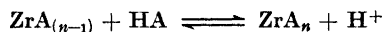


Solvent Extraction Studies of the Formation of Fluoride and Sulphate Complexes of Zirconium (IV)

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The distribution of zirconium(IV) between aqueous solutions containing fluoride or sulphate ions and xylene solutions of thenoyltrifluoroacetone has been studied. All measurements have been performed in a 4 M perchloric acid medium, and at a temperature of 20°C. From the variation of the distribution ratio with the ligand concentration the stability constants K_n^* have been calculated for the complex equilibria



where HA=HF and HSO_4^- . Stability constants K_n^* having $1 \leq n \leq 5$ were obtained for the fluoride system. Three sulphate complexes could be determined within the ligand concentration range used in this investigation. Only small amounts of the third complex were formed and the corresponding stability constant is rather uncertain.

The results of the present investigation are consistent with those obtained from cation exchange¹ and potentiometric methods.²

The present author has previously investigated the fluoride complexes of zirconium(IV) in a 4 M perchloric acid medium and at a temperature of 20°C by two different methods.^{1,2} Using the cation exchange method¹ of Fronæus, the first two stability constants $K_1^* = (9 \pm 1) \times 10^5$ and $K_2^* \simeq 3 \times 10^4$ were obtained. From emf measurements² using the "ferric" method of Brosset and Orring the stability constants K_2^* through to K_6^* were found to have the values: $K_2^* = (2.6 \pm 0.5) \times 10^4$; $K_3^* = (1.0 \pm 0.1) \times 10^3$; $K_4^* = (1.9 \pm 0.3) \times 10^2$; $K_5^* = (3.4 \pm 0.6) \times 10$ and $K_6^* = 2 \pm 1$. Using these methods it was only possible to determine one stability constant (K_2^*) by both methods and it was thus difficult to assess the reliability of the other constants. The value obtained for K_2^* from the cation exchange measurements might involve a certain systematic error. This fact was demonstrated from a corresponding investigation³ of the hafnium(IV) fluoride system, where the experimental conditions were the same as in Ref. 1. The value for this constant using the "ferric" method is also rather uncertain as K_2^* is here calculated from the two intercepts $\beta_{1\text{H}}X_{\text{H}0}^{-1}$ and $\beta_{2\text{H}}X_{\text{H}0}^{-1}$ of which the first one is difficult to obtain accurately;

cf. Ref. 4, p. 2446. The reason for this is the great difference in stability between the first two fluoride complexes of Zr(IV) and the first complex of Fe(III). The present investigation was carried out in order to obtain a better value for K_2^* , and also to determine as many stability constants as possible by more than one method.

The fluoride complexes formed by hafnium(IV) were recently studied by the present author.⁴ The method used involved extraction of Hf(IV) from fluoride solutions into xylene solutions of thenoyltrifluoroacetone (HTTA). By this method the existence of five species (HfF_n , with $n \leq 5$) were proved. The solvent extraction method was originally used by Connick and McVey⁵ to investigate different zirconium(IV) complexes, including among others the fluoride system. Within the range $0 < [\text{HF}] < 10$ mM they showed the existence of three complexes. Since Connick and McVey's measurements were made in 2 M perchloric acid and at a temperature of 25°C, their results could not be used for obtaining a better value of K_2^* , valid under the conditions used in the measurements in Refs. 1 and 2. The solvent extraction technique seems, however, to be the most accurate method for determining K_2^* and was therefore used in the present investigation.

The sulphate complexes formed by zirconium(IV) were studied by the cation exchange method in Ref. 1. The function ϕ_1 was found to increase linearly with increasing concentration of HSO_4^- . It was thus impossible to separate the constants $\beta_{n\text{H}}$ and l_n^* from each other by the calculation method of Fronæus, *cf.* Ref. 3, p. 2450. To compute the stability constants one must

Table 1. Comparison of reported values of the stability constants, K_n^* , for the sulphate complexes of zirconium(IV), hafnium(IV) and neptunium(IV).

