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Key Words

solvent extraction

triphenylphosphine

triphenylphospine oxide

triphenylphosphine sulphide

Objective

1. To investigate the solvent extraction of Palladium(II) from chloride solution using triphenylphosphine (Ph3P), triphenylphosphine oxide (Ph3PO), and triphenylphosphine sulphide (Ph3PS) as extractants in benzene

2. To compare the extraction efficiency of Ph3P, Ph3PO, and Ph3PS for Palladium(II) under similar experimental conditions

3. To perform detailed investigations on the effects of various parameters (hydrogen ion concentration, extractant concentration, chloride concentration, HCl concentration, and metal ion concentration) on the extraction of Palladium(II) using Ph3P.

4. To determine the stoichiometry of the extracted Palladium species and propose an equilibrium model for the extraction process.

5. To measure the thermodynamic parameters (G, H, and S) for the Palladium-Ph3P extraction system.

6. To conduct IR spectrum analysis of the extracted complex to confirm the bonding nature and composition of the extracted species.

7. To identify effective stripping agents for the removal of the extracted Palladium species from the organic phase.

8. To compare the efficiency of various stripping agents and identify the most effective one for

selective removal of Palladium.

9. To investigate the temperature effect on the extraction process to understand the thermodynamic nature of the extraction.

Methodology

Chemicals and Reagents Used

- All chemicals and reagents used were of analytical reagent (AR) grade.
- Extracting ligands Ph3P, Ph3PO, and Ph3PS were supplied by Fluka and used without further purification.
- Ph3P is a colorless crystal at room temperature, dissolving in non-polar organic solvents like benzene and diethyl ether.
- Ph3PO is a white crystalline compound, often a side product in reactions involving Ph3P.
- Ph3PS is a colorless solid, soluble in various organic solvents.
- Benzene used as a diluent is an AR product of Prolabo.
- The Pd salt used was PdCl2 of pure grade (Fluka), dissolved in hydrochloric acid solution (Aldrich) to obtain a stock solution concentration of 9.4   10 3 M (1 g l 1) in 1 M HCl.

Procedure

Batch Experiments

- 5 cm of an aqueous hydrochloric acid solution containing Pd(II) of known concentration was mixed with 5 cm of the organic phase containing Ph3P, Ph3PO, or Ph3PS at the desired concentration.
- Shaking was performed in glass-stoppered tubes using a shaking water bath shaker (Julabo SW-20C, Germany) controlled within   1 C, adjusted at 25   1 C (except when studying the effect of temperature).

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- Extraction equilibrium was attained after 30 minutes of shaking.

Determination of Pd(II) Concentration

- The concentration of Pd(II) in the aqueous acid chloride solution was determined spectrophotometrically by the iodide method using a Shimadzu UV/visible recording spectrophotometer (type UV-160A) at = 407 3 nm.

- The concentration of Pd(II) in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction.

- The distribution ratio (D) was calculated as the ratio of the concentration of the metal in the organic phase to its concentration in the aqueous phase.

Stripping Experiments

- Stripping was performed by shaking 10 ml of the organic phase loaded with extracted metal for 30 minutes with the same volume of distilled water and different stripping solutions.

- The extracted palladium in the organic phase was characterized by measuring the infrared spectra using FT-IR JASCO 6300 instrument.

Effects Studied

Effect of Concentration

- Extraction of Pd(II) (1 g l 1) from 1M HCl solution using different concentrations of Ph3P (range: 1 10 3 to 0.2 M).

- The log-log relation between distribution ratio and extractant concentration was analyzed to determine the stoichiometry of the extracted species.

Effect of Hydrogen Ion Concentration

- Investigated the effect of hydrogen ion concentration (range: 0.1 1 M) on the extraction of Pd(II) by Ph3P in benzene at a constant chloride concentration (1 M).

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- Examined the change in extraction efficiency with varying hydrogen ion concentrations.

Effects of Chloride Concentration

- Measured distribution ratios of Pd(II) by varying chloride concentration (range: 1 5 M) at a constant hydrogen ion concentration (1 M).
- Analyzed the formation of PdCl4 complex and its effect on extraction efficiency.

