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The Hydrolytic Behavior of Zirconium in  
Perchloric Acid Solution

by

R. E. Connick and W. H. Reas

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Abstract

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The polymerization of zirconium(IV) in 1 M and 2 M perchloric acid solutions has been investigated. The extraction of the zirconium chelate of thenoyltrifluoroacetone into benzene was measured as a function of the zirconium concentration. Polymer formation is quantitatively reflected as a decrease in the extraction coefficient of the zirconium, and equations expressing this relationship have been developed and applied to the data.

In 2 M perchloric acid polymers begin to form at zirconium concentrations of approximately  $2 \times 10^{-3}$  M while in 1 M perchloric acid they appear at concentrations as low as  $2 \times 10^{-4}$  M. The dimer was shown to exist. It contains between 3 and 5 hydroxide groups. Higher polymers were formed and it is believed that a continuous series of polymers, starting with the dimer, is formed.

Assuming relatively simple relationships between the successive equilibrium quotients for polymer formation, it was shown that theoretical curves could be deduced which fitted the data within the accuracy of the measurements.

The limits of the extraction coefficient at low zirconium concentrations indicated that the zirconium(IV) monomer in 1 to 2 M perchloric acid solutions is mainly present as unhydrolyzed  $Zr^{+4}$ .

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Because of its high charge and small radius, the ion  $Zr^{+4}$  exhibits a marked tendency to hydrolyze in aqueous solution. Normal compounds of zirconium, such as  $ZrCl_4$ , when dissolved in water, liberate hydrogen ion and even the zirconyl salts, e.g.,  $ZrOCl_2 \cdot 8H_2O$ , which are already half hydrolyzed, produce acidic solutions.

Recently Connick and McVey<sup>1</sup> have shown that in 2 M per-

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<sup>1</sup>R. E. Connick and W. H. McVey, UCRL-101, March 1, 1948.

---

chloric acid at 25°C the average zirconium species at low zirconium concentrations has a charge somewhere between +3 and +4 and is not polymerized. This corresponds to a mixture of  $ZrOH^{+3}$  and  $Zr^{+4}$ . At high zirconium concentrations there is abundant evidence that zirconium is polymerized and considerably more hydrolyzed in the polymers than when present as the monomer. Thus Jander and Jahr<sup>2</sup> found the diffusion coefficient of 0.1 M

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<sup>2</sup>G. Jander and K. F. Jahr, Kolloid-Beihefte, 43, 295 (1935).

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zirconium(IV) to be only half as great as that of uranyl nitrate at acidities ranging from 1.2 M perchloric acid to no added acid. Measurements<sup>3,4</sup> of the pH of aqueous solutions of zirconyl chlor-

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<sup>3</sup>A. W. Laubengayer and R. B. Eaton, J. Am., Chem. Soc., 62, 2704(1940).

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<sup>4</sup>M. Adolf and W. Pauli, Kolloid-Z., 29, 173(1921).

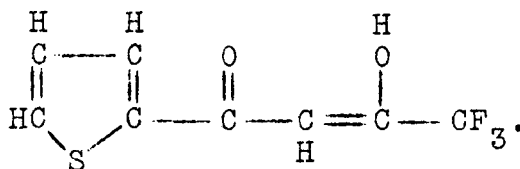
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ide indicate there are approximately three hydroxide ions per zirconium in the polymers. Freezing point studies<sup>4</sup> also indicate extensive polymerization and hydrolysis. In the above cited research the evidence for polymer formation was only qualitative or, if quantitative, could not be uniquely interpreted because of the variation of two or more conditions simultaneously.

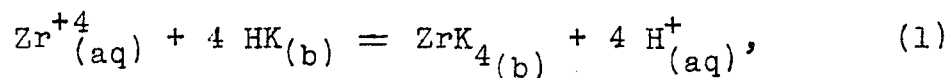
The present research was undertaken to identify, if possible, the polymeric zirconium species which are formed at high zirconium concentrations in solutions of moderate acidity.

## Method

The experimental method, which is similar to that used by Connick and McVey<sup>1</sup>, involves the measurement of the distribution of zirconium between an aqueous phase and a benzene phase containing a chelating agent. The chelating agent used was thenoyltrifluoroacetone (hereafter referred to as TTA). The formula in the enol form is:



It forms a neutral chelate molecule with zirconium(IV), which is very soluble in benzene, but, under the extraction conditions, the TTA does not complex an appreciable fraction of the zirconium in the aqueous phase<sup>1</sup>. Assuming the zirconium species in the aqueous phase to be unhydrolyzed and unpolymerized, the extraction reaction is:



where HK is used to designate TTA. Any polymer formation by the zirconium in the aqueous phase is reflected quantitatively as a decrease of the extraction of zirconium into the benzene phase.

For more details as to the general method and of the properties of TTA and  $\text{ZrK}_4$ , see reference 1.

