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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Hydrolysis and Polymerization of Zirconium in Perchloric Acid Solution[1]

BY ROBERT E. CONNICK AND WILLIAM H. REAS[2]

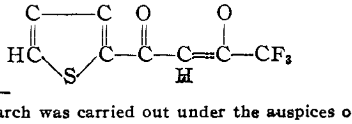
Because of its high charge and small radius, the ion Zr^{+4} exhibits a marked tendency to hydrolyze in aqueous solution. Normal compounds of zirconium, such as $ZrCl_4$, when dissolved in water, liberate hydrogen ion and even the zirconyl salts, *e.g.*, $ZrOCl_2 \cdot 8H_2O$, which are already half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

Recently it has been shown[3] that in 2 *M* perchloric acid at 25° 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 Zr^{+4} and $ZrOH^{+3}$, or possibly ZrO^{++}. 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[4] found the diffusion coefficient of 0.1 *M* 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[5,6] of the *p*H of aqueous solutions of zirconyl chloride indicate there are approximately three hydroxide ions per zirconium in the polymers. Freezing point studies[6] also indicate extensive polymerization and hydrolysis. In the above cited work 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.

Experimental

Method.—The experimental method, which is similar to that used by Connick and McVey,[3] involves the measurement of the distribution of zirconium between an aqueous phase and a benzene phase containing a chelating agent, thenoyltrifluoroacetone (hereafter referred to as TTA). The formula of the enol form is



(1)

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.[3] Assuming the zirconium species in the aqueous phase to be unhydrolyzed and unpolymerized, the extraction reaction is

$$Zr^{+4}_{(aq)} + 4HK_{(b)} = ZrK_{4(b)} + 4H^{+}_{(aq)} \qquad (2)$$

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

For more details as to the general method and of the properties of TTA and ZrK_4, see reference 3.

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, the latter being added to maintain an ionic strength of 2. 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 shaken vigorously in a water thermostat at 25°. 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.

It was necessary to know the TTA concentration in the benzene phase. This could not be obtained readily from the original concentration by difference because it was found, through spectrophotometric measurements, that a small, but unknown, fraction of the zirconium in the aqueous phase was being complexed by TTA in the experiments at high zirconium concentration. 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.

The TTA in the benzene phase was determined spectrophotometrically after diluting the sample with benzene. Correction for the absorption of the zirconium chelate was necessary. Zebroski[7] has measured its spectrum. On repeating his measurements it was found that the molar extinction coefficient appeared to vary with time, probably because of hydrolysis of the chelate in these diluted samples. At 3300 Å. however the absorption remained constant. At this wave length the molar extinction coefficient of ZrK_4 is almost exactly four times that of TTA so that hydrolysis produces no change in the absorption.

From the absorption at 3300 Å. the sum of the TTA and four times the zirconium chelate concentrations was obtained. Subtraction of the zirconium chelate concentration, calculated from the measured extraction coefficient, yielded the TTA concentration.

In theory, it is possible with aid of the Beer law to calcu-

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[1] This research was carried out under the auspices of the United States Atomic Energy Commission.

[2] General Electric Co., Hanford Works, Richland, Washington.

[3] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[4] G. Jander and K. F. Jahr, *Kolloid-Beihefte*, **43**, 295 (1935).

[5] A. W. Laubengayer and R. B. Eaton, THIS JOURNAL, **62**, 2704 (1940).

[6] M. Adolf and W. Pauli, *Kolloid-Z.*, **29**, 173 (1921).

[7] E. L. Zebroski, University of California Radiation Laboratory classified thesis, BC-63, 1947.

late the concentration of both the TTA and the zirconium chelate, providing the molar extinction coefficients are known for both species at two different wave lengths. The results of the calculation were not precise because of the change of the spectrum at wave lengths other than 3300 A., 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, at high zirconium concentrations.

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

The radioactive Zr^{95} tracer, which was obtained from Oak Ridge, was purified by the method used by Connick and McVey.[3] The stock solution in benzene was kept free of the columbium daughter by equilibrating it with an aqueous phase in the presence of TTA. The zirconium remained predominantly in the benzene phase under conditions where the extraction coefficient for columbium greatly favored the aqueous phase. Thus the columbium could be removed as it was formed by shaking the mixture.

