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Key Words

TODGA

DOHyA

trivalent metal ions

nitric acid

phase modifier

third-phase formation

radiolytic stability

density

viscosity

gamma dose

molecular interactions

solvent extraction

high-level liquid waste (HLLW)

lanthanides

actinides

Objective

1. To invetigate the physiochemical properties (density and viscosity) of the combined solvent system (0.15 mol kg 1 of TODGA and 0.29 mol kg 1 of DOHyA in n-DD) and compare these with the individual systems under various temperatures and absorbed gamma doses.

2. To evaluate the stability of the solvent system toward radiation by measuring the changes in density and viscosity after exposure to gamma radiation.

3. To understand the molecular interactions within the solvent system by analyzing thermodynamic

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parameters like the activation energy of viscous flow, molar volume, and excess viscosity

4. To determine the suitability of the solvetn system for industrial-scale applications by assessing its stability and behavior under operational conditions relevant to nuclear reprocessing.

5. To explore the extraction efficienct of the solvent system for trivalent metal ions from nitric acid, focusing on its performance in separating lanthanides and actinides from high-level liquid waste (HLLW).

6. To mitgate third-phase formation during the extraction process by incorporating DOHyA as a phase modifier for the TODGA/n-DD system.

7. To investigate the radiolytic degradation of TODGA and DOHyA and their effects on the solvent extraction efficiency and physicochemical properties.

8. To analyze the impact of temperature on the density and viscosity of the solvent system and understand its implications for solvent extraction processes.

9. To study the aggregation behavior of the solvent system through dynamic light scattering (DLS) and evaluate the size and distribution of reverse micellar aggregates.

10. To assess the thermodynamic stability of the solvent system by calculating excess thermodynamic parameters and understanding the forces acting within the liquid mixture.

Methodology

Materials and Methods

Materials

- Analytical grade chemicals or solvents with purity > 98% were utilized without further purification.
- TODGA was purchased from M/s Orion Chemical Company, Mumbai, India, and further purified by a column chromatographic procedure.
- DOHyA was synthesized and purified by the outlined procedure.

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- The weighed amounts of DOHyA or TODGA were mixed in n-DD (Alfa Aesar, 99%) to make solutions of desired compositions.

- Nitric acid concentration in the stock solution was estimated by conventional acid base titration using phenolphthalein as the indicator.

- The stock solution of Nd(III) was made by weighing a known amount of Nd(NO3)3 6H2O and dissolving it in dilute nitric acid solution.

- Mixing of the aqueous and organic phases during extraction studies was done in a vertical tube vibrating rotator for 30 min.

- Complexometric EDTA titration was used to estimate the concentration of Nd(III) in the aqueous and organic phases using methyl thymol blue as the indicator.

Density and Viscosity Measurements

- Density and viscosity of samples were assessed as per ASTM-D4052 using an Anton Paar DMA 4500 digital vibrating U-tube densitometer with automated viscosity correction in the temperature range of 298 to 323 K.

- Dynamic viscosity was measured using a Hoeppler s principle-based Lovis 2000 ME Anton Paar viscometer.

- The instrument was calibrated daily using ambient air and Millipore quality water.

- At least five measurements were done for each sample to ensure accuracy.

Dynamic Light Scattering (DLS)

- DLS analysis was carried out using a Malvern Zetasizer device.

- The principle involves Brownian motion and scattering of monochromatic light in solution, with fluctuations in scattered light intensity providing information on the diffusion coefficient of aggregates.

- Approximately 0.5 mL of organic phase was filtered through a 0.3 m disposable polypropylene membrane filter before DLS measurements.

- A monochromatic He Ne laser (wavelength 632.8 nm) was used, and the particle size was measured at 298 K.

Irradiation Studies

- The organic solution composed of TODGA, DOHyA, or a combination in n-DD was exposed to various radiation levels using a 60Co -chamber facility with a dosage rate of 1.7 kGy h 1.
- Samples were exposed to radiation at varied absorbed dose levels, and the physicochemical properties of the radiation-exposed samples were measured.

Sample Preparation

- Equal amounts of organic phase (0.15 mol kg 1 of TODGA and 0.29 mol kg 1 of DOHyA in n-DD) and an aqueous phase (different concentrations of nitric acid or Nd(III) in nitric acid) were equilibrated for an hour at 298 K.
- Post-equilibration, the organic phase was subjected to density and viscosity measurements or exposed to various absorbed gamma doses before measurement.

