

Key Words

TODGA

room temperature ionic liquids (RTILs)

actinide extraction

nitrate concentration

cation-exchange mechanism

alkyl chain length

distribution ratios

extraction kinetics

Am³⁺

Pu⁴⁺

UO₂⁺

solvent extraction

stripping studies

high level waste (HLW)

neutral extractant

Objective

1. Investigate the extraction behavior of Am³⁺, Pu⁴⁺, and UO₂⁺ using TODGA as the extractant in various room temperature ionic liquids (RTILs).
2. Compare the extraction efficiency of TODGA in RTILs with that in n-dodecane.
3. Study the effect of nitrate concentration on the extraction efficiency.
4. Determine the mechanism of extraction in RTILs and compare it with the extraction mechanism in n-dodecane.

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5. Analyze the impact of the alkyl chain length of the RTILs on the extraction performance.
6. Conduct kinetic studies to understand the rate of extraction of actinides in different valency states.
7. Examine the nature of the extracted species formed during the extraction process.
8. Perform stripping studies using various complexing agents to evaluate the feasibility of recovering extracted actinides.

Methodology

Materials

TODGA Synthesis: N,N,N',N'-tetraoctyl diglycolamide (TODGA) was synthesized following a previously reported procedure and characterized using NMR, IR, and elemental analysis.

Ionic Liquids: Ionic liquids (C_nmim⁺ NTf₂⁻, and C_nmim⁺ Cl⁻, where n = 4, 6, 8) were procured from Io-Li-Tec, Germany, and used as received.

Radiotracers: ²⁴¹Am, ²³³U, and Pu (mainly ²³⁹Pu) tracers were purified from associated radiotracer impurities by ion-exchange methods.

Stock Solutions: Made in dilute nitric acid and checked for purity by alpha spectrometry. Other reagents were AR grade and used without further purification.

Assaying: ²³³U and Pu were assayed by alpha-liquid scintillation counting using a toluene-based scintillator cocktail, and ²⁴¹Am was assayed by gamma counting using a NaI(Tl) well-type scintillation counter.

Solvent Extraction Studies

Preparation: Extractant solutions with desired concentrations of TODGA in n-dodecane and ionic liquids were prepared.

Agitation: These solutions were agitated with an equal volume of aqueous solutions spiked with radiotracers (²⁴¹Am, ²³³U, or ²³⁹Pu) in a rotary thermostated water bath for an hour at 25.0 ± 0.1

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Pre-equilibration: Organic solutions were pre-equilibrated with the aqueous phase prior to actual experiments containing radiotracers.

Centrifugation: Post equilibration, phases were centrifuged, and aliquots were taken from the aqueous phase for assaying using a liquid scintillation counter.

Distribution Ratio Calculation: The distribution ratio (D) was calculated from the aqueous phase counts

Kinetics of Extraction

- The kinetics of extraction of Am^{3+} , Pu^{4+} , and UO_2^{2+} were investigated using 1.0×10^{-2} M TODGA in $\text{C}_8\text{mim}^+ \text{NTf}_2^-$ at 1 M HNO_3 .

- Equilibrium times: Approximately 10 minutes for Am(III) and 30 minutes for U(VI) and Pu(IV) .

Effect of Aqueous Phase Acidity

Nitrate Ion Concentration: Increasing nitric acid concentration increases extraction in n-dodecane but decreases it in RTILs.

Anion Independence: RTILs showed negligible extraction in the absence of TODGA and marginal increases with higher feed acidity.

Mechanism of Extraction

Cation-Exchange: Demonstrated through distribution coefficient studies at varying C_nmim^+ concentrations in the aqueous phase and confirmed by varying the carbon chain length of the RTILs.

Stoichiometry: Slope analysis method used to determine the number of TODGA molecules

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associated with the extracted species, indicating different species formed in RTILs compared to n-dodecane.

Stripping Studies

- Conducted using complexing agents such as EDTA and DTPA in guanidine carbonate and buffer mixtures.

Efficiency: 0.05 M EDTA in 1.0 M guanidine carbonate was the most effective strippant, achieving cumulative stripping of approximately 91% for Am, 93% for U, and 82% for Pu in three contacts.

Key Findings

Kinetics of Extraction

Faster Extraction in RTILs: The kinetics of extraction for Am(III) were faster compared to U(VI) and Pu(IV). Equilibrium extraction was attained in about 10 minutes for Am(III) and about 30 minutes for U(VI) and Pu(IV).

Lower TODGA Concentration Required: The concentration of TODGA required for quantitative extraction was significantly lower in RTILs compared to n-dodecane, indicating enhanced extractability in RTILs.

Effect of Aqueous Phase Acidity

Decrease in Extraction with Increasing Acidity: The extraction of actinides decreased with increasing feed nitric acid concentration in RTILs, contrary to the behavior observed with n-dodecane, suggesting a different extraction mechanism in RTILs.

Cation-Exchange Mechanism: The extraction mechanism in RTILs was determined to be cation-exchange rather than nitrate ion-assisted complexation, which is prevalent in n-dodecane.

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Mechanism of Extraction

Enhanced Extraction in RTILs: The extraction of actinides by TODGA in RTILs was found to be significantly higher compared to n-dodecane, attributed to the cation-exchange mechanism.

Effect of Carbon Chain Length: Increasing the carbon chain length of the RTILs' alkyl group decreased the distribution coefficients of actinides, further confirming the cation-exchange mechanism.

Nature of the Extracted Species

Stoichiometry of Extracted Species: Slope analysis indicated that Am(III) formed a mixture of di- and tri-solvate species in RTILs, whereas U(VI) formed a mono-solvate, and Pu(IV) formed a mixture of mono- and di-solvate species. These findings differ from those in n-dodecane, where Am(III) forms tetra-solvate and Pu(IV) forms tri-solvate.

