REFERENCE: 20004

Key Words

solvent extraction

intra-lanthanides

Tri(n-butyl)phosphate (TBP)

N,N,N',N'-tetra(n-octyl)diglycolamide (TODGA)

ionic liquid (IL)

trivalent lanthanides

nitric acid solutions

electrically neutral extractants

metal ion extraction

intra-lanthanide ion selectivity

cationic exchange

synergism

distribution ratio (DM)

extraction efficiency

neuclear fuel reprocessing

Objective

1. Invetigate Synergistic Effects: To evaluate the potential synergistic effect between TBP and TODGA in an ionic liquid (IL) medium and determine the optimal ratio of these extractants for enhanced extraction efficiency of lanthanides.
2. Extraction Mechanism: To elucidate the underlying extraction mechanism when using a combination of TBP and TODGA in the IL, focusing on cationic exchange and neutral complex extraction.

REFERENCE: 20004

3. Efficiency Comparison: To compare the extraction efficiencies of lanthanides using the TBP/TODGA/IL system with those using TBP/TODGA in conventional molecular solvents like nonane.

4. Selectivity Studies: To study the selectivity of the TBP/TODGA/IL system towards different lanthanides and determine separation factors for pairs of lanthanides (e.g., Lu/La, Lu/Sm, Lu/Tb).

5. Impact of Nitric Acid: To investigate the effect of varying nitric acid concentrations on the extraction behavior of lanthanides in the TBP/TODGA/IL system.

6. Environmental Considerations: To explore the use of an IL as a more environmentally benign diluent compared to conventional molecular solvents for the extraction process.

7. Structural Analysis: To analyze the chemical structure of extracted lanthanide complexes using TBP and TODGA in IL and conventional solvents.

8. Separation System Development: To contribute to the development of novel, highly efficient separation systems for lanthanides applicable to nuclear fuel reprocessing and metal recycling.

9. Comparison with Previous Studies: To compare the findings with prior studies on similar extraction systems to validate results and identify improvements.

10. Experimental Validation: To perform experimental validation of the extraction process under different conditions and verify reproducibility.

11. Advanced Techniques: To suggest further studies using advanced techniques like synchrotron small-angle X-ray scattering and molecular dynamics calculations for a deeper understanding of the extraction mechanism

12. Optimization: To optimize the TBP/TODGA/IL system for maximum extraction efficiency and selectivity.

13. Role of Ionic Compounds: To understand the role of IL components, particularly the hydrophobic anionic entities, in the extraction mechanism.

REFERENCE: 20004

14. Evaluation of Synergistic Factor: To calculate the synergistic factor for the TBP/TODGA/IL system and compare it with individual extractants to quantify the enhancement in extraction efficiency.

15. Interaction Studies: To study the interactions between metal ions, extractants, and IL components to identify the factors contributing to high extraction efficiency and selectivity.

Methodology

1. Materials:

- TODGA: Prepared, purified, and characterized according to the published method by Sasaki and Choppin.

- TBP and Ionic Liquid ([C4mim][Tf2N]): Purchased from Sigma-Aldrich.

- Ln(III) Salts: Used as supplied

- Nitric Acid (HNO3): Analytical grade concentrared nitrixc acid (65 wt%) from Merck

- Molecular Diluents: Nonane and 1,2-dichloroethane (DCE), used without further purification

- Aqueous Solutions: Prepared using distilled water and conentrated acid

2. Solvent Extraction Procedure:

- Preparation: Stock Ln(III) solution was prepared by dissolving metal nitrate salt to an initial aqueous concentration of 2x10-6 M

- Organic Phase: Prepared by dissolving measured quantities of TODGA and/or TBP in [C4mim][Tf2N], DCE, or nonane

- Mixing: A 1:1 volume ratio of organic and aqueous phases was employed. The biphasic mictures were shaken vigorously using a rotor mizer at 60rpm for 1hr to achieve equilibrium.

- Phase Separation: Promoted by centrifuging the extraction tubes, followed by sampling aliquots of each phase for further analysis.

REFERENCE: 20004

- Distribution Ratio Calculation (DM): Defined as the concentration of the metal ion in the organic phase to that in the aqueous phase, [M]org/[M].

- Reproducibility: Duplicate experiments showed reproducibility of the DM measurements within 10%.

- Metal Ion Concentration Analysis: Conducted using inductively coupled plasma mass spectrometry (ICP-MS) with an X-7 mass spectrometer (Thermo Electron, USA).

3. Additional Experimental Details:

- Experiments were conducted at room temperature (20 25 C).

- Some distribution experiments were performed using Eu(III) as a representative trivalent lanthanide.

- Selectivity studies were conducted with various trivalent lanthanides.

Key Findings

1. Eu(III) Extraction by TODGA and/or TBP

- Efficiency: The distribution ratio (DEu) of Eu(III) with 0.01 M TODGA in nonane is significantly higher (104.7) compared to the same concentration in [C4mim][Tf2N] IL (5.9). This indicates higher extraction efficiency in nonane.

- TBP Alone: TBP in [C4mim][Tf2N] IL shows negligible Eu(III) extraction efficiency (DEu ~0.045).

- Synergistic Effect: A mixture of 0.01 M TODGA and 1.1 M TBP in [C4mim][Tf2N] IL significantly enhances extraction efficiency (DEu ~6.5), indicating a synergistic effect between TODGA and TBP.

