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The Fluoride and Sulphate Complexes of Zirconium(IV)

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The stability constants K_1^* and K_2^* for the complex equilibria

$$\mathrm{M} + \mathrm{HA} \rightleftharpoons \mathrm{MA} + \mathrm{H^+} \quad \text{and}$$
$$\mathrm{MA} + \mathrm{HA} \rightleftharpoons \mathrm{MA_2} + \mathrm{H^+}$$

where $\mathrm{M} = \mathrm{Zr^{4+}}$ and $\mathrm{HA} = \mathrm{HF}$ and $\mathrm{HSO_4^-}$, have been determined by means of cation-exchange measurements. The medium has been 4 M perchloric acid and the temperature 20°C. The results are consistent with those found by Connick and McVey under somewhat different conditions, by use of a solvent extraction method (Table 6). The complexes formed are very strong, as could be expected for an acceptor of small radius and high charge like $\mathrm{Zr^{4+}}$ in connection with F and O as donor atoms.

This study is part of an investigation of the complexes formed by four-valent cations with ligands of various donating properties.

The solution chemistry of four-valent ions has not by far been treated so extensively as that of ions of lower charge. The main reason is obviously the strong tendency towards hydrolysis characteristic of ions of high positive charge. Moreover the hydrolysis involves complicated polynuclear equilibria. If these are superimposed on the equilibria of other ligands, the conditions tend to become hopelessly entangled. In order to avoid the difficulties arising from hydrolysis, the measurements have to be performed in strongly acid solutions and at low concentrations of metal ion. Under such conditions however, only few experimental methods are as a rule applicable for the investigation of the complex formation. In the case of zirconium(IV), which is certainly among the central ions most apt to hydrolyze, only such methods seem in fact to be workable that utilize the variation with complex formation of the distribution of the central ion between different phases.

Thus the comprehensive investigation of zirconium(IV) complexes by Connick and McVey [1] makes use of the competitive formation of thenoyltrifluoroacetone (TTA) complexes, which are extractable into an organic (benzene) phase. Another distribution method of very wide scope consists in measuring the decrease of sorption of zirconium(IV) on a strongly acidic cation exchanger as complex formation proceeds in the outer solution. This method was originally elaborated by Fronæus [2,3] and it has later been used for the investigation of zirconium(IV) (and hafnium(IV)) complexes by Ryabchikov *et al* [4].

The cation exchange method has also been chosen for the present investigation of the complexes formed by zirconium(IV) with fluoride and sulphate ions. These systems belong to those already studied by Connick and McVey [1] by means of solvent extraction. We have, however, decided to reinvestigate them by an independent method of measurement, in order to establish the reliability of both the methods employed under the trying conditions met with in the present experiments, where the extent of hydrolysis is imperfectly known and the concentrations of zirconium are very low and not quite easy to determine correctly.

SPECIES PRESENT IN SOLUTION UNDER THE CONDITIONS CHOSEN FOR THE PRESENT INVESTIGATION

From the measurements of Zielen and Connick [5], and of Larsen and Pei Wang [6], it is evident that even at an acidity as high as 2 M a marked polynuclear hydrolysis exists in non-complex solutions of zirconium(IV) more concentrated than $\approx 10^{-4}$ M. Being polynuclear, the hydrolysis increases rapidly with the concentration of zirconium(IV), C_M. Presumably trimeric and tetrameric species are formed [5,7]. On the other hand mononuclear hydrolytic complexes seem not to exist to a measurable degree so that once the polynuclear complex formation has been suppressed, then Zr^{4+} ought to be the only mononuclear species present [5].

As it is desirable to vary C_M over a rather wide range without the interference of hydrolysis, the acidity has been chosen as high as 4.00 M in the present investigation. Perchloric acid was used to make up this acidity. The acid also served as a medium of constant ionic strength = 4 M.

At this high acidity, the ligands investigated, which are both anions of not very strong acids, exist almost exclusively in the protonated forms HF and HSO_4^-. On account of the strong electrostatic repulsion exerted by Zr^{4+}, it may be presumed that the proton is split off in the process of complex formation. A direct proof for this, however, can only be given by comparison of measurements performed at various acidities, *cf.* the Discussion below.

As only very low values of C_M are used, the chances are that the complex formation is mononuclear and this is also confirmed by the measurements.

Under the present conditions, zirconium(IV) should therefore exist in the solutions as a system of mononuclear species, connected by a set of equilibria which in the case of fluoride may be written:

$$Zr^{4+} + n\mathrm{HF} \rightleftharpoons \mathrm{ZrF}_n^{4-n} + n\mathrm{H}^+ \; (n=1,2....N) \tag{1}$$

and analogously in the case of HSO_4^-. In the following formulas, both HF and HSO_4^- are referred to as HA.

The measurements have been performed at 20°C.

CALCULATION OF THE STABILITY CONSTANTS FROM CATION-EXCHANGE MEASUREMENTS

A full treatment of Fronæus's method applied to four-valent cations has been given by Grenthe and Norén [8]. Only the more important formulas will therefore be collected here, modified so as to fit equilibria of the present type (eqn. (1)). If not otherwise stated, the notation will be that of Ref. [8]

The law of mass action gives, applied to equilibria of the type (1):

$$\frac{[\mathrm{MA}_n]h^n}{[\mathrm{M}][\mathrm{HA}]^n} = \beta_n^* \tag{2}$$

where $h = [\mathrm{H}^+]$. If the equilibrium between two consecutive complexes is considered:

$$\frac{[\mathrm{MA}_n]h}{[\mathrm{MA}_{n-1}][\mathrm{HA}]} = K_n^* \tag{3}$$

Evidently $K_n^* = \beta_n^*/\beta_{n-1}^*$ and $K_1^* = \beta_1^*$ (4a, b)

