5f and 4f Ion Complexes with Dibutylphosphate Ions*

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Important shortcomings of the PUREX process arise because of the degradation of tributylphosphate (TBP) into dibutylphosphoric acid (HDBP) by radiolysis or hydrolysis. HDBP is a strong acidic extractant which retains many metallic species in the organic phase. Its elimination by alkaline washings at each extraction cycle is necessary and produces large amounts of radioactive wastes. Several important dibutylphosphate complexes are scarcely soluble. Their speciation is incomplete and a comprehensive description of the various species is unavailable. This paper is a survey of the literature and it includes recent results obtained in our laboratory concerning the species of actinides and lanthanides formed in aqueous solutions in the presence of DBP^- ions.

Results and Discussion

Dibutylphosphate Complexes of 4f and 5f Trivalent Ions

The reaction between trivalent lanthanides and HDBP gives essentially three species: $M(DBP)^{2+}$ and $M(DBP)_2^+$ (two soluble species) and one insoluble compound $M(DBP)_3$. This feature is illustrated by curves in Fig. 1 where it can be seen that precipitation of $M(DBP)_3$ needs only one additional DBP^- for the soluble complex. The products $\beta_2 pS$ can be calculated from Fig. 1; they are given in Table I, with some results taken from the literature.

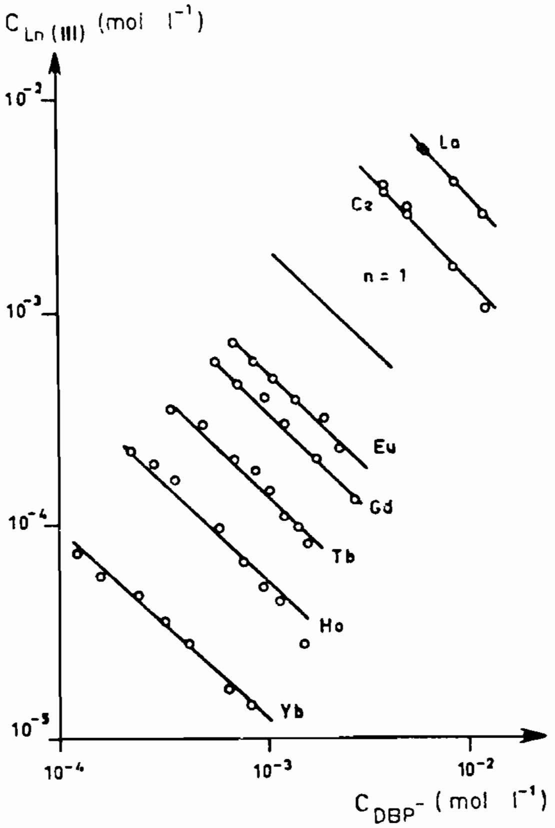

Fig. 1. Solubility of lanthanide $(DBP)_3$ in aqueous solutions as a function of free DBP^- ion concentration; $[NaClO_4]$ = 0.2 M; θ = 21 °C.

TABLE I. Formation Constants for Lanthanides(III)–DBP Complexes

Element	log β_1	log β_2	log β_3	log pS	log $\beta_2 pS$	Reference
La	2.02	3.5	4.6	−9.5	−4.55	1, 2, 3
Ce					−4.95	1
Nd	2.29				−5.8	2, 1
Eu					−6.35	1
Gd					−6.45	1
Tb					−6.75	1
Ho					−7.3	1
Yb	3.49				−7.8	2, 1

$\beta_n = [M(DBP)_n^{(3-n)^+}]/[M^{3+}][DBP^-]^n; pS = [M^{3+}][DBP^-]^3.$

Dibutylphosphate Complexes of 5f Tetravalent Ions

The number of compounds of Th(IV) or Pu(IV) reported in the literature is important; they are listed in Table II. Recently we investigated the behaviour of Th(IV) in order to gain insight into the systematics of Th(IV)–DBP complexes in aqueous solutions. First we measured the solubility of $Th(DBP)_4$, identified by X-ray and chemical analysis, into HCl solutions, because compounds like $Th(DBP)_x(Cl)_y$ are unknown, whereas compounds like $Th(NO_3)_x(DBP)_y$ have been reported by several authors (Table II). The solubility of $Th(DBP)_4$ can be explained quantitatively by the two equilibria:

$$Th(DBP)_4\downarrow + 3HCl \rightleftharpoons ThDBP(HDBP)_3^{3+} + 3Cl^-$$

$$ThDBP(HDBP)_3^{3+} \rightleftharpoons Th^{4+} + 4DBP^- + 3H^+$$

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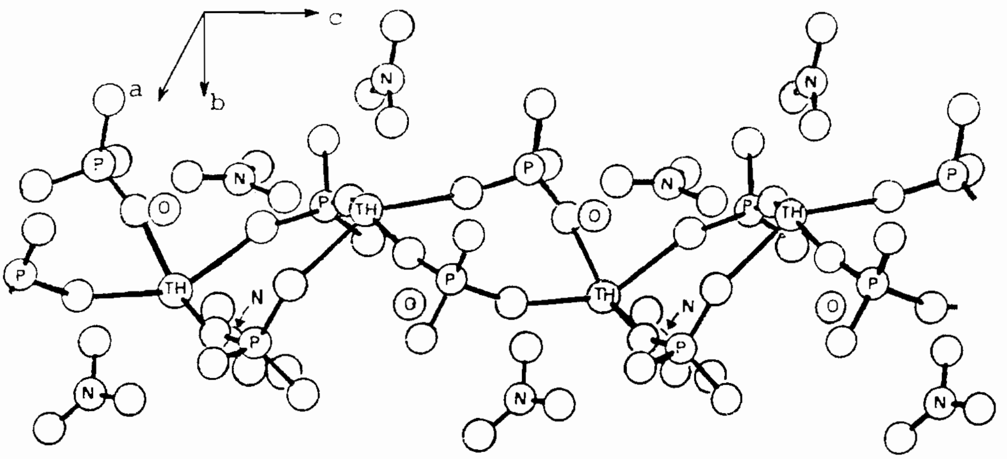

Fig. 2. Chain structure of $Th(DBP)_2(NO_3)_2 \cdot H_2O$ along the *c* axis.

TABLE II. Compounds of Th(IV) and Pu(IV) Formed in the Presence of HDBP

Compounds	Method of identification	Reference
$Th(DBP)_4$	Chemical analysis, X-ray	4, 5, this work
$Th(NO_3)_2(DBP)_2 \cdot H_2O$	Chemical analysis, X-ray diffraction, structure	this work, 6
$Th(DBP)_4 \cdot 2HDBP$	Chemical analysis	5
$Th(NO_3)_3DBP$	Chemical analysis	6
$Th(NO_3)(DBP)_3$	Chemical analysis, X-ray	this work, 6
$Pu(NO_3)_2(DBP)_2$	Chemical analysis	7

with equilibrium constants:

$$ThDBP(HDBP)_3^{3+}/[H^+]^3 = 10^{-6.32}$$

$$Th(HDBP)_3DBP^{3+}/[Th^{4+}][DBP^-]^4[H^+]^3 = 10^{22.13}$$

These constants yield a solubility product:

$$[Th^{4+}][DBP^-]^4 = 10^{-28.45}$$

In nitrate media there are more intricate equilibria because of the existence of other solids: in addition to $Th(DBP)_4$ we found $Th(DBP)_3NO_3$, $Th(DBP)_2(NO_3)_2 \cdot xH_2O$, with $x > 1$, and $Th(DBP)_2(NO_3)_2 \cdot H_2O$. All these compounds can be obtained as crystals and they possess distinct X-ray powder diagrams. $Th(DBP)_2(NO_3)_2 \cdot xH_2O$ is unstable in air because it loses water. The structure of $Th(DBP)_2(NO_3)_2 \cdot H_2O$ has been determined [8]; it is reproduced in Fig. 2. It consists of $Th(DBP)_2^{2+}$ threads; NO_3^- and H_2O complete the coordination sphere of Th^{4+}. Van der Waals interactions weakly hold the threads together. We did not find evidence of solids like $Th(DBP)_4 \cdot 2HDBP$, as described in the literature [5].

