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Key Words

americium

curium

lanthanides

solvent extraction

diglycolamides

Objective

1. Investigate the impact of digicolamides: Study the effects of lipophilicity and steric hindrance of various diglycolamides on the selectivity between Americium (Am) and Curium (Cm) during solvent extraction.

2. Understand TEDGA behavior: Gain a better understanding of the behavior and role of N,N,N',N'-tetraethyl-diglycolamide (TEDGA) in enhancing Am/Cm selectivity during the EXAm process.

3. Establish structure-activity relationships: Establish a relationship between the physico-chemical properties (such as lipophilicity and steric hindrance) of diglycolamide complexing agents and their ability to selectively extract Am over Cm.

4. Evaluate extraction perfromance: Perform liquid-liquid extraction and partitioning experiments under various conditions to evaluate the performance of different diglycolamide derivatives in extracting Am and Cm, as well as lanthanides.

5. Optimize ligand design: Identify potential modifications in the diglycolamide structure that could further optimize Am/Cm selectivity by tuning the lipophilicity and steric properties of the molecule.

6. Perform comparative studies: Compare the performance of TEDGA with other diglycolamides, including N,N,N',N'-tetramethyl-diglycolamide (TMDGA), N,N,N',N'-tetrapropyl-diglycolamide

(TnPDGA), and other analogs to highlight differences in selectivity and extraction behavior.

Methodology

Organic Synthesis:

Synthesis of DGA Derivatives:

- DGAs were synthesized by nucleophilic substitution of diglycolic acid chloride with the corresponding amine.
- Purification was performed using silica-gel chromatography with a cyclohexane and ethyl acetate mixture.
- The purity (>95%) was confirmed using NMR and GC-HRMS.
- TMDGA, TEDGA, and DMDOHEMA were purchased from Pharmasynthese, HDEHP from Sigma Aldrich, and TPH from NOVASEP.

Solvent Extraction

Preparation of Aq Solutions

- Solutions containing 30 mM of DGA derivatives in 6 M nitric acid with 0.1 mM of La, Nd, Sm, Eu, and Y were prepared.
- For Am/Cm separation studies, the solutions were spiked with 241 and 244 (8,000 10,000 Bq/mL).

Preparation of Solvents:

- The solvent was prepared by dissolving 0.6 M DMDOHEMA and 0.45 M HDEHP in TPH.
- For experiments with more lipophilic derivatives, 20 mM DGA extractants were dissolved in a mixture of 1-octanol/TPH (40/60% vol.).

Extraction Experimetns:

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- Aqueous and organic phases were contacted until equilibrium was reached at 25 1 C using an automatic vortex shaker with a thermostated cell.

- After phase separation by centrifugation, the aqueous phase was analyzed by ICP-OES for metal content.

- Organic phase cations were stripped using a solution of TEDGA (0.2 M), oxalic acid (0.5 M), and HEDTA (0.07 M) in 1 M nitric acid, followed by ICP-OES analysis.

Radiometric Analysis:

- Activities of 241 Am and 244Cm were measured using gamma and alpha counting spectrometers to quantify the distribution in aqueous and organic phases.

Calucaltion of Distribution Ratios and Separation Factors:

- Distribution tatios (DM = [M n+]org/[M n+]aq) and separation factors (SF = DM1/DM2) were calculated at equilibrium

- Errors were calculated from standard deviations, assuming maximum erros of about 5% for D-values between 0.1 and 10, and up to 10% for values outside this range

Ligand Partitioning Analysis

- The concentration of complexing agents was quantified by HPLC using a non-polar stationary phase and elution with a water-acetonitrile mixture.

- In aqueous samples, ligand concentration was determined after precipitation with sodium oxalate, centrifugation, and dilution.

- For organic phases, concentration was determined after back extraction with sodium oxalate followed by centrifugation.

Partition Coefficiecnt and Lipophilicity Analysis:

- The partition coefficient (log P) values were predicted using ACD/Labs software to assess the lipophilicity of each ligand.