The exchange equilibria can generally be written:

$$\mathrm{MA}_n^{4-nz} + (4-nz)\mathrm{H}^+(\mathrm{R}) \rightleftharpoons \mathrm{MA}_n^{4-nz}(\mathrm{R}) + (4-nz)\mathrm{H}^+ \tag{5}$$

Here R denotes the resin phase, z is the number of negative charges on the ion A, *i.e.* 1 for F^- and 2 for SO_4^{2-} and n is a positive integer $<4/z$, or 0. The law of mass action gives:

$$\frac{[\mathrm{MA}_n^{4-nz}]_\mathrm{R}}{[\mathrm{MA}_n^{4-nz}]} = k_n \cdot \left(\frac{h_\mathrm{R}}{h}\right)^{4-nz} = l_n \tag{6}$$

If the load on the resin, C_MR, is kept low in comparison with the total capacity, then h_R may be considered constant. The activity coefficients within the resin phase will then be constant, provided that the ion-exchanger is monofunctional. If not, the additional condition C_MR = constant has to be fulfilled in order to achieve constant activity coefficients within the resin [3]. In the outer solution, conditions of constant activity are ensured by the ionic medium. Therefore k_n of (6) may be considered as a constant and if h is kept constant, as has been the case here, l_n will thus be constant.

In the fluoride system three sorbable cationic complexes can exist, *i.e.* l_1, l_2 and l_3 have to be considered. According to previous experience, however, l_n will decrease quite rapidly with the charge of the cation. In the sulphate system on the other hand, only the first complex is a cation and therefore only $l_1 \neq 0$. Even this constant will be comparatively small, as the binding of the first ligand in this case means a decrease of the ionic charge by two units.

Introducing (2) and (6) in the expression for the distribution φ we obtain:

$$\varphi = \frac{C_\mathrm{MR}}{C_\mathrm{M}} = \frac{l_0 + \sum\limits_{n=1}^{3} l_n \cdot \beta_n^* h^{-n}[\mathrm{HA}]^n}{1 + \sum\limits_{n=1}^{N} \beta_n^* h^{-n}[\mathrm{HA}]^n} \tag{7}$$

Furthermore if the composite constants

$$l_o^{-1} \cdot l_n \cdot \beta_n^* h^{-n} = l_n^* \quad (8) \qquad \text{and} \qquad \beta_n^* \cdot h^{-n} = \beta_{n\mathrm{H}} \quad (9)$$

are introduced, then (7) can be written as

$$\varphi = \frac{l_o(1 + \sum\limits_{n=1}^{3} l_n^* [\mathrm{HA}]^n)}{1 + \sum\limits_{n=1}^{N} \beta_{n\mathrm{H}} [\mathrm{HA}]^n} \qquad (10)$$

in complete analogy with eqn. (4) of Ref. [8] Thus, if [HA] is considered as the free ligand concentration, then constants $\beta_{n\mathrm{H}}$, defined by eqn. (9), may be calculated in exactly the same way as the constants β_n of Ref. [8]

From corresponding values of φ and [HA], all the unknown constants may in principle be calculated from (10). In practice however, they have to be determined successively by means of suitable new functions derived from (10). As l_o (= lim φ, when [HA] → 0, *cf.* eqn. (7)) can be determined separately from measurements in ligand free solution, a function φ_1 may be computed:

$$\varphi_1 = \left(\frac{l_o}{\varphi} - 1\right) \cdot \frac{1}{[\mathrm{HA}]} = \frac{\beta_{1\mathrm{H}} - l_1^* - l_2^*[\mathrm{HA}] - l_3^*[\mathrm{HA}]^2 + \beta_{2\mathrm{H}}[\mathrm{HA}] + \sum\limits_{n=3}^{N} \beta_{n\mathrm{H}}[\mathrm{HA}]^{n-1}}{1 + l_1^*[\mathrm{HA}] + l_2^*[\mathrm{HA}]^2 + l_3^*[\mathrm{HA}]^3} \qquad (11)$$

Hence

$$\lim_{[\mathrm{HA}] \to 0} \varphi_1 = \varphi_1^{\circ} = \beta_{1\mathrm{H}} - l_1^* \qquad (12)$$

and

$$\lim_{[\mathrm{HA}] \to 0} \left(\frac{\mathrm{d}\varphi_1}{\mathrm{d}[\mathrm{HA}]}\right) = \beta_{2\mathrm{H}} - l_2^* - l_1^*(\beta_{1\mathrm{H}} - l_1^*) \qquad (13)$$

Once $\beta_{1\mathrm{H}} - l_1^*$ is known, the function f can be computed (*cf.* Ref. [8]) and hence

$$\lim_{[\mathrm{HA}] \to 0} f = f^{\circ} = \beta_{1\mathrm{H}}(\beta_{1\mathrm{H}} - l_1^*) - (\beta_{2\mathrm{H}} - l_2^*) \qquad (14)$$

It is possible to compute the differences $\Delta f = f - f^{\circ}$ and $\Delta\varphi_1 = \varphi_1 - \varphi_1^{\circ}$ which for not too high values of [HA] are connected according to [8]

$$\frac{\Delta f}{[\mathrm{HA}]} = \beta_{1\mathrm{H}} \frac{\Delta\varphi_1}{[\mathrm{HA}]} + (\beta_{1\mathrm{H}} - l_1^*) \cdot l_2^* + l_3^* - \beta_{3\mathrm{H}} \qquad (15)$$

which means that $\Delta f/[\mathrm{HA}]$ is a linear function of $\Delta\varphi_1/[\mathrm{HA}]$ with the slope $\beta_{1\mathrm{H}}$. Once $\beta_{1\mathrm{H}}$ is known, the function g can be calculated which for sufficiently low [HA] will be well approximated by (Ref. [8], p. 2219):

$$g = \beta_{2\mathrm{H}} \cdot \varphi_1 - \beta_{3\mathrm{H}} + l_3^* \qquad (16)$$

A plot of g as a function of φ_1 will thus be a straight line with the slope $\beta_{2\mathrm{H}}$ and the intercept $-(\beta_{3\mathrm{H}} - l_3^*)$. As l_3^* is certainly quite small, this value will be very close to $-\beta_{3\mathrm{H}}$.

