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THE HYDROLYTIC POLYMERIZATION OF ZIRCONIUM

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ABSTRACT

The hydrolysis of zirconium(IV) perchlorate was investigated by means of an organic complexing agent, thenoyltrifluoroacetone, over a range of zirconium concentrations extending from 10^{-5} molar to 0.3 molar and in one and two molar perchloric acid solutions at 25° C. The monomeric zirconium species at these acidities is shown to be the simple Zr^{+4} ion. The formation of hydrolysis polymers was found to commence at approximately 10^{-4} molar zirconium in one molar acid and at approximately 5×10^{-4} molar zirconium in two molar acid. The hydrolysis polymers studied are identified as a trimer and a tetramer and are assinged the formulas, $Zr_3(OH)_4^{+8}$ and $Zr_4(OH)_8^{+8}$. Equilibrium constants for the observed polymer formation are listed. The results of other investigations of zirconium hydrolysis are discussed and compared with the conclusions of this work.

I. INTRODUCTION

The chemical literature contains abundant evidence that zirconium(IV) undergoes extensive hydrolysis in aqueous solutions. Such behavior is, of course, to be expected from an ion of high charge and small radius such as Zr^{+4}. Thus many, if not all[1], the normal zirconium compounds such as $ZrCl_4$ can be prepared only in the absence of water; and even the half-hydrolyzed zirconyl salts such as $ZrOCl_2 \cdot 8H_2O$ produce acidic solutions. The important point is that if an ion is subject to such extensive hydrolysis that the products thereof become major species in solution, then it is imperative that the exact nature of these species be known before any quantitative attack can be made upon the chemistry of the ion.

Early investigations of such properties of zirconium solutions as conductivity[2,3], diffusion coefficients[4], pH[5,6], and freezing points[5] are difficult to interpret quantitatively but have amply indicated extensive hydrolysis and the formation of hydrolysis polymers. Among the recent zirconium work, Connick and his coworkers[7,8] provided a major advance with the first systematic hydrolysis study capable of unambiguous, quantitative interpretation. Other recent and important contributions have come from McVey[9], Larsen and Gammill[10], and Lister and McDonald[1].

The results of the above investigations will be discussed in more detail at the conclusion of this work. Suffice it to say for the moment that the hydrolysis studies of the various investigators have led to interpretations that agree in certain respects and differ considerably in others. Thus this work was undertaken in an effort either to resolve these differences or at least to shed some additional light upon the problem. To that end, the principal objectives in mind were to ascertain

the formulae of the zirconium species present in solutions of moderate acidity and to determine the equilibrium constants for their formation.

II. EXPERIMENTAL METHOD

The experimental method employed in this investigation is similar in many respects to that used by Connick and Reas[8]. They measured the distribution of zirconium between an aqueous phase and a benzene phase containing an organic chelating agent, thenoyltrifluoroacetone (hereafter abbreviated in the text as TTA and as HK in equations). TTA forms a neutral zirconium chelate[7] that is very soluble in benzene. Thus Connick and Reas studied the reaction:

$$Zr^{+4}_{(aq)} + 4HK_{(b)} = ZrK_{4(b)} + 4H^{+}_{(aq)} \qquad (1)$$

and the effects reflected by it as the zirconium and hydrogen ion concentrations were varied.

TTA also forms an aqueous phase complex with zirconium that has been identified by McVey[9] as ZrK^{+3}. This entirely aqueous complexing reaction, assuming for the moment that the zirconium species is unhydrolyzed and unpolymerized, may be represented as:

$$Zr^{+4} + HK = ZrK^{+3} + H^{+} \qquad (2)$$

The above equilibrium reaction served as the basic tool in this work.

A complexing coefficient, E, is defined as follows:

$$E = \frac{(ZrK^{+3})}{\Sigma Zr(HK)} \qquad (3)$$

where ( ) refers to moles per liter and ΣZr represents the formal concentration in moles per liter of the uncomplexed zirconium. By formal it is meant that ΣZr is calculated on the basis of all the zirconium being in the monomeric form.

At constant acidity any polymerization of the zirconium is reflected by a decrease in E. Thus values of E at various zirconium and hydrogen ion concentrations lend themselves to a quantitative treatment nearly identical to that outlined by Connick and Reas[8]. In addition greater experimental accuracy should be obtained since any error in the determination of the TTA concentration is not magnified by a fourth power dependence as in reaction (1). As will be seen in the mathematical development, the effect with regards to hydrogen ion is more complex; but again the aqueous complex reaction favors higher accuracy by lessening the hydrogen ion power dependence.

Experimental Procedures

Complexing coefficients were studied as a function of zirconium concentration in two main series of experiments - one in 2M $HClO_4$ and the other in 1M $HClO_4$ plus 1M $LiClO_4$, which was added to maintain constant ionic strength. In addition a few experiments were performed in 1M $HClO_4$ plus 1M $NaClO_4$. Only perchlorate solutions were employed in an effort to minimize any added complications due to extraneous complexing reactions.

Experimentally the use of TTA as a complexing agent is very convenient since the analysis of species present in equilibrium can be readily handled by spectrophotometric methods. Through the use of suitable blanks and the respective known molar extinction coefficients of ZrK^{+3} and TTA, it was thus possible to obtain the equilibrium concentration of ZrK^{+3} from the total optical density of the experimental solutions. Unless otherwise stated, all optical density measurements were made using a Beckman Model DU Spectrophotometer with the absorption cell compartment thermostated at 25.00 ± 0.05°C.

The equilibrium concentration of free TTA was obtained by a variety of methods. Though reaction (2) represents a homogeneous system, experimentally it was found more convenient to employ a two phase, benzene-aqueous system in the majority of the experiments. Fortunately experimental conditions can be adjusted such that reaction (1) is negligible while (2) still proceeds to a sufficient extent to give the aqueous phase a suitable optical density for the determination of (ZrK^{+3}). Then after correcting the known initial concentration of TTA for the small fraction tied up as ZrK^{+3}, the concentration of free TTA, both in the benzene and aqueous phase, can be calculated from the known distribution coefficient of TTA between benzene and the aqueous phase. A check of this analytical method was made in several of the early experiments by a spectrophotometric analysis of the equilibrium concentration of TTA in the benzene phase. The average deviation of 16 such check analyses from the calculated values amounted to 1.4%, which is well within the limits of error to be expected of the spectrophotometric analysis.

The concentration of free TTA can also be obtained in a one phase experiment by direct difference between the initial TTA concentration and that of ZrK^{+3}. This method was not employed in the majority of the experiments since a large fraction of the initial TTA would have been depleted in the formation of ZrK^{+3}. However under conditions of very low zirconium concentration and high TTA, this disadvantage is overcome; and in addition the two phase system then becomes a problem since reaction (1) starts to have an appreciable effect. In such cases an entirely aqueous experimental system was therefore employed, and this direct difference method was used to calculate the free TTA concentration.

In a typical experiment 75 ml. of benzene containing a known concentration of TTA and 75 ml. of an aqueous phase containing perchloric acid (and lithium or sodium perchlorate in the low acid series) and a known concentration of zirconium perchlorate were placed in an opaque 250 ml. volumetric flask. (Opaque flasks were used as a protective measure against the photochemical decomposition of TTA solutions reported by King and Reas[13].) The stopper was firmly sealed in place with sealing wax and, as an added precaution, tightly bound with waterproof tape. The flask was then mounted on a mechanical shaker and immersed in a water bath thermostated at 25.00 ± 0.05°C. After between 16 to 24 hours of vigorous shaking, a 30 ml. sample of the aqueous phase was removed, subjected to centrifugation to remove air bubbles and to break up any benzene-water emulsion, and analyzed spectrophotometrically. In most of the experiments a second sample was removed after an additional 24 hours of shaking as a check to demonstrate that equilibrium had already been obtained at the time of removal of the first sample. In the case of the one phase experiments, exactly the same procedure was followed with, of course, the exception that the aqueous phase then also contained the known initial TTA concentration.

All concentrations are reported in terms of moles per liter of solution, designated by the symbol M or by ( ).

Materials and Analytical Procedures

Water redistilled from alkaline permanganate was used to prepare all solutions. The water was indicated to be of conductivity grade by resistance measurements that gave a specific conductance of 1.0 x 10^{-6} mhos for typical samples. The benzene was C. P. grade, thiophene free. Perchloric acid solutions were prepared by diluting

G. F. Smith double vacuum distilled perchloric acid. The solutions were standardized by titration with standard, carbonate free sodium hydroxide.

Sodium and lithium perchlorate stock solutions were prepared by adding a small excess of double vacuum distilled perchloric acid to the respective carbonates. After boiling to remove CO_2, the pH of each solution was adjusted to 5 by addition of the respective hydroxides. The solutions were allowed to stand several days and then were filtered through sintered glass. Both solutions were standardized by evaporating aliquots to dryness in the presence of an excess of sulfuric acid and weighing the residue as the respective sulfates[11]. The sodium carbonate was primary standard grade. C. P. grade lithium carbonate, containing sulfate as the principal impurity, was purified by the method of Caley and Elving[12]. The lithium perchlorate stock solution tested free of sulfate when treated with barium nitrate.

TTA was obtained from Dow Chemical Company at supposedly 99.3 to 99.7% purity with acetylthiophene as the main impurity. This material was purified by a series of crystallizations from redistilled hexane (boiling range 59-63°C.). The main TTA stock was put through two such crystallizations and stored in a brown bottle. For use in the experiments, every 6 weeks to two months a small portion of this stock was crystallized once more from hexane and stored in a desiccator.

A melting point determination on a TTA sample after three such crystallizations gave a range of 43.4-43.8°C. The value quoted by the Dow Chemical Company for the true melting point is 43.76 ± 0.005°C. On the basis of our observed melting point range and estimating ΔH of fusion of TTA at about 30 cal./g., the final TTA crystals were estimated to be between 99.8 to 99.9 mole % pure. This calculation also assumes that all the impurity dissolves in the first portion of liquid formed.

Therefore standard solutions of TTA were prepared by dissolving a weighed amount of material and diluting to the desired volume. TTA is readily soluble in benzene but difficultly so in aqueous solutions. In preparing aqueous solutions, it was found expedient to warm the solutions until all the TTA had melted. A few minutes of vigorous shaking then sufficed to produce complete solution.

Due to the slow decomposition of aqueous TTA solutions reported by Zebroski[14] and Mattern[15], neither benzene nor aqueous stock solutions of TTA were maintained. Fresh solutions were prepared for each experiment. Thus the maximum age of all TTA solutions did not exceed four days; and on the basis of the observed rate constants,[14,15] the amount of decomposition should have been negligible.

Zirconyl chloride was obtained from the City Chemical Corp. and contained iron, chromium, and hafnium as the principal impurities. This material was purified by a series of four recrystallizations from 8M HCl, the product separating out in the form of large crystalline needles of $ZrOCl_2 \cdot 8H_2O$. Spectrographic analysis of the final product revealed that all impurities had been removed with the exception of 0.3-0.4 mole % of hafnium. No additional efforts were made to remove the hafnium; the amount present should have had a negligible effect. That this might be especially the case is indicated by the extraction coefficients for zirconium-hafnium mixtures determined by Schutz and Larsen[16] for trifluoroacetylacetone and by Huffman and Beaufait[17] for TTA. Both investigations revealed significantly larger chelating constants for zirconium than hafnium.

Stock solutions of zirconium perchlorate were prepared from zirconyl chloride by repeated fumings with excess perchloric acid. The crystalline product so obtained (still in an excess of $HClO_4$) dissolved readily upon

dilution to give a clear solution which did not show a Tyndall beam and tested free of Cl^- with $AgNO_3$. The zirconium concentration of the stock solutions (approximately 0.6M) was determined by treating aliquots with excess ammonium hydroxide and igniting the zirconium hydroxide so obtained to the dioxide. Small corrections were applied for the hafnium present when the zirconium concentration was calculated.

Various methods of determining the amount of excess perchloric acid in the zirconium stock solutions were investigated. Connick and Reas[8] suggest addition of excess NaF and then titration with NaOH. A rather careful study of this method was made using a Beckman Model G pH meter for a series of potentiometric titrations.

Potentiometric and indicator titrations without added NaF were also studied. Such experiments yield values for the combined zirconium and acid concentrations; the concentration of excess acid is then calculated on the basis of the known zirconium concentration. Both direct and back titrations of this type were employed. In the latter case an excess of standard base was added; the solution was boiled for a few minutes to digest the precipitate, and after cooling, was then titrated with standard acid. The back titrations were performed under an N_2 atmosphere during the entire procedure.

Three sodium fluoride stock solutions, all approximately 0.9M, were prepared by dissolving weighed amounts of C.P. grade Baker and Adamson, Baker's Analyzed, and Mallinckrodt NaF in water. Blank determinations on all three solutions revealed appreciable quantities of free base. All titrations were run with standard, CO_2 free 0.5M NaOH (standardized against potassium acid phthalate). Standard 0.1M $HClO_4$ was used for the back titrations. The zirconium perchlorate stock solution used for all

titrations was 0.6035M in Zr and 0.0025M in Hf. Five ml. and 10 ml. aliquots of this solution were used respectively for titrations without and with NaF added. All solutions were diluted to a total volume of 150 ml. before each titration.

The results of the investigation are summarized in Table 1. The plus or minus values represent average deviations from the mean.

Table 1

Concentration of Excess $HClO_4$ in $Zr(ClO_4)_4$ Stock Solution

Experiment Type	Excess $HClO_4$ (moles/l)	Comments
No added NaF, direct titration.	2.112 ± 0.002	Total of 5 determinations; 2 potentiometric titrations, 3 to bromthymol blue end-point.*
No added NaF, back titration.	2.174 ± 0.002	Total of 3 determinations, all to bromthymol blue end-point.*
NaF added.	2.187 ± 0.012	Total of 13 potentiometric titrations: 2 at 50 ml. added NaF, 7 at 75 ml. NaF, 4 at 100 ml. NaF

*The bromthymol blue end-points were all uncertain to about ± 0.04 ml. of 0.5M NaOH due to fading of the color change near the end-point. In each case titration was run to point of permanent color change.

As indicated by the data, the NaF method is in favorable agreement with the back titration method. Variations in the amount of NaF added produced no noticeable difference provided that a necessary minimum amount was exceeded. This necessary minimum was not measured carefully; but as a convenient rule of thumb, it was found that at least enough NaF solution had to be added to produce a finely divided, white precipitate in the initial zirconium solution. (No attempts were made to

identify the precipitate, but it was considered to be probably Na_2ZrF_6 or perhaps ZrF_4). In all titrations attempted where insufficient NaF had been added to produce this precipitate, zirconium hydroxide commenced to precipitate from solution before the end-point had been reached.

The rather large average deviation observed for the NaF method was due mainly to differences obtained using the three different stock solutions. Results obtained with any one "brand" of NaF were considerably more consistent. This might indicate that the various blanks used were not internally consistent.

The direct titration without added NaF apparently gives low results. This was expected due to the readily observed, complete coagulation of the zirconium hydroxide precipitate shortly before the end-point. This was found to be quite a well-defined point in the careful potentiometric titrations of zirconium solutions by Larsen and Gammill[10] and concerning which they state:

"The appearance of the coagulation point before the theoretical value has been interpreted as signifying the formation of basic salts with the hydroxyl ion deficiency being made up by the anion present in the solution. One could assume as well, however, that the extensively hydrolyzed species already present, reacted further with water to form the neutral metal hydroxide or hydrated oxide and the hydronium ion, the latter ion then being titrated to the end-point."

