

TABLE I

WAVE LENGTH, IN MICRONS, OF STRONG BANDS WHICH DIFFER AMONG THE THREE COMPOUNDS STUDIED

<i>cis</i> - [Co trien Cl ₂]Cl	Violet- trien Br ₂]Br	Green- trien Br ₂]Br
6.15	6.15	6.22
6.30	6.37	6.22
7.39	7.35	No band
7.64	7.64	7.66 (weak)
8.01	8.01	8.05
8.47	8.45	8.47 (weak)
9.34	9.32	9.49
10.06	10.06	9.96
No band	No band	10.11
No band	No band	10.32
12.00	12.01	12.18

proximately 25–30 “strong” or “moderately strong” bands for each compound. Most of these are identical (or very nearly so) for the three compounds but significant differences do occur for the violet and green compounds. This is illustrated by the spectral data reported in Table I, which give the wave lengths of the differentiating bands. A study of this table reveals that the spectrum of the violet dibromo compound is much more like the

spectrum of the *cis*-dichloro compound than either of these is like the spectrum of the green dibromo compound.

It might be pointed out that our spectral results are in accord with the findings of Faust and Quagliano,⁵ who reported that *cis* isomers should contain more absorption peaks than the *trans* since the latter have a center of symmetry while the former do not. Also, the conclusions of Merritt and Wiberley⁶ concerning the distinction of *cis*-*trans* isomers using infrared spectra are borne out here. They reported that in the 6.2 to 6.4 μ region the *trans* isomer always has its maximum at wave lengths 0.04 to 0.08 μ shorter than does the *cis* and that in the 12 μ region the *cis* isomer shows a maximum 0.1–0.2 μ shorter than does the *trans*. In our case the *trans* band is at 6.22 μ while the two *cis* compounds have their bands at 6.30 and 6.37 μ , respectively. Furthermore, the *trans* complex has a band at 12.18 μ while the band of the *cis* complex comes at 12.00 μ .

- (5) J. P. Faust and J. V. Quagliano, *THIS JOURNAL*, **76**, 5346 (1954).
 (6) P. E. Merritt and S. E. Wiberley, *J. Phys. Chem.*, **69**, 55 (1955).

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Polymerization of Uranyl-Tiron Chelates^{1,2}

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The interaction of uranyl ion with Tiron (pyrocatechol-3,5-disodium sulfonate) has been studied potentiometrically and spectrophotometrically in the pH range 2–11. Below pH 3.5 the solutions contain primarily 1:1 mononuclear chelate species although it appears that polymeric forms of the unhydrolyzed chelates may exist to some extent. Further reaction of the monomeric chelate with hydroxide ion results in hydrolysis and polymerization to a ternuclear species which is completely formed at pH 5.3. These reactions are independent of the amount of excess Tiron employed. Equilibrium constants have been calculated which describe the initial buffer region within approximately 0.03 pH unit over a wide range of metal chelate concentration. Further interaction of Tiron with the ternuclear complex in the pH range 5.3–8.5 produces a chelate compound containing 2 $\frac{1}{3}$ moles of Tiron per gram-ion of uranyl salt. The hydrolytic behavior of the UO₂⁺⁺ ion has been investigated in the pH range 2.5–5.5. Evidence for the existence of a mononuclear hydrolyzed species, UO₂(OH)⁺, has been found and equilibrium constants have been calculated for the various hydrolytic and polymeric reactions involved. General equations for deducing the formulas of polynuclear metal chelate species have been derived.

Introduction

It is well known that the uranyl ion undergoes polymerization by the formation of bridges through oxo or hydroxo groups. On the basis of cryoscopic measurements, potentiometric titrations and spectrophotometric evidence, Sutton³ proposed structures corresponding to U₂O₅⁺⁺ and U₃O₈⁺⁺ as well as a number of ions containing additional hydroxo ligands and has calculated equilibrium constants for the formation of the various species involved. Ahrlund, *et al.*,⁴ proposed higher polymers in which the metal ions are arranged in sheet-like structures. The interaction of uranyl ion with citrate, lactate, malate and tartrate ions has been

investigated by potentiometric, spectrophotometric and polarographic techniques by Neuman, Havill and Feldman.^{5–8} Evidence was found for the formation of binuclear and ternuclear chelates having combining ratios of ligand to metal which were equal to or less than unity, the stoichiometry depending upon pH conditions and on the particular ligand used. In no case was a ligand/metal ratio of greater than unity observed.

