

Solvent extraction of hafnium

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Abstract. Mixed chelates of hafnium in benzene medium was studied by the method of solvent extraction. Various β -diketones and their mixtures were used for the study. The equilibrium constants for the mixed complexes were evaluated. Synergism in the extraction of hafnium in the presence of two dissimilar acidic extractants viz. HDEHP and a β -diketone was also investigated. The stoichiometry of the extracted species was determined by graphical method.

Keywords. Hafnium; solvent extraction; mixed chelates; synergism,

1. Introduction

Solvent extraction affords a convenient method for the study of mixed complexes and synergism. Mixed β -diketones of some divalent metals have been studied by Sekine and Dyrssen (1964), Newman and Klotz (1967) and others. Mixed β -diketones of indium have been studied (Sudersanan and Sundaram 1975a) from these laboratories. However, studies on tetravalent metals are few. Extraction studies of hafnium are of interest in view of difficulties associated with its separation from zirconium and other metals. In this paper a study of the mixed chelates of hafnium with a number of β -diketones, viz., thenoyltrifluoroacetone (HTTA), benzoyltrifluoroacetone (HBFA), furoyltrifluoroacetone (HFTA) and dibenzoylmethane (HDBM) has been reported.

Synergism in the extraction of metal ions by a mixture of an alkylphosphoric acid or a β -diketone and an alkylphosphorous ester like tributyl phosphate, tri-*n*-octylphosphine oxide, etc., has been studied (Irving and Edgington 1960, 1961; Healy 1961; Peppard *et al* 1959 a, b). Recently, synergism in the presence of β -diketone and an alkyl phosphoric acid has been reported. This type of synergism was first reported in the case of indium (Sudersanan and Sundaram 1977) and similar results were also observed for scandium. Hence such a study in the case of other metals was desirable. A report on the synergism in the extraction of hafnium by a mixture of di-2-ethyl-hexyl phosphoric acid (HDEHP) and HTTA or HBFA is presented in this paper.

2. Experimental

HTTA and HDBM (Koch-Light Lab.) and HFTA and HBFA (K & K Lab.) were used without further purification. Benzene (BDH Analar) was used as the diluent.

HDEHP (BDH, LR) was purified by the method of Peppard *et al* (1958) and the purity was estimated as over 99% by titration with alkali. Hafnium in the form of $\text{Hf}^{175+181}$, obtained from Isotope Division, BARC, was converted to perchlorate before use.

Ten millilitres of the aqueous phase containing the tracer metal (concentration $\sim 10^{-6}$ M) in 2 M perchloric acid was equilibrated for about 5 hr at room temperature ($23 \pm 1^\circ\text{C}$) with an equal volume of the benzene phase containing the chelating ligand or the mixture of ligands. The phases were separated after extraction and 1 ml aliquots were used for estimations with a γ -ray spectrometer (M/s Electronics Corporation of India Ltd.). The readings were corrected for the background activity.

3. Results and discussion

Larsen and Terry (1953) as well as Huffman *et al* (1955) have studied the distribution of some of these β -diketones in 2 or 4M perchloric acid. The extraction of hafnium by the individual ligands investigated here was studied with a view to obtain data under the present experimental conditions for comparison with those obtained for mixed chelates.

The distribution ratio (D_0) of hafnium was determined as a function of the concentrations of perchloric acid and HTTA, HBFA or HFTA in benzene medium. The partition coefficient (P_{HA}) of HBFA was determined spectrophotometrically as 200 and the reported values of 26.3 for HTTA (Hala 1967), 7.41 for HFTA (Larsen and Terry 1953) and 2.24×10^5 for HDBM (Moucka and Stary 1961) between 2 M perchloric acid and benzene were used for the calculations. The concentration of the β -diketone in the organic phase was calculated from

$$[HA]_0 = [HA]_{\text{tot}} \{P_{HA}/P_{HA} + 1\}, \quad (1)$$

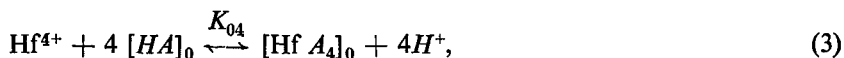
where $[HA]_0$ and $[HA]_{\text{tot}}$ are the concentrations of the chelating agent in the organic phase and its total amount respectively. The plots of $\log D_0$ vs $\log [H]$ or $\log [HA]$ resulted in straight lines with slopes of about 4 indicating the extracted species to be $\text{Hf} A_4$ and the absence of water soluble complexes. The equilibrium constants were calculated from

$$K_{04} = D_0 [H]^4 [HA]_0^{-4} \quad (2)$$

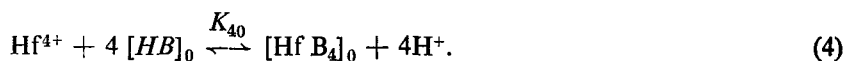
as $10^{7.77}$, $10^{7.28}$ and $10^{6.50}$ for HTTA, HFTA and HBFA systems respectively. The extraction of hafnium by HDBM was negligible under the present experimental conditions.