| Ref. | Method | Medium and temperature | Conc. range of HSO_4^- investigated | $K_1^* \times 10^{-2}$ | $K_2^* \times 10^{-1}$ | $K_3^* \times 10^{-1}$ |
|-----------|---------------|----------------------------|--|------------------------|------------------------|------------------------|
| Zirconium | | | | | | |
| 1 | cation exch. | 4 M HClO_4 , 20°C | ≤ 0.1 M | 7.0 | 7.1 | |
| 7 | cation exch. | 2.3 M HClO_4 | ≤ 0.1 M | 3.6 | 0.6 | 20 |
| 5 | solvent extr. | 2 M HClO_4 , 25°C | ≤ 0.27 M | 4.6 | 5.3 | 0.1 |
| Hafnium | | | | | | |
| 7 | cation exch. | 2.3 M HClO_4 | ≤ 0.1 M | 1.3 | 1.6 | |
| Neptunium | | | | | | |
| 6 | cation exch. | 4 M HClO_4 , 20°C | ≤ 0.5 M | 5.0 | 3.6 | |

assume that none of the complexes are taken up by the cation exchanger. Ahrlund and Brandt,⁶ who recently investigated the sulphate complexes of neptunium(IV), found that the ϕ_1 function exhibited the same behaviour. However, a different result was reported by Ryabchikov *et al.*⁷ For hafnium(IV) ϕ_1 was a straight line but for zirconium(IV) a curved line was obtained.

A comparison of the results, obtained from the various investigations referred to, is given in Table 1; the values calculated by Connick and McVey⁵ from solvent extraction measurements are also included. The formation of at least two sulphate complexes is found in all of the investigations given in Table 1. Only for zirconium(IV) is a third complex reported to be formed. In spite of the almost identical conditions chosen for the measurements of Refs. 5 and 7 the values calculated for K_3^* diverge by a factor of 200. Also the value for K_2^* given in Ref. 7 is remarkably low. These discrepancies justify a reinvestigation of the zirconium(IV) sulphate system.

EXPERIMENTAL

Stock solutions of thenoyltrifluoroacetone (Hopkin & Williams, Ltd.) having the desired concentration were prepared by dissolving a known amount of HTTA in a known volume of xylene.

The ligand solutions were mixed from acids *p.a.*, keeping the hydrogen ion concentration equal to 4.00 M.

The distribution of Zr(IV) between the two phases was determined by radiometrical analysis using the same equipment and technique as in Ref. 4. The nuclide ⁹⁰Zr (β^- ; $t_{1/2} = 65$ d) was used for this purpose. It was obtained in the form of oxalato complexes in an oxalic acid solution from A.E.R.E. Harwell. The oxalic acid was destroyed using conc. nitric acid and 30 % hydrogen peroxide as described in Ref. 1. Finally the tracer was dissolved in 2 M nitric acid.

The daughter ⁹⁰Nb, formed from the disintegration of ⁹⁰Zr, is also radio active (β^- ; $t_{1/2} = 35$ d). Since the distribution of niobium is different from that of zirconium⁸ wrong distribution ratios will be obtained, unless the niobium activity is removed. Just before each series a niobium free ⁹⁰Zr solution was therefore prepared in the following manner:

4 ml 0.5 M HTTA (in xylene) was shaken for 15 min in a centrifuge tube with 3 ml ⁹⁰Zr stock solution (in 2 M HNO₃) and 0.1 ml 30 % H₂O₂. Under these conditions most of the zirconium was extracted into the organic phase, while the niobium remained in the aqueous phase. After centrifugation the xylene phase was transferred to another tube containing 3 ml 2 M HNO₃ and 0.1 ml 30 % H₂O₂. The two phases were again shaken and then separated by centrifugation. This treatment was repeated twice, finally producing a HTTA solution of pure ⁹⁰Zr. Suitable dilution with xylene gave HTTA solutions at the desired concentrations.

In the purification step some of the HTTA is dissolved in the aqueous phase. When calculating the HTTA concentration of the solutions used for the distribution experiments with ligand solutions, a correction was applied for this amount. Since the proportions between the original xylene solution of HTTA and 2 M HNO₃ was kept constant in all of the experiments, C_{HTTA}' was always the same fraction (0.9) of the primary concentration of HTTA. According to eqns. (5) and (8) in Ref. 4 it is evident that the value of X_H will be only slightly influenced by this correction. In some of the series C_{HTTA}' is larger than 0.5 M. For these the removal of ⁹⁰Nb were started using a 2 M HTTA solution.