Experimental Procedure. - The distribution of zirconium between the benzene and water phases was measured in two series of experiments--one at 2 M perchloric acid and the other at 1 M

perchloric acid and 1 M lithium perchlorate, which was added to maintain constant ionic strength. The zirconium concentration was varied over a 3000 fold range in each series.

Equal volumes of a benzene phase, containing a known concentration of TTA and radioactive zirconium tracer, and an aqueous phase, containing perchloric acid (and lithium perchlorate in the low acid series) and zirconium perchlorate, were placed in a long necked flask and shaken vigorously in a water thermostat at 25°C. In every case two or more analyses were made at sufficiently long time intervals to demonstrate that equilibrium had been attained.

The zirconium concentration in each phase was determined by mounting known aliquots on glass cover slides, evaporating to dryness and counting, using a mica window Geiger tube.

When zirconium is extracted into the benzene phase, the TTA concentration is decreased because TTA is used up in forming the chelate. Knowing the distribution ratio of TTA between benzene and 2 M perchloric acid (or 1 M  $\text{HClO}_4$  and 1 M  $\text{LiClO}_4$ ) and making the correction for the amount of TTA used up by zirconium in forming the chelate, it is possible to calculate the concentration of free TTA in the benzene phase, provided there is inappreciable complexing of zirconium by TTA.

in the aqueous phase. It was found, however, by spectrophotometric measurements of the aqueous phase of the experiments at high zirconium concentrations, that a small fraction of the zirconium was being complexed by TTA. Although the fraction of zirconium complexed was quite small, the concentration of TTA in the benzene phase was appreciably altered because of the relatively high zirconium concentration. It was therefore necessary to measure the TTA concentration in the benzene phase experimentally.

The analytical procedure that was adopted consisted in measuring the TTA concentration in the benzene phase spectrophotometrically. It was necessary to correct the observed spectrum for the absorption of light by the zirconium chelate present in the benzene phase. The concentration of  $ZrK_4$  was calculated by the equation:

$$(ZrK_4)_b = \frac{E}{E + I} (Zr)^o \quad (2)$$

where  $(Zr)^o$  represents the original zirconium concentration in moles per liter in the aqueous phase before the extraction. (This equation is only applicable when the volumes of the two phases are equal.)

The zirconium chelate spectrum has been measured by Zebroski<sup>5</sup>. His measurements were repeated, and it was found

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<sup>5</sup>Zebroski, E. L., Thesis, University of California, 1947.

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that the values of the molar extinction coefficient varied with time. A possible reason for this change may be the presence of a small amount of water in the benzene solution, thus allowing the zirconium chelate to hydrolyze slowly. It was noted that the molar extinction coefficient of the zirconium chelate remained constant at  $3300\text{\AA}$ . At this particular wavelength the molar extinction coefficient of the zirconium chelate is almost exactly four times greater than that of pure TTA. Thus as the chelate hydrolyzes TTA is liberated and as a result of the relative values of their extinction coefficients at this wavelength, the concentration of  $\text{ZrK}_4$  appears to remain constant.

It is possible therefore to use results of the spectrophotometric analysis at  $3300\text{\AA}$  in conjunction with the extraction coefficient data to calculate the free TTA concentration in the benzene phase. When the optical density of a sample containing both TTA and chelate is measured, the reading at  $3300\text{\AA}$  is correct even though the chelate may be hydrolyzing. This value can then be corrected for the optical density contributed by the chelate, using the molar extinction coefficient and the concentration of the chelate calculated from the extraction coefficient. The free TTA concentration is then calculated from the residual optical density by means of the known molar extinction coefficient of TTA.

In theory, it is possible with the aid of Beer's Law to calculate the concentration of both the TTA and the zirconium chelate, providing the molar extinction coefficients are known for both species at two different wavelengths. The results of the calculation were not precise because of the slow change of

the spectra at wavelengths other than 3300Å; however they did give approximately the concentrations of TTA and  $ZrK_4$  corresponding to the known total TTA concentration. The calculations therefore indicate that the zirconium species in the benzene phase is  $ZrK_4$ .

The zirconium perchlorate was prepared in the following manner. Zirconyl chloride, which had been purified by recrystallization from hydrochloric acid, was converted to the perchlorate by fuming with perchloric acid. The hot zirconium perchlorate solution was rapidly transferred to a dry box and allowed to cool. The zirconium perchlorate precipitate which formed was very crystalline. The composition was not determined. The crystals were centrifuged away from the concentrated perchloric acid and then dissolved in 2 M perchloric acid. An aliquot of this solution was treated with an excess of sodium fluoride, and then titrated for hydrogen ion with sodium hydroxide. The concentration of perchloric acid in the stock zirconium perchlorate solution (assuming the zirconium to be  $Zr(ClO_4)_4$ ) was calculated to be 2.06 M. The zirconium concentration was found to be 0.229 M by taking an aliquot of the stock solution, converting the zirconium to zirconium hydroxide, and then igniting this to zirconium dioxide.

