

SOLVENT EXTRACTION OF THORIUM(IV) WITH  
DIBUTYLDITHIOPHOSPHORIC ACID IN VARIOUS ORGANIC  
SOLVENTS

M. Curtui, I. Haiduc

Chemistry Department, Babeş-Bolyai University,  
R-3400 Cluj-Napoca, Romania

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The extraction of thorium(IV) from perchlorate solutions with di-n-butyldithiophosphoric acid (HBudtp) in various organic solvents occurs through an ion exchange mechanism. The extracted species in the organic phase is an eight-coordinate complex  $\text{Th}(\text{Budtp})_4$ . The higher values of the distribution ratio obtained in HBudtp-benzene-water system than in HBudtp-n-butanol-water system are explained by higher solubility of the complex species in nonpolar solvents. The position of the extraction curves in the pH-range lower than 0.7 reduces the complexation of thorium(IV) with  $\text{Budtp}^-$  in the aqueous phase and also the hydrolysis process.

#### INTRODUCTION

In previous papers<sup>1,2</sup> we have reported on the extraction of thorium(IV) with diethyldithiophosphoric acid (HETdtp) and di(2-ethylhexyl)dithiophosphoric acid (HEhdtp) in various organic solvents. In both cases it has been noticed that the metal extraction is signifi-

cantly influenced by the nature of the diluent used for the dithiophosphoric extractant, but in a different way. The higher distribution ratios were achieved with oxygen-containing solvents for short chain dithiophosphoric acids (HEtdtp) and with nonpolar-noncoordinating solvents for long branched-chain dithiophosphoric acids (HEhdtp).

In the present work we have investigated the extraction of thorium(IV) from perchlorate solution with di-n-butylldithiophosphoric acid in various organic solvents.

#### EXPERIMENTAL

Materials. All reagents used were of analytical grade purity. Thorium salts and phosphorus pentasulfide were purchased from Aldrich and Ventron A.G., Germany. The di-n-butylldithiophosphoric acid was prepared by reaction of phosphorus pentasulfide with n-butanol and purified by distillation<sup>3</sup>.

A Spekol C. Zeiss Jena (DDR) spectrophotometer was used for the colorimetric determination of thorium(IV). The acidity of the aqueous phase was determined with an Orion Model 611 pH-meter/millivoltmeter.

Operating procedure. A volume of 10 ml of properly diluted HBudtp was equilibrated for five minutes with an equal volume of an aqueous layer containing the desired amount of thorium(IV), hydrogen and perchlorate ions. After the phases were separated by gravity, the concentration of thorium in aqueous phase was determined colorimetrically with Thoron<sup>4</sup> and the distribution was calculated.

In all experiments the ionic strength was kept constant (1M) with perchloric acid and sodium perchlorate.

TABLE 1

Extraction of Th(IV) with di-n-butylthiophosphoric acid in various solvents. ( $C_{Th} = 0.0005M$ ;  $C_{HBudtp} = 0.1M$ ;  $pH \approx 0.8$ )

Solvent	Distribution ratio, D
Heptane	56.20
Cyclohexane	37.66
Benzene	37.60
Carbon tetrachloride	43.70
Chloroform	45.40
Cyclohexanone	7.96
Diethyl ether	0.63
Dibutyl ether	1.15
n-Butanol	3.48

## RESULTS AND DISCUSSION

### Diluent effect

The extraction of thorium(IV) with di-n-butylthiophosphoric acid has been investigated in different partition systems by diluting the complexing reagent with several polar and nonpolar organic solvents.

The data presented in Table 1 show that the highest values of the distribution ratios (D) are obtained with nonpolar (noncoordinating) solvents.

In order to elucidate the extraction mechanism the magnitude of the distribution ratio was determined under various conditions. In this respect the influence of following parameters: the acidity of the aqueous phase, the concentration of HBudtp in the organic phase

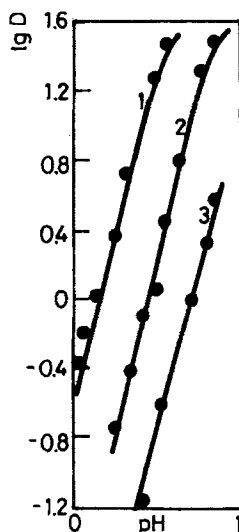


Fig. 1. Extraction of thorium(IV) with di-n-butylthiophosphoric acid in benzene.  $C_{\text{HBudtp}} = 0.1\text{M}$  (curve 1),  $0.05\text{M}$  (curve 2),  $0.03\text{M}$  (curve 3);  $C_{\text{Th}} = 0.0005\text{M}$

and the thorium(IV) concentration in the aqueous phase have been investigated for two extraction systems.

#### HBudtp-benzene-water system

The distribution ratio was determined as a function of aqueous phase acidity for three different concentrations of HBudtp in benzene. The thorium(IV) concentration in the aqueous phase was maintained constant ( $0.0005\text{M}$ ). The results are shown in Fig. 1. The slopes of 3.8, 3.9 and 4.1 for curves 1, 2 and 3, respectively indicate a fourth-order dependence on the pH of the aqueous phase. It follows that four HBudtp molecules are involved in an ion exchange mechanism by neutralizing the positive charge of the  $\text{Th}^{4+}$  ion. This excludes participation of the perchlorate anion  $\text{ClO}_4^-$  in formation of the extracted species.

