

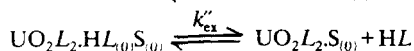
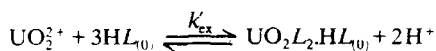
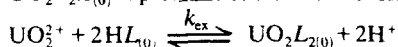
SYNERGISTIC EXTRACTION BEHAVIOUR OF URANIUM-BENZOPHENYL HYDROXYLAMINE COMPLEX WITH TRI-*n*-OCTYL PHOSPHINE OXIDE IN CHLOROFORM

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N-benzoylphenyl hydroxylamine (BPHA) forms extractable complexes with uranium. Studies on synergistic effect on the equilibrium extraction behaviour of uranium have been carried out with chloroform solutions of BPHA (HL) and tri-*n*-octyl phosphine oxide (TOPO; S). The results demonstrate that bivalent uranyl ions are extracted as $UO_2L_2.HL_{(0)}$ in absence of TOPO and as $UO_2L_2.S_{(0)}$ in presence of TOPO. The following equations



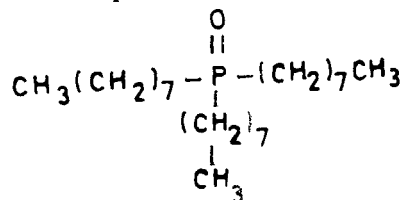
are established to be the overall extraction equilibria for the extraction of UO_2 -BPHA complex in absence and in presence of TOPO. The effects of aqueous phase pH and the bulk organic phase concentration of BPHA and TOPO on the extraction have been investigated. The extraction constants for $UO_2L_{2(0)}$ extraction (as $\log k_{ex}$) is -7.55 whereas that for $UO_2L_2.HL_{(0)}$ ($\log K'_{ex}$) is -4.98 and for $UO_2L_2.S_{(0)}$ ($\log K''_{ex}$) is 0.98. The adduct formation constant with HL ($\log k_{HL}$) is 2.57 and with S ($\log k_S$) is 8.53.

Key Words: Solvent Extraction; Synergistic Extraction; Adduct Formation Constant; Uranium; BPHA; TOPO

Introduction

Solvent extraction technique involving chelating extractants constitutes a separation process of great significance for metal ions. The unquestionable importance of uranium as a strategic metal and as a nuclear fuel together with the comparatively low abundance of the very metal¹ necessitates its economic recovery in the purest form. Hydroxylamines have long been used as spectrophotometric reagents for determination of metal ions²⁻⁵.

The present paper deals with the synergistic effect on the extraction of uranyl-BPHA complexes with a powerful neutral additive, TOPO:



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The evaluation of the equilibrium constants in presence or in absence of TOPO have been done to compare the adduct formation constants.

Experimental

A Shimadzu UV240 spectrophotometer was used to obtain the absorption data. A systronics 335 digital pH meter with a glass calomel electrode pair was used to measure the pH of the solutions. A box-type reciprocating shaker of Sambros (India) with a shaking speed of 200 oscillations per minute was used to equilibrate the aqueous and the organic phases, whenever required.

The extractant BPHA was prepared and purified by known procedure⁵. TOPO was obtained by the recrystallisation of the commercially available Cyanex 921, kindly supplied by Cyanamid. The American Cyanamid Co. N.J., USA. The purity of the reagents were confirmed by elemental analysis, melting point and IR spectra. The stock solution of uranium was prepared from AR grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of BDH and was standardised gravimetrically by 8-hydroxyquinoline⁷. Chloroform, the organic diluent was always distilled and pre-saturated with water prior to use.

Recommended Procedure

Uranium-BPHA Complex System

One ml metal solution of 1.26×10^{-3} M and 4ml of sodium-acetate-acetic acid buffer solution of pH 6.40 were added to 5ml of 2.5×10^{-3} M N-benzoylphenyl hydroxylamine solution in chloroform taken in a 25ml separatory funnel. The two phases were shaken thoroughly for five minutes to reach equilibrium. The chloroform layer was drained out and collected in a 5ml volumetric flask after drying with anhydrous sodium sulphate. The aqueous phase was washed with chloroform and the washing was dried and collected in the volumetric flask. The volume was made upto the mark.