The radioactive  $Zr^{95}$  tracer, which was obtained from Oak Ridge, contained an appreciable fraction of radioactive columbium which is produced by the decay of the zirconium. This mixture of activities was purified by a method developed by Connick and McVey<sup>1</sup>. There was a significant difference, however, in the final step of the purification procedure. Their tracer stock was stored in an aqueous perchloric acid solution; thus as the

zirconium decayed the columbium activity grew. It was therefore necessary to rework this aqueous stock solution occasionally to remove the columbium.

The zirconium tracer used in the experiments described here was prepared in the same manner except the final aqueous solution was extracted with a TTA-benzene solution. The zirconium tracer readily extracted into the organic phase leaving the columbium in the aqueous phase. As columbium was formed by the radioactive decay of zirconium chelate, it was removed from the benzene phase by re-equilibrating the two phase system. With this procedure it was never necessary to rework the zirconium stock solution.

The lithium perchlorate was purified by recrystallization from water.

The interior surface of each flask used in the extraction experiments was coated with Dri-film, which is  $(\text{CH}_3)_2\text{SiCl}_2$ . When the vapors of this chemical are introduced into a flask, the compound reacts rapidly with the water which is normally adsorbed on the surface. The hydrolysis product adheres firmly to the surface and its organic nature prevents water from wetting the glass surface. It was found necessary in trace experiments to use coated flasks because an impurity was being leached off the uncoated flask's surface by the 2 M perchloric acid. It had been found previously that most of this unidentified impurity could be removed by treating the flask with a careful cleaning procedure. These flasks were then treated with dri-film to prevent any residual impurity from being leached off. The pipets used for removing zirconium samples were also treated with Dri-film.

All concentrations are expressed in moles per liter of solution, designated by the symbol M.



## Experimental Results

The data for the 2 M and 1 M perchloric acid series are presented in Tables 1 and 2 respectively. The first column gives the original zirconium concentration in the aqueous phase before extraction. In the second column is the extraction coefficient, defined as the concentration of zirconium in the benzene phase divided by the concentration in the aqueous phase. This value was obtained from the radioactive tracer analyses. The third column lists the optical density at  $3300\text{\AA}$  of a diluted aliquot of the benzene phase and these data were used to calculate the concentration of free TTA in the benzene phase, given in the fourth column, by the method previously described.

The extraction coefficients were all corrected to the values they would have had at unit activity of TTA, assuming a fourth power ketone dependence<sup>1</sup>. The corrected values,  $E^0$ , are given in column 5. In the sixth column is the total concentration of zirconium in the aqueous phase at equilibrium which was calculated from the values of the first and second columns.

In the last two columns are given the minimum and maximum concentrations of hydrogen ion. In the first case it was assumed that none of the zirconium was hydrolyzed and in the second that all of the zirconium was hydrolyzed completely, thus releasing four hydrogen ions for every zirconium ion. The true state of affairs surely lies in between these extremes.

The two or more sets of data at each initial zirconium concentration correspond to repeat analyses of the same experiment after longer shaking times. The first analyses were made 6 hours or longer after the initial mixing; the second analyses at approx-

Table 1

The Hydrolysis and Polymerization of Zirconium in 2 M Perchloric Acid at 25.0°C

Zr, Initial Moles/l	E	D 3300 Å <sup>a</sup>	(HK) <sub>b</sub> Moles/l x 10 <sup>3</sup>	E°	Zr Aq. Moles/l.	(H <sup>+</sup> ) Min.	(H <sup>+</sup> ) Max.
7.63 x 10 <sup>-5</sup>	0.126	0.344	5.97	1.00 x 10 <sup>8</sup>	6.78 x 10 <sup>-5</sup>	2.00	2.00
	0.123	0.346	6.00	0.95 x 10 <sup>8</sup>	6.80 x 10 <sup>-5</sup>		
7.61 x 10 <sup>-4</sup>	0.106	0.344	5.71	1.00 x 10 <sup>8</sup>	6.88 x 10 <sup>-4</sup>	2.00	2.00
	0.101	0.337	5.60	1.02 x 10 <sup>8</sup>	6.91 x 10 <sup>-4</sup>		
2.27 x 10 <sup>-3</sup>	0.073	0.343	5.38	8.7 x 10 <sup>7</sup>	2.11 x 10 <sup>-3</sup>	2.00	2.01
	0.073	0.344	5.39	8.6 x 10 <sup>7</sup>	2.11 x 10 <sup>-3</sup>		
7.63 x 10 <sup>-3</sup>	0.150	0.641	7.19	5.66 x 10 <sup>7</sup>	6.64 x 10 <sup>-3</sup>	2.01	2.03
	0.156	0.638	7.02	6.46 x 10 <sup>7</sup>	6.61 x 10 <sup>-3</sup>		
	0.156	0.640	7.03	6.41 x 10 <sup>7</sup>	6.60 x 10 <sup>-3</sup>		
	0.0397	0.630	6.32	2.51 x 10 <sup>7</sup>	2.94 x 10 <sup>-2</sup>		
3.05 x 10 <sup>-2</sup>	0.0388	0.630	6.42	2.30 x 10 <sup>7</sup>	2.94 x 10 <sup>-2</sup>	2.01	2.13
	0.0415	0.634	6.18	2.87 x 10 <sup>7</sup>	2.93 x 10 <sup>-2</sup>		
	0.0156	0.657	6.77	7.45 x 10 <sup>6</sup>	7.52 x 10 <sup>-2</sup>		
	0.0168	0.660	6.46	9.7 x 10 <sup>6</sup>	7.51 x 10 <sup>-2</sup>		
7.63 x 10 <sup>-2</sup>	0.0166	0.650	6.35	10.2 x 10 <sup>6</sup>	7.51 x 10 <sup>-2</sup>	2.03	2.33
	5.08 x 10 <sup>-3</sup>	0.687	7.34	1.76 x 10 <sup>6</sup>	0.228		
	5.11 x 10 <sup>-3</sup>	0.688	7.33	1.78 x 10 <sup>6</sup>	0.228		
0.229	5.01 x 10 <sup>-3</sup>	0.689	7.45	1.64 x 10 <sup>6</sup>	0.228	2.06	2.98

