex species across different conditions. underscores the robustness of the complexation mechanism against changes in the acidic environment
- detailed analysis of La(III) complexes: for La(III), investigation provided specific insights into stoichiometry and mass-to-charge ratios ( $m/z$ ) of the formed complexes.  $[\text{La}(\text{NO}_3)_2\text{L}_2]^+$  complex at  $m/z$  1137.5 was identified as a significant species, with detailed fragmentation patterns supporting

## REFERENCE: 20037

its structure and stoichiometry

- specific species and m/z values: for Eu(III), specific species were identified along w their m/z values, such as the 1:2[Eu(NO<sub>3</sub>)L<sub>2</sub>]<sup>2+</sup> complex at 544.8, and the 1:3 [Eu(NO<sub>3</sub>)L<sub>3</sub>]<sup>2+</sup> complex at m/z 763.4, among others. findings emphasize the specificity of the ESI-MS technique in resolving complex species at the molecular level
- impact of ligand concentration: highlights the effect of varying the ligand-to-metal ratio on the observed complex species and their relative intensities. an increase in the ligand concentration shifted the equilibrium towards higher stoichiometry complexes, indicating the ligand's capability to form multiple coordination sites w/ the metals
- comparative analysis of La(III) and Eu(III) Speciation: by comparing complexation behavior of La(III) and Eu(III) w PTEH, the study not only identified commonalities in their complexation patterns but also pointed out differences in their preferences for specific stoichiometries. the comparative analysis provides a deeper understanding of the ligand's selectivity towards different lanthanides
- confirmation through mass spectrometry techniques: use of tandem MS/MS techniques further confirmed the composition and structure of the identified complexes, showcasing the utility of ESI-MS in providing molecular-level insights into the complexation behavior of the ligand with lanthanides

## 2. TRLFS: Complexation of Cm(III) and Eu(III) with PTEH

- Formation of Multiple Complex Species: Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) analysis revealed the formation of several complex species between PTEH and both Cm(III) and Eu(III), specifically identifying complexes with stoichiometries of 1:1, 1:2, and 1:3 (M/L ratios).
- Identification of Dominant Complexes: The study identified the [Cm(PTEH)<sub>3</sub>]<sup>3+</sup> and [Eu(PTEH)<sub>3</sub>]<sup>3+</sup> complexes as the dominant species at higher ligand concentrations for both Cm(III)

## REFERENCE: 20037

and Eu(III), indicative of a strong interaction and stable complex formation.

- **Stability Constants Determination:** Logarithmic conditional stability constants ( $\log K'$ ) for the complexes were calculated, highlighting the strong binding affinity between PTEH and the actinides/lanthanides. The values for Cm(III) were higher compared to those for Eu(III), suggesting a stronger complexation of PTEH with Cm(III).
- **Selective Complexation of Actinides Over Lanthanides:** The study provided evidence of the selective complexation behavior of PTEH towards actinides over lanthanides, based on the higher stability constants for Cm(III) complexes. This selectivity is critical for the application of PTEH in actinide-lanthanide separation processes.
- **Spectral Shifts Upon Complexation:** TRLFS data showed spectral shifts upon complexation, which were used to monitor the complexation process and the formation of different species over a range of ligand concentrations.
- **Complexation Mechanism Insights:** The complexation reactions and the associated stability constants offer insights into the molecular mechanisms driving the complexation of Cm(III) and Eu(III) with PTEH, providing a basis for understanding how PTEH can be used in selective extraction processes.
- **Fluorescence Spectrum Evolution:** The evolution of fluorescence spectra with increasing PTEH concentration indicated a stepwise replacement of water molecules in the inner coordination sphere of Cm(III) and Eu(III) by PTEH molecules. This led to distinct spectral shifts that signify the formation of new complex species, showcasing the detailed interaction dynamics between the metal ions and the ligand.
- **Species Distribution Analysis:** The quantitative analysis of species distribution, based on fluorescence spectra deconvolution, allowed for the precise determination of the fractions of different complex species formed at various ligand concentrations. This analysis revealed the

## REFERENCE: 20037

predominance of higher stoichiometry complexes ( $[\text{Cm}(\text{PTEH})_3]^{3+}$  and  $[\text{Eu}(\text{PTEH})_3]^{3+}$ ) at increased ligand concentrations, further confirming the ligand's capacity to form stable complexes with both Cm(III) and Eu(III).

- **Determination of Conditional Stability Constants:** The conditional stability constants for each identified complex species were determined, providing valuable information on the thermodynamics of the complexation reactions. The higher stability constants for complexes involving Cm(III) compared to Eu(III) highlighted the ligand's greater affinity for actinides, supporting its potential utility in the selective separation of actinides from lanthanides in nuclear waste management.

- **Implications for Nuclear Waste Reprocessing:** The results from the TRLFS study, particularly the ligand's selectivity for actinides over lanthanides and the determination of stability constants, have significant implications for the development of more efficient and selective methods for the reprocessing of spent nuclear fuel. This can lead to improved strategies for the recycling of valuable actinides and the reduction of radioactive waste.