During the time (2 h) used for equilibration of the ligand solutions with the initially pure solution of ⁹⁰Zr, only a minor amount of ⁹⁰Nb is formed. Nevertheless, wrong q values will be obtained for high distribution ratios, since all of the niobium activity will be found in the aqueous phase. To determine the highest measurable distribution ratio, for which no correction was necessary, the variation of q^0 with C_{HTTA} was investigated. Determinations were made for a constant hydrogen ion concentration of 4.00 M. The result obtained is shown in Fig. 1, where it can be seen that no deviation occurs from

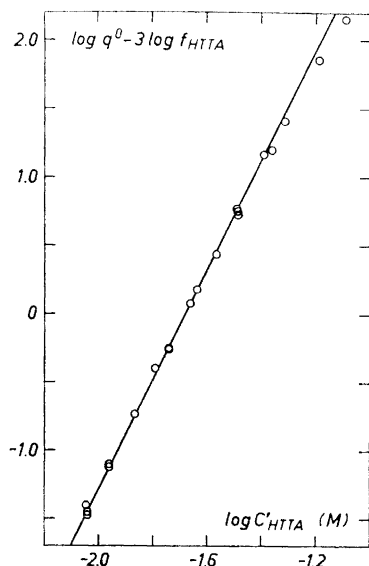


Fig. 1. $\log q^0 - 3 \log f_{HTTA}$ as a function of $\log C'_{HTTA}$. $C_M' = 5 \times 10^{-6}$ M. Aqueous phase: 4.00 M $HClO_4$. $T = 20.0^\circ C$.

the straight line (having the expected slope of 4) until q^0 is higher than 12. It is thus possible to neglect the amount of ^{95}Nb being formed for distribution ratios less than this value.

RESULTS AND CALCULATIONS

The derivation of the stability constants from the extraction data has been described in Ref. 4, where the notations are defined and the equations used are explained.

The fluoride system. The distribution ratio, q , for the different concentrations of hydrofluoric acid used in this investigation is given in Table 2. For the lowest concentration of HTTA ($C_{HTTA}' = 0.0360$ M) measurements were made at three different concentrations of zirconium(IV). By starting the purification procedure (see experimental) from 1, 2, or 5 ml of the radioactive zirconium(IV) stock solution, C_M' was varied within the range 2×10^{-7} M $\leq C_M' \leq 1 \times 10^{-6}$ M. $q^0 = 6.49 \pm 0.15$ was obtained from 9 determinations of the distribution ratio between 36.0 mM HTTA in xylene and 4.00 M $HClO_4$. Since no variation of q^0 with C_M' was found, it was concluded that no polynuclear species of zirconium(IV) existed in the aqueous phase within the range of metal ion concentration investigated. This result is consistent with that obtained in the cation exchange measurements reported in Ref. 1; cf. Fig. 1, p. 418. The values of q obtained for different total hydrofluoric acid concentrations were found to be independent of C_M' . This result indicated that the metal ion concentration was so low that no correction was necessary for the amount of fluoride coordinated due to complex formation. Hence C_{HF}' was substituted for $[HF]$ in the calculations of the stability constants. From the distribution ratios the various values of X_H were calculated using eqn. (4)

Table 2. Corresponding values of $C_{\text{HF}'} \times 10^4 \text{ M}$, q , and X_{H} obtained in the different distribution series made. $100[(q/q_{\text{calc}}) - 1]$, the fourth term in each group of figures, was calculated using the constants $\beta_{1\text{H}} = 1.87 \pm 10^5 \text{ M}^{-1}$; $\beta_{2\text{H}} = 1.14 \times 10^9 \text{ M}^{-2}$; $\beta_{3\text{H}} = 2.85 \times 10^{11} \text{ M}^{-3}$; $\beta_{4\text{H}} = 1.55 \times 10^{13} \text{ M}^{-4}$ and $\beta_{5\text{H}} = 2.2 \times 10^{14} \text{ M}^{-5}$. $C_{\text{HClO}_4} = 4.00 \text{ M}$. $T = 20.0^\circ\text{C}$.

