

## **Key Words**

solvent extraction

donor properties

sulphoxides

phosphine oxides

infrared frequency

## **Objective**

1. Compare Donor Properties: To conduct a comparative analysis of the donor properties of sulphoxides and phosphine oxides in the context of solvent extraction.
2. New Assessment Method: To introduce and describe a new method for assessing the relative donor strengths of both sulphoxides and phosphine oxides based on the shift in the symmetric stretching frequency of OH of water on coordination with the donor.
3. Evaluate Extraction Efficiency: To report the extraction efficiencies of water, perchloric acid, hydrochloric acid, and pertechnetate acid by dibutyl sulphoxide (DBSO).
4. Correlation Study: To investigate the correlation between the infrared frequency of the phosphoryl group and its basicity in the context of solvent extraction, particularly comparing it with sulphoxides.
5. Study Extraction Mechanisms: To understand the mechanisms of extraction for various acids and species by different sulphoxides and phosphine oxides, including examining the formation of coordinated species and their impact on extraction efficiency.

## **Methodology**

### **Experimental Setup**

#### **1. Materials**

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- Dibutyl sulphoxide (DBSO), diphenyl sulphoxide (DPSO), tributyl phosphate (TBP), tri-n-butyl phosphine oxide (TBPO), tri-n-octylphosphine oxide (TOPO), and triphenylphosphine oxide (TPPO) were obtained from Eastman Organic Chemicals.
- Perchloric acid (Baker "Analysed quality"), hydrochloric acid (E. Merck, G. R. grade), and ammonium pertechnetate (Oak Ridge National Laboratory, U.S.A.) were used.
- Benzene solutions of sulphoxides and phosphine oxides were used as the organic phase in solvent extraction experiments.

### 2. Preparation

- Equal volumes of organic and aqueous phases were equilibrated for 10 minutes.
- Phases were separated by centrifuging.
- For infrared (IR) spectroscopy, "Spectro" grade carbon tetrachloride (Eastman Organic Chemicals) was used as the diluent.

## Measurement Techniques

### 1. Infrared Spectroscopy:

- IR spectra of the organic phase in the 3000-4000 cm<sup>-1</sup> region were recorded using a Perkin Elmer recording spectrophotometer (model 21) with a LiCl prism and CaF<sub>2</sub> cell (path length 0.1 mm).
- Carbon tetrachloride pre-equilibrated with triple distilled water was used as the blank.
- The shift in the OH frequency of coordinated water bonded to different extractants was measured and tabulated.

### 2. Extraction Experiments:

- Water Extraction: Different molarities of DBSO (0.75, 1.0, and 2.0 M) in CCl<sub>4</sub> were equilibrated with triple distilled water, and the IR spectra of the organic phase were recorded.
- Acid Extraction: Perchloric acid and hydrochloric acid solutions of varying concentrations were

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prepared. DBSO in benzene was used as the organic phase for acid extraction studies. The concentration of DBSO was varied while keeping the acid concentration constant, and vice versa.

- Technetium Extraction:  $\text{NH TcO}_4$  solutions containing an equivalent amount of HCl were used to investigate the extraction of pertechnic acid by DBSO in benzene. Optical density was measured before and after extraction using a Beckman DU spectrophotometer at 290 nm.

### Data Analysis

#### 1. Donor Properties:

- The donor properties of sulfoxides and phosphine oxides were examined by measuring the shift in the OH stretching frequency in phenol on adduct formation with a donor.
- The relative donor strengths were assessed based on the shift in the symmetric stretching frequency of OH of water on coordination with the donor.

#### 2. Equilibrium Studies:

- For water extraction, the equilibrium constant was determined using the concentration of coordinated water and DBSO.
- For acid extraction, the equilibrium constants for the extraction of perchloric acid and hydrochloric acid were determined by analyzing the dependence of extraction on acid concentration.
- Plots of  $\log[\text{H}_2\text{O} \cdot n\text{DBSO}]$  against  $\log[\text{DBSO}]$  and  $\log[\text{H}^+]$  against  $\log[\text{acid}]$  concentration were used to derive the number of DBSO molecules coordinated with water and to determine the extraction mechanism (ion pair vs. dissociated ions).

### Key Findings

#### 1. Donor Strength Measurement:

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- A new method for assessing the donor strengths of sulfoxides and phosphine oxides was developed, based on the shift in the symmetric stretching frequency of OH of water upon coordination.

- Both sulfoxides and phosphine oxides form a single group, whose solvent extraction properties are determined by their relative donor strengths as measured by this procedure.

### 2. Comparison of Donor Properties:

- Sulfoxides like dibutyl sulfoxide (DBSO) and diphenyl sulfoxide (DPSO) exhibit donor properties that are comparable to those of phosphine oxides such as tributyl phosphate (TBP) and tri-n-butyl phosphine oxide (TBPO).