This research deals with the interaction in aqueous solution of the uranyl ion with Tiron (disodium pyrocatechol-3,5-disulfonate), a bidentate ligand which forms stable uranyl chelates over the whole pH range even at ratios of ligand to metal as low as 1:1 or less. The complexes were studied as a function of pH over a range of concentration

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(2) Abstracted from a dissertation submitted by Richard L. Gustafson to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) J. Sutton, *J. Chem. Soc.*, Supp. No. 2, S275 (1949).

(4) S. Ahrlund, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1907 (1954).

(5) I. Feldman and J. R. Havill, *THIS JOURNAL*, **76**, 2114 (1954).

(6) W. F. Neuman, J. R. Havill and I. Feldman, *ibid.*, **73**, 3593 (1951).

(7) I. Feldman and W. F. Neuman, *ibid.*, **73**, 2312 (1951).

(8) I. Feldman, J. R. Havill and W. F. Neuman, *ibid.*, **76**, 4726 (1954).

to determine the nature of the possible interactions which take place. Because of the interference of hydrolytic reactions of the metal ion itself, it was considered desirable to study the hydrolysis and olation reactions of the uranyl ion in the absence of chelating agent under the same conditions as those used for the uranyl-Tiron chelates.

Experimental

Reagents.—Aqueous stock solutions of uranyl nitrate were prepared from Baker and Adamson analyzed reagent and were standardized gravimetrically by ignition of a suitable aliquot to the oxide, U_3O_8 . The Tiron was obtained from the LaMotte Chemical Products Co., Baltimore, Maryland, and was used without further purification after establishment of its purity and standardization of an aqueous stock solution by potentiometric titration. Since the inflection corresponding to the dissociation of the first phenolic group was not sharp, the equivalence point was determined by the method of Gran.⁹

Potentiometric Titrations.—A Beckman Model G pH meter was used to record hydrogen ion concentrations. Titrations were carried out in a glass, multineck flask of 250 ml. capacity, which was fitted with a mercury seal stirrer, nitrogen inlet and outlet tubes, microburet delivery tube and glass and calomel extension electrodes. Measurements were made at a temperature of $25 \pm 0.05^\circ$. The ionic strength was maintained relatively constant by using a medium of 0.1 M potassium nitrate and relatively low concentrations of ligand and metal ion. Purified nitrogen was bubbled through the solution in order to exclude carbon dioxide. The molar concentration of metal ion was varied between 2×10^{-4} and 5×10^{-3} .

Above pH 5, equilibrium was reached slowly, and several days sometimes were required for the completion of a titration. Under these conditions the procedure was modified by using a series of bottles containing equal aliquots of metal chelate and supporting electrolyte, to which varying amounts of standard base were added. These solutions were allowed to equilibrate for approximately 24 hr. in a nitrogen atmosphere, after which the pH of each sample was recorded. The readings thus obtained were checked for equilibrium by subsequent pH measurements from time to time. In all cases the electrode system was calibrated with standard acetate buffer according to the method of Michaelis.¹⁰

Spectrophotometric Determinations.—The uranyl-Tiron system was investigated by Job's¹¹ method of continuous variations modified as outlined by Vosburgh and Cooper.¹² Determinations were made at pH 3.00, 4.00, 5.30 and 8.50, with ratios of $T_A/(T_A + T_M)$ which varied from 0.25 to 0.80 (where T_A and T_M represent total concentrations of Tiron and uranyl species, respectively). Samples were allowed to equilibrate for several days and absorbancy measurements were made in 10 mm. Corex cells with a Cary Model 14 recording spectrophotometer.

In addition to the above measurements, the absorbancy was determined for a series of solutions containing equal amounts of uranyl ion but varying in ligand concentration, according to the method outlined by Meyer and Ayres.¹³ Data of this type were obtained over a wide pH range while values of T_A/T_M were varied from 0.5 to 3.0.

Results and Discussion

In the discussion and mathematical treatment of data, the symbols employed are:

m = number of moles of standard base added per mole of metal ion.

T_M = total analytical concentration of metal ion in all forms.

