

**Synergistic and Antagonistic Effects in the Extraction of
^{175,181}Hf(IV) by Dibutylphosphate (HDBP) and Di(2-ethyl-
hexyl)phosphate (HDEHP) in the Presence of Trioctyl-
phosphineoxide (TOPO) or Trioctylamine (TOA)
in Hexane and Toluene**

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The extraction has been studied of ^{175,181}Hf(IV) from 1.0(0.5) M H₂SO₄ and 1.0 M HClO₄ aqueous solution into hexane and toluene by dibutylphosphate (HDBP) or di(2-ethylhexyl)phosphate (HDEHP), in the presence of trioctylphosphineoxide (TOPO) or trioctylamine (TOA). The results show that the combination HDEHP + TOA may cause antagonistic, while HDBP + TOPO may cause both synergistic and antagonistic effects in hafnium extraction. The distribution data have been analyzed with the LETAGROPVRID computer program. They indicate the formation of the following extractable Hf(IV)-species:

1) in hexane with HA = HDBP and B = TOPO: HfA₄, HfA₄(HA), HfSO₄A₂(HA)₂, HfSO₄A₂(HA)₃ (cf. Ref. 1); Hf(SO₄)₂B, Hf(SO₄)₂B₂, Hf(SO₄)₂B₃; Hf(ClO₄)₄B₂, Hf(ClO₄)₄B₃; Hf(SO₄)₂HAB, Hf(SO₄)₂HAB₂, Hf(SO₄)₂HAB₃, HfA₄B; Hf(ClO₄)₃AB₃ and Hf(ClO₄)₂A₂B₂.

2) in toluene with HA = HDEHP and B = TOA: HfA₄(HA), HfA₄(HA)₂ (cf. Ref. 1), (BH)₂Hf(SO₄)₃ and (BH)₂Hf(SO₄)₂A₂.

A summary of the equilibrium constants for the formation of the various Hf(IV)-species is given in Table 13.

In recent years there has been considerable interest in studying metal extraction with a combination of an acidic extractant (= HA) (e.g. thenoyl-trifluoroacetone (TTA), dialkylphosphoric acid) and a neutral or basic extractant (= B), e.g. tributylphosphate (TBP), trioctylphosphineoxide (TOPO)² or trioctylamine (TOA).^{3,4}

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In previous studies ^{5,6} one of us has shown that in metal extraction with a dialkylphosphate, the presence of a neutral organophosphorus extractant may cause either a synergistic effect (the distribution ratio D is greater than the sum of the distribution ratios with the individual extractants), or an antagonistic effect (the combination of HA and B leads to a decrease in D). Liem and Dyrssen ^{17,18,6} have also shown that in the case with U(VI)-extraction these effects may be explained quantitatively in terms of mixed complex formation between UO_2^{2+} ions, HA, B, and the inorganic anions in the aqueous medium.

Navrátil ⁷ found indications that TBP would cause an antagonistic effect in the extraction of Hf(IV) with dialkylphosphates. Hála ⁸ reported from a study of the extraction of Hf(IV) by TTA or *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) from 1–4 M HClO_4 or HNO_3 solutions that the presence of TBP may cause both antagonistic or synergistic effects, depending on the concentrations of TBP used. He also indicated that the combination TTA + HDBP and BPHA + HDBP gave rise to a marked synergistic effect. However, Hála drew no definite conclusions on the Hf-species extracted and gave no equilibrium constants.

The purpose of the present work is to study the nature of the extracted Hf(IV)-species in the extraction of ^{175,181}Hf(IV) from sulfuric and perchloric acid medium into hexane or toluene by dibutylphosphoric acid and di(2-ethylhexyl)phosphoric acid in the presence of trioctylphosphine oxide or trioctylamine.

Previously we reported the extraction of Hf(IV) from 1.0(0.5) M and 1.0 M HClO_4 aqueous solution into hexane and toluene by HDBP or HDEHP in the absence of B (= TOPO, TOA).¹ The complex formation between HDBP and TOPO in hexane and between HDEHP and TOA in toluene has been determined by one us in previous distribution studies ^{9,10} (*cf.* Table 8).

EXPERIMENTAL

Reagents. Trioctylphosphineoxide (TOPO), $(n\text{-C}_8\text{H}_{17})_3\text{PO}$, from Eastman Kodak Company, USA, was found by titration with NaOH solution to be practically free from acidic components and at least 99.7 % pure. It was used without further purification.

Trioctylamine, TOA, $(n\text{-C}_8\text{H}_{17})_3\text{N}$, from Eastman Kodak Company, USA, was used without further purification. The TOA-toluene solution was always pre-equilibrated with 1 M H_2SO_4 solution before being used for the distribution experiments.

The quality and method of purification of the HDBP, HDEHP, hexane, toluene, ^{175,181}Hf(IV), HClO_4 , NaClO_4 , H_2SO_4 , and Na_2SO_4 used and other details of the distribution experiments have been described previously.¹

SYMBOLS AND EQUILIBRIUM CONSTANTS

HA = dibutylphosphoric acid $(n\text{-C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{OH}$, (HDBP), or di(2-ethylhexyl)phosphoric acid $((\text{C}_8\text{H}_{17}\text{O})_2\text{P}(\text{O})\text{OH})$, (HDEHP).

B = trioctylphosphineoxide $(n\text{-C}_8\text{H}_{17})_3\text{P}=\text{O}$, (TOPO), or trioctylamine $(n\text{-C}_8\text{H}_{17})_3\text{N}$, (TOA).

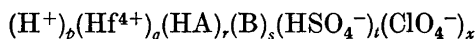
[] = equilibrium concentration in the aqueous phase.

[]_{org} = equilibrium concentration in the organic phase.

- C_A = initial total concentration of HA in the organic phase.
 C_B = initial total concentration of B in the organic phase.
 K_a = $[H^+][A^-]/[HA]$ stoichiometric acid dissociation constant.
 I_{aq}, I_{org} = gamma-activity of $^{175}, ^{181}\text{Hf}$ in the aqueous and organic phase in cpm for equal volumes of samples.
 $K_{pqrstx} = \frac{[(H^+)_p(Hf^{4+})_q(HA)_r(B)_s(HSO_4^-)_t(ClO_4^-)_x]_{org}}{[H^+]^p[Hf^{4+}]^q[HA]^r[B]_{org}^s[HSO_4^-]^t[ClO_4^-]^x}$
 formation constant of the extractable complexes
 $(H^+)_p(Hf^{4+})_q(HA)_r(B)_s(HSO_4^-)_t(ClO_4^-)_x$
 $D = \frac{\sum[Hf]_{org}}{\sum[Hf]} = I_{org}/I_{aq}$ net distribution ratio of Hf(IV).
 $U = \sum_1^{Np} (\log D_{calc} - \log D_{exp})^2$ the error-square sum of $\log D$ for Np experimental points.

CHEMICAL MODEL

The aqueous phase is assumed to contain Hf^{4+} ions in perchloric acid solution and Hf^{4+} , $Hf(SO_4)^{2+}$, and $Hf(SO_4)_2$ species in sulfuric acid medium (*cf.* Ref. 1). By the (p, q, r, s, t, x) complex in the organic phase we mean a complex of the general formula



The extracted complex is assumed to be uncharged and since $[Hf^{4+}]$ is always less than 10^{-7} M, we assume that $q=1$. The concentration of a $(p, 1, r, s, t, x)$ complex in the organic phase is given as:

$$\begin{aligned} [(H^+)_p Hf(HA)_r(B)_s(HSO_4^-)_t(ClO_4^-)_x]_{org} &= C_{p1rstx}(org) \\ &= K_{p1rstx}^{org} [H^+]^p [Hf^{4+}] [HA]^r [B]_{org}^s [HSO_4^-]^t [ClO_4^-]^x \end{aligned} \quad (1)$$

Using (1) we may express the distribution ratio as:

$$\begin{aligned} D_{calc} &= \frac{\sum [(H^+)_p Hf(HA)_r(B)_s(HSO_4^-)_t(ClO_4^-)_x]_{org}}{[Hf^{4+}] + [Hf(SO_4)^{2+}] + [Hf(SO_4)_2]} \\ &= \frac{\sum K_{p1rstx}^{org} [H^+]^p [HA]^r [B]_{org}^s [HSO_4^-]^t [ClO_4^-]^x}{1 + \beta_1 [H^+]^{-1} [HSO_4^-] + \beta_2 [H^+]^{-2} [HSO_4^-]^2} \end{aligned} \quad (2)$$

The amounts of A and B bound by the Hf-species may be neglected in comparison with the total concentrations of A and B, since in the experiments the total concentration of Hf(IV) was always less than 10^{-7} M. We may thus write for the mass balance equations for HA and B:

$$\begin{aligned} C_A &= \sum r [(H^+)_p (HA)_r] + \sum r [(HA)_r (B)_s]_{org} \\ &= \sum r K_{p0r000}^{aq} [H^+]^p [HA]^r + \sum r K_{00rs00}^{org} [HA]^r [B]_{org}^s \end{aligned} \quad (3)$$

$$C_B = \sum s [(HA)_r (B)_s]_{org} = \sum s K_{00rs00}^{org} [HA]^r [B]_{org}^s \quad (4)$$

Given the values of $[H^+]$, C_A , C_B , $C_{SO_4^-}$, $C_{ClO_4^-}$ for each point, $*\beta_1$, $*\beta_2$, K_{p1rstx}^{org} for the formation of the Hf(IV)-species, and the equilibrium constants K_{p0r000}^{aq} , K_{00rs00}^{org} for the formation of the species $(H^+)_p(HA)_r(aq)$ and $(HA)_rB_s(org)$ (cf. Table 8), we may calculate D_{calc} from (2), (3), and (4).

COMPUTER ANALYSIS OF THE DATA

The data for the Hf(IV)-extraction were treated by means of an improved version of the LETAGROPVRID computer program developed by Sillén *et al.*¹²⁻¹⁴ with which are calculated the set of values of the constants K_1 , K_2 , \dots , K_N for the formation of the extractable complexes $(H^+)_pHf(HA)_rB_s(HSO_4^-)_t(ClO_4^-)_z$ in the organic phase which will minimize the error square sum: $U = \sum(\log D_{calc} - \log D_{exp})^2$.

The input data for the computer were:

- 1) $\log [H^+]$
- 2) $C_{Hf(IV)}$, initial total concentration of Hf(IV) in the aqueous solution, which may be given any arbitrary small value, e.g. $10^{-10}M$, in case only mono-nuclear Hf(IV)-species are assumed to be formed.
- 3) C_A , initial total concentration of HA in the organic phase.
- 4) C_B , initial total concentration of B in the organic phase.
- 5) $I_{aq}^{(175,181)Hf}$ activity in the aqueous phase in cpm).
- 6) $I_{org}^{(175,181)Hf}$ activity in the organic phase in cpm).