4. Study of mixed chelates

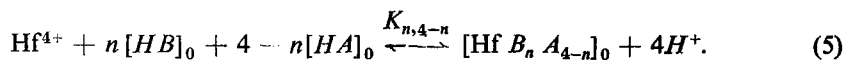
The extraction of hafnium by a β -diketone HA can be written as



and by another β -diketone HB as



It is assumed that (i) hydrolysis of hafnium does not occur in view of the high acidity (ii) hafnium exists in the aqueous phase as the uncomplexed metal ion and (iii) the extractants do not interact. In the presence of both the extractants, mixed chelates are formed, the reaction being



The equilibrium constant for the formation of the mixed chelate can be written as

$$K_{n,4-n} = [\text{Hf B}_n \text{A}_{4-n}]_0 [\text{H}]^4 [\text{Hf}]^{-1} [\text{HB}]_0^{-n} [\text{HA}]_0^{-(4-n)} \quad (6)$$

Substituting in terms of the distribution ratio D and the equilibrium constants, one gets on rearranging

$$F_0 = D[\text{H}]^4 [\text{HA}]_0^{-4} = K_{04} + K_{13} [\text{L}] + K_{22} [\text{L}]^2 + K_{31} [\text{L}]^3 + K_{40} [\text{L}]^4, \quad (7)$$

where L represents $[\text{HB}]_0/[\text{HA}]_0$. This function can be solved for the individual equilibrium constants.

Mixed chelates of hafnium with β -diketones were studied by choosing the ligands in such a manner that (i) the two chelating agents form chelates of almost equal stability, e.g., HTTA-HBFA, HTTA-HFTA and HFTA-HBFA and (ii) the two parent ligands differ in stability, one forming a comparatively weaker chelate, e.g., HDBM-HFTA and HDBM-HTTA.

5. Chelates of equal stability

5.1. Hafnium-HTTA-HBFA system

The extraction of hafnium by a mixture of HTTA (HB) and HBFA (HA), both containing $-\text{CF}_3$ groups, and having similar extracting abilities was studied at an acidity of 2.0 M perchloric acid by varying the concentration of one ligand keeping that of the other constant. The ratio $[L]$ was varied from 0.05 to 20. A considerable increase in extraction was observed as compared to the sum of the extractabilities of the individual ligands. The function F_0 given by (7) was calculated (table 1) at different values of $[L]$ and the equilibrium constants for the various species were evaluated by the graphical method (table 2, figure 1). The values for the parent complexes obtained from these data agreed well with those obtained for simple chelates indicating the absence of any interaction between the ligands or the chelates. The absence of chelates of the type $\text{MB}_n\text{A}_{4-n}$. HA is also indicated from the plot of F_0 vs $[L]$.

Table 1. Extraction of hafnium by HTTA and HBFA

 $P_{\text{HTTA}} = 26.3$; $P_{\text{HBFA}} = 200$; $(\text{HClO}_4) = 2.0 \text{ M}$

$[\text{HTTA}]_0$ $\times 10^2 \text{ M}$	$[\text{HBFA}]_0$ $\times 10^2 \text{ M}$	$-\text{Log } D$	$-\text{Log } [L]$	$\text{Log } F_0$
0.10	1.99	1.31	1.32	6.70
0.15	1.99	1.26	1.14	6.75
0.19	1.99	1.15	1.01	6.86
0.24	1.99	1.10	0.92	6.91
0.39	1.99	0.91	0.71	7.10
0.48	1.99	0.76	0.62	7.25
0.58	1.99	0.69	0.54	7.32
0.77	1.99	0.51	0.41	7.50
0.96	1.99	0.29	0.32	7.72
1.16	1.99	0.12	0.24	7.89
1.45	1.99	-0.06	0.14	8.07
1.93	1.99	-0.38	0.01	8.39
1.93	1.49	-0.24	-0.11	8.74
1.93	1.00	-0.05	-0.29	9.26
1.93	0.50	0.13	-0.59	10.29
1.93	0.25	0.23	-0.89	11.39
1.93	0.10	0.29	-1.29	12.92