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Additional Experiements:

Water Soluble Analogues:

- Water-soluble ligands (TMDGA, TnPDGA, and TiPDGA) were evaluated in aqueous phase with the EXAm solvent.

- Experimental conditions were chosen to achieve distribution ratios close to 1, with low element concentrations and 6 M nitric acid to maintain solubility and prevent precipitation.

Tetrabutyl Analogues

- Tetrabutyl analogues, which are poorly soluble in water, were evaluated as extractants in an organic phase mixture of 1-octanol and TPH.

Key Findings

Water Soluble Analogues

Distribution Ratios and Separation Factors:

- TMDGA, TEDGA, and TnPDGA partially complex Am and Cm in 6 M HNO_3.

- TEDGA showed the lowest distribution ratios for Am and Cm, indicating a higher affinity.

- Both TMDGA and TEDGA improved Am/Cm separation with separation factors ($SF_{Am/Cm}$) higher than 1.4.

- TnPDGA had a separation factor close to 1, indicating poor selectivity

Evaluation of Lanthanides and Yttrium

- TMDGA and TEDGA exhibited stronger affinity towards heavier lanthanides.

- TEDGA showed the strongest masking effect on heavy lanthanides.

- TnPDGA showed a general decrease in extraction for all cations, indicating low selectivity

Ligand Partitioning

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- TEDGA demonstrated the highest partitioning value despite higher lipophilicity compared to TMDGA and TnPDGA.

- Additional mechanisms beyond lipophilicity influenced TEDGA's behavior

Complexation with Extractants

- TEDGA can be extracted by DMDOHEMA, and its extraction is enhanced by Ln cations.

- Formation of mixed solvated Ln(NO3)3-TEDGAn-DMDOHEMA in the organic phase was considered .

Tetrabutyl Analogues

Evaluation of Solubility and Extraction

- TnBDGA, TiBDGA, and TsBDGA were evaluated as extractants in the organic phase due to poor water solubility.

- -ramifications (TiBDGA) decreased Am and Cm extraction.

- -ramifications (TsBDGA) increased distribution ratios but reduced selectivity .

Lanthaides and Yttrium Extraction

- All tested extractants showed higher extraction efficiency than TODGA.

- TsBDGA showed poor selectivity among lanthanides, while TnBDGA and TiBDGA showed selectivity towards heavier lanthanides .

Impact of Steric Hindrance

- Introduction of steric hindrance in positions (TsBDGA) led to a significant increase in distribution ratios but a loss of selectivity.

- -ramifications (TiBDGA) decreased extraction efficiency but maintained selectivity .

Conclusions

Optimal Ligand Structure

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- The study confirmed that 2-carbon symmetrical alkyl chains (ethyl groups) on DGA are optimal for Am/Cm selectivity in EXAm process conditions.
- Shorter alkyl chains (TMDGA) resulted in lower selectivity, while longer chains (TnPDGA) almost lost selectivity .

Complexity of TEDGA Partitioning

- TEDGA must be co-extracted with Ln/An cations forming mixed solvates in the organic phase with DMDOHEMA.
- The complex speciation involving TEDGA likely plays a significant role in Am/Cm selectivity .

Evaluation of Tetrabutyl Derivatives

- Tetrabutyl derivatives showed varied extraction efficiencies based on their structural modifications.
- Introduction of and ramifications had distinct impacts on extraction efficiency and selectivity .

