Key Words

Europium (Eu3+)

HEH[EHP] (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester)

diluents

solvent extraction

stoichiometry

radiotracer

Luminescence spectroscopy

slope analysis

coordination sphere

thermodynamics

Objective

1. To investigate the effect of different organic diluents on the extraction efficiency of Europium (Eu3+) using HEH[EHP].

2. To analyze the apparent stoichiometry of the extracted Eu3+ complex by using slope analysis techniques.

3. To compare the pH dependence and extractant dependence of the extraction process across various diluents.

4. To characterize the primary coordination sphere of the Eu3+ complex in selected diluents using luminescence spectroscopy.

5. To train new scientists in handling radioactivity and in solvent extraction techniques by using radiotracer 152/154Eu.

6. To establish the effect of diluent properties such as hydrogen donor/acceptor behavior, polarity,

polarizability, and molecular dimensions on the extraction process.

7. To determine the extraction equilibrium constants (Koex) for different diluents and refine them based on the experimentally observed stoichiometries.

8. To assess potential changes in the Eu-O bonding stoichiometry within the first coordination sphere of the extracted complex using luminescence data.

9. To develop a conceptual framework for understanding the diluent effects on the extraction process.

10. To contribute to the knowledge base in memory of Professor Jan Rydberg, emphasizing both educational and scientific advancements in solvent extraction chemistry .

Methodology

1. Materials Preparation

Organic Diluents: Obtained from various suppliers, used without further purification.

HEH[EHP] Extractant: Purified to >99% using a third phase formation procedure, with purity verified by phosphorus NMR spectroscopy.

Aqueous Solutions: Prepared using standardized $Eu(NO_3)_3$ stocks, with metal, nitrate, and proton concentrations determined by ICP-MS, ion exchange chromatography, and potentiometric titrations.

Radiotracer 152/154Eu: Produced by neutron activation of Eu_2O_3 and dissolved in HNO_3.

2. Slope Analysis

- The organic phase samples were prepared gravimetrically and aqueous solutions by volume.

- All experiments were conducted at a 1:1 (Vaqueous

) phase ratio, with variations in pH and ligand concentration in 20 different organic diluents.

- The aqueous phase ionic strength was fixed at 0.1 mol L 1 by adding $NaNO_3$.

- Radiotracer experiments used 152/154Eu and were analyzed using a gamma counter. Extractions were done at room temperature (23 2 C) and run in triplicate.

- Phases were mixed on a vortex mixer for 15 minutes, then separated after centrifugation at 1600 rpm for 10 minutes. Aliquots of each phase were assayed for total gamma activity.

3. Distribution Ratio Calculation

- The distribution ratios (D) were defined by the quotient of specific radioactivity of the europium radiotracer in the organic and aqueous phases.

4. Luminescence Spectroscopy:

- Eu^{3+} luminescence spectra were used to probe changes in the first coordination sphere of the metal center in different diluents.

- Luminescence spectra were taken on a fluorimeter with specific settings for excitation and emission wavelengths.

5. Data Analysis

- Slope analysis was used to determine the apparent stoichiometry of the extracted metal complex by plotting log D vs. log [H+] and log [(HA)2].

- Extraction equilibrium constants (Koex) were calculated based on the experimentally observed stoichiometries.

- The apparent stoichiometry of the extraction reaction was investigated through acid and extractant dependencies.

- Equilibrium constants for different diluents were refined and reported.

Key Findings

Slope Analysis

Apparent Stoichiometry

- Extraction of Eu3+ by HEH[EHP] shows variation in the number of extractant molecules.

- Expected stoichiometry is 1:3 (Eu

), but experimental results range between 2.5 and 3.0 extractant molecules per metal ion.

- Indicates formation of both Eu(A)3 (HA)3 and Eu(A)3 (HA)2 complexes depending on the diluent.

Extraction Equilibrium Constant Calculations

Koex Values:

- Extraction equilibrium constants (Koex) calculated assuming EuA3 (HA)3 as the dominant species.

- Adjustments for variable stoichiometry refined the constants, improving precision.

- Koex values generally decrease with an increase in protonated extractants, indicating reduced metal-ligand complex strength with increased inter-extractant hydrogen bonding.

Europium Luminescence

First Coordination SPhere:

- Luminescence spectra of Eu-HEH[EHP] complexes in n-octane and toluene are nearly identical.

- Suggests no significant changes in the primary coordination environment of Eu3+ with different diluents.

- Minor peaks in the D0 F0 transition suggest slight variations in symmetry environments around the metal center due to different binding modes of the extractant.

Linear Gibbs Energy Correlations

Thermodynamic Consistency:

- Linear Free Energy Relationships (LFER) show consistent trends between Gibbs energy and extraction equilibrium constants for various diluents.

- Stronger extraction observed in aliphatic diluents, weaker in aromatic diluents.

