Aqueous Chemistry of Protactinium(IV). 5. Benzoylacetone Complexes of Pa(IV) and Hf(IV)

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The liquid-liquid distribution systems M-HBA in C_6H_6-1 M $(Na,H)ClO_4$, where M = Pa(IV) or Hf(IV) and HBA = benzoylacetone, were studied at 25 °C in the ph range $0-10$. The experimental results indicated that $Pa(BA)_4$ and PaO^{2+} (or $Pa(OH)_2^{2+}$), and $Hf(BA)_4$ and HfO^{2+} (or $Hf(OH)_2^{2+}$) were the competing dominating species in aqueous phase. The extraction constants $(K_D(Pa) = [Pa(BA)_4(org)][H^+]^2[H_2O]/[PaO^{2+}][HBA(org)]^4$ or $[Pa(Ba)_4(org)]$ $[H^+]^2$ $[H_2O]^2/[Pa(OH)_2^{2+}]$ $[HBA(org)]^4)$ were found to be log $K_D(Pa) = -0.7 \pm 0.1$ and log $K_D(Hf) = 0.6 \pm 0.2$, for Pa(IV) and Hf(IV), respectively. The distribution constant $(\lambda_{4,-2} = [Hf(BA)_4(org)]/[Hf(BA)_4])$ for the hafnium benzoylacetone complex was determined to be log $\lambda_{4,-2} = 3.6 \pm 0.1$. The stability constant β_4' for the aqueous reaction $HfO^{2+} + 4BA^- + 2H^+ \rightleftharpoons Hf(BA)_4 + H_2O$ (or $Hf(OH)_2^{2+} + 4BA^- + 2H^+ \rightleftharpoons Hf(BA)_4 + 2H_2O$) was calculated to be log $\beta_4' = 41.8 \pm 0.2$.

Pa(IV) has been found to form different types of β-diketonate complexes; tetrakis thenoyltrifluoroacetone[1] (TTA) and bisacetylacetone[2] (HAA) complexes. The unexpected formation of only a twofold coordination of acetylacetone needs further information, *i.e.* the composition of other β-diketone complexes, in order to be understood. Benzoylacetone (HBA) is a β-diketone with a configuration rather close to acetylacetone and which might be looked upon as an intermediary between TTA and HAA. A liquid-liquid distribution study of the complex formation between Pa(IV) and HBA was therefore undertaken. In order to compare the aqueous chemistry of Pa(IV) with other tetravalent metals a re-investigation of the corresponding Hf(IV) system was also made. The hafnium(IV)-benzoylacetone extraction system has been the subject of a previous study.[3]

EXPERIMENTAL

Chemicals. A mixture of the isotopes [175]Hf (3.8 mCi) and [181]Hf (26.3 mCi) was supplied from R.C.C. Amersham as an 8.5 ml 2 M HCl solution, where [Hf] ~ 0.4 mg/ml. High resolution gamma spectroscopy with a Ge(Li)-detector showed that the hafnium was radiochemically pure. Benzene solutions of benzoylacetone (Merck, *p.a.*) of various concentrations up to saturation (~3 M HBA, yellowish solution) were prepared. The preparation of other chemicals used has been described elsewhere.[2,4]