Relevance to Study

Selective Extraction: The study identifies TEDGA (N,N,N',N'-tetraethyl-diglycolamide) as a key ligand for selectively maintaining curium in the aqueous phase while extracting americium into the organic phase. This selectivity is crucial for separating these two elements effectively in nuclear fuel reprocessing

Optimal Alkyl Chain Length: It was found that the optimal symmetrical alkyl chain length for achieving Am/Cm selectivity is two carbons (ethyl groups). Shorter (e.g., TMDGA) or longer chains (e.g., TnPDGA) significantly reduce selectivity, impacting the efficiency of the separation process

Lipophilicity and Partitioning: TEDGA's complex behavior, including its co-extraction with lanthanide and actinide cations forming mixed solvates, is highlighted. This behavior underscores the importance of understanding and optimizing the lipophilicity of ligands to enhance their performance in solvent extraction processes

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Impact of Steric Hindrance: The introduction of steric hindrance in the ligands' side chains impacts their extraction efficiency and selectivity. For example, alpha-branched chains (TsBDGA) increase distribution ratios but decrease selectivity, while beta-branched chains (TiBDGA) decrease extraction efficiency

Radiolytic Stability: DGAs, including TEDGA, exhibit good radiolytic stability, making them suitable for use in the highly radioactive environments of nuclear fuel reprocessing. This stability ensures the long-term effectiveness of the separation process

Thermodynamic and Speciation Studies: Ongoing studies aim to improve the thermodynamic models and better understand the complexation and speciation behaviors of TEDGA and other DGAs. These studies are crucial for predicting the behavior of lanthanides and actinides in the extraction process, leading to more efficient ligand designs

Comparison with Other Ligands: The study compares TEDGA with other diglycolamides like TMDGA and TnPDGA, providing insights into how variations in structure affect performance. Such comparisons help in identifying the most effective ligands for specific separation tasks in nuclear fuel reprocessing

Critical Parameters Identified

High Importance

Chemial Stability

Hydrolysis: TiPDGA was quickly hydrolyzed in 6 M HNO3, indicating poor stability due to steric hindrance from branched alkyl chains. Other ligands, such as TMDGA and TEDGA, showed stability even after 12 hours in 6 M HNO3

Steric Hindrance: The introduction of steric hindrance in and positions of amide groups affected the ligands' stability and extraction performance. TiPDGA's quick hydrolysis highlights the

importance of chemical stability under highly acidic conditions

Radiolysis Resistance:

TEDGA Stability: TEDGA and other DGAs demonstrated good radiolytic stability, with no degradation observed after gamma irradiation at 100 kGy. This property is crucial for maintaining separation efficiency in radioactive environments

Thermodynamics

Selectivity and Biding Strength: The study established that 2-carbon symmetrical alkyl chains (ethyl groups) on DGAs provide optimal Am/Cm selectivity. This finding underlines the importance of thermodynamic principles in ligand design for effective metal ion separation

Partition Coefficients: The calculated log P values for DGAs helped predict their lipophilicity and interaction with organic phases, impacting their thermodynamic behavior in extraction processes

Medium Importance

Kinetics

Equilbrium Conditions: Experimental conditions were chosen to achieve distribution ratios close to 1, ensuring efficient separation kinetics. These conditions are vital for practical and reversible separation processes

Loading Capacity:

Complexation Efficiency: The study evaluated the chelating ability of DGAs (e.g., TEDGA, TMDGA, TnPDGA) towards Am and Cm, impacting the ligands' loading capacity. The higher the chelating ability, the greater the loading capacity

Operational Condition Range:

Acid Concentrations: The ligands were tested in various acidic conditions (up to 6 M HNO_3), demonstrating their ability to operate under highly acidic environments typical of nuclear fuel

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Solvent Combinations: The study assessed different combinations of solvents (e.g., DMDOHEMA/HDEHP in TPH, 1-octanol/TPH), showing the flexibility of DGAs under different operational conditions

Low Importance

Solubility

Water Solubility: DGAs like TnPDGA showed lower solubility in water compared to TMDGA and TEDGA. While solubility is important, it was managed by dissolving more lipophilic derivatives in organic diluents

Dispersion Numbers: The study did not specifically discuss dispersion numbers, but this factor is less critical compared to others evaluated

Phase Disengagement:

Extraction/Stripping Procedures: The phase disengagement process was managed through careful phase separation by centrifugation and back extraction methods, but this aspect was not a primary focus