$C_{\text{HTTA}'} = 0.0360 \text{ M}$; $2 \times 10^{-7} \text{ M} \leq C_{\text{M}'} \leq 1 \times 10^{-6} \text{ M}$
 0.0174, 5.02, 1.29, 3; 0.0276, 3.74, 1.74, -9; 0.0341, 3.99, 1.63, 1; 0.0422, 3.73, 1.74, 4;
 0.0502, 3.41, 1.90, 4; 0.0599, 2.82, 2.31, -6; 0.0599, 3.06, 2.12, 2; 0.0619, 3.01, 2.16, 2;
 0.0693, 2.82, 2.31, 2; 0.0806, 2.53, 2.57, 0; 0.0809, 2.52, 2.58, 0; 0.0809, 2.60, 2.49, 4;
 0.0985, 2.26, 2.87, 3; 0.1154, 1.89, 3.43, -4; 0.1267, 1.82, 3.58, -1; 0.1286, 1.73, 3.75,
 -4; 0.1286, 1.78, 3.65, -2; 0.1515, 1.62, 4.00, 2; 0.1774, 1.40, 4.64, 1; 0.1946, 1.27, 5.10,
 -1; 0.2220, 1.10, 5.91, -3; 0.2220, 1.14, 5.69, 0; 0.2534, 1.00, 6.49, 0; 0.3036, 0.839,
 7.73, 0; 0.3036, 0.864, 7.51, 3; 0.3550, 0.714, 9.09, 0; 0.3842, 0.668, 9.71, 2; 0.4177, 0.607,
 10.7, 1; 0.4435, 0.567, 11.5, 1; 0.4728, 0.517, 12.6, -1; 0.4728, 0.526, 12.3, 1; 0.503,
 0.479, 13.6, -2; 0.532, 0.462, 14.1, 1; 0.572, 0.430, 15.1, 3; 0.601, 0.411, 15.8, 4; 0.659,
 0.358, 18.1, 1; 0.659, 0.354, 18.3, 0; 0.710, 0.318, 20.4, -1; 0.775, 0.294, 22.1, 2; 0.997,
 0.205, 31.6, -1; 1.234, 0.155, 41.9, 0;

$C_{\text{HTTA}'} = 0.0720 \text{ M}$; $C_{\text{M}'} = 2 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-2}$
 0.548, 6.94, 0.141, 4; 0.741, 4.70, 0.209, 2; 1.110, 2.83, 0.346, 5; 1.365, 2.09, 0.468, 4;
 1.548, 1.68, 0.583, 0; 1.909, 1.30, 0.756, 6; 2.283, 0.946, 1.04, 2; 2.956, 0.614, 1.60, 2;
 4.143, 0.338, 2.91, 1; 5.22, 0.214, 4.59, -2; 7.15, 0.119, 8.27, 0; 7.76, 0.101, 9.72, 0; 9.79,
 0.0611, 16.1, -3; 11.45, 0.0435, 22.6, -4; 13.41, 0.0309, 31.8, -4; 16.76, 0.0191, 51.4,
 -3;

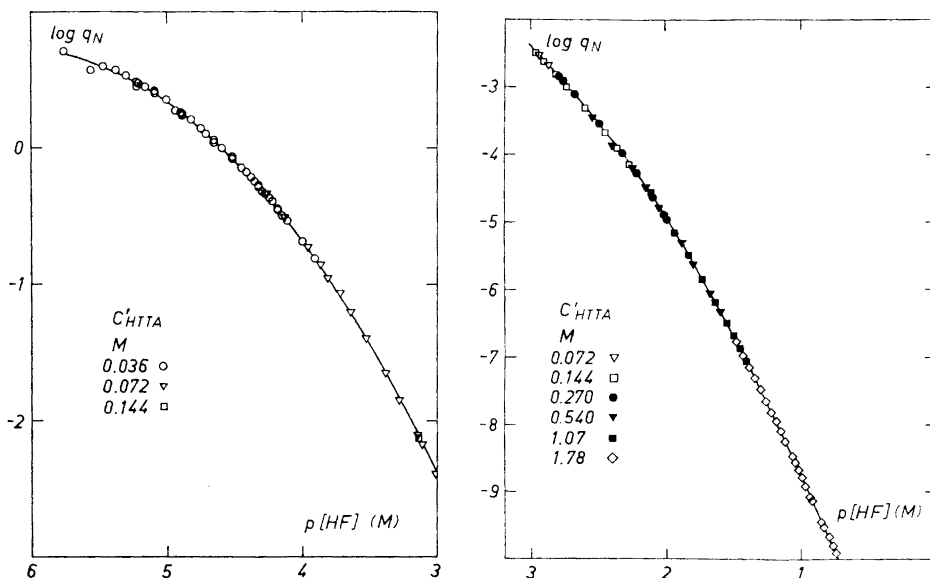
$C_{\text{HTTA}'} = 0.144 \text{ M}$; $C_{\text{M}'} = 4 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-3}$
 7.24, 1.66, 0.866, -2; 10.84, 0.707, 2.03, -5; 12.50, 0.515, 2.79, -6; 15.24, 0.339, 4.24,
 -5; 18.31, 0.222, 6.47, -6; 25.13, 0.107, 13.5, -5; 35.37, 0.0467, 30.8, -2; 43.33, 0.0277,
 51.8, -1; 53.0, 0.0157, 91.3, -3;