Experimentally, φ is measured as a function of the total concentration of ligand C_{HA}. However, it is often possible to choose C_{M} so low that $[\mathrm{HA}] \approx C_{\mathrm{HA}}$. In other cases, where the part of C_{HA} consumed by complex formation is not quite negligible, a sufficiently good correction can be calculated from the slope of the function φ, according to a formula deduced by Fronæus [2]. It must then be presumed, however, that [HA] is not very different from C_{HA}. In the case of extremely strong complexes, as in the zirconium fluoride system, C_{HA} has however to start at such a low value in order to cover the initial stages of the complex formation that the part of C_{HA} bound in complexes will be very considerable in the beginning. It may then be possible to find [HA] by an extrapolation method, analogous to that used by Fronæus for finding the free ligand concentration from emf measurements of the concentration of the free central ion [9]. The distribution φ is determined as a function of C_{HA} for several values of total metal concentration, C'_{M}. The resulting family of curves is cut at a number of suitably chosen values of φ, and C_{HA} then plotted as a function of C_{M} with φ as parameter. Extrapolation of these curves to $C_{\mathrm{M}} = 0$ will give $C_{\mathrm{HA}} = [\mathrm{HA}]$ for the corresponding value of φ.

There is however an important restriction on the use of the function φ in this way. As is evident from eqn. (10), the constants l_n^* have to be independent of the load C_{MR}, *i.e.* the ion-exchanger has to be monofunctional, if φ is to be a function of [HA] only, and this is a necessary condition if an extrapolation to $C_{\mathrm{M}} = 0$ of C_{HA} as a function of C_{M} should be permitted, because otherwise the course of this function will not be known. Only if a certain value of φ means a constant [HA], and thus a constant ligand number $\bar{n}$, *cf.* Ref. [9], the connection between C_{HA} and C_{M} will be the straight line

$$C_{\mathrm{HA}} = [\mathrm{HA}] + \bar{n} \cdot C_{\mathrm{M}} \tag{17}$$

with the intercept [HA] and the slope $\bar{n}$.

Fortunately there are several criteria available to test if the ion exchanger behaves monofunctionally. Firstly, l_0 should be independent of C'_{M}, *i.e.* of C_{MR}. Secondly, φ should be independent of C'_{M} at values of C_{HA} so high that the part consumed by complex formation becomes negligible. This means that for a monofunctional resin the functions φ for various C'_{M} should start at the same value l_0 for $C_{\mathrm{HA}} = 0$, then possibly separate as the complex formation sets in and finally coincide again. An ultimate check of the method is obtained by comparing the values of $\bar{n}$ found from the slopes with those calculated from the determined stability constants. An agreement does not only show that the extrapolation did give the right [HA], but also that the complex formation is mononuclear within the range of C_{M} studied [9].

EXPERIMENTAL

Preparation of active zirconium solutions. As very low concentrations of zirconium(IV) have to be determined in the presence of agents forming very strong complexes, analysis by means of tracer seems to be the method of choice. The β-emitting ^{95}Zr, with a half-life of 65 d, can be used for the purpose though it has the serious drawback that the daughter ^{95}Nb is also a β-emitter with a somewhat shorter half-life of 35 d. A niobium activity will therefore very soon be noticeable in an originally pure zirconium tracer, and this activity will presumably have quite a different distribution φ. The half-life of ^{95}Nb is on the other hand much too long for the measurements to be postponed until that niobium has decayed which has been partitioned between the phases according to its own rules. Moreover the β-energies of the two nuclides are not different enough to ensure a complete discrimination of the ^{95}Nb activity with simple means, and the accompanying γ-energies are practically the same for both. The best way, therefore, seems to be to determine the distribution with a solution that has just been purified from ^{95}Nb, and then introduce a correction for the activity of ^{95}Nb formed during the experiment. This has been done as follows (*cf.* Refs. [1,10]):

A tracer solution of ^{95}Zr in oxalic acid (Harwell) was evaporated to dryness with conc. nitric acid and 30 % hydrogen peroxide in order to destroy the organic matter. The tracer was taken up in 2 M nitric acid and ^{95}Zr extracted by an equal volume of 0.3 M thenoyltrifluoroacetone (TTA) in benzene which extracts only very little of the niobium. As need arose, aqueous tracer solutions were prepared by reextracting ^{95}Zr from portions of this stock solution. Then all niobium formed on standing (or extracted from the original aqueous solution) was first removed by washing with freshly prepared 1 % hydrogen peroxide in 2 M nitric acid. As observed by Moore [10], the small amount of niobium extracted into a TTA-benzene phase cannot be reextracted merely by 2 M acid, and according to our experience the same is true for the niobium formed in this phase. The hydrogen peroxide treatment is thus essential for the preparation of a pure ^{95}Zr-tracer. The benzene phase was then diluted twentyfold with xylene in order to decrease the concentration of TTA so that ^{95}Zr could be extracted by half the volume of 8 M hydrochloric acid. By repeated evaporation almost to dryness with conc. perchloric acid, the hydrochloric acid was then removed and traces of organic matter simultaneously destroyed. The zirconium tracer was taken up in 8 M perchloric acid, inactive zirconium solution added to achieve the total concentration of zirconium wanted and the acidity finally adjusted to 4 M.