T_A = total analytical concentration of ligand in all forms.

(9) G. Gran, *Analyst*, **77**, 661 (1952).

(10) L. Michaelis, "Physical Methods of Organic Chemistry," Vol. I, 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1950, p. 1727.

(11) P. Job, *Ann. Chem.*, **11**, 97 (1936).

(12) W. C. Vosburgh and G. R. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

(13) A. S. Meyer, Jr., and G. H. Ayres, *ibid.*, **79**, 49 (1957).

t = number of hydroxo groups bound per polynuclear link in a "core plus links" type complex.

n = number of "links" per complex.

i = number of gram-ions of titratable hydrogen per mole of organic ligand.

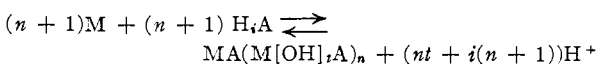
$Z = \frac{T_{OH} + [H^+] - [OH^-]}{T_M}$ = average number of protons which are neutralized or hydroxyl ions which react per metal ion in the formation of a metal complex molecule or ion.

T_{OH} = total concentration of KOH added to the experimental solution

A General Formula for Polynuclear Metal Chelate Formation.—Recently Sillén¹⁴ and Hietanen and Sillén¹⁵ have described methods for determining the general formulas of "core plus links" types of polymeric olated metal species of the general formula $M([OH]_iA)_n$. They found in a number of cases that the curves obtained by plotting Z (which is the average number of hydroxo groups bound per mole of metal ion) as ordinate *vs.* $-\log [H^+]$ as abscissa for different values of the total metal ion concentration, T_M , were essentially parallel and that the horizontal spacing between the two curves was proportional to the difference between the two values of $-\log T_M$. Mathematically this may be expressed by the relationship

$$\left(\frac{\partial \log T_M}{\partial \log [H^+]} \right)_Z = t \quad (1)$$

where t is number of hydroxo bridges per link in the polymeric complex. Unfortunately such a treatment does not yield valid results for systems in which chelation and polymerization occur simultaneously and both the ligand and metal ion concentrations are varied. Under these conditions the extent to which both reactions occur is dependent on the total metal ion concentration. It is possible, however, to derive expressions which will aid in the selection of general formulas for polynuclear olated chelate compounds. For the general reaction



the equilibrium constant $K_{(n+1)}$ may be expressed as

$$K_{(n+1)} = \frac{[MA(M[OH]_iA)_n][H^+]^{(nt+i(n+1))}}{[M]^{(n+1)}[H_iA]^{(n+1)}} \quad (2)$$

where M is the aquo metal ion, H_iA is an organic ligand containing i replaceable protons and $MA(M[OH]_iA)_n$ is the general formula of a "core plus links" type complex which contains t hydroxo bridges per link. In this and in forthcoming discussions, ionic charges will be omitted for purposes of clarity. Also

$$T_M = (n+1)[MA(M[OH]_iA)_n] + [M] \quad (3)$$

$$T_A = (n+1)[MA(M[OH]_iA)_n] + [H_iA] \quad (4)$$

where T_M and T_A are the total concentrations of metal ion and organic ligand, respectively. If $T_M = T_A$, equation 2 becomes

$$K_{(n+1)} = \frac{(T_M - [M])[H^+]^{(nt+i(n+1))}}{(n+1)[M]^{(2n+2)}} \quad (5)$$

It may be shown that at constant Z , $T_M/[M]$ is a constant which is represented by X . This is true

(14) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954).

(15) S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954).