The details of the computer program, called DISTR, will be published elsewhere.¹³

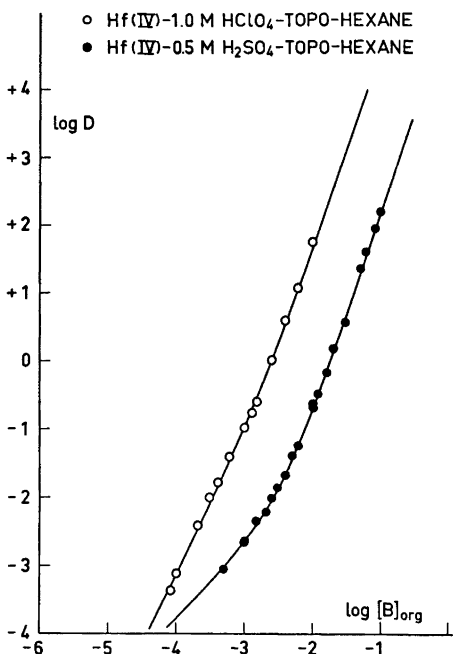


Fig. 1. The distribution of Hf(IV) between TOPO-hexane solution and 1.0 M HClO₄ (○) or 0.50 M H₂SO₄ (●) as a function of $[B]_{org}$. The distribution data are given in Tables 5 and 1. The curves have been calculated assuming the Hf(IV)-TOPO species and equilibrium constants in Table 13.

Calculations of distribution curves. The calculated distribution curves are given as full lines in the different figures. These have been calculated using the HALTAFALL program¹⁶ assuming the set of $(\text{H}^+)_p, (\text{Hf})_q, (\text{HA})_r, (\text{B})_s, (\text{HSO}_4^-)_t, (\text{ClO}_4^-)_x$ species and the equilibrium constants given in Tables 8 and 13.

RESULTS AND DISCUSSION

Extractable Hf(IV)-TOPO complexes

Extraction from sulfate medium. Fig. 1 shows the distribution of Hf(IV) between 0.5 M H_2SO_4 and TOPO-hexane solution, given as $\log D = f(\log [\text{B}]_{\text{org}})$. The data (21 experimental points) were computer analyzed assuming the extraction of $\text{Hf}(\text{SO}_4)_2\text{B}$ species in the organic phase. In the computer treatment of this set of data we may use $C_{\text{Hf}}(\text{aq}) (= \sum [\text{Hf}(\text{IV})])$ as a species component, since both $[\text{H}^+]$ and $[\text{HSO}_4^-]$ were kept constant. A good fit to the

Table 1. The distribution of $^{175,181}\text{Hf}(\text{IV})$ between solutions of TOPO in hexane and 0.50 M H_2SO_4 at 25°C. Data given as $\log D_{\text{exp}}$, $\log [\text{B}]_{\text{org}}$ and $\log D_{\text{calc}} D_{\text{exp}}^{-1}$.
 $\log [\text{H}^+] = -0.265$.

-3.048, -3.302, +0.037; -2.626, -3.001, -0.017; -2.648, -3.001, +0.005; -2.353,
-2.825, -0.043; -2.205, -2.693, +0.017; -2.017, -2.603, -0.014; -1.851, -2.524,
-0.032; -1.653, -2.395, +0.032; -1.658, -2.395, +0.036; -1.381, -2.302, -0.033;
-1.232, -2.220, +0.010; -0.669, -1.997, +0.013; -0.608, -1.997, -0.048; -0.467,
-1.919, +0.021; -0.155, -1.794, +0.056; +0.205, -1.696, -0.029; +0.575, -1.524,
+0.097; +1.368, -1.298, -0.037; +1.618, -1.219, -0.054; +1.957, -1.094, -0.023;
+2.213, -0.997, +0.008.

distribution data is found assuming the extraction of $\text{Hf}(\text{SO}_4)_2\text{B}$, $\text{Hf}(\text{SO}_4)_2\text{B}_2$, and $\text{Hf}(\text{SO}_4)_2\text{B}_3$ complexes, as is shown from the value of the error-square sum $U = 0.030$ and $\sigma(y) = 0.041$.

Table 2 shows distribution data for the system Hf(IV)-1.0 M(Na,H)HSO₄- 1.006×10^{-2} M TOPO-hexane, at varying hydrogen ion con-

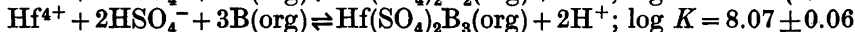
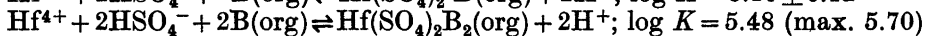
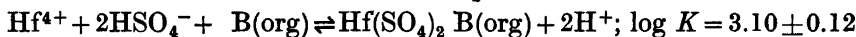
Table 2. Distribution of $^{175,181}\text{Hf}(\text{IV})$ between 1.006×10^{-2} M TOPO hexane solution and 1.0 M (H,Na)HSO₄ at 25°C. Data given as $\log D$, $\log [\text{H}^+]$, $\log [\text{HSO}_4^-]$.

-0.645, -0.027, -0.017; -0.652, -0.034, -0.057; -0.667, -0.041, -0.102; -0.718,
-0.051, -0.147; -0.704, -0.061, -0.199; -0.718, -0.075, -0.251; -0.750, -0.090,
-0.311; -0.694, -0.131, -0.440.

centrations ($-\log [\text{H}^+] = 0.017 - 0.440$). As can be seen the distribution ratio D is practically constant for the pH-range studied, since the major part of Hf(IV) in the aqueous phase was in the form of $\text{Hf}(\text{SO}_4)_2$. This indicates that the extracted Hf(IV) species may be represented as $\text{Hf}(\text{SO}_4)_2\text{TOPO}$, $\text{Hf}(\text{SO}_4)_2(\text{TOPO})_2$ and $\text{Hf}(\text{SO}_4)_2(\text{TOPO})_3$. Using the values of the equilibrium

constants for the formation of $\text{Hf}(\text{SO}_4)_2^{2+}$ and $\text{Hf}(\text{SO}_4)_2$ found previously (cf. Ref. 1) we computer calculated the following equilibrium constants which

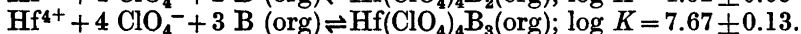
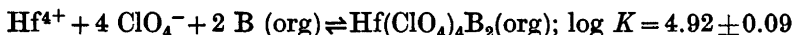
minimized the error-square sum $U = \sum_1^{21} (\log D_{\text{calc}} - \log D_{\text{exp}})^2 (= 0.030)$:



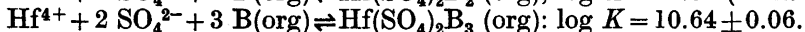
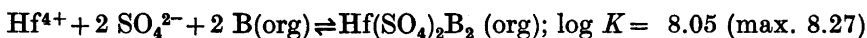
The free-energy $\Delta G = -RT \ln K$ for the formation of the Hf(IV)-complexes can be calculated as -4.23 , -7.48 , and -11.01 kcal. As may be expected the value of ΔG decreases as the number of TOPO coordinated to the Hf-species increases, *i.e.* the extraction of Hf(IV)-TOPO complex becomes easier. The decrease in the value ΔG may thus be approximated as 3–4 kcal/TOPO coordinated.

Extraction from 1 M HClO₄. The extraction of Hf(IV) from 1 M HClO_4 by TOPO was also studied. In this medium and $[\text{H}^+] = 1$ M we may assume that Hf(IV) is predominantly in the form of Hf^{4+} . In Fig. 1 the distribution of Hf(IV) is given as a function of $[\text{B}]_{\text{org}}$. The data ($N_p = 13$ points) was Letagrop analyzed with various assumptions of the extraction of Hf(IV)-TOPO species.

The results show that for the concentration of TOPO studied ($C_B = 8.08 \times 10^{-5} - 1.00 \times 10^{-2}$ M) the distribution data can be described satisfactorily with the extraction of $\text{Hf}(\text{ClO}_4)_4(\text{TOPO})_2$ and $\text{Hf}(\text{ClO}_4)_4(\text{TOPO})_3$ ($U = 0.044$ and $\sigma(\log D) = 0.053$). The equilibrium constants found have the following values:



The equilibrium constants found for the formation of the (1,2) and (1,3) Hf(IV)-TOPO species from perchloric acid medium may be compared with those found previously for the formation from 0.5 M sulfuric acid medium:



The significant differences in the formation constants thus indicate the effect of the inorganic ligand on the formation of the Hf-species, sulfate being more strongly complexed by Hf(IV) than the ClO_4^- ligand. For the reaction $\text{Hf}(\text{ClO}_4)_4 \text{B}_2(\text{org}) + \text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{ClO}_4)_4 \text{B}_3(\text{org})$, we find $K = 10^{2.75} \text{ M}^{-1}$ which may be compared with the value $10^{2.59}$ found for the Hf(IV)-sulfate complexes.

Hafnium(IV) complexes with HDBP and TOPO. Trioctylphosphine oxide, TOPO, was found previously by one of us⁵ to form UO_2^{2+} -HDBP-TOPO mixed complex species and to cause a stronger synergistic effect compared with other organophosphorous compounds with less basic character, such as tributylphosphate, TBP. Moreover it seems to form extractable uranyl mixed-ligand complexes of the substitution type rather than complexes of the addition type.

A study from this laboratory⁶ has shown previously that TBP, while showing a synergistic effect in the extraction of UO_2^{2+} with HDBP, shows an antagonistic effect in the extractions of a four-valent metal ion, such as Th^{4+}

Table 3. The distribution of Hf(IV) between solutions of HDBP in hexane and 0.50 M H_2SO_4 for different constant initial concentrations of TOPO at 25°C. The data are given as $\log D_{exp}$, C_A M, $\log [HA]$, $\log [B]_{org}$ and $\log D_{calc} D_{exp}^{-1}$. $\log [H^+] = -0.265$.

$$C_B = 4.933 \times 10^{-4} M$$

-2.576, 9.959×10^{-5} , -4.181, -3.316, +0.031; -1.812, 1.992×10^{-4} , -3.886, -3.330, -0.028; -1.451, 2.490×10^{-4} , -3.792, -3.336, -0.036; +0.187, 5.985×10^{-4} , -3.431, -3.379, -0.090; +0.773, 7.990×10^{-4} , -3.316, -3.402, -0.141; +1.674, 1.496×10^{-3} , -3.076, -3.470, +0.101.

$$C_B = 1.997 \times 10^{-3} M$$

-1.837, 9.959×10^{-5} , -4.353, -2.709, -0.047; -1.715, 1.494×10^{-4} , -4.177, -2.714, -0.045; +0.228, 7.990×10^{-4} , -3.461, -2.772, -0.029; +1.363, 1.496×10^{-3} , -3.200, -2.829, -0.035.

$$C_B = 5.033 \times 10^{-3} M$$

-1.356, 9.959×10^{-5} , -4.575, -2.304, +0.127; -1.244, 1.494×10^{-4} , -4.399, -2.307, +0.081; -1.143, 2.490×10^{-4} , -4.177, -2.313, +0.097; -0.238, 7.980×10^{-4} , -3.670, -2.344, -0.011; +0.688, 1.496×10^{-3} , -3.396, -2.382, +0.045; +1.626, 2.493×10^{-3} , -3.173, -2.435, +0.014.

$$C_B = 1.003 \times 10^{-2} M$$

-0.763, 9.959×10^{-5} , -4.796, -2.002, +0.184; -0.740, 1.494×10^{-4} , -4.620, -2.004, +0.196.