Table 2. Equilibrium constants for mixed chelates of hafnium

System	Equilibrium constant (log)	$\text{Log } (K_{n, 4-n})$ stat	$\text{Log } K_M$	$\text{Log } K_S$	
Hf-HTTA-HBFA	K_{04}	6.54			
	K_{13}	7.40	7.47	0.53	-0.07
	K_{22}	8.00	7.97	0.80	0.03
	K_{31}	7.18	8.12	-0.34	-0.95
	K_{40}	7.85			
Hf-HTTA-HFTA	K_{04}	7.26			
	K_{13}	8.15	8.02	0.73	0.13
	K_{22}	8.23	8.36	0.65	-0.13
	K_{31}	7.48	8.34	-0.26	-0.86
	K_{40}	7.90			
Hf-HFTA-HBFA	K_{04}	6.48			
	K_{13}	7.20	7.30	0.50	-0.11
	K_{22}	7.66	7.70	0.73	-0.04
	K_{31}	7.52	7.75	0.37	-0.23
	K_{40}	7.37			
Hf-HDBM-HFTA	K_{04}	7.27			
	K_{13}	6.89	7.36	0.13	-0.47
	K_{22}	5.78	7.02	-0.46	-1.24
	K_{31}	5.86	6.32	0.14	-0.46
	K_{40}	5.20			
Hf-HDBM-HTTA	K_{04}	7.70			
	K_{13}	7.22	7.68	0.14	-0.46
	K_{22}	6.81	7.23	0.36	-0.42

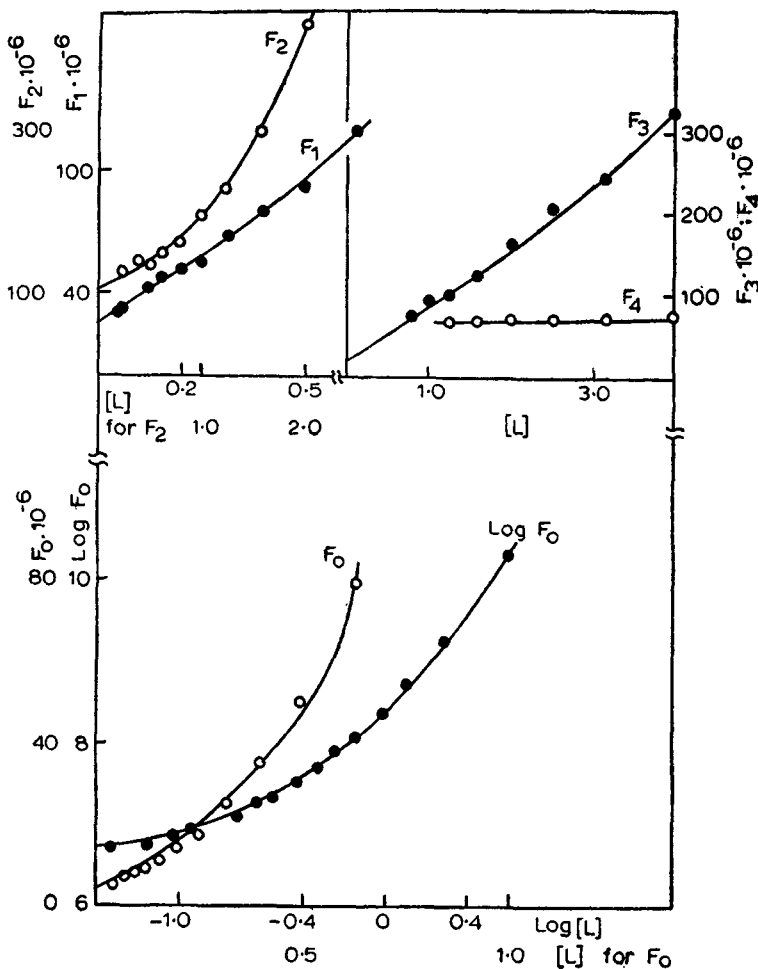


Figure 1. Extraction of hafnium by HTTA and HBFA

5.2 Hafnium—HTTA—HFTA and HFTA—HBFA systems

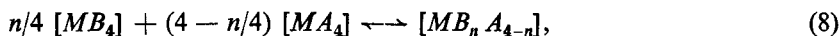
Experiments were carried out in a similar manner, the ratio $[L]$ being varied in the range of 0.07 to 4. The equilibrium constants were evaluated from the plots of $\log F_0$ vs $[L]$ and are given in table 2.