Key Findings

Density and Viscosity Measurements

Density of Individual and Combined Solvent Systems

Temperature Dependence

- Density of neat TODGA decreases from 905 to 888 kg/m and DOHyA from 902 to 885 kg/m as temperature increases from 298 to 323 K.
- Combined System: Density variation in 0.15 mol/kg of TODGA in n-DD, 0.29 mol/kg of DOHyA in n-DD, and their combination shows that the combined system exhibits higher densities due to polar-polar interactions.

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- Addition of n-DD helps to increase the disparity between the densities of both aqueous and organic phases, facilitating quicker phase disengagement during solvent extraction.

Impact of Gama Irradiation on Density

- Slight increase in density with absorbed gamma dose; higher for combined TODGA+DOHyA system compared to individual systems.
- Density of the organic phase increases with increasing absorbed dose, attributed to the formation of polar degradation products from irradiation.
- Density values decrease as a function of temperature

Viscosity of Individual and Combined Solvent Systems

Temperature Dependence

- Viscosity of neat TODGA decreases from 0.132 to 0.036 Pa s and DOHyA from 0.023 to 0.008 Pa s as temperature increases from 298 to 323 K.
- The combined system exhibits higher viscosities than the individual systems, due to stronger molecular interactions between TODGA and DOHyA.
- Viscosity decreases with increasing temperature for both individual and combined systems

Impact of Gamma Irradiation on Viscosity

- Viscosity increases with absorbed gamma dose, likely due to formation of polar degradation products that enhance polar-polar interactions.
- Combined TODGA+DOHyA system shows less variation in viscosity, indicating better stability under irradiation compared to individual systems

Effects of Gamma Irradiation

Density and Viscosity Changes Post-Irradiation

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- Density and viscosity of all systems increase with gamma dose, attributed to the formation of polar degradation products that enhance polar-polar interactions.
- Combined TODGA+DOHyA system demonstrates minimal changes in density and viscosity, signifying exceptional stability under irradiation

Extraction Efficiency and Stability

Third-Phase Formation

- DOHyA effectively mitigates third-phase formation in TODGA solutions by modifying phase behavior, which is crucial for maintaining efficiency in metal ion extraction.
- Dynamic Light Scattering (DLS) analysis shows that DOHyA reduces the size of reverse micellar aggregates, thus stabilizing the solvent system

Thermodyanmic Parameters

Activation Energy

- Decreases with increasing gamma dose, indicating reduced molecular interactions facilitating viscous flow under irradiated conditions.
- Higher activation energy for combined system shows it is less vulnerable to changes in viscosity with temperature

Entropy and Enthalpy

- Variations suggest weak molecular interactions in the combined system, corroborating stability and reduced sensitivity to temperature changes

Extraction of Metal Ions

Efficiency

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- Combined TODGA+DOHyA system shows superior performance in extracting Nd(III) from nitric acid solutions, attributed to stronger interactions within the solvent system

Overall Stability

Radiolytic Stability

- Combined solvent system exhibits minimal changes in density and viscosity even at high radiation doses, demonstrating exceptional stability and suitability for nuclear reprocessing applications

Conclusion

Combined Solvent System

- The combination of TODGA and DOHyA in n-dodecane (n-DD) forms a robust solvent system exhibiting superior physicochemical properties compared to individual components.
- Enhanced density and viscosity characteristics were observed, contributing to the overall stability of the solvent system under various operational conditions .

Impact on Temperature

- Both density and viscosity decrease with an increase in temperature for neat TODGA and DOHyA solutions as well as their combination in n-DD.
- The combined solvent system exhibits higher densities and viscosities than individual systems, suggesting stronger molecular interactions between TODGA and DOHyA .

Gamma Irradiation

- Density and viscosity of the solvent systems increase slightly with gamma irradiation dose due to the formation of polar degradation products, enhancing polar-polar interactions.
- The combined TODGA+DOHyA system shows minimal variation in properties, indicating better radiolytic stability compared to individual components .

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Third-Phase Formation

- The addition of DOHyA effectively prevents third-phase formation in the TODGA/n-DD system, crucial for maintaining extraction efficiency.
- Dynamic Light Scattering (DLS) analysis indicates that DOHyA reduces the size of reverse micellar aggregates, stabilizing the solvent system .

Extraction Efficiency

- The combined TODGA+DOHyA system demonstrates superior performance in extracting Nd(III) from nitric acid solutions, attributed to stronger interactions within the solvent system.
- The extraction efficiency improves with the use of DOHyA, which acts as a phase modifier and enhances the overall extraction process .

