ACTA CHEMICA SCANDINAVICA 21 (1967) 2457–2462

The Fluoride Complexes of Zirconium (IV)

A Potentiometric Investigation

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The fluoride complexes formed by zirconium(IV) have been studied by means of potentiometric measurements (using the Fe^{3+}/Fe^{2+} electrode). The stability constants K_n^* for the complex equilibria

$$ZrF_{(n-1)} + HF \rightleftharpoons ZrF_n + H^+$$

where $2 \leq n \leq 6$, have been determined. The results refer to 4 M $HClO_4$, and a temperature of 20°C.

The fluoride complexes formed by zirconium(IV) in a 4 M perchloric acid medium have been investigated previously by means of the cation exchange method.[1] Only the first two stability constants could be calculated from the data obtained. The stability constants, $K_n^*(3 \leq n \leq 6)$, have been determined by Buslaev[2] using the "ferric" method of Brosset and Orring.[3] The results refer to 0.5 M NH_4ClO_4 and a hydrogen ion concentration of 10^{-2} M. In a solvent extraction investigation, Connick and McVey[4] studied the distribution of zirconium(IV) between 2 M $HClO_4$ and a benzene solution of thenoyltrifluoroacetone (HTTA), there being varying concentrations of hydrofluoric acid in the aqueous phase. From the results of that work, the first three stability constants may be calculated. Thus, no complete complex formation curve has been determined in the same medium. The reason for the present investigation was to obtain as large a part of the Zr^{4+}...HF formation curve as possible, in the same medium.

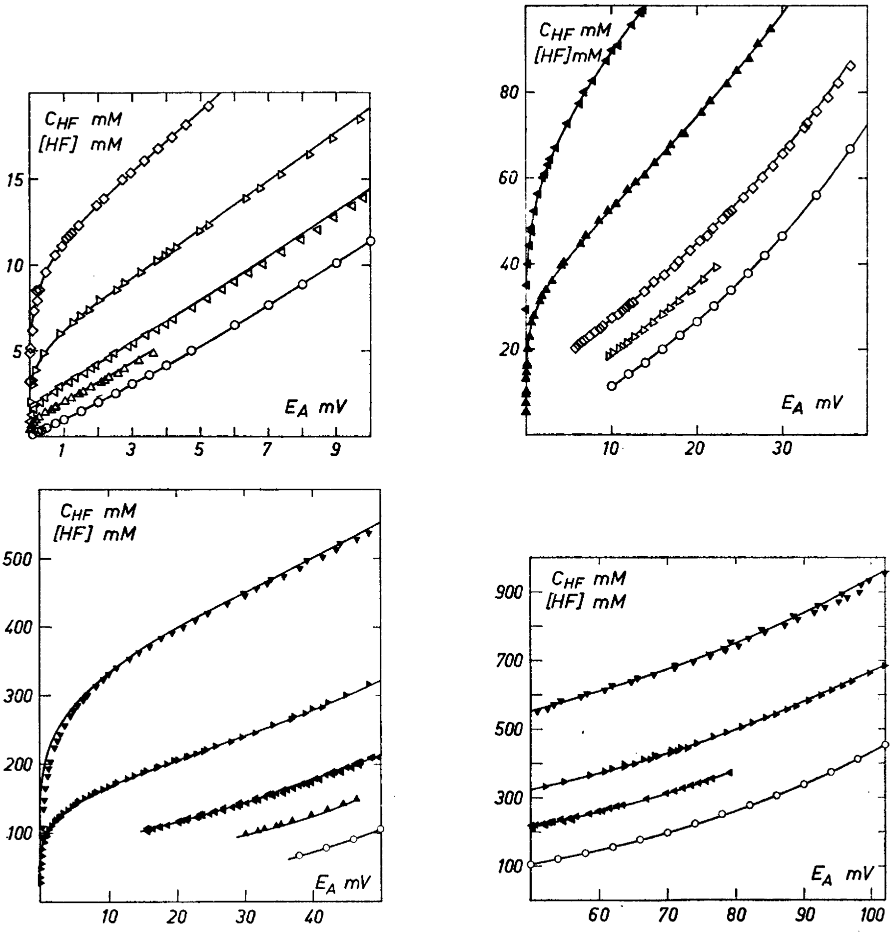
A 4 M $HClO_4$ medium was selected in order to minimize the hydrolysis of Zr(IV) and also in order to be able to compare the results with those obtained for Hf(IV).[5] In the previous Hf^{4+}...HF investigation it was found that the measurements could be extended to higher ligand concentrations by the "ferric" method than by the solvent extraction method using HTTA. The stability constants where $n \geq 3$ are also determined with better accuracy using the former method. For these reasons it was decided to study the zirconium(IV) fluoride complexes by the "ferric" method.

