SOLVENT EXTRACTION OF THORIUM(IV)
WITH DIALKYLDITHIOPHOSPHORIC ACIDS

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Solvent extraction of thorium(IV) from aque-
ous solution with dialkyldithiophosphoric
acids $(RO)_2P(S)SH$, (abbreviated Hdtp) in
different organic solvents shows that the
chain length in Hdtp significantly influence
the magnitude of the distribution ratio. The
diluent effect and the influence of the in-
organic anion present in the aqueous phase
was investigated in the Th - di(2-ethyl-
hexyl)dithiophosphoric acid (HEhdtp) extrac-
tion system. The treatment of the partition
data shows that the extraction of Th(IV) in
benzene, cyclohexane, chloroform, carbon
tetrachloride and n-butanol from perchlo-
rate, chloride and nitrate media occurs via
an ion-exchange mechanism. Inorganic anions
present in the aqueous phase do not parti-
cipate in the formation of the extracted
species but influence the magnitude of the
distribution ratios.

INTRODUCTION

In our earlier work we studied extensively the ex-
traction of uranium(VI) with different dialkyldithio-
phosphoric acids from various aqueous solutions[1-6].

Further on, we extended these investigations to the
solft extraction of rare earths and thorium(IV)[7-9].
In a previous work[7] we reported on the extraction of
thorium(IV) with diethyldithiophosphoric acid (HEtdtp)
in different organic solvents. As has been noticed, the
extraction was significantly influenced by the nature
of diluent used for HEtdtp. Higher distribution ratios
were obtained in extractions with oxygen-containing
solvents than in extractions with nonpolar non-coordi-
nating solvents.

The aim of this work is to investigate the extrac-
tion of thorium(IV) with longer chain dialkyldithio-
phosphoric acid.

EXPERIMENTAL

Materials

The dialkyldithiophosphoric acids were synthesized
by the reaction of phosphorus pentasulfide with the
appropriate alcohol, according to published proce-
dures[10-11]. Thorium salts and phosphorus pentasulfide
were supplied by Aldrich Chemie and Ventron A.G., Ger-
many. A stock solution of 0.05M thorium salt was stan-
dardized gravimetrically. Solutions of exactly known
concentrations of perchloric acid and sodium perchlo-
rate, hydrochloric acid and sodium chloride or nitric
acid and sodium nitrate were prepared from chemicals
of analytical grade purity and used for the adjustment
of the pH and/or the ionic strength.

A Spekol C. Zeiss Jena spectrophotometer was used
for colorimetric determination of thorium. The concen-

tration of hydrogen ions in the aqueous phase was de-
termined with on Orion Model 611 pH-meter/millivolt-
meter.

Procedure

Equal volumes (10 cm^3) of the aqueous and the organ-
ic phases were shaken together at room temperature
(20-21 ^{O}C) for about 5 min to complete the equilibra-
tion. The two phases were separated and suitable ali-
quots of each were used for photometrically determina-
tion of thorium(IV) with thoron[12]. In all experiments
the ionic strength was kept constant (1M).

RESULTS AND DISCUSSION

Preliminary experiments on the extraction of thori-
um(IV) with different dialkyldithiophosphoric acids
showed that the length of the alkyl chain in
(RO)$_2$P(S)SH significantly influences the magnitude of
the distribution ratio (Fig. 1). An increase in the
chain length causes an increase of the distribution ra-
tio.

In the present work we selected di(2-ethylhexyl)di-
thiophosphoric acid (HEhdtp) as extractant for thori-
um(IV). The extraction of the metal from aqueous solu-
tions was carried out comparatively using HEhdtp in
nonpolar non-coordinating solvents and oxygen-contain-
ing solvents. The extractions were performed from aque-
ous perchlorate, chloride or nitrate solutions of 1M
ionic strength.

The data presented in Table 1 show that the highest
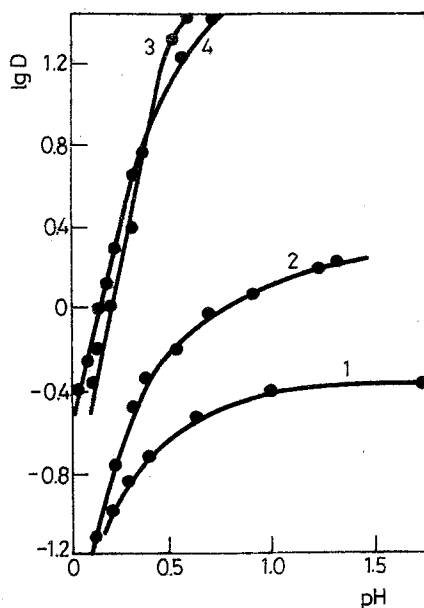values of the distribution ratio are obtained when non-