By varying the concentration of perchloric acid and the time of the final dissolution it was checked that the preceding treatment had not resulted in slowly reacting products of hydrolysis.

Procedure of the distribution measurements. The solutions were prepared by mixing 2 ml of the active zirconium solution with 10 ml of ligand solution of various concentration, but always of the acidity 4 M. For the determination of l_0, the second solution was just 4 M perchloric acid. The resin was added (m = 0.500 or 1.000 g) and the phases equilibrated by mechanical shaking. Equilibrium was reached when the activity of the solution started to increase linearly, due to the steady formation of ^{95}Nb, as elaborated below. This happened after one to two days. In most experiments recorded here two days time of shaking has been used.

Samples of 5 ml of the solutions were then measured in a γ-scintillation counter (Tracerlab P-20). After the measured activities had been corrected for the influence of ^{95}Nb as described below, φ was calculated according to [8]:

$$\varphi = \frac{v}{m}\left(\frac{C'_\mathrm{M}}{C_\mathrm{M}} - \delta\right) = \frac{v}{m}\left(\frac{I^\circ}{I} - \delta\right) \tag{18}$$

where v = volume of solution (12 ml) and δ = the swelling factor of the resin.

Influence of niobium on the activity measurements. As ^{95}Nb was formed anew, the activity of all solutions was steadily increasing. Over a period of 8 days the increase was found to be approximately linear.

If no sorption takes place, the activity I_t°, measured at a time t which is short compared with the half-lives, should be connected with the initial activity I° of the solution, due only to zirconium, according to the formula

$$I_t^\circ = I^\circ [1 + t\left(\frac{1}{t''_{½}} - \frac{1}{t'_{½}}\right) \ln 2] \tag{19}$$

where $t''_{½}$ and $t'_{½}$ are the half-lives of ^{95}Nb and ^{95}Zr, respectively. If 35 and 65 days are inserted for these, (19) gives a linear increase of 0.9 %/d, in good agreement with the value of 0.8 % found experimentally in this case.

With ion-exchanger present, the rate of increase of the activity in solution will be more rapid, the stronger the zirconium is sorbed, due to the fact that niobium is not at all taken up by the resin in the same degree as zirconium. If the ratio $C'_\mathrm{M}/C_\mathrm{M}$ is denoted by Q' and Q'' for zirconium and niobium respectively, then eqn. (19) will be modified as follows:

$$I_t = I[1 + t\left(\frac{Q'/Q''}{t''_{½}} - \frac{1}{t'_{½}}\right) \ln 2] \tag{20}$$

The activity will still increase linearly, but at a faster rate than when no resin is present, as $Q'/Q'' > 1$. Experimentally, the rate of increase, k, can be determined for various values of $Q' = I^\circ/I$ which are themselves found by extrapolation of the functions (19) and (20) to $t = 0$. Knowing $t''_{1/2}$ and $t'_{1/2}$ it is then possible to calculate the corresponding value of Q''. This has been done for two different values of Q':

Table 1.

Q'	k (%/d)	Q''
1.78	2.0	1.15
3.39	4.3	1.25

These values of Q'' may be somewhat in error on account of the fact that $t''_{1/2}$ is not quite accurately known. If $t''_{1/2}$ is 37 instead of 35 days [11], then Q'' will come out 0.06 lower than tabulated above. In any case it is evident that the sorption of niobium by the resin is quite low as compared with that of zirconium.

The eqns. (19) and (20) have been deduced on the assumption that the counting efficiency is the same for ^{95}Zr and ^{95}Nb. This is certainly true as the γ-energies are very much the same.

In practice, the niobium correction is found graphically. I_t is determined as a function of t for some different Q' and the values of k that should be applied for intermediate values of Q' may then be found by interpolation.

Determination of the range of zirconium concentrations that can be used for the present measurements. In order to avoid disturbances caused by the polynuclear hydrolysis, rather low values of C_M have to be chosen. On the other hand, very low values of C_M tend to amplify any tendency of the ion-exchanger towards a non-monofunctional behaviour, which will make the evaluation of the results difficult, or even impossible (*cf. p.* 415). It is known that the uniformity of the exchange sites may vary considerably between different resins. For this investigation, Dowex 50W—X8 (Dow Chemical Co) and Amberlite IR—120 (Rohm and Haas) were tested. In Fig. 1, l_0 is plotted against log C_M.

For Dowex, l_0 is almost constant over a wide range of C_M, and even at tracer concentrations (of the order of magnitude 10^{-10} M), the increase is quite modest which indicates a virtually monofunctional resin. As C_M exceeds $\approx 2 \times 10^{-4}$ M on the other hand, l_0 starts increasing at a rate which soon grows very fast. This must be due to the hydrolysis and evidently the polynuclear hydrolytic complexes are more strongly sorbed than the monomer Zr^{4+}, which may seem a little surprising.

On the other hand, no monofunctional region exists for Amberlite. As C_M decreases, l_0 increases very markedly, reaching an extremely high value at tracer concentrations. For values of C_M exceeding $\approx 3 \times 10^{-4}$, an increase of l_0 with C_M is found, as was the case for Dowex, though not quite so steep.

As to the monofunctionality of the resins, our results are consistent with those found by Fronaeus [3] for other exchange reactions at higher pH. The increase of l_0 as hydrolysis sets in seems on the other hand not to be compatible with the results reported for Amberlite IR-120 by Larsen and Pei Wang [6], who find a decrease of their distribution coefficient under similar circumstances. This discrepency cannot be solved at present.

For our purpose, the monofunctional Dowex is to be preferred, and it has been used in all the following measurements.