$C_{\text{HTTA}'} = 0.270 \text{ M}$; $C_{\text{M}'} = 4 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-4}$
 16.00, 3.56, 0.447, 0; 17.49, 2.93, 0.543, 1; 21.11, 1.92, 0.829, 2; 32.01, 0.711, 2.24, 4;
 47.34, 0.257, 6.18, 5; 60.4, 0.128, 12.5, 2; 79.5, 0.0565, 28.2, 1; 96.3, 0.0311, 51.1, 1; 101.3,
 0.0266, 59.7, 1;

$C_{\text{HTTA}'} = 0.540 \text{ M}$; $C_{\text{M}'} = 4 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-5}$
 28.64, 11.5, 0.185, -4; 39.88, 5.11, 0.417, -1; 56.0, 2.07, 1.03, 0; 70.2, 1.08, 1.96, 1;
 87.9; 0.533, 4.00, -3; 130.1, 0.158, 13.5, 0; 157.6, 0.0783, 27.2, -5; 210.0, 0.0291, 73.2,
 -4; 249.8, 0.0158, 135, -1;

$C_{\text{HTTA}'} = 1.07 \text{ M}$; $C_{\text{M}'} = 4 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-6}$
 73.9, 10.6, 0.238, -3; 115.1, 2.70, 0.935, -3; 145.0, 1.26, 2.01, -4; 184.8, 0.554, 4.55,
 -2; 228.8, 0.256, 9.86, -2; 280.0, 0.126, 20.1, 2; 314.4, 0.0817, 30.3, 4; 350.4, 0.0528,
 47.7, 2; 390.7, 0.0347, 72.6, 3;

$C_{\text{HTTA}'} = 1.78 \text{ M}$; $C_{\text{M}'} = 7 \times 10^{-6} \text{ M}$; $X_{\text{H}} \times 10^{-9}$
 330.3, 0.378, 0.0383, 0; 330.3, 0.379, 0.0387, 0; 370.4, 0.237, 0.0618, -2; 410.3, 0.161,
 0.0908, 0; 450.7, 0.111, 0.133, 0; 500, 0.0755, 0.194, 5; 548, 0.0510, 0.287, 4; 599, 0.0339,
 0.433, 0; 652, 0.0249, 0.589, 6; 702, 0.0178, 0.822, 4; 755, 0.0125, 1.17, 0; 853, 0.00758,
 1.93, 4; 894, 0.00610, 2.40, 2; 951, 0.00468, 3.13, 3; 1003, 0.00365, 4.01, 2; 1071, 0.00268,
 5.47, 1; 1151, 0.00186, 7.89, -4; 1195, 0.00164, 8.96, 1; 1400, 0.000803, 18.2, 2; 1465,
 0.000671, 21.8, 5; 1598, 0.000482, 30.4, 13; 1702, 0.000349, 41.9, 9; 1805, 0.000272, 53.3,
 12;