Extraction procedure. The extraction procedure for Pa(IV) in presence of 0.01 M Cr^{2+} under continuous electrolysis was carried out as before.[2,4] Concerning Hf(IV), it was observed that no reproducible distribution values were obtained if the back extraction technique was not used (*i.e.* the hafnium was pre-extracted into the organic phase before equilibrating with fresh inactive aqueous phase). The back extraction technique was especially important in order to obtain the maximum distribution values. The organic phases were prepared by shaking 16 ml benzene solutions of benzoylacetone with 4 ml 1 M $NaClO_4$ + 20 μl 2 M HCl stock solution of [175,181]Hf. Equal volumes of organic phase and 1 M $(Na,H)ClO_4$ were mixed in two different ways: either by shaking 1.29 ml phases in 5 ml glass tubes closed with polyethylene caps for $1-66$ h at 23 ± 1 °C (batch experiments) or by stirring 15 ml phases $5-30$ min at 25.0 °C in a glass vessel, the latter technique allowing investigation at different ph $(= -\log [H^+])$ or [HBA] in the same run. The distribution of hafnium was calculated from the measured gamma activity, using a well type NaI(Tl) crystal, for equal samples (0.400 ml) of each
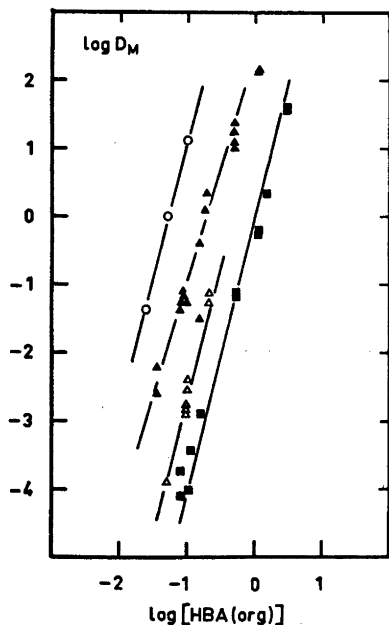
Fig. 1. The distribution of ²³³Pa(IV) and ¹⁷⁵,¹⁸¹Hf(IV) between dilute solutions of benzoyl-acetone in benzene and 1 M (Na, H)ClO$_4$ as a function of the benzoylacetone concentration [HBA(org)] at 25 °C and different hydrogen ion concentrations. △Pa(IV), ph 1.03; ○Pa(IV), ph 3.00; ▲Hf(IV), ph 1.00; ■Hf(IV) ph 0.00.

phase. Normally about 400 000 cpm were measured for each pair of samples. The background was about 130 cpm.

EXTRACTION OF Pa(IV) AND Hf(IV) WITH BENZOYLACETONE

The distribution of ²³³Pa(IV) and ¹⁷⁵,¹⁸¹Hf(IV) between dilute solutions of HBA in C$_6$H$_6$ and 1 M (Na,H)ClO$_4$ was studied at 25 °C. The influence of the concentration of HBA in the organic phase [HBA(org)] on the distribution D_M (M = Pa(IV) or Hf(IV)) was determined at different hydrogen concentrations, see Fig. 1.

Linear relationships between log D_M and log [HBA(org)] were found for the investigated ph ranges (1 − 3 for Pa(IV) and 0 − 1 for Hf(IV)). The slopes of the lines, ∂ log D_M/∂ log [HBA(org)] were close to 4 indicating that four molecules of HBA per molecule of metal were involved in the extraction mechanism. To further examine the composition of the ex-

tracted species the ph dependence of the distribution was measured at 0.096 M [HBA(org)] for Pa(IV) and at 0.147 M [HBA(org)] for Hf(IV), see Fig. 2. Also here linear relationships were found. The slope of the lines ∂ log D_M/∂ log ph being +2. The extraction of Hf(IV) was somewhat higher than for Pa(IV) but, in all the behaviour of the two metals was similar. The highest ph investigated in the case of Pa(IV) was around 3 because Cr²⁺ (present for reduction of Pa) forms Cr-HBA complexes at higher ph. However, there was no such ph limit for Hf(IV) and therefore a more thorough investigation of the ph dependence of the distribution of Hf(IV) was undertaken at different concentrations of HBA, see Fig. 3. All extraction curves rise with ph (the limiting slope for decreasing ph being ∂ log D_{Hf}/∂ ph = +2) and reach a plateau with a very high distribution factor (log D_{Hf} = 3.6). No decrease from this plateau value at ph up to 10 was found. The time for reaching equilibrium was studied by shaking or stirring for 5 min up to 66 h. The time needed for equilibrium seemed to be less than 5 min in most cases and was not found to depend on ph. However, a rather strong adsorp-

