Key Words

AmSel

Am/Cm separation

SO3-Ph-BTBP

TODGA

BTBP

Objective

1. Develop a new process for the selective separation of americium (Am(III)) from curium (Cm(III)) and lanthanides (Ln(III)) in the PUREX (Plutonium-Uranium Recovery by Extraction) raffinate.

2. Investigate the use of N,N,N ,N -tetraoctyl-diglycolamide (TODGA) for coextracting actinides (An(III)) and lanthanides (Ln(III)).

3. Utilize a water-soluble bis-triazinyl-bipyridin ligand (sodium 3,3 ,3 ,3 -([2,2 -bipyridine]-6,6 -diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate, SO3-Ph-BTBP) for the selective stripping of Am(III).

4. Achieve high selectivity for Am(III) over Cm(III) and Ln(III) in acidic conditions using nitric acid as the aqueous phase without additional salting out agents.

Methodology

Methodology

Aqueous Phase:

- Consisted of 241Am(III), 244Cm(III), 152Eu(III) (1kbq/ml each)

- Included 6 mg/L of each Y(III) and La(III)   Lu(III) in either 20 mmol/L SO3-Ph-BTBP in nitric acid (varied concentrations) or in 0.5 mol/L nitric acid with varied SO3-Ph-BTBP concentrations.

Organic Phase

- Composed of 0.2 mol/L TODGA + 5 vol.% 1-octanol in Exxsol D80 (a kerosene diluent).

- Octan-1-ol was added to avoid third phase formation.

Procedure:

- A mixture of 500 L aqueous and 500 L organic phase was shaken on a vortex shaker (40 Hz) for 30 minutes.

- Phases were separated after centrifugation.

- 241 Am and 152Eu activities were measured using a gamma counter

- Alpha activies of 241Am and 244Cm were determined by alpha spectroscopy

- Organic samples for alpha spectroscopy were stripped into 0.5 mol/L ammonium glycolate (pH = 4) (A = 10), and aqueous samples were diluted by a factor of 10 using 0.5 mol/L ammonium glycolate (pH = 4) before measurement.

- Y(III), La(III), and Ce(III) Lu(III) were determined by ICP-MS, with ammonium glycolate solutions diluted by a factor of 100 with 2% HNO3 (suprapure).

Stripping Kinetics

Loading the Prganic Phase:

- the organic phase was loaded with 241Am(III) and 152Eu(III) (1kBq/mL each) by extraction from 3 mol/L nitric acid

- 500 L of this loaded organic phase was contacted with an aqueous phase consisting of 20 mmol/L SO3-Ph-BTBP in 0.29 mol/L HNO3.

- The resulting nitric acid concentration was approximately 0.5 mol/L after stripping.

Shaking Devices:

- Two different shakers (40 Hz and 5 Hz) were used, with varying contacting times to observe equilibrium.

Chemicals

- SO3-Ph-BTBP was synthesized as described by M llich et al.

- Other chemicals (e.g., lanthanide nitrates) were purchased from Alfa Aesar or Sigma Aldrich and used as received.

- 244Cm(III) stock solution for TRLFS studies contained 3.34×10^{-6} mol/L 244Cm(III) in 15.7 mmol/L HCl04

- For 152Eu(III) TRLFS studies, a stock solution of 1.1 mmol/L Eu(ClO4)3 in 10 mmol/L HClO4 was used.

- Radionuclides were taken from laboratory stock.

- All solutions were prepared with ultrapure water (Millipore, Billerica, USA; 18.2 M cm).

TRLFS Setup

- TRLFS studies were performed using a Nd laser-pumped dye laser system with a repetition rate of 10 Hz.

- A wavelength of 396.6 nm was used for the excitation of 244Cm(III) and 394nm for 152Eu(III)

- Spectral decomposition was done by a spectrograph with 1199 lines mm-1 grating, recorded by an ICCD camera with an integrated delay controller.

- The fluorescence signal was detected after a delay time of 1 s to discriminate short-lived fluorescence of organic compounds.

Preparation of TRLFS Samples

- Analogous to batch extraction experiments, with the aqueous phase consisting of 20 mmol/L SO3-Ph-BTBP and 1×10^7 mol/L 244Cm(III) or 5×10^{-6} mol/L 152Eu(III) in 0.5mol/L HNO3

- The organic phase consisted of 0.2 mol/L TODGA + 5 vol.% 1-octanol in Exxsol D80.

- Aliquots (500 L) of each phase were contacted for 30 minutes and separated after centrifugation.

- Both aqueous and organic phases were then investigated separately by TRLFS.

Precipitation Test

- The organic phase consisted of 0.2 mol/L TODGA + 5 vol.% 1-octanol in Exxsol D80 was contacted with an aqueous phase containing various concentrations of lanthanides and nitric acid.

- The presence of any precipitate was observed and noted to ensure it did not interfere with the process.

Key Findings

1. Selective Separation:

- The AmSel system successfully demonstrated the selective separation of Am(III) from PUREX raffinate using TODGA for coextraction of An(III) and Ln(III), followed by selective stripping of Am(III) with SO3-Ph-BTBP.

- Achieved a selectivity factor of SFCm(III)/Am(III) 2.5 due to the inverse selectivity of TODGA and SO3-Ph-BTBP.

2. Efficiency:

- The separation factor for Eu(III) from Am(III) reached up to 1200, indicating a high degree of separation efficiency.

- The system performed well under acidic conditions (using nitric acid as the aqueous phase) without the need for additional salting out agents.