Fig. 1. Extraction of Th(IV) from perchlorate solutions
with dialkyldithiophosphoric acids in benzene.
Curves: 1 - ethyl, 2 - iso-propyl, 3 - n-butyl,
4-ethylhexyl. C_{Th} - 0.0004M; C_{Hdtp} = 0.1M

TABLE 1

Extraction of Th(IV) from perchlorate solutions with
HEhdtp in various solvents. (C_{Th} = 0.001M;
C_{HEhdtp} = 0.2M; pH = 0.8)

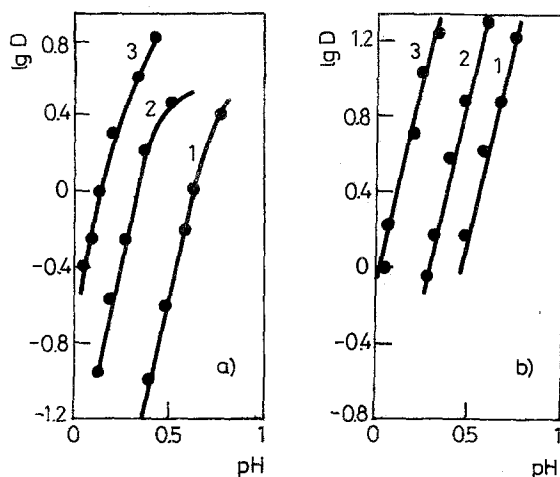| Solvent	Distribution ratio (D)
Cyclohexane	35.80
Benzene	12.60
Chloroform	3.50
Carbon tetrachloride	2.95
Diethyl ether	0.27
Dibutyl ether	0.27
n-Butanol	0.84
Cyclohexanone	4.88.

Fig. 2. Extraction of Th(IV) from perchlorate solutions
with HEhdtp in benzene (a) and cyclohexane (b).
C_{HEhdtp} = 0.03M (curve 1); 0.05M (curve 2);
0.1M (curve 3). C_{Th} = 0.0005M

polar (noncoordinating, oxygen-free) solvents are used
as diluents for HEhdtp.

Extraction in non-coordinating solvents

Benzene, cyclohexane. The distribution ratio was de-
termined as a function of aqueous phase acidity for
different concentrations of HEhdtp varying from 0.03M -
0.1M in benzene and cyclohexane, respectively. The re-
sults presented in Fig. 2 indicate a fourth order pH
dependence in both cases. This suggests an ionexchange
mechanism in which four molecules of dithioacid parti-
cipate in the formation of the extracted species by
neutralizing the positive charge of Th^{4+} ion. It fol-
lows that the perchlorate anion present in the aque-
ous phase does not participate in the extraction pro-
cess.
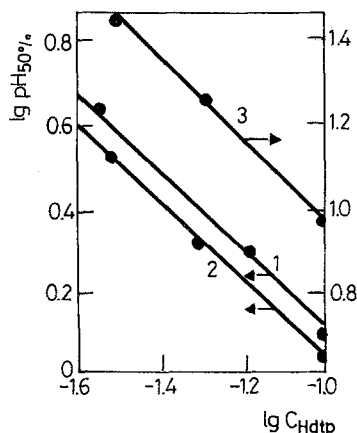
Fig. 3. Dependence of $pH_{50\%}$ on the concentration of HEhdtp in benzene (curve 1) and cyclohexane (curve 2)

A linear plot of $pH_{50\%}$ against the concentration of di(2-ethylhexyl)dithiophosphoric acid with a slope of 1 (Fig. 3) suggests that in the extraction process no other molecules of HEhdtp are involved.

The pH dependence of the distribution ratio at various metal concentrations in the aqueous phase was investigated. The data obtained show that in the 0.0005M-0.01M concentration range no polymeric species are formed in either the aqueous or organic phase.

Chlorocarbons. The extraction of Th(IV) with di(2-ethylhexyl)dithiophosphoric acid in chloroform and carbon tetrachloride was also studied. Slope analysis of the data presented in Fig. 4 indicates that the extraction mechanism is similar to that found in benzene and cyclohexane but the magnitude of the distribution ratio is different from those in other systems.
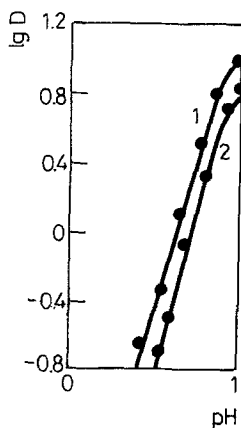
Fig. 4. Extraction of Th(IV) from perchlorate solutions in chloroform (curve 1) and carbon tetrachloride (curve 2). C_{Th} = 0.001M; C_{HEhdtp} = 0.1M