a. The optical density was measured in a 5 cm. cell after a 10<sup>3</sup> fold dilution. The following molar extinction coefficients were used:

$$E_{ZrK_4} = 46,000$$

$$E_{HK} = 11,460$$

Table 2

The Hydrolysis and Polymerization of Zirconium in 1 M HClO<sub>4</sub> and 1 M LiClO<sub>4</sub> at 25.0° C.

Zr, Initial Moles/l	E	D <sub>3300 Å</sub> <sup>a</sup>	(HK) <sub>b</sub> Moles/l x 10 <sup>3</sup>	E°	Zr Aq. Moles/l.	(H <sup>+</sup> ) Min.	(H <sup>+</sup> ) Max.
1.312 x 10 <sup>-5</sup>	0.323	b	4.35	9.1 x 10 <sup>8</sup>	9.92 x 10 <sup>-6</sup>	1.001	1.001
	0.346	0.499	4.35	9.7 x 10 <sup>8</sup>	9.75 x 10 <sup>-6</sup>		
3.93 x 10 <sup>-5</sup>	0.390		4.32	1.12x 10 <sup>9</sup>	2.83 x 10 <sup>-5</sup>	1.002	1.002
	0.378	0.498	4.33	1.08x 10 <sup>9</sup>	2.85 x 10 <sup>-5</sup>		
1.313 x 10 <sup>-4</sup>	0.401	0.491	4.21	1.31x 10 <sup>9</sup>	9.37 x 10 <sup>-5</sup>	1.000	1.000
	0.379	0.491	4.22	1.20x 10 <sup>9</sup>	9.52 x 10 <sup>-5</sup>		
3.94 x 10 <sup>-4</sup>	0.327		4.15	1.10x 10 <sup>9</sup>	2.97 x 10 <sup>-4</sup>	1.000	1.001
	0.327	0.498	4.15	1.10x 10 <sup>9</sup>	2.97 x 10 <sup>-4</sup>		
1.313 x 10 <sup>-3</sup>	0.166	0.495	3.94	6.87x 10 <sup>8</sup>	1.126x 10 <sup>-3</sup>	1.001	1.006
	0.152	0.498	4.00	5.96x 10 <sup>8</sup>	1.140x 10 <sup>-3</sup>		
3.94 x 10 <sup>-3</sup>	0.0611		3.88	2.69x 10 <sup>8</sup>	3.71 x 10 <sup>-3</sup>	1.001	1.016
	0.0591	0.497	3.89	2.58x 10 <sup>8</sup>	3.72 x 10 <sup>-3</sup>		
1.313 x 10 <sup>-2</sup>	0.0201	0.504	3.87	9.0 x 10 <sup>7</sup>	1.287x 10 <sup>-2</sup>	1.001	1.053
	0.0214	0.494	3.76	10.7 x 10 <sup>7</sup>	1.286x 10 <sup>-2</sup>		
3.94 x 10 <sup>-2</sup>	0.0118		4.14	4.03x 10 <sup>7</sup>	3.89 x 10 <sup>-2</sup>	1.002	1.158
	0.0102	0.579	4.25	3.14x 10 <sup>7</sup>	3.90 x 10 <sup>-2</sup>		

a. The optical density was measured in a 5 cm. cell after a 500-fold dilution.

b. Where no measurement of the optical density was taken in the first analysis, it was assumed to be the same as in the second analysis.

imately twice this time interval; etc. In no case was there evidence that equilibrium had not been attained at the time of the first analysis.

## Discussion

The decrease of  $E^\circ$  at high zirconium concentration concentrations in each series of experiments is clear evidence of polymer formation. In order to consider the data quantitatively it is necessary to derive several equations.