Table 4. The distribution of Hf(IV) between solutions of TOPO in hexane and 0.50 M H_2SO_4 for different constant initial concentrations of HDBP at 25°C. The data are given as $\log D_{exp}$, C_B M, $\log [HA]$, $\log [B]_{org}$ and $\log D_{calc} D_{exp}^{-1}$. $\log [H^+] = -0.265$.

$$C_A = 1.494 \times 10^{-4} M$$

-2.558, 4.990×10^{-5} , -3.942, -4.326, +0.166; -2.280, 4.993×10^{-4} , -4.008, -3.323, +0.066; -1.731, 1.997×10^{-3} , -4.177, -2.714, -0.029; -1.058, 4.993×10^{-3} , -4.397, -2.310, -0.111; +0.239, 2.010×10^{-2} , -4.877, -1.700, -0.022.

$$C_A = 3.990 \times 10^{-4} M$$

-0.722, 1.996×10^{-5} , -3.533, -4.762, +0.222; -0.640, 2.996×10^{-4} , -3.571, -3.580, +0.047; -0.662, 4.993×10^{-4} , -3.596, -3.355, +0.009; -0.670, 4.993×10^{-3} , -3.970, -2.325, -0.201; +0.010, 1.501×10^{-2} , -4.337, -1.834, -0.036.

$$C_A = 4.988 \times 10^{-3} M$$

-0.060, 2.994×10^{-5} , -3.446, -4.599, -0.015; -0.172, 4.990×10^{-5} , -3.448, -4.377, +0.089; -0.177, 1.997×10^{-4} , -3.468, -3.771, +0.038; -0.216, 2.996×10^{-4} , -3.480, -3.593, +0.042; -0.229, 4.993×10^{-4} , -3.505, -3.367, -0.012; -0.529, 1.997×10^{-3} , -3.660, -2.746, -0.071; +0.340, 2.006×10^{-2} , -4.350, -1.707, -0.041; +0.862, 3.009×10^{-2} , -4.511, -1.528, -0.113.

$$C_A = 9.975 \times 10^{-4} M$$

+1.237, 1.997×10^{-4} , -3.199, -3.829, -0.084; +1.095, 2.996×10^{-4} , -3.209, -3.650, +0.020; +1.160, 4.993×10^{-4} , -3.230, -3.423, -0.119; +0.563, 1.997×10^{-3} , -3.368, -2.789, +0.031; +0.309, 2.996×10^{-3} , -3.444, -2.599, +0.066; +0.018, 4.993×10^{-3} , -3.571, -2.358, +0.055; +0.313, 2.006×10^{-2} , -4.047, -1.717, +0.084; +0.815, 3.009×10^{-2} , -4.208, -1.535, -0.007; +1.447, 5.015×10^{-2} , -4.417, -1.308, -0.056.

Table 5. The distribution of $^{175,181}\text{Hf(IV)}$ between solutions of TOPO in hexane and 0.975 M HClO_4 at 25°C. Data given as $\log D_{\text{exp}}$, $\log [\text{B}]_{\text{org}}$ and $\log D_{\text{calc}} D_{\text{exp}}^{-1}$.

-3.364, -4.093, +0.070; -3.109, -3.995, +0.014; -2.409, -3.694, -0.061; -2.002, -3.519, -0.097; -1.782, -3.393, -0.044; -1.400, -3.217, -0.035; -0.973, -2.998, +0.045; -0.752, -2.886, +0.091; -0.587, -2.822, +0.032; +0.025, -2.602, +0.026; +0.598, -2.397, -0.006; +1.804, -2.222, -0.012; +1.761, -2.000, -0.066.

Table 6. The distribution of $^{175,181}\text{Hf(IV)}$ between solutions of HDBP in hexane and 0.975 M HClO_4 for different constant initial concentrations of TOPO at 25°C. Data given as $\log D_{\text{exp}}$, C_A M, $\log [\text{HA}]$, $\log [\text{B}]_{\text{org}}$ and $\log D_{\text{calc}} D_{\text{exp}}^{-1}$.

$C_B = 1.005 \times 10^{-3}$ M

+0.224, 9.959×10^{-5} , -4.221, -3.011, +0.054; +0.402, 1.245×10^{-4} , -4.124, -3.014, +0.028; +0.567, 1.494×10^{-4} , -4.046, -3.017, -0.008; +0.710, 1.992×10^{-4} , -3.923, -3.023, +0.062; +1.003, 2.490×10^{-4} , -3.828, -3.030, -0.057; +1.173, 2.988×10^{-4} , -3.750, -3.036, -0.075; +1.460, 3.984×10^{-4} , -3.629, -3.048, -0.098; +1.685, 4.980×10^{-4} , -3.535, -3.059, -0.087.

$C_B = 2.501 \times 10^{-3}$ M

+1.032, 9.959×10^{-5} , -4.380, -2.611, +0.003; +1.213, 1.245×10^{-4} , -4.284, -2.613, -0.060; +1.298, 1.494×10^{-4} , -4.205, -2.615, -0.043; +1.464, 1.992×10^{-4} , -4.080, -2.620, -0.039; +1.584, 2.490×10^{-4} , -3.983, -2.642, -0.022; +1.664, 2.988×10^{-4} , -3.905, -2.629, +0.015; +1.756, 3.984×10^{-4} , -3.780, -2.637, +0.113; +1.880, 4.980×10^{-4} , -3.684, -2.646, +0.142.

Table 7A. The distribution of $^{175,181}\text{Hf(IV)}$ between solutions of TOA in toluene and 1.0 M H_2SO_4 at 25°C. Data given as $\log D_{\text{exp}}$, C_B M, $\log [\text{B}]_{\text{org}}$ and $\log D_{\text{calc}} D_{\text{exp}}^{-1}$. $\log [\text{H}^+] = 0.032$.

-2.407, 2.050×10^{-4} , -3.744, -0.024; -1.920, 4.058×10^{-4} , -3.487, +0.003; -1.320, 1.006×10^{-3} , -3.175, +0.027; -0.820, 2.030×10^{-3} , -2.956, -0.036; -0.217, 6.039×10^{-3} , -2.649, -0.025; +0.396, 2.013×10^{-2} , -2.343, -0.024; +0.814, 6.005×10^{-2} , -2.082, +0.079.

Table 7B. The distribution of Hf(IV) between solutions of HDEHP and 1.0 M H_2SO_4 for different constant initial concentrations of TOA at 25°C. The data are given as $\log D_{\text{exp}}$, C_A M, $\log [\text{HA}]$, $\log [\text{B}]_{\text{org}}$ and $\log D_{\text{calc}} D_{\text{exp}}^{-1}$. $\log [\text{H}^+] = 0.0319$.

$C_B = 2.030 \times 10^{-4}$ M

-2.728, 1.992×10^{-3} , -8.878, -5.224, -0.023; -2.433, 2.988×10^{-3} , -8.780, -5.319, +0.117; -1.431, 5.976×10^{-3} , -8.620, -5.477, -0.051; -1.101, 7.968×10^{-3} , -8.555, -5.541, -0.028; -0.777, 1.006×10^{-2} , -8.503, -5.592, -0.063; +1.158, 4.026×10^{-2} , -8.196, -5.896, -0.274; -0.121, 1.611×10^{-2} , -8.398, -5.696, -0.136; +0.295, 2.517×10^{-2} , -8.299, -5.794, +0.002.

$C_B = 4.060 \times 10^{-4}$ M

-2.468, 1.245×10^{-3} , -9.043, -4.764, -0.225; -2.462, 1.494×10^{-3} , -8.987, -4.818, -0.193; -2.157, 3.486×10^{-3} , -8.758, -5.040, +0.041; -1.719, 4.980×10^{-3} , -8.671, -5.125, -0.002; -0.908, 1.006×10^{-2} , -8.507, -5.287, +0.048; +0.027, 2.013×10^{-2} , -8.351, -5.441, -0.019; +0.566, 2.996×10^{-2} , -8.262, -5.529, -0.060; +1.311, 5.035×10^{-2} , -8.148, -5.643, -0.151.

$C_B = 6.039 \times 10^{-3}$ M

-0.530, 1.006×10^{-2} , -8.693, -3.932, +0.169; -0.489, 4.980×10^{-3} , -9.574, -3.133, +0.040; -0.325, 1.245×10^{-3} , -10.591, -2.711, +0.012; -0.403, 2.490×10^{-3} , -10.208, -2.794, -0.001; -0.438, 3.486×10^{-3} , -9.970, -2.887, -0.013; -0.269, 2.013×10^{-2} , -8.423, -4.197, +0.187; +0.085, 2.996×10^{-2} , -8.308, -4.311, +0.257; +0.643, 5.035×10^{-2} , -8.174, -4.445, +0.386;

from perchloric acid medium. To study whether a more basic P = O group may be more effective in the formation of mixed ligand complexes with a four-valent metal ion, we studied the extraction of Hf(IV) by HDBP into hexane in the presence of TOPO from 0.5 M H_2SO_4 and 1.0 M $HClO_4$ solution.

Extraction from 0.50 M H_2SO_4 medium. Fig. 2 shows the distribution of Hf(IV) as a function of [HA] for different constant total concentrations of

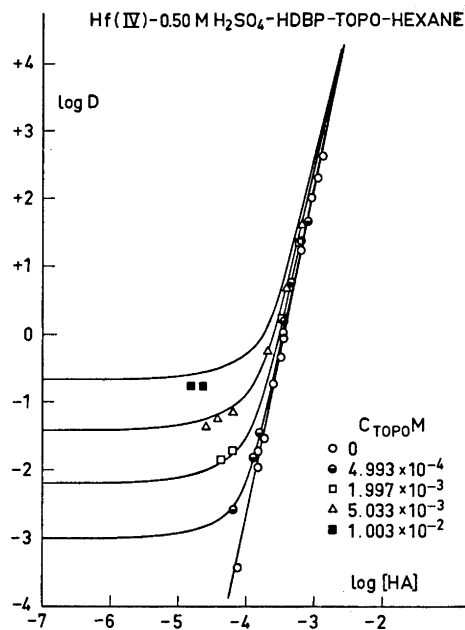


Fig. 2. The distribution of Hf(IV) between HDBP-TOPO hexane and 0.50 M H_2SO_4 as a function of [HA] at different constant initial concentrations of TOPO in the organic phases C_B : O (○) (cf. Ref. 1), 4.993×10^{-4} (●), 1.997×10^{-3} (□), 5.033×10^{-3} (△), and 1.003×10^{-2} M (■). The distribution data are given in Table 3. The curves have been calculated assuming the HDBP-TOPO species in Table 8 and the Hf(IV)-HDBP-TOPO complexes in Table 13.

