REFERENCE: 20042

Key Words

diglycolamides

actinide partitioning

solvent extraction

TODGA

radiolytic stability

Objective

1. To review the development of diglycolamides (DGAs): The article aims to provide a historical perspective on the development of DGAs as extractants, focusing on their synthesis and characterization.

2. To highlight the complexation chemistry of DGAs: It discusses the basic complexation studies of DGAs with various metal ions, including aqueous complexation, theoretical calculations, and spectroscopic studies.

3. To evaluate the solvent extraction properties of DGAs: The article assesses the effectiveness of DGAs, particularly TODGA, in solvent extraction studies for the partitioning of actinides from nuclear waste solutions.

4. To examine the stability of DGAs: The stability of DGAs under hydrolytic and radiolytic conditions is analyzed to ensure their suitability for long-term use in nuclear waste management.

5. To explore alternative separation techniques using DGAs: The potential applications of DGAs in liquid membrane studies and extraction chromatography for actinide partitioning are investigated.

6. To provide insights into the future directions: The article outlines the future research directions that could further enhance the understanding and application of DGAs in actinide partitioning processes.

REFERENCE: 20042

Methodology

1. Synthesis and Characterization of DGAs:

- DGAs were synthesized by reacting diglycolic anhydride with secondary amines in the presence of dicyclohexylcarbodiimide (DCC).

- An alternative single-step synthesis involved reacting diglycolyl chloride with dialkyl amines in the presence of triethylamine.

- The synthesized DGAs were characterized using techniques like NMR spectroscopy to confirm their structure and purity.

2. Basic Complexation Studies:

- Aqueous complexation studies involved examining the binding affinity of water-soluble DGAs with various metal ions, including actinides.

- Spectroscopic techniques such as time-resolved laser-induced fluorescence spectroscopy (TRLFS) and extended X-ray absorption fine structure (EXAFS) were used to study the metal-ligand complexes.

- Theoretical calculations, including molecular dynamics simulations and density functional theory (DFT), were performed to understand the stability and geometry of DGA complexes with metal ions.

3. Solvent Extraction Studies:

- Solvent extraction experiments were conducted using DGAs dissolved in various organic diluents to evaluate their extraction efficiency for different metal ions, including trivalent actinides.

- The effect of different parameters, such as acid concentration, diluent nature, and the presence of phase modifiers, on the extraction behavior was systematically studied.

- Dynamic light scattering and small-angle neutron scattering (SANS) techniques were employed to investigate the aggregation behavior of DGAs in organic solvents.

4. Evaluation of Phase Modifiers:

REFERENCE: 20042

- Various phase modifiers, such as N,N-dihexyl octanamide (DHOA) and tri-n-butyl phosphate (TBP), were evaluated for their ability to prevent third-phase formation and enhance the loading capacity of DGAs.

5. Hydrolytic and Radiolytic Stability Tests:

- The hydrolytic stability of DGAs was assessed by keeping them in contact with nitric acid for extended periods and analyzing for degradation products using gas chromatography-mass spectrometry (GC-MS).
- Radiolytic stability was tested by irradiating DGA solutions with gamma rays and helium ion beams, followed by analysis of degradation products and extraction efficiency post-irradiation.

6. Countercurrent Extraction Studies

- Countercurrent extraction experiments were performed using mixer-settler units or centrifugal contactors to simulate continuous extraction processes.
- These studies involved using simulated or genuine high-level waste (HLW) solutions to evaluate the efficiency and selectivity of DGAs in removing actinides and lanthanides from the waste streams.

7. Comparative Performance Evaluation:

- The performance of DGAs was compared with other known extractants, such as CMPO, TRPO, and DMDBTDMA, in terms of their extraction efficiency, stability, and decontamination factors for actinide partitioning.

Key Findings

1. Effectiveness of DGAs:

- Diglycolamides (DGAs), particularly TODGA (Tetraoctyl diglycolamide), have demonstrated superior extraction properties for actinides and lanthanides compared to other extractants like CMPO and TRPO.

REFERENCE: 20042

2. Complexation Chemistry:

- DGAs show high affinity for trivalent actinides and lanthanides. Their complexation behavior is influenced by the nature of the diluent and the type of acid used.

- Aqueous complexation studies and spectroscopic analyses (TRLFS and EXAFS) confirmed the formation of stable metal-DGA complexes, with varying stoichiometries depending on the experimental conditions.

3. Aggregation Phenomenon:

- TODGA exhibits aggregation behavior in nonpolar solvents, forming monomers, dimers, and tetramers. The presence and size of these aggregates depend on the acidity of the aqueous phase and the polarity of the organic diluent.

4. Diluent Effect:

- The extraction efficiency of TODGA is significantly influenced by the choice of diluent. Polar diluents like 1-octanol and nitrobenzene enhance the extraction of Am(III) compared to nonpolar diluents like n-dodecane.

- The nature of the diluent affects the stoichiometry of the extracted complexes, with polar diluents favoring fewer TODGA molecules per complex.

5. Radiolytic and Hydrolytic Stability:

- DGAs, especially TODGA, exhibit excellent hydrolytic stability when in contact with nitric acid. Radiolytic stability is also high, with degradation products being minimal even after exposure to significant radiation doses.

- The addition of phase modifiers like DHOA (N,N-dihexyl octanamide) and TBP (tri-n-butyl phosphate) can further enhance the stability and performance of the extraction system.

6. Third-Phase Formation and Phase Modifiers:

- The propensity for third-phase formation in TODGA systems can be mitigated using phase modifiers such as DHOA and TBP, which increase the loading capacity and prevent the formation of unwanted phases.