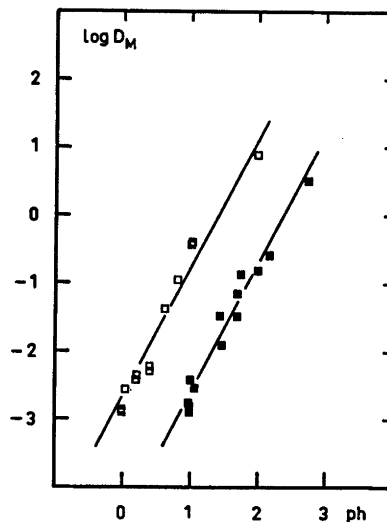Fig. 2. The influence of the hydrogen ion concentration on the distribution of ²³³Pa(IV) and ¹⁷⁵,¹⁸¹Hf(IV) between benzoylacetone in benzene and 1 M (Na,H)ClO$_4$ at 25 °C. ■Pa(IV) [HBA(org)] = 0.096 M; □Hf(IV) [HBA(org)] = 0.147 M.
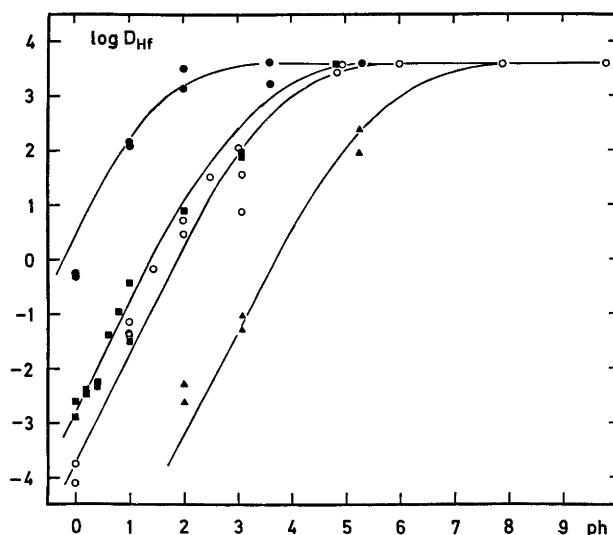
Fig. 3. The distribution of ^{175,181}Hf(IV) between benzene solutions of benzoylacetone and 1 M (Na,H)ClO$_4$ at 25 °C as a function of the hydrogen ion concentration at various benzoylacetone concentrations [HBA(org)]. [HBA(org)]: ●1.16 M, ■0.147 M, ○0.078 M, ▲0.0101 M.

tion of Hf on the glass walls was observed at ph 1−3 depending on the concentration of HBA. High concentrations reduced the adsorption and for lower and higher ph the adsorption was negligible. Similar observations concerning the adsorption of Th, in trace concentrations, on glass in the presence of acetylacetone has been made.[5] The distribution of Hf was not found to be affected by the adsorption.

The metal concentration was kept at trace levels; [Pa(IV)] ≈ 10^{-10} M and [Hf(IV)] ≈ 10^{-6} M. Changes of the metal concentrations did not influence the distribution.

EVALUATING THE EXTRACTION MECHANISM

The theory for extraction of a metal (M^{i+}) from an aqueous medium into an organic solvent in the presence of a chelating agent has been outlined in an earlier paper.[4] One can conclude from the partial derivatives ∂ log D_M/∂ log [H$^+$] = −2 and ∂ log D_M/∂ log [HBA]$_{org}$ = 4 of the linear parts of the corresponding distribution functions for Pa(IV) and Hf(IV), that the metals are extracted with HBA according to the following formula:

$$M^{i+} + 4HBA(org) - 2H^+ \rightleftharpoons$$
$$M(HBA)_4H_{-2}^{(i-2)+}(org)$$
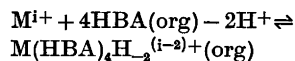
Only one extractable species is indicated. The electroneutrality criterium for the extracted species requires that the charge of the metal ion is 2. M^{2+} is then to be identified with HfO^{2+} (or Hf(OH)$_2$$^{2+}$) or PaO^{2+} (or Pa(OH)$_2$$^{2+}$). The formation of benzoylacetone complexes of Pa(IV) and Hf(IV), respectively, in aqueous phase can then be described by the formation constants $\beta_{x,y}$ related to the equilibria

$$M^{2+} + xHBA - yH^+ \rightleftharpoons M(HBA)_xH_{-y}.$$
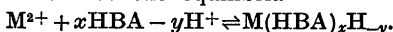
Possible values of x and y are listed in Table 1, taking Hf(IV) as an example.