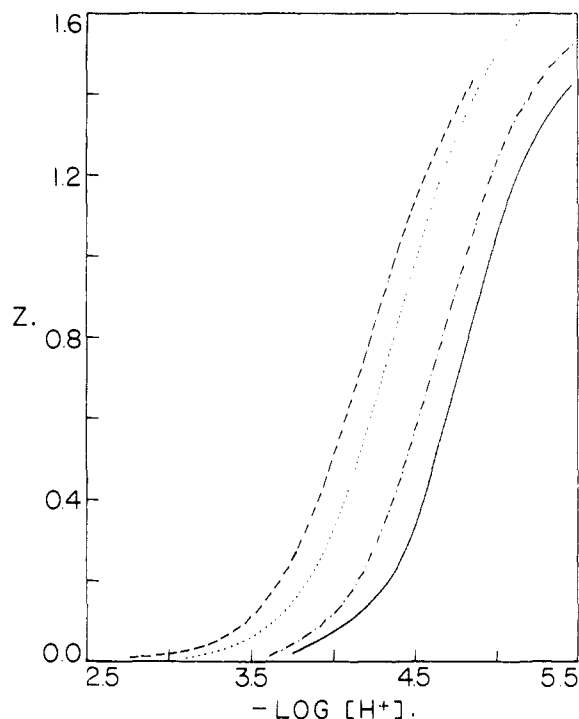


Fig. 1.—Plot of $Z = (T_{OH} + [H^+])/T_M$ = average number of hydroxyl groups bound per mole of UO_2^{+2} vs. $-\log [H^+]$; , $T_M = 5 \times 10^{-3} M$; , $T_M = 2 \times 10^{-3} M$; - · - · - , $T_M = 5 \times 10^{-4} M$; ——— , $T_M = 2 \times 10^{-4} M$; $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3).

if only a single species corresponding to the general formula $MA(M[OH]_iA)_n$ exists in equilibrium with the aquated metal ion. Then multiplication of both sides of equation 5 by $T_M^{(2n+1)}$ gives

$$K_{(n+1)}T_M^{(2n+1)} = \frac{[H^+]^{(nt+i(n+1))}X^{(2n+1)}(X-1)}{(n+1)} \quad (6)$$

or

$$\begin{aligned} \log T_M^{(2n+1)} &= \log [H^+]^{(nt+i(n+1))} + \log X^{(2n+1)}(X-1) \\ &\quad - \log(n+1)K_{(n+1)} \\ &= \log [H^+]^{(nt+i(n+1))} + C \end{aligned} \quad (7)$$

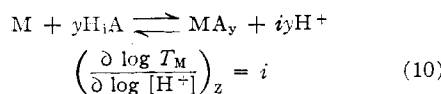
where C is a constant. Equation 7 may be rearranged to give

$$\log T_M = \log [H^+]^{\frac{nt+i(n+1)}{(2n+1)}} + C' \quad (8)$$

therefore

$$\left(\frac{\partial \log T_M}{\partial \log [H^+]}\right)_Z = \frac{(nt+i(n+1))}{(2n+1)} \quad (9)$$

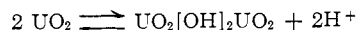
From equation 9, it is seen that a plot of $-\log [H^+]$ as abscissa vs. $-\log T_M$ as ordinate at constant Z will give a straight line of slope $[nt+i(n+1)]/(2n+1)$, provided that $[MA(M[OH]_iA)_n]$ is the only complex formed to an appreciable extent. In a similar manner it may be shown that for the reaction



and for $(n+1)MA \rightleftharpoons MA_y(M[OH]_iA_y)_n + ntH^+$

$$\left(\frac{\partial \log T_M}{\partial \log [H^+]}\right)_Z = t \quad (11)$$

Hydrolysis of the Uranyl Ion.—In Fig. 1 are plotted data obtained from potentiometric titration of uranyl nitrate with KOH. Here $Z = (T_{OH} + [H^+])/T_M$ = the average number of hydroxo groups bound per mole of metal ion. A plot of $-\log T_M$ as ordinate vs. $-\log [H^+]$ as abscissa at constant Z (equation 1) gave slopes of 2.08, 2.16, 2.20, 2.25, 2.34 and 2.39 at Z values of 0.20, 0.40, 0.60, 0.80, 1.00 and 1.20, respectively. These values are somewhat higher than the value of 2.00 which would be predicted on the basis of polymers containing two hydroxo bridges per link. A simple qualitative explanation of this behavior is based on the fact that the presence of complexes such as $UO_2[OH]^{+1}$ (which would appear to be the precursor of the polymer) would tend to produce a closer spacing of the curves in Fig. 1 than would be observed if only polynuclear complexes existed, thus giving a higher value of t . Calculations based on the assumption that the only reaction taking place in the early stage of the titration is

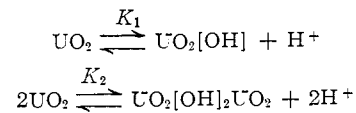


gave these K values at various concentrations:

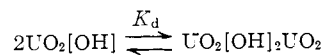
$T_M(M)$	$K \times 10^3$
5×10^{-3}	1.48 ± 0.01
2×10^{-3}	$1.51 \pm .03$
5×10^{-4}	$1.68 \pm .04$
2×10^{-4}	$1.98 \pm .05$

Such an upward trend in the values of the equilibrium constant could be explained on the basis of the existence of a simple monohydroxo complex, the relative concentration of which increases as the total uranyl concentration decreases.