6. Chelates of unequal stability

6.1. Hafnium—HDBM (HB) and HFTA/HTTA (HA) systems

These systems have been studied as examples of the case where the extractabilities of the two chelating agents are different. From the measured values of the distribution ratio as a function of $[L]$, the equilibrium constants were evaluated (table 2).

The formation of mixed complexes has also been considered on statistical grounds. For a reaction



the mixing constant K_M which gives a measure of the stability of the mixed complex, is given by

$$(K_M)_{n, 4-n} = [MB_n A_{4-n}] [MB_4]^{-n/4} [MA_4]^{-(4-n)/4} \quad (9)$$

or in terms of the equilibrium constants as

$$(K_M)_{n, 4-n} = K_{n, 4-n} K_{40}^{-n/4} K_{04}^{-(4-n)/4}. \quad (10)$$

The stabilisation factor K_s defined by

$$K_s = (K_{BA})_{\text{obs}} / (K_{BA})_{\text{stat}} \quad (11)$$

is a measure of the stabilisation of the complex over the statistical value. K_{stat} for the present system is defined as

$$(K_{n, 4-n})_{\text{stat}} = \frac{4!}{n! (4-n)!} \{ K_{40}^n K_{04}^{4-n} \}^{1/4}. \quad (12)$$

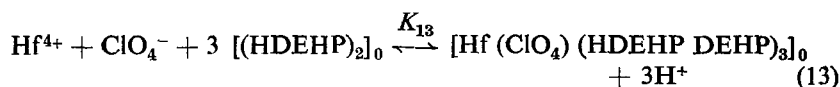
The calculated values of K_M , K_s , and K_{stat} for the mixed chelates of hafnium are also presented in table 2. It can be seen that chelates of the type MA_2B_2 have a higher stability in systems where the ligands are of unequal strength. For most of the systems the equilibrium constants obtained are nearly the same as for the parent chelates on statistical considerations. K_M gives a measure of compatibility of different ligands in the inner sphere of the metal ion. β -diketones being compatible on the basis of structural and geometric considerations form mixed chelates and the value of K_M is greater than unity for most of the species.

7. Synergism in the presence of HDEHP and HTTA/HBFA

Synergism was observed in the extraction of hafnium in the presence of a mixture of two acidic reagents HDEHP and a β -diketone like HTTA or HBFA, a phenomenon first reported in the case of indium.

The distribution of hafnium was studied as a function of the concentrations of perchloric acid and the extractants. The log-plots indicate that three molecules each of HDEHP and hydrogen ions are involved in the extraction process. Alkylphosphoric acids are known to exist as dimers or polymers in organic solvents. It was confirmed that HDEHP existed as a dimer from the measurement of molecular weight of HDEHP using a Perkin-Elmer molecular weight apparatus (Sudersanan 1975b) It was also observed (Navratil 1967; Peppard 1959 b, 1960) that in the case of extrac-

tion of highly charged cations by dialkylphosphoric acids, the aqueous phase anions accompanied the extracted species. Since only three hydrogen ions are involved in the extraction reaction it was assumed that the extraction reaction could be represented by



The equilibrium constant, K_{13} , given by

$$K_{13} = D_0 [\text{H}]^3 [(\text{HDEHP})_2]_0^{-3} [\text{ClO}_4]^{-1} \quad (14)$$

has been calculated in the formality scale as $10^{8.15}$.

8. Extraction of hafnium by HDEHP and HTTA/HBFA

The extraction of hafnium by a mixture of HDEHP and HTTA or HBFA was studied in benzene medium as a function of the concentrations of the extractants and perchloric acid by varying the concentration of one, keeping those of the other two constant. The distribution ratio in the presence of the mixture was higher than the sum of the individual values and at a constant acidity can be equated as

$$D = (D_0)_{\text{HTTA}} + (D_0)_{\text{HDEHP}} + D_{\text{syn}} \quad (15)$$

where D_{syn} represents the distribution ratio of the synergic species and can be evaluated from the values due to HDEHP and HTTA or HBFA alone. It was assumed that the two reactants did not react with each other and no aqueous phase complexes were present. Figure 2 represents the plots of $\log D_{\text{syn}}$ vs $\log [(\text{HDEHP})_2]_0$ and $\log [(\text{HTTA})_0]$ while figure 3 represents the corresponding plots for HBFA. The slopes of about three for plot 1 and about one for plots 2 and 3 indicate that the