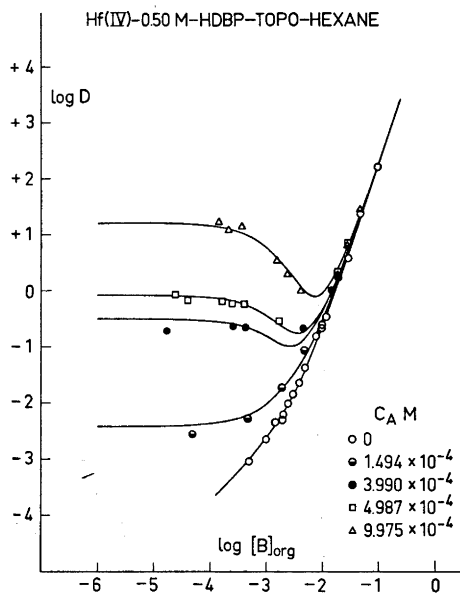


Fig. 3. The distribution of Hf(IV) between HDBP-TOPO-hexane and 0.50 M H_2SO_4 as a function of $[B]_{org}$ at different constant initial concentrations of HDBP in the organic phase, C_A : O (○), 1.494×10^{-4} (●), 3.990×10^{-4} (○), 4.988×10^{-4} (□), 9.975×10^{-4} M (△). The distribution data are given in Table 4. The curves have been calculated assuming the HDBP-TOPO species in Table 8 and the Hf(IV)-HDBP-TOPO complexes in Table 13.

TOPO, $C_B = 4.993 \times 10^{-4}$, 1.997×10^{-3} , 5.033×10^{-3} , and 1.003×10^{-2} M, and Fig. 3 gives the extraction of Hf(IV) as a function of $[B]_{org}$ for different constant total concentrations of HDBP, $C_A = 1.494 \times 10^{-4}$, 3.990×10^{-4} , 4.988×10^{-4} , and 9.975×10^{-4} M. The [HA] and $[B]_{org}$ were computer calculated assuming the formation constants for the $(H^+)_p(HA)_qB_r$, given in Ref. 9 summarized in Table 8. The data plotted in Fig. 2 indicate the possible formation of Hf(IV)-

Table 8. Equilibrium constants for the formation of HDBP-TOPO species in hexane (cf. Refs. 9, 15) and HDEHP-TOA species in toluene (cf. Ref. 10) used in the present work for computer calculations of H(IV)-extraction data.

| System | Equilibrium constant | |
|--|---|--|
| HDBP-hexane/1.0 M (Na,H)ClO ₄ | $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{A}^-$ | $K_a = 0.1318 \text{ M}$ |
| | $\text{HA}(\text{aq}) \rightleftharpoons \text{HA}(\text{org})$ | $K_d = 4.471 \times 10^{-3}$ |
| | $2 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_2\text{A}_2(\text{org})$ | $K_2 = 169 \text{ M}^{-1}$ |
| | $10 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_{10}\text{A}_{10}(\text{org})$ | $K_{10} = 6.824 \times 10^{15} \text{ M}^{-9}$ |
| | $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{A}^-$ | $K_a = 0.1318 (0.1253) \text{ M}$ |
| HDBP-hexane/1.0(0.5) M (Na,H)SO ₄ | $\text{HA}(\text{aq}) \rightleftharpoons \text{HA}(\text{org})$ | $K_d = 6.572 \times 10^{-3}$ |
| | $2 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_2\text{A}_2(\text{org})$ | $K_2 = 196.6 \text{ M}^{-1}$ |
| | $4 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_4\text{A}_4(\text{org})$ | $K_4 = 7.780 \times 10^5 \text{ M}^{-3}$ |
| | $\text{HA}(\text{aq}) + \text{B}(\text{org}) \rightleftharpoons \text{HAB}(\text{org})$ | $K_{11} = 49.875 \text{ M}^{-1}$ |
| HDBP-TOPO-hexane/0.5 M H ₂ SO ₄ /or 1.0 M HClO ₄ | $2 \text{HA}(\text{aq}) + \text{B}(\text{org}) \rightleftharpoons \text{H}_2\text{A}_2\text{B}(\text{org})$ | $K_{21} = 267.27 \text{ M}^{-2}$ |
| | $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{A}^-$ | $K_a = 0.7127 \text{ M}^{-1}$ |
| HDEHP-toluene/1.0 M (H,Na)HSO ₄ /or (H,Na)ClO ₄ | $2 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_2\text{A}_2(\text{aq})$ | $K_{\text{aaq}} = 8.0 \times 10^{12} \text{ M}^{-1}$ |
| | $\text{HA}(\text{aq}) \rightleftharpoons \text{HA}(\text{org})$ | $K_d = 6.157 \times 10^4$ |
| | $2 \text{HA}(\text{aq}) \rightleftharpoons \text{H}_2\text{A}_2(\text{org})$ | $K_2 = 4.81 \times 10^{14} \text{ M}^{-1}$ |
| | $2 \text{BH} \cdot \text{HSO}_4(\text{org}) \rightleftharpoons (\text{BH})_2 \cdot \text{SO}_4(\text{org}) + \text{H}^+ + \text{HSO}_4^-$ | $K_4[\text{H}^+]^{-1}[\text{HSO}_4^-]^{-1} = 377.21 \text{ M}^{-1}$ |
| HDEHP-TOA toluene/1.0 M H ₂ SO ₄ | $\text{HA}(\text{aq}) + \text{BH} \cdot \text{HSO}_4(\text{org}) \rightleftharpoons \text{HAB}(\text{org}) + \text{H}^+ + \text{HSO}_4^-$ | $K_{11}[\text{H}^+]^{-1}[\text{HSO}_4^-]^{-1} = 2.493 \times 10^{10} \text{ M}^{-1}$ |

mixed ligand species, since the experimental points seem not to fall on a single straight line with increasing [HA]. Another indication for metal mixed ligand complex formation is found in Table 10, model (10, I and II), which shows that no good fit to the data with both HA and B present is obtained when only the extraction of Hf(IV)-HDBP species ($\text{Hf}(\text{HA})_4 + \text{Hf}(\text{HA})_5$) and Hf(IV)-TOPO species (HfB , HfB_2 , and HfB_3) found previously are assumed.

We computer treated the data ($N_p = 60$ points) to find the possible extractable Hf(IV)-HDBP-TOPO mixed complexes. From graphical analysis of the data: $\log \Delta D = f(\log[\text{HA}])$ at constant C_B and $\log \Delta D = f(\log[\text{B}]_{\text{org}})$ at constant C_A values, where ΔD represent the calculated contribution on the distribution ratio D by the $\text{Hf}(\text{HA})_q\text{B}_r$ species, we found indications of the possible formation of the species $\text{Hf}(\text{HA})_4\text{B}$ and $\text{Hf}(\text{HA})\text{B}_3$.

The data (60 points) were analyzed using the species selector (rejection factor $F_\sigma = 1.0$, i.e. only species with $K > F_\sigma \times \sigma(K)$ are accepted, assuming the extraction of the possible $\text{Hf}(\text{HA})_q\text{B}_r$ species. The results for the systems where q and r may take the values: $q = 0$ to 5 and $r = 0$ to 3 are summarized in Table 9.

Table 9. Equilibrium constants $\log \beta_{*q*r}$ for the formation of $(\text{H}^+)_* \text{Hf}(\text{HSO}_4)_* \text{B}_r$ species in the system Hf(IV)-0.50 M H_2SO_4 -HDBP-TOPO-hexane for various assumptions of extractable Hf(IV)-species which minimize the error-square sum

$$U = \sum_{i=1}^{60} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$$

| Model No. | $(*, q, *, r) \log \beta_{*q*r}$ | U_{min} | $\sigma(\log D)$ |
|----------------|---|------------------|------------------|
| I ^b | $c(*, 0, *, 1) 0.05; c(*, 0, *, 2) 2.43; c(*, 0, *, 3) 5.01;$ | 1.351 | 0.155 |
| | $c(*, 5, *, 0) 17.05; c(*, 4, *, 0) 12.75;$ $(*, 4, *, 1) 16.52 \pm 0.24; (*, 1, *, 1) 4.75, \text{max. } 5.16;$ $(*, 1, *, 2) 7.30, \text{max. } 7.80; (*, 1, *, 3) 9.26, \text{max. } 9.68.$ | | |
| rejected: | $(*, 3, *, 1) \text{max. } 13.47; (*, 3, *, 2) \text{max. } 15.44;$ $(*, 2, *, 1) \text{max. } 9.24; (*, 4, *, 2) \text{max. } 19.02;$ $(*, 2, *, 2) \text{max. } 11.73; (*, 2, *, 3) \text{max. } 13.84.$ | | |
| II | $c(*, 0, *, 1) 0.05; c(*, 0, *, 2) 2.43; c(*, 0, *, 3) 5.01;$ | 1.351 | 0.153 |
| | $c(*, 5, *, 0) 17.05; c(*, 4, *, 0) 12.75; c(*, 4, *, 1) 16.52;$ $c(*, 1, *, 1) 4.75; c(*, 1, *, 2) 7.30; c(*, 1, *, 3) 9.26;$ $(*, 2, *, 2) \beta = 0, \text{max. } 11.62; (*, 2, *, 3) \beta = 0,$ $\text{max. } 13.74;$ $(*, 3, *, 2) \beta = 0, \text{max. } 15.53; (*, 3, *, 3) \beta = 0,$ $\text{max. } 17.75.$ | | |
| III | $c(*, 0, *, 1) 0.05; c(*, 0, *, 2) 2.43; c(*, 0, *, 3) 5.01;$ | 1.351 | 0.153 |
| | $c(*, 5, *, 0) 17.05; c(*, 4, *, 0) 12.75; c(*, 4, *, 1) 16.52;$ $c(*, 1, *, 1) 4.75; c(*, 1, *, 2) 7.30; c(*, 1, *, 3) 9.26;$ $(*, 4, *, 2) \beta = 0, \text{max. } 19.32; (*, 4, *, 3) \beta = 0,$ $\text{max. } 21.40;$ $(*, 5, *, 1) \beta = 0, \text{max. } 20.10; (*, 5, *, 2) \beta = 0,$ $\text{max. } 22.58.$ | | |

^a $\beta_{*q*r} = [(\text{H}^+)_* \text{Hf}(\text{HA})_q (\text{HSO}_4)_* \text{B}_r]_{\text{org}} [\text{Hf}(\text{IV})]^{-1} [\text{HA}]^{-q} [\text{B}]_{\text{org}}^{-r}$, where $[\text{Hf}(\text{IV})] = [\text{Hf}^{4+}] + [\text{Hf}(\text{SO}_4)^{2+}] + [\text{Hf}(\text{SO}_4)_2]$.