Lithium perchlorate was purified by recrystallization from water.

Difficulty was experienced with an unidentified impurity (see also ref. 3) which appeared to be present on the glass walls of the containers. A careful cleaning procedure decreased its effect. In addition all vessels and pipets were coated with Dri-film, $(CH_3)_2SiCl_2$.

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

Results

The data for the 2 M and 1 M perchloric acid series are presented in Tables I and II, respectively. The first column lists the original zirconium concentration in the aqueous phase before extraction. The extraction coefficient, E, defined as the concentration of zirconium in the benzene phase divided by the concentration in the aqueous phase, was corrected to the value it would have had at unit activity of TTA, assuming a fourth power ketone dependence.[3] These corrected values are designated as E^0. In the last two columns are given the minimum and maximum concentrations of hydrogen ion, assuming in the first case 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 value surely lies 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 approximately twice this time interval. In no case was there evidence that equilibrium had not been attained at the time of the first analysis.

Discussion

The decrease of E^0 at high zirconium 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

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

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

$$nZr = Zr_n \quad (4)$$

$$K_n = (Zr_n)/(Zr)^n \quad (5)$$

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 (3)

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

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

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

where k is a constant.

Replacing E by E^0, to correspond to constant TTA activity, and substituting from equation (7) gives

$$E^0 = \frac{k(Zr)}{\sum\limits_{n=1} nK_n(Zr)^n} \quad (8)$$

Differentiating

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

which may be written as

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

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

The experimental data of Table I and II have been plotted in Fig. 1 with log E^0 as ordinate and the logarithm of the total aqueous zirconium concentration, *i.e.*, log $\Sigma n(Zr_n)$, as abcissa. According to equation 10 the slope 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 in this region because of an impurity in the solutions. Exactly the same effect was noted previously[3] and it was most plausibly interpreted as arising

TABLE I

THE HYDROLYSIS AND POLYMERIZATION OF ZIRCONIUM IN 2 *M* PERCHLORIC ACID AT 25.0°

Zr, initial, moles/l.	E	$(HK)_b$ moles/l. × 10^3	E^0	Zr aq. moles/l.	(H^+) Min.	(H^+) Max.
7.63×10^{-5}	0.126	5.97	1.00×10^8	6.78×10^{-5}	2.00	2.00
	.123	6.00	0.95×10^8	6.80×10^{-5}		
7.61×10^{-4}	.106	5.71	1.00×10^8	6.88×10^{-4}	2.00	2.00
	.101	5.60	1.02×10^8	6.91×10^{-4}		
2.27×10^{-3}	.073	5.38	8.7×10^7	2.11×10^{-3}	2.00	2.01
	.073	5.39	8.6×10^7	2.11×10^{-3}		
7.63×10^{-3}	.150	7.19	5.66×10^7	6.64×10^{-3}	2.01	2.03
	.156	7.02	6.46×10^7	6.61×10^{-3}		
	.156	7.03	6.41×10^7	6.60×10^{-3}		
3.05×10^{-2}	.0397	6.32	2.51×10^7	2.94×10^{-2}	2.01	2.13
	.0388	6.42	2.30×10^7	2.94×10^{-2}		
	.0415	6.18	2.87×10^7	2.93×10^{-2}		
7.63×10^{-2}	.0156	6.77	7.45×10^6	7.52×10^{-2}	2.03	2.33
	.0168	6.46	9.7×10^6	7.51×10^{-2}		
	.0166	6.35	10.2×10^6	7.51×10^{-2}		
0.229	5.08×10^{-3}	7.34	1.76×10^6	0.228	2.06	2.98
	5.11×10^{-3}	7.33	1.78×10^6	0.228		
	5.01×10^{-3}	7.45	1.64×10^6	0.228		

