Studies of the Solvent Extraction of ^{175,181}Hf(IV) by Dibutylphosphate (HDBP), Di(2-ethylhexyl)phosphate (HDEHP) in Hexane and Toluene

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The extraction of ^{175,181}Hf(IV) has been studied from 1.0(0.5)
M H_2SO_4 and 1.0 M $HClO_4$ aqueous solution into hexane and toluene
by dibutylphosphate or di(2-ethylhexyl)phosphate ($=$HA). The
distribution data have been computer-analyzed with the LETA-
GROPVRID program and the results indicate the formation of
$Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ complexes in the aqueous phase and the
following extractable Hf(IV)-species:
1) in hexane with HA$=$HDBP: HfA_4, $HfA_4(HA)$, $HfSO_4A_2(HA)_2$,
and $HfSO_4A_2(HA)_3$.
2) in toluene with HA$=$HDEHP: $HfA_4(HA)$ and $HfA_4(HA)_2$.
A summary of the equilibrium constants for the formation of the
Hf(IV)-species found is given in Table 8.

The extraction of hafnium(IV) by dialkylphosphate has been studied by several authors. [1-4,19] However, opinions differ about the composition and formation constants of the Hf(IV) species extracted. Peppard and Ferraro [1] studied the extraction of Zr(IV) and Hf(IV) in 0.2 — 0.3 mM concentrations into toluene from chloride and nitrate medium with di(2-ethylhexyl)phosphate (HDEHP). From the analytical data for the solids isolated in the saturated organic phase and their infrared spectra, they concluded that the extracted species are: ZrA_4 and $(ZrO_{0.5}NO_3A_2)_n$ for Zr(IV); HfA_4 and $Hf(NO_3)A_3$ for Hf(IV). Dyrssen [19] reported the formation of extractable Hf(IV) — HDBP species in chloroform or hexone as $HfA_4(HA)$ or a mixture of HfA_4 and $HfA_4(HA)_2$. Navrátil [2-4] studied the extraction of ^{175,181}Hf(IV) from several acid media (HCl, HBr, HI, $HClO_4$, H_2SO_4) by dibutyl-, diamyl-, di(2-ethyl-hexyl)-, and dioctylphosphoric acid into several organic solvents (benzene, chloroform, CCl_4, cyclohexane, toluene, and octane). From his equilibrium

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data he concluded that hafnium(IV) is predominantly extracted as $HfXA_3(HA)_2$ from $2-2.5$ M $HClO_4$ or $C_{HCl} < 3.5$ M; as $HfX_4(HA)_4$ from media more acidic than 4 M $HClO_4$, 4.5 M HCl or 1.5 M HNO_3; as $HfXA_3(HA)_x + HfX_4(HA)_y$ from HX $(X = Br^-,\ I^-)$ and $HfA_4(HA)_y + Hf(SO_4)_2$ $(HA)_y$ from H_2SO_4 solution.

In the present work we have tried to make a systematic study of 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 analyzing our equilibrium data we have the advantage of having available the constants for the distribution equilibria of HDBP and HDEHP which have been determined in previous distribution studies.[5,6]

The equilibrium constants for the formation of the Hf(IV)-species found in the present work will be used in analyzing the distribution data on the extraction of Hf(IV) into hexane (toluene) by HDBP (HDEHP) in the presence of TOPO or TOA.[16]

EXPERIMENTAL

Reagents..The HDBP, $(n\text{-}C_4H_9O)_2P(O)OH$, (HDEHP), $(C_8H_{17}O)_2P(O)OH$, (Albright and Wilson Ltd, London) with a purity of approximately 95 %, was further purified by the procedure described previously.[7] Potentiometric titrations indicated that the purified product was free from monobutylphosphate or mono-2-ethylhexylphosphate, and at least 99 % pure. H_2SO_4 and $HClO_4$ (*p.a.* Merck, Darmstadt) were used without further purification. The hexane, boiling range $68-69°C$, had a purity of at least 99 % (*puriss.* KEBO). We purified it before use by washing it several times with 0.1 M NaOH solution, with dilute mineral acid, and finally with distilled water. The toluene was of analytical grade (*p.a.* Merck, Darmstadt) with at least 99 % purity according to gas-chromatographical analysis and was used without further purification.

$NaClO_4$ was prepared from Na_2CO_3 (*p.a.* Merck-Darmstadt) and $HClO_4$ (*p.a.* Merck, Darmstadt) as described in Ref. 8. Na_2SO_4 (*p.a.* Merck, Darmstadt) was dried at 120°C and used without further purification.

The radioactive [181,175]Hf was obtained in the form of [181,175]$HfCl_4$ in 2.15 M HCl solution from the Radiochemical Centre, Amersham, England. Solutions of [181,175]Hf(IV) in 0.5 M and 1.0 M H_2SO_4 or 1.0 M $HClO_4$ were prepared by adding appropiate amounts of sulfuric or perchloric acid to the [181,175]$HfCl_4$ hydrochloric acid solution, evaporating nearly to dryness and diluting the product with distilled water so that the solutions obtained became 0.5 or 1.0 M in H_2SO_4 or $HClO_4$. The [181,175]Hf(IV) acid solutions made in this way were always left to equilibrate for at least $3-4$ days before being used in the experiments.

In the distribution experiments the initial concentration of Hf(IV) in the aqueous phase was always $\leq 0.723 \times 10^{-7}$ M and may thus be considered negligible as compared with the total concentrations of HA or B.

Ionic strength and acidity constants. The values of $K_a = [H^+][SO_4^{2-}]/[HSO_4^-]$ for 0.5 M and 1.0 M H_2SO_4 were calculated from the value at infinite dilution $K° = 1.01 \times 10^{-2}$ M (*cf.* Ref. 9) and the activity factors given by Kielland.[10] Using the value $K_a = [H^+][SO_4^{2-}]/[HSO_4^-] = 5.192 \times 10^{-2}$ M we calculated the ionic strength $I = \frac{1}{2}\sum c_i z_i^2 = 0.587$ M for 0.5 M H_2SO_4 and with $K_a = 6.270 \times 10^{-2}$ M the ionic strength $I = 1.123$ M for 1.0 M H_2SO_4 solution.

In the experiments with 0.5 M (Na,H)HSO_4 or 1.0 M (Na,H)HSO_4, where the hydrogen-ion concentration was varied, the solutions were made from the appropriate amounts of 0.5 M (or 1.0 M) H_2SO_4 and 0.5 M (or 1.0 M) Na_2SO_4 solutions, such that the (Na,H)HSO_4 solutions obtained would have the calculated ionic strength $I = 0.587$ M or 1.123 M. For the acidity constant of HDBP we used the value $K_a = 0.1253$ M for $I = 0.5$ M and 0.1318 M for $I = 1$ M (cf. Refs. 11, 10). For HDEHP we used the value $K_a = 0.7127$ M for $I = 1$ M (*cf.* Refs. 6, 10). Even if these values of the acid constants are slightly in error, this will

only appear as a constant factor in the equilibrium constants and will not affect the conclusions regarding the species present.

Distribution experiments. Equal volumes of aqueous and organic phases were shaken for at least 2 h in a glass-stoppered centrifuge tube. The two phases were separated by centrifugation. Samples of the solutions were pipetted out into polyethylene tubes and the gamma-radioactivity measured in a Tracerlab SC-57 low background well scintillation counter with a Tl-activitated NaI crystal which is connected with a Tracerlab SC-70 Compu/Matic V scaler. All experiments were carried out in rooms thermostated at 25°C.

SYMBOLS AND EQUILIBRIUM CONSTANTS

HA
: = dibutylphosphoric acid $(n\text{-}C_4H_9O)_2P(O)OH$, (HDBP), or di(2-ethylhexyl)phosphoric acid $(C_8H_{17}O)_2P(O)OH$, (HDEHP)

[ ]
: = equilibrium concentration in the aqueous phase

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

C_A
: = initial total concentration of HA in the organic phase

K_a
: = $[H^+][A^-]/[HA]$ stoichiometric acid dissociation constant

I_{aq}, I_{org}
: = gamma-activity of ^{181,175}Hf in the aqueous and organic phase, cpm for equal volumes of samples.

$K_{klmn}{}^{aq}$
: = $[(H^+)_k(Hf^{4+})_l(HA)_m(HSO_4^-)_n][H^+]^{-k}[Hf^{4+}]^{-l}[HA]^{-m}[HSO_4^-]^{-n}$ formation constant of the complex $(H^+)_k(Hf)_l(HA)_m(HSO_4)_n$ in the aqueous phase.

$K_{pqrst}{}^{org}$
: = $[(H^+)_p(Hf^{4+})_q(HA)_r(HSO_4^-)_s(ClO_4^-)_t]_{org}[H^+]^{-p}[Hf^{4+}]^{-q}[HA]^{-r}[HSO_4^-]^{-s}[ClO_4^-]^{-t}$ formation constant of the complex $(H^+)_p(Hf^{4+})_q(HA)_r(HSO_4^-)_s(ClO_4^-)_t$ in the organic phase

D
: = $\sum[Hf]_{org}/\sum[Hf] = I_{org}/I_{aq}$ net distribution ratio of Hf(IV)

CHEMICAL MODEL

The species in the aqueous phase may be represented by the general formula

$$(H^+)_k(Hf^{4+})_l(HA)_m(HSO_4^-)_n$$
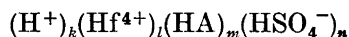
leaving out complex formation with H_2O, Na^+ and ClO_4^-.

For instance the $(-1, 1, 0, 1)$ complex in the aqueous phase represents the 1:1 Hf sulfate species $Hf(SO_4)^{2+}$.