- **Theoretical Separation Factor:** The study provided a theoretical separation factor based on the differences in stability constants between Cm(III) and Eu(III) complexes, quantifying the selectivity of PTEH for actinides over lanthanides. This factor is crucial for evaluating the efficiency of PTEH in separating actinides from lanthanides in practical applications.

### 3. Conclusions

- **Promising Selectivity of PTEH:** The study concluded that 26-bis(2-ethylhexyl-1H-123-triazol-4-yl)pyridine (PTEH) demonstrates promising extracting performances, making it a potential candidate for a regular-Selective Actinides EXtraction (SANEX) process aimed at extracting actinides from spent nuclear fuel.

- **Complexation Behavior and Metal/Ligand Stoichiometry:** ESI mass spectrometry provided initial insights into the metal/ligand stoichiometry, identifying specific complexes formed upon

## REFERENCE: 20037

complexation with PTEH. Notably, the 1:2  $[ML_2(NO_3)_2]^+$  complex was identified as a significant species for both La(III) and Eu(III).

- Dominant Complex Species and Stability Constants: Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) analyses revealed the formation of  $[Cm(PTEH)_3]^{3+}$  and  $[Eu(PTEH)_3]^{3+}$  as the dominant species, with stability constants indicating a strong binding affinity and selectivity of PTEH towards actinides over lanthanides.

- NMR Spectroscopy Insights: NMR spectroscopy provided insights into the bonding of PTEH with Lu(III) and Am(III), highlighting significant differences in chemical shifts for the coordinating nitrogen atoms, which suggest a higher covalent bond character in the Am(III) complex. This finding underpins the ligand's selectivity towards actinides.

- Potential for Large-Scale Implementation: The study encourages the consideration of PTEH for potential large-scale implementation in advanced nuclear fuel reprocessing strategies, based on its extraction efficiency, remarkable actinide selectivity, fast extraction kinetics, and good radiochemical stability.

- Advancement in Nuclear Waste Reprocessing Technologies: The findings contribute to the development of more sustainable and efficient methods for managing spent nuclear fuel by enhancing the selectivity and efficiency of actinide-lanthanide separation processes.

## Relevance to Study

- \*- Demonstrating Ligand Effectiveness: Shows the effectiveness of PyTri-Ethyl-Hexyl-PTEH as a selective ligand for actinide partitioning from spent nuclear fuel, relevant for improving separation processes.

- Highlighting Selectivity Towards Actinides: Provides evidence of the ligand's selectivity for actinides over lanthanides, a crucial characteristic for efficient reprocessing and recycling of nuclear

## REFERENCE: 20037

fuel.

- Advancing Reprocessing Technologies: Supports the development of advanced nuclear fuel reprocessing technologies, specifically through the potential implementation of SANEX-like processes using the ligand.
- Offering Insights into Complexation Mechanisms: Offers detailed insights into the complexation mechanisms and stability of metal-ligand complexes, aiding in the understanding of ligand behavior in nuclear waste management.
- Facilitating Sustainable Nuclear Waste Management: Contributes to efforts in making nuclear energy more sustainable by enhancing the efficiency and selectivity of spent nuclear fuel reprocessing and reducing long-term radio-toxicity.

### Critical Parameters Identified

#### High Importance

- Chemical Stability: The study's focus on the complexation behavior of PyTri-Ethyl-Hexyl-PTEH under various conditions (with and without HNO<sub>3</sub>) indirectly touches upon its chemical stability in the reprocessing environment.
- Radiolysis Resistance: While not directly addressed, the investigation into the ligand's performance in a nuclear context suggests an underlying consideration of its radiolysis resistance.
- Thermodynamics: The determination of stability constants for metal-ligand complexes directly relates to the thermodynamics of the separation process, highlighting the ligand's selectivity and binding affinity which are crucial for thermodynamic feasibility.

#### Medium Importance

- Kinetics (forwards and reverse): The study's analysis, especially using TRLFS to monitor complexation over time, gives insights into the kinetics of ligand-metal interaction, albeit not explicitly

## REFERENCE: 20037

focusing on forward and reverse kinetics.

- Loading Capacity: While not specifically quantified, the examination of different metal-ligand stoichiometries and the ligand's ability to form stable complexes suggest implications for the ligand's loading capacity.
- Operational Condition Range: Investigations into ligand complexation in the presence and absence of nitric acid and at various ligand-to-metal ratios hint at the operational condition range, showcasing the ligand's adaptability to different chemical environments

### Low Importance

- Solubility: Indirectly referenced through the study's methodology and experimental setups, solubility is implied as a factor in the ligand's effectiveness, though it is not the main focus.
- Dispersion Numbers (for applied systems with conditional values): This aspect is not directly covered in the study, as the focus is more on molecular-level interactions rather than system-wide physical properties.
- Phase Disengagement (for applied systems with conditional values): Similar to dispersion numbers, phase disengagement is outside the scope of this detailed chemical investigation, focusing instead on the ligand's chemical and physical interactions with target metals.

### Primary Categories

- Chemical Parameters
- Process Parameters
- Physical Parameters