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Key Words

nitric acid extraction

TODGA

1-octanol

solvent phase

equilibrium model

SANEX process

adducts

temperature range

antagonistic effects

synergistic effects

activation energy

arrhenius expression

phase modifier

third-phase formation

empirical model

Objective

1. To generate distribution data for the partition of nitric acid between aqueous and solvent phases comprising various combinations of TODGA, octanol, and kerosene diluent across a range of conditions.

2. To derive a model describing the equilibrium of nitric acid between phases suitable for incorporation in process models like the innovative SANEX process.

3. To investigate the formation of nitric acid/octanol adducts and their impact on extraction

efficiency.

4. To identify and model the synergistic and antagonistic effects in nitric acid extraction when using TODGA and octanol mixtures.

5. To determine the effect of temperature on the extraction of nitric acid using an Arrhenius type expression.

6. To ensure the model accounts for the presence of different adducts in the extracted nitric acid and predict the prevalence of these adducts under varying conditions.

7. To explore the applicability and limitations of the model under conditions not directly covered by the experimental data.

8. To assess the impact of varying acidity and extractant concentrations on the distribution ratios of nitric acid.

9. To validate the model against experimental data and refine it for practical applications in solvent extraction processes.

Methodology

1. Experimental Setup

Materials: TODGA was synthesized or bought, Exxsol D80 and TPH were used as diluents, and 1-octanol and nitric acid were used as received.

Aqueous Phase: Nitric acid concentrations ranged from 0.1 to 9 mol/L.

Organic Phase: TODGA concentrations ranged from 0.05 to 0.4 mol/L, with or without 5 v/v% octanol.

2. Procedures

Mixing and Contacting: Equal volumes of aqueous and organic phases were contacted on an orbital shaker for 15 minutes at various temperatures (20   0.5 C, 22   1 C, or ambient).

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Centrifugation: Following mixing, the samples were centrifuged.

Stripping and Titration: Organic-phase aliquots were stripped into water, and nitric acid concentrations were determined by duplicate potentiometric titration with NaOH.

3. Temperature Effect Studies:

- Experiments were performed at temperatures ranging from 10 to 50 C to quantify the effect of temperature on nitric acid extraction.

- Samples were shaken in a temperature-controlled water bath and left overnight for phase disengagement.

4. Data Collection:

Distribution Data: The data collected covered a range of conditions from 0 to 9 mol/L HNO3(aq), 0 100% octanol, and 0 0.4 mol/L TODGA.

Temperature Range: Data included variations in temperature from 10 C to 50 C.

5. Modelling Approach

Model Derivation: The equilibrium model was derived using the experimental data.

Adduct Formation: The model considered the formation of multiple nitric acid/TODGA and nitric acid/octanol adducts.

Empirical Fitting: The model was empirically fitted to the experimental data using gPROMS software to estimate parameters and variances.

6. Validation

Comparison with Experimental Data: The derived models were validated against experimental results to ensure accuracy and applicability.

Key Findings

Extraction of Nitric Acid into Octanol

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- The extraction of nitric acid into octanol involves the formation of HNO3 Octanol and HNO3 2Octanol adducts.

- The empirical model indicates a better fit when considering an HNO3 3Octanol adduct as well .

Extraction of Nitric Acid into TODGA

- Nitric acid extraction into TODGA involves the formation of multiple adducts, including 4HNO3 TODGA.

- The model developed fits the available data well, but there are limitations due to potential other unidentified adducts .

Extraction of Nitric Acid into TODGA-Octanol Solvents

- The model shows that extraction of nitric acid into TODGA is generally more significant than into octanol, except when high concentrations of octanol are used.

- The addition of cross-adducts (iHNO3 jTODGA kOctanol) improves the model's accuracy significantly .

Performance of Correlations Neglecting SYnergistic Effects

- Models that neglect the synergistic effects of TODGA and octanol tend to under-predict nitric acid extraction at high concentrations and over-predict at lower concentrations.

- Inclusion of synergistic effects yields better agreement with experimental data .

Inclusion of Synergistic Extraction of Acid by TODGA-Octanol Mixtures

- Synergistic effects between TODGA and octanol significantly influence the extraction process.

- The improved model accounts for these effects and better predicts nitric acid extraction across various conditions .

Predicted Prevalence of Different Adducts in Extracted Nitric Acid

- A significant fraction of octanol remains unbound, with various adducts contributing to the overall extraction efficiency.

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- The 4HNO3 TODGA adduct is notable only at the highest acidity levels, while HNO3 2Octanol and HNO3 3Octanol adducts are significant only at high octanol concentrations .

Temperature Effects

- Temperature significantly affects the extraction process, with data collected over a range of 10 50 C.
- The model includes temperature dependence, improving the accuracy of predictions for different conditions .