Uranium-BPHA-TOPO System

One ml metal solution of 1.26×10^{-3} M and 4ml of buffer solution of pH 3.2 were added to 2.5ml of 1.25×10^{-2} M BPHA in chloroform and 2.5ml of 1.8×10^{-3} M TOPO in chloroform taken in a 25ml separatory funnel. The two phases were shaken thoroughly for 5 minutes to reach equilibrium. The chloroform layer was drained out and collected in a 5ml volumetric flask after drying with anhydrous sodium sulphate. The aqueous phase was washed with chloroform and the washing was dried and collected in the volumetric flask. The volume was then made upto the mark.

Results and Discussion

Absorbance Curve

UV-VIS spectra of the extracted yellow coloured complexes following the recommended procedures were obtained in the wave-length region of 300nm to 600nm. The absorbance maxima (λ_{max}) for both the cases were found to be

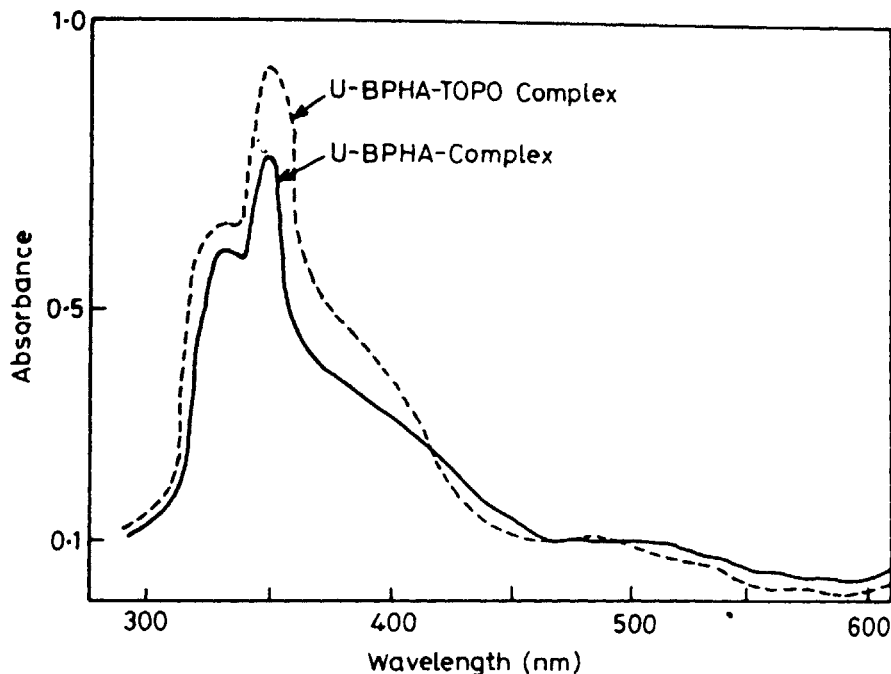


Fig 1 Absorbance spectral curve of U-BPHA and U-BPHA-TOPO complex against corresponding reagent blank

350nm against the respective reagent blanks. The absorbance spectral curve are shown in Fig. 1. A significant enhancement in the absorbance due to the introduction of TOPO has been observed, though the λ_{max} remains the same. The increase could well be attributed to the formation of a tertiary adduct compound of uranium-BPHA complex with TOPO. The absorbance spectra of chloroform solution of BPHA against chloroform and of TOPO against chloroform do not show any noteworthy absorbance. Hence, 350nm has been chosen as the experimental wave length for further studies. Moreover, the colour intensity of the complex was found to remain constant for over 24 hours at room temperature ($\sim 25^{\circ}\text{C}$).

Role of BPHA

The extraction of uranium as a function of BPHA concentration in the bulk organic phase was studied. Absorbance of the extracted complex was found to increase steadily with increasing reagent concentration. The calculated values of $\log D_U$ when plotted against the corresponding $\log \text{BPHA}_{(0)}$ values, yields an interesting observation (Fig. 2). In the lower concentration range of the reagent a straight line with a slope value of about two was obtained. Thereafter, the slope becomes even steeper and was calculated to be three. Hence, two molecules of the reagent are bound to the central metal at lower reagent concentrations and a third reagent molecule forms an adduct at somewhat

