REFERENCE: 20040

Key Words

organophosphorus extractants

actinides/lanthides separation

tributyl phosphate (TBP)

phosphorus oxide extractants

chemical stablity

Objective

1. Examine the Application Scope of Organophosphorus Extractants: Discuss the use of specific organophosphorus extractants like tributyl phosphate (TBP), bis(2-ethylhexyl) phosphate (HDEHP), octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), trialkyl phosphine oxide (TRPO), and purified Cyanex 301 in the separation of actinides and lanthanides.
2. Analyze Extraction Mechanisms and Structure-Function Relationships: Explore the mechanisms by which these extractants work and their structure-function relationships to understand how they can effectively separate actinides from lanthanides.
3. Review Design Criteria and Properties of New Organophosphorus Extractants: Evaluate newly developed organophosphorus extractants, such as CMPO-modified calixarene/pillarene, phenanthroline-derived organophosphorus extractants, and phosphate-modified carborane, focusing on their design criteria, extraction properties, and mechanisms.
4. Identify Roles and Potential Applications in Advanced Nuclear Fuel Cycles: Emphasize the significant roles these extractants play in the current processes and identify potential applications for future advanced nuclear fuel cycle systems.
5. Address Challenges in Design and Application: Discuss unresolved challenges in the design and practical application of organophosphorus extractants for actinides/lanthanides separation,

highlighting the need for more precise studies and better understanding of extraction mechanisms at the microscopic and mesoscopic levels.

Methodology

1. Literature Review and Conceptual Analysis:

- A comprehensive review of existing literature and studies related to organophosphorus extractants is conducted.

- The scope of various organophosphorus extractants such as TBP, HDEHP, CMPO, TRPO, and Cyanex 301 is introduced, focusing on their chemical properties, extraction mechanisms, and practical applications.

2. Structural and Mechanistic Analysis:

- Detailed structural analysis of organophosphorus extractants is performed to understand their coordination chemistry and extraction efficiency.

- Mechanistic insights into the extraction process, including the formation of extracted complexes and the role of side chains and functional groups, are provided.

3. Evaluation of New Extractants:

- Newly developed organophosphorus extractants are reviewed, including CMPO-modified calixarene/pillarene, phenanthroline-derived organophosphorus extractants, and phosphate-modified carborane.

- The design criteria, extraction properties, and mechanisms of these new extractants are analyzed.

4. Comparison and Analysis of Extractant Performance:

- The performance of traditional and new organophosphorus extractants is compared based on their extraction efficiency, selectivity, and stability.

- The impact of structural modifications on the extraction ability and selectivity of these extractants is

REFERENCE: 20040

assessed.

5. Theoretical and Experimental Studies:

- Theoretical studies, including Density Functional Theory (DFT) calculations, are used to support the experimental findings and provide deeper insights into the extraction mechanisms.

-Single-crystal structure analysis and UV-vis titration studies are conducted to elucidate the coordination modes between extractants and metal ions.

6. Addressing Practical Challenges:

- Practical challenges in the application of organophosphorus extractants, such as chemical stability, radiolysis resistance, and solubility in organic solvents, are discussed.

- Suggestions for future research directions are provided to address these challenges and improve the design of high-efficiency extractants.

Key Findings

1. HA301 (Bis(2,4,4-trimethylpentyl)dithiophosphinic acid) Extractants:

- HA301 shows strong affinity for lighter lanthanides and forms 1:3 metal-to-ligand complexes.

- The extraction mechanism varies due to lanthanide contraction, with lighter lanthanides forming inner-sphere complexes and heavier lanthanides forming outer-sphere complexes.

- Problems in practical application include low operating acidity and inadequate structural stability under irradiation and acidic conditions.

- Dialkyl and diaryl substituted dithiophosphonic acid extractants were synthesized to overcome these issues, with the introduction of electron-donating groups enhancing extraction ability and electron-withdrawing groups improving selectivity between Am(III) and Ln(III).

- Synergistic extractants like TBP can enhance the extraction ability of HA301 systems .

2. Pre-Organized Organophosphorus Extractants:

REFERENCE: 20040

- The degree of pre-organization in the extractant skeleton significantly affects extraction performance, including ability, rates, and selectivity.
- Rigid structures reduce both the flexibility and the complexation ability of the extractant, but can enhance selectivity by preventing undesired interactions.
- Pillararene-based organophosphorus extractants exhibit higher extraction efficiency, better separation performance, and stronger irradiation stability compared to traditional organophosphorus extractants.
- The functional side chains on pillararenes significantly influence their extraction properties, with symmetrical anchoring at the edges improving extraction performance in both organic solvents and ionic liquids .

3. Phenanthroline-derived Organophosphorus Extractants:

- Phenanthroline-based extractants (POPhen, BPPhen, PIPhen) show strong affinity for actinides and lanthanides, but their separation ability varies.
- The structure-activity relationship is crucial for understanding and improving their performance, with factors such as side chain length and substituent groups playing significant roles.
- The introduction of phenyl-armed phosphorus oxide groups enhances extraction ability but reduces the Am(III)/Eu(III) separation factor.
- Counter anions also impact coordination ability, with some anions promoting better coordination than others .