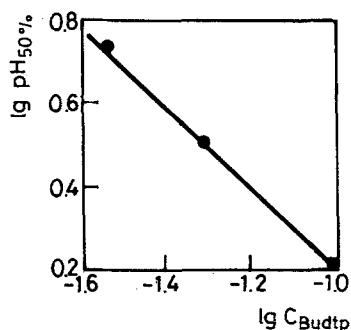


Fig. 2. Dependence of  $\text{pH}_{50\%}$  on the concentration of di-n-butyldithiophosphoric acid in benzene  
 $C_{\text{Th}} = 0.0005\text{M}$

In order to establish the stoichiometric composition of the extracted species, the  $\text{pH}_{50\%}$  values (from Fig. 1) were plotted against the concentration of HBudtp in benzene. The data are presented in Fig. 2. The slope of 1 obtained for the straight line suggests that only four molecules are involved in the ion exchange participate in the formation of the species extracted in benzene<sup>5</sup>.

In the concentration range investigated (0.0005 to 0.001M) the distribution ratio is not influenced by the metal concentration in the aqueous phase (Fig. 3). It follows that no polymeric species are formed in the aqueous and organic phases.

#### HBudtp-n-butanol-water system

The extraction of thorium(IV) from perchlorate solutions with di-n-butyldithiophosphoric acid in n-butanol was performed. The data obtained are plotted in Fig. 4. A fourth order dependence of distribution ratio on the aqueous phase acidity indicates an ion-exchange mechanism with the formation of a thorium(IV) complex in which the metal coordinates four ligand groups. The

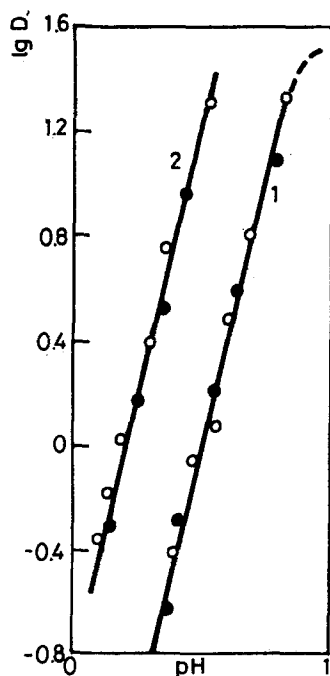


Fig. 3. Dependence of  $\lg D$  on metal concentration.  
 $C_{\text{HBudtp}} = 0.05\text{M}$  (curve 1),  $0.1\text{M}$  (curve 2);  
 $C_{\text{Th}} = 0.0001\text{M}$  (o),  $0.005\text{M}$  (●)

slope analysis of the other partition data including variation of the distribution ratio on HBudtp concentration in n-butanol and thorium concentration in the aqueous phase shows that thorium(IV) extraction with HBudtp in n-butanol follows the same mechanism as in benzene.

#### CONCLUSIONS

The extraction of thorium(IV) with di-n-butyldithiophosphoric acid in benzene or n-butanol takes place through an ion-exchange mechanism involving four molecules of dithiophosphoric acid, which forms a neutral

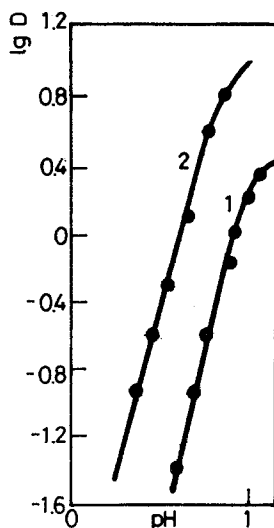


Fig. 4. Extraction of thorium(IV) with di-n-butyldithiophosphoric acid in butanol.  $C_{\text{HBudtp}} = 0.05\text{M}$  (curve 1),  $0.1\text{M}$  (curve 2);  $C_{\text{Th}} = 0.005\text{M}$

complex  $\text{Th}(\text{Budtp})_4$ . The high values of the distribution ratio obtained in the  $\text{HBudtp}$ -benzene-water system are explained by the high solubility of the complex species in nonpolar solvents. In this complex thorium(IV) achieved a coordination number of 8, which is common for this metal<sup>6</sup> and it is in agreement with the X-ray structure of one of the thorium(IV) dithiophosphinates<sup>7</sup>.

The shift of the extraction curves towards the more acidic range reduces the amount of  $\text{HBudtp}$  in the aqueous phase. Therefore, the complexation of thorium(IV) in the aqueous phase with  $\text{Budtp}^-$  anions takes place to a very limited extent and does not affect metal distribution in the organic phase. Also the hydrolysis processes are suppressed.

The smaller values of the distribution ratio in  $\text{HBudtp}$ -n-butanol-water system can be explained by dimin-

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ished solubility of  $\text{Th}(\text{Budtp})_4$  complex in the polar solvent. The extraction curves are situated in a less acidic range, in which the  $\text{HBudtp}$  concentration in the aqueous phase is increased<sup>8</sup>. In the pH range above 1, a decrease of the distribution ratio is observed because of thorium(IV) complexation in the aqueous phase with  $\text{Budtp}^-$  ion.

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