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Key Words

solvent extraction

thorium nitrates

eurpium nitrates

TPPO

thermodynamic parameters

enthalpy change

ntropy change

gibbs free energy

extraction equilibriametal-ligand ratio

dichloromethane

1,2-dichloroethane

neutral phosphorylated ligands

temperature influence

coordination behavior

Objective

1. To evaluate the extractive properties of triphenylphosphine oxide (TPPO) towards thorium and europium nitrates.

2. To calculate the thermodynamic parameters (G , H , and S) of the extraction process using the influence of the temperature on extraction equilibria.

3. To compare the extraction efficiency and thermodynamic parameters of TPPO with those of two other phosphorylated ligands, tri-n-octylphosphine oxide (TOPO) and diphenyl-N,N-dimethylcarbamoylmethylphosphine oxide (D DMCMPO).

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4. To study the extraction of europium to provide a model for the behavior of Ac(III) species

Methodology

1. Materials and Reagents

- Triphenylphosphine oxide (TPPO) was used without further purification.

- Dichloromethane and 1,2-dichloroethane were washed with distilled water to remove solvent stabilizers and ensure saturation with respect to water content.

- Europium solutions were prepared by dissolving europium oxide in hot concentrated nitric acid and diluting to a known volume.

- Thorium solutions were prepared from $Th(NO_3)_4 \cdot 6H_2O$ and standardized by complexometric titration with EDTA.

- Other reagents used were laboratory reagent grade.

2. Solvent Extraction Experiments

- Equal volumes (5 ml) of the organic and aqueous phases were used in stoppered glass tubes immersed in a thermostated water bath (0.1 C).

- Equal volumes (5 ml) of the organic and aqueous phases were used in stoppered glass tubes immersed in a thermostated water bath (0.1 C).

- After phase separation, the concentration of the remaining cation in the aqueous phase was measured spectrophotometrically using Arsenazo III.

3. Spectrophotometric Analysis

- A volume of 5 ml of Arsenazo III solution (6.10^-4 M) was added to a 1 ml aliquot of the aqueous phase.

- The volume was adjusted to 25 ml with either a 4M nitric acid solution (for thorium determination) or a sodium formate/formic acid buffer (pH 2.80) for europium determination.

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- Absorbance was measured at 660 nm for thorium and 655 nm for europium. The standard deviation for the lowest distribution coefficient (D) values was calculated to be less than 0.01.

4. Data Analysis

- The distribution coefficient (D) of thorium and europium cations between the 1M sodium nitrate aqueous solution and the dichloromethane phases as a function of ligand concentration in the organic phase was measured at 293 K

- The extraction equilibrium constant (Kex) was defined and calculated using the distribution ratios and ligand concentrations.

- Plots of logD vs. log[L] provided the metal/ligand ratio of the extracted species.

- The effect of temperature on the extraction process was studied in the range of 293 313 K using 1,2-dichloroethane as the solvent.

5. Thermodyanmic Parameter

- The enthalpy (H) and entropy (S) changes associated with the extraction process were calculated using the van't Hoff isochore.

- The Gibbs free energy (G) was calculated using the Gibbs-Helmholtz equation.

Key Findings

1. Efficiency of TPPO

- Triphenylphosphine oxide (TPPO) is more efficient for extracting europium(III) than thorium(IV) from nitrate media into dichloromethane.

- The extraction takes place via the formation of species with a 1:2 metal to ligand ratio for both thorium and europium.

2. Comparison with Other Ligands

- Compared to other phosphorylated ligands, such as tri-n-octylphosphine oxide (TOPO) and

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diphenyl-N,N-dimethylcarbamoylmethylphosphine oxide (D DMCMPO), TPPO shows different extraction efficiencies and thermodynamic behaviors.

- TOPO extracts both thorium and europium via a 1:3 metal to ligand ratio.

- D DMCMPO forms 1:3 complexes with thorium and 1:2 complexes with europium.

3. Thermodynamic Parameters

- The extraction of europium by TPPO is controlled by enthalpy changes (exothermic process).

- The extraction of thorium by TPPO is driven by entropy changes (endothermic process).

- For TOPO and D DMCMPO, the extraction of europium and thorium shows varying enthalpy and entropy changes.

5. Temperature Influence

- The equilibrium constants for the distribution of Eu(III) and Th(IV) between 1M NaNO3 and 1,2-dichloroethane solutions of TPPO were evaluated over the temperature range of 293 313 K.

- Extraction of Eu(III) by TOPO is less efficient at higher temperatures, while the opposite is true for Th(IV).

5. Enthalpy and Entropy Changes

- More negative enthalpy changes and lower entropy changes for the extraction of europium by TPPO compared to D DMCMPO indicate bidentate binding of D DMCMPO.

- Higher enthalpy changes and lower entropy changes for the extraction of thorium by D DMCMPO compared to TOPO support the bidentate binding nature of CMPO-type ligands.

6. Hydration Effects

- The more negative extraction enthalpy for Eu(III) compared to Th(IV) correlates with the hydration enthalpy differences between these ions.

- The release of a greater number of water molecules during the complexation process contributes to the positive entropy changes for Th(IV) extraction by TPPO and D DMCMPO.

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Relevance to Study

Extraction Efficiency: Demonstrates that triphenylphosphine oxide (TPPO) is more efficient for europium(III) than thorium(IV), highlighting the importance of ligand efficiency in selective extraction processes.

Thermodynamic Parameters: Provides detailed thermodynamic data (G , H , S) for the extraction processes, which are critical for understanding the energetics and feasibility of ligand-metal interactions in nuclear fuel reprocessing.

Temperature Dependence: Evaluates the impact of temperature on the extraction equilibria, emphasizing the need for temperature control and optimization in solvent extraction operations.

Comparison with Other Ligands: Compares TPPO with other ligands like TOPO and D DMCMPO, offering insights into the relative performance and binding characteristics of different phosphorylated ligands, aiding in the selection of the most suitable ligand.

Hydration and Coordination Behavior: Discusses the role of ligand hydration and coordination mode, indicating how these factors influence the extraction efficiency and selectivity, which are vital for designing ligands that can effectively separate actinides from lanthanides.

Critical Parameters Identified

High Importance

Thermodynamics

- Detailed thermodynamic parameters (G , H , S) for the extraction of thorium and europium nitrates using TPPO.

- Identification that the extraction of europium is exothermic (enthalpy-driven) while the extraction of thorium is endothermic (entropy-driven).

- Comparative analysis of thermodynamic data with other ligands (TOPO and D DMCMPO).

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Medium Importance

Kinetics: The study discusses the equilibrium reached after 30 minutes under continuous magnetic stirring, suggesting efficient kinetics for practical extraction processes.

Loading Capacity: The metal to ligand ratio (1:2 for both thorium and europium with TPPO) implies the ligand's loading capacity, although not explicitly quantified.

Operational Condition Range: Extraction experiments were performed in a temperature range of 293 313 K, indicating the ligand's performance under different thermal conditions.

Low Importance

Solubility: The use of dichloromethane and 1,2-dichloroethane as solvents, and their preparation, ensures the solubility of ligands, though specific solubility values are not highlighted.

Dispersion Numbers: Not specifically discussed in the study, but the efficiency of phase mixing and separation during the extraction process can be inferred from the experimental setup.

Phase Disengagement: The practical separation of phases post-extraction (measured concentrations in the aqueous phase) indirectly indicates successful phase disengagement.