Although Larsen and Gammill did not do so, their data allow a test of these two hypotheses. Their observed difference between coagulation point and the theoretical value amounted to about 1 ml. of 0.1M NaOH, and the total solution volume was roughly 100 ml. Therefore if the latter case is correct, the observed coagulation pH should have been approximately 3 and actually it was about 5. Thus one must conclude that the precipitate formed at the coagulation point is indeed a basic salt. This produces low results for the excess acid found in

the direct titration since the precipitated zirconium was assumed to be $Zr(OH)_4$ or the hydrated oxide equilvalent.

Of course, high results would be obtained in both the back titration and the NaF methods if in the former any insoluble zirconates are formed and in the latter if either oxyfluoride complexes or precipitate are formed. In any event the various methods must certainly bracket the correct answer to within a few percent - an accuracy quite sufficient for this work since in nearly all the experiments, the excess acid of the zirconium stock solution contributed but a small fraction to the total acidity.

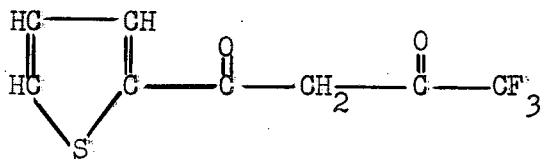
The NaF titration need not be potentiometric. A much simpler and nearly as accurate method is to titrate to the phenolphthalein end-point. This procedure was used to determine the excess $HClO_4$ in all other zirconium perchlorate stock solutions.

III. TTA: SPECIES IN SOLUTION AND OPTICAL PROPERTIES

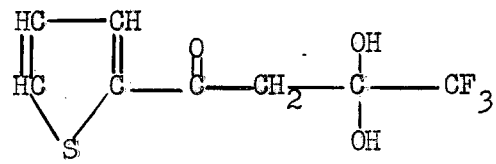
As a prerequisite to the use of TTA as a complexing agent, it was necessary to know: the species present in benzene and aqueous solutions, absorption spectra of TTA and ZrK^{+3}, and distribution coefficients for TTA between benzene and various aqueous phases. These topics will be discussed in this and the following two sections of this thesis.

Species in Solution

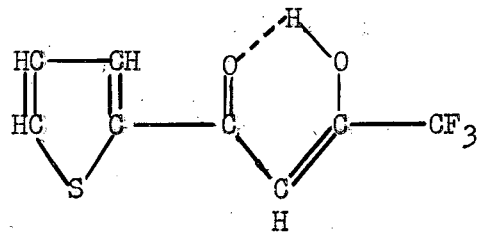
A number of detailed investigations[14,18,19] have been made concerning TTA species in solution. The results can be summarized as: approximately 98% keto-hydrate and 2% enol in aqueous solutions, at least 97% enol and possibly 3% keto in "dry" benzene, and approximately 90% enol and 10% keto-hydrate in benzene solutions which have been previously equilibrated with an aqueous phase. The formulas assigned to the various species are:



keto form



keto-hydrate form



enol form

An additional species, the enolate ion, is of importance only in basic solutions (acid dissociation constant of TTA[15]: $HK = H^+ + K^-$ $K_{25°} = 2.96 \times 10^{-7}$).

Molar Extinction Coefficients

Due to a certain amount of discrepancy in TTA spectral data reported by a number of authors,[14,15,20,21] it was deemed advisable to determine experimentally TTA molar extinction coefficients at all wavelengths pertinent to this research. This was done for all types of aqueous phases employed since Mattern[15] has reported changes in molar extinction coefficients with the ionic media.

By definition the optical density, D_λ, is equal to the logarithm (base ten) of the quotient of the incident light intensity, I^o, by the transmitted light intensity, I. Through application of Beer's and Lambert's laws, the optical density is also shown to be equal to the product of the molar extinction coefficient, ϵ_λ, the cell length, l, in centimeters, and the molar concentration, c, of the absorbing species. Thus:

$$D_\lambda = \epsilon_\lambda l\, c = \log I^o/I \qquad (4)$$

The experimentally determined molar extinction coefficients and the necessary data for their calculation are presented in Tables 2-5. A summary of the results and comparison with those of other authors is given in Table 6. The four wavelengths listed (266.5, 292, 314.1, and 366 mμ) correspond respectively to the two TTA absorption peaks, equal molar extinction coefficients for TTA and ZrK^{+3}, and the ZrK^{+3} absorption peak. The absorption spectra of TTA and ZrK^{+3} are presented in Figure 3 (Section V of this thesis). The appropriate blank corrections have been applied to all listed optical density values.

Table 2

Molar Extinction Coefficients of TTA at 266.5 Millimicrons and 25°C.

Media	(TTA) moles/l x 10^5	l (cm.)	D	ε
2M $HClO_4$	0.9596	5	0.485	10110
"	0.7191	5	0.359	9980
"	0.9604	5	0.483	10060
"	2.316	2	0.469	10110
"	1.854	2	0.369	9940
"	2.316	2	0.459	9900

Table 3

Molar Extinction Coefficients of TTA at 292 Millimicrons and 25°C.

Media	(TTA) moles/l x 10^5	l (cm.)	D	ε
2M $HClO_4$	4.638	2	0.7235	7800
"	5.713	2	0.8975	7855
"	4.707	2	0.7375	7830
1M $HClO_4$	4.769	2	0.7545	7910
+	7.333	2	1.1515	7850
1M $LiClO_4$	4.720	2	0.7485	7930
1M $HClO_4$	6.157	2	0.9555	7750
+	4.607	2	0.7205	7810
1M $NaClO_4$	4.665	2	0.7335	7855

Table 4

Molar Extinction Coefficients of TTA at 314.1 Millimicrons and 25°C.

Media	(TTA) moles/l x 10^5	l (cm.)	D	ε
2M $HClO_4$	6.724	2	0.547	4062
"	8.674	2	0.712	4099
"	6.867	2	0.556	4043

Table 5

Molar Extinction Coefficients of TTA at 366 Millimicrons and 25°C.

Media	(TTA) moles/l x 10^3	l (cm.)	D	ϵ
2M $HClO_4$	2.207	2	0.3785	85.7
"	2.382	2	0.4095	86.0
"	1.982	2	0.3395	85.7
"	4.644	2	0.7935	85.4
"	5.718	2	0.9855	86.2
"	4.711	2	0.8025	85.2
"	5.974	1	0.511	85.5
"	1.193	10	1.014	85.0
1M $HClO_4$	4.775	2	0.740	77.5
+	7.339	2	1.152	78.5
1M $LiClO_4$	4.724	2	0.732	77.5
1M $HClO_4$	3.086	2	0.4155	67.3
+	5.557	2	0.7555	67.9
1M $NaClO_4$	4.671	2	0.6265	67.0

Table 6

Summary of TTA Molar Extinction Coefficients at 25°C.

Reference	Media	$\epsilon_{266.5}$	ϵ_{292}	$\epsilon_{314.1}$	ϵ_{366}
This Work	2M $HClO_4$	10020 ± 80	7830 ± 20	4068 ± 21	85.6 ± 0.3
"	1M $HClO_4$ + 1M $LiClO_4$	-	7900 ± 30	-	77.8 ± 0.4
"	1M $HClO_4$ + 1M $NaClO_4$	-	7805 ± 40	-	67.4 ± 0.3
9	4M $HClO_4$	-	-	-	213.2
14	0.001M $HClO_4$	10080	7940	-	-
15	0.02M to 1M $HClO_4$	10045 ± 70	7850 ± 20	-	-
20	0.133M HCl	10140 ± 110	8010 ± 45	-	-
21	0.01M HCl	10000	7840	-	-

The experimentally determined molar extinction coefficients at the two TTA absorption peaks are seen to be in good agreement with the values reported by Mattern[15] and Orr[21] but less so with those of Zebroski[14] and King and Reas.[20] Variations of the ionic media apparently have but a small effect at the absorption peaks. That this is not the case when working at the absorption side-bands is amply demonstrated and in agreement with Mattern.[15]

IV. TTA: DISTRIBUTION COEFFICIENTS AND SALT EFFECTS

The determination of the equilibrium concentration of free TTA_{aq} in the complexing experiments required a knowledge of TTA distribution coefficients between benzene and various aqueous phases. As has been previously noted, such distribution coefficients were found to be markedly dependent upon the nature of the aqueous phase. All TTA distribution coefficient data that could be located are compiled here, and it is shown that the observed variations can be explained on the basis of salting out (and in) effects.

TTA Distribution Coefficients

The equilibrium distribution of TTA between benzene and an aqueous phase may be expressed as:

$$\beta = \frac{(TTA)_b}{(TTA)_{aq}} \tag{5}$$

where β is the distribution coefficient. The β values for various aqueous phases were measured by spectrophotometric analysis of the equilibrium aqueous phase. The 292 mμ TTA peak was used for all analyses. The observed optical densities, in combination with the appropriate molar extinction coefficients listed in Table 6, yield values of $(TTA)_{aq}$. If initially all the TTA was in the benzene phase, then it is readily shown that:

$$\beta = \frac{(TTA)^{\circ}_b}{(TTA)_{aq}} - A \tag{6}$$

where A equals the ratio of aqueous phase volume to benzene phase volume. If all the TTA was started in the aqueous phase, then:

$$\beta = \frac{A(TTA)^{\circ}_{aq}}{(TTA)_{aq}} - A \tag{7}$$

Unless otherwise noted, the following experimental conditions were observed in the determination of all β values: two centimeter spectrophotometer cells, all TTA initially in the benzene phase, A = 1 (equal benzene and aqueous phase volumes). The experimental procedure, without the addition of zirconium perchlorate, is identical to that outlined in Section II of this thesis. The data are presented in Tables 7-9.

Table 7

TTA Distribution Coefficient between Benzene and 2M $HClO_4$ at 25°C.

$(TTA)_b^\circ$ moles/l x 10^4	D_{292}	$(TTA)_{aq}$ moles/l x 10^5	β
15.03	0.642	4.100	35.7
15.03	0.646	4.125	35.4
14.50	0.619	3.953	35.7
14.50	0.613	3.914	36.0
4.974	0.5305*	1.354	35.8
5.599	0.5975*	1.525	35.7
7.618	0.8135*	2.076	35.7
	*5 cm. cell.	Mean Value:	35.7 ± 0.1

Table 8

TTA Distribution Coefficient between Benzene and 1M $HClO_4$ + 1M $LiClO_4$ at 25°C.

$(TTA)_b^\circ$ moles/l x 10^3	D_{292}	$(TTA)_{aq}$ moles/l x 10^5	β
1.509	0.499	3.159	46.8
1.509	0.508	3.216	45.9
1.387	0.458	2.900	46.8
1.146	0.382	2.419	46.4
1.397	0.455	2.881	47.5
1.397	0.472	2.988	45.7
		Mean Value:	46.5 ± 0.5

Table 9

TTA Distribution Coefficient between Benzene and 1M $HClO_4$ + 1M $NaClO_4$ at 25°C.

$(TTA)^{o}_{b}$ moles/l x 10^3	D_{292}	$(TTA)_{aq}$ moles/l x 10^5	β
3.086*	0.502	3.212	47.5
1.520	0.483	3.091	48.2
1.767	0.556	3.558	48.7
		Mean Value:	48.1 ± 0.4

*$(TTA)^{o}_{aq}$ - all TTA started in aqueous phase; A = 0.5

Salt Effects on TTA Activity

The data presented above illustrate the strong influence of ionic media on the value of β. As will be seen shortly, even more extreme variations in β have been observed. Since it does not seem reasonable that comparatively minor changes in the aqueous phase, such as replacement of half the hydrogen ions by lithium or sodium ions, can drastically affect the benzene phase, then the variations in β are apparently reflections of changes in the aqueous TTA activity coefficient. If this is the case, then it can be argued that the complexing coefficient E should be defined in terms of the benzene phase TTA concentration or:

$$E = \frac{(ZrK^{+3})}{(HK)_b \, \Sigma Zr} \qquad (8)$$

Since E is actually an arbitrary quantity that can be defined exactly in terms of solution concentrations, there might not at first sight appear to be any reason to consider thermodynamic activities. However the experimental E values and the equation defining them will later be used in equations containing various equilibrium constant expressions. Because of a lack of the required activity coefficients,

these equilibrium constants are all necessarily expressed in terms of the concentrations of species in solution instead of the respective thermodynamic activities. This will not affect the conclusions of this work as long as the activity coefficients of all pertinent species remain reasonably constant. However if the activity coefficient of any one species such as HK_{aq} is known to be changing, then, and for later convenience only, this variation could be removed by defining E in terms of the benzene TTA concentration, thereby assuming that the benzene TTA activity coefficient remains constant. However there is also another factor to consider. Namely that regardless if E is defined in terms of $(HK)_b$ or $(HK)_{aq}$, the concentration of the zirconium-TTA complex appears in all equations as the ratio $(ZrK^{+3})/(HK)$. Now if the activity coefficient of ZrK^{+3} is also varying in a similar fashion as that of the aqueous TTA, then both effects can be removed simply by defining E as in equation (3) and using the aqueous TTA concentration.

As a preliminary to any definite conclusions in regard to this problem, it was necessary to express β as a thermodynamic function of the activities of all pertinent TTA species. The β data were then analyzed in terms of the expression so obtained in an effort to find a rational explanation for the observed variations in the TTA distribution coefficient.

In the following equations, all activity coefficients are on the moles per liter scale and are indicated by the symbol f with suitable subscripts. The standard state of all species, including water dissolved in benzene, is the hypothetical one molar solution with infinite dilution properties. In the aqueous phase, the standard

state of water is the pure liquid.

As summarized in Section III of this thesis, the keto-hydrate and enol forms of TTA are the only species that need be considered. Then letting (E) equal concentration of TTA enol and (KH) equal concentration of TTA keto-hydrate:

$$\beta = \frac{(TTA)_b}{(TTA)_{aq}} = \frac{(E)_b + (KH)_b}{(E)_{aq} + (KH)_{aq}} \tag{9}$$

Since the enol form comprises no more than 2% of the aqueous TTA, as the first approximation it will be assumed that:

$$\beta = \frac{(E)_b + (KH)_b}{(KH)_{aq}} \tag{10}$$

(King and Reas[13,19] state that the amount of enol in an aqueous solution could range from 0 to 3% and assumed the former figure in their successful analysis of the anomalous approach to equilibrium of TTA distribution coefficients.)