Accordingly it is assumed that the reactions taking place in the region of the titration where $Z < 0.3$ are



or



where

$$K_1 = \frac{[UO_2[OH]][H^+]}{[UO_2]} \quad (12)$$

$$K_2 = \frac{[UO_2[OH]_2UO_2][H^+]^2}{[UO_2]^2} \quad (13)$$

and

$$K_d = \frac{[UO_2[OH]_2UO_2]}{[UO_2[OH]]^2} \quad (14)$$

These equations also hold for this system

$$T_{OH} + [H^+] = [UO_2[OH]] + 2[UO_2[OH]_2UO_2] \quad (15)$$

$$T_M = [UO_2] + [UO_2[OH]] + 2[UO_2[OH]_2UO_2] \quad (16)$$

Combination of equations 12, 13, 15 and 16 yields the expression

$$K_1 + 2K_2[UO_2]/[H^+] = [H^+](T_{OH} + [H^+])/[UO_2] \quad (17)$$

Hence if a binuclear diolate species is formed a plot of $[UO_2]/[H^+]$ as abscissa vs. $[H^+](T_{OH} + [H^+])/[UO_2]$ as ordinate should yield a straight line with a slope equal to $2K_2$ and an intercept equal to

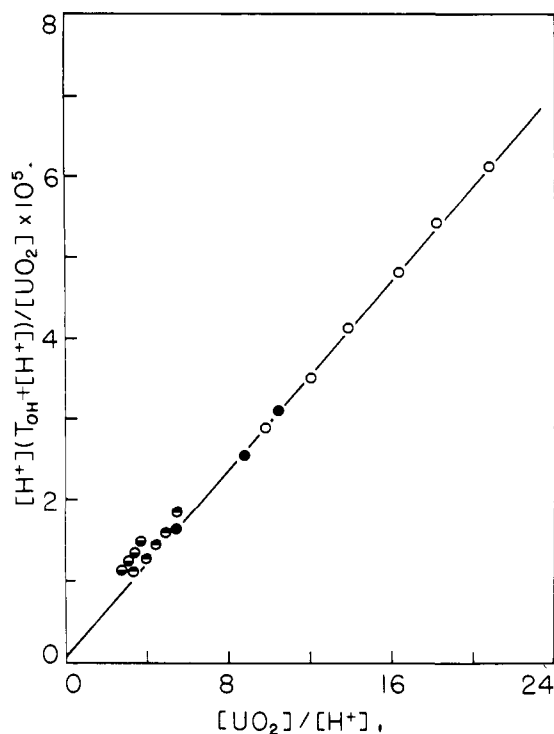


Fig. 2.—Plot of data of Fig. 1 illustrating presence of the binuclear olated species, $[\text{UO}_2(\text{OH})_2\text{UO}_2]$, in the pH range 3-4. Points calculated from data at the following concentrations: \circ , $T_M = 5 \times 10^{-3} M$; \bullet , $T_M = 2 \times 10^{-3} M$; \ominus , $T_M = 5 \times 10^{-4} M$; $\omin�$, $T_M = 2 \times 10^{-4} M$.

K_1 . As may be seen in Fig. 2, a straight line is obtained indicating a value of K_2 of 1.45×10^{-6} . Algebraic solution of equation 17 using the above value of K_2 gave a better value of K_1 than could be determined by graphical extrapolation. A summary of the values obtained are

$$\begin{aligned} pK_1 &= 6.10 \\ pK_2 &= 5.84 \\ \log K_d &= 6.36 \end{aligned}$$

The value $pK_2 = 5.84$ compares with Sutton's 5.94 and Ahrland's 6.05 (at 20° in $1 M \text{NaClO}_4$). It is of interest to note that the value of K_d for the uranyl ion is considerably greater than those calculated for aluminum, cupric, ferric, scandium¹⁶ or thorium¹⁷ ions, indicating that the monohydroxo species of the uranyl ion has a relatively greater tendency to form polynuclear complexes.