For a given acidity we shall represent the total concentration of all polymers containing  $n$  zirconium atoms by  $(Zr_n)$ . Assuming only  $ZrK_4$  to be present in the benzene phase, the extraction coefficient  $E$  is:

$$E = \frac{(ZrK_4)_b}{(Zr) + 2(Zr_2) + 3(Zr_3) + \dots} = \frac{(ZrK_4)_b}{\sum_{n=1} n (Zr_n)} \quad (3)$$

The equilibria between the polymers may be represented at constant acidity by the equations:

$$n Zr = Zr_n \quad (4)$$

$$K_n = \frac{(Zr_n)}{(Zr)^n} \quad (5)$$

(The values of  $K_n$  will be constant if the activity coefficients of all species remain constant, to which end the ionic strength was maintained constant in the experiments.)

Substituting from equation (5) into equation (3):

$$E = \frac{(ZrK_4)_b}{\sum n K_n (Zr)^n} \quad (6)$$

At constant activity of hydrogen ion and TTA the following relationship holds:

$$(ZrK_4)_b = k(Zr) \quad (7)$$

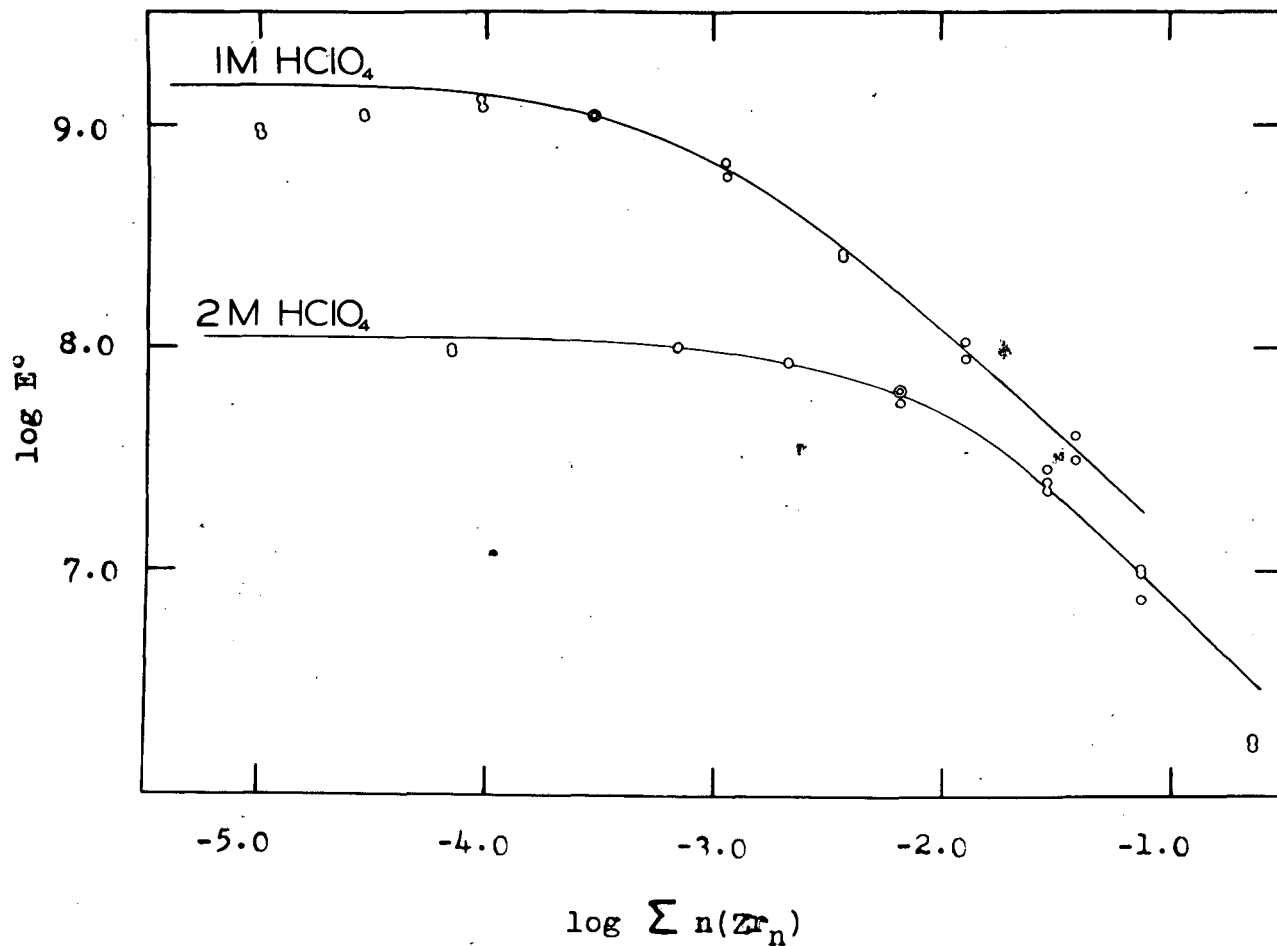


Figure 1

Extraction Coefficient of Zirconium at Unit Activity of TTA  
 in Benzene Phase and 1 M and 2 M Perchloric Acid in  
 Aqueous Phase.