Consider next the equilibria:

$$E_b + H_2O_b = KH_b \tag{11}$$

$$H_2O_{aq} = H_2O_b \tag{12}$$

and the respective equilibrium constants, K_1 and K_2:

$$K_1 = \frac{(KH)_b \, f_{KH_b}}{(E)_b \, f_{E_b} \, (H_2O)_b \, f_{H_2O_b}} \tag{13}$$

$$K_2 = \frac{(H_2O)_b \, f_{H_2O_b}}{[H_2O]} \tag{14}$$

where $[H_2O]$ = activity of water in the aqueous phase. A thermodynamic distribution coefficient for the keto-hydrate form only is defined as:

$$\beta^{o}_{KH} = \frac{(KH)_b \, f_{KH_b}}{(KH)_{aq} \, f_{KH_{aq}}} \tag{15}$$

Substitution of (13)-(15) in (10) yields, after suitable manipulation:

$$f_{KH_{aq}} = \frac{\beta \, [H_2O] \, f_{E_b}}{\beta^{o}_{KH} \left[\frac{[H_2O] \, f_{E_b}}{f_{KH_b}} + \frac{1}{K_1 K_2} \right]} \tag{16}$$

Since

$$\frac{1}{K_1 K_2} = \frac{(E)_b \, f_{E_b} \, [H_2O]}{(KH)_b \, f_{KH_b}} \tag{17}$$

and assuming $[H_2O]$ to be approximately one and the activity coefficients of E_b and KH_b to be roughly equal, then on the basis of 9 to 12% of KH_b and 91 to 88% of E_b as reported by King and Reas,[19] the value of $1/K_1K_2$ is estimated to be 9. The value of β^{o}_{KH} can also be estimated on the basis of the percentages of KH_b and KH_{aq} and the fact that β at low TTA concentration and low aqueous phase ionic strength approaches the value of 40. β^{o}_{KH} is thus taken equal to 4. (King and Reas[19] estimated 5.3 at a TTA benzene concentration of 0.5M). Substituting these values in (17) and again assuming that the activity coefficients of E_b and KH_b cancel, we obtain:

$$f_{KH_{aq}} = \frac{\beta \, [H_2O] \, f_{E_b}}{4\left\{[H_2O] + 9\right\}} \tag{18}$$

Table 10 presents a summary of $f_{KH_{aq}}$ values calculated on the basis of equation (18) from all TTA distribution coefficient data that could be located in the literature. King and Reas[20] have determined

the average activity coefficient of all TTA species in the benzene phase as a function of TTA concentration, and their values were used as an estimate for f_{E_b}. Solution densities for molal-molar scale conversions and osmotic coefficients for calculation of water activities were obtained from: Markam,[22] Stonehill,[23] Robinson and Baker,[24] for $HClO_4$; Lange,[25] Jones[26] for $NaClO_4$; Mazzucchelli and Rossi,[27] Jones,[26] for $LiClO_4$; Harned and Owen,[28] Robinson and Stokes,[29] for HCl and NaCl. In the cases where the aqueous phase contained mixed electrolytes, water activities were calculated as mean values. (Thus in 1M HCl + 1M NaCl, the value of $[H_2O]$ was assumed to be the average of the water activity in 2M HCl and in 2M NaCl). The last column of Table 10 represents the quotient of log $f_{KH_{aq}}$ by the ionic strength μ. As such it demonstrates the use of the Setschenow salting equation, log f = kc, which is generally applicable for the salt effect upon neutral molecules (c is the molar concentration of the salt and k, a constant dependent upon the salt and the neutral molecule, is the salting coefficient). Randall and Failey[30] have shown that this equation is not strictly valid, but it remains a useful first approximation.

Table 10

Benzene-Aqueous TTA Distribution Coefficients
and Activity Coefficients of Aqueous TTA at 25°C.

Reference	β	$(TTA)_b$ moles/l	fE_b	Aqueous Phase	$[H_2O]$	$f_{KH_{aq}}$	$\frac{\log f_{KH_{aq}}}{\mu}$
31	40.0	0.0109	0.99	0.0157M $HClO_4$	0.999	0.99	-0.28
31	37.4	0.0108	0.99	1M "	0.961	0.89	-0.051
31	37.1	0.0108	0.99	2M "	0.905	0.84	-0.038
TW.*	35.7	0.0015	1.00	2M "	0.905	0.82	-0.043
7	35	?	1 (?)	2M "	0.905	0.80	-0.048
32	37.0	0.0730	0.94	2M "	0.905	0.80	-0.048
31	45.7	0.0109	0.99	4M "	0.727	0.84	-0.019
31	84.9	0.0110	0.99	6.54M "	0.388	0.87	-0.009
33	49	0.490	0.82	0.5M $NaClO_4$ + 0.09M $HClO_4$	0.980	0.98	-0.015
33	57	0.491	0.82	1M " + "	0.962	1.13	0.049
33	76	0.494	0.82	2M " + "	0.923	1.45	0.077
33	167	0.497	0.82	4M " + "	0.826	2.87	0.112
33	443	0.499	0.82	6M " + "	0.698	6.52	0.134
TW.*	48.1	0.0017	1.00	1M $HClO_4$ + 1M $NaClO_4$	0.917	1.11	0.023
TW.*	46.5	0.0015	1.00	1M $HClO_4$ + 1M $LiClO_4$	0.904	1.06	0.013
20	40.0	0	1	0.115M HCl	0.996	1.00	0.00
34	58	0.0393	0.97	2M HCl	0.914	1.29	0.055
34	59	0.0983	0.93	"	0.914	1.26	0.050
34	61	0.216	0.88	"	0.914	1.24	0.047
34	62	0.295	0.86	"	0.914	1.23	0.045
34	65	0.0394	0.97	1.6M HCl + 0.4M NaCl	0.917	1.45	0.081
34	71	0.296	0.86	" + "	0.917	1.41	0.075
34	75	0.0395	0.97	1.2M HCl + 0.8M NaCl	0.920	1.68	0.113
34	77	0.0987	0.93	" + "	0.920	1.66	0.110
34	79	0.296	0.86	" + "	0.920	1.57	0.098
34	85	0.217	0.88	1M HCl + 1M NaCl	0.921	1.74	0.120
34	87	0.0395	0.97	0.8M HCl + 1.2M NaCl	0.922	1.96	0.146
34	89	0.0989	0.93	" + "	0.922	1.92	0.142
34	94	0.297	0.86	" + "	0.922	1.88	0.137
34	91	0.0396	0.97	0.4M HCl + 1.6M NaCl	0.926	2.05	0.156
34	110	0.297	0.86	" + "	0.926	2.20	0.171
34	97	0.0396	0.97	2M NaCl	0.928	2.19	0.170
34	113	0.0991	0.93	"	0.928	2.45	0.195
34	126	0.298	0.86	"	0.928	2.53	0.201

TW.* = This Work

The values listed in the last column of Table 10 represent quite reasonable salting coefficients for the respective electrolytes (see Harned and Owen[35] for an extensive list of salting coefficients). Thus the observed variations in β can be adequately interpreted as a combination of salting out (and in) effects plus accompanying changes in the water activity.

Provided that the Setschenow equation is valid, the calculated salting coefficients should be constant in the $HClO_4$ series of data and nearly so in the $NaClO_4$ plus 0.09M $HClO_4$ series. The fact that there is considerable variation is not considered unreasonable in view of the empirical nature of the Setschenow equation and the number of approximations and estimations employed in the derivation of equation (18). Also the HCl-NaCl series indicates the inadequacy of replacing f_{E_b} with the average activity coefficients of King and Reas.[20] Or possibly it is an indication that these activity coefficients are strictly valid only when the aqueous phase corresponds to that of their experiments (0.115M HCl).

The next problem to consider involves the complexing coefficient E and the salting effects on aqueous TTA activity. Specifically it is necessary to decide if the salting effects should be ignored - on the basis that they are canceled by an equal effect on the similar species ZrK^{+3} - or if they should be removed, either by use of the activity coefficients in Table 10 or the approximately equivalent procedure of equation (8). Direct experimental evidence to resolve this problem does not exist. However an answer can be obtained from the considerable quantity of data in the literature for the analogous situation of salting effects on the dissociation constants of weak acids.

The dissociation of a weak acid and the corresponding equilibrium

constant are represented by:

$$HA = H^+ + A^- \tag{19}$$

$$K_a = K_c \frac{f_{H^+}f_{A^-}}{f_{HA}} \tag{20}$$

Where K_a is the thermodynamic dissociation constant and K_c is the so-called concentration "constant", i.e.:

$$K_c = \frac{(H^+)\ (A^-)}{(HA)} \tag{21}$$

Principally through E.M.F. studies of cells with and without liquid junctions, values for the activity coefficient ratio $f_{H^+}f_{A^-}/f_{HA}$ - at infinite dilution of the acid and in various salt solutions - have been evaluated for a large number of weak acids. The observed activity coefficient ratios vary with the salt employed and the ionic strength. However at a fixed concentration of any given salt, the value of $f_{H^+}f_{A^-}/f_{HA}$ is nearly independent of the weak acid. This has been found to be so even though the salting effects on the undissociated part of the various weak acids (as represented by f_{HA}) vary widely. On the basis of this experimental fact, Larsson and Adell[36] have suggested that the activity coefficient of the weak acid anion should be represented as the product of two factors representing respectively the salting and charge effect or:

$$f_{A^-} = f_A f_- \tag{22}$$

This salting factor in f_{A^-} is then largely canceled by f_{HA}, leaving the activity coefficient ratio as:

$$\frac{f_{H^+}f_{A^-}}{f_{HA}} = \frac{f_{H^+}f_A f_-}{f_{HA}} = f_{H^+}f_- \tag{23}$$

and f_- is presumably approximated by the activity coefficient of a small minus one ion in the same salt solution. (It is interesting to

note that in the recent theoretical equation for salting coefficients derived by McDevit and Long,[37] salt effects are predicted to vary as the partial molar volume of the salted out (or in) species. The salt effects on species of closely related dimensions such as HA and A^- would thus be expected to be very similar.) Equation (23) indicates that the activity coefficient ratio should be independent of the weak acid and in addition should assume values very similar to the activity coefficient product of 1-1 electrolytes at infinite dilution in the same salt solution.

Figures 1 and 2 illustrate how well the above conditions are obeyed in sodium and potassium chloride solutions. Utilizing the data of Larsson and Adell,[36] the average of the logarithm of the activity coefficient ratios for 24 organic acids are plotted versus the square root of the ionic strength. Where they become appreciable, average deviations from the mean value are indicated by vertical lines. For comparison to the activity coefficient product of a 1-1 electrolyte at infinite dilution in the same salt solutions, the smooth curve in each case represents values of log $f_{H^+}f_{OH^-}$ as calculated from the very accurate data that exist on the ionization constant of water.[38] (In similar plots Harned and Owen[39] use the square of the mean activity coefficient of HCl at infinite dilution in the salt solution).

The deviations produced by applying salting out corrections for the undissociated part of the weak acid only are illustrated in the case of two of the acids - acetic and benzoic. The former is an example of a small to moderate salting effect (salting coefficients approximately 0.04 in KCl and 0.08 in NaCl) and the latter of a fairly large one (salting coefficient approximately 0.14 in KCl and 0.18 in

NaCl). The values of f_{HA} for these calculations were obtained from Randall and Failey[30] for acetic acid and from Kilpatrick[40] for benzoic acid. All data in Figures 1 and 2 are at 25°C. and are on the moles per liter scale. The necessary solution densities and osmotic coefficients were obtained from the sources quoted for the data in Table 10.

On the basis of the above discussion of salt effects on weak acids, all values of the complexing coefficient E were calculated from the equation:

$$E = \frac{(ZrK^{+3})}{(HK)_{aq}\ \Sigma Zr} \qquad (24)$$

It was thereby assumed that the salting effects on TTA activity are canceled by an equal effect on the TTA complex ZrK^{+3}. The resultant residual activity coefficient, as in equation (23), of ZrK^{+3} would then be expected to be that of a small +3 ion.

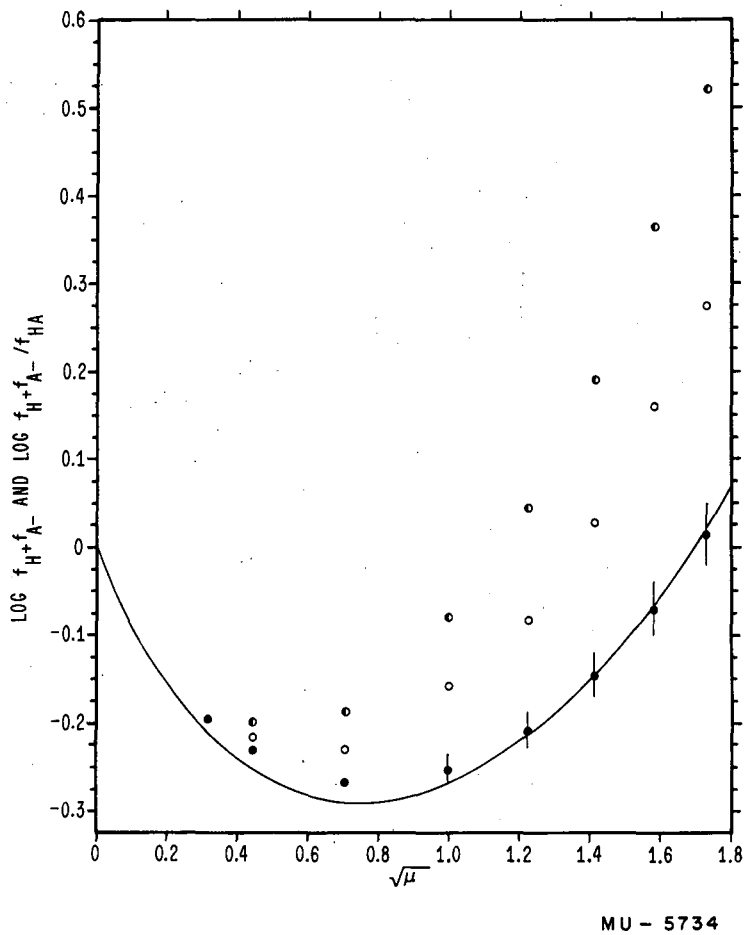


Fig. 1. Smooth curve, log $f_{H^+}f_{OH^-}$; ●, average of log $f_{H^+}f_{A^-}/f_{HA}$ for 24 organic acids; O and ◐, log $f_{H^+}f_{A^-}$ for acetic and benzoic acids.

Salt Effects in NaCl Solutions

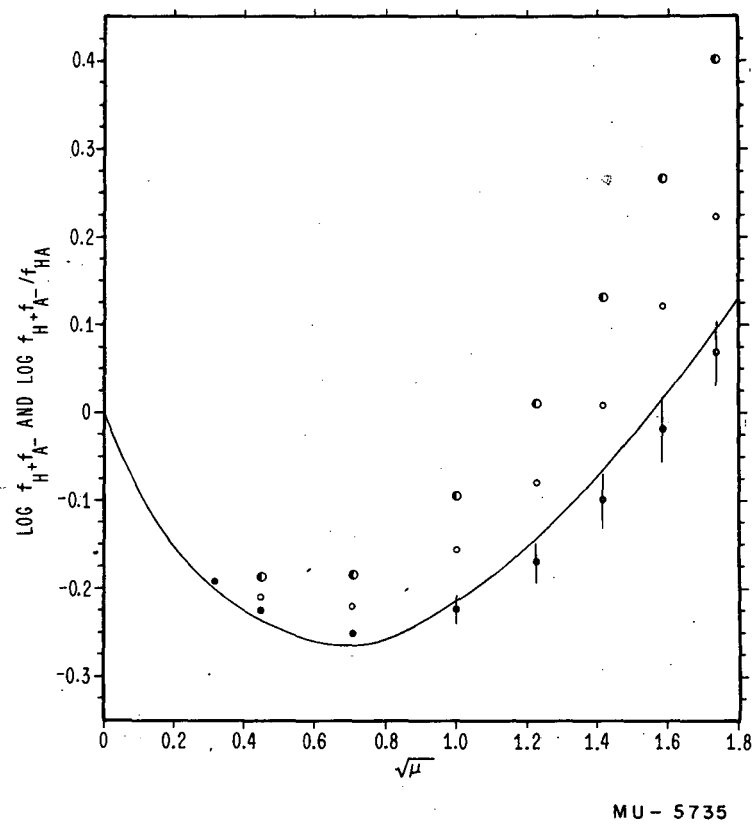


Fig. 2. Smooth curve, log $f_H + f_{OH^-}$; ●, average of log $f_H + f_{A^-}/f_{HA}$ for 24 organic acids; O and ◐, log $f_H + f_{A^-}$ for acetic and benzoic acids.