For the complex in the organic phase we may use the general formula:

$$(H^+)_p(Hf^{4+})_q(HA)_r(HSO_4^-)_s(ClO_4^-)_t$$
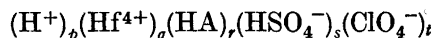
Thus the $(-4, 1, 4, 0, 0)$ complex in the organic phase is the extractable HfA_4.

We make the reasonable assumption that the species extracted are uncharged and since $C_{Hf} < 10^{-7}$ M, that l and q can only have the values 0 or 1.

The concentration of a $(k, 1, m, n)$ complex in the aqueous phase is given as:

$$[(H^+)_k Hf(HA)_m(HSO_4^-)_n] = C_{k1mn}(aq) = K_{k1mn}{}^{aq}[H^+]^k[Hf^{4+}][HA]^m[HSO_4^-]^n \quad (1)$$

and that of a $(k, 0, m, 0)$ complex as:

$$[(H^+)_k(HA)_m] = C_{k0m0}(aq) = K_{k0m0}{}^{aq}[H^+]^k[HA]^m \quad (2)$$

The concentration of a $(p, 1, r, s, t)$ complex in the organic phase is given as:

$$[(H^+)_p Hf(HA)_r(HSO_4^-)_s(ClO_4^-)_t]_{org} = C_{p1rst}(org) =$$
$$K_{p1rst}{}^{org}[H^+]^p[Hf^{4+}][HA]^r[HSO_4^-]^s[ClO_4^-]^t \qquad (3)$$

and using (1) and (3) we can express the distribution ratio as:

$$D_{calc} = \frac{\sum[(H^+)_p Hf(HA)_r(HSO_4^-)_s(ClO_4^-)_t]_{org}}{\sum[(H^+)_k Hf(HA)_m(HSO_4^-)_n]} =$$
$$= \frac{\sum K_{p1rst}{}^{org}[H^+]^p[HA]^r[HSO_4^-]^s[ClO_4^-]^t}{\sum K_{k1mn}{}^{aq}[H^+]^k[HA]^m[HSO_4^-]^n} \qquad (4)$$

The mass balance for HA is given by the equation:

$$C_A = \sum m[(H^+)_k(HA)_m] + \sum r[(HA)_r]_{org} =$$
$$= \sum m K_{k0m0}{}^{aq}[H^+]^k[HA]^m + \sum r K_{00r00}{}^{org}[HA]^r \qquad (5)$$

Given the values of $[H^+]$, C_A, $C_{SO_4{}^{--}}$, $[ClO_4^-]$ for each point and $K_{p1rst}{}^{org}$, $K_{k1mn}{}^{aq}$ for the formation of the Hf(IV)-species and moreover $K_{00r00}{}^{org}$, K_{k0m0} for the formation of (HA)$_r$ species in the organic phase and $(H^+)_k(HA)_m$ in the aqueous phase (cf. Refs. 5 – 7, Table 9), we may calculate D_{calc} from (4) and (5).

The amounts of A bounded by the Hf-species may be neglected compared with the total concentration of A, since in the distribution experiments $C_{Hf} < 10^{-7}$ M.

COMPUTER ANALYSIS OF DISTRIBUTION DATA

The extraction data have been analyzed using an improved version of the LETAGROPVRID computer program developed by Sillén and coworkers.[12–14] The program consists of a main part, which is a general minimizing program common for all kind of problems, and a special part (UBBE) which describes the kind of special problem to be dealt with, e.g. in this work the relationship between the experimental data and chemical models in a two phase-distribution experiment. Using this LETAGROPVRID program the computer calculated the set of values of the constants K_1, $K_2...K_n$ for the formation of the $(H^+)_k(Hf)_l(HA)_m(HSO_4^-)_n$ species in the aqueous phase and the extractable $(H^+)_p(Hf)_q(HA)_r(HSO_4)_s(ClO_4)_t$ complexes in the organic phase which will minimize the error-square sum:

$$U = \sum_1^{Np} (\log D_{calc} - \log D_{exp})^2 \text{ for the } Np \text{ experimental points available.}$$

The details of the computer program will be published elsewhere.[14]

Calculations of distribution curves. The final refined equilibrium constants given in Table 8 have been used to calculate distribution curves, using mostly the HALTAFALL program.[15] These calculated distribution curves are given as full lines in the different figures.

RESULTS AND DISCUSSION

Hf—HDBP species in hexane

Extraction from 1 M $(Na, H)ClO_4$. Fig. 1 shows the distribution of Hf(IV) between 1 M $HClO_4$ and HDBP (= HA) hexane solutions as a function of [HA].
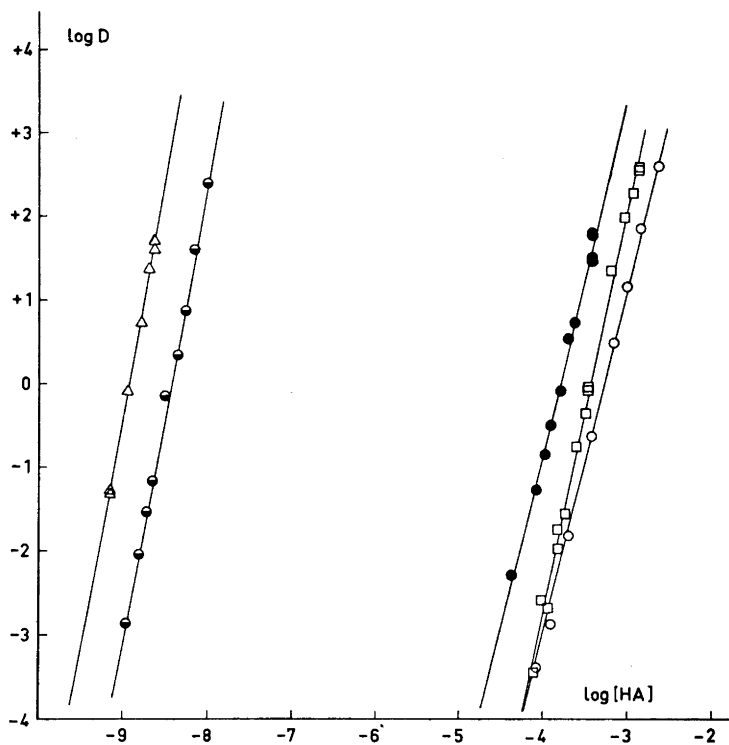

Fig. 1. The distribution of Hf(IV) as a function of [HA] in the two-phase systems 0.50 M H_2SO_4/HDBP-hexane (O); 1.0 M H_2SO_4/HDBP-hexane (□); 0.975 M $HClO_4$/HDBP-hexane (●); 1.0 M H_2SO_4/HDEHP toluene (△), and 0.975 M $HClO_4$/HDEHP-toluene (◖). The distribution data are given in Tables 1—5. The lines have been calculated assuming the HDBP, HDEHP species in Table 9 and the set of Hf(IV)-HSO_4-HA species in Table 8.

In Table 10 we give a summary of the values of U_{min} ($Np = 11$ points) for the formation of $(H^+)_* Hf(HA)_q (ClO_4)_*$ species in the system Hf(IV) − 1 M $HClO_4$ − HDBP-hexane for various assumptions of extractable Hf(IV)-species in hexane. The subscript $_*$ for p and r in the complex $(H^+)_p Hf(HA)_q (ClO_4^-)_r$, indicates that in the experiment the values of $[H^+]$ and $[ClO_4^-]$ have been kept constant. The distribution data thus gave no information about the possible values of p and r. In the computer calculations in Table 10 we have arbitrarily put $p = q = 0$, and the values of the equilibrium constants thus correspond to $\beta_{*q*} = [Hf(HA)_q]_{org}/[Hf^{4+}][HA]^q$.

Table 1 A. The distribution of ^{175,181}Hf(IV) between solutions of HDBP in hexane and 0.975 M HClO$_4$ at 25°C. Data given as log D_{exp}, C_A M, log [HA] and log $D_{calc}D_{exp}^{-1}$.

-2.276, 4.979×10^{-5}, -4.365, -0.117; -1.260, 9.959×10^{-5}, -4.069, $+0.085$; -0.825, 1.245×10^{-4}, -3.974, $+0.045$; -0.483, 1.494×10^{-4}, -3.898, $+0.025$; -0.065, 1.992×10^{-4}, -3.777, $+0.116$; $+0.561$, 2.490×10^{-4}, -3.685, -0.114; $+0.745$, 2.988×10^{-4}, -3.610, $+0.025$; $+1.594$, 4.980×10^{-4}, -3.405, $+0.080$; $+1.833$, 4.980×10^{-4}, -3.405, -0.159; $+1.818$, 4.980×10^{-4}, -3.405, -0.144; $+1.542$, 4.980×10^{-4}, -3.405, $+0.132$; $+1.544$, 4.980×10^{-4}, -3.405, $+0.130$; $+1.143$, 3.486×10^{-4}, -3.548, -0.100.

Table 1 B. The distribution of ^{175,181}Hf(IV) between 1.0 M (Na,H)ClO$_4$ and 9.96×10^{-5} M HDBP-hexane solution at 25°C. Data given as log D, log [H$^+$] and log [HA].

-1.479, -0.033, -4.071; -1.445, -0.057, -4.074; -1.288, -0.082, -4.077; -1.127, -0.108, -4.081; -1.051, -0.166, -4.089; -0.638, -0.233, -4.100; -0.388, -0.312, -4.115; -0.239, -0.409, -4.137.

Table 2 A. The distribution of ^{175,181}Hf(IV) between solutions of HDBP in hexane and 1.0 M H$_2$SO$_4$ at 25°C. Data given as log D_{exp}, C_A M, log [HA] and log $D_{calc}D_{exp}^{-1}$. log [H$^+$] = 0.032.