3. Stripping Kinetics:

- Stripping of Am(III) by SO3-Ph-BTBP was efficient, with equilibrium reached within 7 minutes using a fast shaker (40 Hz) and within 15 minutes using a slower shaker (5 Hz).

4. Nitric Acid Influence

- the distribution ratios of Am(III), Cm(III), and Eu(III) increased with rising nitric acid concentration

due to increased formation of the M(TODGA)33 complex.

- High separation factors between Ln(III) and An(III) were observed at 0.5 mol/L HNO3, with SFEu(III)/Am(III)=600.

5. SO3-Ph-BTBP Concentration:

- Increasing SO3-Ph-BTBP concentration led to a decrease in distribution ratios, with separation factors SFCm(III)/Am(III) in the range of 2.5 3.

- TRLFS studies confirmed the formation of 1:2 M(III)-BTBP complexes in the aqueous phase during extraction.

6. Ln(III) Behavior:

- Light Ln(III) showed a linear increase in distribution ratios with increasing nitric acid concentration.

- Heavy Ln(III) displayed a non-linear trend, with distribution ratios initially increasing and then dropping at higher nitric acid concentrations.

7. Precipitation Issues:

- Initial experiments with high M(III) concentrations led to precipitation, which did not dissolve even after 7 days.

- No precipitation was observed at process conditions in subsequent experiments, suggesting that precipitation is not expected to impede the AmSel process.

8. AmSel Process Viability:

- The inverse selectivities of SO3-Ph-BTBP and TODGA were effective, with SFCm(III)/Am(III) 2.5 and high separation factors between Am(III) and Ln(III).

- The AmSel process was considered a promising alternative to existing processes for Am(III)-only separation due to its robustness and lack of need for additional chemicals.

Relevance to Study

Innovative Separation Process:

- Presents a new system (AmSel) for selectively extracting americium (Am(III)) from PUREX raffinate, highlighting the need for effective ligands in nuclear fuel reprocessing.

Use of TODGA and SO3-Ph-BTBP:

- Demonstrates the use of N,N,N ,N -tetraoctyl-diglycolamide (TODGA) for coextracting actinides (An(III)) and lanthanides (Ln(III)).

- Utilizes a water-soluble bis-triazinyl-bipyridin (SO3-Ph-BTBP) for selective stripping of Am(III), showing the importance of ligand selectivity and stability in acidic conditions.

Selectivity and Efficiency:

- Highlights the high selectivity factor for Am(III) over Cm(III) and Ln(III), critical for efficient ligand design.

- Achieves a separation factor up to 1200 for Eu(III) from Am(III), demonstrating the potential of these ligands for effective separation processes.

Robustness in Acidic Conditions:

- The system works well even in acidic conditions (nitric acid), a common environment in nuclear fuel reprocessing, underlining the need for ligands that maintain functionality under such conditions.

Absence of Additional Salting Agents:

- Does not require additional salting out agents, indicating the potential for simplified processing and reduced chemical use.

Stripping Kinetics and Distribution Ratios:

- Provides insights into the kinetics of ligand stripping and the influence of nitric acid concentration on distribution ratios, essential for understanding ligand performance in real-world applications.

Precipitation Behavior:

- Investigates the precipitation behavior of Ln(III) complexes, emphasizing the need for ligands that

avoid precipitation issues in process conditions.

Hydrophilic and Hydrophobic Ligands:

- Combines hydrophilic (SO3-Ph-BTBP) and hydrophobic (TODGA) ligands, demonstrating the complementary roles different ligands can play in enhancing separation efficiency.

Critical Parameters Identified

High Importance

1. Chemical Stability:

- The study confirms that the AmSel process works well in acidic conditions using nitric acid as the aqueous phase without the need for additional salting out agents. This indicates chemical stability of the ligands under these conditions.

- No significant precipitation issues were observed at process conditions, suggesting that the ligands maintain their stability and functionality throughout the separation process.

2. Radiolysis Resistance:

- The article does not specifically address radiolysis resistance, but the use of ligands in the context of nuclear fuel reprocessing implies a need for ligands that can withstand radiation. Further studies would be needed to explicitly confirm radiolysis resistance.

3. Thermodynamics:

- The selectivity factor for Am(III) over Cm(III) and the high separation factor for Eu(III) from Am(III) indicate favorable thermodynamic properties. The ability to achieve high selectivity and binding strength is crucial for the feasibility of the separation process.

Medium Importance

1. Kinetics:

- Stripping kinetics were efficient, with equilibrium reached within 7 minutes using a fast shaker and within 15 minutes using a slower shaker. This demonstrates that the separation process can occur within practical time frames and suggests reversibility.

2. Loading Capacity:

- The study does not explicitly discuss loading capacity. However, the ability to achieve high separation factors and maintain functionality in the presence of multiple metal ions suggests that the ligands can handle significant loading before saturation.

3. Operational OCndition Range:

- The ligands were tested under varying concentrations of nitric acid, demonstrating their ability to operate effectively across a range of acidic conditions. This flexibility enhances the applicability of the separation process.

Low Importance

1. Solubility:

- While initial experiments showed some precipitation at high M(III) concentrations, no precipitation was observed at typical process conditions. This suggests that solubility issues are manageable under the conditions tested.

2. DIspersion Numbers:

- The study does not provide specific information on dispersion numbers. This parameter is less critical in the context of the findings presented.

3. Phase Disengagement

- Phase disengagement was not a primary focus of this study. The separation and measurement techniques used indicate that phase disengagement was successfully achieved, but detailed analysis would be needed for specific system designs.