^b Application of species-selector in LETAGROP analysis with rejection factor $F_\sigma = 1.0$.

^c The equilibrium constant is not varied during the course of the computer calculation.

The subscript * for p and t in the extractable complex $(\text{H}^+)_{p,t} \text{Hf}(\text{HA})_q \text{B}_r$, $(\text{HSO}_4^-)_t$, indicates that in this experiment the values of $[\text{H}^+]$ and $[\text{HSO}_4^-]$ have been kept constant. This set of distribution data thus gave no information about the possible values of p and t . During the computer calculations we arbitrarily put $p=t=0$. The equilibrium constant given in Table 9 corresponds to $\beta_{*q**} = [\text{Hf}(\text{HA})_q \text{B}_r]_{\text{org}} [\text{Hf}^{4+}]^{-1} [\text{HA}]^{-q} [\text{B}]_{\text{org}}^{-r}$.

The results in Table 9 indicate that with $F_\sigma = 1.0$, only the following Hf-HA-TOPO complexes are retained in the calculations: $\text{Hf}(\text{HA})\text{B}$, $\text{Hf}(\text{HA})\text{B}_2$, $\text{Hf}(\text{HA})\text{B}_3$, and $\text{Hf}(\text{HA})_4\text{B}$ and the following Hf-species are rejected: $\text{Hf}(\text{HA})_2\text{B}$, $\text{Hf}(\text{HA})_2\text{B}_2$, $\text{Hf}(\text{HA})_2\text{B}_3$, $\text{Hf}(\text{HA})_3\text{B}$, $\text{Hf}(\text{HA})_3\text{B}_2$, $\text{Hf}(\text{HA})_3\text{B}_3$, $\text{Hf}(\text{HA})_4\text{B}_2$ (model 9 I).

Adding the combinations $\text{Hf}(\text{HA})_2\text{B}_2 + \text{Hf}(\text{HA})_2\text{B}_3 + \text{Hf}(\text{HA})_3\text{B}_2 + \text{Hf}(\text{HA})_3\text{B}_3$ (model 9 II) or $\text{Hf}(\text{HA})_4\text{B}_2 + \text{Hf}(\text{HA})_4\text{B}_3 + \text{Hf}(\text{HA})_5\text{B} + \text{Hf}(\text{HA})_5\text{B}_2$ (model 9 III) to the Hf-HA-B species retained in model 9 I, resulted in values for $\beta = 0$ for all the species added and thus gave no improvement to the value of the error-square sum $U = 1.351$ found previously in model 9 I.

During the computer analysis of model II and model III the equilibrium constants for the formation of the Hf(IV)-species retained in model I had not been varied, since these values of the constants may be expected not to vary in any significant degree which would justify the extra computer time needed.

In Table 10 we also summarize the result of an analysis with 46 selected points, in which the different species which have been rejected in the first run using the species-selector are again added one by one to the combination of species retained. As can be seen from Table 10 no improvement of either U_{min} or $\sigma(\log D)$ is found. We thus conclude that the main Hf-HA-TOPO mixed complexes extracted for the extraction conditions studied are the (1,1,1), (1,1,2), (1,1,3), and (1,4,1) species (model IV) which may be represented with the chemical formula $(\text{H}^+)_p \text{Hf}(\text{HSO}_4^-)_{4+p} (\text{HA})\text{B}$, $(\text{H}^+)_p \text{Hf}(\text{HSO}_4^-)_{4+p} (\text{HA})\text{B}_2$, $(\text{H}^+)_p \text{Hf}(\text{HSO}_4^-)_{4+p} (\text{HA})\text{B}_3$, and $(\text{H}^+)_p \text{Hf}(\text{HSO}_4^-)_{4+p} (\text{HA})_4\text{B}$. Since the distribution of Hf(IV) in this set of experiment was studied at constant values of $[\text{H}^+]$ ($= 0.5436 \text{ M}$) and $[\text{HSO}_4^-]$ ($= 0.4564 \text{ M}$), the value of p cannot be determined from the data available. Assuming the probable value $p = -2$ for the (1,1,1), (1,1,2), and (1,1,3) species and $p = -4$ for the (1,4,1) complex, we may formally describe the formation of the Hf-HA-TOPO complexes with the following equilibrium reactions:

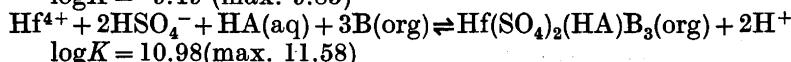
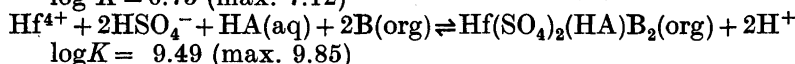
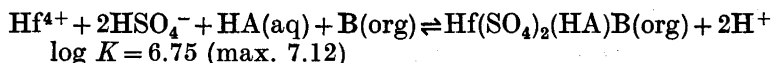


Fig. 4 shows the mole percentage of Hf(IV)-species in the system $\text{Hf}(\text{IV}) - 0.50 \text{ M H}_2\text{SO}_4 - 5.165 \times 10^{-4} \text{ M HDBP-TOPO-hexane}$, as a function of $[\text{TOPO}]_{\text{org}}$. This figure shows the competition in formation between the

Table 10. Equilibrium constants $^a \log \beta_{*q*r}$ for the formation of $(\text{H}^+)_* \text{Hf}(\text{HA})_q (\text{HSO}_4)_r \text{B}_r$ species in the system $\text{Hf(IV)}\text{-}0.50 \text{ M H}_2\text{SO}_4\text{-HDBP-TOPO-hexane}$ for various assumptions of extractable Hf(IV) -species which minimize the error-square sum

$$U = \sum_1^{46} (\log D_{\text{calc}} - \log D_{\text{exp}})^2.$$

| Model No. | $(*, q, *, r) \log \beta_{*q*r}$ | U_{min} | $\sigma (\log D)$ |
|-----------------|---|------------------|-------------------|
| I | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75.$ | 7.334 | |
| II | $(*, 0, *, 1) 0.76, \text{max. } 1.19; (*, 0, *, 2) 3.04, \text{max. } 3.69;$ $(*, 0, *, 3) 5.27, \text{max. } 5.60; (*, 5, *, 0) 17.24, \text{max. } 17.51;$ $(*, 4, *, 0) 13.15, \text{max. } 13.80.$ | 1.895 | 0.215 |
| III | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.45 \pm 0.24;$ $(*, 1, *, 3) 9.56 \pm 0.20; (*, 2, *, 1) 9.02 \pm 0.24.$ | 0.487 | 0.106 |
| IV ^b | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.15;$ $(*, 1, *, 1) 4.60, \text{max. } 4.96; (*, 1, *, 2) 7.39, \text{max. } 7.71;$ $(*, 1, *, 3) 9.28, \text{max. } 9.59.$ | 0.353 | 0.092 |
| V | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.23;$ $(*, 1, *, 1) 4.58, \text{max. } 5.22; (*, 1, *, 2) 7.39, \text{max. } 7.74;$ $(*, 1, *, 3) 9.28, \text{max. } 9.60;$ $(*, 2, *, 1) 7.48, \text{max. } 9.19 (\sigma(\beta) > 8.5\beta).$ | 0.353 | 0.093 |
| VI | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.15;$ $(*, 1, *, 1) 4.60, \text{max. } 4.96; (*, 1, *, 2) 7.39, \text{max. } 7.72;$ $(*, 1, *, 3) 9.28, \text{max. } 9.60; (*, 2, *, 3) \beta=0, \text{max. } 13.74.$ | 0.353 | 0.093 |
| VII | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.16;$ $(*, 1, *, 1) 4.60, \text{max. } 4.96; (*, 1, *, 2) 7.39, \text{max. } 7.72;$ $(*, 1, *, 3) 9.28, \text{max. } 9.59; (*, 4, *, 2) \beta=0, \text{max. } 18.93.$ | 0.353 | 0.093 |
| VIII | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75;$ $(*, 4, *, 1) 16.54, \text{max. } 16.83;$ $(*, 1, *, 1) 4.61, \text{max. } 4.97; (*, 1, *, 2) 7.39, \text{max. } 7.71;$ $(*, 1, *, 3) 9.28, \text{max. } 9.59; (*, 5, *, 1) \beta=0, \text{max. } 18.64.$ | 0.353 | 0.093 |
| IX | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.15;$ $(*, 1, *, 1) 4.60, \text{max. } 4.96; (*, 1, *, 2) 7.39, \text{max. } 7.72;$ $(*, 1, *, 3) 9.28, \text{max. } 9.59; (*, 2, *, 2) \beta=0, \text{max. } 11.65.$ | 0.353 | 0.093 |
| X | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.16;$ $(*, 1, *, 1) 4.60, \text{max. } 4.97; (*, 1, *, 2) 7.39, \text{max. } 7.73;$ $(*, 1, *, 3) 9.28; \text{max. } 9.59; (*, 3, *, 1) \beta=0; \text{max. } 13.00.$ | 0.353 | 0.093 |
| XI | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.15;$ $(*, 1, *, 1) 4.60; \text{max. } 4.96; (*, 1, *, 2) 7.39; 7.72;$ $(*, 1, *, 3) 9.28; \text{max. } 9.59; (*, 3, *, 3) \beta=0, \text{max. } 17.53.$ | 0.353 | 0.093 |
| XII | $^c (*, 0, *, 1) 0.05; ^c (*, 0, *, 2) 2.43; ^c (*, 0, *, 3) 5.01;$ $^c (*, 5, *, 0) 17.05; ^c (*, 4, *, 0) 12.75; (*, 4, *, 1) 16.56 \pm 0.16;$ $(*, 1, *, 1) 4.60, \text{max. } 4.97; (*, 1, *, 2) 7.39, \text{max. } 7.72;$ $(*, 1, *, 3) 9.28, \text{max. } 9.59; (*, 3, *, 2) \beta=0, \text{max. } 15.35.$ | 0.353 | 0.093 |

^a $\beta_{*q*r} = [(\text{H}^+)_* \text{Hf}(\text{HA})_q (\text{HSO}_4)_r \text{B}_r]_{\text{org}} [\text{Hf(IV)}]^{-1} [\text{HA}]^{-q} [\text{B}]_{\text{org}}^{-r}$, where $[\text{Hf(IV)}] = [\text{Hf}^{4+}] + [\text{Hf}(\text{SO}_4)^{2+}] + [\text{Hf}(\text{SO}_4)_2]$.

^b The "best" model assumed.

^c The equilibrium constants are not varied during the course of the computer calculation.