Figs. 2 and 3. $\log q_N$ (q normalized to $C_{\text{HTTA}}' = 36.0$ mM) as a function of $p[\text{HF}]$ (M). The curve was calculated using the constants $\beta_{1\text{H}} = 1.87 \times 10^5 \text{ M}^{-1}$; $\beta_{2\text{H}} = 1.14 \times 10^9 \text{ M}^{-2}$; $\beta_{3\text{H}} = 2.85 \times 10^{11} \text{ M}^{-3}$; $\beta_{4\text{H}} = 1.55 \times 10^{13} \text{ M}^{-4}$ and $\beta_{5\text{H}} = 2.2 \times 10^{14} \text{ M}^{-5}$.

of Ref. 4 for $C_{\text{HTTA}}' = 36.0$ mM, and eqn. (5) of Ref. 4 for the series performed at higher concentrations of HTTA. By using the relationship

$$q_N = q \left(\frac{[\text{HTTA}]_{\text{org}}^0}{[\text{HTTA}]_{\text{org}}} \right)^4 \left(\frac{f_{\text{HTTA}}^0}{f_{\text{HTTA}}} \right)^3 \quad (1)$$

all of the measured distribution ratios were normalized to the same concentration of HTTA (36.0 mM). In Figs. 2 and 3 the logarithms of the normalized distribution ratios are plotted against $-\log [\text{HF}]$. These diagrams show that the q_N values obtained from different C_{HTTA}' coincide. This observation led us to conclude that the species extracted into the xylene phase contained no fluoride ions as ligands.

The constants, $\beta_{n\text{H}}$, were computed from corresponding values of X_{H} and $[\text{HF}]$ by the usual extrapolation method of Fronæus. The following constants were obtained:

$$\begin{array}{ll} \beta_{1\text{H}} = (1.9 \pm 0.1) \times 10^5 \text{ M}^{-1}; & K_1^* = (7.6 \pm 0.4) \times 10^5 \\ \beta_{2\text{H}} = (1.1 \pm 0.1) \times 10^9 \text{ M}^{-2}; & K_2^* = (2.3 \pm 0.3) \times 10^4 \\ \beta_{3\text{H}} = (2.8 \pm 0.4) \times 10^{11} \text{ M}^{-3}; & K_3^* = (1.0 \pm 0.2) \times 10^3 \\ \beta_{4\text{H}} = (1.5 \pm 0.5) \times 10^{13} \text{ M}^{-4}; & K_4^* = (1.8 \pm 0.5) \times 10^2 \\ \beta_{5\text{H}} = (2 \pm 1) \times 10^{14} \text{ M}^{-5}; & K_5^* = (0.7 \pm 0.5) \times 10^2 \end{array}$$

The constants, K_n^* , were calculated using eqns. (4) and (9) of Ref. 1.

The full drawn curves in Figs. 2 and 3 were calculated using the experimental values of the stability constants.

Table 3. Corresponding values of $C_{\text{HSO}_4^-} \times 10^3$ M, q , and X_{H} obtained in the different distribution series made. $100[(q/q_{\text{calc}})-1]$, the fourth term in each group of figures, was calculated using the constants $\beta_{1\text{H}}=1.6 \times 10^2 \text{ M}^{-1}$; $\beta_{2\text{H}}=3.5 \times 10^3 \text{ M}^{-2}$ and $\beta_{3\text{H}}=2 \times 10^3 \text{ M}^{-3}$. $[\text{H}^+]=4.00 \text{ M}$. $T=20.0^\circ\text{C}$.

$$C_{\text{HTTA}}' = 0.0360 \text{ M}$$

1.917, 4.76, 1.36, -3; 2.684, 4.57, 1.42, 2; 3.833, 3.81, 1.71, -3; 5.37, 3.40, 1.91, 3; 6.39, 2.93, 2.22, -2; 8.05, 2.81, 2.31, 9; 9.58, 2.33, 2.79, 2; 13.42, 1.65, 3.93, -4; 16.61, 1.41, 4.61, 0; 19.17, 1.32, 4.92, 9; 20.76, 1.12, 5.81, 1; 23.96, 0.994, 6.53, 5; 26.83, 0.863, 7.52, 4; 31.94, 0.659, 9.85, -1; 35.78, 0.623, 10.4, 9; 39.93, 0.501, 13.0, 1; 44.72, 0.455, 14.3, 7; 47.92, 0.376, 17.3, -2; 55.9, 0.315, 20.6, 3; 63.9, 0.252, 25.7, 1; 67.1, 0.236, 27.5, 2; 71.9, 0.207, 31.3, 0; 76.7, 0.192, 33.8, 3; 79.9, 0.168, 38.6, -4; 95.8, 0.130, 49.9, 1; 103.8, 0.107, 60.6, -5; 124.6, 0.0802, 80.9, -2; 143.7, 0.0581, 112, -9; 167.7, 0.0458, 142, -4; 199.7, 0.0324, 200, -6; 223.6, 0.0252, 258, -9; 239.6, 0.0229, 284, -6; 279.5, 0.0159, 408, -11; 319.4, 0.0120, 541, -12;