Thermodynamoc Stability

- The activation energy for viscous flow decreases with increasing gamma dose, indicating reduced molecular interactions.
- The combined system shows higher activation energy, reflecting less sensitivity to temperature changes and better stability under irradiated conditions .

Radiolytic Stability

- The combined solvent system exhibits exceptional radiolytic stability, with minimal changes in density and viscosity even at high radiation doses.
- This stability makes it an excellent candidate for nuclear reprocessing applications, ensuring consistent performance under operational conditions .

Relevance to Study

Physiochemical Properties: The study provides detailed insights into the density and viscosity of the TODGA+DOHyA/n-DD solvent system, essential for understanding molecular interactions and stability. This information is critical for selecting ligands that maintain favorable physicochemical properties under operational conditions

Radiolytic Stability: The exceptional radiolytic stability of the TODGA+DOHyA system under gamma irradiation is highlighted. Ligand stability under radiation is crucial for long-term use in nuclear fuel reprocessing, ensuring consistent performance without significant degradation

Third-Phase Formation: The addition of DOHyA prevents third-phase formation, a common issue in solvent extraction processes. Understanding how phase modifiers like DOHyA enhance phase stability helps in selecting ligands that can operate efficiently without phase separation issues

Thermodynamic Parameters: The study includes extensive data on activation energy, enthalpy, and entropy of the combined solvent system. These thermodynamic parameters provide insights into the energy requirements and molecular behavior of the solvent, aiding in the selection of ligands that optimize extraction processes

Extraction Efficiency: The combined TODGA+DOHyA system demonstrates superior extraction efficiency for trivalent metal ions like Nd(III) from nitric acid. High extraction efficiency is a key criterion for ligand selection, ensuring effective separation of actinides and lanthanides

Aggregate Behavior: Dynamic Light Scattering (DLS) analysis shows that DOHyA reduces the size of reverse micellar aggregates, indicating better control over molecular aggregation. Controlling aggregate size is important for maintaining solvent performance and preventing clogging or phase separation

Operational Conditions: The document discusses the performance of the solvent system under various temperatures and radiation doses, providing a comprehensive view of its robustness. Ligands that perform well under diverse operational conditions are preferred for the nuclear fuel cycle

Long-Term Stability: The combined solvent system's minimal changes in density and viscosity under irradiation underscore its long-term suitability for nuclear reprocessing applications, a crucial factor in ligand selection

Critical Parameters Identified

High Importance

Chemical Stability: The study indicates that the TODGA+DOHyA solvent system exhibits strong resistance to acid and base hydrolysis. The addition of DOHyA helps mitigate third-phase formation, ensuring the chemical stability of the solvent system in the presence of high metal ion concentrations from nitric acid

Radiolysis Resistance: The combined TODGA+DOHyA system shows minimal changes in density and viscosity even at high gamma radiation doses, demonstrating exceptional radiolytic stability. This ensures that the ligands maintain their separation efficiency under radiation exposure

Thermodynamics: The study provides extensive data on the thermodynamic parameters, including activation energy, enthalpy, and entropy, indicating that the TODGA+DOHyA system has favorable thermodynamic properties for metal ion extraction. These properties influence the selectivity and binding strength of ligands towards specific metal ions, making the separation process feasible

Medium Importance

Kinetics (forwards and reverse): The study discusses the kinetics of the extraction process, noting that the combined solvent system facilitates efficient forward and reverse reactions. This ensures that the separation occurs within practical time frames and is reversible if necessary

Loading Capacity: The combined TODGA+DOHyA system demonstrates a high loading capacity for Nd(III) from nitric acid solutions, indicating that it can process significant amounts of material before becoming saturated. This is important for the efficiency of the separation process

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Operational Condition Range: The solvent system performs well under a broad range of temperatures and radiation doses, indicating its robustness and flexibility. This increases the applicability of the separation process under various operational conditions encountered in nuclear fuel reprocessing

Low Importance

Solubility: While the solubility of TODGA and DOHyA in n-dodecane is adequate for the extraction process, it is less critical compared to other parameters. Solubility can often be modified through solvent selection or operational conditions

DIspersion Numbers (for applied systems with conditional values): The study briefly mentions the impact of molecular interactions on the efficiency of mass transfer between phases, but this is specific to the system setup and thus ranked lower in importance

Phase Disengagement (for applied systems with conditional values): The ability of DOHyA to prevent third-phase formation is critical for practical phase separation after extraction. However, this is highly dependent on system design and operation parameters, making it less critical than the other parameters