TABLE II

THE HYDROLYSIS AND POLYMERIZATION OF ZIRCONIUM IN 1 *M* $HClO_4$ AND 1 *M* $LiClO_4$ AT 25.0°

Zr, initial, moles/l.	E	$(HK)_b$ moles/l. × 10^3	E^0	Zr aq. moles/l.	(H^+) Min.	(H^+) Max.
1.312×10^{-5}	0.323	4.35	9.1×10^8	9.92×10^{-6}	1.001	1.001
	.346	4.35	9.7×10^8	9.75×10^{-6}		
3.93×10^{-5}	.390	4.32	1.12×10^9	2.83×10^{-5}	1.002	1.002
	.378	4.33	1.08×10^9	2.85×10^{-5}		
1.313×10^{-4}	.401	4.21	1.31×10^9	9.37×10^{-5}	1.000	1.000
	.379	4.22	1.20×10^9	9.52×10^{-5}		
3.94×10^{-4}	.327	4.15	1.10×10^9	2.97×10^{-4}	1.000	1.001
	.327	4.15	1.10×10^9	2.97×10^{-4}		
1.313×10^{-3}	.166	3.94	6.87×10^8	1.126×10^{-3}	1.001	1.006
	.152	4.00	5.96×10^8	1.140×10^{-3}		
3.94×10^{-3}	.0611	3.88	2.69×10^8	3.71×10^{-3}	1.001	1.016
	.0591	3.89	2.58×10^8	3.72×10^{-3}		
1.313×10^{-2}	.0201	3.87	9.0×10^7	1.287×10^{-2}	1.001	1.053
	.0214	3.76	10.7×10^7	1.286×10^{-2}		
3.94×10^{-2}	.0118	4.14	4.03×10^7	3.89×10^{-2}	1.002	1.158
	.0102	4.25	3.14×10^7	3.90×10^{-2}		

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.[3] 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 curves of Fig. 1 it is found that the extraction coefficient E^0 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^0 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 3.9×10^{-4} *M* zirconium. Therefore the hydrogen ion dependence

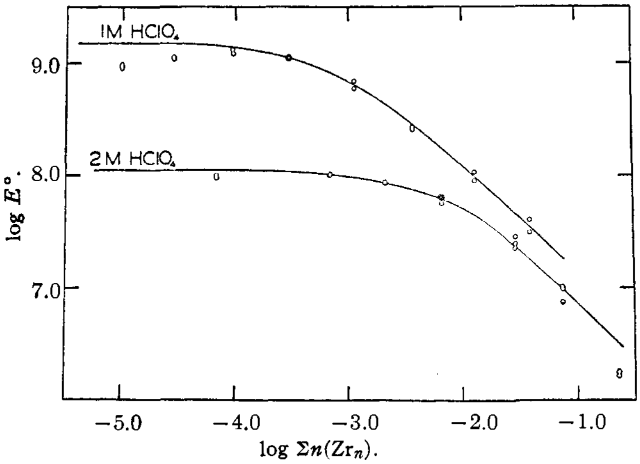

Fig. 1.—Extraction coefficient of zirconium at unit activity of TTA in benzene phase and 1 *M* and 2 *M* perchloric acid in aqueous phase.

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 data with macro amounts of zirconium indicated less than one hydroxide ion per zirconium ion, in agreement with the present results.

Polymer Formation.—The 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 II. The zirconium is practically all polymerized and, if the number of hydroxide ions per zirconium ion in the polymers is four, the acidity is 2.98 *M* rather than 2.00.

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

$$\Sigma n f_n = \frac{1}{\text{slope} + 1} \qquad (11)$$

The data are presented in Table III in column 5. It is clear 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 $\Sigma n f_n$ 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 $\Sigma n f_n$ of 10 rather than 300 for the point at 10^{-1} *M* zirconium concentration in the 2 *M* perchloric acid series.

