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Key Words

actinides

Am(III)

Pu (IV)

U(VI)

TODGA

thermodynamics

extraction constant (log K ex)

enthalpy

entropy

Gibbs free energy

nitric acid medium

n-dodecane

distribution ratio (DM)

loading of Nd(III)

diluent

Objective

1. Study the effect of temperature on the extraction behavior of Am(III), Pu(IV), and U(VI) from a nitric acid medium using TODGA in n-dodecane.

2. Calculate and compare the two-phase equilibrium constants (log K ex) of TODGA with those of other extractants proposed for actinide partitioning, such as CMPO and DMDBTDMA.

3. Determine thermodynamic parameters, including Gibbs free energy (G), enthalpy (H), and entropy (S), for the extraction of actinides by TODGA and compare them with those of CMPO and

DMDBTDMA.

4. Investigate the role of diluent on the loading of Nd(III) in 0.1 M TODGA dissolved in different diluents

Methodology

1. Reagents and Radionuclides

2.

- TODGA was synthesized at the Chemistry Department, University of Delhi. The details of the synthesis procedure, analytical data, and PMR data are provided elsewhere.
- The diluent, n-dodecane, was used without further purification.
- Other chemicals used were of analytical reagent grade.
- 241Am was tested for its purity by and -spectrometry.
- Radiotracer 233U was prepared by irradiation of 232Th in a nuclear reactor and separated by the THOREX process.
- 239Pu was purified and its radiochemical purity was ascertained by gamma ray spectrometry to ensure the absence of 241Am. The valency of Pu in the aqueous phase was adjusted and maintained in the tetravalent state by adding 0.05 M NaNO2 and 0.005 M NH4VO3 as holding oxidants.

2. Distribution Studies

- A suitable volume of the aqueous phase, spiked with radiotracers, was agitated with an equal volume of pre-equilibrated organic phase (0.1 M TODGA/n-dodecane) in stoppered glass tubes for 45 minutes.
- The studies were conducted at constant temperatures maintained within 1 C using a thermostated water bath.

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- The two phases were then centrifuged and assayed radiometrically.

- 241Am was estimated by gamma counting using a well-type NaI(Tl) scintillation counter.

- Liquid scintillation counting was used for 233U and 239Pu, employing a toluene-based scintillator.

- The distribution ratio of the metal ion (DM) was calculated as the ratio of the concentration of metal ions in the organic phase to that in the aqueous phase.

3. Loading Studies

- Loading of Nd(III) in 0.1 M TODGA dissolved in different diluents was carried out from an aqueous phase containing 2 M Nd(III) at 3 M HNO3.

- The third

phase obtained was dissolved by adding fresh organic phase. If no third phase formation was observed, repeated loading experiments were performed with fresh aqueous phase each time until the Nd(III) concentration in the organic phase was constant, determined by complexometric titration employing standard EDTA solution and xylenol orange as indicator.

4. Calculation of Thermodynamic Parameters

- The two-phase equilibrium representing the extraction of metal ions from nitric acid medium with TODGA was represented and the equilibrium constant (Kex) calculated using specific assumptions and approximations.

- The Van t Hoff equation was used to calculate the enthalpy change (H) associated with the extraction process.

- The concentration of the free ligand A was calculated from the basicity of the extractant, considering the extraction of HNO3 by neutral ligand TODGA.

- The predominant extracted species in the organic phase were identified for Am(III), Pu(IV), and U(VI), and the extraction equilibria were established.

- The Gibbs energy change (G) associated with the extraction process was calculated from the value of the extraction constant (K ex).

- From the knowledge of the Gibbs energy change (G) and the enthalpy change (H), the entropy change (S) of the system was calculated using Gibbs s Helmholtz equation .

Key Findings

Effect of Temperature on Distribution of Metal Ions

- The extraction of Am(III), Pu(IV), and U(VI) decreases with an increase in temperature, indicating the exothermic nature of the extraction equilibria.
- The calculated extraction constants (log K ex) for Am(III), Pu(IV), and U(VI) using TODGA are higher than those for CMPO and DMDBTDMA, suggesting TODGA is a more effective extractant .

Thermodynamic Parameters (G, H, and S)

- The Gibbs energy change (G) follows the order: Am(III) > Pu(IV) > U(VI), indicating that the formation of the Am(III) TODGA complex is thermodynamically more favored.
- The extraction of Am(III) and U(VI) is enthalpy-driven, while the extraction of Pu(IV) is driven by both enthalpy and entropy.
- Higher exothermic enthalpy values (H) for Am(III) suggest stronger binding with TODGA compared to Pu(IV) and U(VI) .