EXPERIMENTAL

Chemicals. Stock solutions of Zr(IV) in 4.00 M $HClO_4$ were prepared from $ZrOCl_2.8H_2O$, Merck, *pro analysi* in the same manner as the Hf(IV) stock solutions used in Ref. 5. The Zr(IV) stock solutions were analysed according to Fritz and Johnson.[6] The other chemicals were the same as used in Ref. 5.

Procedure. The measurements were performed as described before.[5] To compensate for the increase in acidity, caused by the hydrogen ions set free in the complex formation reaction, the solution T_2 had the composition:

$$T_2\text{: } C_{HF}' \text{ M HF, } (4.00-k\ C_{HF}') \text{ M } HClO_4$$



Figs. 1, 2, 3, and *4.* The connection between C_{HF} and E_A. For the lowest curve $C_M = 0$ This curve has been calculated using the constants $\beta_{1H}^{III} = 40.3\ M^{-1}$ and $\beta_{2H}^{III} = 180\ M^{-2}$. Circles represent the free ligand concentrations, obtained in the present investigation from corresponding values of C_{HF} and C_M. The experimental data were obtained in titration series having $C_{III} = 0.379$ mM, $C_{II} = 0.478$ mM and the following concentrations (in mM) of Zr(IV): 0.497 △; 0.991 ◁; 2.477 ▷; 4.974 ◇; 13.14 ▲; 24.77 ◀; 49.54 ▶ and 102.7 ▼. The curves have been calculated using the constants obtained.

Table 1. Corresponding values of $\bar{n}$, [HF] and the functions X_{I}, X_{II}, X_{III}, X_{IV}, X_{V}, X_{VI}.

E_A mV	[HF] mM	$\bar{n}$	$X_I \times 10^{-7}$ M^{-1}	$X_{II} \times 10^{-9}$ M^{-2}	$X_{III} \times 10^{-11}$ M^{-3}	$X_{IV} \times 10^{-12}$ M^{-4}	$X_V \times 10^{-13}$ M^{-5}	$X_{VI} \times 10^{-13}$ M^{-6}
	0.000		*0.00066*	*0.0429*	*0.1040*	*0.485*	*0.418*	*0.22*
0.10	0.092	1.35	0.00105	0.0427				
0.15	0.136	1.46	0.00126	0.0439				
0.25	0.230	1.63	0.00168	0.0446				
0.35	0.318	1.74	0.00213	0.0461				
0.50	0.462	1.83	0.00285	0.0474				
0.75	0.702	1.97	0.00416	0.0499				
1.00	0.943	2.08	0.00566	0.0530				
1.50	1.459	2.19	0.00934	0.0595				
2.00	1.972	2.31	0.01355	0.0654	0.1141			
2.50	2.483	2.41	0.01850	0.0718	0.1164			
3.00	3.021	2.49	0.02452	0.0790	0.1195			
3.50	3.548	2.56	0.03126	0.0862	0.1220			
4.00	4.134	2.60	0.03969	0.0944	0.1246			
5.00	5.34	2.72	0.06068	0.1125	0.1304			
6.00	6.51	2.82	0.08621	0.1315	0.1362			
7.00	7.68	2.92	0.1174	0.1521	0.1423			
8.00	8.86	3.00	0.1554	0.1746	0.1486			
9.00	10.11	3.07	0.2032	0.2003	0.1557	0.511		
10.00	11.41	3.13	0.2619	0.2289	0.1630	0.517		
12.00	14.07	3.26	0.4158	0.2950	0.1792	0.534		
14.00	16.86	3.36	0.6323	0.3746	0.1967	0.550		
16.00	19.94	3.45	0.9483	0.4752	0.2168	0.566		
18.00	23.22	3.54	1.388	0.5973	0.2388	0.580		
20.00	26.37	3.62	1.929	0.7311	0.2610	0.595		
22.00	30.01	3.69	2.720	0.9064	0.2877	0.612		
24.00	33.85	3.75	3.775	1.115	0.3168	0.629	0.425	
26.00	37.79	3.81	5.134	1.358	0.3481	0.646	0.426	
28.00	42.04	3.88	6.953	1.654	0.3832	0.664	0.426	
30.00	46.49	3.93	9.314	2.003	0.4217	0.683	0.426	
34.00	56.2	4.03	16.46	2.928	0.5131	0.728	0.432	
38.00	66.9	4.11	28.13	4.205	0.6223	0.775	0.434	
42.00	79.1	4.19	47.80	6.045	0.7591	0.828	0.434	
46.00	91.5	4.28	76.69	8.386	0.9123	0.884	0.436	0.20
50.00	106.0	4.35	125.4	11.83	1.112	0.951	0.440	0.21
54.00	121.5	4.43	199.3	16.40	1.347	1.023	0.443	0.21
58.00	138.4	4.49	313.1	22.62	1.632	1.104	0.447	0.21
62.00	156.9	4.56	487.8	31.09	1.979	1.195	0.453	0.22
66.00	177.4	4.61	758.2	42.74	2.407	1.298	0.458	0.23
70.00	199.0	4.66	1152	57.89	2.907	1.408	0.464	0.23
74.00	222.7	4.70	1744	78.31	3.515	1.531	0.470	0.23
78.00	249.8	4.73	2675	107.1	4.285	1.674	0.476	0.23
82.00	276.8	4.78	3934	142.1	5.133	1.817	0.481	0.23
86.00	306.7	4.80	5807	189.3	6.172	1.979	0.487	0.22
90.00	338.6	4.84	8482	250.5	7.397	2.154	0.493	0.22
94.00	373.4	4.86	12370	331.3	8.871	2.348	0.499	0.22
98.00	412.0	4.87	18100	439.3	10.66	2.562	0.504	0.21
102.0	455.0	4.86	26570	584.0	12.83	2.798	0.508	0.20