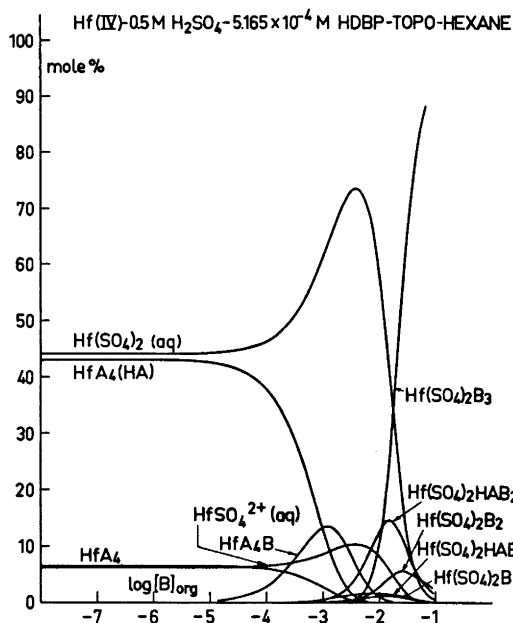


Fig. 4. The mole percentage of different Hf(IV) species in the two-phase systems HDBP-TOPO-hexane/0.50 M H_2SO_4 , as a function of $[B]_{org}$ at $C_A = 5.165 \times 10^{-4}$ M. The curves have been calculated assuming the HDBP-TOPO complexes given in Table 8 and the extraction of the Hf(IV)-HDBP-TOPO species found in Ref. 1 and in the present work (cf. Table 13).

different Hf(IV) species with increasing value of $[B]_{org}$. Fig. 4 is to be related with Fig. 5 which shows the variation of the percentage of metal extracted as a function of $[B]_{org}$ for different constant values of C_A . In Fig. 6 is plotted the mole percentage of the Hf(IV)-species formed in the system Hf(IV)–0.50 M H_2SO_4 – 2.018×10^{-2} M TOPO-HDBP-hexane as a function of $[HA]$. This is to be related to Fig. 7, which shows the percentage of Hf(IV) extracted as a function of $[HA]$ for different constant values of C_B .

Extraction from 1.0 M $HClO_4$. To investigate the effect of the ionic medium on the formation of extractable Hf(IV)-HDBP-TOPO mixed complexes, we studied the extraction of Hf(IV) by HDBP from 1.0 M $HClO_4$ aqueous solution in the presence of TOPO. Fig. 8 shows the distribution of Hf(IV) given as $\log D$ versus $\log[HA]$ at constant total concentration of TOPO, $C_B = 0, 1.005 \times 10^{-3}$, and 2.501×10^{-3} M. The data clearly show the formation of extractable Hf(IV)-mixed ligand complexes and the limiting slope indicates the possible extraction of the Hf(IV)-species $Hf(HA)_p B_q$ with $p = 1$ and 2. In Table 11 we summarize the results of the computer analysis on the available data ($N_p = 16$ points) assuming the extraction of a set of $(H^+)_p Hf(HA)_q (ClO_4^-)_s B_r$ complexes. The subscript * for p and s for the complex $(H^+)_p Hf(HA)_q (ClO_4^-)_s B_r$ indicates

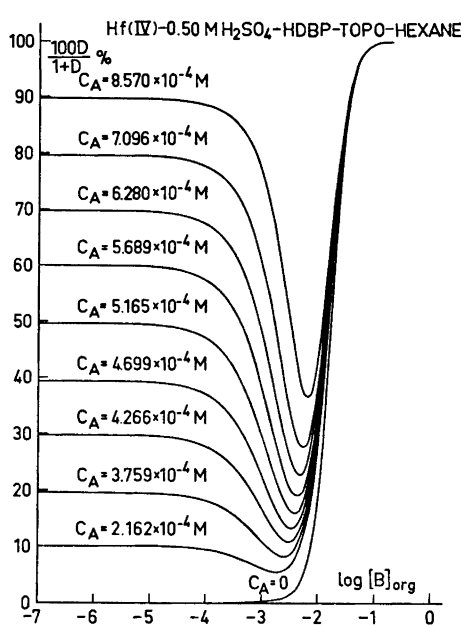


Fig. 5. Calculated curves for metal extraction in the system Hf(IV)-0.5 M H_2SO_4 -HDBP-TOPO-hexane as a function of the concentration of TOPO and different constant values of C_A . The curves have been calculated assuming the HDBP-TOPO complexes given in Table 8 and the extraction of the Hf(IV)-HDBP-TOPO species found in Ref. 1 and in the present work (Table 13).

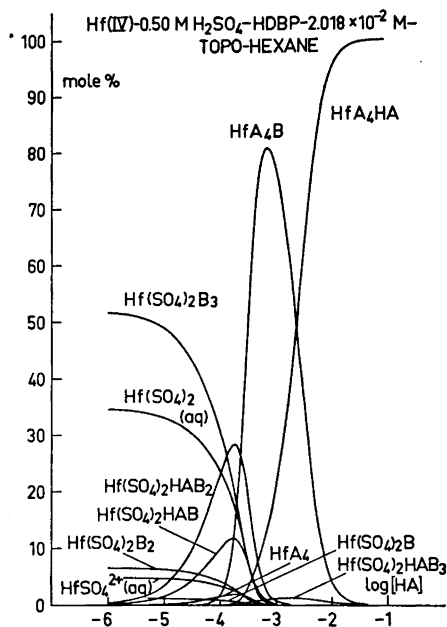


Fig. 6. The mole percentage of different Hf(IV) species in the two-phase system HDBP-TOPO-hexane/0.50 M H_2SO_4 as a function of $[\text{HA}]$ at $C_B = 2.018 \times 10^{-2}$ M. The curves have been calculated assuming the HDBP-TOPO complexes given in Table 8 and the extraction of Hf(IV)-HDBP-TOPO species found in Ref. 1 and in the present work (Table 13).

that in the experiments $[\text{H}^+]$ and $[\text{ClO}_4^-]$ have been kept constant. The values of p and s thus cannot be determined from this set of distribution data. In the computer calculation we arbitrarily put $p = s = 0$, and the equilibrium constants given in Table 11 correspond to $\beta_{*q*r} = [\text{Hf}(\text{HA})_q \text{B}_r]_{\text{org}} / [\text{Hf}^{4+}]^{-1} [\text{HA}]^{-q} [\text{B}]_{\text{org}}^{-r}$.

As can be seen the combination $\text{Hf}(\text{HA})\text{B}_3 + \text{Hf}(\text{HA})_2\text{B}_2$ is found to give a better U value compared with the other models tried. No improvement of the error-square sum U is found by adding the $\text{Hf}(\text{HA})\text{B}_2$ species. We may conclude that in the concentration ranges of HDBP ($C_A = 10^{-4} - 4.98 \times 10^{-4}$ M) and TOPO ($C_B = 10^{-3} - 2.5 \times 10^{-3}$ M) studied the distribution data show synergistic effects in the extraction of Hf(IV) and can be described satisfactorily with the extraction of $\text{Hf}(\text{HA})_4$, $\text{Hf}(\text{HA})_5$, HfB_2 , HfB_3 , $\text{Hf}(\text{HA})\text{B}_3$ and $\text{Hf}(\text{HA})_2\text{B}_2$ complexes.

Since the experiment is carried out at constant $[\text{H}^+] = 1$ M and $[\text{ClO}_4^-] = 1$ M we are not able to determine the values of x in the extracted Hf(IV)-species

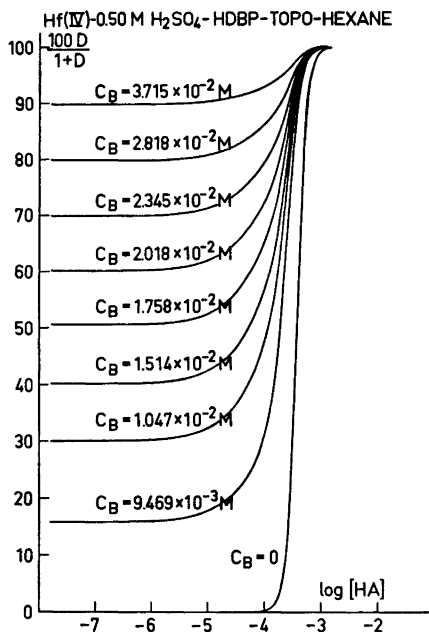


Fig. 7. Calculated curves for metal extraction in the system Hf(IV)-0.50 M H₂SO₄-HDBP-TOPO-hexane as a function of [HA] and different constant values of C_B. The curves have been calculated assuming the HDBP-TOPO complexes given in Table 8 and the extraction of Hf(IV)-HDBP-TOPO-species found in Ref. 1 and in the present work (Table 13).

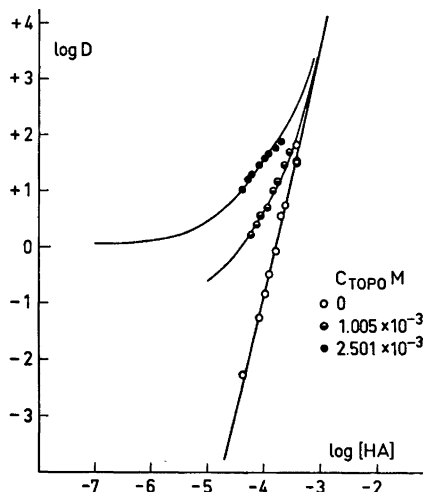


Fig. 8. The distribution of Hf(IV) between HDBP-TOPO hexane and 1.0 M HClO₄ as a function of [HA] at different constant initial concentrations of TOPO in the organic phase, C_B: O (○) (cf. Ref. 1), 1.005 × 10⁻³ M (◐) and 2.501 × 10⁻³ M (●). The distribution data are given in Table 6. The curves have been calculated assuming the HDBP-TOPO species in Table 8 and the Hf(IV)-HDBP-TOPO species in Table 13.