The distribution of the metal may be written

$$D_M = \frac{\lambda_{4,-2}\beta_{4,-2}[HBA]^4[H^+]^{-2}}{\sum^{x,y}\beta_{x,y}[HBA]^x[H^+]^y}$$

where $\lambda_{4,-2}$ is the distribution constant for the extracted species M(HBA)$_4$H$_{-2}$. The distribution data of Hf(IV) was analysed using an iterative least squares method of the same type as had been used previously in determining the stability constants for Pa(V) acetylacetone complexes.[6] It turned out that within the accuracy of the primary data, the extraction

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Table 1. Possible composition of the hafnium benzoylacetone complexes in aqeous phase. Negative complexes as well as adduct formation on charged complexes are neglected.

x values	Possible species	Derived y values
4	$Hf(BA)_4$, $HfO(BA)_2(HBA)_2$ (or $Hf(OH)_2(BA)_2(HBA)_2$)	-2
3	$Hf(BA)_3{}^+$, $HfO(BA)_2HBA$ (or $Hf(OH)_2(BA)_2(HBA)$, $Hf(OH)$ $(BA)_3$)	$-1, -2$
2	$Hf(BA)_2{}^{2+}$, $HfO(BA)_2$ (or $Hf(OH)_2(BA)_2$, $Hf(OH)$ $(BA)_2{}^+$)	$0, -2, -1$
1	$Hf(BA)^{3+}$, $HfO(BA)^+$ (or $Hf(OH)_2BA^+$), $Hf(OH)BA^{2+}$	$1, -1, 0$
0	HfO^{2+} (or $Hf(OH)_2{}^{2+}$)	0

system could be described with only the two species M^{2+} and $M(HBA)_4H_{-2}$. No reasonable reliable conclusions concerning the presence of intermediate complexes could be made.

Assuming M^{2+} and $M(HBA)_4H_{-2}$ to be the main species the distribution function is simplified to

$$D_M = \frac{\lambda_{4,-2}\beta_{4,-2}([HBA][H^+]^{-1/2})^4}{1+\beta_{4,-2}([HBA][H^+]^{-1/2})^4}$$

It is found that all data (different [HBA] and [H$^+$]) coincide within experimental scatter with a single curve when plotting log D as a function of log $[HBA][H^+]^{-1/2}$, see Fig. 4.

The distribution constant $\lambda_{4,-2}$ for the hafnium benzoylacetone complex was found to be log $\lambda_{4,-2} = 3.6 \pm 0.1$. The extraction constant, $K_D(M) = [M(HBA)_4H_{-2} \text{ (org)}] [H^+]^2/ [M^{2+}][HBA(org)]^4$, for Pa(IV) and Hf(IV) was calculated to be log $K_D(Pa) = -0.7 \pm 0.1$ and log $K_D(Hf) = 0.6 \pm 0.2$.

Using the value log $k_D = 2.97 \pm 0.06$ for the partition constant of HBA [7] (25 °C, 1 M $NaClO_4 - C_6H_6$, $[HBA(org)] = 0.01 - 0.1$ M) log $\beta_{4,-2}$ can be calculated to be 8.9 ± 0.2. The stability constant, log $\beta_4' = 41.8 \pm 0.2$, for the reaction $M^{2+} + 4BA^- + 2H^+ \rightleftharpoons M(HBA)_4H_{-2}$ for hafnium was obtained using literature data for the dissociation of benzoylacetone,[8] $pK_a = 8.24$.

DISCUSSION

From the present investigation it was concluded that Pa(IV) in trace concentrations exists as PaO^{2+} (or $Pa(OH)_2{}^{2+}$) in perchlorate media in conformity with several other observations.[9] Similar species were also found for Hf(IV). Further, no hydrolysis of the species was observed, in the presence of
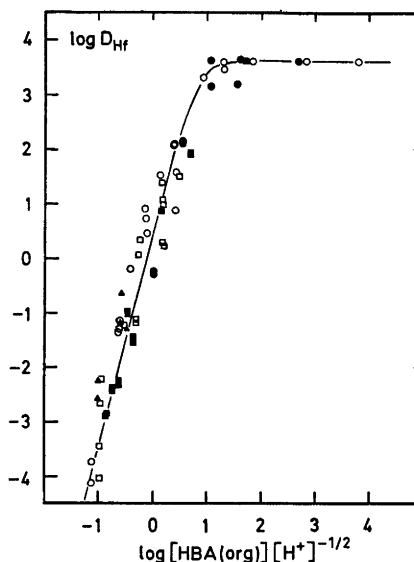