Replacing  $E$  by  $E^\circ$ , to correspond to constant TTA activity, and substituting from equation 7 we have:

$$E^\circ = \frac{k(Zr)}{\sum_{n=1}^{\infty} n K_n (Zr)^n} \quad (8)$$

Differentiating we obtain:

$$\frac{d \log E^\circ}{d \log \sum n K_n (Zr)^n} = -1 + \frac{\sum n K_n (Zr)^n}{\sum n^2 K_n (Zr)^n} \quad (9)$$

which may be written as

$$\frac{d \log E}{d \log \sum n (Zr_n)} = -1 + \frac{1}{\sum n f_n} \quad (10)$$

where  $f_n$  is the fraction of the total zirconium in the aqueous phase which exists in polymers containing  $n$  zirconium atoms. The expression  $\sum n f_n$  represents the size of the polymer in which a zirconium ion will be found on the average. This quantity we shall call the average degree of polymerization.

The experimental data of Tables 1 and 2 have been plotted in Fig. 1 with  $\log E^\circ$  as ordinate and  $\log \sum n (Zr_n)$  as abscissa. According to equation 10 the slope of the curves should be zero at low zirconium concentrations where the monomer is the only important species. As the zirconium concentration is increased the slope should become negative where polymers begin to form and should approach minus one at high zirconium concentrations, if the polymers approach infinite size.

The solid curves of Fig. 1 have been drawn with zero slope at low zirconium concentrations, in agreement with the theory.

It is believed that the experimental points fall below the lines of zero slope in this region because of an impurity in the solutions. Exactly the same effect has been noted previously<sup>1</sup> and it was most plausibly interpreted as arising from the complexing of an appreciable fraction of the zirconium, by an impurity, at low zirconium concentrations. The concentration of the impurity is sufficiently low that its effect becomes small at ca.  $10^{-3}$  M zirconium concentrations. In the present experiments in 2.00 M perchloric acid the effect is not as great as observed in the previous work<sup>1</sup>. The presence of the impurity obviously introduces considerable uncertainty into the drawing of the curve at 1 M perchloric acid and some even at 2 M perchloric acid.

Formula of Monomer. - From the limiting values of the extraction coefficient at low zirconium concentration in the two sets of experiments, the degree of hydrolysis of the monomeric ion of zirconium may be calculated. Taking the limiting values of the solid curves of Fig. 1 it is found that the extraction coefficient  $E^{\circ}$  has an inverse 3.8 power dependence on the hydrogen ion concentration. The uncertainty in drawing the curves is greatest for the experiments in 1 M perchloric acid, where, if anything, the limiting value of  $E^{\circ}$  should probably be higher than shown, since there may have been an appreciable lowering of the extraction coefficient by the impurity at the experiment with  $3.94 \times 10^{-4}$  M zirconium. Therefore the hydrogen ion dependence could be as high as an inverse 4th power, corresponding to a formula of  $Zr^{+4}$ , assuming that perchlorate ion does not complex zirconium. In any case the hydrogen ion dependence appears to



lie between 3.7 and 4.0 so that in 2 M perchloric acid most of the zirconium is present as  $Zr^{+4}$ .

In the previous work by Connick and McVey the species in 2.00 M perchloric acid appeared to be  $ZrOH^{+3}$  when trace concentrations of zirconium were used. Presumably the interference of the impurity was the cause of this apparent hydrolysis. The effect is in the expected direction, as they pointed out. Their few results with macro amounts of zirconium indicated less than one hydroxide ion per zirconium ion, in agreement with the present results.

Polymer Formation. - The set of points at the highest zirconium concentration of the 2 M perchloric acid series are so low on the plot that a slope more negative than -1 would be required to fit a curve through them. Such a slope is not allowable according to equation (10) and the obvious explanation for the deviation of the data is the high acidity of this solution, as shown in the last column of Table 2. In this solution the zirconium is practically all polymerized and, if the number of hydroxide ions per zirconium ion in the polymers is four, the acidity would be 2.98 M rather than 2.00. Therefore it is not surprising that these points at 0.229 M initial zirconium concentration do not fall on the curve.

From equation (10) the average degree of polymerization may be calculated, i.e.,

$$\sum n f_n = \frac{1}{\text{slope} + 1} \quad (11)$$

The data are presented in Table 3 in column 5. It is clear

Table 3

The degree of Polymerization of Zirconium in Aqueous Perchloric Acid Solution  
at 25°C