RESULTS

The fluoride system. φ as a function of C_{HA} for three different values of C'_M is given in Table 2 and, partly, in Fig. 2. The resin works monofunctionally, as is seen from the constant value of l_0 found for the two series of lowest C_M. These also coincide at high C_{HA}. For the series of $C'_M = 125 \times 10^{-6}$ M, corresponding to $C_M = 31.5 \times 10^{-6}$ M (and log $C_M = 4.50$) for $C_{HA} = 0$, a slight influence of hydrolysis is already observed (*cf.* Fig. 1), indicated by a somewhat higher

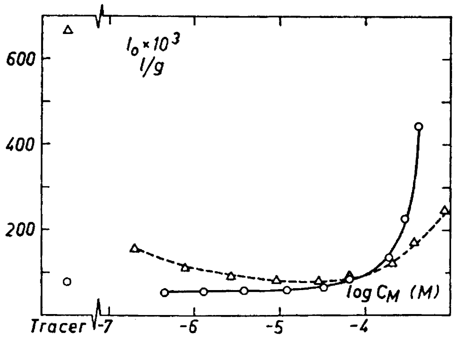

Fig. 1. l_0 as a function of C_M for: a) Dowex 50W—X8, 50—100 mesh, exchange capacity 4.21 meq/g: ——— ○. b) Amberlite IR-120, 20—50 mesh, exchange capacity 3.65 meq/g: — — — △.

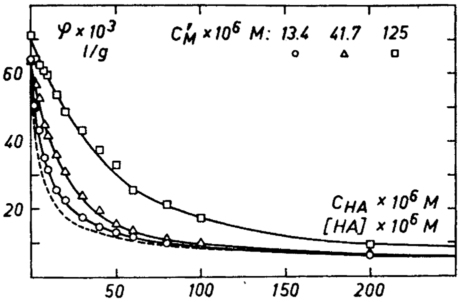

Fig. 2. φ as a function of C_{HA} for the fluoride system at various values of C'_M. Extrapolation to $C_M = 0$ gives φ as a function of [HA], dashed curve.

value of l_0. As the complex formation goes on, the hydrolysis is suppressed, however, which is evident from the final coincidence of this series with the others (Table 2).

It is thus possible to determine [HA] by cutting the two curves of lowest C'_M at constant φ and extrapolating to $C_M = 0$. The values of C_M wanted are found from eqn (18). The resulting function φ([HA]) has been drawn in Fig. 2. It is also tabulated in Table 3, together with the values of $\bar{n}$ found from the slopes of C_{HA}, C_M-lines.

The function φ_1 then formed (Table 3, Fig. 3) is decreasing which is unusual (*cf.*, *e.g.*, Ref. [2,8,12]). As is clear from an examination of eqn (11), a decrease of φ_1 implies that the constants l_n^* are unusually large in relation to the constants β_{2H}, β_{3H} etc. More specifically it is evident from eqn. (13) that φ_1 will start as a decreasing function if

Table 2. φ as a function of the total fluoride concentration for different values of C'_M.

$C'_M \times 10^6$ M →	13.4	41.7	125
$C_{HA} \times 10^6$ M	$\varphi \times 10^3$ l/g		
0	63.9	63.4	71.4
1	51.3	56.9	
2	50.5	57.2	
3	50.0	56.8	63.9
5	43.2	52.7	62.7
8	35.2	44.9	60.9
10	31.7	41.7	59.6
15	25.7	36.1	53.7
20	22.7	31.0	48.9
30	17.6	24.1	43.2
40	15.0	19.7	37.5
50	13.2	15.8	33.1
60	12.0	13.8	25.8
80	10.2	11.4	21.5
100	9.22	10.0	17.4
200	6.18	6.60	9.52
500	4.02	3.79	4.95
1000	3.04	2.84	3.06
2000	2.08	1.77	2.17

Table 3. Corresponding values of φ, [HA] and $\bar{n}$ for the fluoride system. The functions φ_1, f, $\Delta\varphi_1/[\mathrm{HA}]$, $\Delta f/[\mathrm{HA}]$ and g used for the calculation of the constants $\beta_{1\mathrm{H}}$, $\beta_{2\mathrm{H}}$ and l_1^*.

$\varphi \times 10^3$ l/g	[HA] $\times 10^6$ M	$\bar{n}$	$\varphi_1 \times 10^{-5}$ M^{-1}	$f \times 10^{-9}$ M^{-2}	$-\dfrac{\Delta\varphi_1}{\Delta[\mathrm{HA}]} \times 10^{-9}$ M^{-2}	$-\dfrac{\Delta f}{\Delta[\mathrm{HA}]} \times 10^{-14}$ M^{-3}	$g \times 10^{-15}$ M^{-3}
62	*0*		*1.8*	*39*			
60	0.3	0.07					
55	0.9	0.17					
50	1.6	0.28	1.5				
45	2.6	0.37	1.5				
40	3.8	0.46	1.5	35			
35	4.9	0.63	1.6	33			
30	6.1	1.8	1.8	33			
25	9.3	1.0	1.6	31			
22	13.3	1.0	1.4	28			
20	17.6	0.9	1.2	25	3.41	7.96	
18	17.9	1.5	1.4	27	2.24	6.71	
16	25.3	1.3	1.14	23	2.62	6.34	
14	38.0	1.1	0.90	18.5	2.36	5.40	0.176
12	52	1.0	0.80	16.3	1.92	4.36	0.157
10	77	1.1	0.68	13.7	1.46	3.29	0.137
8	117		0.58	11.5	1.04	2.35	0.117
6	200		0.47	9.0	0.67	1.50	0.094
4	470		0.31	5.9	0.32	0.71	0.064
3	990		0.20	3.7	0.16	0.36	0.041
2	2030		0.15	2.7	0.08	0.18	0.030