-3.381, 9.959×10^{-5}, -4.067, $+0.124$; -2.858, 1.494×10^{-4}, -3.897, $+0.287$; -1.802, 2.490×10^{-4}, -3.687, $+0.082$; -0.608, 4.980×10^{-4}, -3.411, $+0.012$; $+0.515$, 9.975×10^{-4}, -3.150, -0.034; $+1.192$, 1.496×10^{-3}, -3.007, -0.111; $+1.894$, 2.493×10^{-3}, -2.837, -0.091; $+2.636$, 4.986×10^{-3}, -2.625, $+0.086$.

Table 2 B. The distribution of ^{175,181}Hf(IV) between 2.490×10^{-4} M HDBP hexane and 1.0 M (Na,H)HSO$_4$ at 25°C. Data given as log D_{exp}, [HSO$_4^-$], log [H$^+$], log [HA] and log $D_{calc}D_{exp}^{-1}$.

-1.899, 0.9459, $+0.032$, -3.687, $+0.179$; -1.724, 0.9399, -0.017, -3.691, $+0.057$; -1.637, 0.9250, -0.057, -3.696, $+0.018$; -1.468, 0.9109, -0.102, -3.701, -0.099; -1.391, 0.8898, -0.147, -3.707, -0.120; -1.312, 0.8699, -0.199, -3.715, -0.139; -1.238, 0.8411, -0.251, -3.723, -0.148; -1.072, 0.8129, -0.310, -3.734, -0.243; -0.973, 0.7781, -0.373, -3.746, -0.264; -0.899, 0.7393, -0.440, -3.762, -0.255; -0.832, 0.6958, -0.514, -3.781, -0.232.

Table 3 A. The distribution of ^{175,181}Hf(IV) between solutions of HDBP in hexane and 0.50 M H$_2$SO$_4$ at 25°C. Data given as log D_{exp}, C_A M, log [HA], log $D_{calc}D_{exp}^{-1}$. log [H$^+$] = 0.265.

-3.441, 9.950×10^{-5}, -4.105, $+0.239$; -2.666, 1.494×10^{-4}, -3.934, $+0.246$; -2.570, 1.245×10^{-4}, -4.011, -0.202; -1.957, 1.992×10^{-4}, -3.814, $+0.093$; -1.726, 1.992×10^{-4}, -3.814, -0.139; -1.540, 2.490×10^{-4}, -3.722, $+0.108$; -0.727, 3.486×10^{-4}, -3.585, -0.056; -0.335, 4.482×10^{-4}, -3.484, $+0.034$; -0.058, 4.980×10^{-4}, -3.442, -0.042; $+0.033$, 4.980×10^{-4}, -3.442, -0.133; $+1.242$, 9.975×10^{-4}, -3.177, -0.052; $+1.384$, 9.975×10^{-4}, -3.177, -0.193; $+2.018$, 1.496×10^{-3}, -3.031, -0.109; $+2.308$, 1.995×10^{-3}, -2.931, $+0.092$; $+2.585$, 2.493×10^{-3}, -2.857, $+0.183$; $+2.626$, 2.493×10^{-3}, -2.857, $+0.142$.

Table 3 B. The distribution of ^{175,181}Hf(IV) between 1.982×10^{-4} M HDBP-hexane solution and 0.50 M (Na,H)HSO$_4$ at 25°C. Data given as log D_{exp}, [HSO$_4^-$], log [HA], log [H$^+$] and log $D_{calc}D_{exp}^{-1}$.

-1.639, 0.4444, -3.821, -0.296, -0.191; -1.805, 0.4312, -3.827, -0.323, $+0.020$; -1.717, 0.4235, -3.835, -0.366, -0.019; -1.709, 0.4111, -3.843, -0.404, $+0.026$; -1.647, 0.4013, -3.855, -0.454, $+0.018$; -1.542, 0.3898, -3.868, -0.507, -0.030; -1.476, 0.3772, -3.885, -0.568, -0.036; -1.409, 0.3633, -3.907, -0.638, -0.041.

Table 4 A. The distribution of ^{175,181}Hf(IV) between solutions of HDEHP in toluene and 0.975 M HClO$_4$ at 25°C. Data given as log D_{exp}, C_A M, log [HA] and log $D_{calc}D_{exp}^{-1}$.

−1.302, 5.021 × 10^{-4}, −9.140, +0.075; −1.256, 5.021 × 10^{-4}, −9.140, +0.029; −0.077, 1.245 × 10^{-3}, −8.936, −0.011; +0.728, 2.490 × 10^{-3}, −8.782, +0.059; +1.379, 3.735 × 10^{-3}, −8.692, −0.078; +1.719, 5.035 × 10^{-3}, −8.626, −0.038; +1.609, 5.035 × 10^{-3}, −8.626, +0.072.

Table 4 B, The distribution of ^{175,181}Hf(IV) between 5.021 × 10^{-4} M HDEHP-toluene solution and 1.0 M (Na,H)ClO$_4$ at 25°C. Data given as log D_{exp}, log [HA], log [H$^+$] and log $D_{calc}D_{exp}^{-1}$.

−1.051, −9.140, −0.033, −0.087; −0.934, −9.140, −0.057, −0.109; −0.852, −9.140, −0.082, −0.093; −0.716, −9.140, −0.108, −0.124; −0.566, −9.140, −0.166, −0.042; −0.367, −9.140, −0.233, +0.027; −0.115, −9.140, −0.312, +0.093; +0.133, −9.140, −0.409, +0.231.

Table 5. A. The distribution of ^{175,181}Hf(IV) between solutions of HDEHP in toluene and 1.0 M H$_2$SO$_4$ at 25°C. Data given as log D_{exp}, C_A M, log [HA], and log $D_{calc}D_{exp}^{-1}$. log [H$^+$] = 0.032.

−2.857, 1.245 × 10^{-3}, −8.960, −0.038; −2.040, 2.490 × 10^{-3}, −8.806, −0.049; −1.527, 3.735 × 10^{-3}, −8.716, −0.088; −1.160, 4.979 × 10^{-3}, −8.653, −0.117; −0.104, 1.006 × 10^{-2}, −8.497, −0.338; +0.351, 2.013 × 10^{-2}, −8.346, +0.034; +0.879, 2.996 × 10^{-2}, −8.259, −0.013; +1.607, 5.035 × 10^{-2}, −8.146, −0.107; +2.397, 0.1001, −7.996, −0.050.

Table 5 B. The distribution of ^{175,181}Hf(IV) between 1.006 × 10^{-2} M HDEHP-toluene solution and 1.0 M (H,Na)HSO$_4$ at 25°C. Data given as log D_{exp}, [HSO$_4^-$], log [H$^+$], log [HA] and log $D_{calc}D_{exp}^{-1}$.

−0.299, 0.9399, −0.018, −8.498, −0.039; −0.224, 0.9250, −0.057, −8.498, −0.015; −0.165, 0.9109, −0.102, −8.498, +0.032; −0.074, 0.8898, −0.147, −8.498, +0.056; +0.030, 0.8699, −0.199, −8.498, +0.079; +0.107, 0.8411, −0.251, −8.498, +0.137; +0.245, 0.8129, −0.310, −8.498, +0.151; +0.513, 0.7393, −0.441, −8.498, +0.235.

Table 6. The distribution of ^{175,181}Hf(IV) between 1 M H(HSO$_4^-$, ClO$_4^-$) and 4.980 × 10^{-4} M HDBP-hexane solution. The data are given as log [H$^+$], log [HSO$_4^-$], log D_{exp} and log $D_{calc}D_{exp}^{-1}$.

0.000, [HSO$_4^-$] = 0, +1.833, −0.109; 0.000 [HSO$_4^-$] = 0, +1.818, −0.094; −0.011, −3.028, +1.667, +0.067; −0.011, −3.028, +1.593, +0.141; −0.010, −2.551, +1.566, +0.108; −0.003, −2.186, +1.454, +0.104; −0.003, −2.186, +1.472, +0.086; −0.008, −2.183, +1.525, +0.047; −0.019, −2.028, +1.365, +0.178; −0.019, −2.028, +1.390, +0.154; −0.019, −2.028, +1.512, +0.032; −0.009, −1.852, +1.335, +0.088; 0.000, −1.729, +1.326, −0.006; 0.000, −1.729, +1.365, −0.045; 0.000, −1.729, +1.403, −0.083; −0.010, −1.551, +1.317, −0.101; 0.000, −1.451, +1.187, −0.080; −0.001, −1.252, +0.994, −0.080; −0.008, −1.183, +0.846, +0.017; −0.007, −1.028, +0.703, −0.015; −0.006, −0.904, +0.608, −0.070; 0.000, −0.797, +0.502, −0.105; −0.004, −0.726, +0.174, +0.141; −0.004, −0.652, +0.232, −0.010; −0.007, −0.571, +0.039, +0.084; −0.008, −0.512, −0.029, +0.079; −0.011, −0.461, −0.140, +0.128; −0.015, −0.404, −0.035, −0.044; −0.015, −0.373, −0.235, +0.117; −0.019, −0.300, −0.312, +0.107; −0.022, −0.283, −0.217, −0.005; −0.023, −0.238, −0.326, +0.048; −0.026, −0.120, −0.375, +0.064; −0.028, −0.184, −0.333, −0.008; −0.030, −0.159, −0.409, +0.040; −0.032, −0.134, −0.412, +0.015; −0.034, −0.113, −0.409, −0.012; −0.036, −0.092, −0.427, −0.018; −0.001, −0.053, −0.504, −0.025; +0.023, −0.026, −0.608, +0.022.

Table 7. The distribution of ^{175,181}Hf(IV) between 1 M H(HSO$_4^-$,ClO$_4^-$) and 5.035 × 10^{-3} M HDEHP-toluene solution. The data given as log [H$^+$], log [HSO$_4^-$], log D_{exp} and log $D_{calc}D_{exp}^{-1}$.