TABLE III

THE DEGREE OF POLYMERIZATION OF ZIRCONIUM IN AQUEOUS PERCHLORIC ACID SOLUTION AT 25°

(H⁺) moles/l.	log E	log $\Sigma_{n=1}\, n(\mathrm{Zr}_n)$	Slope	$\Sigma_{n=1}\, nf_n$	f_1	g
2	7.975	−3.00	−0.138	1.16	0.86	2.2
2	7.89	−2.50	− .245	1.32	.71	2.1
2	7.713	−2.00	− .515	2.06	.47	3.0
2	7.35	−1.50	− .890	9	.20	11
2	6.865	−1.00	− .997	*ca.* 300	.067	*ca.* 320
1	9.13	−4.00	− .133	1.15	.90	2.6
1	9.03	−3.50	− .283	1.39	.72	2.4
1	8.83	−3.00	− .529	2.12	.45	3.0
1	8.51	−2.50	− .770	4.4	.21	5.3
1	8.09	−2.00	− .889	9	.082	10
1	7.63	−1.50	− .944	*ca.* 18	.029	*ca.* 19

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

$$g = [\Sigma n f_n - f_1]\frac{1}{1 - f_1} \qquad (12)$$

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

$$f_1 = E^0/E^0_0 \qquad (13)$$

where E^0_0 is the limiting value of E^0 at low zirconium concentration, *i.e.*, it is the extraction coefficient of the monomer.

It is clear that the values of *g* which appear in the last column of Table III are not precise as the trend is inverted in the first two points of each series of experiments. This inversion 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 *g* could have would be three, corresponding to the trimer.

It can also be seen from Table III that the dimer is not the only polymer present, as the value of *g* 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 *g*, *i.e.*, from three up, are only order of magnitude values because the calculation is extremely sensitive to the slope of the curve as it 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 Fig. 1 that the two curves approach each other at high zirconium concentrations. If they coincided this would mean that the large polymers contained four hydroxide ions per zirconium. The observed limiting separation (at a given zirconium concentration) is 0.29 logarithm unit which is almost exactly a factor of two. Assuming that activity coefficients are the same in the two sets of solutions this result corresponds to polymers containing three hydroxide ions for every zirconium, a formula which is in agreement with the results of *p*H measurements cited earlier.[5,6] Presumably these large polymers approximate to the stoichiometric formula $(\mathrm{Zr(OH)_3 \cdot }x\mathrm{H_2O})_n^{+n}$ and in addition may contain perchlorate ions to neutralize some of the charge.

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

$$\frac{E^0_0}{E^0} = \frac{(\mathrm{Zr}) + 2K_2(\mathrm{Zr})^2}{(\mathrm{Zr})} = 1 + 2K_2(\mathrm{Zr}) \qquad (14)$$

If one chooses the same value of E^0_0/E^0 for 1 *M* and 2 *M* perchloric acid

$$K_{2(1\,\mathrm{M})}(\mathrm{Zr})_{(1\,\mathrm{M})} = K_{2(2\,\mathrm{M})}(\mathrm{Zr})_{(2\,\mathrm{M})} \qquad (15)$$

Still applying the above condition, it may be shown that

$$\left[\frac{(\mathrm{Zr})}{\Sigma n(\mathrm{Zr_n})}\right]_{1\,M} = \left[\frac{(\mathrm{Zr})}{\Sigma n(\mathrm{Zr_n})}\right]_{2\,M} \tag{16}$$

Substituting into equation (15) and letting x be the exponent of the hydrogen ion dependence of K_2 one obtains

$$\frac{K_{2_{(1\,\mathrm{M})}}}{K_{2_{(2\,\mathrm{M})}}} = \frac{\Sigma n(\mathrm{Zr_n})_{(2\,\mathrm{M})}}{\Sigma n(\mathrm{Zr_n})_{(1\,\mathrm{M})}} = 2^x \tag{17}$$

or

$$x = \frac{\log \Sigma n(\mathrm{Zr_n})_{(2\,\mathrm{M})} - \log \Sigma n\,(\mathrm{Zr_n})_{(1\,\mathrm{M})}}{0.301} \tag{18}$$

The above equation applies where polymer formation is very slight. 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 found 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.[8]