- DHOA was found to be particularly effective as it does not coextract unwanted metal ions and improves the extraction capacity of TODGA.

7. Countercurrent Extraction Studies:

- Countercurrent extraction experiments using TODGA demonstrated efficient extraction and stripping of lanthanides and actinides, achieving high decontamination factors for fission products and structural elements.

- The TODGA-based processes showed promising results for actinide partitioning from genuine PUREX raffinate and simulated high-level waste solutions.

8. Comparative Performance:

- TODGA outperformed other extractants like DMDBTDMA and DMDOHEMA in terms of extraction efficiency, decontamination factors, and stability under high acidity conditions.

- The use of TODGA in combination with suitable phase modifiers presents a viable solution for the partitioning of minor actinides from high-level nuclear waste.

9. Future Directions:

- The article highlights the need for further research to optimize the composition of TODGA-based solvents and improve their performance for large-scale applications.

- Investigating alternative separation techniques such as liquid membranes and extraction chromatography with DGAs could provide additional benefits in reducing volatile organic compounds (VOCs) and secondary waste.

Conclusion

1. Hgi hExtraction Efficiency:

REFERENCE: 20042

- Diglycolamides, particularly TODGA, have shown high extraction efficiency for trivalent actinides (Am(III), Cm(III)) and lanthanides from nitric acid solutions.

2. Versatility and STability:

- TODGA exhibits excellent hydrolytic and radiolytic stability, making it suitable for long-term applications in nuclear waste management. It is effective under a wide range of conditions, including high acidity.

3. Aggregation and Solvent Effects:

- The unique aggregation behavior of TODGA in nonpolar solvents contributes to its high extraction efficiency. The extraction properties are influenced by the nature of the diluent, with polar diluents enhancing performance.

4. Use of Phase Modifiers:

- The use of phase modifiers such as DHOA and TBP can mitigate third-phase formation and improve the loading capacity of TODGA, enhancing its applicability in industrial-scale processes.

5. Comparative Advantage:

- Compared to other extractants like CMPO, TRPO, and DMDBTDMA, TODGA demonstrates superior extraction properties, stability, and decontamination factors, making it a more effective choice for actinide partitioning.

6. Process Optimization:

- The study emphasizes the need for optimizing TODGA-based solvent compositions and conditions to further enhance performance and reduce secondary waste generation.

7. Future Research Directions

- Further research is encouraged to explore alternative separation techniques using diglycolamides, such as liquid membrane studies and extraction chromatography, to improve efficiency and sustainability in radioactive waste management.

REFERENCE: 20042

Relevance to Study

High Extraction Efficiency: Diglycolamides (DGAs), particularly TODGA, exhibit high efficiency in extracting trivalent actinides (Am(III), Cm(III)) and lanthanides from nitric acid solutions, making them suitable candidates for nuclear waste reprocessing .

Stability and Versatility: TODGA demonstrates excellent hydrolytic and radiolytic stability, which are critical for maintaining performance in the harsh conditions of nuclear waste processing .

Aggregation Behavior: The unique aggregation properties of TODGA in nonpolar solvents enhance its extraction efficiency and provide insights into designing ligands with optimal performance for specific applications .

Compatability with Phase Modifiers: The use of phase modifiers like DHOA and TBP with TODGA helps prevent third-phase formation and increases the loading capacity, which is important for industrial-scale applications .

Future Research Directions: The article highlights the need for further research to optimize TODGA-based solvents and to explore alternative separation techniques such as liquid membranes and extraction chromatography, which could enhance the efficiency and sustainability of nuclear waste management processes .

Critical Parameters Identified

High Impoetance

1. Chemical Stability:

- TODGA exhibits excellent hydrolytic stability when in contact with nitric acid, maintaining functionality over long durations (Section 4.5: Stability of TODGA).

2. Radiolysis Resistance:

- TODGA shows high radiolytic stability, with minimal degradation products even after exposure to significant radiation doses (Section 4.5: Stability of TODGA).

3. Thermodynamics:

- The study of complexation chemistry and thermodynamics of DGAs highlights their high affinity and selective binding towards trivalent actinides and lanthanides (Section 3: Basic Complexation Studies with Diglycolamides).

Medium Importance

1. Kinetics:

- Kinetics of the extraction process, including the formation of metal-ligand complexes and aggregation behavior of TODGA in nonpolar solvents, affects the speed and efficiency of separation (Section 4.1: Role of Nature of Acid and Aggregation Phenomenon).

2. Loading Capacity:

- The loading capacity of TODGA, including the use of phase modifiers like DHOA to enhance loading and prevent third-phase formation, is critical for processing large volumes of nuclear waste (Section 4.4: Evaluation of Phase Modifiers).

3. Operational Condition Range:

- TODGA operates effectively under a wide range of conditions, including high acidity levels typical of nuclear waste solutions, providing flexibility in its application (Section 4.2: Effect of Nature of Diluent on Extraction of Americium).

Low Importance

1. Solubility:

- The solubility of TODGA in various organic solvents is discussed, with polar diluents enhancing extraction efficiency, but solubility can often be managed through solvent selection (Section 4.2:

REFERENCE: 20042

Effect of Nature of Diluent on Extraction of Americium).

2. Dispersion NUmbers:

- While the aggregation behavior and formation of micelles are mentioned, these aspects are specific to the system setup and have less impact on the overall importance compared to other factors (Section 4.1: Role of Nature of Acid and Aggregation Phenomenon).

3. Phase Disengagement:

- The study addresses third-phase formation and phase disengagement, but these are highly dependent on the system design and specific operational parameters