Salt Effects in KCl Solutions

V. ABSORPTION SPECTRUM OF ZrK^{+3}

McVey[9] has reported that the first zirconium-TTA chelate, ZrK^{+3}, exhibits a maximum light absorption at 366 millimicrons. By a method involving the equilibrium constant of reaction (2):

$$K = \frac{(ZrK^{+3})\ (H^{+})}{(Zr^{+4})\ (HK)} \tag{25}$$

and known initial concentrations of zirconium and TTA, McVey determined K and ϵ_{366} of ZrK^{+3} by a series of optical density measurements in 4M perchloric acid solutions. His reported values, all at 25°C., are K = 1084 and ϵ_{366} of ZrK^{+3} = 2.34×10^4.

Since the spectrophotometric method of analysis was used exclusively in the study, the molar extinction coefficient of ZrK^{+3} is necessarily a constant of prime importance. It was thus desirable to check McVey's results by a new determination at the ionic strength of two employed in this work.

Efforts to do so by use of McVey's method were not successful since as a necessary prerequisite, one must have a fairly wide working range of zirconium concentrations where the monomer is the only important zirconium species. Such a range is available in 4M but not 2M acid because of the high hydrogen ion dependence of zirconium polymerization. Therefore it was necessary to devise a new method for the determination of the ZrK^{+3} molar extinction coefficient. Briefly this method gives a measure of $\epsilon_{ZrK^{+3}}$ by the change produced in the optical density of an aqueous TTA solution by the addition of zirconium.

The optical density, including solution background and cell blank, of a TTA solution of concentration (HK)' and at any wavelength x may be expressed as:

$$D^x_{A_1} = l\epsilon^x_{HK} (HK)' + D^x_{cell} \tag{26}$$

where D^x_{cell} represents the combined blank contribution of solution and cell. The optical density, in the same cell, of an identical solution plus added zirconium is:

$$D^x_{B_1} = l\left[\epsilon^x_{HK} (HK) + \epsilon^x_{ZrK^{+3}} (ZrK^{+3})\right] + D^x_{cell} \tag{27}$$

where (HK) and (ZrK^{+3}) are related by:

$$(ZrK^{+3}) = (HK)' - (HK) \tag{28}$$

(Actually the D^x_{cell} value of equation (27) is identical to that of (26) only after a very small correction has been applied for the additional absorption caused by the zirconium.)

Equations (26)-(28) can be combined to give:

$$D^x_{B_1} - D^x_{A_1} = \Delta D^x_1 = l\left[\epsilon^x_{ZrK^{+3}} - \epsilon^x_{HK}\right](ZrK^{+3}) \tag{29}$$

If optical density measurements are made on the same pair of solutions at any other wavelength y and if x is taken equal to 366 mμ, the results can be combined to give:

$$\frac{\Delta D^{366}_1}{-\Delta D^y_1} = \frac{\epsilon^{366}_{ZrK^{+3}} - \epsilon^{366}_{HK}}{\epsilon^y_{HK} - \epsilon^y_{ZrK^{+3}}} = k_1^{\ y} \tag{30}$$

If y is such a wavelength that the molar extinction coefficient of ZrK^{+3} is negligibly small compared to that of TTA, then equation (30) in combination with the independently measurable values of ϵ^{366}_{HK} and ϵ^y_{HK} would allow an immediate determination of $\epsilon^{366}_{ZrK^{+3}}$. Regrettably no such wavelength was found to exist, and hence a second series of experiments must be performed in order to utilize equation (30). This second series is very similar in principle to the first but employes a two phase, benzene-aqueous system. Optical density measurements are again made on the aqueous phase with and without added zirconium.

However in this case the benzene phase acts as a reservoir for TTA, and hence all optical density values are increased by the addition of zirconium.

Let $(HK)^{\circ}$ equal the total initial concentration of TTA - all in the benzene phase - and $(HK)'$ equal the equilibrium concentration of aqueous TTA with no added zirconium and (HK) equal the equilibrium concentration of aqueous TTA with added zirconium. Then by equation (5) and if the benzene and aqueous phase volumes are equal:

$$\beta = \frac{(HK)^{\circ} - (HK)'}{(HK)'} = \frac{(HK)^{\circ} - (HK) - (ZrK^{+3})}{(HK)} \quad (31)$$

The difference of equations exactly similar in form to (26) and (27) yields:

$$D^{x}_{B_2} - D^{x}_{A_2} = \Delta D^{x}_{2} = l\left\{\epsilon^{x}_{ZrK^{+3}} (ZrK^{+3}) - \epsilon^{x}_{HK} \left[(HK)' - (HK)\right]\right\} \quad (32)$$

Substituting (31) into (32), we obtain:

$$\Delta D^{x}_{2} = l\left[\epsilon^{x}_{ZrK^{+3}} - \frac{\epsilon^{x}_{HK}}{\beta + 1}\right] (ZrK^{+3}) \quad (33)$$

Again if optical density measurements are made on the same pair of solutions at another wavelength y and if x is taken to be 366 mμ, the quotient of the ΔD_2 values gives:

$$\frac{\Delta D^{366}_{2}}{\Delta D^{y}_{2}} = \frac{(\beta + 1)\ \epsilon^{366}_{ZrK^{+3}} - \epsilon^{366}_{HK}}{(\beta + 1)\ \epsilon^{y}_{ZrK^{+3}} - \epsilon^{y}_{HK}} = k_2^{\ y} \quad (34)$$

At any given y, the value of $\epsilon^{366}_{ZrK^{+3}}$ can now be obtained by simultaneous solution of (30) and (34):

$$\epsilon^{366}_{ZrK^{+3}} = \frac{\beta k_1^{\ y} k_2^{\ y} \epsilon^{y}_{HK} + \epsilon^{366}_{HK}\left[k_1^{\ y} + k_2^{y} (\beta + 1)\right]}{(\beta + 1)\ (k_1^{\ y} + k_2^{y})} \quad (35)$$

For the case where $\epsilon^{y}_{HK} = \epsilon^{y}_{ZrK^{+3}}$ or $k_1^{\ y} = \infty$, equation (35) reduces

to:

$$\epsilon^{366}_{ZrK^{+3}} = \frac{\beta k_2^{y} \epsilon^{y}_{HK} + \epsilon^{366}_{HK}}{\beta + 1} \qquad (36)$$

To utilize equation (35), aqueous phase optical density measurements were made on pairs of solutions from one and two phase equilibrium systems. One solution from each pair contained added zirconium perchlorate and the other did not. Since for the most part the ΔD values so obtained represent rather small differences, the experimental error for any one determination could be quite large. Therefore several solutions were analyzed at a total of 3 wavelengths (in addition to the necessary 366 mμ) in order to obtain a reliable average value for $\epsilon^{366}_{ZrK^{+3}}$. The 3 wavelengths selected - 266.5, 292, and 314.1 mμ - correspond to the two TTA absorption peaks and the wavelength where $\epsilon_{HK} = \epsilon_{ZrK^{+3}}$. This last wavelength is indicated by a ΔD value of zero in the one phase experiments. As such it was first determined approximately from experiments using a Cary Recording Spectrophotometer. More precise measurements with a Beckman Model DU Spectrophotometer, and on 3 independent solution pairs, gave an average value of 314.1 ± 0.1 mμ.

All aqueous solutions were 2M in perchloric acid. The zirconium concentration varied roughly from 0.01M to 0.04M and the initial TTA concentration from 0.7×10^{-5}M to 2×10^{-5}M in the one phase runs and 3×10^{-4}M to 5×10^{-4}M in the two phase experiments. (This method does not require a knowledge of the TTA or zirconium concentrations; the only restriction is that the initial TTA concentration in each solution pair must be identical.) Equal benzene and aqueous phase volumes were used, and all experiments were performed at 25.00 ± 0.05°C. Five cm. and two cm. absorption cells were employed respectively in runs

1-3 and 4-6; and unless otherwise indicated, two cm. cells were used for runs 7-12. The experimental procedure was identical to that outlined in Section II of this thesis.

The data and calculated results are presented in Tables 11A-11C. The necessary values of ϵ^{y}_{HK} and β are given in Tables 6 and 7. The plus or minus values listed in Table 11C were obtained as follows: For k_1 and k_2, they are average deviations from the mean experimental values. For $\epsilon^{366}_{ZrK^{+3}}$, they are calculated as probable errors, utilizing as uncertainties the average deviations listed for k_1, k_2, ϵ^{y}_{HK}, and β. Since the wavelength were $\epsilon_{HK} = \epsilon_{ZrK^{+3}}$ was found to be uncertain by 0.1 mμ, the uncertainty in $\epsilon^{314.1}_{HK}$ was increased to ± 60 for these calculations. The final value of $\epsilon^{366}_{ZrK^{+3}}$ represents the average of the listed values, each weighted inversely according to the calculated probable error. This final value is considered to be in sufficiently good agreement with McVey's[9] value of $\epsilon^{366}_{ZrK^{+3}} = 2.34 \times 10^4$ since an examination of his data shows that this result is uncertain by at least 3%. In addition there may be an effect due to the 4M perchloric acid medium employed in his work and the 2M perchloric acid used in this determination. It should also be mentioned that the ZrK^{+3} absorption peak was found to occur at 365 mμ in this work in comparison to McVey's result of 366 mμ.

Once the value of $\epsilon^{366}_{ZrK^{+3}}$ has been determined, equation (30) allows the calculation of $\epsilon_{ZrK^{+3}}$ at any other wavelength by the one phase, k_1 experiments only. The absorption spectrum of ZrK^{+3} was thus obtained by running suitable solution pairs on a Cary Recording Spectrophotometer. The smooth curve, average result of two such determinations is illustrated in Figure 3. The absorption spectrum of TTA is also presented for comparison.

Table 11A

Determination of $\epsilon^{366}_{ZrK^{+3}}$ in 2M $HClO_4$ - One Phase Data

Run	ΔD_1^{366}	$-\Delta D_1^{292}$	$-\Delta D_1^{266.5}$	k_1^{292}	$k_1^{266.5}$
1	0.709	0.0735	0.189	9.65	3.75
2	0.525	0.057	0.136	9.21	3.86
3	0.6325	0.0705	0.1715	8.97	3.69
4	0.7145	0.071	0.1905	10.06	3.75
5	0.573	0.055	0.1455	10.42	3.94
6	0.5735	0.0585	0.1495	9.80	3.84

Table 11B

Determination of $\epsilon^{366}_{ZrK^{+3}}$ in 2M $HClO_4$ - Two Phase Data

Run	ΔD_2^{366}	$\Delta D_2^{314.1}$	ΔD_2^{292}	$\Delta D_2^{266.5}$	$k_2^{314.1}$	k_2^{292}	$k_2^{266.5}$
7	0.615	-	0.1155	-	-	5.32	-
8	0.7165	-	0.137	0.1035	-	5.23	6.92
9	0.5555	-	0.1125	-	-	4.94	-
10	0.5705	0.2325*	0.2855*	0.078	6.13	5.00	7.31
11	0.5005	0.213*	0.2455*	0.0645	5.87	5.10	7.76
12	0.5835	0.2385*	0.275*	0.0905	6.12	5.30	6.45

* 5 cm. cell-multiply ΔD by 0.4 to calculate k_2

Table 11C

Determination of $\epsilon^{366}_{ZrK^{+3}}$ in 2M $HClO_4$ - Summary and Calculated Results

y (mμ)	k_1	k_2	$\epsilon^{366}_{ZrK^{+3}} \times 10^{-4}$
314.1	∞	6.04 ± 0.11	2.39 ± 0.06
292	9.68 ± 0.41	5.15 ± 0.14	2.56 ± 0.09
266.5	3.80 ± 0.07	7.11 ± 0.43	2.42 ± 0.18

Weighted average: 2.45 ± 0.09

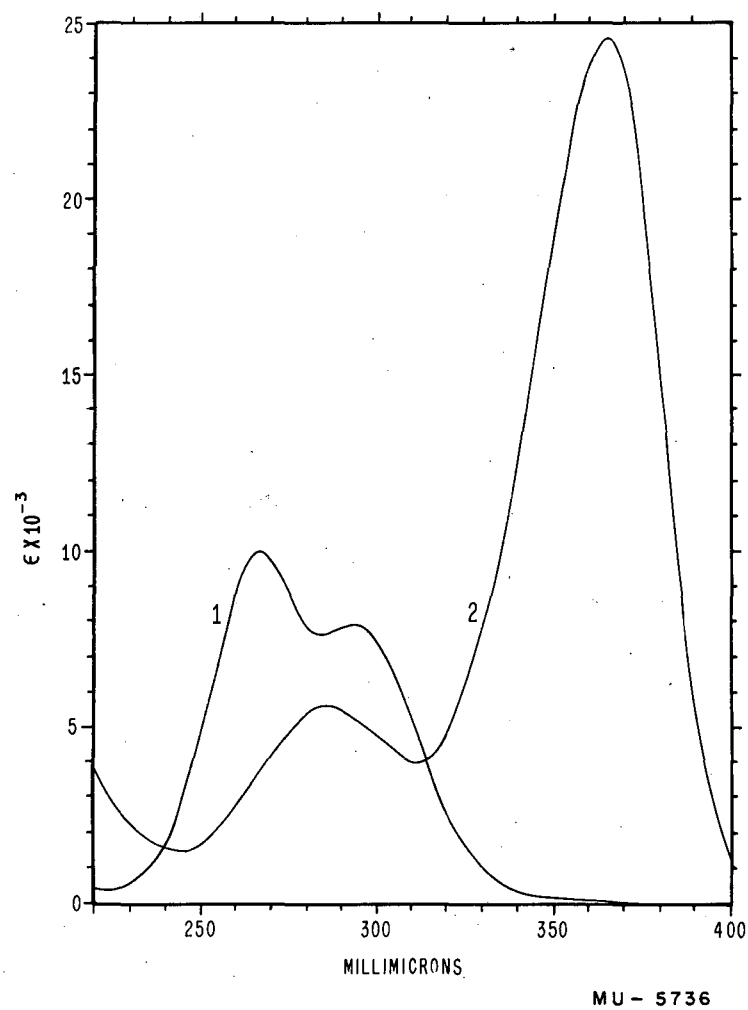


Fig. 3. Absorption Spectrum of TTA (1) and ZrK^{+3} (2) in 2 M $HClO_4$

VI. ZIRCONIUM-TTA COMPLEXING COEFFICIENTS

Sufficient information is now available to determine values of the complexing coefficient E as defined by equations (3) and (24). In the following equations $(HK)^\circ$ refers to the initial concentration of TTA in both the one phase and two phase experiments (in the two phase experiments it will be understood that all TTA was initially in the benzene phase). The equilibrium aqueous phase concentration of TTA and the first zirconium chelate are always represented by (HK) and (ZrK^{+3}). The initial and equilibrium aqueous phase concentrations of zirconium perchlorate are given by ΣZr° and ΣZr. In the two phase experiments the ratio of aqueous phase volume to benzene phase volume is abbreviated as A.

