REFERENCE: 20030

Key Words

ALSEP

T2EHDGA

speciation model

trivalent actinides and lanthanides

extraction constant

Objective

1. Investigate the Liquid-Liquid Distribution Behavior: The primary objective is to study the distribution behavior of nitric acid (HNO3) and water by the diglycolamide (DGA) ligand, N,N,N ,N -tetra-2-ethylhexyldiglycolamide (T2EHDGA), into an n-dodecane diluent.

2. Characterize Organic Extraction Solutions: The study employs spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) to characterize the organic extraction solutions and understand the coordination of T2EHDGA with HNO3.

3. Model Nitric Acid Distribution: The research aims to model the experimentally observed distribution of HNO3 using the computer program SXLSQI, identifying the formation of organic-phase species such as HNO3 T2EHDGA and (HNO3)2 T2EHDGA.

4. Determine Thermodynamic Extraction Constants: The study includes temperature-dependent solvent extraction studies to determine the thermodynamic extraction constants, as well as the enthalpy (H) and entropy (S) parameters for the corresponding extractive processes.

5. Understand Water Extraction Behavior: It examines how the presence of HNO3 affects water extraction and characterizes the behavior of water extraction in the presence of nitric acid.

Methodology

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Materials

- T2EHDGA: Purchased from Eichrom Technologies and purified by column chromatography.

- Aqueous Solutions: Prepared using distilled, deionized water. Nitric acid (HNO3) was standardized using a Metrohm 905 Automatic Titrator.

- Organic Solvent: n-Dodecane obtained from Alfa Aesar.

Solvent Extraction Experiments

1. Kinetic Experiments:

- Determined the equilibrium contact time for HNO3 extraction.

- Equal volumes of 0.1 M T2EHDGA in n-dodecane and 1.5 M HNO3 were contacted at 25 C for different times (1 min to 6 hours).

- Equilibrium was achieved after 5 minutes.

2. Mechanism Determination

- Samples of 0.1 M T2EHDGA in n-dodecane were contacted with 0.1 3 M HNO3.

- Experiments were conducted at temperatures ranging from 25 to 50 C to avoid third-phase formation.

3. Ligand Concentration Dependence

- The extractant concentration was varied from 0.01 to 0.2 M T2EHDGA in n-dodecane, with a fixed aqueous phase acid concentration of 2.08 M HNO3.

4. Ion Chromatography (ID):

- Used for determining the concentration of NO_3^- in stock HNO3 solutions, post-contacted aqueous phases, and stripped aqueous samples.

Modeling and Data Analysis

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Thermodynamic Analysis:

- Equilibrium HNO3 distribution data was modeled using the SXLSQI program, which considers activity coefficients and other solute species interactions.
- Two organic-phase species (HNO3 T2EHDGA and (HNO3)2 T2EHDGA) were assumed for modeling.

Vapor Pressure Osmometry (VPO):

- Evaluated the aggregation behavior of T2EHDGA in n-heptane.
- Measurements were performed for T2EHDGA solutions contacted with 0 5 M HNO3.

Spectroscopic Characterization

1. FTIR Spectroscopy:

- Conducted using a Bruker ALPHA Platinum ATR module.
- Measured changes in T2EHDGA speciation upon equilibration with water and HNO3.

2. NMR Spectroscopy

- Heteronuclear (13C, 1H, and 15N) NMR measurements were run with a 500 MHz Oxford magnet and Agilent DD2 console.
- 15N-labeled HNO3 was used to investigate extraction speciation.

Water Partitioning Studies

Karl FIscher Titration:

- Analyzed the partitioning of water into T2EHDGA solutions in n-dodecane under variable extractant and HNO3 concentrations.

Key Parameters for Modeling

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Pitzer Parameters and Masson Coefficients: Used for the activity coefficients of solute species in the aqueous phase.

Hildebrand-Scott Treatment: Applied for activity effects in the organic phase.

Key Findings

1. Extraction of Water by T2EHDGA

Water Extraction Behavior: The study found that organic-phase water concentrations increased with the T2EHDGA concentration. When 2 M HNO3 was present, the water concentration in the organic phase increased significantly from 30 mM to over 80 mM.