Stripping Studies

Effective Stripping Agent: Among the strippants tested, 0.05 M EDTA in 1.0 M guanidine carbonate was found to be the most effective, achieving cumulative stripping of approximately 91% for Am, 93% for U, and 82% for Pu in three contacts. This suggests that quantitative stripping is possible by increasing the number of stripping stages.

Conclusion

Enhanced Extraction Efficiency: The extraction efficiency of actinides (Am^{3+} , Pu^{4+} , and UO_2^{2+}) using TODGA in room temperature ionic liquids (RTILs) was significantly higher compared to conventional molecular diluents like n-dodecane.

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Dependence on Feed Nitric Acid Concentration: The extraction efficiency decreased with increasing feed nitric acid concentration, suggesting a different extraction mechanism in RTILs compared to n-dodecane.

Mechanism of Extraction: The extraction mechanism in RTILs was identified as cation-exchange, as opposed to the nitrate ion-assisted complexation mechanism in n-dodecane. This was supported by the effect of the alkyl chain length of the RTILs on the extraction performance.

Nature of Extracted Species: The stoichiometry of the extracted complexes differed between RTILs and n-dodecane. In RTILs, Am(III) formed di- and tri-solvate species, U(VI) formed a mono-solvate, and Pu(IV) formed mono- and di-solvate species, which are different from the species formed in n-dodecane.

Stripping Studies: The use of complexing agents like EDTA and DTPA in guanidine carbonate was effective in stripping the extracted actinides. 0.05 M EDTA in 1.0 M guanidine carbonate was found to be the most effective, achieving cumulative stripping efficiencies of approximately 91% for Am, 93% for U, and 82% for Pu in three contacts.

Relevance to Study

Enhanced Actinide Extraction: The study demonstrates that TODGA in room temperature ionic liquids (RTILs) significantly improves the extraction efficiency of actinides (Am^{3+} , Pu^{4+} , and UO_2^{2+}) compared to conventional molecular diluents like n-dodecane, which is critical for effective ligand selection in nuclear fuel cycle applications

Mechanism of Extraction: The extraction mechanism in RTILs was identified as cation-exchange, differing from the nitrate ion-assisted complexation seen with n-dodecane. This finding is essential for understanding how different ligands interact with actinides and can guide the selection of ligands based on the desired extraction mechanism

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Effect of Aqueous Phase Acidity: The study shows that the extraction efficiency of actinides decreases with increasing feed nitric acid concentration in RTILs, which is an important consideration for optimizing ligand performance under varying acidity conditions typical in nuclear fuel reprocessing

Stoichiometry of Extracted Species: The nature of the extracted species formed in RTILs is different from those formed in n-dodecane. This includes variations in the number of TODGA molecules associated with the extracted actinide species, providing insights into the coordination environment and stability of the complexes formed, which is vital for selecting ligands that form stable complexes with actinides

Stripping Efficiency: Effective stripping of extracted actinides using complexing agents like EDTA and DTPA in guanidine carbonate highlights the feasibility of recycling and reusing the extractant systems. This aspect is crucial for sustainable ligand use in nuclear fuel cycle chemistry

Role of Carbon Chain Length: The study indicates that the carbon chain length of the RTILs' alkyl group significantly affects the extraction performance of TODGA. This suggests that ligand design can be tailored to optimize extraction efficiency by modifying the hydrophobicity of the extraction medium

Critical Parameters Identified

High Importance

Chemical Stability

RTIL Stability: The study indicates that RTILs with PF₆⁻ counter anions are unstable at moderate to high concentrations of nitric acid, suggesting the need for RTILs with other counter anions like NTf₂⁻ and Cl⁻ for better stability

TODGA Stability: The use of TODGA in RTILs showed enhanced extraction efficiency, indicating its

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stability and functionality under the studied conditions

Radiolysis Resistance

Implicit Relevance: While not directly studied, the enhanced performance of TODGA in RTILs under various conditions suggests potential radiolysis resistance, an important factor for nuclear applications

Thermodynamics

Extraction Mechanism: The study found that TODGA in RTILs follows a cation-exchange mechanism, which differs from nitrate ion-assisted complexation in n-dodecane. This thermodynamic behavior influences selectivity and binding strength

Effect of Aqueous Phase Acidity: The extraction efficiency decreasing with increasing feed nitric acid concentration suggests specific thermodynamic properties of the system

Medium Importance

Kinetics (forwards and reverse)

Extraction Kinetics: The study shows that the extraction of Am(III) is faster compared to U(VI) and Pu(IV), with equilibrium times of 10 minutes for Am(III) and 30 minutes for U(VI) and Pu(IV)

Loading Capacity

Implicit in Distribution Ratios: The study mentions high distribution ratios for actinides using TODGA in RTILs, implying a high loading capacity under the studied conditions

Operational Condition Range

Effect of Alkyl Chain Length: The study highlights the impact of the alkyl chain length of RTILs on extraction performance, indicating that TODGA can operate under various conditions by modifying the hydrophobicity of the RTILs

Stripping Studies: Successful stripping using complexing agents like EDTA and DTPA in guanidine

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carbonate demonstrates operational flexibility and efficiency

Low Importance

Solubility

RTILs and TODGA: The solubility of TODGA in RTILs was sufficient for effective extraction, although solubility was not a primary focus of the study

Dispersion Numbers:

Not Directly Addressed: The study does not provide specific details on dispersion numbers but focuses on the overall extraction efficiency and mechanisms

Phase Disengagement

Centrifugation Method: Phase disengagement was achieved by centrifugation, indicating practical separation, although detailed metrics on phase disengagement efficiency are not provided