Since the chief purpose of obtaining data for the uranyl nitrate system was to obtain constants which could be used in correcting uranyl chelate data for the effect of the unchelated ion, it was felt that the mathematical approach derived by Silén^{14,15} would suit the purpose satisfactorily. Accordingly the constants obtained were

$$\begin{aligned} K_2 &= 10^{-5.83 \pm 0.01} \\ K_3 &= 0 \\ K_4 &= 10^{-17.6 \pm 0.2} \end{aligned}$$

(16) See review by L. Pokras, *J. Chem. Educ.*, **33**, 223 (1956).

(17) R. F. Bogucki and A. E. Martell, *THIS JOURNAL*, **80**, 4170 (1958). Calculated from data of K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

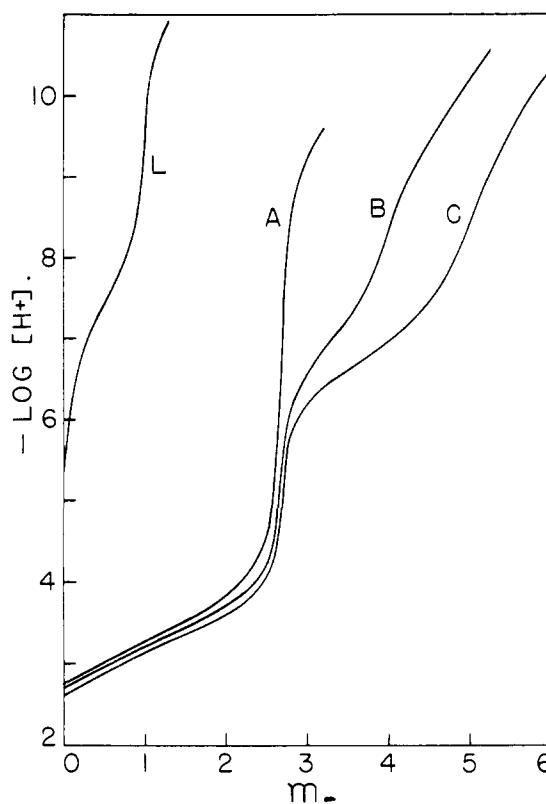


Fig. 3.—Potentiometric titration of uranyl-Tiron chelates: L, free ligand; A, B and C represent 1:1, 2:1 and 3:1 ratios of ligand to uranyl ion, respectively; $T_M = 5 \times 10^{-3} M$; m = number of moles of standard KOH added per mole of metal ion except for free ligand curve where m = number of moles of base added per mole of ligand; $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3).

where

$$K_{n+1} = \frac{[\text{UO}_2(\text{OH})_2\text{UO}_2]_n [\text{H}^+]^{2n}}{[\text{UO}_2]^{(n+1)}}$$

The arbitrary assignment of $K_3=0$, as made by Ahrland, *et al.*,⁴ allows a good fit of the experimental data up to pH 4.5. In the solution of equations involving the uranyl-Tiron system, it is necessary to allow for the contributions of the species $[\text{UO}_2(\text{OH})]$, $[\text{UO}_2(\text{OH})_2\text{UO}_2]$ and $[\text{UO}_2(\text{OH})_2\text{UO}_2]_3$. An excellent approximation may be made by assuming that the concentration of the monohydroxo species is equal to zero and that except in the pH range greater than 4, the concentration of $[\text{UO}_2(\text{OH})_2\text{UO}_2]_3$ is equal to zero also.

