REFERENCE: 20001

KEYWORDS:

Am^{3+}

Cm^{3+}

Diglycolamides (DGA)

N,N,N',N'-tetra-n-octyldiglycolamide (TODGA)

N,N,N',N'-tetra-2-ethylhexyldiglycolamide (T2EHDGA)

Hydrophilic 2,6-bis(1,2,4-triazinyl)pyridine (SO3PhBTP)

nitric acid medium

selectivity

liquid-liquid extraction

computational studies

radiotoxic elements

minor actinides (Am, Cm, Np)

oxidation states

solvent extraction

OBJECTIVES:

1. **Evaluation of Ligands**: The study aims to evaluate N,N,N',N'-tetra-n-octyldiglycolamide (TODGA) and N,N,N',N'-tetra-2-ethylhexyldiglycolamide (T2EHDGA) for the separation of Am^{3+} and Cm^{3+} in the presence of a hydrophilic 2,6-bis(1,2,4-triazinyl)pyridine (SO3PhBTP) derivative in the aqueous phase.
2. **Understanding Selectivity**: To understand the selectivity of the two DGA ligands (TODGA and T2EHDGA) for Am^{3+} and Cm^{3+}, and how the presence of SO3PhBTP affects this selectivity.

3. **Temperature-Dependent Studies**: To carry out temperature-dependent liquid–liquid extraction studies to determine the thermodynamic parameters (enthalpy, Gibbs free energy, and entropy) for the extraction of Am^{3+} and Cm^{3+}.
4. **Computational Studies**: To perform computational studies to support the experimental findings, including geometry optimization and energy calculations for the complexes formed between the ligands and metal ions.
5. **Optimization of Extraction Conditions**: To optimize the conditions for the liquid–liquid extraction process, including the concentrations of nitric acid, DGA ligands, and SO_3PhBTP, and to investigate the effect of different organic diluents on the extraction efficiency.
6. **Improving Separation Factors**: To enhance the separation factors (S.F.) for Am^{3+} and Cm^{3+} by using different combinations of ligands and solvents, aiming for better selectivity and efficiency in the separation process.
7. **Mechanistic Insights**: To gain insights into the mechanism of the extraction process, including the nature of the complexes formed and the factors influencing the selectivity and efficiency of the extraction.

METHODOLOGY:

1. **Reagents and Chemicals**:

   - Synthesized N,N,N',N'-tetra-n-octyldiglycolamide (TODGA) and N,N,N',N'-tetra-2-ethylhexyldiglycolamide (T2EHDGA) using established procedures.

   - Used ^{241}Am and ^{244}Cm radiotracers from laboratory stock solutions.
2. **Liquid-Liquid Extraction Studies**:

   - Equal volumes (0.5 mL) of the aqueous phase containing the radiotracer in 3 M HNO_3 and the organic phase containing 0.1 M DGAs in n-dodecane were equilibrated in plastic tubes for an hour at 25 ± 0.1 °C.

   - Tubes were centrifuged, and the distribution ratio (D) values of the metal ions were calculated based on the concentration of the radiotracer in both phases.
3. **Temperature-Dependent Extraction Studies**:

   - Conducted to determine the thermodynamic parameters (enthalpy, Gibbs free energy, entropy) for the extraction of Am^{3+} and Cm^{3+}.

   - The extraction constant values (K_{ex}) were calculated and plotted against the inverse of temperature in the Kelvin scale.
4. **Effect of Nitric Acid Concentration**:

   - Studied by varying the aqueous phase nitric acid concentration from 0.5 to 2.5 M in the presence of 5 mM SO3PhBTP at a fixed TODGA and T2EHDGA concentration of 0.2 M in n-dodecane.

5. **Effect of DGA and SO3PhBTP Concentrations**:
   - Measured the distribution ratio of both metal ions as a function of ligand concentration at a fixed HNO3 concentration of 1.5 M in the presence of 0.007 M SO3PhBTP.
6. **Effect of Diluents**:
   - Evaluated different organic diluents (e.g., toluene, tBu-benzene, Tri-iPr-Benzene, n-dodecane) for the extraction of Am3+ and Cm3+ with the DGA derivatives.
7. **Computational Studies**:
   - Used n-butyl (TBDGA) and iso-butyl (TiBDGA) derivatives of the diglycolamides as model ligands.
   - Geometries of the free ligands and their complexes with Am3+ and Cm3+ were optimized using def-SV(P) basis sets and TURBOMOLE-7.2.1 suites.
   - Single point energies of the free ligands and complexes were calculated using the hybrid functional B3LYP and valence triple zeta (def-TZVP) basis sets.
8. **Analysis of Natural Charges and Interaction Energies**:
   - Natural charges were calculated using natural population analysis.
   - Interaction energies for complexation were calculated for the complexes of Am3+ and Cm3+ with the DGA ligands and the bis-triazinyl pyridine (BTP) in the absence and presence of competition from BTP.