$$l_1^*(\beta_{1\mathrm{H}}-l_1^*)>\beta_{2\mathrm{H}}-l_2^* \tag{21}$$

or, approximately,

$$l_1^*>\beta_{2\mathrm{H}}/\beta_{1\mathrm{H}} \tag{22}$$

The introduction of eqns. (8), (9) and (4) in (22) finally yields

$$l_0^{-1}\cdot l_1>K_2^*/K_1^* \tag{23}$$

Now this condition is especially likely to be fulfilled in the case of zirconium fluoride, because the distribution coefficient l_1 of the first complex should be unusually large on account of the high cationic charge of ZrF^{3+} and moreover fluoride systems are known[13] to have unusually low values of the ratios K_{n+1}^*/K_n^*.

In general, a decreasing function φ_1 may be expected for systems characterized by a central ion of high charge, a ligand of low charge and a not very steep complex formation curve.

As the complex formation proceeds however, those terms of eqn. (11) will become more important which refer to higher complexes of low affinity to the resin. With increasing [HA], the numerator of (11) will therefore at last grow at a faster rate than the denominator and φ_1 will thus pass through a minimum. In the general case, the expression for [HA] in this minimum will be very complicated. If it is assumed however that the second and third complexes

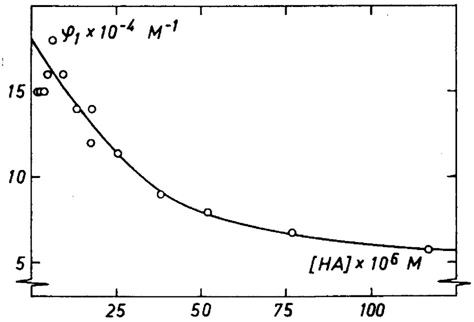

Fig. 3. φ_1 as a function of [HA] for the fluoride system.

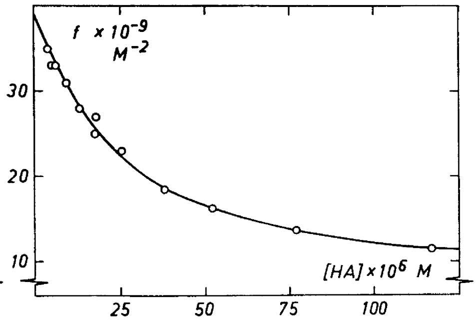

Fig. 4. *f* as a function of [HA] for the fluoride system.

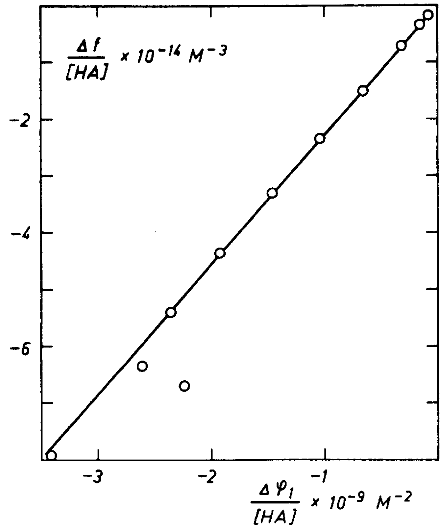

Fig. 5. Δf/[HA] as a function of $\Delta\varphi_1$ /[HA] for the fluoride system.

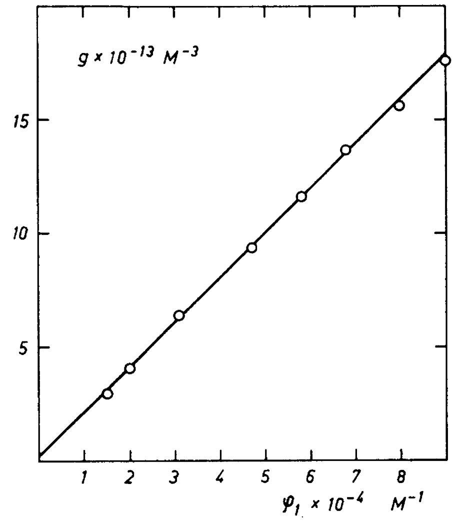

Fig. 6. *g* as a function of φ_1 for the fluoride system.

are not appreciably sorbed and that only the first three complexes exist in the actual range of [HA], then the following approximative formula can be derived:

$$[\mathrm{HA}]_{\varphi_1\,\mathrm{min}} = \sqrt{\frac{\beta_{3\mathrm{H}}/l_1^* + l_1^*(\beta_{1\mathrm{H}} - l_1^*) - \beta_{2\mathrm{H}}}{l_1^* \cdot \beta_{3\mathrm{H}}}} - \frac{1}{l_1^*} \tag{24}$$

The validity of the assumptions introduced is borne out by the results given below. They also show that the terms $\beta_{3\mathrm{H}}/l_1^*$ and $1/l_1^*$ are negligible in the case of the present system.

From extrapolation of φ_1, $\beta_{1\mathrm{H}} - l_1^* = (1.8 \pm 0.2) \times 10^5\ \mathrm{M}^{-1}$. The function *f* then formed is also decreasing with [HA] (Table 3, Fig. 4), for the same reasons as φ_1. Extrapolation of *f* gives $f^\circ = \beta_{1\mathrm{H}}(\beta_{1\mathrm{H}} - l_1^*) - (\beta_{2\mathrm{H}} - l_2^*) = (39 + 3)$

Table 4. φ as a function of the total sulphate concentration for different values of C'_M.