Impact of HNO3: There was a notable increase in water extraction when aqueous HNO3 concentrations exceeded 1 M. The water content in the organic phase correlated linearly with the concentration of HNO3 extracted, maintaining a constant ratio of [HNO3]/[H2O] = 3.6 0.2 for aqueous acidities above 1 M HNO3.

Spectroscopic Analysis: FTIR and Raman spectroscopies did not show characteristic O H vibrational envelopes, suggesting significant alterations in the symmetry of water in the organic phase, making its vibrational modes spectroscopically silent .

2. Aggregation of T2EHDGA in n-Dodecane by VPO

Aggregation Behavior: Vapor Pressure Osmometry (VPO) showed that T2EHDGA tended to form a mixture of monomeric and higher-order dimeric species in pristine solutions. Upon water washing, the aggregation number dropped to indicate primarily monomeric species.

Effect of HNO3: At HNO3 concentrations of 3 M and higher, the study observed extensive aggregation, with visible third-phase formation above 5 M HNO3. This suggests the formation of high-order aggregates with greater than 1:1 stoichiometry in T2EHDGA solutions contacted with high HNO3 concentrations .

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3. HNO3 Distribution Studies

Distribution Ratio: The study measured the distribution ratio (D) of HNO3 as a function of initial HNO3 concentration and T2EHDGA concentration at 25 C. The best fit model assumed the formation of 1:1 and 2:1 HNO3 complexes

Equilibrium Constants: Refined equilibrium constants for the extraction of HNO3 by T2EHDGA were determined, showing good agreement with experimental data up to 2 M HNO3. The study observed that the organic phase was likely saturated with HNO3 at higher concentrations due to the formation of larger aggregates.

Temperature Dependence: The extraction of HNO3 decreased slightly with increasing temperature, indicating exothermic behavior. The Van't Hoff plot suggested that both 1:1 and 2:1 complex formations were driven by exothermic enthalpy terms, compensating for unfavorable entropy terms .

4. FTIR Characterization of the Organic Extraction Solutions

Spectral Changes: The FTIR spectrum showed significant changes upon equilibration with HNO3. Key vibrational bands of T2EHDGA shifted upon contact with HNO3, indicating interactions such as hydrogen bonding between the carbonyl oxygen and the proton from HNO3. These changes were not observed upon contact with water alone .

5. NMR Spectroscopy

Chemical Shifts: NMR spectroscopy revealed distinct chemical shifts in T2EHDGA upon contact with HNO3. The carbonyl carbon shifted downfield, consistent with hydrogen bonding, while other carbons exhibited shifts due to the -effect.

Aggregation Effects: Significant broadening of NMR resonances at higher HNO3 concentrations indicated changes in T2EHDGA speciation, consistent with the formation of (HNO3)2 T2EHDGA and possibly higher-order aggregates .

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Conclusion

1. HNO3 Extraction Mechanism: The extraction of HNO3 by T2EHDGA in n-dodecane is adequately described by the formation of two organic species: HNO3 T2EHDGA and (HNO3)2 T2EHDGA. These species were identified through a combination of FTIR, 13C, 1H, and 15N NMR spectroscopies, which provided evidence of interactions between HNO3 and the T2EHDGA carbonyl group, along with successive binding of HNO3.

2. Aggregation Behavior: As aqueous acidity approaches 3 M HNO3, there is evidence of significant aggregation behavior in the organic phase, leading to third-phase formation. This aggregation is dependent on both the extractant concentration and the aqueous acidity.

3. Water Co-Extraction: HNO3 co-extracts a significant amount of water into the organic phase. This finding is important for understanding the overall extraction mechanism and the role of water in the process.

4. Thermodynamic Analysis: Variable-temperature studies on the extraction of HNO3 indicate that the reactions are exothermic. The enthalpy (H) and entropy (S) parameters for the corresponding extractive processes were determined, with a slightly greater temperature dependence observed for the higher-order HNO3 species.

5. Modeling and Experimental Validation: The experimentally observed distribution of HNO3 was successfully modeled using the computer program SXLSQI. The model's predictions matched well with the experimental data, validating the formation of 1:1 and 2:1 HNO3

complexes in the organic solutions equilibrated with aqueous HNO3 solutions below 3 M.