- The infrared frequency of the phosphoryl group in phosphine oxides was found to correlate with their basicity, while the S=O frequency in sulfoxides did not show a significant variation and thus could not be used as a reliable measure of their donor properties.

### 3. Extraction of Water:

- The extraction of water by DBSO involved the coordination of two DBSO molecules with one water molecule, forming a species represented as  $\text{H}_2\text{O} \cdot 2\text{DBSO}$ .

- This behavior is different from TBP and TOPO, which coordinate with water in a 1:1 ratio.

### 4. Extraction of Acids:

- Perchloric acid is extracted by DBSO as an ion pair, rather than as dissociated ions.

- The study showed that one DBSO molecule is associated with one ion pair of perchloric acid, forming a species represented as  $\text{DBSO} \cdot \text{HClO}_4$ .

- Hydrochloric acid extraction by DBSO did not show any saturation effect at higher molarities, indicating efficient extraction even at high acid concentrations.

### 5. Technetium Extraction:

- No extraction of pertechnic acid ( $\text{HTcO}_4$ ) was observed with DBSO, either in the presence or

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absence of HCl.

- This contrasts with the extraction behavior of technetium by organophosphorus compounds like TOPO and TPPO, where TOPO showed significantly higher extraction efficiency compared to TPPO, despite TPPO being more basic.

### 6. Reliability of Donor Strength Indicators:

- The study concluded that the shift in the OH frequency of coordinated water is a more reliable indicator of solvent donor strength than the infrared frequency of the functional groups (P=O and S=O) alone.
- This finding is particularly important for sulfoxides, where the S=O frequency remains nearly constant across different compounds.

## Relevance to Study

**Donor Properties Comparison:** Provides a method to assess the donor properties of sulfoxides and phosphine oxides, crucial for ligand selection based on their ability to form stable complexes with metal ions.

**Extraction Efficiency:** Demonstrates how different ligands (sulfoxides and phosphine oxides) extract water, acids, and technetium, highlighting their suitability for various stages of the nuclear fuel cycle.

**Stability and Coordination:** Highlights that sulfoxides and phosphine oxides form stable complexes with specific ratios, impacting their effectiveness in separating specific nuclear materials.

**Mechanistic Insights:** Offers insights into the coordination chemistry and mechanisms of extraction, aiding in the prediction of ligand behavior under nuclear fuel cycle conditions.

**Infrared Spectroscopy as a Tool:** Suggests that the shift in OH frequency upon coordination is a reliable indicator of donor strength, useful for selecting ligands with optimal performance under

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radiolytic and chemical conditions in the nuclear fuel cycle.

### Critical Parameters Identified

#### High Importance

##### 1. Chemical Stability:

- The study discusses the chemical stability of sulphoxides and phosphine oxides in various acidic conditions, showing that these ligands remain functional under the chemical conditions present in nuclear fuel reprocessing.
- The non-extraction of technetium by DBSO indicates potential limitations in chemical stability or reactivity with certain species.

##### 2. Radiolysis Resistance:

- While the study does not directly address radiolysis resistance, the discussion on donor properties and the stability of sulphoxides and phosphine oxides under different chemical conditions provides indirect insights into their potential behavior under radiation.

##### 3. Thermodynamics:

- The study's method of assessing donor strengths through the shift in OH frequency upon coordination is fundamental to understanding the thermodynamics of ligand-metal interactions.
- The equilibrium studies and the resulting data on donor properties contribute to understanding the thermodynamic feasibility of using these ligands for separation processes.

#### Medium Importance

##### 1. Kinetics

- The study mentions the equilibration time (10 minutes) for the solvent extraction experiments, which provides some information on the kinetics of the extraction process.

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- The linear relationship observed in the equilibrium plots indicates predictable kinetic behavior, essential for practical applications.

### 2. Loading Capacity:

- The study does not explicitly address loading capacity, but the detailed examination of the coordination ratios (e.g., H O 2DBSO) implies that different ligands have varying capacities for binding metal ions or other species.

### 3. Operational Condition Range:

- The extraction experiments were conducted under various conditions (different acid concentrations, ligand concentrations), showing the ligands' ability to operate across a range of conditions.
- The study highlights how different conditions affect the extraction efficiency, indicating the flexibility and applicability of these ligands in various scenarios.

## Low Importance

### 1. Solubility:

- The use of benzene and carbon tetrachloride as solvents in the extraction experiments provides information on the solubility of the ligands, though it is not a primary focus of the study.
- Solubility in these solvents is mentioned but not deeply explored, indicating it is a manageable parameter.

### 2. Dispersion Numbers:

- The study does not address dispersion numbers directly, as the focus is more on the fundamental donor properties and extraction efficiencies.

### 3. Phase Disengagement

- Phase separation by centrifuging is mentioned as part of the experimental procedure, but specific

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details on phase disengagement efficiency are not provided.

- This aspect is less critical in the context of the study's primary focus on donor properties and extraction mechanisms.