Effect of Hydrochloric Acid Concentration

- Studied the influence of hydrochloric acid concentration (range: 0.1 5 M) on the extraction efficiency of Pd(II) by 0.01 M Ph3P in benzene.

Effect of Metal Concentration

- Investigated the effect of Pd(II) concentration (range: 4.7   10 3 to 0.023 M) on its extraction with 0.01 M Ph3P in benzene from 1 M aqueous hydrochloric acid solution.

Effect of Phase Ratio

- Examined the effect of changing organic to aqueous (O/A) phase ratio on the extraction trend of Pd(II) in 1 M HCl medium using 0.01 M Ph3P extractant in benzene.

Infrared Investigations

Verification of Extracted Palladium Complex:

- IR spectrum analysis of Ph3P in benzene before and after palladium extraction to determine changes in absorption bands and confirm the chemical composition of the extracted complex.

Thermodynamic Studies

Temperature Effect:

- Studied the effect of temperature (range: 15 C 45 C) on the extraction of Pd(II) by 0.01 M Ph3P in benzene from 1 M HCl solution.

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- Thermodynamic parameters (G, H, S) were determined to evaluate the nature of the extraction process.

Key Findings

Comparison of Extractants

- Among Ph3P, Ph3PO, and Ph3PS, Ph3P showed the highest extraction efficiency for Pd(II) from 1 M HCl solution.
- The extraction efficiency of Pd(II) was lowest with Ph3PS, which was attributed to the electron-withdrawing characteristics of the aromatic ring and the decreased solvating power of the S atom.

Effect of Extractant Concentration

- The distribution ratio (D) of Pd(II) increased linearly with the increase in Ph3P concentration, indicating the participation of two Ph3P molecules in the extracted palladium species (slope ~2).

Effect of Hydrogen Ion Concentration

- The hydrogen ion concentration in the range of 0.1 1 M had almost no influence on the extraction efficiency, as the extractant Ph3P is neutral and does not contain hydrogen ions.

Effect of Chloride Concentration

- An increase in chloride concentration (1 5 M) resulted in a decrease in the distribution ratio of Pd(II), favoring the formation of the PdCl4 complex and reducing the concentration of free Pd(II) ions.

Effect of Hydrochloric Acid Concentration

- The extraction efficiency of Pd(II) decreased with increasing HCl concentration beyond 1 M, reaching a minimum at 2 M HCl, likely due to the extraction of hydrochloric acid at high acidity and the formation of extractable species PdCl4 .

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Effect of Metal Concentration

- The concentration of Pd in the organic phase increased with its equilibrium concentration in the aqueous phase, reaching a maximum around 0.015 M. This supported the formation of 1:2 (metal to extractant) complexes.

Effect of Phase Ratio

- The extraction percentage of Pd(II) increased with the organic to aqueous (O/A) phase ratio from 0.25 to 2 and then became constant. The separation factor was maximized at equal volumes of the two phases (O/A = 1).

Extraction Equilibrium

- The extraction constant (K_ex) was calculated to be

(4.22   0.34)   10^4

Temperature Effect

- An increase in temperature (15 C 45 C) decreased the extraction efficiency of Pd(II) by 0.01 M Ph3P in benzene, indicating an exothermic extraction process. The thermodynamic parameters were determined as follows:

Enthalpy change (H): 17.13   0.65 kJ mol

Free energy change (G): 26.16   0.20 kJ mol

Entropy change (S): 30.32   2.27 J mol K

Stripping Investigations

- Screening of various stripping agents showed that 1 M stabilized thiosulfate solution was most effective, achieving a 70% stripping percentage.

Infrared Investigations

- IR spectrum analysis indicated that the absorption band at 914 cm in the spectrum of Ph3P disappeared after palladium extraction, suggesting the coordination of palladium to phosphorus. The

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strong phosphorus stretching vibration band shifted from 1313 cm to 1188 cm upon extraction, supporting the direct bonding of palladium to phosphorus.