Stoichiometric Ratios of Tiron and Uranyl Ions in Their Chelates.—The titration curves shown in Fig. 3 for 1:1, 2:1 and 3:1 ratios of ligand to metal ion exhibit steep inflections at $m = 2\frac{2}{3}$ in each case. Since little may be said on the basis of the data presented in Fig. 3 as to the nature of the complexes formed, it was necessary to investigate the uranyl-Tiron system spectrophotometrically. In Fig. 4 are plotted continuous variations data obtained at $-\log[\text{H}^+] = 5.3$, which is the pH corresponding to the midpoint of the first inflection of the titration curves of Fig. 3. At all wave lengths studied (500-600 $m\mu$), maximum absorption was observed for solutions containing approxi-

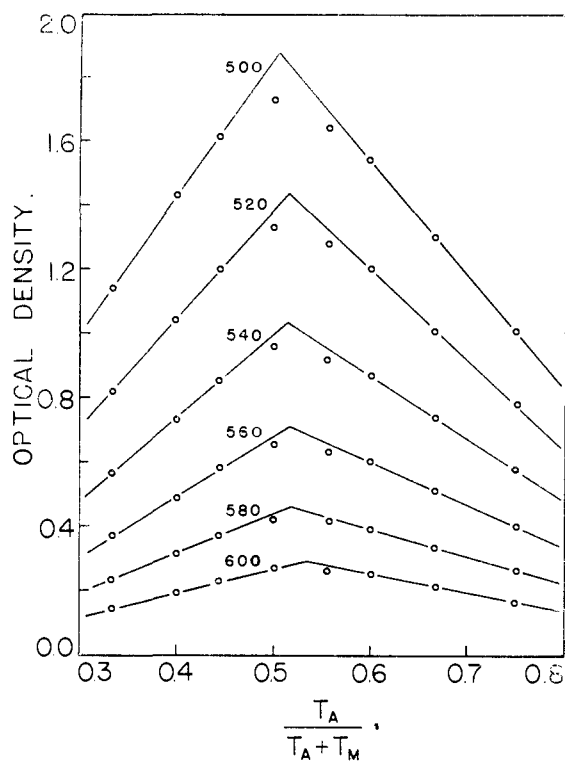


Fig. 4.—Continuous variations measurements of the uranyl-Tiron system at $-\log [H^+] = 5.3$ and at various wave lengths: $T_A + T_M = 1.01 \times 10^{-2} M$; all solutions $0.1 M$ in KNO_3 .

mately equivalent amounts of ligand and metal ion, indicating the presence of a 1:1 chelate. Continuous variations measurements at $-\log[H^+] = 4.0$ also indicated formation of a 1:1 complex while results at $-\log[H^+] = 3.0$ were inconclusive. At $-\log[H^+] = 8.5$ corresponding to the midpoint of the second inflection in the 2:1 and 3:1 titration curves, a maximum absorption was obtained for solutions containing a $T_A/(T_A + T_M)$ ratio of 0.7 (Fig. 5), indicating the presence of a complex containing the unusual number of seven ligand groups per three uranyl ions. At wave lengths shorter than $560 m\mu$ the interpretation of the continuous variations data becomes indefinite presumably because of the fact that two or more chelate species absorb rather strongly in this region.

It was hoped that the application of the mole ratio technique for determining the stoichiometry of complex ions might be of value in the present study. Accordingly solutions $1.20 \times 10^{-2} M$ in uranyl ion, but varying in ligand concentration, were prepared at $-\log[H^+] = 8.5$ and were equilibrated for several days. A plot of the optical densities obtained at wave lengths of 520, 600 and $640 m\mu$ is shown in Fig. 6. Only a single definite break is observed at a T_A/T_M ratio of 2.3, again corresponding to the presence of a chelate containing approximately seven Tiron molecules per three uranyl ions or some multiple thereof. Although the expected behavior is observed at $520 m\mu$ in that there is no increase in absorption beyond the maximum at $T_A/T_M = 2.3$, the curves