Two Phase Experiments

In the case of unequal benzene and aqueous phase volumes, equation (31) is modified to:

$$\beta = \frac{(HK)^\circ - A\left[(HK) + (ZrK^{+3})\right]}{(HK)} \qquad (37)$$

From optical density measurements of the equilibrium aqueous phase - all at 366 mμ:

$$(ZrK^{+3}) = \frac{D/l - (HK)\,\epsilon_{HK}}{\epsilon_{ZrK^{+3}}} \qquad (38)$$

and D is understood to be the residual optical density after all necessary blank corrections, including the small absorption of the zirconium at high zirconium concentration. Simultaneous solution of (37) and (38) yields:

$$(HK) = \frac{(HK)^\circ\,\epsilon_{ZrK^{+3}} - AD/l}{(\beta + A)\,\epsilon_{ZrK^{+3}} - A\epsilon_{HK}} \qquad (39)$$

After obtaining (HK) from (39) and then (ZrK^{+3}) from (38), ΣZr is simply

obtained by:

$$\Sigma Zr = \Sigma Zr^{\circ} - (ZrK^{+3}) \tag{40}$$

One Phase Experiments

Equation (38) also applies in the one phase experiments and since:

$$(HK) = (HK)^{\circ} - (ZrK^{+3}) \tag{41}$$

then substitution of (41) in (38) gives:

$$(ZrK^{+3}) = \frac{D/l - (HK)^{\circ}\,\epsilon_{HK}}{\epsilon_{ZrK^{+3}} - \epsilon_{HK}} \tag{42}$$

and ΣZr is again obtained by equation (40).

All quantities are now available for calculation of the complexing coefficient E by equation (24). The experimental procedure has been described in Section II of this thesis, and the data are presented in Tables 12-14. One phase experiments are indicated by an A value of ∞. The necessary values of ϵ^{366}_{HK}, β, and $\epsilon^{366}_{ZrK^{+3}}$ are as listed in Sections III-V. In certain of the two phase experiments where high TTA concentrations were used, it was necessary to apply small corrections for zirconium extracted into the benzene phase as ZrK_4 - see reaction (2). Such corrections were applied by utilizing the data of Connick and Reas[8] for a successive approximation calculation of the ZrK_4 concentration. Corrected "initial" concentrations of TTA and zirconium were then employed to calculate E.

Table 12

Zirconium-TTA Complexing Coefficients in 2M $HClO_4$ at 25°C

Run	ΣZr° moles/l x 10^3	$(HK)^{\circ}$ moles/l x 10^4	A	l (cm)	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
2-1	0.02069	11.99	∞	5	0.974	119.5	3.78	0.01691	187
					0.971	119.5	3.75	0.01694	185
2-2	0.03211	8.994	∞	5	0.941	89.48	4.56	0.02755	185
					0.941	89.48	4.56	0.02755	185
2-3	0.03924	6.314	∞	5	0.752	62.75	3.95	0.03529	178.5
					0.749	62.75	3.92	0.03532	177
2-4	0.06419	5.996	∞	5	1.009	59.34	6.17	0.05802	179
					1.011	59.34	6.18	0.05801	180
2-5	0.09505	25.25	1	10	0.318	6.87	1.06	0.09362	164*
					0.323	6.87	1.08	0.09359	168*
2-6	0.1956	1.263	∞	5	0.543	12.23	4.01	0.1916	171
					0.545	12.23	4.02	0.1916	172
2-7	0.3153	23.87	1	10	0.843	6.48	3.21	0.3111	159.5*
2-8	0.5208	0.5052	∞	5	0.516	4.647	4.05	0.5167	169
					0.516	4.647	4.05	0.5167	169
2-9	0.7875	5.024	1	10	0.417	1.364	1.65	0.7858	154
2-10	1.299	3.680	2.5	5	0.241	0.951	1.93	1.297	157
					0.237	0.951	1.90	1.297	154

*Corrected for $(ZrK_4)_b$ - see text

Table 12-2

Run	ΣZr^{o} moles/l x 10^3	$(HK)^{o}$ moles/l x 10^4	A	l (cm)	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
2-11	2.597	3.680	2.5	5	0.421	0.941	3.40	2.594	139.5
					0.416	0.941	3.36	2.594	138
2-12	3.871	3.680	2.5	5	0.5395	0.934	4.37	3.867	121
2-13	6.278	1.459	1	2	0.1202	0.391	2.44	6.276	99.4
2-14	6.297	3.879	1	2	0.3125	1.040	6.34	6.291	97.0
					0.3095	1.040	6.28	6.291	96.0
2-15	12.44	1.459	1	2	0.1645	0.388	3.34	12.44	69.2
2-16	12.46	5.071	1	2	0.578	1.350	11.8	12.45	69.9
2-17	13.09	4.964	1	2	0.573	1.321	11.6	13.08	67.3
2-18	18.10	4.784	1	2	0.617	1.269	12.5	18.09	54.6
2-19	24.19	4.784	1	2	0.7185	1.264	14.6	24.18	47.8
2-20	24.69	3.879	1	2	0.5855	1.024	11.9	24.68	47.1
2-21	26.18	3.310	1	2	0.502	0.874	10.2	26.17	44.6
2-22	31.03	5.071	1	2	0.832	1.336	16.9	31.01	40.9
2-23	39.28	3.310	1	2	0.585	0.870	11.9	39.27	34.8
2-24	61.98	3.879	1	2	0.821	1.011	16.7	61.96	26.7
					0.805	1.012	16.4	61.96	26.1

Table 12-3

Run	ΣZr° moles/l x 10^3	$(HK)^{\circ}$ moles/l x 10^4	A	$l_{(cm)}$	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
2-25	154.8	2.070	1	2	0.655	0.528	13.4	154.8	16.3
					0.647	0.528	13.2	154.8	16.1
2-26	310.1	2.070	1	2	0.955	0.511	19.5	310.1	12.3
					0.952	0.511	19.4	310.1	12.25

Table 13

Zirconium-TTA Complexing Coefficients in 1M $HClO_4$ + 1M $LiClO_4$ at 25° C

Run	ΣZr° moles/l x 10^3	$(HK)^{\circ}$ moles/l x 10^4	A	$l_{(cm)}$	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
1-1	0.02097	10.06	∞	5	0.875	100.2	3.96	0.01701	232
					0.875	100.2	3.96	0.01701	232
1-2	0.03920	6.289	∞	5	0.986	62.28	6.07	0.03313	294
					0.984	62.28	6.05	0.03315	293
1-3	0.05223	2.516	∞	5	0.541	24.80	3.63	0.04860	301
					0.541	24.80	3.63	0.04860	301
1-4	0.07811	1.529	∞	5	0.487	14.94	3.50	0.07461	314
					0.488	14.94	3.51	0.07460	315
1-5	0.1302	0.956	∞	5	0.500	9.18	3.79	0.1264	327
					0.501	9.18	3.80	0.1264	327

Table 13-2

Run	ΣZr^{o} moles/l x 10^3	$(HK)^{o}$ moles/l x 10^4	A	l (cm)	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
1-6	0.1953	0.956	∞	5	0.718	9.00	5.57	0.1897	326
					0.720	9.00	5.59	0.1897	328
1-7	0.3255	18.52	2.4	5	0.489	3.74	3.87	0.3203	323*
					0.471	3.74	3.73	0.3204	311*
1-8	0.3255	17.90	2.4	5	0.471	3.62	3.73	0.3206	321*
					0.452	3.62	3.58	0.3207	308*
1-9	0.4672	18.52	2.4	5	0.649	3.73	5.18	0.4604	302*
					0.625	3.73	4.98	0.4606	290*
1-10	0.4673	17.90	2.4	5	0.623	3.61	4.97	0.4609	299*
					0.603	3.61	4.81	0.4610	289*
1-11	0.6486	18.52	2.4	5	0.787	3.72	6.31	0.6404	265*
1-12	0.6487	17.90	2.4	5	0.779	3.60	6.24	0.6408	271*
					0.770	3.60	6.17	0.6408	268*
1-13	1.038	7.246	2.4	5	0.4125	1.465	3.32	1.035	219
					0.4095	1.465	3.30	1.035	217
1-14	1.619	7.246	2.4	5	0.5195	1.461	4.19	1.615	178
					0.4955	1.462	4.00	1.615	169
1-15	3.209	7.246	2.4	5	0.6695	1.455	5.42	3.204	116
					0.6625	1.455	5.36	3.204	115
1-16	5.187	5.010	2.4	5	0.555	1.002	4.50	5.183	86.6
					0.553	1.002	4.48	5.183	86.3

*Corrected for $(ZrK_4)_b$ - see text

Table 13-3

Run	ΣZr° moles/l x 10^3	$(HK)^{\circ}$ moles/l x 10^4	A	l (cm)	D_{366}	(HK) moles/l x 10^5	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^3	E
1-17	7.758	5.010	2.4	5	0.620	1.000	5.03	7.753	64.9
					0.617	1.000	5.00	7.753	64.6
1-18	12.90	3.999	2.5	5	0.588	0.792	4.78	12.90	46.8
					0.593	0.791	4.82	12.90	47.2
1-19	19.40	5.010	2.4	5	0.855	0.990	6.95	19.39	36.2
					0.854	0.990	6.94	19.39	36.15
1-20	32.28	3.999	2.5	5	0.824	0.782	6.70	32.27	26.6
					0.835	0.781	6.79	32.27	26.9
1-21	48.28	2.016	2.4	5	0.489	0.393	3.98	48.28	21.0
					0.505	0.392	4.11	48.28	21.7
1-22	64.32	3.999	2.5	5	1.084	0.771	8.82	64.31	17.8
					1.089	0.771	8.86	64.31	17.9
1-23	80.17	2.016	2.4	5	0.603	0.388	4.91	80.16	15.8
					0.609	0.388	4.96	80.16	15.95
1-24	128.6	2.016	2.4	5	0.749	0.382	6.10	128.6	12.4
					0.750	0.382	6.11	128.6	12.4

Table 14

Zirconium-TTA Complexing Coefficients in 1M $HClO_4$ + 1M $NaClO_4$ at 25°C

Run	ΣZr moles/l x 10^4	(HK)° moles/l x 10^4	A	$l_{(cm)}$	D_{366}	(HK) moles/l x 10^4	(ZrK^{+3}) moles/l x 10^6	ΣZr moles/l x 10^4	E
1'-1	0.7775	2.387	∞	5	0.751	2.332	5.49	0.7226	326
					0.749	2.332	5.47	0.7228	325
1'-2	1.295	1.492	∞	5	0.754	1.435	5.76	1.237	324.5
					0.751	1.435	5.74	1.238	323
1'-3	1.944	0.5959	∞	5	0.433	0.5621	3.38	1.910	315
					0.433	0.5621	3.38	1.910	315

The data at low zirconium concentrations in the 1M $HClO_4$ + 1M $LiClO_4$ series of experiments indicate that another type of correction must be applied. As will be seen shortly in the theoretical treatment, at constant acidity E must approach a constant value as the zirconium concentration is decreased. This condition is met fairly well in the 2M acid series, but in 1M acid the E values reach a maximum and start to decrease. Exactly this same behavior has been observed by Connick and McVey[7] and Connick and Reas.[8] In each case it has been attributed to the complexing of a small amount of the zirconium by an impurity in the solutions. The amount of zirconium "lost" to this impurity complex is negligibly small until the zirconium concentration is decreased to about 10^{-4}M.

This impurity remains unidentified, but there is some evidence[8] that it is leached off of glass surfaces. As a precaution against this, all bottles, flasks and pipettes used for zirconium solutions were coated with "Dri-Film", which is $SiCl_2(CH_3)_2$. This compound is hydrolyzed by the thin film of water present on an air-dried glass surface to give a hydrocarbon surface which is not wet by water. In addition a careful cleaning procedure, which included a 24 hour treatment with potassium dichromate-sulfuric acid cleaning solution and a final 30 minute steam-rinsing, was used on all glass apparatus. These precautions apparently met with a fair amount of success since no evidence of the zirconium-impurity complex was observed in 2M perchloric acid. Since the impurity effect was thus limited to the 1M acid experiments, the lithium perchlorate stock solution is suspected as the source of the impurity - despite the considerable effort that was expended in an effort to obtain a pure solution (see Section II).

The presence of the impurity certainly introduces a considerable uncertainty in the 1M acid values of E at low zirconium concentration. However a quantitative correction for this effect can be made. This correction is based on the simplest possible assumption: that the amount of zirconium complexed by the impurity is constant in all the 1M $HClO_4$ + 1M $LiClO_4$ experiments. If this is the case, then over the zirconium concentration range where the complexing coefficient is constant, which corresponds to zirconium monomer as the only important species - see Section VII:

$$E^\circ = \frac{E\Sigma Zr}{\Sigma Zr - k} \qquad (43)$$

where E° is the true (constant) value of the complexing coefficient, E' is the experimentally observed value, and k represents the constant concentration of zirconium in the form of the impurity complex. Equation (43) can be rearranged to give:

$$\Sigma Zr = E\Sigma Zr/E^\circ + k \qquad (44)$$

Thus a plot of ΣZr versus $E\Sigma Zr$ should be linear with a slope equal to $1/E^\circ$ and intercept equal to k. The excellent straight line obtained with such a plot is illustrated in Figure 4, using the five points of lowest zirconium concentration from the 1M $HClO_4$ + 1M $LiClO_4$ series. At higher concentrations, polymerization of the zirconium becomes appreciable. The values of E° and k obtained from the slope and intercept are $E^\circ = 341$ and $k = 5.3 \times 10^{-6}$M. If it is assumed that the slope of Fig. 4 can be determined more accurately than the intercept, then on the basis of $E^\circ = 341$ the calculated value of k from the same five points is $(5.35 \pm 0.36) \times 10^{-6}$M; and this value of k was used to correct runs 1-1 through 1-6.

At higher zirconium concentrations, the correction is negligible. The corrected results are presented in Table 15. No impurity complex corrections have been applied to the 2M acid series or to the results in sodium perchlorate solutions.

Table 15

Zirconium Impurity Complex Corrections in 1M $HClO_4$ + 1M $LiClO_4$

Run	ΣZr moles/l x 10^4	E	ΣZr-k moles/l x 10^4	$E_{corrected}$
1-1	0.1701	232	0.1166	339
	0.1701	232	0.1166	339
1-2	0.3313	294	0.2778	351
	0.3315	293	0.2780	350
1-3	0.4860	301	0.4325	338
	0.4860	301	0.4325	338
1-4	0.7461	314	0.6926	338
	0.7460	315	0.6925	339
1-5	1.264	327	1.211	341
	1.264	327	1.211	342
1-6	1.897	326	1.844	336
	1.897	327.5	1.844	337

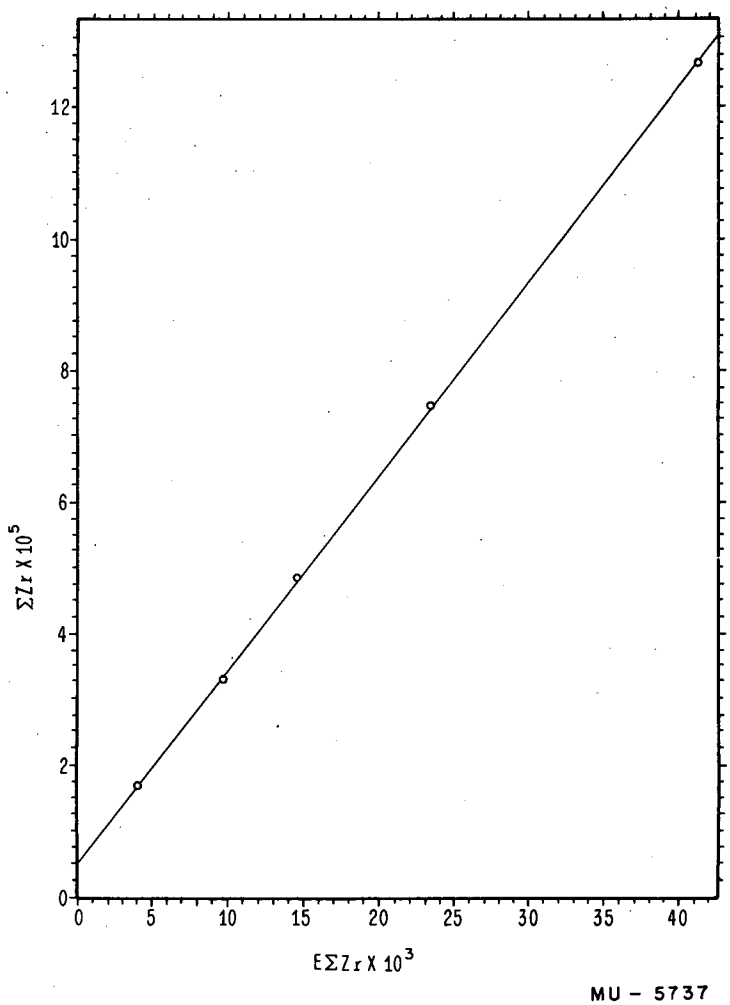


Fig. 4. Zr Impurity Complex in 1 M $HClO_4$ + 1 M $LiClO_4$

VII. ZIRCONIUM SPECIES IN SOLUTION AS OBTAINED FROM ZIRCONIUM-TTA COMPLEXING COEFFICIENTS.

Interpretation of the complexing coefficient data in terms of all possible zirconium hydrolytic species will now be made. The general case of combined hydrolysis and polymerization of zirconium is represented by the reaction(s):

$$n\ Zr^{+4} + m\ H_2O = Zr_n\ (OH)_m^{\ +4n-m} + m\ H^+ \qquad (45)$$

and the corresponding equilibrium constant(s):

$$K_{nm} = \frac{\left[Zr_n(OH)_m^{\ +4n-m}\right](H^+)^m}{(Zr^{+4})^n} \qquad (46)$$

Consideration is thereby given to all possible integral values of n, starting with one, and all corresponding m values, starting with zero, for each n.