$$C_{\text{HTTA}}' = 0.0900 \text{ M}; X_{\text{H}} \times 10^{-2}$$

38.30, 19.8, 0.118, 5; 69.8, 8.05, 0.290, 3; 134.2, 2.70, 0.864, 5; 255.6, 0.774, 3.02, 1; 287.5, 0.632, 3.69, 4; 319.4, 0.499, 4.68, 1; 383.4, 0.326, 7.16, -4; 552, 0.148, 15.8, -5; 575, 0.134, 17.5, -7; 639, 0.118, 19.8, 4; 690, 0.0938, 24.9, -2; 747, 0.0754, 30.9, -6; 767, 0.0667, 35.0, -12; 799, 0.0674, 34.6, -2; 862, 0.0550, 49.2, -12; 958, 0.0500, 46.7, 10; 1278, 0.0193, 121, -16; 1437, 0.0156, 150, -10;

$$C_{\text{HTTA}}' = 0.180 \text{ M}; X_{\text{H}} \times 10^{-2}$$

286.2, 9.04, 3.76, 1; 351.4, 6.37, 5.33, 8; 373.7, 5.17, 6.57, 0; 415.2, 4.45, 7.63, 7; 498.2, 3.29, 10.3, 16; 543, 2.72, 12.5, 15; 598, 2.29, 14.8, 20; 652, 2.15, 15.8, 36; 716, 1.79, 19.0, 39; 799, 1.07, 31.7, 7; 844, 1.15, 29.5, 30; 894, 1.11, 30.5, 44; 1038, 0.680, 49.9, 24;

The sulphate system. The distribution ratio for the sulphate system was also determined using different concentrations of HTTA. The results are given in Table 3. Since all the measurements were performed keeping the metal ion concentration in the region of 10^{-6} M no correction was necessary for the sulphate ions bound in the complexes formed. As previously observed with the fluoride system, the value of q_{N} obtained was independent of the concentration of HTTA used. Consequently no sulphate-containing species exists in the xylene phase. The logarithms of the normalized distribution ratios are plotted against $-\log [\text{HSO}_4^-]$ in Fig. 4.

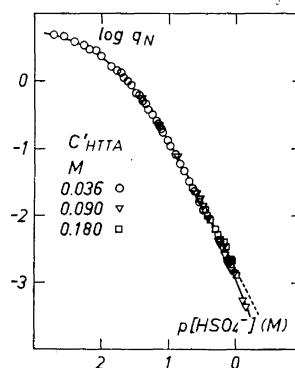


Fig. 4. $\log q_{\text{N}}$ (q normalized to $C'_{\text{HTTA}} = 36.0$ mM) as a function of $p[\text{HSO}_4^-]$ (M). The full drawn curve was calculated using the constants $\beta_{1\text{H}}=1.6 \times 10^2 \text{ M}^{-1}$; $\beta_{2\text{H}}=3.5 \times 10^3 \text{ M}^{-2}$ and $\beta_{3\text{H}}=2 \times 10^3 \text{ M}^{-3}$. The dashed curve was calculated using the constants $\beta_{1\text{H}}=1.6 \times 10^2 \text{ M}^{-1}$ and $\beta_{2\text{H}}=4.0 \times 10^3 \text{ M}^{-2}$.