0.000, [HSO$_4^-$] = 0, + 1.719, − 0.101; 0.000, [HSO$_4^-$] = 0, + 1.590, + 0.028; 0.000, [HSO$_4^-$] = 0, + 1.609, + 0.009; − 0.011, − 3.028, + 1.677, − 0.046; − 0.011, − 3.028, + 1.610, + 0.020; 0.001, − 2.553, + 1.523, + 0.003; 0.001, − 2.553, + 1.589, − 0.062; − 0.001, − 2.186, + 1.455, − 0.010; − 0.003, − 2.186, + 1.455, − 0.010; − 0.019, − 2.028, + 1.271, + 0.163; − 0.018, − 2.028, + 1.407, + 0.028; 0.000, − 1.729, + 1.311, − 0.117; 0.000, − 1.729, + 1.161, + 0.033; − 0.010, − 1.551, + 1.061, + 0.023; − 0.008, − 1.329, + 0.956, − 0.094; − 0.008, − 1.183, + 0.638, + 0.057; − 0.007, − 1.028, + 0.436, + 0.059; − 0.030, − 0.852, + 0.227, + 0.076; − 0.037, − 0.726, + 0.045, + 0.083; − 0.002, − 0.630, − 0.157, + 0.043; − 0.007, − 0.571, − 0.178, − 0.021; − 0.011, − 0.461, − 0.379, + 0.002; − 0.015, − 0.373, − 0.524, + 0.002; − 0.020, − 0.301, − 0.637, − 0.003; − 0.023, − 0.238, − 0.747,   0.000; − 0.028, − 0.184, − 0.831, − 0.006; + 0.023, − 0.026, − 1.160, − 0.080.

In the following text a subscript $_*$ for p, q, r, or s in the complex (H$^+$)$_p$Hf(HA)$_4$(HSO$_4^-$)$_r$(ClO$_4^-$)$_s$ will be understood to have a meaning similar to that described previously, and in the computer calculation of the data the coefficient which is symbolized by the subscript $_*$ has been arbitrarily given the value equal zero unless otherwise stated.

The computer analysis shows that, out of the different combinations tried, the lowest error-square sum U was found by assuming the extraction of the complexes Hf(HA)$_4$ + Hf(HA)$_5$ (model V). Adding Hf(HA)$_3$ to Hf(HA)$_4$ and Hf(HA)$_5$ (model VI) gave a slight improvement to the U-value from 0.123 to 0.114, but caused an increase in $\sigma(y)$ from 0.117 to 0.128. Moreover, the formation constant for Hf(HA)$_3$ found in this combination had a standard deviation $\sigma(K) > K$. In Fig. 2 the extraction of Hf(IV) from 1 M (Na,H)ClO$_4$ with 1.982 × 10^{-4} M HDBP hexane solutions is shown as a function of log [H$^+$] In the [H$^+$]-range studied ($pH = 0.033 - 0.409$) the value of [HA] = 10$^{-4.10}$ M is practically constant. The plot log D *versus* − log [H$^+$] shows a slope of approximately 4, indicating a possible extraction of the species (H$^+$)$_{-4}$Hf(HA)$_4$ and (H$^+$)$_{-4}$Hf(HA)$_5$.

In Table 11 we summarize the values of U_{min} found for 8 experimental points assuming the values − 3 and − 4 for p in the formula of the extracted species (H$^+$)$_p$Hf(HA)$_4$ and (H$^+$)$_p$Hf(HA)$_5$. The result of the computer calculations indicates that $p = -4$ gives definitely a better description of the data than $p = -3$.

In the computer calculation (Table 11) we arbitrarily put $r = 0$ and the values of the equilibrium constants thus correspond to

$$\beta_{pq*} = [(H)_p Hf(HA)_q]_{org}[H^+]^{-p}[Hf^{4+}]^{-1}[HA]^{-q}$$

Using only this data ($Np = 8$ points) the distribution of Hf(IV) may satisfactorily be explained by assuming the formation of either HfA$_4$ (model II) or HfA$_4$(HA) (model III). However, the analysis of $D = f([HA])$ given in Table 10 indicates that the extraction of both 1:4 and 1:5 Hf−HA species gives a better fit to the data.

We thus conclude the following extraction equilibrium for hafnium:
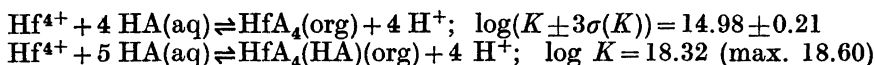
Hf^{4+} + 4 HA(aq) ⇌ HfA$_4$(org) + 4 H$^+$; log$(K \pm 3\sigma(K)) = 14.98 \pm 0.21$

Hf^{4+} + 5 HA(aq) ⇌ HfA$_4$(HA)(org) + 4 H$^+$; log $K = 18.32$ (max. 18.60)

Table 8. The extraction of Hf(IV) by HDBP or HDEHP into hexane or toluene. Equilibrium constants ^{a} for formation of sets of Hf(IV) complexes which were found to give the minimum error-square sum $U = \sum_1^{Np} (\log D_{calc} - \log D_{exp})^2$. The total concentration of Hf(IV) was less than 10^{-7} M.

System		
Hf(IV) – 1 M H(HSO₄,ClO₄)	$Hf^{4+} + HSO_4^- \rightleftharpoons HfSO_4^{2+} + H^+$	$\log {}^*\beta_1 = 1.88 \pm 0.30$
	$Hf^{4+} + 2\ HSO_4^- \rightleftharpoons Hf(SO_4)_2 + 2\ H^+$	$\log {}^*\beta_2 = 2.80\ (\text{max. } 2.94)$
Hf(IV) – 1 M (Na,H)(HSO₄,ClO₄)- HDBP-hexane	$Hf^{4+} + 4\ HA(aq) \rightleftharpoons HfA_4(org) + 4\ H^+$	$\log K = 15.37 \pm 0.09$
	$Hf^{4+} + 4\ HA(aq) + HSO_4^- \rightleftharpoons HfSO_4A_2(HA)_2(org) + 3\ H^+$	$\log K = 15.72 \pm 0.19$
	$Hf^{4+} + 5\ HA(aq) + HSO_4^- \rightleftharpoons HfSO_4A_2(HA)_3(org) + 3\ H^+$	$\log K = 18.32\ (\text{max. } 18.79)$
Hf(IV) - 0.50 M (Na,H)HSO₄- HDBP-hexane	$Hf^{4+} + 4\ HA(aq) \rightleftharpoons HfA_4(org) + 4\ H^+$	$\log K = 14.90\ (\text{max. } 15.16)$
	$Hf^{4+} + 5\ HA(aq) + HSO_4^- \rightleftharpoons HfSO_4A_2(HA)_3(org) + 3\ H^+$	$\log K = 19.62 \pm 0.17$
Hf(IV)-1 M (Na,H)ClO₄- HDBP-hexane	$Hf^{4+} + 4\ HA(aq) \rightleftharpoons HfA_4(HA)(org) + 4\ H^+$	$\log K = 14.98 \pm 0.21$
	$Hf^{4+} + 5\ HA(aq) \rightleftharpoons HfA_4(HA)(org) + 4\ H^+$	$\log K = 18.32\ (\text{max. } 18.60)$
Hf(IV)-1 M (Na,H)(HSO₄, ClO₄)- HDEHP-toluene	$Hf^{4+} + 5\ HA(aq) \rightleftharpoons HfA_4(HA)(org) + 4\ H^+$	$\log K = 44.69 \pm 0.14$
	$Hf^{4+} + 6\ HA(aq) \rightleftharpoons HfA_4(HA)_2(org) + 4\ H^+$	$\log K = 53.05 \pm 0.23$

^{a} The limits given correspond 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.

Table 9. Equilibrium constants for the formation of HDBP species in hexane and HDEHP species in toluene used in the present work for computer calculations of Hf(IV)-extraction data.

System		Equilibrium constants	Ref.
HDBP-hexane/1.0 M (Na,H)ClO_4	$HA(aq) \rightleftharpoons H^+ + A^-$	$K_a = 0.1318$ M	7
	$HA(aq) \rightleftharpoons HA(org)$	$K_d = 4.471 \times 10^{-3}$	
	$2\ HA(aq) \rightleftharpoons H_2A_2(org)$	$K_2 = 159$ M^{-1}	
	$10\ HA(aq) \rightleftharpoons H_{10}A_{10}(org)$	$K_{10} = 6.824 \times 10^{15}$ M^{-9}	
HDBP-hexane/1.0(0.5) M (Na,H)HSO_4	$HA(aq) \rightleftharpoons H^+ + A^-$	$K_a = 0.1318(0.1253)$M	5
	$HA(aq) \rightleftharpoons HA(org)$	$K_d = 6.572 \times 10^{-3}$	
	$2\ HA(aq) \rightleftharpoons H_2A_2(org)$	$K_2 = 196.6$ M^{-1}	
	$4\ HA(aq) \rightleftharpoons H_4A_4(org)$	$K_4 = 7.780 \times 10^5$ M^{-3}	
HDEHP-toluene/1.0 M (H,Na)HSO_4 or (H,Na)ClO_4	$HA(aq) \rightleftharpoons H^+ + A^-$	$K_a = 0.7127$ M	6
	$2\ HA(aq) \rightleftharpoons H_2A_2(aq)$	$K_{2aq} = 8.0 \times 10^{12}$ M^{-1}	
	$HA(aq) \rightleftharpoons HA(org)$	$K_d = 6.157 \times 10^4$	
	$2\ HA(aq) \rightleftharpoons H_2A_2(org)$	$K_2 = 4.81 \times 10^{14}$ M^{-1}	

Table 10. Equilibrium constants [a] log β_{*q*} for the formation of $(H^+)_* Hf(HA)_q(ClO_4)_*$ species in the system Hf(IV)-1 M $HClO_4$-HDBP-hexane for various assumptions of extractable Hf(IV)-species in hexane, which minimize the error-square sum

$$U = \sum_{1}^{11} (\log D_{calc} - \log D_{exp})^2.$$

Model No.	(*, q, *) log β_{*q*}	U_{min}	$\sigma(\log D)$
I	(*, 3, *) 11.47, max. 11.73	1.680	0.410
II	(*, 4, *) 15.19 ± 0.15	0.176	0.138
III	(*, 5, *) 18.91 ± 0.26; rej. (*, 6, *)	0.802	0.283
IV	(*, 4, *) 15.19 ± 0.15; rej. (*, 3, *) max. 10.90	0.176	0.140
V [b]	(*, 4, *) 15.05, max. 15.27; (*, 5, *) 18.27, max. 18.70; rej. (*, 6, *) max. 22.62	0.123	0.117
VI	(*, 3, *) 10.39, max. 11.13; (*, 4, *) 14.85, max. 15.43; (*, 5, *) 18.46, max. 18.93; rej. (*, 6, *) max. 22.77	0.114	0.123
VII	(*, 4, *) 15.10 ± 0.16; (*, 6, *) 21.60, max. 22.00	0.126	0.118

[a] The limits of β_{*q*} ($=[Hf(HA)_q]_{org}[Hf^{4+}]^{-1}[HA]^{-q}$) 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.