It will be noted that because of a lack of the necessary activity coefficients, all K_{nm} equilibrium constants - and the K of equation (25) - are expressed in terms of concentrations instead of thermodynamic activies; but as mentioned in Section IV, the conclusions of this work will not be affected as long as the activity coefficients of all pertinent species remain reasonably constant. Despite its possible high power dependence and the fact that it is considerably less than one in these solutions, the activity of water has also not been included in K_{nm}. However this should introduce no relative error since the water activities in 2M $HClO_4$ and in 1M $HClO_4$ plus 1M $LiClO_4$ are nearly identical (see Table 10, Section IV). The variations produced by salting effects in the activity coefficients of HK_{aq} and ZrK^{+3} have been discussed in Section IV and have presumably been canceled out by defining E as in equation (24).

In regard to possible activity coefficient changes of the charged species in solution, no definite answer can be given other than that the customary precaution of maintaining constant ionic strength was observed. Indeed, this procedure may have been especially successful here since only positive ions are concerned in all equilibria considered. In such cases, according to Olson and Simonson[41], concentration equilibrium constants are primarily a function of the negative ion concentration, which was maintained constant in this investigation. The addition of zirconium perchlorate produces a negligible effect on both the ionic strength and perchlorate ion concentration until (ca) 0.02M ΣZr. The possible error introduced by solutions containing higher zirconium concentrations is discussed in Section VII. Also it should be strongly emphasized that the effects of replacing hydrogen ion by lithium (or sodium) ion is of concern here only in the determination of the hydrogen ion dependence of the zirconium monomer and polymers. The data from the 2M and 1M acid series are analyzed independently to determine the number of zirconium atoms in the polymers.

The total (formal) concentration of zirconium is obtained by solving (46) for the concentration of $Zr_n(OH)_m^{+4n-m}$ and summing over all values of n and m. Thus:

$$\Sigma Zr = \sum_{n=1} \sum_{m=0} \frac{nK_{nm} (Zr^{+4})^n}{(H^+)^m} \qquad (47)$$

Through use of the equilibrium constant of reaction (2), as given by equation (25), and the definition of E - equation (24) - we obtain:

$$(Zr^{+4}) = \frac{(ZrK^{+3}) \quad (H^+)}{K \ (HK)} = \frac{E(H^+) \ \Sigma Zr}{K} \qquad (48)$$

Substitution of (48) into (47) gives:

$$\Sigma Zr = \sum_{n,\ m} \frac{n\ K_{nm}\ E^n\ (\Sigma Zr)^n}{K^n\ (H^+)^{m-n}} \tag{49}$$

Differentiating (49) partially with respect to ΣZr at constant (H^+), the results can be expressed as:

$$1 = \left\{ \left[\frac{\partial \ln E}{\partial \ln \Sigma Zr} \right]_{(H^+)} + 1 \right\} \sum_{n,\ m} \frac{n^2 K_{nm} E^n (\Sigma Zr)^{n-1}}{K^n\ (H^+)^{m-n}} \tag{50}$$

and since it is readily seen that:

$$\left[Zr_n (OH)_m^{+4n-m} \right] = \frac{K_{nm} (Zr^{+4})^n}{(H^+)^m} = \frac{K_{nm} E^n (\Sigma Zr)^n}{K^n\ (H^+)^{m-n}} \tag{51}$$

then substitution of (51) into (50) and changing ln to log:

$$\left[\frac{\partial \log E}{\partial \log \Sigma Zr} \right]_{(H^+)} = -1 + \frac{\Sigma Zr}{\sum_{n,\ m} n^2 \left[Zr_n (OH)_m^{+4n-m} \right]} \tag{52}$$

Equation (52) can also be expressed in the useful form:

$$\left[\frac{\partial \log E}{\partial \log \Sigma Zr} \right]_{(H^+)} = -1 + \frac{1}{\sum_{n,\ m} n f_{nm}} \tag{53}$$

where each f_{nm} represents the fraction of the total zirconium which exists in a polymer containing n zirconium atoms and m hydroxide groups. The weighted summation of all such fractions, as given by $\Sigma n f_{nm}$, is called the weight average degree of polymerization and represents the size of the polymer in which a zirconium ion will be found on the average. (If there is but one zirconium polymer - or only the monomer - regardless of any differences due to the number of hydroxide groups, $\Sigma n f_{nm}$ gives the

exact degree of polymerization.) Thus if a plot of log E versus log ΣZr is made, the slope of the curves so obtained serves as a direct measure of the amount of polymerization. At low zirconium where the monomer is the only important species - thus $\Sigma nf_{nm} = 1$ - equation (53) demands a zero slope. As the zirconium concentration is increased and polymers begin to form, the slope should become negative, approaching minus one as a limiting value if the polymers are of infinite size.

All of the complexing coefficient data in 1M and 2M acid are shown in such plot in Figure 5. The majority of the points are the average of at least two experimental values. At low zirconium concentrations in the 1M acid series, the plotted points represent E values corrected for the impurity complex as listed in Table 15. The smooth curves are drawn in accord with the theoretical restrictions of equation (53) and represent calculated values that will be discussed shortly. Because of the hydrolysis of the zirconium, a correction due to increased acidity over the nominal values of 1M and 2M has been applied to several of the points at high zirconium concentration. This hydrolysis correction will also be discussed shortly.

Formula of Monomer

The limiting values of the complexing coefficient, designated as E^o, at low zirconium concentration in 1M and 2M acid allow a calculation of the amount of hydrolysis of the monomeric species. For this simple case, after expansion and rearrangement, we obtain from equation (49):

$$E^o = \frac{K}{(H^+) + K_{11} + K_{12}/(H^+) + K_{13}/(H^+)^2 + \quad \cdots} \qquad (54)$$

(K_{10} does not appear in the above equation since it is necessarily equal to one.) Equation (54) indicates that if a number of hydrolysis products

of comparable importance are present, then values of E° would be quite a complicated function of hydrogen ion concentration. A clear-cut case with a minimum of data can be found if, and only if, the observed hydrogen ion dependence of E° is an inverse first power, corresponding to Zr^{+4} as the monomeric species. That such appears to be the case in this work can be seen in Figure 5 where the theoretical curves have been drawn with E° values of 341 in 1M acid and 170.5 in 2M acid.

The amount of spread of the 2M acid points indicates a possible error in the E° value of about 5%. (The 4 points at lowest zirconium concentration, which also contained the highest TTA concentration, show a small trend beyond this 5% error limit. This is presumed due to the formation of a small amount of the second zirconium - TTA chelate, ZrK_2^{+2}. A high value for E would then be obtained since the molar extinction coefficient of such a species is expected to be roughly twice that of ZrK^{+3}.) Using this figure, an estimated upper limit for the monomer hydrolysis can be calculated from equation (54). Assuming $Zr(OH)^{+3}$, we obtain $K_{11} \leq 0.1$. If a higher hydrolysis product such as $Zr(OH)_2^{+2}$ is assumed, a smaller K_{1m} value is obtained. The estimated error in the E° values should perhaps be greater than 5% due to the zirconium impurity complex correction that was applied to the 1M acid series; however it is assumed that this correction was made with fair accuracy. In any event there can be no doubt that the data indicate Zr^{+4} as the most important monomeric species in 1M and 2M perchloric acid solutions.

Additional support for Zr^{+4} as the monomeric species, and also for the important assumption that changes in the ionic media at constant ionic strength produce no significant change in the activity coefficients of the various species, is obtained from the results of the experiments

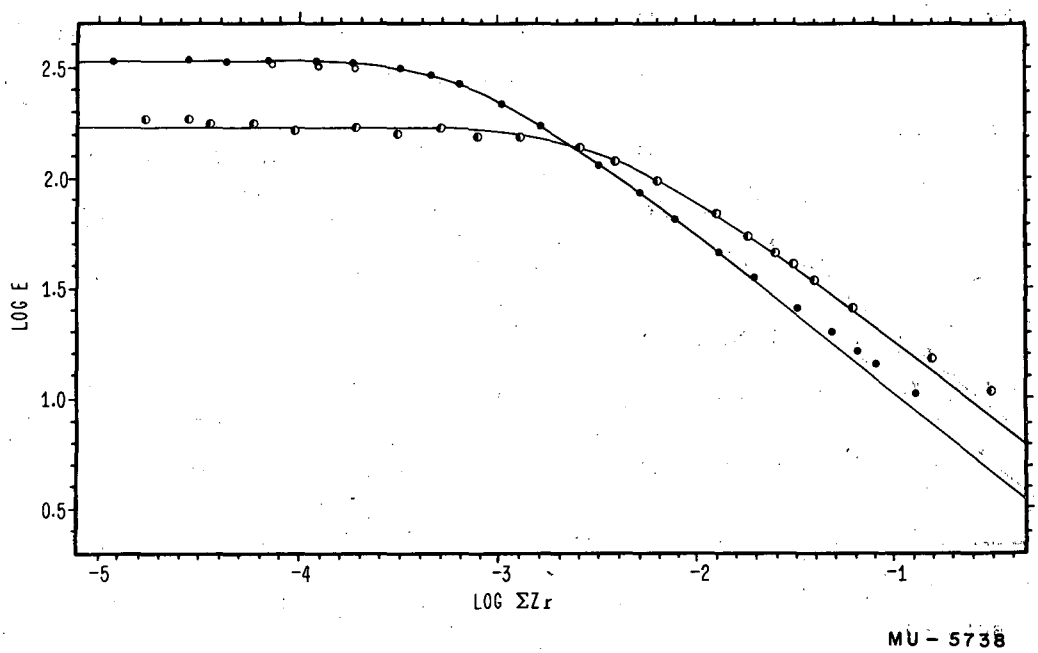


Fig. 5. ◐, 2 M $HClO_4$; ●, 1 M $HClO_4$ + 1 M $LiClO_4$; O, 1 M $HClO_4$ + 1 M $NaClO_4$.

Hydrolytic Polymerization of Zirconium.

in 1M $HClO_4$ plus 1M $NaClO_4$. The E values of the solutions containing sodium ion appear to be about 5% lower than those in the corresponding lithium ion solutions; however such a deviation is what might be expected on grounds of specific ionic effects. Also the sodium perchlorate solutions were not extended to low enough zirconium concentrations to detect if any correction for a zirconium-impurity complex was necessary in these solutions. If so, this would bring the E° values of the two 1M acid series in even closer agreement.

In this identification of Zr^{+4} as the monomeric species, it has been implicitly assumed that there is no appreciable complexing of the zirconium by perchlorate ion; and this will also be the case in the discussion of the polymeric species. However such complexing would have no affect on the identification of species in solution as long as the perchlorate ion concentration is maintained constant.

Polymeric Species

The weight average degree of polymerization, as calculated from the slopes of Figure 5 by equation (53), can be analyzed in terms of possible species in solution; and this method was largely used by Connick and Reas[8] in their treatment of zirconium-TTA extraction coefficients. However since the measurement of slopes from any but linear plots is liable to a good deal of personal error, a more analytical treatment of the data is made here.

Equation (49) can be rewritten in form:

$$1/E = \sum_{n=1} \sum_{m=0} \frac{nK_{nm} (E\Sigma Zr)^{n-1}}{K^n (H^+)^{m-n}} \qquad (55)$$

which when expanded is:

$$1/E = a_1 + a_2 (E\Sigma Zr) + a_3 (E\Sigma Zr)^2 + \ldots \qquad (56)$$

and where each a_n is defined by:

$$a_n = \frac{n}{K^n} \sum_{m=0} \frac{K_{nm}}{(H^+)^{m-n}} \qquad (57)$$

At constant hydrogen ion concentration, all a_n values in equation (56) can be considered as constant coefficients. Thus a plot of 1/E versus $E\Sigma Zr$ gives a simple polynomial curve whose terms and coefficients are directly related to the polymeric species in solution. When such plots were made, it was found that 1/E represented a cubic equation in $E\Sigma Zr$ - corresponding to the tetramer as the highest polymer present at appreciable concentrations under the experimental conditions of this work. In addition it was found that the value of a_2, the coefficient of the dimer term, is negligibly small. Thus assuming the polymeric species to consist of a trimer-tetramer mixture only, equation (56) can be placed in the linear form:

$$(1/E - a_1)\ (1/E\Sigma Zr)^2 = a_3 + a_4\ (E\Sigma Zr) \qquad (58)$$

and a plot of the left hand member of (58) versus $(E\Sigma Zr)$, at constant acidity, should give a straight line with slope equal to a_4 and intercept equal to a_3.

Such plots for the 1M and 2M acid data are shown respectively in Figures 6 and 7. The value of a_1, as indicated by a comparison of equations (54) and (57), is simply $1/E°$. As such it has been taken equal to 341 in 1M acid and 170.5 in 2M acid. Only a somewhat limited range of the complexing coefficient is shown in these plots for two reasons. First, because of the $(1/E - a_1)$ term in equation (58), the amount of polymerization must be appreciable before any reasonable accuracy can be obtained. Second, a definite trend at high zirconium concentrations is caused by a combination of increased acidity due to

hydrolysis and an increase in ionic strength due to the addition of zirconium perchlorate. A hydrolysis correction has been applied, and a rough estimate of the possible deviation due to the ionic strength increase is indicated in Figures 6 and 7. Both of these effects are discussed below.

For these reasons the range of points in Figures 6 and 7 is restricted to runs 1-7 through 1-20 and runs 2-8 through 2-23. The range of zirconium concentrations covered is thus about 3×10^{-4} M to 0.04M. Nearly all the points represent the average of two or more experimental values. Probable uncertainties in the individual points are indicated by vertical lines. These uncertainties were calculated on the basis of an estimated possible error of 3% in the E values and of 5% in each a_1. The possible errors at low zirconium concentration are seen to be quite large.