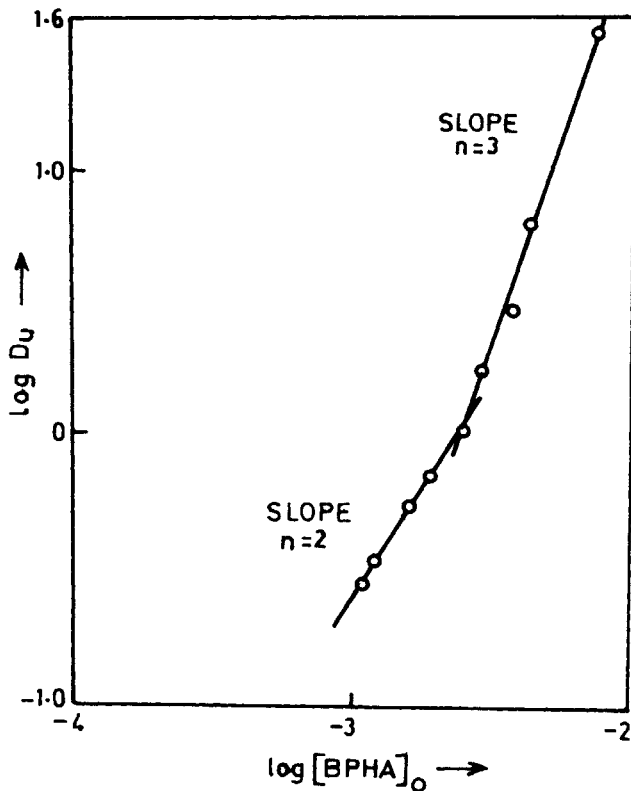
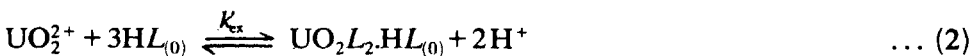
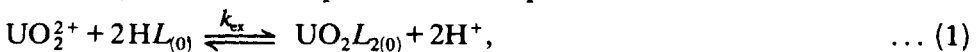


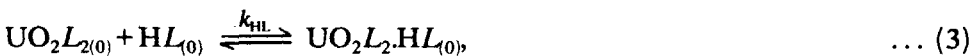
Fig 2 $\log D_U$ vs $\log[\text{BPHA}]_0$ plot

higher concentration range. This phenomenon was confirmed by the results obtained when the distribution of the metal was studied as a function of aqueous hydrogen ion concentration. The $\log D_U$ vs. pH plot gave a straight line (Fig. 3) with a slope of 2.16. Two ligand molecules instead of three therefore could be predicted to be deprotonated to form the complex with dipositive uranyl cation.

Thus, the extraction equilibria can be represented as:



and



$\log k_{\text{ex}}$ and $\log k'_{\text{ex}}$, the corresponding conditional extraction constants and $\log K_{\text{HL}}$, the self adduct formation constant were calculated to be -7.55 , -4.98 and 2.57 respectively.