Relevance to Study

1. Understanding Extraction Mechanisms:

- The study elucidates the extraction mechanisms of nitric acid (HNO3) by T2EHDGA, showing the

formation of specific organic-phase species (HNO3 T2EHDGA and (HNO3)2 T2EHDGA). This understanding is crucial for selecting ligands that can efficiently manage the acid environment in nuclear reprocessing

2. Aggregation Behavior

- Insights into the aggregation behavior of T2EHDGA in the presence of HNO3 provide valuable information for predicting phase behavior and avoiding issues such as third-phase formation, which can complicate the extraction processes in nuclear fuel reprocessing

3. Temperature and Solubility Effects

- The study highlights the exothermic nature of the extraction reactions and the impact of temperature on the distribution ratios. This information helps in designing processes that remain efficient across a range of operational temperatures

4. Thermodynamic Parameters

- Determining the thermodynamic parameters (H and S) for the extraction processes aids in predicting the behavior of extraction systems under different conditions, essential for robust ligand selection

5. Co-Extraction of Water

- The study shows that HNO3 co-extracts significant amounts of water into the organic phase, which can affect the efficiency and selectivity of the extraction process. Understanding this behavior is key to selecting ligands that minimize undesirable co-extraction

6. Spectroscopic Characterization

- Detailed FTIR and NMR spectroscopic characterization of the organic extraction solutions provide insights into the molecular interactions and stability of the ligands under extraction conditions, critical for selecting ligands with the desired chemical properties

7. Comparative Performance of DGAs:

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- The comparison with other diglycolamide (DGA) ligands, such as TODGA, and the specific performance of T2EHDGA in different contexts, inform the selection process by highlighting the strengths and limitations of various DGAs for actinide and lanthanide separation

8. Application in ALSEP Process

- The study supports the development of the Actinide Lanthanide Separation Process (ALSEP), which combines T2EHDGA with acidic extractants for selective co-extraction. Understanding T2EHDGA's behavior helps in optimizing this process for nuclear fuel reprocessing

Critical Parameters Identified

High Importance

1. Chemical Stability

Aggregation Behavior: The study found that T2EHDGA aggregates significantly at high HNO3 concentrations, forming high-order aggregates and potentially a third phase. This indicates a need for chemical stability under varying acid concentrations to prevent phase separation issues

FTIR and NMR Spectroscopy: Characterization using FTIR and NMR revealed that T2EHDGA forms stable complexes with HNO3 (HNO3 T2EHDGA and (HNO3)2 T2EHDGA). The chemical stability of these complexes is crucial for the ligand s performance in the separation process

2. Radiolysis Resistance

Not directly addressed: The study does not directly investigate the radiolysis resistance of T2EHDGA. However, the chemical stability insights can indirectly inform the selection of ligands with potential radiolysis resistance.

3. Thermodynamics

Thermodynamic Parameters: The study provides detailed thermodynamic parameters (H and S) for the extraction processes. The exothermic nature of these processes indicates their feasibility and

helps in understanding the selectivity and binding strength of T2EHDGA towards HNO3

Temperature Dependence: The findings show that the extraction reactions are exothermic and slightly temperature-dependent, crucial for designing efficient separation processes under various thermal conditions

Medium Importance

1. Kinetics

Equilibrium Contact Time: The study determined that equilibrium for HNO3 extraction is achieved within 5 minutes, indicating efficient kinetics for the forward extraction process

2. Loading Capacity

HNO3 Loading: The formation of higher-order aggregates at high HNO3 concentrations suggests a high loading capacity for HNO3. This is essential for processing large amounts of material before the ligand becomes saturated

3. Operational Condition Range

Variable Aqueous HNO3 Concentrations: The study examines the behavior of T2EHDGA under a range of HNO3 concentrations (0.1 3 M), showing its ability to operate under varying acidic conditions, which increases the flexibility of the separation process

Low Importance

1. Solubility

Water Co-Extraction: The study finds that HNO3 co-extracts significant amounts of water into the organic phase, impacting the solubility of the system. Although important, this can be managed through solvent selection and process conditions

2. Dispersion Numbers

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Not specifically addressed: The study does not focus on dispersion numbers or their impact on mass transfer efficiency.

3. Phase Disengagement

Aggregation and Third-Phase Formation: The findings about aggregation behavior and third-phase formation are related to phase disengagement. Proper ligand selection can mitigate these issues, although it is highly dependent on system design and operational parameters