Hf(ClO₄)_{4-*x*}A_{*x*}(HA)_{1-*x*}B₃ and Hf(ClO₄)_{4-*x*}A_{*x*}(HA)_{2-*x*}B₂. Thus with the data available no distinction can be made regarding the possible extractable species: Hf(ClO₄)₄(HA)B₃, Hf(ClO₄)₃AB₃, Hf(ClO₄)₄(HA)₂B₂, Hf(ClO₄)₃A(HA)B₂, and Hf(ClO₄)₂A₂B₂. Making the reasonable assumption that A⁻ will be stronger coordinated than ClO₄⁻ by Hf⁴⁺, we tentatively described the extraction with the following probable equilibrium reactions:

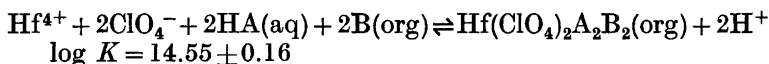
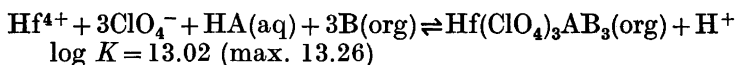


Table 11. Equilibrium constants $^a \log \beta_{*q*r}$ for the formation of $(\text{H}^+)_* \text{Hf}(\text{HA})_q (\text{ClO}_4^-)_r \text{B}$, species in the system Hf(IV)-0.975 M HClO_4 -HDBP-TOPO-hexane for various assumptions of extractable Hf(IV) complexes which minimize the error-square sum

$$U = \sum_1^{16} (\log D_{\text{calc}} - \log D_{\text{exp}})^2.$$

| Model No. | (* , q , * , r) | $\log \beta_{*q*r}$ | U_{min} | $\sigma (\log D)$ |
|-----------------|-------------------|---|------------------|-------------------|
| I | $^c (*, 4, *, 0)$ | 14.95; $^c (*, 5, *, 0)$ 18.60; $^c (*, 0, *, 2)$ 4.87; | 0.779 | 0.228 |
| | $^c (*, 0, *, 3)$ | 7.62; $(*, 1, *, 3)$ 13.52 \pm 0.20. | | |
| II | $^c (*, 4, *, 0)$ | 14.95; $^c (*, 5, *, 0)$ 18.60; $^c (*, 0, *, 2)$ 4.87; | 0.356 | 0.154 |
| | $^c (*, 0, *, 3)$ | 7.62; $(*, 1, *, 2)$ 10.74 \pm 0.13. | | |
| III | $^c (*, 4, *, 0)$ | 14.95; $^c (*, 5, *, 0)$ 18.60; $^c (*, 0, *, 2)$ 4.87; | 0.244 | 0.128 |
| | $^c (*, 0, *, 3)$ | 7.62; $(*, 2, *, 2)$ 14.72 \pm 0.10. | | |
| IV ^b | $^c (*, 4, *, 0)$ | 14.95; $^c (*, 5, *, 0)$; 18.60; $^c (*, 0, *, 2)$ 4.87; | 0.074 | 0.076 |
| | $^c (*, 0, *, 3)$ | 7.62; $(*, 2, *, 2)$ 14.55 \pm 0.14; | | |
| | $(*, 1, *, 3)$ | 13.00, max. 13.21; rej. $(*, 1, *, 2)$ max. 10.41. | | |

^a The limits of β_{*q*r} ($= [\text{Hf}(\text{HA})_q \text{B}_r]_{\text{org}} [\text{Hf}^{4+}]^{-1} [\text{HA}]^{-q} [\text{B}]_{\text{org}}^{-r}$) given correspond to $\log(\beta + 3\sigma(\beta))$ and if $\sigma(\beta) > 0.2\beta$, the maximum value $\log(\beta + 3\sigma(\beta))$ is given.

^b The "best" model assumed.

^c The equilibrium constant is not varied during the course of the computer calculations.

Table 12. Equilibrium constants $^a \log \beta_{*p*q}$ for the formation of $(\text{H}^+)_* \text{Hf}(\text{HA})_p (\text{HSO}_4)_q \text{B}$ species in the system Hf(IV)-1.0 M H_2SO_4 -HDEHP-TOA toluene for various assumptions of extractable Hf(IV)-species which minimize the error-square sum $U = \sum_1^{24} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$ with the assumption of the formation of $\text{Hf}(\text{SO}_4)_2^{2+}$, $\text{Hf}(\text{SO}_4)_2$ and HDEHP-TOA species with equilibrium constants in Tables 13 and 8.

| Model No. | (* , p , * , q) | $\log \beta_{*p*q}$ | U_{min} | $\sigma (\log D)$ |
|----------------|-------------------|---|------------------|-------------------|
| I ^b | $(*, 0, *, 2)$ | 7.89, max. 8.15; $(*, 5, *, 0)$ 44.13, max. 44.53; | 0.515 | 0.160 |
| | $(*, 6, *, 0)$ | 52.71, max. 53.04; $(*, 2, *, 2)$ 27.67 \pm 0.26. | | |
| II | $^c (*, 5, *, 0)$ | 44.67; $^c (*, 6, *, 0)$ 53.00; | 3.171 | 0.371 |
| | $^c (*, 0, *, 2)$ | 7.86; $(*, 2, *, 2)$ 27.56, max. 27.97. | | |
| III | $(*, 5, *, 0)$ | 44.13; $(*, 6, *, 0)$ 52.71; | 0.510 | 0.149 |
| | $(*, 0, *, 2)$ | 7.89; HAB(org) 10.67, max. 11.44; | | |
| | $(*, 2, *, 2)$ | 28.20 \pm 0.23. | | |

^a The limits of β_{*p*q} ($= [\text{Hf}(\text{HA})_p \text{B}_q]_{\text{org}} [\text{Hf}^{4+}]^{-1} [\text{HA}]^{-p} [\text{B}]_{\text{org}}^{-q}$) given correspond to $\log(\beta \pm 3\sigma(\beta))$ and if $\sigma(\beta) > 0.2\beta$, the maximum value $\log(\beta + 3\sigma(\beta))$ is given.

^b The "best" model assumed.

^c The equilibrium constant is not varied during the course of the computer calculation.

Table 13. The extraction of Hf(IV) by HDBP or HDEHP into hexane or toluene in the presence of TOPO or TOA. The total concentration of Hf(IV) was less than 10^{-7} M. Equilibrium constants σ for formation of sets of Hf(IV) complexes which were found to give the minimum error-square sum $U = \sum_1^{Np} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

| System | Chemical Reaction | $\log^* \beta_i$ | Ref. | |
|---|--|---|----------------------|-----------|
| Hf(IV)-0.50 M H_2SO_4 - HDBP-TOPO-hexane | $\text{Hf}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{HfSO}_4^{2+} + \text{H}^+$ | 1.88 ± 0.30 | 1 | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Hf}(\text{SO}_4)_2 + 2\text{H}^+$ | 2.81 (max. 2.94) | 1 | |
| | $\text{Hf}^{4+} + 4 \text{HA}(\text{aq}) \rightleftharpoons \text{HfA}_4(\text{org}) + 4 \text{H}^+$ | 14.90 (max. 15.16) | 1 | |
| | $\text{Hf}^{4+} + 5 \text{HA}(\text{aq}) + \text{HSO}_4^- \rightleftharpoons \text{HfSO}_4\text{A}_4(\text{HA})_3(\text{org}) + 3 \text{H}^+$ | 19.62 ± 0.17 | This work | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- + \text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{SO}_4)_2\text{B}(\text{org}) + 2\text{H}^+$ | 3.10 ± 0.12 | " | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- + 3\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{SO}_4)_3\text{B}_3(\text{org}) + 2\text{H}^+$ | 5.48 (max. 5.70) | " | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- + \text{HA}(\text{aq}) + \text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{SO}_4)_2(\text{HA})\text{B}(\text{org}) + 2\text{H}^+$ | 8.07 ± 0.06 | " | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- + \text{HA}(\text{aq}) + 2\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{SO}_4)_2(\text{HA})\text{B}_2(\text{org}) + 2\text{H}^+$ | 6.75 (max. 7.12) | " | |
| | $\text{Hf}^{4+} + 2\text{HSO}_4^- + \text{HA}(\text{aq}) + 3\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{SO}_4)_3(\text{HA})\text{B}_3(\text{org}) + 2\text{H}^+$ | 9.49 (max. 9.85) | " | |
| | $\text{Hf}^{4+} + 4\text{HA}(\text{aq}) + \text{B}(\text{org}) \rightleftharpoons \text{HfA}_4\text{B}(\text{org}) + 4\text{H}^+$ | 10.98 (max. 11.58) | " | |
| | $\text{Hf}^{4+} + 4\text{HA}(\text{aq}) \rightleftharpoons \text{HfA}_4(\text{org}) + 4\text{H}^+$ | 18.21 ± 0.14 | " | |
| | $\text{Hf}^{4+} + 5\text{HA}(\text{aq}) \rightleftharpoons \text{HfA}_5(\text{HA})(\text{org}) + 4\text{H}^+$ | 14.98 ± 0.21 | 1 | |
| | Hf(IV)-1 M HClO_4 -HDBP- -TOPO-hexane | $\text{Hf}^{4+} + 4\text{ClO}_4^- + 2\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{ClO}_4)_2\text{B}_2(\text{org})$ | 18.32 (max. 18.60) | 1 |
| | | $\text{Hf}^{4+} + 4\text{ClO}_4^- + 3\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{ClO}_4)_3\text{B}_3(\text{org})$ | 4.92 ± 0.09 | This work |
| $\text{Hf}^{4+} + 3\text{ClO}_4^- + \text{HA}(\text{aq}) + 3\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{ClO}_4)_2\text{A}_3\text{B}_3(\text{org}) + \text{H}^+$ | | 7.67 ± 0.13 | " | |
| $\text{Hf}^{4+} + 2\text{ClO}_4^- + 2\text{HA}(\text{aq}) + 2\text{B}(\text{org}) \rightleftharpoons \text{Hf}(\text{ClO}_4)_2\text{A}_2\text{B}_2(\text{org}) + 2\text{H}^+$ | | 13.02 (max. 13.26) | " | |
| $\text{Hf}^{4+} + 5\text{HA}(\text{aq}) \rightleftharpoons \text{HfA}_5(\text{HA})(\text{org}) + 4\text{H}^+$ | | 14.55 ± 0.16 | " | |
| Hf(IV)-1 M H_2SO_4 -HDEHP- -TOA-toluene | $\text{Hf}^{4+} + 6\text{HA}(\text{aq}) \rightleftharpoons \text{HfA}_6(\text{HA})_3(\text{org}) + 4\text{H}^+$ | 44.69 ± 0.14 | 1 | |
| | $\text{Hf}^{4+} + \text{HSO}_4^- + 2 \text{BH} \cdot \text{HSO}_4(\text{org}) \rightleftharpoons (\text{BH})_2\text{Hf}(\text{SO}_4)_3(\text{org}) + 3\text{H}^+$ | 53.05 ± 0.23 | 1 | |
| | $\text{Hf}^{4+} + 2\text{HA}(\text{aq}) + 2\text{BH} \cdot \text{HSO}_4(\text{org}) \rightleftharpoons (\text{BH})_2\text{Hf}(\text{SO}_4)_2\text{A}_2(\text{org}) + 4 \text{H}^+$ | 7.98 ± 0.05 | This work | |
| | $\text{Hf}^{4+} + 2\text{HA}(\text{aq}) + 2\text{BH} \cdot \text{HSO}_4(\text{org}) \rightleftharpoons (\text{BH})_2\text{Hf}(\text{SO}_4)_2\text{A}_2(\text{org}) + 4 \text{H}^+$ | 27.67 ± 0.26 | " | |

σ The limits given corresponds approximately to $\log(K \pm 3 \sigma(K))$ and if $\sigma(K) > 0.2 K$, the maximum value $\log(K + 3\sigma(K))$ is given.