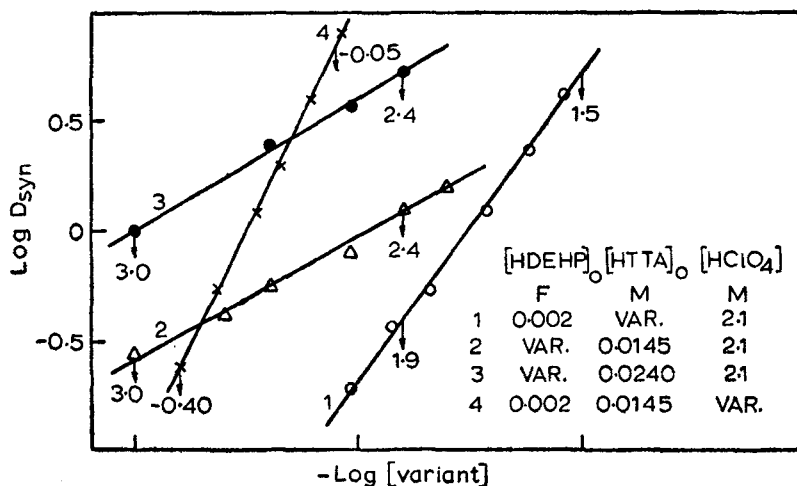


Figure 2. Extraction of hafnium by HDEHP and HTTA

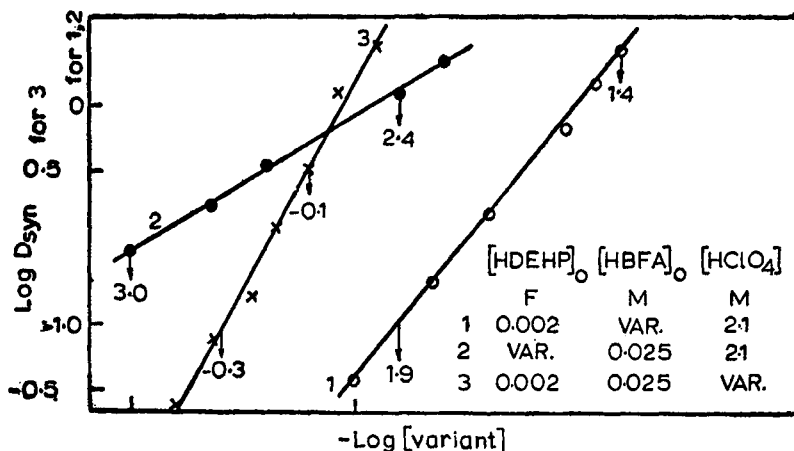
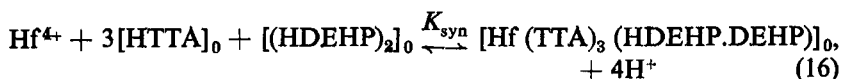


Figure 3. Extraction of hafnium by HDEHP and HBFA

synergic species contains three molecules of HTTA or HBFA and one of HDEHP. Plot 4 represents the dependence of hydrogen ions on the reaction, the slope of four indicating the liberation of four hydrogen ions. Hence the synergic reaction can be written as



and the distribution ratio D_{syn} of the synergic species by

$$D_{\text{syn}} = [\text{Hf}(\text{TTA})_3(\text{HDEHP}.\text{DEHP})]_0 [\text{Hf}^{4+}]^{-1} \quad (17)$$

The equilibrium constant for the synergic reaction represented by

$$K_{\text{syn}} = D_{\text{syn}} [\text{H}]^4 [\text{HTTA}]_0^{-3} [(\text{HDEHP})_2]_0^{-1} \quad (18)$$

was also calculated (table 3).

It can be seen from table 3 that the synergic species are more stable than the simple chelates. The extracted species has been found to be mixed chelate where one of the co-ordinated ligands is replaced by the other extractant. The increased stability may

Table 3. Values of equilibrium constants

System	log equilibrium constant
Hf-HDEHP	8.15
Hf-HTTA	7.77
Hf-HBFA	6.50
Hf-HDEHP-HTTA	9.21
Hf-HDEHP-HBFA	8.49

be due to a greater asymmetry of the charge distribution and other steric factors. In the case of indium (Sudersanan *et al* 1977) it was found that the enthalpy of reaction remains almost same while the entropy effect was predominant in stabilising the complex. Similar effects may be operating in this system as well.

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