From the data given in Table 3 the stability constants, β_{nH} , were computed in the manner described earlier. It was found that the measurements could be described by the formation of three complexes, and the respective stability constants are given as follows:

$$\begin{array}{ll} \beta_{1H} = (1.6 \pm 0.2) \times 10^2 \text{ M}^{-1}; & K_1^* = (6 \pm 1) \times 10^2 \\ \beta_{2H} = (3.5 \pm 0.5) \times 10^3 \text{ M}^{-2}; & K_2^* = (9 \pm 2) \times 10 \\ \beta_{3H} \simeq 2 \times 10^3 \text{ M}^{-3}; & K_3^* \simeq 2 \end{array}$$

Only an approximative value could be obtained for β_{3H} . For some unexplainable reason the accuracy of the determinations of the q values were not as good as for the corresponding fluoride system, in spite of the fact that extreme distribution ratios were avoided for the higher concentrations of HSO_4^- by increasing the HTTA concentration to 0.180 M.

DISCUSSION

For the fluoride system the stability constants found agree closely with those obtained in Refs. 1 and 2, where the measurements were performed under the same conditions as in the present work, *i.e.* 4 M HClO_4 ; $T=20^\circ\text{C}$. Also for the corresponding hafnium(IV) system consistent results were obtained for the three different methods tried; *cf.* Refs. 3 and 4. In two of the methods of investigation (cation exchange and solvent extraction) a rather low concentration of metal ion ($<10^{-5}$ M) was used, while the potentiometric measurements were performed keeping this concentration within the range 5×10^{-4} M $< C_M < 1 \times 10^{-1}$ M. K_2^* was the only stability constant which could be determined in all of the measurements. Since essentially the same value was obtained for this constant and also because of the agreement between the higher constants found both in the solvent extraction and potentiometric investigations, it may be concluded that all of the reported constants represent the formation of mononuclear fluoride complexes.

A choice can now be made among the various constants determined for the zirconium(IV) fluoride system in the present work and in Ref. 2. For the reasons given in Ref. 4, p. 2446 the following values of the constants are considered to be the most reliable ones:

$$\begin{array}{l} K_1^* = (7.6 \pm 0.4) \times 10^5 \\ K_2^* = (2.3 \pm 0.3) \times 10^4 \\ K_3^* = (1.0 \pm 0.1) \times 10^3 \\ K_4^* = (1.9 \pm 0.3) \times 10^2 \\ K_5^* = (3.4 \pm 0.6) \times 10 \\ K_6^* = 2 \pm 1 \end{array}$$

In the cation exchange investigation¹ referred to previously, K_1^* was found to be $(9 \pm 1) \times 10^5$. Within the limits of random errors this value coincides with that obtained in the present work. However, $K_1^* = 7.6 \times 10^5$ is preferred since the calculation of the stability constant from the cation exchange data was complicated by the sorption of more than one species onto the resin.

For the sulphate system the formation of the first two complexes was proved without doubt. The values found for $K_1^* = (6 \pm 1) \times 10^2$ and $K_2^* = (9 \pm 2) \times 10$ are in close agreement with those obtained from the cation exchange measurements reported in Ref. 1; cf. Table 1. Within the limits of random errors both methods give the same values for these constants. It may therefore be concluded that the assumption ($l_1^* = 0$) involved in the calculations of the stability constants from the cation exchange data was valid. The same approximation was also made in the corresponding investigation of the sulphate complexes of neptunium(IV).⁶

An attempt was made to describe the measurements of the sulphate system assuming that only two complexes were formed. Values of q_N were therefore calculated using the constants $\beta_{1H} = 1.6 \times 10^2 \text{ M}^{-1}$ and the maximum value of $\beta_{2H} = 4.0 \times 10^3 \text{ M}^{-2}$. The result is shown in Fig. 4 as the dashed curve. This curve agrees with the experimental q_N values quite well upto $[\text{HSO}_4^-] \simeq 0.25 \text{ M}$. For larger ligand concentrations most of the q_N values are decidedly smaller. Thus the present investigation indicates the formation of $\text{Zr}(\text{SO}_4)_3^{2-}$. The value found for K_3^* ($\simeq 2$) is, however, uncertain because very little of the third complex is formed in the ligand concentration range investigated.

As can be seen in Table 1 the results of the present investigation are much more related to those obtained by Connick and McVey⁵ than to those found by Ryabchikov *et al.*⁷ Thus the large value given in Ref. 7 for K_3^* ($= 200$) is probably in error. Evidently the difference in ability between Zr(IV) and Hf(IV) to form sulphate complexes is not as pronounced as suggested in Ref. 7.

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