where $k = 1-[HF]C_{HF}^{-1}$. It can be shown that $\lim_{[HF]\to 0} k = \beta_{1H}C_M(1 + \beta_{1H}C_M)^{-1}$. As $C_M \geq 0.497 \times 10^{-3}$ M and $\beta_{1H} = 2.3 \times 10^5$ M^{-1} k is almost equal to 1 for low values of C_{HF}. Therefore, the titrations were initiated using a T_2 solution having $k = 1$. From the $C_{HF}(E_A)$ curve thus obtained, it was easy to see when a new solution, having a lower k value, was needed. When this was the case a new cell was set up. The last part of the previous $C_{HF}(E_A)$ curve was remeasured, using the new T_2 solution, before the titration was continued to higher ligand concentrations. The different k values used were 1, 0.8, 0.7, 0.75, 0.6, 0.5, 0.4, and 0. Depending on the actual C_M value being investigated, a selection amongst these was taken. The differences between the results obtained from T_2 solutions having adjacent k values were about 1 % for ligand concentrations corresponding to k values between the ones used.

RESULTS

The derivation of the stability constants from the emf data has been described in Ref. 5, which ought to be consulted concerning details of the calculations. The notations will be the same as in Ref. 5.

The experimental data obtained in the various titration series are given in Figs. 1, 2, 3, and 4. Values of $\bar{n}$ and [HF] were calculated graphically as described before. These values are given in Table 1. For high values of C_M, the $E_A(C_{HF})$ curves increase very fast in the beginning, giving uncertain values of C_{HF} for small values of E_A. Thus for [HF] < 0.5 mM only results from titration series having $C_M \leq 4.97$ mM were used. Since the values of $\bar{n}$ found for a certain [HF] turn out to be independent of C_M, it may be concluded that only mononuclear complexes are formed under the present conditions. The limits of error of both $\bar{n}$ and [HF] were less than 2 %. By graphical integration of $\bar{n}$ [HF]$^{-1}$ as a function of [HF], $X_H X_{H0}^{-1}$ was obtained. The lower limit of integration was chosen to be $[HF]_0 = 0.919 \times 10^{-4}$ M. When calculating X_I, the term X_{H0}^{-1} was neglected, since no value of $X_{H0}^{-1} \neq 0$ could be obtained from plotting $X_H X_{H0}^{-1}$ against [HF]. The functions X_I, X_{II} *etc.* are also included in Table 1. By extrapolating these to [HF] = 0, the following constants were obtained:

$$\beta_{1H}X_{H0}^{-1} = (0.7 \pm 0.1) \times 10^4 \text{ M}^{-1}$$
$$\beta_{2H}X_{H0}^{-1} = (0.43 \pm 0.02) \times 10^8 \text{ M}^{-2}$$
$$\beta_{3H}X_{H0}^{-1} = (1.04 \pm 0.06) \times 10^{10} \text{ M}^{-3}$$
$$\beta_{4H}X_{H0}^{-1} = (0.49 \pm 0.04) \times 10^{12} \text{ M}^{-4}$$
$$\beta_{5H}X_{H0}^{-1} = (0.42 \pm 0.04) \times 10^{13} \text{ M}^{-5}$$
$$\beta_{6H}X_{H0}^{-1} = (0.2 \pm 0.1) \times 10^{13} \text{ M}^{-6}$$

The limits of error were estimated graphically. The $E_A(C_{HF})$ curves calculated using these constants are given in Figs. 1, 2, 3, and 4. The experimental values obtained for the various titration series are also included. Using $\beta_{1H}^{III} = 40.3$ M^{-1} and $\beta_{2H}^{III} = 180$ M^{-2} for the fluoride complexes of Fe^{3+}, the E_A([HF]) curve having $C_M = 0$ was calculated. For a comparing with this curve, the free ligand concentrations, obtained in the present investigation from corresponding values of C_{HF} and C_M, are also plotted.