(H <sup>+</sup> )	log E	Log. $\sum_{m=1}^{\infty} n(Zr_n)$	slope	$\sum_{m=1}^{\infty} n f_m^2$	f <sub>1</sub>	N
2	7.975	-3.00	-0.138	1.16	0.86	2.2
2	7.89	-2.50	-0.245	1.32	0.71	2.1
2	7.713	-2.00	-0.515	2.06	0.47	3.0
2	7.35	-1.50	-0.890	9.1	0.20	11.0
2	6.865	-1.00	-0.997	ca 300.	0.067	ca 320.
1	9.13	-4.00	-0.133	1.15	0.90	2.6
1	9.03	-3.50	-0.283	1.39	0.72	2.4
1	8.83	-3.00	-0.529	2.12	0.45	3.0
1	8.51	-2.50	-0.770	4.4	0.21	5.3
1	8.09	-2.00	-0.889	9.0	0.082	10.0
1	7.63	-1.50	-0.944	18.0	0.029	19.0

that polymers of zirconium containing several zirconium atoms are formed. The values are dependent on the way the curves were drawn and, as can be seen from Fig. 1, the data are not sufficiently accurate to fix the curves at all precisely. Therefore the values of  $\sum n f_n$  are only approximate and especially so at high zirconium concentrations, where the slope approaches minus one. For example the data could probably be fitted with a curve which would give a value of  $\sum n f_n$  of 10 rather than 300 for the point at  $10^{-1}$  M zirconium concentration in the 2 M perchloric acid series.

The average degree of polymerization, excluding the monomer, may be calculated. This quantity, designated by N, is given by the equation:

$$N = \left[ \sum n f_n - f_1 \right] \frac{1}{1 - f_1} \quad (12)$$

The fraction of monomer,  $f_1$ , is calculated from the equation

$$f_1 = \frac{E^\circ}{E_0^\circ} \quad (13)$$

where  $E_0^\circ$  is the limiting value of  $E^\circ$  at low zirconium concentration, i.e., it is the extraction coefficient of the monomer.

It is clear that the values of N which appear in the last column of Table 4 are not precise as the trend is inverted in the first two points of each series of experiments. This inversion of values indicates that the curve was drawn with too great a curvature in the region where the polymers are beginning to form. The data do indicate, however, that a zirconium dimer does exist in these solutions. If the dimer did not make an appreciable contribution to the total zirconium concentration,

the lowest value N could have would be three, corresponding to the trimer.

It can also be seen from Table 4 that the dimer is not the only polymer present, as the value of N increases as the zirconium is increased. Since large polymers are formed at high zirconium concentrations and since the dimer exists, there is every reason to believe that all intermediate polymers also exist. The higher values of N, i.e., from three up, are only order of magnitude values. The calculation of these higher values is extremely sensitive to the slope of the curve as the slope approaches minus one. The formation of polymers above the trimer appears, from the data, to be more sudden with increasing zirconium concentration at 2 M than at 1 M perchloric acid. However, because of the uncertainty in drawing the curves, there is in reality no significant difference.

It can be seen in Figure 1 that the two curves are approaching each other at high zirconium concentrations. This means that the value of the hydrogen ion dependence of the extraction coefficient is approaching zero, which in turn requires that the successive polymers approach the composition of the neutral hydroxide, i.e.,  $[\text{Zr}(\text{OH})_4]_x$ .

From the data it is possible to obtain a rough value of the number of hydroxide ions in the dimer. This value is related to the zirconium concentrations at which polymers first begin to form at the two different acidities. Under conditions where only the monomer and dimer are important, i.e., where only a small amount of polymerization has taken place:

$$\frac{E_0^0}{E^0} = \frac{(\text{Zr}) + 2K_2(\text{Zr})^2}{(\text{Zr})} = 1 + 2K_2 (\text{Zr}) \quad (14)$$

If we choose the same value of  $E^{\circ}/E^{\circ}$  for 1 M and 2 M perchloric acid

$$K_2(1M) \frac{(Zr)}{\sum n (Zr_n)(1M)} = K_2(2M) \frac{(Zr)}{\sum n (Zr_n)(2M)} \quad (15)$$

Still applying the above condition, it may be shown that

$$\left[ \frac{(Zr)}{\sum n (Zr_n)} \right]_{1M} = \left[ \frac{(Zr)}{\sum n (Zr_n)} \right]_{2M} \quad (16)$$

Substituting into equation (15) and letting  $x$  be the exponent of the hydrogen ion dependence of  $K_2$  we obtain

$$\frac{K_2(1M)}{K_2(2M)} = \frac{\sum n (Zr_n)(2M)}{\sum n (Zr_n)(1M)} = 2^x, \quad (17)$$

or

$$x = \frac{\log \sum n (Zr_n)(2M) - \log \sum n (Zr_n)(1M)}{0.301} \quad (18)$$

The above equation applies where polymer formation is very slight, i.e., where only the monomer and dimer are important species. The difference in the logarithms of the total zirconium concentration must be taken where each curve has decreased the same amount from the limiting value of the extraction coefficient of the monomer. From Fig. 1 it is evident that polymer formation begins to occur approximately 1 to 1.5 logarithmic units higher in the 2 M than in the 1 M perchloric acid series. Therefore there are of the order of 3 to 5 hydroxide ions in the dimer.

Equilibrium Constants for Polymer Formation. - The precision of the data does not allow accurate calculation of the equilibrium constants for polymerization. Rough values of  $K_2$  were calculated to be  $10^2$  and  $10^3$  for 2 M and 1 M perchloric acid respectively.