4. Carborane-based Extractants:

- Carborane-based extractants can selectively capture and release metal ions through electrochemical adjustments of their conformation.
- An ortho-substituted nido-carborane anion demonstrates strong selective extraction for UO2^2+ ions, with its conformation changing from nido to closo to adjust coordination ability.

REFERENCE: 20040

- This selective capture-release system is effective for UO_2^{2+} over other metal ions like Cs(I), Th(IV), Sm(III), and Nd(III) .

Relevance to Study

Extraction Efficiency:

- Demonstrates the high extraction efficiency of various organophosphorus extractants such as TBP, HDEHP, CMPO, TRPO, and HA301 for actinides over lanthanides
- Highlights the importance of selecting ligands with strong extraction capabilities to achieve effective separation of actinides in nuclear fuel reprocessing

Chemical Stability:

- Discusses the chemical stability of organophosphorus extractants under harsh conditions, such as high acidity and radiation, which is crucial for maintaining their functionality during the separation process
- Presents new extractants with improved stability, such as CMPO-modified calixarene/pillarene and phenanthroline-derived organophosphorus extractants

Selectivity:

- Emphasizes the role of ligand selectivity in achieving the desired separation of actinides from lanthanides, with specific examples of extractants showing high selectivity for Am(III) over Eu(III)
- Provides insights into the design of ligands with tailored selectivity through structural modifications and the use of pre-organized skeletons

Mechanistic Understanding:

- Explores the extraction mechanisms and structure-function relationships of various organophosphorus extractants, aiding in the rational design of new ligands with enhanced performance

REFERENCE: 20040

- Combines theoretical studies, such as Density Functional Theory (DFT) calculations, with experimental data to deepen the understanding of coordination chemistry and extraction processes

Practical Applications:

- Identifies potential applications of organophosphorus extractants in advanced nuclear fuel cycles, highlighting their importance in current and future nuclear fuel reprocessing technologies

- Addresses practical challenges, such as low solubility in organic solvents and the need for synergistic extractants to enhance extraction performance

Critical Parameters Identified

High Importance

1. Chemical Stability:

- Findings:

-- The article discusses the stability of various organophosphorus extractants under different chemical conditions, highlighting the need for ligands that maintain functionality during nuclear fuel reprocessing.

-- New extractants such as CMPO-modified calixarene/pillarene and phenanthroline-derived organophosphorus extractants show improved stability under harsh conditions .

- Relevance:

-- Ensures ligands remain functional throughout the separation process.

-- Critical for long-term effectiveness in nuclear fuel reprocessing.

2. Radiolysis Resistance

- Findings:

-- The study addresses the resistance of organophosphorus extractants to radiolysis, noting that radiation stability is crucial for maintaining extraction efficiency.

REFERENCE: 20040

-- Pillararene-based extractants exhibit stronger irradiation stability compared to traditional extractants .

- Relevance:

-- Necessary for maintaining separation efficiency under radioactive conditions.

3. Thermodynamics

- Findings:

-- Thermodynamic properties of extractants, such as binding strength and selectivity towards specific metal ions, are explored using theoretical and experimental approaches.

-- The study highlights the importance of understanding the thermodynamics of extraction mechanisms to improve ligand design .

- Relevance:

-- Influences the feasibility and efficiency of separation processes.

Medium Importance

1. Kinetics

- Findings:

-- The kinetics of extraction processes, including forward and reverse reactions, are discussed.

-- Efficient kinetics are necessary for practical time frames and reversible separation processes .

- Relevance

-- Affects the speed and efficiency of the separation process.

2. Loading Capacity

- Findings:

-- Loading capacity of ligands is mentioned as an important factor for processing large volumes of material before saturation occurs.

REFERENCE: 20040

-- New extractants are evaluated for their ability to handle higher loading capacities .

- Relevance:

-- Determines how much material can be processed efficiently.

3. Operational Condition Range:

- Findings:

-- The study emphasizes the importance of ligands that can operate under a broad range of conditions, including varying acidity and temperature.

-- Extractants like TRPO and CMPO are highlighted for their broad operational ranges .

- Relevance: Increases the flexibility and applicability of the separation process.

Low Importance

1. Solubilty:

- Findings:

-- Solubility of extractants in organic solvents is discussed, with some extractants showing low solubility that can be improved through structural modifications.

-- The article notes that solubility issues can often be managed by selecting appropriate solvents .

- Relevance: Important but can be modified or managed through other means.

2. Dispersion Numbers:

- Findings:

-- The efficiency of mass transfer between phases, influenced by dispersion numbers, is mentioned as a factor in the performance of extraction systems.

-- Specific to particular system setups and less critical compared to other parameters .

- Relevance:

REFERENCE: 20040

-- Influences mass transfer efficiency but is often system-specific.

3. Phase Disengagement:

- Findings:

-- Phase disengagement is discussed as critical for the practical separation of phases after extraction.

-- Dependent on system design and operational parameters, making it less universally critical .

- Relevance: Important for practical separation but highly system-dependent.