The values of the equilibrium constants are the computer calculated values for $Np = 13$ points (Hf distribution as a function of C_A at constant $[H^+] = 1$ M) assuming the extraction of HfA_4 and HfA_4HA) ($U = 0.147$, $\sigma(\log D) = 0.116$).

Table 11. Equilibrium constants ^{a} $\log \beta_{pq*}$ for the formation of $(H^+)_p Hf(HA)_q (ClO_4)_*$ in the system Hf(IV)-1 M $(Na,H)ClO_4$-1.982×10^{-4} M HDBP-hexane, which minimize the error-square sum $U = \overset{8}{\underset{1}{\sum}} (\log D_{calc} - \log D_{exp})^2$.

Model No.	$(p, q, *) \log \beta_{pq*}(org)$	U_{min}	$\sigma(\log D)$
I	$(-3, 4, *)$ 14.86, max. 15.36 $(-3, 5, *)$ 18.02, max. 19.27	0.233	0.199
II ^{b}	$(-4, 4, *)$ 14.72 ± 0.10 rej.: $(-4, 5, *)$ max. 19.45; $(-3, 5, *)$ max. 18.80	0.046	0.087
III	$(-4, 5, *)$ 18.80 ± 0.13 rej.: $(-3, 4, *)$ max. 14.78	0.058	0.096

^{a} The limits of $\beta_{pq*}(=[Hf(HA)_q]_{org}[Hf^{4+}]^{-1}[HA]^{-q})$ 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.

Extraction from 1.0 M $(Na,H)HSO_4$.

Hf(IV) − sulfate species in aqueous solution. Ryabchikov *et al.*[17] from ion-exchange experiments reported that in sulfate medium hafnium forms the sulfate complexes $Hf(SO_4)^{2+}$

$(*\beta_1 = [Hf(SO_4)^{2+}][H^+][Hf^{4+}]^{-1}[HSO_4^-]^{-1} = 130)$ and $Hf(SO_4)_2$
$(*\beta_2 = [Hf(SO_4)_2][H^+]^2[Hf^{4+}]^{-1}[HSO_4^-]^{-2} = 2090)$. Peshkova and An Pen [18,9] from distribution studies reported the formation of hafnium-sulfate complexes with $*\beta_1 = 10^{2.03}$ and $*\beta_2 = 10^{3.42}$.

In the present work an attempt was made to study the formation of Hf(IV)-sulfate complexes by measuring the distribution ratio of Hf(IV) in the systems 5×10^{-4} M HDBP hexane/1.0 M $H(ClO_4, HSO_4)$ (40 points) and 5×10^{-3} M HDEHP toluene/1.0 M $H(ClO_4, HSO_4)$ (27 points) as a function of varying concentrations of sulfate in the aqueous medium. In each set of experiment the value of [HA] and [H$^+$] may be considered practically constant, *i.e.* we may assume that the Hf(IV) distribution will mainly be affected by the change of sulfate concentration. In Tables 12 and 13 we summarize the results of our computer calculations for different assumed sets of $(H^+)_* Hf(HA)_* (HSO_4^-)$, complexes in the organic and aqueous phase.

In this calculation we assumed the formation of $Hf(SO_4)^{2+}$, $Hf(SO_4)_2$ and $Hf(SO_4)_3^{2-}$ in the aqueous medium and of $(H^+)_p Hf(HA)_s$, $(H^+)_p Hf(HSO_4)(HA)_s$ and $(H^+)_p Hf(HSO_4)_2(HA)_s$ in the organic phase.

Conclusions from extraction data with HDBP as extractant. In the extraction system Hf(IV) − 1 M $H(ClO_4, HSO_4)/5 \times 10^{-4}$ M HDBP hexane the results of the computer-analysis ($Np = 40$ points, Table 12) indicate that model (12,II) gives a lower error-square sum U and $\sigma(\log D)$ than model (12,I). In model (12,II) we assumed the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ species in the aqueous phase and the extraction of sulfate-containing Hf(IV) complexes in the hexane phase.

Table 12. Equilibrium constants [a] $\log \beta_{***,r}$ for the formation of $(H^+)_*Hf(HA)_*(HSO_4)_r$ species in the system Hf(IV)·1 M H(HSO₄⁻, ClO₄⁻)-HDBP-hexane for various assumptions of Hf(IV)-species in the aqueous and organic phase, which minimize

$$U = \sum_1^{40} (\log D_{calc} - \log D_{exp})^2; \quad C_{HDBP} = 5 \times 10^{-4}\ M.$$

Model No.	$(H^+)_*Hf(HA)_*(HSO_4)_r$ (aq)	$(H^+)_*Hf(HA)_*(HSO_4)_r$ (org)	U_{min}	$\sigma(y)$
I	(*,,1) 1.96±0.21; (*,*,2) 2.22±0.19; rej. (*,*,3) max. 2.42;	(*,*,0) 1.73±0.11	0.271	0.087
II[b]	(*,*,1) 1.78, max. 2.00; (*,*,2) 2.84, max. 3.15	(*,*,0) 1.69±0.11; (*,*,1) 2.15, max. 2.53	0.203	0.075
III	(*,,1) 1.85±0.22; (*,*,3) 3.72, max. 3.97; rej. (*,*,2) max. 3.24;	(*,*,0) 1.70±0.10; (*,*,2) 3.13, max. 3.40	0.173	0.070
IV	(*,*,1) 1.97, max. 2.18; (*,*,3) 4.26±0.09; rej. (*,*,2) max. 3.74	(*,*,0) 1.71±0.11; (*,*,1) 2.63, max. 2.94; (*,*,2) 3.63±0.14	0.167	0.070

[a] The limits of $\beta_{***,r}$ $(=[Hf(HSO_4)_r]_{org}[Hf^{4+}]^{-1}[HSO_4^-]^{-r})$ 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.

Table 13. Equilibrium constants [a] $\log \beta_{***,r}$ for the formation of $(H^+)_*Hf(HA)_*(HSO_4)_r$ species in the system Hf(IV)·1 M H(HSO₄⁻, ClO₄⁻)-HDEHP-toluene for various assumptions of Hf(IV)-species in the aqueous and organic phase, which

$$\text{minimize } U = \sum_1^{27} (\log D_{calc} - \log D_{exp})^2; \quad C_{HDEHP} = 5 \times 10^{-3}\ M.$$

Model No.	$(H^+)_*Hf(HA)_*(HSO_4)_r$ (aq)	$(H^+)_*Hf(HA)_*(HSO_4)_r$ (org)	U_{min}	$\sigma(y)$
I[b]	(*,*,1) 1.93±0.15; (*,*,2) 2.80±0.10 rej. (*,*,3) max. 2.69	(*,*,0) 1.65±0.06	0.065	0.053
II	(*,*,1) 1.90±0.22; (*,*,2) 3.02, max. 2.39; (*,*,3) 3.22, max. 3.77	(*,*,0) 1.64±0.07; (*,*,1) 2.15, max. 2.65	0.063	0.053
III	(*,*,1) 1.99±0.24; (*,*,2) 3.34, max. 3.75; (*,*,3) 4.10, max. 4.39	(*,*,0) 1.65±0.07; (*,*,1) 2.90, max. 3.27; (*,*,3) 3.34, max. 3.75	0.064	0.055

[a] The limits of $\beta_{***,r}$ $(=[Hf(HSO_4)_r]_{org},log[Hf^{4+}]^{-1}[HSO_4^-]^{-r})$ 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.

Further improvements in the value of U are found for model (12,III) and model (12,IV). However, these new assumptions did not give any significant change in the value of $\sigma(\log D)$ compared with model (12,II).

Conclusions from extraction data with HDEHP as extractant. For the extraction with HDEHP the results of the computer analysis (Table 13) show that out of the different mechanism tried the best description of the data was found for model (13,II) with $U_{min} = 0.063$ $(\sigma(\log D) = 0.053)$ and the assumptions that we have $Hf(SO_4)^{2+}$, $Hf(SO_4)_2$ and $Hf(SO_4)_3^{2-}$ in the aqueous phase and the extraction of $Hf(HSO_4)$-species in the organic phase. Comparing the different models tried we found, however, that they only show slight differences in the values of the error-square sum and $\sigma(\log D)$. We may conclude from these calculations that within the experimental error, the data available with HDEHP as extractant may be described equally well with several models (*cf.* Tables 12 and 13). However, out of the different possible models the simplest description of the available data would be by assuming model (12,II) and model (13,I), *i.e.* the assumptions that Hf(IV) forms the species $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ in the aqueous phase and that only with HDBP are Hf-HSO_4-HA species extracted in hexane.