Since the successive polymers differ only in the addition of one more zirconium ion and an unspecified number of hydroxide ions, it would seem likely that there should be a fairly simple relationship between the successive equilibrium constants, especially the higher ones. With this in mind it was of interest to try to fit the experimental data with theoretical polymerization curves calculated on the basis of several assumptions concerning the K's.

Case 1. Assume  $K_n = k^{n-1}$ . This assumption is equivalent to saying that the free energy change on the addition of each successive zirconium ion (along with the accompanying hydroxide ions) is constant. The constant,  $k$ , is raised to the  $n-1$  power rather than the  $n$ 'th power so that  $K_1$  will equal unity, as it must.

The total zirconium concentration is:

$$\sum n (Zr_n) = \sum n K_n (Zr)^n = \sum n k^{n-1} (Zr)^n \quad (19)$$

$$\frac{E^\circ}{E^\circ} = \frac{\sum n (Zr_n)}{(Zr)} = \sum n [k (Zr)]^{n-1} \quad (20)$$

This series when summed is equal to:

$$\frac{E^\circ}{E^\circ} = \frac{1}{[1 - k (Zr)]^2} = \frac{\sum n (Zr_n)}{(Zr)} \quad (21)$$

$$\sum n (Zr_n) = \left[ 1 - \left( \frac{E^\circ}{E_0^\circ} \right)^{1/2} \right] \frac{E_0^\circ}{k E^\circ} \quad (22)$$

This equation contains two arbitrary parameters  $E^\circ$  and  $k$  which are to be fitted to the data.

Case 2. Assume  $K_n = n k^{n-1}$ . This assumption implies that the free energy of addition of each successive zirconium ion is somewhat more positive, the change becoming negligible at high values of  $n$ . Thus each successive zirconium atom is less stably held on the polymer.

Proceeding as before,

$$\sum n (Zr_n) = \sum n^2 k^{n-1} (Zr)^n \quad (23)$$

$$\frac{E_0^\circ}{E^\circ} = \sum n^2 [k (Zr)]^{n-1} \quad (24)$$

This series when summed is

$$\frac{E_0^\circ}{E^\circ} = \frac{1 + k (Zr)}{[1 - k (Zr)]^3} = \frac{\sum n (Zr_n)}{(Zr)} \quad (25)$$

Case 3. Assume  $K_n = n^{-1} k^{n-1}$ . This assumption means that the free energy of addition of each successive zirconium ion is more negative than that of the preceding one, the difference becoming negligible at high values of  $n$ . Thus each successive zirconium is more stably bound in the polymer.

With the above assumption we write:

$$\sum n (Zr_n) = \sum k^{n-1} (Zr)^n \quad (26)$$

$$\frac{E_0^\circ}{E^\circ} = \sum [k (Zr)]^{n-1} \quad (27)$$

On summing the series we obtain:

$$\frac{E_0^\circ}{E^\circ} = \frac{1}{1 - k (Zr)} = \frac{\sum n (Zr_n)}{(Zr)} \quad (28)$$

$$\sum n (Zr_n) = \frac{E_0^\circ - E^\circ}{k E^\circ} \quad (29)$$

Theoretical curves of  $\log E^\circ/E_0^\circ$  versus  $\log \sum n(Zr_n)$  for cases 1, 2 and 3 were plotted on transparent graph paper. For these curves the value of  $k$  for each case was assumed to be unity. The curves were then shifted horizontally and vertically over a plot of the experimental points, on the same scale, until the best fit was obtained. The horizontal placement of the theoretical curve relative to the experimental points determines the value of  $k$  in each case.

It was found that case 2 did not give a good fit while cases 1 and 3 did represent the data within the accuracy of the measurements. Case 3 appeared to give slightly better agreement than case 1. For case 3 the best values of  $k$  are approximately  $1.2 \times 10^3$  and  $1.3 \times 10^2$  for the 1 M and 2 M perchloric acid series respectively. The corresponding values of  $\log E_0^\circ$  are 9.21 and 8.05.



Polymer Formation in Other Systems. - The present study constitutes to the authors knowledge the first systematic investigation of polymer formation of a +4 ion. All +4 ions are known to exhibit strong tendencies towards such behavior, as shown, for example, by their ease of formation of colloidal solutions. Almost certainly the other +4 ions when studied in detail will be found to hydrolyze and polymerize in a manner qualitatively similar to that of zirconium. The ease of hydrolysis and polymerization appears to depend strongly on the size and charge of the ion as well as the electronic structure.

Recently  $\text{Bi}^{+3}$  has been studied in detail by Graner and L. G. Sillen who showed that it simultaneously hydrolyzes and polymerizes like zirconium. Other ions which are known to exhibit such

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<sup>6</sup>F. Graner and L. G. Sillen, Acta Chem Scand. 1, 631 (1947).

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a behavior are  $\text{UO}_2^{++}$  and  $\text{Be}^{++}$ . It seems likely that such a behavior is more common than is generally assumed and that many more of the common cations when carefully studied will be found to act similarly.

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