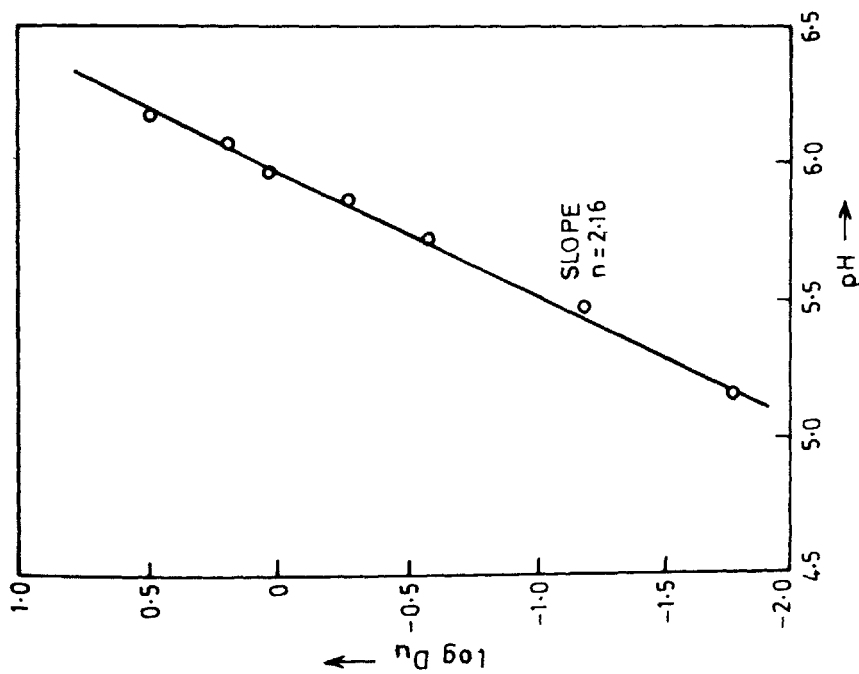


Fig. 3 $\log D_t$ vs pH plot

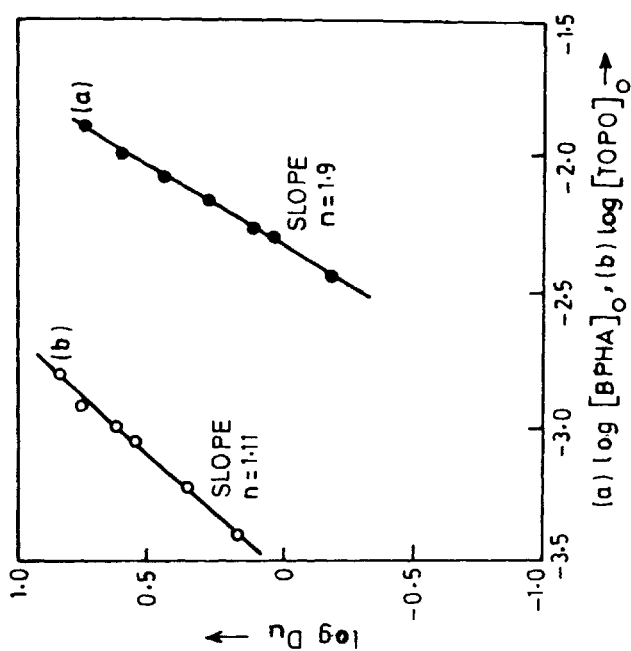


Fig. 4 $\log D_t$ plot as a function of (a) $\log [\text{BPHA}]_0$ and (b) $\log [\text{TOPO}]_0$

Role of TOPO

Taking the tendency of uranyl complex to form adduct compounds into account, the synergistic effect on the overall extraction due to a strong donor molecule, tri-*n*-octylphosphine oxide (TOPO) has been studied. The primary aim of the introduction of TOPO was to achieve a more effective extraction through the adduct formation.

In the presence of TOPO as a secondary ligand, $\log D_U$ vs. $\log \text{BPHA}$ (Fig. 4a) plot gave a straight line with a single slope of 1.9 throughout the entire range of BPHA concentration. The distribution of the metal as a function of TOPO concentration at a fixed BPHA concentration was studied. $\log D_U$ when plotted against $\log \text{TOPO}_{(0)}$ yields a straight line with a slope of 1.11 (Fig. 4b). To consider the extraction equilibrium in the mixed ligand system of uranium-BPHA-TOPO, the distribution ratio of the metal ($D_{U,S}$) is given by

$$D_{U,S} = \frac{P_U \beta_2 [L^-]^2 \{1 + \sum K_{S,m} [S]^2\}}{1 + \sum \beta_n [L^-]^n} \quad \dots (4)$$

where β_n = the stability constant of the chelate,

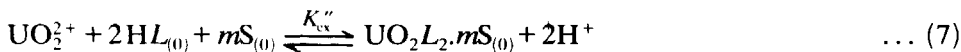
P_U = the distribution coefficient of the chelate,

and $K_{S,m}$ = the formation constant of the following addition reaction in the organic phase:



$$\text{and } K_S = \frac{[\text{UO}_2\text{L}_2.m\text{S}]_0}{[\text{UO}_2\text{L}_2]_0 [S]_0^m} \quad \dots (6)$$

Otherwise, the overall extraction equilibrium in the presence of the additive can be written as



$$\text{where } K_{\text{ex}}'' = \frac{[\text{UO}_2\text{L}_2.m\text{S}]_0 [\text{H}^+]^2}{[\text{UO}_2^{2+}] [\text{HL}]^2 [\text{S}]^m} \quad \dots (8)$$

K_{ex}'' is the synergic extraction constant. The $\log K_{\text{ex}}''$ and $\log K_S$ were found to be 0.98 and 8.53 respectively.

Hence, it can be concluded that even in presence of TOPO, BPHA serves the role of the primary ligand to neutralise the positive charges of uranyl ion and still, an adduct is formed with TOPO instead of BPHA. The remarkably higher value of K_{ex}'' in comparison to K_{ex} and K_{ex}' indicates a more effective extraction of the metal in presence of TOPO. Thus, using TOPO as the adduct

forming agent a synergistic extraction was achieved by increasing the efficiency of the extraction.

Acknowledgement

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