From the values found in model (12,II) and model (13,I) we calculate the mean values of the equilibrium constant for the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$, using the values of $1/\sigma^2$ as the weight factors. The equilibrium reactions in the aqueous medium can now be described as:

$$Hf^{4+} + HSO_4^- \rightleftharpoons Hf(SO_4)^{2+} + H^+ \qquad \log(^*\beta_1 \pm 3\sigma) = 1.88 \pm 0.30$$
$$Hf^{4+} + 2HSO_4^- \rightleftharpoons Hf(SO_4)_2 + 2H^+ \qquad \log(^*\beta_2) = 2.80, \ (\log(^*\beta_2 + 3\sigma) = 2.94)$$
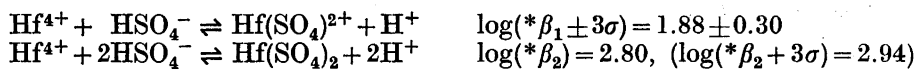
Comparing these values with those reported by Ryabchikov et al.[17] $(\log^*\beta_1 = 2.11, \log^*\beta_2 = 3.32)$, we find that the differences are not insignificant, although the value of the ratio $^*\beta_2/^*\beta_1 = 10^{1.21}$ is comparable with that found in the present work $(= 10^{1.08})$.

Conclusions about the extracted Hf(IV) − HDBP − species. The computer analysis of the data for the system Hf(IV)-1 M $H(HSO_4, ClO_4)$-5 × 10⁻⁴ M HDBP-hexane, thus indicate that the best description of the data (*cf.* Table 12), is found when we assume the extraction of $(H^+)_p Hf(HA)_q + (H^+)_p Hf(HSO_4)(HA)_q$ species in the organic phase, and the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ in the aqueous phase. To draw more definite conclusions about the composition of the Hf(IV)-species extracted we must find the values of p and q, *i.e.* the number of moles of H^+ and HA bound per mole of Hf(IV)-complex. To determine q, we studied the extraction of Hf(IV) from 1.0 M H_2SO_4 solution as a function of C_A. The extraction was thus carried on at constant $[H^+] = 1.08$ M and $[HSO_4^-] = 0.95$ M. In Fig. 1 we plot $\log D = f(\log [HA])$ and the experimental points seem to fall on a straight line with a slope of approximately 4. In Table 14 we summarize the Letagrop analysis for 8 experimental points, assuming the extraction of different "$Hf(HA)_q$" species, where q may take the values from 3 to 6. The equilibrium constants in Table 14 were calculated assuming the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ with Ryabchikov's constants (*cf.* Ref 17). Even if Ryabchikov's equilibrium constants are slightly in error, this will only appear as a constant factor in the equilibrium constant

Table 14. Equilibrium constants [a] log β_{*q*} for formation of $(H^+)_*Hf(HA)_q(HSO_4)_*$ species in the system Hf(IV)-1.0 M H_2SO_4-HDBP-hexane for various assumptions of extractable Hf(IV)-species in hexane, which minimize the error-square sum $U = \sum_1^8 (\log D_{calc} - \log D_{exp})^2$, with the assumption of the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_*$-complexes in the aqueous phase with Ryabchikov's equilibrium constants (*cf.* Ref. 17).

Model No.	(*, q, *) log β_{*q*} (org)	U_{min}	σ (log D)
I	(*, 3, *) 12.94, max. 13.37	3.210	0.677
II	(*, 4, *) 16.32 ± 0.10; rej. (*, 3, *)	0.215	0.175
III	(*, 5, *) 19.66, max. 19.94; rej. (*, 6, *)	0.972	0.373
IV	(*, 6, *) 22.95, max. 23.45	5.481	0.885
V	(*, 3, *) 12.35, max. 12.76; (*, 6, *) 22.16, max. 22.57	0.785	0.362
VI [b]	(*, 4, *) 16.10, max. 16.31; (*, 5, *) 18.98, max. 19.35 rej. (*, 3, *) max. 12.27	0.084	0.129
VII	(*, 4, *) 16.20 ± 0.26; (*, 6, *) 21.49, max. 22.01 rej. (*, 3, *)	0.147	0.172

[a] The limits of $\beta_{*q*}(=[Hf(HA)_q]_{org}[Hf^{4+}]^{-1}[HA]^{-q})$ 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.

and will not affect the conclusions on the Hf species present, since in this set of data $[SO_4^{2-}]$ has been kept constant.

In the computer calculation we arbitrarily put $p = r = 0$ and the equilibrium constants given in Table 14 thus correspond to $\beta_{*q*} = [Hf(HA)_q]_{org}[Hf^{4+}]^{-1}[HA]^{-q}$. The computer calculations indicate that the combinations $Hf(HA)_4 + Hf(HA)_5$ (model 14,VI) gives a lower error-square sum U and $\sigma(\log D)$ than the other combinations tried. The extracted Hf(IV) species may now be represented as $(H^+)_pHf(HSO_4^-)_r(HA)_q$ with $r = 0$ or 1 and $q = 4$ and 5. To find out the best value of p we studied the distribution of Hf(IV) in the system Hf(IV)-1 M (Na,H)HSO$_4$-2.5 × 10^{-4} M HDBP-hexane. Assuming that p may have the possible values: −1, −2, −3, and −4 and neglecting the small variations in $[HSO_4]$ in the pH-range (0 – 0.5) studied, we analyzed the data $D = f([H^+])_{C_A}$ and $D = f(C_A)_{[H^+]}$. The results of the calculation for 19 experimental points are given in Table 15. The combination $(H^+)_{-4}Hf(HA)_4 + (H^+)_{-4}Hf(HA)_5$ (model 15,V) seems to give a lower U-value than the other models tried.

We may thus conclude that the main Hf(IV)-species extracted can be represented as $(H^+)_{-4}Hf(HSO_4)_r(HA)_q$ with $r = 0$ or 1, and $q = 4$ or 5, and making the reasonable assumption that the extracted species must be uncharged then the probable extracted species when $r = 1$, $q = 4$ or 5, will be $(H^+)_{-3}Hf(HSO_4)(HA)_q$, *i.e.* $Hf(SO_4)A_2(HA)_2$ and $Hf(SO_4)A_2(HA)_3$.

Table 15. Equilibrium constants ^{a} log β_{pq*} for the formation of $(H^+)_p Hf(HA)_q(HSO_4)_*$-species in the system Hf(IV)-1 M (Na,H)HSO$_4$-HDBP-hexane for various assumptions of extractable Hf(IV)-HDBP species in hexane which minimize the error-square sum
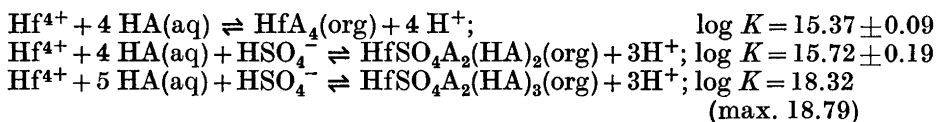
$$U = \sum_1^{19} (\log D_{calc} - \log D_{exp})^2,$$ with the assumption of the formation of Hf(SO$_4$)$^{2+}$ and Hf(SO$_4$)$_2$ in the aqueous phase using Ryabchikov's constant.[17]

Model No.	$(p, q, *)$ log β_{pq*} (org)	U_{min}	σ (log D)
I	$(-2, 4, *)$ 16.77, max. 17.02; rej. $(-1, 5, *)$ max. 21.03	1.416	0.397
II	$(-4, 4, *)$ 16.31 $\pm$ 0.08; $(-1, 5, *)$ 18.85, max. 19.14	0.146	0.093
III	$(-3, 4, *)$ 16.37, max. 16.61; $(-4, 5, *)$ 19.15, max. 19.74	0.689	0.201
IV	$(-4, 4, *)$ 16.31 $\pm$ 0.08; $(-2, 5, *)$ 18.90, max. 19.19	0.143	0.092
V^b	$(-4, 4, *)$ 16.28 $\pm$ 0.09; $(-4, 5, *)$ 19.04, max. 19.30	0.126	0.086
VI	$(-4, 4, *)$ 16.30 $\pm$ 0.08; $(-3, 5, *)$ 18.96, max. 19.24	0.138	0.090

^{a} The limits of $\beta_{pq*}(=[(H^+)_p Hf(HA)_q]_{org}[H^+]^{-p}[Hf^{4+}]^{-1}[HA]^{-q})$ given correspond to log ($\beta \pm 3$ $\sigma(\beta)$) and if $\sigma(\beta) > 0.2$ β, the maximum value log ($\beta + 3$ $\sigma(\beta)$) is given.
^{b} The "best" model assumed.

We finally calculated the equilibrium constants which minimize U (59 points), assuming the extraction of HfA$_4$, HfA$_4$(HA), HfSO$_4$A$_2$(HA)$_2$ and HfSO$_4$A$_2$(HA)$_3$ while keeping constant the values of the equilibrium constant for the formation of Hf(SO$_4$)$^{2+}$ and Hf(SO$_4$)$_2$ found previously. Using this set of data, the species HfA$_4$(HA) was found to be rejected, since the value of the equilibrium constant for its formation was reduced to zero. The value for $U_{min} = 0.755$ (σ(log D) = 0.098) was found for the following extraction equilibria:

$$Hf^{4+} + 4 \, HA(aq) \rightleftharpoons HfA_4(org) + 4 \, H^+; \qquad \log K = 15.37 \pm 0.09$$
$$Hf^{4+} + 4 \, HA(aq) + HSO_4^- \rightleftharpoons HfSO_4A_2(HA)_2(org) + 3H^+; \log K = 15.72 \pm 0.19$$
$$Hf^{4+} + 5 \, HA(aq) + HSO_4^- \rightleftharpoons HfSO_4A_2(HA)_3(org) + 3H^+; \log K = 18.32$$
$$(\text{max. } 18.79)$$

The absence of any indication of the formation of the HfA$_4$(HA) species in hexane when Hf(IV) is extracted from sulfate medium is surprising and should not be taken as conclusive, since it is reasonable to assume that the formation of the species HfA$_4$ and HfA$_4$(HA) in hexane may be expected not to be dependent on the ionic medium used. It is most probable that by using distribution data with a broader range of HDBP concentration, one might be able to find indications of the extraction of HfA$_4$(HA) species in hexane even from sulfate medium.