$C'_M \times 10^6$ M →	13.4	41.7	125
$C_{HA} \times 10^3$ M	$\varphi \times 10^3$ l/g		
0	58.7	64.3	66.9
0.5	53.0	56.3	62.5
1	50.6	51.0	58.5
1.5	46.9	50.0	52.8
2	43.9	46.8	49.4
3	38.6	39.7	43.2
5	31.4	30.9	34.4
7	26.1	27.2	28.2
10	20.4	20.9	21.9
15	15.0	14.4	15.1
20	10.6	10.6	10.6
30	6.82	6.50	6.70
50	3.67	3.71	3.67
70	2.24	2.06	2.21
100	1.21	1.31	1.26

Table 5. Corresponding values of φ, [HA] and φ_1 for the sulphate system.

$\varphi \times 10^3$ l/g	[HA] $\times 10^3$ M	φ_1 M^{-1}
62	0	*175*
55	0.5	
50	1.1	
45	1.9	
40	2.9	193
35	3.9	197
30	5.4	197
25	7.6	195
20	10.5	200
15	14.7	213
10	21.1	246
8	25.8	262
6	34.1	273
4	47.3	306
2	73.4	408
1.2	102	497

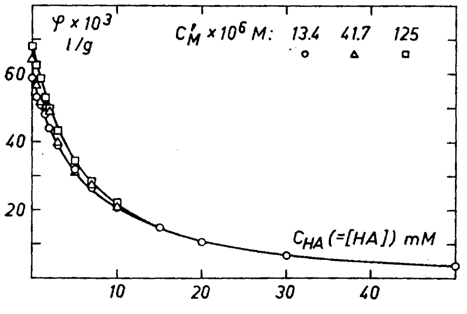

Fig. 7. φ as a function of C_{HA}(=[HA]) for the sulphate system at various values of C'_M.

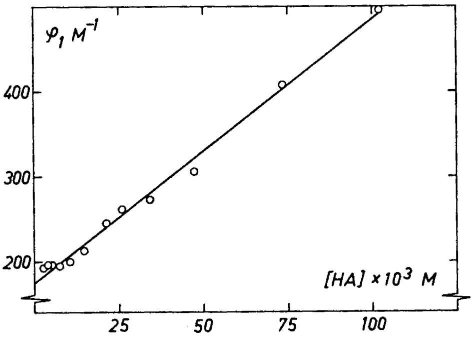

Fig. 8. φ_1 as a function of [HA] for the sulphate system.

$\times 10^9$ M^{-2}. It is then possible to compute corresponding values of Δf/[HA] and $\Delta \varphi_1$/[HA], Table 3, which show the expected linear relation, Fig. 5. The slope yields $\beta_{1H} = (2.3 \pm 0.2) \times 10^5$ M^{-1}. Thus the most probable value of l_1^* is 0.5×10^5 M^{-1}. From f°, a value of $\beta_{2H} - l_2^* = 2 \times 10^9$ M^{-2} is calculated. Then the function g can be formed. Its slope yields $\beta_{2H} = 2 \times 10^9$ M^{-2}

i.e. l_2^* is negligible compared with β_{2H}. As demanded by (22), the ratio $\beta_{2H}/\beta_{1H} = 0.9 \times 10^4$ M^{-1} is smaller than the found value $l_1^* = 5 \times 10^4$ M^{-1}. The intercept of the function g is quite small, and yields rather a positive than a negative value. Evidently β_{3H} is too small to give a significant deviation of g from the origin. This precludes a calculation of $[HA]_{\varphi_1,\min}$ according to eqn. (24) from experimental data. If however K_3^* is assumed to have a value of $\approx 10^3$ in the present medium, which seems reasonable considering the data presented in Table 6, then $\beta_{3H} \approx 5 \times 10^{11}$ M^{-3} and $[HA]_{\varphi_1\min} = 0.5$ mM. The minimum should thus occur in the upper part of the range of [HA] investigated here. Experimentally it does not show up however, Table 3. This may either be due to the choice of a wrong value of β_{3H}, or, perhaps, to large errors in the determinations of the low values of φ for the highest [HA] used.

The sulphate system. In Table 4, φ is given as a function of C_{HA} for three different C'_M. Here the curves of the two lowest C'_M virtually coincide along their whole course, Fig. 7 (though l_o comes out somewhat low for $C'_M = 13.4 \times 10^{-6}$ M, *cf.* the corresponding fluoride series). The monofunctional behaviour found for the fluoride system is thus confirmed and moreover the approximation $[HA] = C_{HA}$ is evidently valid, the complexes formed being much weaker than in the case of fluoride. For the series of $C'_M = 125 \times 10^{-6}$ M, a deviation due to hydrolysis is found in the beginning but, as may be expected, it gradually disappears as the complex formation proceeds. With a value of $l_o = (62 \pm 2) \times 10^{-3}$ l/g, the function φ_1 is calculated from a mean of the coinciding curves, Table 5. Here this function is found to increase, as is the general rule. Thus $l_1^* < \beta_{2H}/\beta_{1H}$. Clearly the double charge of SO_4^{2-} will make l_1^* comparatively much smaller than in the fluoride system. Moreover the complex formation curve is as a rule steeper in the case of sulphate, resulting in a larger value of the ratio β_{2H}/β_{1H}. Within the limits of experimental error, φ_1 is also linear, Fig. 8. Remembering that $l_2^* = 0$, the slope is found from eqn. (13) as $\beta_{2H} - l_1^*$ $(\beta_{1H} - l_1^*)$. Furthermore, as $l_1^* \ll \beta_{1H}$ and $< \beta_{2H}/\beta_{2H}$,one may in the first approximation even put the intercept $= \beta_{1H}$ and the slope $= \beta_{2H}$, thus neglecting the sorption of the complex. This yields $\beta_{1H} = 175 \pm 15$ M^{-1}

Table 6. The constants β_n^* and K_n^* for the zirconium fluoride and sulphate systems, determined by us in 4 M perchloric acid at 20°C and by Connick and McVey [1] in 2 M perchloric acid at 25°C.