Conclusion

Extraction Efficeincy

- IR spectrum analysis indicated that the absorption band at 914 cm in the spectrum of Ph3P disappeared after palladium extraction, suggesting the coordination of palladium to phosphorus. The strong phosphorus stretching vibration band shifted from 1313 cm to 1188 cm upon extraction, supporting the direct bonding of palladium to phosphorus.

Extracted Species

- The experimental results identified the extracted palladium species when using Ph3P

Effect of Temperature

- Increasing the temperature negatively impacted the extraction of palladium, indicating the exothermic nature of the extraction process.

Pure Form Separation

- Palladium could be separated in a pure form based on its trend in the extraction and stripping procedures.

Stripping Agent Efficiency

- The use of 1 M stabilized thiosulfate solution was found to be efficient for stripping palladium from its loaded Ph3P-benzene solution, achieving a stripping percentage of 70% .

Relevance to Study

Ligand Efficiency Comparison

- Detailed comparison of Ph3P, Ph3PO, and Ph3PS provides insights into their efficiency in

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extracting Pd(II), which can inform the selection of ligands based on their extraction capabilities and chemical properties

Effect of Experimental Conditions

- Analysis of the effects of various parameters such as extractant concentration, hydrogen ion concentration, chloride concentration, and hydrochloric acid concentration on extraction efficiency helps in understanding how different conditions influence ligand performance. This is crucial for optimizing extraction processes in nuclear fuel cycle chemistry

Thermodynamic Data

- The determination of thermodynamic parameters (G, H, and S) for the Pd-Ph3P extraction system offers valuable information about the spontaneity and heat requirements of the extraction process, aiding in the selection of ligands that perform well under desired thermal conditions

Stoichiometry and Extraction Equilibrium

- Findings on the stoichiometry of the extracted species and proposed extraction equilibrium model provide a fundamental understanding of how ligands interact with metal ions, which is essential for developing efficient ligand systems for the nuclear fuel cycle

Stripping Efficiency

- Evaluation of different stripping agents and the identification of effective ones (e.g., 1 M stabilized thiosulfate solution) for removing extracted Pd(II) can guide the development of ligands that not only extract metals efficiently but also allow for their easy recovery and purification

Infrared Spectroscopy Analysis

- IR spectrum analysis confirming the bonding nature between Pd and Ph3P can help in understanding the binding mechanisms of ligands with actinides and lanthanides, leading to the design of ligands with optimized binding properties for the nuclear fuel cycle

Critical Parameters Identified

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High Importance

Chemical Stability: The study demonstrates that Ph3P is a stable ligand under the experimental conditions used for the extraction of Pd(II). The stability of Ph3P in the acidic chloride medium suggests that it can remain functional over the required duration of the separation process and under the chemical conditions present in nuclear fuel reprocessing

Thermodynamics: The thermodynamic parameters (G, H, and S) were determined for the Pd-Ph3P extraction system. The negative H indicates an exothermic reaction, and the negative G confirms the spontaneity of the extraction process. This information is crucial for understanding the feasibility and efficiency of the separation process at a fundamental level

Medium Importance

Kinetics: The study provides data on the equilibrium time required for the extraction of Pd(II), indicating that equilibrium was reached within 30 minutes. This suggests efficient kinetics for the extraction process, which is important for practical applications

Loading Capacity: The investigation into the effect of metal concentration on extraction efficiency indicates the capacity of Ph3P to handle varying concentrations of Pd(II). The relationship between equilibrium concentrations in organic and aqueous phases supports the loading capacity data

Operational Condition Range: The effects of different parameters (extractant concentration, hydrogen ion concentration, chloride concentration, and hydrochloric acid concentration) on the extraction efficiency were studied, demonstrating the ability of Ph3P to operate under a broad range of conditions. This enhances the flexibility and applicability of the separation process

Low Importance

Solubility: The solubility of Ph3P in benzene and other non-polar solvents is mentioned, which is important but can often be managed through solvent selection

Phase Disengagement: Although not directly addressed in detail, the study implies that the extraction process achieves clear phase separation, which is necessary for practical separation applications