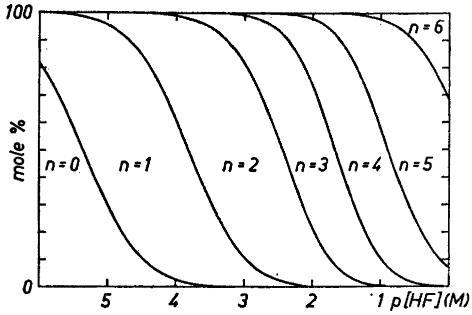


Fig. 5. The distribution of Zr(IV) between different fluoride complexes, ZrF_n, calculated from the stability constants found ($K_1^* = 9 \times 10^5$ M^{-1} has been taken from the cation exchange investigation).

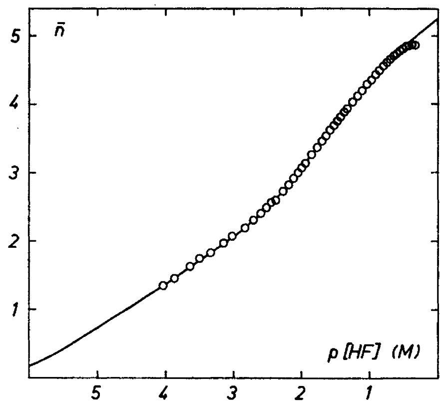


Fig. 6. Complex formation curve for the zirconium(IV) fluoride system. The circles represent corresponding values of $\bar{n}$ and [HF] experimentally measured. The curve has been calculated from the stability constants found ($K_1^* = 9 \times 10^5$ M^{-1} has been taken from the cation exchange investigation).

DISCUSSION

The stability constants, K_n^* where $2 \leq n \leq 6$, determined in the present work are given in Table 2. The results conform closely with those obtained in Refs. 2 and 4 under somewhat different conditions. Undoubtedly, six complexes are formed within the ligand concentration range investigated. The distribu-

Table 2. The stability constants K_n^* for the fluoride complexes of Zr(IV) in 4 M $HClO_4$ and at 20°C obtained in the present investigation. The results reported in Refs. 4 and 2, valid in 2 M $HClO_4$, 25°C and 0.5 M NH_4ClO_4, 10^{-2} M $HClO_4$, 25°C, respectively, are also given. The corresponding constants for Hf(IV), determined in Ref. 5 are included for comparison.

Ref.	Method	$K_1^* \times 10^{-5}$	$K_2^* \times 10^{-4}$	$K_3^* \times 10^{-3}$	$K_4^* \times 10^{-2}$	$K_5^* \times 10^{-2}$	K_6^*
				Hafnium			
Ref. 5	extr. and emf	3.3 ± 0.2	1.1 ± 0.2	1.1 ± 0.2	1.6 ± 0.3	0.5 ± 0.1	3 ± 2
				Zirconium			
This work	emf		2.6 ± 0.5	1.0 ± 0.1	1.9 ± 0.3	0.34 ± 0.06	2 ± 1
Ref. 1	cation exch.	9 ± 1	3				
Ref. 4	extr.	6.3 ± 0.63	2.10 ± 0.21	0.67 ± 0.20			
Ref. 2	emf			0.50	0.672	0.320	7.2

tion of zirconium(IV) between these complexes is shown in Fig. 5. Using the K_n* values determined in the present investigation together with K_1* calculated from the cation exchange measurements of Ref. 1, the complex formation curve has been calculated and is shown in Fig. 6. This curve describes the experimentally obtained $\bar{n}$ and [HF] values very well. The small deviation at the highest $\bar{n}$ and [HF] values was also observed for hafnium (IV)[5] and is just outside the experimental error limits. The deviation may be due to medium changes.

The investigation of the Hf(IV) fluoride complexes, reported in Ref. 5, was carried out in the same medium as that used in the present investigation. The stability constants, K_n*, $n \geq 3$, for both systems are very close to each other, *cf.* Table 2, reflecting the similarities in chemical properties of the two elements. The first and second constants are much larger for Zr(IV) than for Hf(IV). The lower stability of the hafnium(IV) complexes may be associated with the greater size of the Hf^{4+} ion.

Statens naturvetenskapliga forskningsråd (The Swedish Natural Science Research Council) has supported this investigation by a grant which is gratefully acknowledged. I wish to express my gratitude to Professor S. Fronæus, Dr. Sten Ahrland, and Dr. Ingmar Grenthe for their kind interest and many fruitful discussions. My thanks are also due to Fil.kand. Christer Hellner for his skilful technical assistance, and to Dr. David Williams for his linguistic revision of the manuscript.

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Received June 9, 1967.