- Correlation reinforces the significant role of the diluent in determining extraction efficiency.

Correlation with Hildebranc Solubility Parameter

Solvation Effects

- Inverse relationship between Hildebrand solubility parameter and extraction equilibrium constants.

- Stronger solvation parameters correlate with weaker Eu3+ extraction.

- Data suggest two distinct families of diluents, each affecting the extraction process differently, indicating complex interactions between solvation properties and extraction process.

Interpretation of Luminescence Data

Coordination Sphere Symmetry

- Luminescence data suggest changes in extractant dependency may not involve the primary coordination sphere of Eu3+.

- Variations in stoichiometry could occur in the "outer" coordination sphere, influenced by hydrogen bonding between the protonated extractant and the metal complex.

Conclusion

Effect of Organic Diluent

- Characterized the effect of 20 different organic diluents on the extraction of Eu3+ by HEH[EHP].

- Functional groups, dielectric constants, polarizability, shape, and size of the diluents were considered.

Number of Extractant Molecules

- The number of extractant molecules in the complex changes with different diluents.

- The number of protons exchanged for Eu3+ remains constant at three.

- The number of protonated adduct ligands varies from 2 in aliphatic diluents to 3 in aromatic diluents, showing continuous variation.

Eu3+ Luminescence Spectra:

- No clear evidence for a change in the first coordination sphere of the Eu3+ metal center.

- Suggests changes in stoichiometry do not involve the primary solvation sphere.

Extraction Equilibrium Constanst (Kex):

- Kex value generally decreases as the number of protonated extractants in the complex increases.

- Indicates reduced metal-ligand complex strength with increased inter-extractant hydrogen bonding.

Considerations and Limitations:

- Dimerization of the extractant likely changes with the diluent.

- Other factors such as interfacial behavior, pKa, and the amount of water solubilized in the organic phase are diluent-dependent and affect extraction and dimerization equilibria.

- Further studies are needed to determine these and other organic phase parameters in various diluents and extractants.

Relevance to Study

Diluents' Impact on Extraction Efficiency

- Demonstrates significant effects of different organic diluents on the extraction efficiency of europium (Eu3+) by HEH[EHP].

- Important for selecting appropriate diluents to maximize extraction efficiency in nuclear fuel cycle processes.

Variable Stoichiometry

- Shows stoichiometry of extracted Eu3+ complex varies with diluent type.

- Critical for designing ligands and choosing diluents that ensure optimal extraction performance and predictability.

Thermodynamic Considerations

- Provides insights into the thermodynamic stability of metal-ligand complexes by calculating and comparing extraction equilibrium constants (Koex).

- Essential for selecting ligands that form stable complexes with actinides and lanthanides in the nuclear fuel cycle.

Luminescence Spectroscopy:

- Uses europium luminescence spectroscopy to probe the first coordination sphere of the metal-ligand complex.

- Valuable for designing ligands that maintain desired coordination environments.

Correlation with Solvating Properties:

- Correlates extraction efficiencies with Hildebrand solubility parameters of diluents.

- A systematic approach to predict and select diluents based on their solvating properties.

Practical Implications for Nuclear Fuel Cycle

- Emphasizes need for careful selection of diluents and ligands in solvent extraction processes used in the nuclear fuel cycle.

- Ability to fine-tune extraction processes by choosing the right combination of extractants and diluents can improve efficiency and safety of nuclear fuel reprocessing and waste management.

Critical Parameters Identified

High Importance

1. Chemical Stability: The study did not directly address chemical stability under acid/base hydrolysis or reaction with other chemicals.

2. Radiolysis Resistance: The study did not directly evaluate the radiolysis resistance of the ligands or diluents.

3. Thermodynamics

Extraction Equilibrium Constants (Koex): The study calculated and compared extraction equilibrium constants for different diluents, providing insights into the thermodynamic stability of the metal-ligand complexes.

Thermodynamic Consistency: Linear Free Energy Relationships (LFER) between Gibbs energy and extraction equilibrium constants indicate consistent thermodynamic trends.

Medium Importance

1. Kinetics (forwards and reverse):

Slope Analysis: The study used slope analysis to determine the apparent stoichiometry of the extraction process, indirectly providing insights into the kinetics of the extraction.

2. Loading Capacity: The study did not directly address the loading capacity of the ligands.

3. Operational Condition Range

Variability in Diluents: The study used 20 different organic diluents with various functional groups, dielectric constants, polarizability, shape, and size, showcasing the flexibility of the extraction process under a broad range of conditions.

Low Importance

1. Solubility

Solvation Effects: The study correlated extraction efficiencies with Hildebrand solubility parameters of the diluents, providing insights into the solubility characteristics of the diluents.

2. Dispersion Numbers (for applied systems with conditional values): The study did not address dispersion numbers.

3. Phase Disengagement (for applied systems with conditional values): The study did not address phase disengagement.