The effect that would be produced in Figures 6-7 by the presence of appreciable quantities of the dimer and/or higher polymers than the tetramer can be expressed by writing equation (58) in its complete form:

$$(1/E - a_1)(1/E\Sigma Zr)^2 = a_2/(E\Sigma Zr) + a_3 + a_4(E\Sigma Zr) + a_5(E\Sigma Zr)^2 + \ldots \quad (59)$$

Thus if a_2 is not negligibly small, the ordinate term of Fig. 6-7 would commence to increase at low values of $(E\Sigma Zr)$, producing a minimum in the curve. Higher polymers than the tetramer would be indicated by an upward curvature at high values of $(E\Sigma Zr)$. Neither of these effects is observed though a small amount of the latter one may be masked because of the ionic strength error. An estimated upper limit for a_2 may be made by a plot of the quantity $(1/E - a_1)(1/E\Sigma Zr)$ versus $E\Sigma Zr$. The curve from such a plot should have an ordinate intercept equal to a_2.

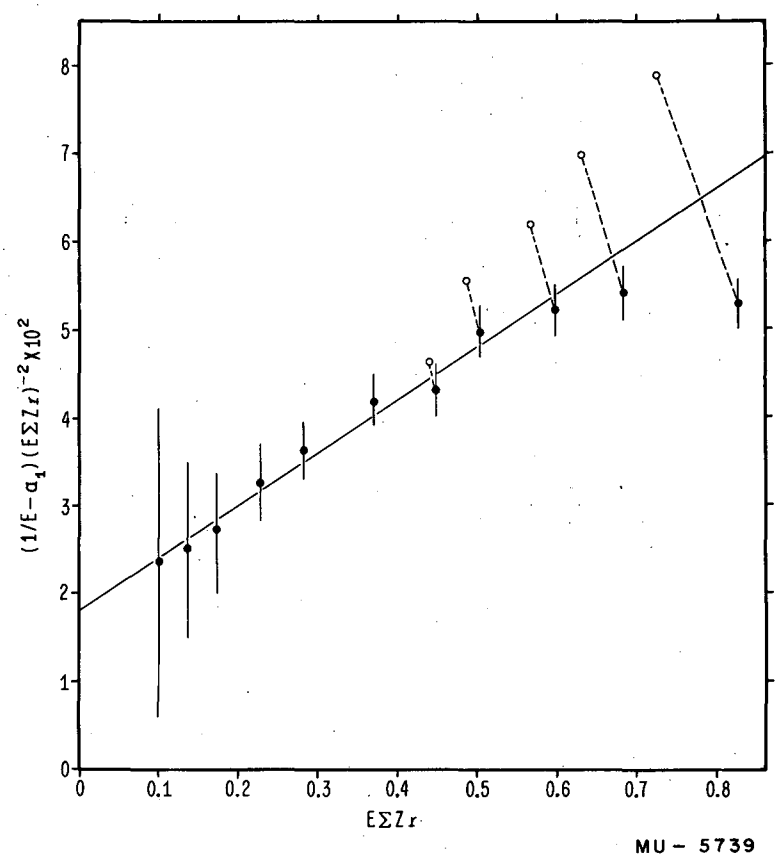


Fig. 6. ●, observed values; O, ionic strength correction

Trimer and Tetramer Zr Polymers in 1 M $HClO_4$ + 1 M $LiClO_4$

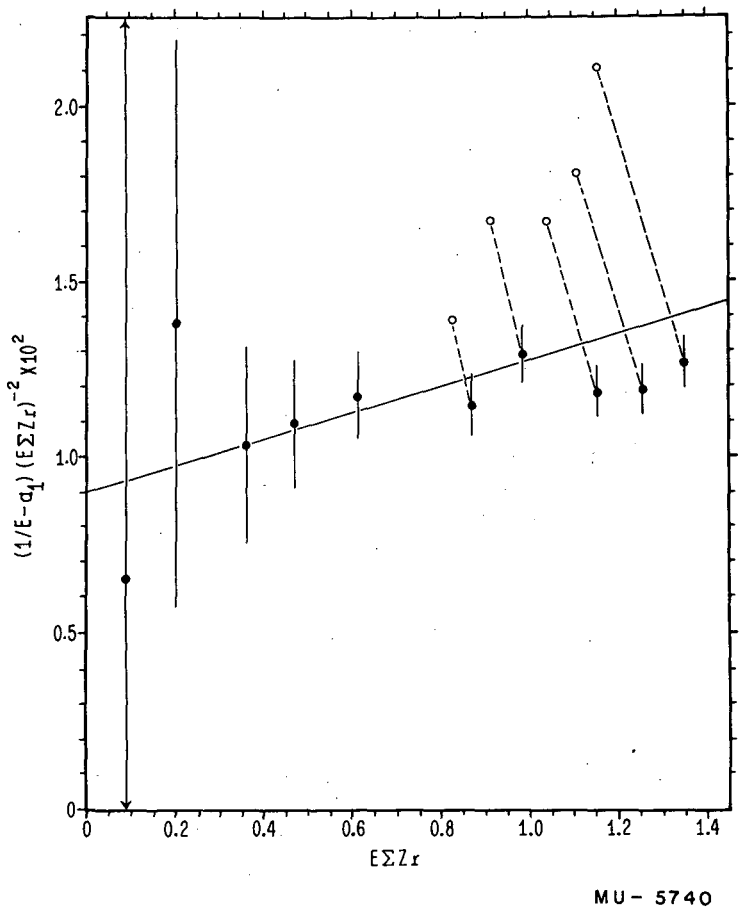


Fig. 7. ●, observed values; O, ionic strength correction

Trimer and Tetramer Zr Polymers in 2 M $HClO_4$

The observed value is a zero intercept, but estimated possible errors approximately place the limit on a_2 (in 1M acid) as no greater than 5×10^{-4}. By use of equation (57) and taking K = 341, the upper limit of the sum of the dimerization equilibrium constants is calculated to be:

$$\sum_{m=0} K_{2m} \leq 30 \qquad (60)$$

As mentioned above, a rather large error has been attributed to ionic strength effects. This is not too unreasonable when it is noted a typical experimental solution such as $\Sigma Zr = 0.025M$ in 2M $HClO_4$ would actually be 2.1M in ClO_4^-. That this could be the source of a fairly large error is indicated by comparison of the K value of 1084 determined by McVey[9] at an ionic strength of four and the value of 341 found in this work. To obtain a better picture of this ionic strength effect, we utilize equation (49), assuming average values of n and m at any given hydrogen ion and zirconium concentration:

$$E = \frac{K\,(H^+)^{m/n - 1}}{(nK_{nm})^{1/n}\,(\Sigma Zr)^{1-1/n}} \qquad (61)$$

Assuming a linear relationship between the two K values at μ equal four and two and then estimating the ionic strength to be equal to the perchlorate ion concentration, E values can be corrected back to an ionic strength of two from the corresponding change in K. The ionic strength corrections illustrated in Figures 6 and 7 are calculated on this basis. Obviously they are but crude estimates and are only intended to show that the observed deviations from linearity at high zirconium concentrations can be adequately explained on the basis of the increased ionic strength. In addition they should be looked upon as upper limits since the value of E at constant (H^+) and ΣZr varies not as K but as

$K/(nK_{nm})^{1/n}$. Analysis in Section VIII of some additional work by McVey[9] at $\mu = 4$ shows that the polymerization constants also increase with ionic strength and thus, partially at least, tend to cancel the increase in K. The true corrected value of the points is expected to lie somewhere on the dotted line joining the observed and corrected values in Fig. 6-7. If the plots included the additional E data at higher zirconium concentration, these points would continue to fall further below the straight lines drawn in Fig. 6-7; however the ionic strength correction is always more than adequate to account for the deviation.

The intercepts and slopes from Fig. 6-7, corresponding to the respective a_3 and a_4 values, and their estimated error limits are:

$$a_3 = (1.8 \pm 0.6) \times 10^{-2}$$
$$a_4 = (6.0 \pm 1.4) \times 10^{-2}$$
1M acid

$$a_3 = (9.0 \pm 2.6) \times 10^{-3}$$
$$a_4 = (3.75 \pm 3.0) \times 10^{-3}$$
2M acid

These values of a_3 and a_4, plus $a_2 = 0$ and the a_1 values as listed previously, were employed to calculate the theoretical curves shown in the log E versus log ΣZr plots of Fig. 5. Equation (56), assuming all a_n values equal to zero for n equal to or greater than five, was used for this purpose.

The a_3 and a_4 values can also serve to calculate the average degree of hydrolysis of the trimer and tetramer polymers. Expanding equation (57) we obtain:

$$a_3 = 3/K^3 \left[K_{30}(H^+)^3 + K_{31}(H^+)^2 + K_{32}(H^+) + K_{33} + K_{34}/(H^+) + K_{35}/(H^+)^2 + \ldots\right] \quad (62)$$

$$a_4 = 4/K^4 \left[K_{40}(H^+)^4 + K_{41}(H^+)^3 + \ldots + K_{44} + K_{45}/(H^+) + K_{46}/(H^+)^2 + \ldots\right] \quad (63)$$

Even though a number of the K_{nm} values in the above equations could be set equal to zero as corresponding to unlikely species, still it is impossible to establish definitely the number of hydroxide groups in the trimer(s) and tetramer(s) with data at only two acidities. However the values of a_3 are observed to have roughly an inverse first power hydrogen ion dependence and those of a_4 to have an inverse fourth power dependence. The straight lines drawn in Fig. 6-7 thus correspond to the polymeric species $Zr_3(OH)_4^{+8}$ and $Zr_4(OH)_8^{+8}$.

Interpretation of the data in terms of but one trimer and one tetramer could easily be an oversimplification of a complicated system, but the above species at least represent the average degree of hydrolysis of the polymers as observed in this work. Understanding then that the constants so calculated are perhaps to be regarded as only average values, K_{34} and K_{48} can be obtained from equations (62) and (63) by assuming all other K_{nm} values to be zero:

$$a_3 = \frac{3K_{34}}{K^3(H^+)} \tag{64}$$

$$a_4 = \frac{4K_{48}}{K^4(H^+)^4} \tag{65}$$

Utilizing the observed values of a_3, a_4 and K, we obtain:

$$K_{34} = \frac{\left[Zr_3(OH)_4^{+8}\right](H^+)^4}{(Zr^{+4})^3} = (2.4 \pm 0.8) \times 10^5 \tag{66}$$

$$K_{48} = \frac{\left[Zr_4(OH)_8^{+8}\right](H^+)^8}{(Zr^{+4})^4} = (2.0 \pm 0.5) \times 10^8 \tag{67}$$

And the above limits represent the corresponding uncertainties in the a_3 and a_4 values from the 1M acid series.

Though the trimer and the tetramer respectively with 4 and 8 hydroxide groups give the best fit to the data, the uncertainties in

a_3 and a_4 indicate that the trimer could have from 3 to 5 hydroxide groups and the tetramer from 6 to 11 hydroxide groups. The case of the tetramer is especially uncertain because of the small slope observed in Fig. 7 (the ordinate scale has been magnified beyond the expected accuracy of the data in order to emphasize the slope).

Hydrolysis Correction

The hydrolysis correction that has been mentioned several times previously can now be calculated from the values of K_{34} and K_{48}. The effect on E produced by changes in the hydrogen ion concentration can be obtained by taking the partial derivative of equation (49) with respect to hydrogen ion concentration at constant ΣZr. By a procedure very similar to that used in the derivation of equation (53), we obtain:

$$\left[\frac{\partial \log E}{\partial \log (H^+)}\right]_{\Sigma Zr} = -1 + \frac{\sum_{n,m} mf_{nm}}{\sum_{n,m} nf_{nm}} \tag{68}$$

where f_{nm} and Σnf_{nm} are defined for equation (53) and Σmf_{nm} represents the sum of m times the fraction of the zirconium atoms present in species containing n zirconiums and m hydroxides. If for any given ΣZr (and over a small range of hydrogen ion concentration) an average number of hydroxides per zirconium is assumed, then equation (68) can be integrated to give:

$$E = C(H^+)^{-1 + \Sigma mf_{nm}/\Sigma nf_{nm}} \tag{69}$$

where C is the integration constant. The acid concentration in the hydrolyzed zirconium solution is calculated by simultaneous use of equations (66) and (67). The concentrations of Zr^{+4}, $Zr_3(OH)_4^{+8}$, and $Zr_4(OH)_8^{+8}$ are also calculated, and a value of $\Sigma mf_{nm}/\Sigma nf_{nm}$ is thus obtained. This calculation is then repeated for the desired hydrogen

ion concentration, i.e., 1M or 2M, to obtain the other limiting value of $\Sigma mf_{nm}/\Sigma nf_{nm}$. The calculated hydrogen ion concentration and mean value of $\Sigma mf_{nm}/\Sigma nf_{nm}$ are then used to correct the E values to 1M or 2M acid by equation (69). The results of such calculations for the concentrated zirconium solutions are summarized in Tables 16A and 16B.

Table 16A

Zirconium Hydrolysis Correction in 1M $HClO_4$ + 1M $LiClO_4$ at 25°C

Run	ΣZr moles/l	(H^+) moles/l	$\frac{\Sigma mf_{nm}}{\Sigma nf_{nm}}$	E	$E_{corrected}$
1-24	0.1286	1.224	1.851	12.4 12.4	10.45 10.45
1-23	0.08016	1.138	1.841	15.8 15.95	14.15 14.3
1-22	0.06431	1.110	1.834	17.8 17.9	16.3 16.4
1-21	0.04828	1.082	1.824	21.0 21.7	19.7 20.4
1-20	0.03227	1.053	1.804	26.6 26.9	25.5 25.8
1-19	0.01939	1.031	1.772	36.2 36.15	35.35 35.3
1-18	0.01290	1.019	1.738	46.8 47.2	46.2 46.6

Table 16B

Zirconium Hydrolysis Correction in 2M $HClO_4$ at 25°C

Run	ΣZr moles/l	(H^+) moles/l	$\frac{\Sigma mf_{nm}}{\Sigma nf_{nm}}$	E	$E_{corrected}$
2-26	0.3101	2.462	1.653	12.3 12.25	10.75 10.7
2-25	0.1548	2.224	1.623	16.3 16.1	15.3 15.1
2-24	0.06196	2.082	1.551	26.7 26.1	26.1 25.6
2-23	0.03927	2.049	1.498	34.8	34.4
2-22	0.03101	2.037	1.465	40.9	40.5
2-21	0.02617	2.030	1.438	44.6	44.3
2-20	0.02468	2.028	1.428	47.1	46.8
2-19	0.02418	2.028	1.424	47.8	47.5
2-18	0.01809	2.019	1.370	54.6	54.4

VIII. SUMMARY AND DISCUSSION OF THE CONTRIBUTIONS OF OTHER INVESTIGATORS ON THE HYDROLYSIS OF ZIRCONIUM

McVey[9] has recently made a study of zirconium hydrolysis, utilizing the identical experimental tool that has been employed in this work: the aqueous equilibrium reaction between zirconium and its first TTA chelate. However in McVey's work, constant zirconium concentration was employed and the hydrogen ion concentration was varied. This method serves best to indicate the average number of hydroxides per zirconium ion in the polymers, while that employed in this work indicates the number of zirconium atoms in the polymeric species.