Case 1.—Assume $K_\mathrm{n} = k^{n-1}$. 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

$$\Sigma n(\mathrm{Zr_n}) = \Sigma n K_\mathrm{n}(\mathrm{Zr})^n = \Sigma n k^{n-1}\,(\mathrm{Zr})^n \tag{19}$$

$$\frac{E_0^0}{E^0} = \frac{\Sigma n(\mathrm{Zr_n})}{(\mathrm{Zr})} = \Sigma n\,[k(\mathrm{Zr})]^{n-1} \tag{20}$$

This series when summed is equal to

$$\frac{E_0^0}{E^0} = \frac{1}{[1 - k(\mathrm{Zr})]^2} = \frac{\Sigma n(\mathrm{Zr_n})}{(\mathrm{Zr})} \tag{21}$$

$$\Sigma n(\mathrm{Zr_n}) = \left[1 - \left(\frac{E^0}{E_0^0}\right)^{1/2}\right]\frac{E_0^0}{kE^0} \tag{22}$$

This equation contains two arbitrary parameters E_0^0 and *k* which are to be fitted to the data.

Case 2.—Assume $K_\mathrm{n} = nk^{n-1}$. 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

$$\Sigma n(\mathrm{Zr_n}) = \Sigma n^2 k^{n-1}\,(\mathrm{Zr})^n \tag{23}$$

$$E_0^0/E^0 = \Sigma n^2\,[k(\mathrm{Zr})]^{n-1} \tag{24}$$

This series when summed is

$$\frac{E_0^0}{E^0} = \frac{1 + k(\mathrm{Zr})}{[1 - k(\mathrm{Zr})]^3} = \frac{\Sigma n(\mathrm{Zr_n})}{(\mathrm{Zr})} \tag{25}$$

Case 3.—Assume $K_\mathrm{n} = n^{-1}k^{n-1}$. 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

$$\Sigma n(\mathrm{Zr_n}) = \Sigma k^{n-1}\,(\mathrm{Zr})^n \tag{26}$$

$$E_0^0/E^0 = \Sigma[k(\mathrm{Zr})]^{n-1} \tag{27}$$

On summing the series we obtain

$$\frac{E_0^0}{E^0} = \frac{1}{1 - k(\mathrm{Zr})} = \frac{\Sigma n(\mathrm{Zr_n})}{(\mathrm{Zr})} \tag{28}$$

$$\Sigma n(\mathrm{Zr_n}) = (E_0^0 - E^0)/(kE^0) \tag{29}$$

Theoretical curves of log E^0/E_0^0 *versus* log $\Sigma n(\mathrm{Zr_n})$ 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 represented 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 1.2×10^3 and 1.3×10^2 for the 1 *M* and 2*M* perchloric acid series, respectively. The corresponding values of log E_0^0 are 9.21 and 8.05.

Polymer Formation in Other Systems.—All simple +4 ions exhibit strong tendencies toward polymerization accompanied by hydrolysis, as shown, for example, by their ready formation of colloidal solutions. Cerium(IV), which is considerably hydrolyzed even in 1 *M* perchloric acid,[9] forms a dimer and higher polymers[10] of undetermined composition. The ions of uranium(IV) and plutonium(IV) polymerize under approximately the same conditions as cerium(IV)[11] but the equilibria have not been investigated. The formula of the plutonium polymer formed in perchloric acid solutions has been reported[11] to be $(\mathrm{Pu(OH)_{3.85}})_n^{+0.15n}$. Zirconium polymerizes somewhat more readily than the above three ions as would be expected from its smaller size.

Recently $\mathrm{Bi^{+3}}$ has been studied in detail by Graner and L. G. Sillen[8] who showed that it simultaneously hydrolyzes and polymerizes like zir-

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[8] See F. Graner and L. G. Sillen (*Acta Chem. Scand.*, **1**, 631 (1947)) for a similar treatment of bismuth polymerization.

[9] M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

[10] L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948).

[11] K. A. Kraus and F. Nelson, U. S. Atomic Energy Commission Declassified Report, AECD-1888.

conium. Other ions which are known to react in this manner are UO_2^{++} and Be^{++}. It seems likely that such a behavior is more common than is generally assumed and that more cations when carefully studied will be found to act similarly.