Hf(IV)-extraction from 0.5 M (Na,H)HSO$_4$. To study the effect of the ionic medium in the aqueous phase we also studied the distribution of Hf(IV) in the system Hf(IV)-0.5 M H$_2$SO$_4$-HDBP-hexane. In Fig. 1 we plot log $D = f$(log [HA]) at constant log [H$^+$] = 0.265, and the experimental points appear to fall on a straight line with a slope of approximately 4.

Table 16. Equilibrium constants [a] log β_{*p*} for the formation of $(H^+)_*Hf(HA)_q(HSO_4)_*$ species in the system Hf(IV)-0.5 M H_2SO_4-HDBP-hexane for various assumptions of extractable Hf(IV)-species in hexane, which minimize the error-square sum $U = \sum_{1}^{16}(\log D_{calc} - \log D_{exp})^2$, with the assumption of the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ in the aqueous phase using Ryabchikov's equilibrium constants.[17]

Model No.	$(*, q, *)$ log β_{*p*} (org)	U_{min}	$\sigma(\log D)$
I	(*, 3, *) 13.41, max. 13.78	8.962	0.773
II	(*, 4, *) 16.87, max. 17.08; rej. (*, 3, *)	2.039	0.369
III	(*, 5, *) 20.33 ± 0.12; rej. (*, 6, *) max. 23.00	0.378	0.159
IV	(*, 6, *) 23.79, max. 24.07	3.980	0.515
V	(*, 3, *) 11.73, max. 12.38; (*, 5,*) 20.30 ± 0.17	0.350	0.158
VI	(*, 3, *) 12.57, max. 12.89; (*, 6, *) 23.39, max. 23.66	1.343	0.310
VII[b]	(*, 4, *) 15.95, max. 16.41; (*, 5, *) 20.25 ± 0.18 rej. (*, 3, *) max. 12.69; rej. (*, 6, *) max. 23.26	0.325	0.152
VIII	(*, 4, *) 16.56, max. 16.78; (*, 6, *) 23.16, max. 23.45 rej. (*, 3, *) max. 12.55	0.705	0.225

[a] The limits of $\beta_{*q*}(=[Hf(HA)_q]_{org}[Hf^{4+}]^{-1}[HA]^{-q})$ 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.

Computer analysis of the data given in Table 16 for 16 points showed that out of the different mechanisms tried the lowest error-square sum was found when the extraction of the species $(H^+)_pHf(HA)_q(HSO_4)_s$ with $q = 4$ and 5 was assumed (model 16,VII). This agrees with the results found for Hf(IV)-extraction from 1.0 M H_2SO_4 aqueous medium. In order to determine the values of p the data $D = f(C_A,[H^+])$ consisting of 24 points was computer treated assuming the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ in the aqueous phase, as indicated previously, and assuming that p may have the values -1, -2, -3, and -4. The results of the computer calculations which are summarized in Table 17 show that the lowest value for the error-square sum $U = \sum_{1}^{24}(\log D_{calc} - \log D_{exp})^2 = 0.376$ $(\sigma(y) = 0.131)$ and $U = \sum_{1}^{24}[(D_{calc}/D_{exp}) - 1]^2 = 1.722$ $(\sigma(y) = 0.280)$ was found for the combination $(H^+)_{-4}Hf(HA)_4$-$(HSO_4)_s + (H^+)_{-4}Hf(HA)_5(HSO_4)_s$ (model 17,IX). We may thus conclude that the Hf(IV)-HDBP species extracted from 1.0 M H_2SO_4 and 0.5 M H_2SO_4 apparently have mainly the same compositions. Using the reasonable assumption that the same set of Hf(IV)-species (HfA$_4$, HfSO$_4$A$_2$(HA)$_2$, HfSO$_4$A$_2$(HA)$_3$)
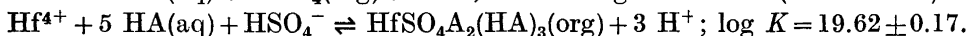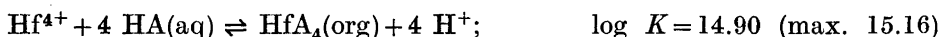
Table 17. Equilibrium constants [a] log β_{pq*} for the formation of $(H^+)_p Hf(HA)_q(HSO_4)_*$ species in the system Hf(IV)- 0.50 M (Na,H)HSO$_4$-HDBP-hexane for various assumptions of extractable Hf(IV)-species which minimize the error-square sum $U = \sum_1^{24} (\log D_{calc} - \log D_{exp})^2$ $(U = \sum_1^{24} (D_{calc}/D_{exp} - 1)^2)$, with the assumption of the formation of Hf(SO$_4$)$^{2+}$ and Hf(SO$_4$)$_2$ in the aqueous phase using Ryabchikov's constants.[17]

Model No.	$(p, q, *)$ log β_{pq*} (org)	U_{min}	$\sigma(y)$
I	$(-1, 4, *)$ 16.42, max. 16.72 (15.74, max. 16.12)		
	$(-1, 5, *)$ 19.82, max. 20.21 (19.94, max. 20.15)	2.090 (5.456)	0.308 (0.498)
II	$(-1, 4, *)$ 15.95, max. 16.55		
	$(-2, 5, *)$ 19.82, max. 20.12	1.526	0.264
III	$(-1, 4, *)$ 15.38, max. 16.23 (15.48, max. 16.06)		
	$(-3, 5, *)$ 19.58 $\pm$ 0.22 (19.47 $\pm$ 0.18)	0.742 (3.309)	0.184 (0.388)
IV	$(-1, 4, *)$ 15.65, max. 16.12 (15.42, max. 15.95)		
	$(-4, 5, *)$ 19.23 $\pm$ 0.15 (19.19 $\pm$ 0.13)	0.392 (1.982)	0.134 (0.300)
V	$(-2, 4, *)$ 15.58, max. 16.07 (15.36, max. 15.83)		
	$(-3, 5, *)$ 19.51 $\pm$ 0.26 (19.44 $\pm$ 0.19)	0.683 (3.142)	0.176.(0.378)
VI	$(-2, 4, *)$ 15.44, max. 15.87 (15.23, max. 15.71)		
	$(-4, 5, *)$ 19.21 $\pm$ 0.16 (19.18 $\pm$ 0.14)	0.383 (1.929)	0.132 (0.296)
VII	$(-3, 4, *)$ 15.71 $\pm$ 0.23 (15.41, max. 15.70)		
	$(-1, 5, *)$ 19.83, max. 20.04 (19.87, max. 20.08)	0.743 (4.157)	0.184 (0.435)
VIII	$(-3, 4, *)$ 15.65, max. 15.86 (15.35, max. 15.66)		
	$(-2, 5, *)$ 19.61 $\pm$ 0.26 (19.64 $\pm$ 0.24)	0.670 (3.621)	0.175 (0.406)
IX[b]	$(-4, 4, *)$ 14.88, max. 15.28 (14.82, max. 15.18)		
	$(-4, 5, *)$ 19.19 $\pm$ 0.18 (19.15 $\pm$ 0.15)	0.376 (1.722)	0.131 (0.280)
X	$(-3, 4, *)$ 15.48, max. 15.78		
	$(-3, 5, *)$ 19.42 $\pm$ 0.23	0.523	0.154

[a] The limits of $\beta_{pq*}(= [(H^+)_p Hf(HA)_q]_{org}[H^+]^{-p}[Hf^{4+}]^{-1}[HA]^{-q})$ 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.

were extracted as from 1 M H$_2$SO$_4$ medium we finally calculate the following equilibrium constants for the formation of the Hf(IV)-species which minimize U for $Np = 24$:

Hf^{4+} + 4 HA(aq) $\rightleftharpoons$ HfA$_4$(org) + 4 H$^+$;   log $K = 14.90$ (max. 15.16)

Hf^{4+} + 5 HA(aq) + HSO$_4^-$ $\rightleftharpoons$ HfSO$_4$A$_2$(HA)$_3$(org) + 3 H$^+$; log $K = 19.62 \pm 0.17$.

The HfSO$_4$A$_2$(HA)$_2$ species found previously for Hf-extraction from 1 M H$_2$SO$_4$ was rejected in the computer analysis of the extraction data for 0.5 M H$_2$SO$_4$ ($K = 0$).

In this analysis of the extraction data of Hf(IV) we have used the values of the constants for the formation of Hf(SO$_4$)$^{2+}$ and Hf(SO$_4$)$_2$ found previously for 1.0 M H$_2$SO$_4$ medium. This assumption is of course not strictly correct,

since the activity-factors of the reagents species will be dependent on the ionic strength of the aqueous medium. This slight error may in part explain the small deviations found for the formation constants of HfA_4 and $HfSO_4A_2(HA)_3$ for the extraction from 0.50 M $(Na,H)SO_4$ compared with that from 1.0 M $(Na, H)SO_4$ medium.

Hf(IV) - HDEHP species in toluene

Hf(IV)-extraction from 1 M $(Na,H)ClO_4$. Fig. 1 shows the distribution of Hf(IV) in the extraction system HDEHP toluene/1 M $HClO_4$, given as log D *versus* log [HA]. The values of [HA] were calculated using the equilibrium constants from Ref. 6, which are given in Table 9. The experimental points in Fig. 1 are seen to fall on a straight line with a slope of approximately 5. In Fig. 2 we further represent the distribution of Hf(IV) as a function of $[H^+]$ at a constant value of $C_A = 5.021 \times 10^{-4}$ M As can be seen the data log $D = f(-\log[H^+])$ can be fitted to a straight line with a slope of 4.