Model Applicability and Limitations

- The empirical nature of the model limits its applicability beyond the range of data used for fitting.
- The model performs well within the tested ranges of 0.05 0.3 mol/L TODGA, 5 50 v/v% octanol, 0 5 mol/L HNO3, and 10 50 C, but may not extrapolate reliably beyond these conditions .

Conclusion

Sophisticated Models Developed: Models for the extraction of nitric acid into octanol, TODGA, and TODGA + 5 v/v% octanol were developed, encompassing a range of nitric acid and TODGA concentrations and temperatures relevant to process modeling.

reasonable Agreement with Experimental Data: The additive model for TODGA/octanol solvents predicted nitric acid extraction into TODGA plus nitric acid extraction into octanol, showing reasonable agreement with experimental data.

Systematic Under- and OverPrediction: Nitric acid extraction was systematically under-predicted for aqueous nitric acid concentrations above about 1.5 mol/L HNO3 and over-predicted for lower nitric acid concentrations.

Improved Accuracy with Cross-Adducts: Including cross-adducts (iHNO3 jTODGA kOctanol) significantly improved the model's accuracy.

Temperature Dependence: Fitting of temperature series data (10 50 C) showed a temperature dependence dictated by the relationship:

No Diluent Dependence Found: The model found no dependence on the diluent for nitric acid extraction.

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Relevance to Study

Comprehensive Data on Nitric Acid Extraction: The study provides extensive data on the extraction of nitric acid into TODGA, octanol, and their mixtures, covering a range of concentrations and temperatures

Equilibrium Models: Development of sophisticated equilibrium models describing the extraction behavior of nitric acid into these solvents. These models are essential for designing and optimizing solvent extraction processes in nuclear fuel reprocessing

Adduct Formation: Identification of various nitric acid/TODGA and nitric acid/octanol adducts, including complex cross-adducts. Understanding these interactions helps in predicting extraction efficiencies and improving ligand formulations

Synergistic Antagonistic Effects: The study highlights the synergistic and antagonistic effects observed in the extraction process when using TODGA and octanol mixtures. These effects influence the overall efficiency and selectivity of the extraction process

Temperature Dependence: Detailed analysis of the temperature dependence of nitric acid extraction, providing an Arrhenius type expression for modeling purposes. This information is crucial for process optimization under different operational conditions

Impact on Process Modeling: The derived models are suitable for incorporation into process models such as SANEX, which are used in advanced nuclear fuel reprocessing to separate actinides from

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lanthanides

Model Limitation and Applicability: The study discusses the applicability and limitations of the developed models, emphasizing the need for empirical adjustments and validations under different conditions. This insight is valuable for extending the models to other solvent systems and operational scenarios

Critical Parameters Identified

High Importance

Chemical Stability

Adduct Formation: Identification of stable nitric acid/TODGA and nitric acid/octanol adducts, ensuring the ligands remain functional under various conditions

Equilibrium Models: Models describing the stable equilibrium of nitric acid extraction into different solvents, which are essential for predicting and ensuring the stability of the ligands during the process

Radiolysis Resistance

Not specifically addressed in the study. The focus is on chemical interactions and thermodynamics rather than radiolysis resistance.

Thermodynamics

Temperature Dependence: Analysis of the temperature dependence of nitric acid extraction, providing an Arrhenius type expression for modeling purposes, which is crucial for understanding the fundamental feasibility and efficiency of the separation process

Synergistic and Antagonistic Effects: Understanding the thermodynamic interactions between TODGA and octanol, which influence the overall extraction efficiency and selectivity

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Medium Importance

Kinetics

Equilibrium and Contact Time: The study includes data on the equilibrium times for the extraction process, which relates to the kinetics of the system, ensuring practical time frames for separation

Loading Capacity

Adduct Saturation: The formation and prevalence of various adducts under different conditions provide insights into the loading capacity of the ligands, indicating how much nitric acid can be extracted before saturation

Operational Condition Range:

Temperature and Concentration Ranges: The study covers a broad range of nitric acid and TODGA concentrations and temperatures, indicating the flexibility and applicability of the ligands under different operational conditions

Low Importance

Solubility

Not explicitly addressed in the study. Solubility of the ligands and solvents can be managed through the selection of appropriate solvents and conditions.

Dispersion Numbers:

Not specifically discussed. The study does not focus on the dispersion numbers or mass transfer efficiency between phases.

Phase Disengagement

Third-Phase Formation: Mention of the tendency for TODGA-diluent mixtures to form a third phase at moderate loadings of nitric acid, which is relevant for phase disengagement and practical separation but is considered of lower importance