Summary

The polymerization of zirconium(IV) in 1 *M* and 2 *M* perchloric acid solutions has been investigated by measurement of the extraction of the zirconium chelate of thenoyltrifluoroacetone into benzene 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 2×10^{-3} *M* while in 1 *M* perchloric acid they appear at concentrations as low as 2×10^{-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, exists.

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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Ion Exchange Measurements of Activity Coefficients and Association Constants of Cerous Salts in Mixed Electrolytes[1]

BY ROBERT E. CONNICK AND STANLEY W. MAYER

Introduction.—In the study of equilibria involving polyvalent ions it is often important to know the activity coefficients of such ions in mixed electrolytes. In many cases the deviations of activity coefficients from normal behavior are caused by complex-ion formation and a knowledge of the dissociation constants of such species is equally desirable. These data are not available except for a few cases, particularly insoluble salts.[2]

It has been pointed out by several investigators[3a,b,4] that measurements of ion exchange equilibria provide a convenient method of obtaining such information and it was adopted in the present work for the study of cerous salts.

Theory.—It has been shown by Bauman and Eichhorn[5] that a cation exchange resin of the Dowex type may be thought of as a highly concentrated salt phase in which the negative ions are fixed in position but the positive ions move more or less freely, as in a normal aqueous phase. In order to neutralize the negative charges of the resin an equal number of positive charges must always be present within the resin and, therefore, the normality of positive ions is fixed by the "capacity" of the resin.

The exchange equilibrium of +3 and +1 positive ions between a resin and an aqueous phase may be represented by

$$M^{+3} + 3N^{+} = M^{3+}_{R} + 3N^{+} \qquad (1)$$

where the subscript R represents the resin phase. The equilibrium constant for this reaction is

$$K = \frac{[M_R^{+3}][N^+]^3}{[M^{+3}][N_R^+]^3} = \frac{(M_R^{+3})(N^+)^3\gamma_{M_R^{+3}}\gamma^3_{N^+}}{(M^{+3})(N_R^+)^3\gamma_{M^{+3}}\gamma^3_{N_R^+}} \qquad (2)$$

where brackets indicate activities, parentheses represent concentrations and γ is the activity coefficient of the species indicated.

Multiplying numerator and denominator of equation (2) by $\gamma^3_{X^-}$ gives

$$K = \frac{(M_R^{+3})(N^+)^3\gamma_{M_R^{+3}}\gamma_{\pm NX}}{(M^{+3})(N_R^+)^3\gamma^4_{\pm MX_3}\gamma^{3}_{N_R^+}} = \frac{Q\gamma_{M_R^{+3}}\gamma^6_{\pm NX}}{\gamma^4_{\pm MX_3}\gamma^3_{N_R^+}} \qquad (3)$$

The quantity *Q* is experimentally measurable. If in a series of experiments the concentration of M^{+3} is kept small relative to that of N^+ in both phases, $\gamma_{N_R^+}$ and $\gamma_{M_R^{+3}}$ should remain constant and $\gamma_{\pm NX}$ should be equal to that for solutions containing only NX. Then

$$\gamma_{\pm MX_3} = k_{N^+}[Q\gamma^6_{\pm NX}]^{1/4} \qquad (4)$$

where k_{N^+} is a constant for a given temperature if the resin is nearly all in the N^+ form. Similar equations are readily derived for other types of electrolytes.

Experimental.—The experimental method was the same as that described by Tompkins and Mayer[3] except that the temperature was maintained within ±0.5° at 25° in all experiments.

Materials.—A single, large batch of Dowex 50 resin, 100–200 mesh, was the source of resin for all experiments. It was thoroughly washed with 6 molar hydrochloric acid and water and dried in air at 99% relative humidity in the acid form. The capacity of this resin was 2.700 equivalents per 1000 g. For equilibrations involving sodium salts, a portion of this resin was neutralized with sodium hydroxide, washed and air-dried. The

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(1) Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapt. 14.

(3) (a) G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947); (b) E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

(4) J. Schubert, *J. Phys. Colloid Chem.*, **52**, 340 (1948).

(5) W. C. Bauman and J. Eichhorn, THIS JOURNAL, **69**, 2830 (1947).