- Comparison with TBP: When comparing the distribution ratios, TODGA in nonane shows the highest efficiency, but the combination of TODGA and TBP in IL provides a notable synergistic improvement compared to using TBP alone

2. Effect of HNO3 Concentration on Eu(III) Extraction by TODGA and/or TBP

REFERENCE: 20004

- HNO3 Dependence: For TODGA/TBP in nonane, DEu increases with increasing HNO3 concentration, indicating nitrate anions and/or nitric acid molecules play a crucial role.

- Ionic Liquid System: For the IL system, DEu decreases with increasing HNO3 concentration up to 4 M, then increases, suggesting a shift in the extraction mechanism from cation exchange to neutral complex formation.

- Comparison Across Systems: The differing behaviors between nonane and IL systems underscore the unique extraction mechanisms at play, with IL showing a complex dependency on acid concentration that involves cation exchange and neutral complex extraction

3. Intra-lanthanide Selectivity with TODGA and/or TBP Extractants

- General Trend: Distribution ratios increase across the lanthanide series for solvent phases composed of TODGA in molecular solvents.

- Enhancement by TBP: Adding TBP to TODGA in IL enhances extraction efficiency, particularly for middle and heavy lanthanides. The TODGA/TBP/IL system shows significantly higher selectivity (e.g., Lu/La separation factor of 1622) compared to other systems.

- Separation Factors: The separation factors for Lu/La, Lu/Sm, and Lu/Tb in the TODGA/TBP/IL system are 1622, 45, and 4.8, respectively. This demonstrates the system's superior selectivity for heavy lanthanides

4. Stoichiometry of Extraction Metal Complexes with TODGA and TBP Ligands:

- Slope Analysis: Slope analysis of logDM versus log[TODGA] indicates the number of TODGA molecules associated with light lanthanides (La, Ce, Pr) is close to 2.5, and 3 for other metals (Nd, Eu, Tb, Ho, Lu).

- Mechanisms: Higher extraction efficiencies in the IL-based system are explained by the exchange between cationic metal-organic ligand species and IL cations, and/or ion pairing with Tf2N and NO3 anions.

REFERENCE: 20004

- Inner and Outer Coordination: The study suggests that Tf2N anions are likely involved in the outer coordination sphere of the extracted lanthanide species, affecting the extraction efficiency and selectivity

Relevance to Study

High Extraction Efficiency: The study demonstrates that the combination of TBP and TODGA in an ionic liquid significantly enhances the extraction efficiency of lanthanides, which is critical for effective separation processes in nuclear fuel reprocessing .

Synergistic Effects: The research highlights the synergistic effects between TBP and TODGA, leading to improved metal ion extraction and selectivity, which can optimize ligand selection strategies in nuclear applications .

Ionic Liquid as Diluent: Using ionic liquids (ILs) as diluents instead of conventional solvents reduces environmental impact and enhances the stability and efficiency of the extraction process, aligning with the principles of green chemistry in nuclear fuel cycles .

Selectivity Improvement: The study shows enhanced selectivity for heavy lanthanides using TODGA/TBP/IL systems, which is essential for the selective recovery of specific elements in nuclear fuel reprocessing .

Mechanistic Insights: Detailed mechanistic insights into the extraction processes, including cation exchange and neutral complex formation, provide a deeper understanding necessary for designing efficient extraction systems for nuclear materials .

Environmental Considerations: The use of ILs as more environmentally benign solvents supports the development of safer and more sustainable extraction methods in nuclear chemistry .

- Optimization Potential: Findings suggest optimization strategies for ligand combinations (e.g., TODGA and TBP) that can be tailored to improve extraction performance in nuclear fuel cycle applications .

- Application to Actinide Separation: The results contribute to improving separation processes for actinides and lanthanides, which are crucial for handling nuclear waste and recycling nuclear materials .

Critical Parameters Identified

High Importance

Chemical Stability: The study investigates the stability of the extraction process in both molecular solvents and ionic liquids, highlighting the robust performance of TODGA and TBP even in highly acidic conditions (up to 7 M HNO3).

Radiolysis Resistance: While not directly addressed, the use of ionic liquids as diluents may imply enhanced radiolysis resistance due to their known stability under radiation compared to conventional organic solvents.

Thermodynamics: The study provides detailed thermodynamic insights into the extraction efficiency and selectivity of Eu(III) and other lanthanides, indicating strong binding affinities of TODGA and TBP in ILs, which are crucial for effective separation processes.

Medium Importance

Kinetics (forwards and reverse): The extraction experiments are conducted with phase contact times sufficient to reach equilibrium, implying practical kinetics for the separation process, although specific kinetic rates are not detailed.

Loading capacity: The study mentions the distribution ratios (DM) and the enhancement of extraction efficiency through synergistic effects, which indirectly relate to the loading capacity of the extraction system.

Operational Condition Range: The use of TODGA and TBP in both nonane and ionic liquids under varying nitric acid concentrations demonstrates the broad operational condition range of the extraction system, making it adaptable to different separation scenarios.

Low Importance

Solubility: The solubility of TODGA and TBP in different solvents (nonane, DCE, and ILs) is addressed, but this is not a primary focus compared to extraction efficiency and selectivity.

Dispersion Numbers (for applied systems with conditional values): Not specifically discussed in the study, making it less relevant to the primary findings.

Phase Diengagement (for applied systems with conditional values): The study mentions the use of centrifugation to promote phase separation, but this is a standard procedure and not a focal point of the research.