In brief, McVey found the average number of hydroxides per zirconium ion to vary from zero to two as the acidity was changed from 4M to 0.012M - all at $\mu = 4$ in $HClO_4$ plus $LiClO_4$ solutions. McVey realized from two series of experiments at different zirconium concentrations that polymers were being formed in his solutions; nevertheless he chose to interpret his results in terms of Zr^{+4} and $Zr(OH)_2^{+2}$ as the only important species. It is equally possible - and in the light of this work, more probable - to fit his data by assuming hydrolyzed polymers and Zr^{+4} as the only monomer. McVey is also now in agreement that this is the more likely interpretation.[42]

McVey utilized a complexing coefficient F, which is defined identically as the E of this work. Small improvements in his calculated F values can be made by taking into account the amount of zirconium tied up as ZrK^{+3}, and in addition there is a small hydrolysis correction at the two lowest acidities of his work. For these reasons McVey's data and the recalculated results are presented in Table 17. All the experiments represent one phase systems and hence

equations (40)-(42) can be used directly for the necessary calculations. All the optical density measurements were made at 366 mμ, using 5 cm. absorption cells. McVey's reported values of the TTA and ZrK^{+3} molar extinction coefficients (cf. Sections III and V) at an ionic strength of 4 were employed in the calculations. The last column of Table 17 represents the result of assuming an average species in solution and then applying the integrated form of equation (53). The values of the weight average degree of polymerization so calculated were obtained from each pair of F_I and F_{II} values.

Table 17

Zirconium-TTA Complexing Coefficients as a Function of Acidity

Temperature = 25°C; μ = 4.0 ($HClO_4$ + $LiClO_4$)

I $\Sigma Zr^\circ = 2.50 \times 10^{-4}\underline{M}$; $(HK)^\circ = 4 \times 10^{-5}\underline{M}$

II $\Sigma Zr^\circ = 1.25 \times 10^{-4}\underline{M}$; $(HK)^\circ = 2 \times 10^{-5}\underline{M}$

(H^+) moles/l	D_I	F_I	D_{II}	F_{II}	Σnf_{nm}
4	0.325	262	0.101	286	1.1
3	0.400	338	0.114	335	1.0
2	0.530	478	0.151	478	1.0
1	0.791	790	-	-	-
0.5	0.640	604	-	-	-
0.3	0.481	424	0.202	685	3.3
0.2	0.375	312.5	-	-	-
0.15	0.298	235	0.124	373	3.0
0.05*	0.145	90.6	0.067	161	5.8
0.012*	0.070	23.8	0.040	65	$>\infty$

*Assuming $2OH^-$ groups per Zr, corrected acidities in I series are 0.0505$\underline{M}$ and 0.0125$\underline{M}$.

Unfortunately McVey did not adjust his experimental conditions for the II series to obtain the greatest possible accuracy (note low D_{II} values). However, the limited number of Σnf_{nm} values that could be calculated show the expected monomer at high acid; and at low

acid, they are in reasonable agreement with the trimer-tetramer results of this work. The Σnf_{nm} value at lowest acidity is an impossible answer but easily accountable for because of the high probable error with such low optical densities.

Utilizing the I series of data in Table 17, a plot of log F versus log (H^+) is illustrated in Fig. 8. The two limiting slopes of the plot are +1 and -1. According to equation (68), the average number of hydroxide groups per zirconium ion at low acid is thus indicated to be two and at high acid to be zero. The latter value indicates Zr^{+4} as the monomer. Analytical treatments of the data, similar to those discussed in Section VII, to determine the polymeric species quickly indicated two facts. First, that plots such as Fig. 8 are sensitive only to the number of hydroxides per zirconium ion, showing but little change regardless of the size of the polymers assumed - as witnessed by McVey's success in fitting the data with $Zr(OH)_2^{+2}$. And second, that the data require, in addition to Zr^{+4}, a minimum of two hydrolyzed species - one containing 2 hydroxide groups per zirconium and the other between 1.6 to 1.8 hydroxides per zirconium.

With only these limitations, it is not surprising that several combinations of species can be found that fit the data equally well. Such fits were found with the pairs: $Zr_3(OH)_5^{+7}$ and $Zr_3(OH)_6^{+6}$, $Zr_4(OH)_7^{+9}$ and $Zr_4(OH)_8^{+8}$, $Zr_3(OH)_5^{+7}$ and $Zr_4(OH)_8^{+8}$. Undoubtedly even others could be found; but if limited to a trimer-tetramer pair, the best fit and the corresponding equilibrium constants are:

$$K_{35} = \frac{\left[Zr_3(OH)_5^{+7}\right] (H^+)^5}{(Zr^{+4})^3} = 4.0 \times 10^6 \qquad (70)$$

$$K_{48} = \frac{\left[Zr_4\ (OH)_8^{+8}\right]\ (H^+)^8}{(Zr^{+4})^4} = 1.4 \times 10^9 \qquad (71)$$

These values of K_{35} and K_{48} plus the value $K = 1.03 \times 10^3$ - see equation (25) - are the parameters employed to calculate the smooth curve of Fig. 8. (The value of K reported by McVey from independent experiments is 1084 at $\mu = 4$. However an examination of his data shows that the best-fit value selected here is within his experimental accuracy. In any event the value of K is only of importance in the high acid region of the curve.) Also the equilibrium concentration of ΣZr was assumed to be 2.5×10^{-4}M. Since the experimental values of ΣZr vary between 0.1% to 2.6% less than this value, a correction could be applied by use of the integrated form of equation (53). This was not done in Fig. 8 but it would have served to lower all the experimental points slightly, with the largest correction occuring near the curve maximum.

In general then, it is seen that the results of McVey's experiments provide considerable support for the conclusions of this work. His evidence for Zr^{+4} as the principle monomeric species at moderate acidities is especially strong. Agreement as to the number of zirconium ions in the polymer is also obtained. The different number of hydroxide groups in the trimer found from McVey's data is within the experimental error of this work. Also it should be repeated that the type of experiment performed by McVey gives a better measure of the hydroxide dependence. Combining the best features of both investigations, we thus obtain $Zr_3(OH)_5^{+7}$ and $Zr_4(OH)_8^{+8}$ as the most likely polymeric zirconium species in solutions of moderate acidity.

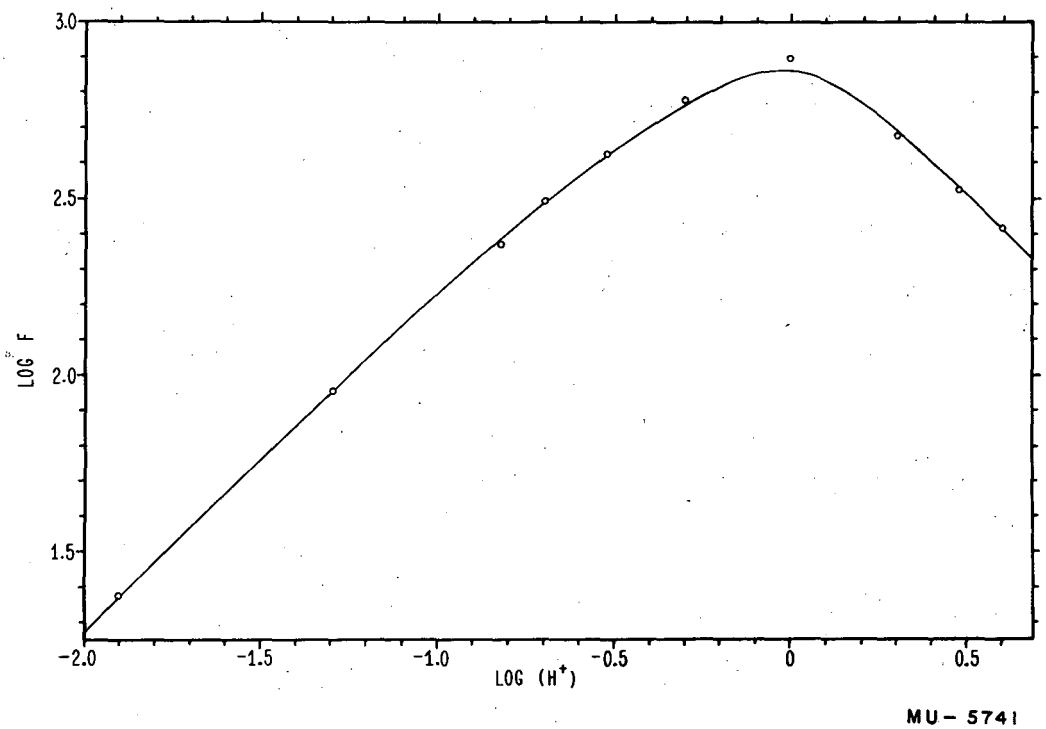


Fig. 8. Hydrogen Ion Dependence of Zr Hydrolysis.

(2.5×10^{-4} M Zr; $\mu = 4$)

Support for the monomeric species Zr^{+4} is also obtained from the work of Connick and McVey[7] and Connick and Reas.[8] Both investigations employed the TTA extraction technique that is represented by reaction (1). Employing trace concentrations of zirconium in 2M perchloric acid, Connick and McVey found $Zr(OH)^{+3}$ as the apparent monomeric species. However they also observed the impurity effect that has been discussed in Section VI and attributed this apparent hydrolysis to it. Their few results with macro concentrations of zirconium indicated less than one hydroxide per zirconium ion.

Repeated reference has been given to the work of Connick and Reas[8] since their experimental method and goals were so similar to those of the present work. Their results in 2M and 1M perchloric acid are in good agreement with Zr^{+4} as the monomer. They observed a 3.8 power hydrogen ion dependence in comparison to the theoretical value of 4 required by reaction (1) for the Zr^{+4} species; and since also troubled by the ever-present impurity, they concluded that the observed hydrogen ion dependence could have been as high as the necessary 4th power. However their reported results for polymer formation are not in very good agreement with this work. They interpreted their data in terms of the formation of a continuous series of polymers, starting with a dimer that contained between 3 and 5 hydroxide groups.

For the treatment of their data they defined a distribution coefficient E' as:

$$E' = \frac{(ZrK^{+3})}{(HK)_b^4 \quad \Sigma Zr} \tag{72}$$

It can be shown that if plots of log E and log E' versus log ΣZr at constant acidity - as in Fig. 5 - are made, the curves so obtained should be identical in shape and superimposable by shifting the ordinates only. Such plots were made and it was indeed found that the 2M acid data of Connick and Reas are in very good agreement with those of this work. Serious differences only occur at zirconium concentrations higher than 0.03M where errors due to ionic strength effects and hydrolysis render the results of both investigations highly uncertain.

This was not found to be the case for the 1M acid curves. The one obtained from the data of Connick and Reas commences to bend down, i.e., indicates polymer formation, at a lower zirconium concentration and continues with a steeper slope. To express the observed deviations in a more quantitative manner, their 1M acid data would indicate but 50% of ΣZr remaining in the monomeric form at $\Sigma Zr = 0.8 \times 10^{-3}$M and the results of this work indicate the same fraction of monomer at $\Sigma Zr = 1.7 \times 10^{-3}$M. This discrepancy remains unexplained and is especially perplexing in view of the excellent agreement of the 2M acid data. Both investigations had to contend with rather serious impurity effects in 1M $HClO_4$ + 1M $LiClO_4$, and this fact may eventually afford the solution.

Evidence that the polymers remain small even at high zirconium concentrations, instead of the continuous series of polymers suggested by Connick and Reas, is also obtained from the ultracentrifugal equilibrium experiments of Johnson and Kraus.[43] They have reported the molecular weight of the zirconium polymeric species in 1M HCl + 1M NaCl to be about 600 and have interpreted this result as the species $\left[Zr(OH)_{2.33}\ Cl_{1.67}\right]^{3+}$. At 0.05M Zr in 0.1M HCl + 1.9M NaCl, they

find a higher polymeric species with an average molecular weight of about 1000. In experiments at 0.12M Zr in 1M $HClO_4$ + 1M $NaClO_4$, the polymers were found to carry such a substantial charge that assignment of a definite molecular weight was not possible. Nonetheless they do state:

"There seems little question, however, that continuous polymerization of the type postulated by Connick and Reas for similar conditions does not occur."

It is also interesting to note that in the recent crystal structure determination of $ZrOCl_2 \cdot 8H_2O$ and $ZrOBr_2 \cdot 8H_2O$ by Clearfield and Vaughan,[44] it is reported that zirconyl ions appear in the structure as the tetramer $(ZrO)_4$ rings. They mention that this structure shows no evidence of highly polymeric species and that viscosity measurements on zirconyl chloride solutions also indicate the absence of high polymers.

In contrast to the number of independent determinations that have indicated Zr^{+4} as the principle monomeric species in solutions of moderate acidity, Lister and McDonald[1] by use of ion exchange resin techniques have reported ZrO^{+2} as the only monomeric form in solutions up to 6M in perchloric acid. They performed a number of different types of experiments, but the most crucial one of their entire investigation involved a determination of the average charge per zirconium ion of the species adsorbed on a cation exchange resin. This was done by eluting the water washed zirconium-hydrogen form of the resin with NaCl solutions and determining the number of acid equivalents so released. The total number of resin equivalents was then determined by a second elution with NaCl after the resin had been stripped of zirconium and returned to the hydrogen ion form. Difference of the two values gave the resin equivalents occupied by

the known amount of zirconium and hence the average charge per zirconium ion of the resin adsorbed species. The average charge values so obtained varied from 1.7 at 6M $HClO_4$ to 1.3 at 2M $HClO_4$ and all solutions were 0.04M in Zr. Lister and McDonald interpreted these results to indicate an equilibrium mixture of ZrO^{+2} and an additional species such as $Zr_2O_3^{+2}$.

In a criticism of this work, Connick[45] has pointed out that the above technique will not differentiate between the reactions (assuming Zr^{+4} and ZrO^{+2} for simplicity):

$$H_R^+ + Na^+ = Na_R^+ + H^+ \qquad (73)$$

$$Zr_R^{+4} + H_2O + 2Na^+ = ZrO_R^{+2} + 2Na_R^+ + 2H^+ \qquad (74)$$

Therefore reaction (74) indicates how the sodium ion elution could increase the degree of hydrolysis of the zirconium and hence produce the low average charge per zirconium ion found by Lister and McDonald. Connick[45] has also suggested that stripping the resin of hydrogen ions would be equivalent to lowering the acidity of a solution containing the adsorbed ion, thus increasing the tendency for extensive zirconium hydrolysis as indicated by equation (74). In view of these factors it is readily understood why Lister and McDonald did not observe the zirconium monomer Zr^{+4}. It should also be mentioned that at a concentration of 0.04M Zr, the results of this work indicate but 20% of the total zirconium in the monomeric form in 2M $HClO_4$; and hence the average charge per zirconium ion is much less than +4.

In conclusion it can be stated that the preponderance of experimental evidence available has served to support the major conclusions of this work. In solutions of moderate acidity, the existence of Zr^{+4}

as the principal monomeric species is strongly established. A wide range of experimental evidence supports the small size of the zirconium polymers, and indicates the trimer and/or tetramer as the most likely species. The number of hydroxide groups in the polymers is less certain, but the average result appears to be about two hydroxides per zirconium ion. More extensively hydrolyzed species, and perhaps larger polymers, undoubtedly exist in solutions of very low acidity. Thus pH measurements of zirconyl chloride solutions by Laubengayer and Eaton[6] have indicated 3 hydroxides per zirconium ion. Also Larsen and Gammill[10] have shown from their electrometric titrations of zirconium perchlorate solutions that the average formula of the species in solution over 3/4 of the precipitation pH range is $\left[Zr(OH)_{3.4}^{+0.6}\right]_n$.

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