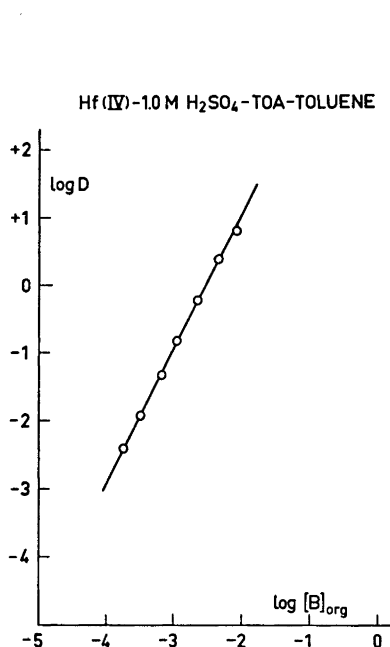


Fig. 9. The distribution of Hf(IV) between TOA-toluene solution and 1.0 M H_2SO_4 aqueous solution as a function of $[\text{BH}^+\text{HSO}_4^-]_{\text{org}}$. The distribution data are given in Table 7. The line has been calculated assuming the formation $(\text{BH})_2\text{SO}_4$ with the dimerization constant given in Table 8 and the extraction of $(\text{BH}^+)_2\text{Hf}(\text{SO}_4)_3^{3-}$ with the equilibrium constant given in Table 13.

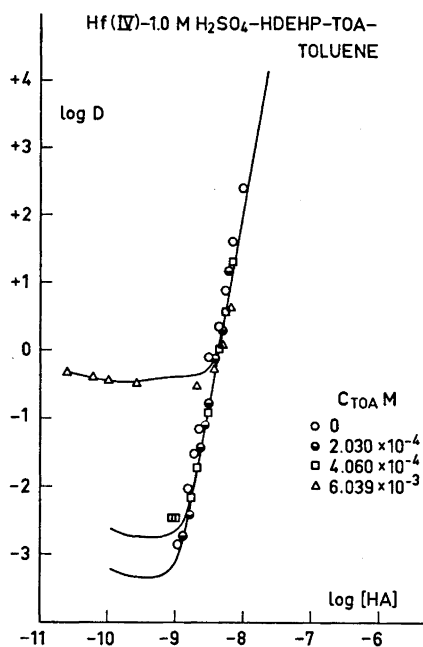


Fig. 10. The distribution of Hf(IV) between HDEHP-TOA-toluene and 1.0 M H_2SO_4 as a function of $[\text{HA}]$ at different constant initial concentrations of TOA in the organic phase, C_{TOA} : 0 (O), 2.030×10^{-4} (●), 4.060×10^{-4} (□) and 6.039×10^{-3} M (Δ). The distribution data are given in Table 7A. The lines have been calculated assuming the HDEHP-TOA species in Table 8 and the extraction of Hf(IV)-HDEHP-TOA species in Table 12 (model I).

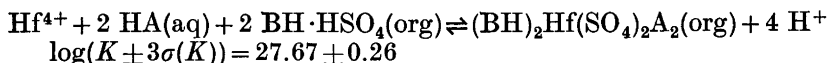
Extractable Hf(IV)-TOA complexes in toluene. Fig. 9 shows the distribution of Hf(IV) as a function of $[\text{BH}^+\text{HSO}_4^-]_{\text{org}}$ in the system Hf(IV)-1 M H_2SO_4 -TOA-toluene. The values for $[\text{BH}^+\text{HSO}_4^-]_{\text{org}}$ were calculated assuming the formation of $(\text{BH})_2\text{SO}_4$ in the toluene phase with the dimerization constant $K_2[\text{H}^+]^{-1}[\text{HSO}_4^-]^{-1} = [(\text{BH})_2\text{SO}_4]_{\text{org}}[\text{BH}\cdot\text{HSO}_4]_{\text{org}}^{-2} = 377.21 \text{ M}^{-1}$ found in a separate study by one of us for the two-phase system TOA-toluene/0.1 M $(\text{Na},\text{H})\text{ClO}_4$ (cf. Ref. 10). The data plotted in Fig. 9 is seen to fit to a straight line with a slope of approximately 2, indicating the extraction of HfB_2 -species.

We computer refined the equilibrium constant for the formation of the HfB_2 -complex using 7 experimental points and found that the value $\log(K_{12} \pm 3 \sigma(K_{12})) = 8.31 \pm 0.13$ gives a rather good fit to the data ($U = 0.0207$,

$\sigma(y) = 0.064$). We thus conclude that the available data indicate the extraction of $(\text{BH})_2\text{Hf}(\text{SO}_4)_3$ complex into toluene.

The antagonistic effect of TOA on Hf(IV)-extraction by HDEHP in toluene

Some authors^{3,4} have reported that trioctylamine may form mixed ligand metal complexes and would thus cause a possible synergistic effect in metal extractions with acidic complexing agents. In order to investigate a possible formation of Hf(IV)-HDEHP-TOA species we studied the extraction of Hf(IV) from 1 M H_2SO_4 by HDEHP in toluene in the presence of TOA. Fig. 10 shows the distribution data as a function of $[\text{HA}]$ for different constant total concentrations of TOA ($C_p = 2.030 \times 10^{-4}$, 4.060×10^{-4} , and 6.039×10^{-3} M). The values of $[\text{HA}]$ were calculated from the equilibrium constants in Ref. 10 given in Table 8. Assuming only the extraction of the $\text{Hf}(\text{HA})_p\text{B}_q$ species $(1,5,0) + (1,6,0) + (1,0,2)$ with the equilibrium constants found previously, the data ($Np = 24$ points) showed deviations which exceeded the expected experimental error ($U = 4.432$, $\sigma(\log D) = 0.430$). Applying the species-selector procedure in the Letagrop program and taking the rejection factor $F_\sigma = 1.0$, we found that the species $(1,2,2)$ was accepted with improvement of the error-square sum $U = 3.171$, and $\sigma(\log D) = 0.371$ (Table 12, model II), whereas the following Hf-HDEHP-TOA species tried were rejected during the computer calculations: $(1,1,1)$, $(1,1,2)$, $(1,1,3)$, $(1,2,1)$, $(1,2,3)$, $(1,3,1)$, $(1,3,2)$, and $(1,4,1)$. In model I (Table 12) the values of the equilibrium constants for the formation of the species $(1,5,0)$, $(1,6,0)$, $(1,0,2)$, and $(1,2,2)$ were varied and a considerable improvement of the error-square sum was obtained ($U = 0.515$ and $\sigma(\log D) = 0.160$). A slight improvement of U was found in model III, where the constant for the formation of HAB, the species $(0,1,1)$, and $\text{Hf}(\text{HA})_2\text{B}_2$, $(1,2,2)$, were varied during the computer calculations. However, this made $\sigma(K) > K$ for the formation of HAB. The equilibrium constants for the formation of $(1,5,0)$ and $(1,6,0)$ found in model III differed somewhat from those found in model II, which may indicate that some other unaccounted Hf-species are extracted. We may conclude that in the system Hf(IV) - 1.0 M H_2SO_4 -HDEHP-TOA-toluene, the greater part of the data available may be explained by the extraction of the Hf-species $\text{Hf}(\text{HA})_5$, $\text{Hf}(\text{HA})_6$, HfB_2 , and $\text{Hf}(\text{HA})_2\text{B}_2$. In this experiment, since $[\text{H}^+]$ has been kept constant, we are not able to differentiate between the two possible extractable mixed-species $\text{HfSO}_4\text{A}_2\text{B}_2$ or $(\text{BH})_2\text{Hf}(\text{SO}_4)_2\text{A}_2$. Making the reasonable assumption that TOA will form a relative strong bond with H^+ , we tentatively describe the extraction of the Hf-mixed species with the following equilibrium reaction:



The lines in Fig. 10 have been calculated assuming the extraction of $\text{Hf}(\text{HA})_5$, $\text{Hf}(\text{HA})_6$, HfB_2 , and $\text{Hf}(\text{HA})_2\text{B}_2$ species with equilibrium constants found for model I in Table 12.

The fact that the combination HDBP + TOPO gives synergistic effects in the extraction of hafnium, while on the other hand HDEHP + TOA gives an antagonistic effect may be understood by considering the following equilibrium reaction: $\frac{1}{2}\text{H}_2\text{A}_2(\text{org}) + \text{B}(\text{org}) \rightleftharpoons \text{HAB}(\text{org})$ for which we may calculate the following value of the equilibrium constant K : 35.6 M^{-1} (HDBP-TOPO-hexane)⁹ and 1137 M^{-1} (HDEHP-TOA-toluene).¹⁰ This big difference in the values of K indicates a much stronger hydrogen-bond between HDEHP and TOA than HDBP and TOPO in the species HAB. This strong bond, $>\text{P}(=\text{O})\text{O}\cdots\text{HN}\angle$, may in part explain why under the extraction conditions studied, mixed complexes are formed to lesser extent in Hf-HDEHP-TOA than in the system Hf-HDBP-TOPO.

CONCLUSIONS

With TOPO hafnium is found to be extracted as $\text{Hf}(\text{SO}_4)_2\text{B}$, $\text{Hf}(\text{SO}_4)_2\text{B}_2$ and $\text{Hf}(\text{SO}_4)_2\text{B}_3$ from sulfuric acid and as $\text{Hf}(\text{ClO}_4)_4\text{B}_2$ and $\text{Hf}(\text{ClO}_4)_4\text{B}_3$ from perchloric acid medium. The nature of the inorganic ligand seems to affect the equilibrium constant for the formation of the Hf-TOPO species, indicating a stronger Hf(IV)-sulfate bond than Hf(IV)- ClO_4^- bond in the extracted species. Hafnium is mainly extracted as $(\text{BH})_2\text{Hf}(\text{SO}_4)_3$ from sulfate medium into toluene by TOA. The combined use of HDBP + TOPO as extractant gives rise to synergistic and antagonistic effects due to the extraction of mixed ligand Hf-species: HfA_4B , $\text{Hf}(\text{SO}_4)_2(\text{HA})\text{B}$, $\text{Hf}(\text{SO}_4)_2(\text{HA})\text{B}_2$, and $\text{Hf}(\text{SO}_4)_2(\text{HA})\text{B}_3$ from sulfate and $\text{Hf}(\text{ClO}_4)_3\text{AB}_3 + \text{Hf}(\text{ClO}_4)_2\text{A}_2\text{B}_2$ from perchlorate medium. With HDEHP + TOA the data indicate the extraction of the species $(\text{BH})_2\text{Hf}(\text{SO}_4)_2\text{A}_2$ in toluene from sulfate medium. The combination of HDEHP + TOA as extractant in hafnium extraction, however, causes mainly antagonistic effects for the concentration ranges of HDEHP and TOA studied. This may in part be due to the strong hydrogen-bond, $>\text{P}(=\text{O})\text{O}\cdots\text{HN}\equiv$, in the HAB species.

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