SPECTROSCOPIC STUDIES OF THE BEHAVIOUR OF THE
AgNO₃ – HNO₃ – TETRABUTYL DITHIOPYROPHOSPHATE
EXTRACTION SYSTEM

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A very efficient extraction of silver with tetrabutyl dithiopyrophosphate (TBDTPP) is followed by dramatic changes in the structure of the extractant molecule. The IR and NMR spectroscopic studies have revealed that in the presence of Ag⁺ and NO₃⁻ ions the TBDTPP molecule rearranges first into a molecule containing a P–S–P bridge and one P=O group instead of P–O–P and P=S, respectively, and then into a molecule containing two P–S–C and two P=O groups at a P–O–P bridge.

Introduction

In a search for a selective extractant for the metals belonging to Groups IB (Cu, Ag, Au), IIB (Zn, Cd, Hg) and IIIA (Ga, In, Tl) of the periodic table, it was found that TBDTPP ensures high distribution coefficients for Cu(I), Hg(II) (both extracted from HCl) and particularly for Ag(I) (extracted from HNO₃). The effect of concentration of particular components of the system on the extraction was reported earlier.¹ It has been found that extraction of silver results in nontrivial structural changes of the solvent molecule. Basing on the IR and ³¹P NMR spectroscopic data two possible mechanisms for these changes were suggested.² The objective of the present work was to confirm or rule out any of the mechanisms discussed previously² or to suggest a new one based on extended spectroscopic data.

Experimental

Chemicals. Inorganic phase

AgNO₃, analytical grade, supplied by Merck was used without further purification. HNO₃, analytical grade, supplied by POCh (Polish reagents) was distilled prior to measurement. All the solutions were prepared using doubly distilled water.
Chemicals. Organic phase

The extractant (TBDTPP, yellowish viscous liquid, b.p. 126–128 °C under 0.01 mm Hg \( n_d^{22.5} = 1.4712 \)) was synthesized in the Institute of Organic Chemistry of the Technical University, Łódź. It was purified on a column and by distillation by a supplier. The purity was checked by means of IR and \( ^{31}P \) NMR spectroscopy.

The diluent, CCl₄ (POCh, chemically pure) was boiled with 5% Na₂CO₃, dried with P₂O₅ and distilled before use.

Sample preparation

Ag⁺ ions were extracted from 0.1M aqueous solution of AgNO₃ in 3M HNO₃ by 0.1M TBDTPP solution in CCl₄ by mechanically shaking the mixture for 40 minutes. The organic phase containing the Ag·TBDTPP complex was separated and filtered through a paper filter before being subjected to spectral measurements.

The Ag·TBDTPP complex was destroyed by shaking the organic phase with an equivalent amount of 1M HCl. The precipitated AgCl was centrifuged and the water phase was separated. The organic phase was washed several times with water to remove traces of HCl, and filtered through a paper filter. The resultant organic solution was subject to spectral measurements either after a few hours or 3–4 weeks of aging.

IR and NMR measurements

The IR spectra were measured within the region of 450–4000 cm⁻¹ with a Perkin–Elmer grating spectrometer in Řež near Prague (Czechoslovakia). A cell with KBr windows, having a path length of 0.16 mm was used; the absorption of the solvent was compensated using a variable path length cell.

The \(^{31}P \) NMR spectra were taken for the liquid samples in Technical University, Łódź, on a 24 MHz JEOL spectrometer. The Internal standard H₃PO₄ was used in all scans.

The \(^{13}C \) NMR spectra were recorded in Technical University, Łódź, on 22.63 MHz Bruker spectrometer with proton noise decoupling. Tetramethylsilane was used as an internal standard; all samples were diluted with hexadeutero-benzene.