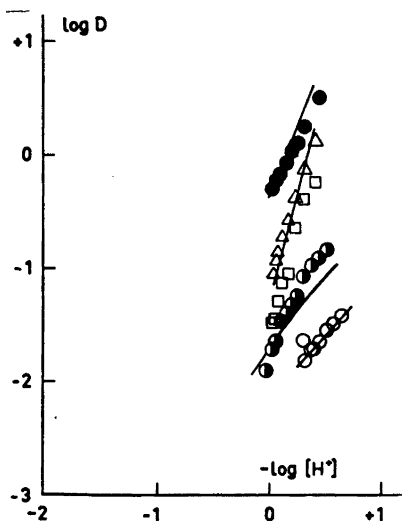*Fig. 2.* The distribution of Hf(IV) as a function of $-\log [H^+]$ in the two-phase systems 0.5 M $(H,Na)HSO_4/2 \times 10^{-4}$ M HDBP-hexane (O); 1.0 M $(H,Na)HSO_4/2.5 \times 10^{-4}$ M HDBP-hexane (◑); 1.0 M $(H,Na)ClO_4/10^{-4}$ M HDBP-hexane (▣); 1.0 M $(H,Na)HSO_4/10^{-2}$ M HDEHP-toluene (●), and 1.0 M $(H,Na)ClO_4/5 \times 10^{-4}$ M HDEHP-toluene (△). The distribution data are given in Tables 1 − 5. The lines have been calculated assuming the HDBP, HDEHP species in Table 9 and the set of Hf(IV)-HSO_4^--HA species in Table 8.

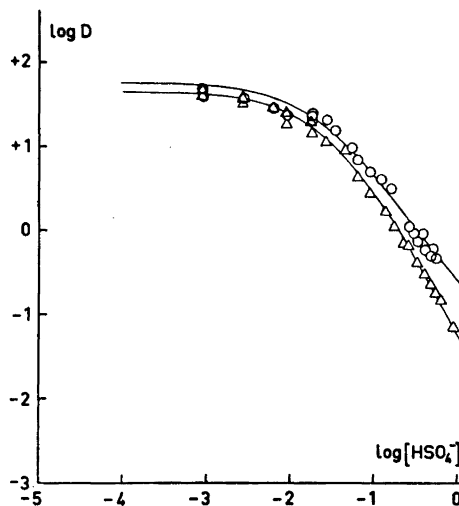*Fig. 3.* The distribution of Hf(IV) between 1 M H(HSO_4, ClO_4) and 4.98×10^{-4} M HDBP-hexane (O) or 5×10^{-2} M HDEHP-toluene (△) as a function of $[HSO_4^-]$. The distribution data are given in Tables 6 and 7. The curves have been calculated assuming the Hf(IV)-HA-HSO_4^- species in Table 8 and the HDBP or HDEHP species in Table 9.

The data $D = f(C_A, [H^+])$ were computer analyzed for various assumptions of the extractions of $(H^+)_{-4}Hf(HA)_q$ species, where q may take the values 5 and 6. The results of the computer calculations for 15 experimental points as shown in Table 18 indicate that the combination $(H^+)_{-4}Hf(HA)_5 + (H^+)_{-4}Hf(HA)_6$ with $U = 0.131$ $(\sigma(y) = 0.10)$ definitely gives a better fit to the data than assuming the extraction of either $(H^+)_{-4}Hf(HA)_5$ $(U = 0.359,$ $\sigma(y) = 0.168)$ or $(H^+)_{-4}Hf(HA)_6 (U = 0.486,$ $\sigma(y) = 0.121)$ separately.

Table 18. Equilibrium constants [a] $\log \beta_{q*}$ for the formation of $(H^+)_{-4}Hf(HA)_q(ClO_4)_*$-species in the system Hf(IV)-1.0 M (Na,H)ClO$_4$-HDEHP-toluene for various assumptions of extractable Hf(IV)-species in toluene, which minimize $U = \sum_{1}^{15} (\log D_{calc} - \log D_{exp})^2$.

Model No.	$(q, *) \log \beta_{q*}$ (org)	U_{min}	$\sigma(\log D)$
I	(5, *) 44.62 ± 0.13	0.359	0.168
II	(6, *) 53.63 ± 0.15	0.486	0.121
III[b]	(5, *) 44.10, max. 44.41	0.131	0.100
	(6, *) 53.29, max. 53.53		

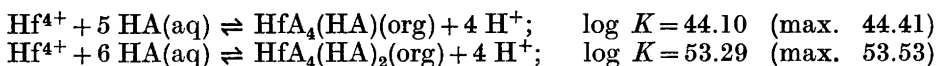[a] The limits of $\beta_{q*}(=[(H^+)_{-4}Hf(HA)_q]_{org}[H^+]^{-4}[Hf^{4+}]^{-1}[HA]^{-q})$ given correspond to $\log (\beta \pm 3\sigma(\beta))$ and if $\sigma(\beta) > 0.2 \beta$, the maximum value $\log (\beta + 3\sigma(\beta))$ is given.
[b] The "best" model assumed.

The values of the equilibrium constants given in Table 18 correspond to:

$$\beta_{q*} = [(H^+)_{-4}Hf(HA)_q]_{org}[H^+]^{-4}[Hf^{4+}]^{-1}[HA]^{-q}$$

Assuming the formation of H_2A^+ in the aqueous phase and $HA \cdot HClO_4$ in the organic phase, as was indicated at low pH and $C_A < 5 \times 10^{-4}$M (cf. Ref. 6), we found in some preliminary calculations no improvement of the U value. This may indicate that at higher values of C_A the formation of $HA \cdot HClO_4$ is depressed by the H_2A_2 formation.
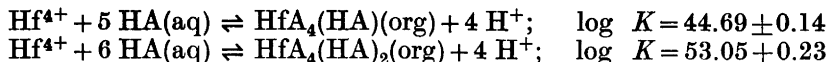
We may thus conclude that the extraction of Hf(IV) from 1 M (Na,H)ClO$_4$ by HDEHP may be described satisfactorily by the following equilibrium reactions:

$Hf^{4+} + 5\,HA(aq) \rightleftharpoons HfA_4(HA)(org) + 4\,H^+$; $\log K = 44.10$ (max. 44.41)
$Hf^{4+} + 6\,HA(aq) \rightleftharpoons HfA_4(HA)_2(org) + 4\,H^+$; $\log K = 53.29$ (max. 53.53)

Hf(IV)-extraction from 1 M H$_2$SO$_4$. The extraction of Hf(IV) by HDEHP in toluene was also studied from 1 M H$_2$SO$_4$ aqueous medium. In Fig. 1 the distribution data for 1 M H$_2$SO$_4$ are given as a function of HA. Slope analysis of the data indicates the extraction of Hf(HA)$_p$-species with $p \approx 5$. To find the "best" values of p we computer-analyzed the available data $(Np = 8)$ assuming p may take the values 5 and 6. The calculation shows that we can

describe the data satisfactorily by assuming the extraction of $Hf(HA)_5 + Hf(HA)_6$ species, ($U = 0.09$ and $\sigma(y) = 0.123$). Assuming the extraction of either $Hf(HA)_5$, ($U = 0.176$, $\sigma(y) = 0.158$), or $Hf(HA)_6$, ($U = 0.279$, $\sigma(y) = 0.20$), alone, gives higher values for U and $\sigma(y)$.

The final calculation of all the data available ($Np = 42$ points), assuming the extraction of the species $HfA_4(HA)[= (H^+)_{-4}Hf(HA)_5] + HfA_4(HA)_2$ $[= (H^+)_{-4}Hf(HA_6)]$ and the formation of $Hf(SO_4)^{2+}$ and $Hf(SO_4)_2$ in the aqueous phase as concluded previously, gives a $U_{min} = 0.191$, ($\sigma(y) = 0.069$) and the following equilibrium constants:

$$Hf^{4+} + 5\ HA(aq) \rightleftharpoons HfA_4(HA)(org) + 4\ H^+; \quad \log\ K = 44.69 \pm 0.14$$
$$Hf^{4+} + 6\ HA(aq) \rightleftharpoons HfA_4(HA)_2(org) + 4\ H^+; \quad \log\ K = 53.05 \pm 0.23$$

CONCLUSIONS

The results of our present work indicate that hafnium is extracted by HDBP into hexane mainly as HfA_4, $HfSO_4A_2(HA)_2$, and $HfSO_4A_2(HA)_3$ complexes from sulfate medium and as $HfA_4 + HfA_4(HA)$ from perchlorate medium.

With HDEHP hafnium is extracted in toluene mainly as $HfA_4(HA)$ and $HfA_4(HA)_2$ from both sulfate and perchlorate medium. At higher concentrations of HDBP ($C_A > 3 \times 10^{-3}M$) both in Hf-extraction from sulfate and from perchlorate medium we found indications of the formation of Hf(IV)-HA aqueous complexes, since the distribution ratio D tends to decrease with increasing C_A. No attempt has been made to deduce the possible species formed from the data available. We may conclude that for the extraction of HA in non-polar organic solvent both the nature of the dialkylphosphate and of the ionic medium may be significant for the composition of the extractable hafnium species. Navrátil's [3,4] report on the extraction of, among other species, like $HfClA_3(HA)_2$ and $HfClA_3$ from HCl medium and $Hf(NO_3)_4(HA)_2$ from nitric acid medium, may support our conclusions. The number of HA complexed in the Hf-species extracted is found to be $4-6$, which agrees with the results reported by Peppard and Ferraro,[1] Dyrssen,[19] and Navrátil.[2-4]

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