KEY FINDINGS:

- **Effects of Nitric Acid Concentration**
  - The extraction of both Am3+ and Cm3+ increases with rising nitric acid concentration when using both TODGA and T2EHDGA.
  - At 2.5 M HNO3, distribution ratios become too high for mutual separation, so 1.5 M HNO3 was chosen for further studies.
  - T2EHDGA showed marginally higher selectivity for Am3+ over Cm3+, with the highest selectivity factor (S.F.) value of 2.0 at 1 M HNO3.
  - In the absence of SO3PhBTP, the highest S.F. was 1.13 at 0.2 M T2EHDGA concentration
- **Effects of Diluents**
  - Different organic diluents impact the extraction efficiency of Am3+ and Cm3+.
  - Extraction efficiency increased in the order: toluene < tBu-benzene < Tri-iPr-Benzene

< n-dodecane.

- The dielectric constant and solubility parameters play a role, with higher extraction efficiency observed with n-dodecane due to lower solubility parameters and dielectric constants compared to toluene.

- Despite solvesso-100 showing the highest S.F., n-dodecane was chosen for further studies due to its overall extraction efficiency

- **Effects of DGA and SO3PhBTP Concentrations**

  - The distribution ratios of both metal ions were measured as a function of ligand concentration.

  - TODGA and T2EHDGA extracted both metal ions predominantly as 1:2 and 1:3 complexes.

  - SO3PhBTP's stability constant values indicated 1:2 complexes for both Am3+ and Cm3+ with comparable stability constants.

  - DGA-based systems showed that tetradentate bistriazinyl bipyridine (BTBP) or phenanthroline (BTPhen) derivatives preferred Am3+ over Cm3+

- **Role of Temperature**

  - Extraction of Am3+ and Cm3+ by TODGA and T2EHDGA decreases with increasing temperature, indicating an exothermic process.

  - Enthalpy values ranged from -22 to -26 kJ mol^-1 for TODGA and T2EHDGA in the absence of SO3PhBTP and -16 to -19 kJ mol^-1 in its presence.

  - Temperature-dependent extraction studies suggest the enthalpic competition between SO3PhBTP and DGA ligands, with the extraction becoming less enthalpically favored in the presence of SO3PhBTP

- **Computational Studies**

  - The n-butyl (TBDGA) and iso-butyl (TiBDGA) derivatives were used for computational cost reduction.

  - Geometry optimization and single point energy calculations were performed using TURBOMOLE with BP86 and B3LYP functionals.

  - Natural population analysis revealed higher ligand-to-metal electron transfer in Am3+ complexes compared to Cm3+ complexes.

  - Interaction energies showed that Cm3+ forms stronger complexes than Am3+ with both DGA ligands, but the selectivity for Am3+ by T2EHDGA in the presence of SO3PhBTP is attributed to entropy factors favoring Am3+ extraction

- **Conclusion**

  1. **Evaluation of TODGA and T2EHDGA**: TODGA and T2EHDGA were evaluated for the

separation of Am^{3+} and Cm^{3+} from nitric acid medium, both in the presence and absence of the aqueous complexant SO3PhBTP. A reversal of extraction selectivity was observed with T2EHDGA showing marginal selectivity for Am^{3+} over Cm^{3+} in the presence of SO3PhBTP.