Extraction in oxygen-containing solvents

The extraction of thorium(IV) with HEhdtp in n-butanol was investigated. The variation of the distribution ratio against aqueous phase acidity is presented in Fig. 5. The slope of the linear part of the curves obtained for different acid concentrations has the values of 3.8 (curve 1), 3.9 (curve 2) and 3.6 (curve 3). Within experimental error this suggests a fourth order dependence between the distribution ratio and the aqueous phase acidity. It follows that the extraction of Th(IV) takes place also via an exchange mechanism and four molecules of HEhdtp participate in the ion exchange reaction.

The dependence of the distribution ratio on HEhdtp concentration (Fig. 3, curve 3) and on the thorium concentration indicates that the species formed in the organic phase is a complex of the type $Th(Ehdtp)_4$. The results are similar to those obtained in non-coordinating solvents.

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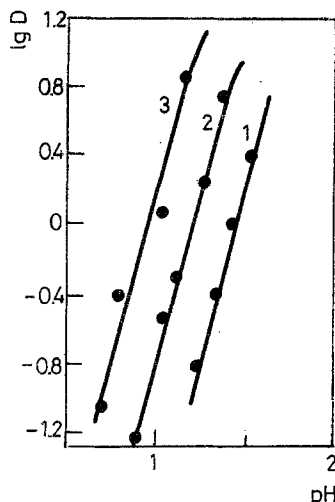Fig. 5. Extraction of Th(IV) from perchlorate solutions with HEhdtp in n-butanol. C_{HEhdtp} = 0.03M (curve 1); 0.05 (curve 2); 0.1M (curve 3). C_{Th} = 0.0005M

Aqueous phase effect

   The partition data presented in Table 2 show that the inorganic anion present in the aqueous phase does influence the extraction of thorium(IV). The distribu- tion ratios in the extraction carried out from chloride and nitrate media are smaller than that from perchlo- rate media.

   Slope analysis of the results presented in Fig. 6 suggests that thorium(IV) is extracted in the organic phase as Th(Ehdtp)$_4$ and the participation of nitrate or chloride anions in the formation of the extracted spe- cies is unlikely. The lower values of the distribution ratio obtained for nitrate and chloride media than for perchlorate media are due to the complexation of Th(IV) in the aqueous phase by these anions. Thus, the concen- tration of thorium(IV) available for extraction is de-
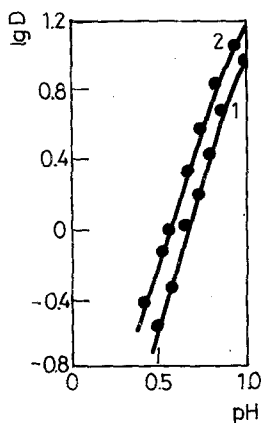
Fig. 6. Extraction of Th(IV) from nitrate (curve 1) and chloride (curve 2) solutions with HEhdtp in benzene. C_{Th} = 0.0005M; C_{HEhdtp} = 0.1M

TABLE 2

Influence of the inorganic anions upon the extraction of Th(IV) with HEhdtp in benzene. (C_{Th} = 0.001M; C_{HEhdtp} = 0.1M; pH = 0.8)
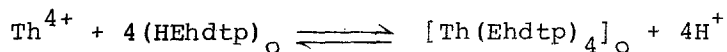
Inorganic anion	Distribution ratio (D)
Perchlorate	12.60
Chloride	4.80
Nitrate	2.74

creased. Both chloride and nitrate anions are known to form stable complexes in aqueous solution with Th(IV)[13-15].

CONCLUSIONS

The extraction of Th(IV) with di(2-ethylhexyl)dithio-phosphoric acid in different organic solvents (nonpolar noncoordinating or polar oxygen-containing solvents)

occurs via an ion-exchange mechanism described by the equation:

$$Th^{4+} + 4(HEhdtp)_o \rightleftharpoons [Th(Ehdtp)_4]_o + 4H^+$$

The inorganic anions present in the aqueous phase do not participate in the formation of the extracted species in the organic phase, but influence the magnitude of the distribution ratios by complexation phenomena occurring in aqueous solution.

The high values of the distribution ratios obtained in Th^{4+}- HEhdtp extraction system can be explained by the high solubility of the neutral chelate complex $Th(Ehdtp)_4$ in organic solvents. This is favored by the presence of a long branched chain in the organic side of the ligand, producing a strongly hydrophobic character of the extracted species.

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