Dibutylphosphate Complexes of Pentavalent Np [1]

The solubility of NpO_2^+ ions as a function of DBP^- concentration is plotted in Fig. 3. The solubility variation can be attributed to the formation of two species: $NpO_2DBP \cdot xH_2O$ and $NpO_2(DBP)_2Na$. The solubility product of NpO_2DBP has a value of 5.2×10^{-7}. This compound probably contains water but there is no available data to prove this.

Dibutylphosphate Complexes of Hexavalent 5f Ions

The solubility of UO_2^{2+} ions as a function of DBP^- in a perchloric solution at pH 3 is shown in Fig. 4. This solubility can be explained by the formation of the scarcely soluble $UO_2(DBP)_2$ ($pS = 7 \times 10^{-12}$) and the soluble complexes UO_2DBP^+ and $UO_2(DBP)_4^{2-}$ ($\beta_1 = 10^{4.3}$, $\beta_4 = 10^{8.4}$). According to the literature [7], other insoluble complexes are formed in nitrate

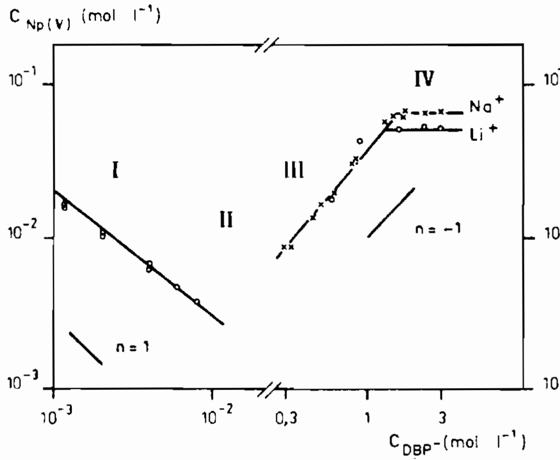

Fig. 3. Solubility of NpO_2^+ ions in aqueous solutions as a function of DBP^- ion concentrations; pH 3.0; $\theta = 21$ °C; $[Na(ClO_4, DBP)] = 0.2$ M (parts I and II); $[Na(ClO_4, DBP)] = 3$ M (parts III and IV).

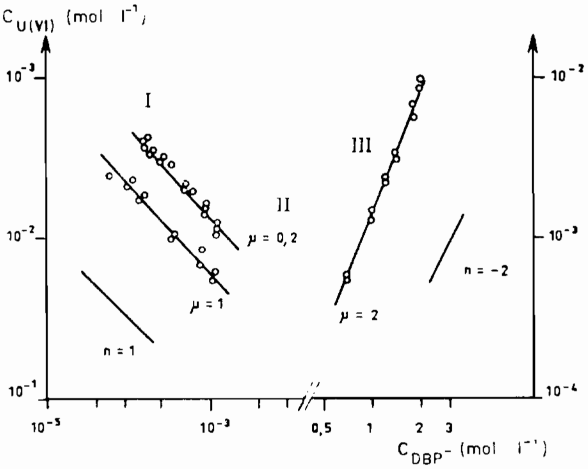

Fig. 4. Solubility of UO_2^{2+} ions in aqueous solutions as a function of DBP^- ion concentrations; pH = 3.0; θ = 21 °C; ionic strength as quoted adjusted with $NaClO_4$.

media in addition to $UO_2(DBP)_2$; they are $UO_2H(DBP)_2NO_3$, $UO_2H(DBP)_2NO_3 \cdot 2HDBP$ and $UO_2(DBP)NO_3$.

Conclusions

This short survey of data dealing with the 5f and 4f ion dibutylphosphate complexes shows that much more work is necessary in order to have a comprehensive insight into these complexes and their equilibrium relationships. Especially for the solids, X-ray diffraction data is missing and in its absence, unambiguous identification of the insoluble compounds is difficult. The knowledge of DBP^- complexes of actinides in aqueous solutions is important for nuclear fuel reprocessing in order to predict or prevent the formation of precipitates.

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