Effect of Diluent on Nd(III) Loading

- The limiting organic concentration (LOC) for Nd(III) is low in n-dodecane but increases significantly in polar solvents like 1-octanol.
- The order of Nd(III) loading observed for different diluents is: n-dodecane < nitrobenzene < toluene 1,2-dichloroethane < 1-octanol.
- The Nd(III)-TODGA complex involves two extractant molecules in the inner coordination sphere in polar solvents and additional molecules in the outer sphere for non-polar solvents .

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Conclusion

- The extraction process of Am(III), Pu(IV), and U(VI) by TODGA is exothermic.
- The extraction of Am(III) and U(VI) is primarily driven by enthalpy, while entropy counteracts the extraction.
- In the case of Pu(IV), both enthalpy and entropy favor the extraction process.
- The extracted species of Am(III) changes depending on the diluent used.
- The nature of the diluent and the stoichiometry of the extracted species affect the loading of Nd(III) in the organic phase.
- At 3 M HNO3, the loading of Nd(III) by 0.1 M TODGA dissolved in different diluents follows the order: 1-octanol > toluene   1,2-dichloroethane > nitrobenzene > n-dodecane

Relevance to Study

Effectiveness of TODGA: The study demonstrates that TODGA is a highly effective extractant for trivalent actinides (Am(III), Pu(IV), U(VI)) from nitric acid medium, showing higher extraction constants (log K ex) compared to other extractants like CMPO and DMDBTDMA. This indicates its potential for efficient actinide partitioning in nuclear fuel reprocessing

Thermodynamic Parameters: The research provides detailed thermodynamic data (G, H, S) for the extraction processes, showing that the extraction of Am(III) and U(VI) is enthalpy-driven while the extraction of Pu(IV) is both enthalpy and entropy-favored. This information is crucial for understanding the energy dynamics and optimizing extraction processes in nuclear fuel cycles

Role of Diluent: The study investigates the impact of different diluents on the loading of Nd(III) in TODGA solutions, revealing that the choice of diluent significantly affects the extraction efficiency and stoichiometry of the extracted species. This insight helps in selecting appropriate solvent systems for specific extraction requirements in the nuclear fuel cycle

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Comparative Analysis: By comparing TODGA with other extractants like CMPO and DMDBTDMA, the study highlights the superior performance of TODGA in terms of extraction efficiency and thermodynamic stability. This comparative analysis aids in making informed decisions about ligand selection for actinide partitioning

Temperature Effects: The research emphasizes the exothermic nature of the extraction processes with TODGA and the decrease in extraction efficiency with increasing temperature. Understanding these temperature effects is vital for designing and operating extraction processes under varying thermal conditions in nuclear fuel reprocessing

Critical Parameters Identified

High Imporance

Thermodynamics

- The study provides detailed thermodynamic parameters (G, H, S) for the extraction of Am(III), Pu(IV), and U(VI) using TODGA, showing that the extraction of Am(III) and U(VI) is enthalpy-driven while Pu(IV) extraction is both enthalpy and entropy-favored
- Extraction constants (log K ex) indicate the strong binding and efficiency of TODGA in extracting actinides compared to other extractants like CMPO and DMDBTDMA

Medium Importance

Kinetics

- While specific kinetic data is not deeply explored in the study, the temperature-dependent extraction behavior suggests the importance of understanding kinetic factors for practical applications

Loading Capacity

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- While specific kinetic data is not deeply explored in the study, the temperature-dependent extraction behavior suggests the importance of understanding kinetic factors for practical applications

Operational Condition Range

- The effect of temperature on the extraction process indicates that TODGA can operate under varying thermal conditions, which is crucial for flexibility in nuclear fuel reprocessing operations

Low Importance

Solubility

- The study notes the role of different diluents on the extraction efficiency, indirectly addressing the solubility of the extracted species in various solvents

Dispersion Numbers

- Not specifically addressed in the study, but the efficiency of mass transfer could be inferred from the distribution ratios and loading capacities in different diluents.

Phase Disengagement

- Mentioned in terms of the loading studies, where the formation of a third phase was noted and managed by adding fresh organic phase, highlighting practical aspects of phase separation in the extraction process