2. **Effect of Diluents**: Among various diluents studied, n-dodecane was found to be the most suitable, achieving an S.F. value of 2.4 for Am^{3+} over Cm^{3+} using 0.2 M T2EHDGA in n-dodecane from a 1.5 M HNO_3 medium with 7 mM SO3PhBTP.
3. **Complexation Behavior**: Both TODGA and T2EHDGA extracted Am^{3+} and Cm^{3+} predominantly as 1:3 complexes, while in the aqueous phase, the metal ions were present as 1:2 complexes with SO3PhBTP. Stability constant values for these complexes were determined, indicating the formation of stable 1:2 complexes in the presence of SO3PhBTP.
4. **Temperature-Dependent Studies**: The extraction of Am^{3+} and Cm^{3+} by TODGA and T2EHDGA was found to be an exothermic process, with no significant difference in the enthalpy of extraction between the two DGA derivatives. The selectivity of T2EHDGA for Am^{3+} over Cm^{3+} in the presence of SO3PhBTP was attributed to the entropy effect, where the extraction of Am^{3+} was more entropy-favored compared to Cm^{3+}.
5. **Computational Studies**: Computational studies supported the experimental findings, indicating that the selectivity for Am^{3+} over Cm^{3+} with T2EHDGA in the presence of SO3PhBTP could be attributed to differences in the entropy of extraction.

The study suggests further investigation into DGA ligands with additional branching in the alkyl chain in combination with hydrophilic complexants like SO3PhBTP for improved separation of Am^{3+} and Cm^{3+}.

RELEVANCE TO STUDY:

Objective: The study aims to improve the separation of Am^{3+} and Cm^{3+} using diglycolamides (DGA), crucial for managing radiotoxic elements in the nuclear fuel cycle.

Ligands Evaluated: The study evaluates N,N,N’,N’-tetra-n-octyldiglycolamide (TODGA) and N,N,N’,N’-tetra-2-ethylhexyldiglycolamide (T2EHDGA) in combination with a hydrophilic SO3PhBTP derivative.

Nitric Acid Concentration: Extraction efficiency increases with higher nitric acid concentration, with 1.5 M HNO_3 chosen for further studies due to optimal separation factors.

Diluents: n-Dodecane was identified as the most effective diluent for extraction, providing the best balance between extraction efficiency and selectivity.

Ligand Concentrations: The study finds that DGA ligands predominantly form 1:2 and 1:3 complexes with Am3+ and Cm3+, while SO3PhBTP forms 1:2 complexes, enhancing selectivity.

Temperature Effects: The extraction process is exothermic, with decreasing efficiency at higher temperatures, suggesting optimal operational temperatures for separation.

Computational Support: Computational studies corroborate experimental findings, indicating higher ligand-to-metal electron transfer for Am3+ complexes and highlighting the importance of entropy in achieving selectivity.

Future Directions: The study suggests further exploration of DGAs with more branching in combination with hydrophilic complexants like SO3PhBTP for enhanced separation efficiency

Critical Parameters Identified:

High Importance

Chemical Stability:

- Acid/Base Hydrolysis**:** The study investigates the stability of TODGA and T2EHDGA in nitric acid medium, crucial for their function during the separation process under nuclear reprocessing conditions.

- Reactive Chemicals**:** The interaction between the ligands and nitric acid, as well as the effect of various diluents, ensures that the ligands maintain stability during the separation process

Radiolysis Resistance:

- Durability under Radiation**:** Although not explicitly discussed in terms of radiolysis resistance, the study implies the importance of ligand stability under conditions prevalent in nuclear fuel reprocessing environments

Thermodynamics:

- Enthalpy and Entropy: The study provides detailed thermodynamic parameters, including enthalpy (ΔH) and entropy (ΔS) of the extraction processes, which are fundamental for understanding ligand selectivity and binding strength towards Am3+ and Cm3+

Medium Importance

Kinetics (Forwards and Reverse)

- Efficiency of Separation**:** While specific kinetic data is not detailed, the study mentions the equilibration time for achieving extraction equilibrium, indicating practical considerations for process speed and efficiency

Loading Capacity

- Extraction Efficiency**:** The study evaluates the concentration of TODGA and T2EHDGA and their ability to extract Am3+ and Cm3+ effectively, which indirectly addresses the loading capacity of these ligands

Operational Condition Range

- Temperature and Acid Concentration**:** The study examines a range of nitric acid concentrations and temperatures, showcasing the operational flexibility of the ligands under various conditions

Low Importance

Solubility:

- Ligand Solubility in Diluents**:** The study discusses the solubility of ligands in various organic diluents, which is essential for optimizing extraction conditions but can be adjusted through solvent selection

Dispersion Numbers (for Applied System with Conditional Values)

- Separation of Phases**:** The centrifugation step after equilibration indicates practical considerations for phase disengagement, ensuring clear separation of organic and aqueous phases for measurement