	$\beta_1^*(=K_1^*)$	β_2^*	K_2^*	K_3^*	K_1^*/K_2^*	K_2^*/K_3^*
	Fluoride					
This work	9.2×10^5	3.2×10^{10}	3.5×10^4	—	26	—
C. and McV.	6.3×10^5	1.32×10^{10}	2.10×10^4	6.7×10^2	30	31
	Sulphate					
This work	7.0×10^2	5.0×10^4	71	—	9.9	—
C. and McV.	4.6×10^2	2.4×10^4	53	1	8.7	53

and $\beta_{2H} = (3.1 \pm 0.3) \times 10^3$ M^{-2}. Thus $\beta_{2H}/\beta_{1H} = 18 > l_1^*$ which will be inside the limits of error for β_{1H}. Calculation of the function $\Delta f/[HA]$ does not yield any further information in this case, only a very rough value of β_{1H} is obtained, of the same order of magnitude as before. Nor is it possible to find a useful value of β_{2H} from f°. For β_{2H}, the value found at the first approximation has thus to be accepted. From the reasoning in Ref. [8] about the decreases of sorption when a fourvalent ion takes up two negative charges one may conclude with a certain confidence, however, that the error of β_{2H} will not be too large.

DISCUSSION

In Table 6, the constants β_1^* $(= K_1^*)$, β_2^* and K_2^*, calculated from eqns. (9) and (4) have been tabulated, as well as the ratios K_1^*/K_2^*. They are compared with the data found by Connick and McVey for 2 M perchloric acid by means of solvent extraction. The constants K_n^* for the consecutive steps are throughout found to be some 50 % higher in our measurements. This is what

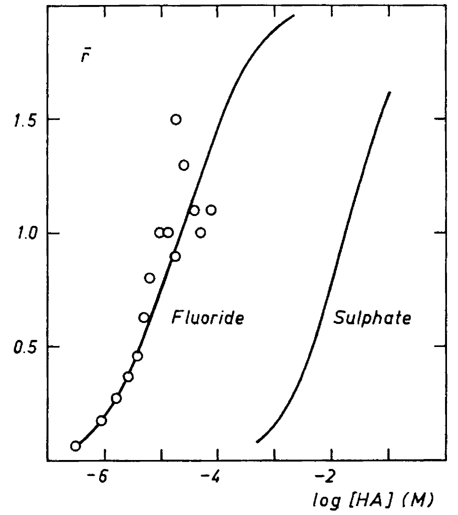

Fig. 9. The complex formation functions of the zirconium fluoride and sulphate systems. The circles refer to the values of $\bar{n}$ for the fluoride system found from the slopes of the C_{HA}, C_M-lines of constant φ.

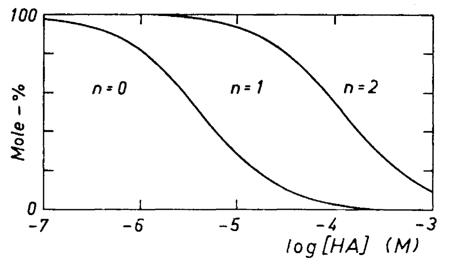

Fig. 10. The distribution of zirconium between different species in fluoride solution.

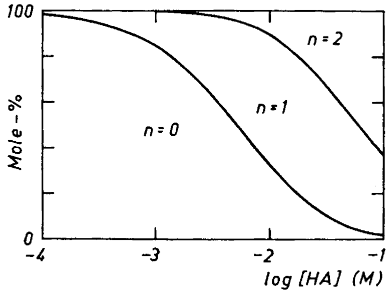

Fig. 11. The distribution of zirconium between different species in sulphate solution.

may be expected from the increase of the ionic strength. The two methods employed may therefore be considered as giving consistent results, which is also expressed by the good agreement of the ratios K_1^*/K_2^*. It may then be inferred that the assumptions underlying these methods are really true and the results thus reliable.

The fact that consistent values of the constants are found for 4 M and 2 M acid implies moreover that the complexes formed have the formulas postulated in eqn. (1), *i.e.* that the protons are split off in the process of complex formation.

From the formula

$$\bar{n} = \frac{\beta_{1H}[HA] + 2\beta_{2H}[HA]^2}{1 + \beta_{1H}[HA] + \beta_{2H}[HA]^2} \qquad (25)$$

the complex formation functions have been computed and drawn in Fig. 9, where also those values of $\bar{n}$ have been plotted that were found from the slopes of the C_{HA}, C_M-lines of constant φ for the fluoride system (Table 3). The experimental values fall along the computed curve as well as could be expected. The resin thus works monofunctionally and only mononuclear complexes are formed. For fluoride, the value of K_1^*/K_2^* is just high enough for an inflexion to develop around $\bar{n} = 1$ (Ref. [14 p. 24]), which is not prominent enough, however, to be noticeable on Fig. 9. In the sulphate system the value of K_1^*/K_2^* is lower and the formation curve thus steeper, with no inflexion around $\bar{n} = 1$.

In Figs. 10 and 11, the distribution of the zirconium between various species is given as a function of log [HA] (*cf. e.g.* Ref. [14 p. 286]).

Among all acceptors, zirconium(IV) forms the strongest fluoride complexes known so far. Also the sulphate complexes are among the strongest found. The strong affinity to F and O as donor atoms is typical of acceptors of high charge and small radius [15,16] and as Zr^{4+} possesses these two qualities to an unusual degree, the strong complex formation is certainly expected.

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