Fig. 4. The relationship between the distribution of [175,181]Hf(IV), between benzene solutions of benzoylacetone and 1 M (Na,H)ClO$_4$ at 25 °C, at various benzoylacetone [HBA(org)] and hydrogen ion concentrations, and the function $[HBA(org)][H^+]^{-1/2}$. The line is calculated from estimated stability constants. [HBA(org)]; ●1.16 M, ■0.147 M, ○0.078 M, ▲0.0101 M, □0.035 − 3.03 M.

benzoylacetone, for ph up to at least 10. The distribution of the elements was not affected by changes in the concentration of the elements indicating that no polynuclear species were developed. Neither is this to be expected due to the low concentrations ([Pa] ≈ 10^{-10} M, [Hf] ≈ 10^{-6} M) used. The polymerisation of Pa(IV) or Hf(IV) in 1 M HClO$_4$ is reported to be negligible [10,3] for [Pa] < 10^{-6} M or [Hf] < 10^{-3} M. The mononuclear hydrolysis of Hf(IV) has been the subject of several in-

vestigations [11] but conflicting conclusions were reached. Reported values of the first hydrolysis constant are disparate. A recent investigation [11] using both solvent extraction and potentiometric measurements shows that the hydrolysis of Hf(IV) is not so severe as previously believed. Only one set of hydrolysis constants has been reported. The constants being calculated from a rather limited solvent extraction study [3] using benzoylacetone and acetylacetone as extrating agents. The results were interpreted as a stepwise hydrolysation of Hf^{4+}. The reported data for benzoylacetone agrees with the present investigation. Except for the highest D-values, which were too low because the back extraction technique was not used, all data (ph 0 − 3) fitted the function $\partial \log D_{Hf} = 2\ \partial ph$. A similar linear relationship between $\log D$ and ph was also obtained from the acetylacetone data and this suggests that the extent of hydrolysis of Hf(IV) was not changed. The similar chemical properties of Zr and Hf justifies a comparison of the results from studies of Zr. Using oxine as extracting agent [12] ZrO^{2+} (or $Zr(OH)_2^{2+}$) was assumed to dominate at ph 0.8 − 1.5. No further hydrolysis for ph less than 4 was observed. Another solvent extraction study [13] of Zr with acetylacetone and benzoylacetone indicated the existence of ZrO^{2+} (or $Zr(OH)_2^{2+}$.) By titration of zirconyl compounds in neutral solutions with potassium fluoride the number of OH groups displaced was determined and it was concluded that $Zr(OH)_2^{2+}$ rather than ZrO^{2+} existed. [14]

Pa(IV) and Hf(IV) are here shown to be extracted in a similar fashion. The extracted complex can be written in the general form $M(HBA)_4H_{-2}$. The formula for this species may be written in several equal forms. Taking Pa as an example: $Pa(BA)_4$ or $PaO(BA)_2(HBA)_2$ (or $Pa(OH)_2(BA)_2(HBA)_2$) which also can be written $Pa(BA)_4(H_2O)_n$, where $n = 0,1,2$. Complexes with benzoylacetone adducts are not expected according to the theory [15] of solvent extraction, as the maximum distribution ($D = \lambda_{4,-2}$) was not dependent on the HBA concentration ($[HBA]_{org} = 0.03 − 3$ M). On the other hand $Pa(BA)_4$ and $Hf(BA)_4$ are expected from the comparison with other β-diketonates of Zr(IV) and Hf(IV). Tetrakis diketonates [16] with acetylacetone, trifluoroacetylacetone, 2-

furoylacetone, 2-furoyltrifluoroacetone, 2-thenoylacetone, 2-pyrroyltrifluoroacetone and 2-thenoyltrifluoroacetone have been prepared. Contradictory to this $ZrO(BA)_2$ has been prepared [17] in the excess of Zr relative to HBA, but in general $Me(diket)_4$ is expected to be formed.

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