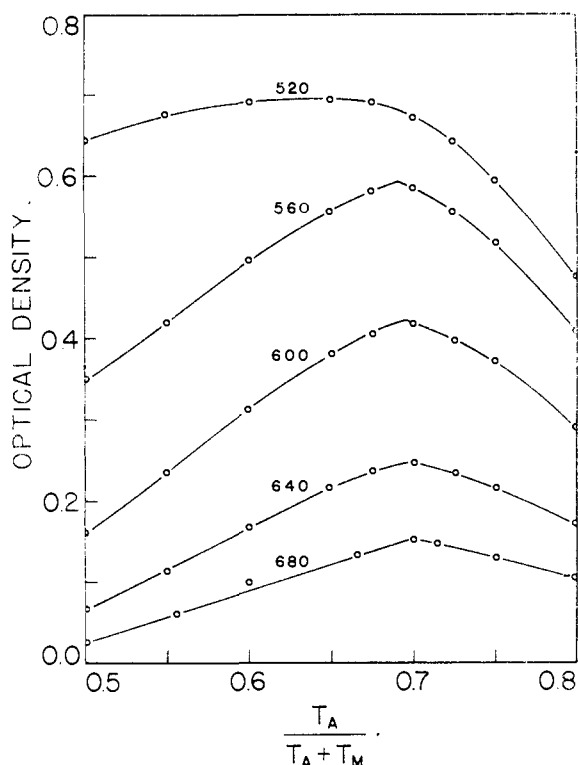


Fig. 5.—Continuous variations measurements of the uranyl-Tiron system at $-\log [H^+] = 8.5$; for $520, 560, 600$ and $640 m\mu$ $T_M + T_A = 4.00 \times 10^{-2} M$; for $680 m\mu$ $T_M + T_A = 2.02 \times 10^{-2} M$. Optical densities plotted are only $1/3$ actual value in the latter case. All solutions $0.10 M$ in KNO_3 .

for the 600 and $640 m\mu$ data actually show a decrease in absorption.

Uranyl-Tiron Interactions in the Low pH Region.

—Since it has been demonstrated that the complex formed below $pH 5.3$ in solutions containing ligand to metal ratios greater than or equal to unity is a 1:1 type, it now becomes necessary to deduce the formulas of the polynuclear complexes formed and if possible to calculate the equilibrium constants involved. First a series of 1:1 titration curves were obtained over a 25-fold range of concentration. A plot of Z vs. $-\log[H^+]$ for these data is shown in Fig. 7 while a plot of $-\log T_M$ vs. $-\log[H^+]$ for data obtained at constant Z is shown in Fig. 8. The values of $(\partial \log T_M / \partial \log [H^+])_Z$ were found to be 1.69, 1.76, 1.83, 1.88 and 1.82 at Z values of 0.75, 1.00, 1.25, 1.50 and 1.75, respectively. Before attempting to give any significance to these values, it is of interest to consider the various possible "core plus links" species which would yield inflection points at $m = 2^{2/3}$ for solutions containing 1:1 ratios of ligand to metal ion. In Table I are listed the m values at which inflections would be observed for various complexes of the general formula $[MA([OH]_t MA)_n]$ on the basis of various values of n , i and t in the formation reaction. It will be noticed that only three types (indicated by asterisks) predict inflections in the region $m = 2.6$ to 2.7 , namely, those corresponding to the formulas $[MA(M[OH]A)_2]$, $[MHA(M[OH]_2 HA)_4]$ and $[MHA(M[OH]_2 HA)_5]$.

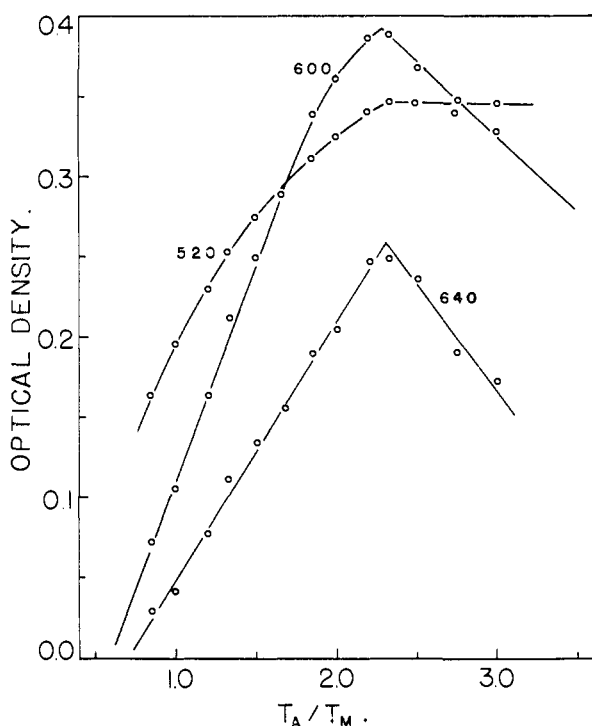


Fig. 6.—Plot of absorption vs. T_A/T_M for uranyl-Tiron chelates: $T_M = 1.20 \times 10^{-2} M$; path length = 1.001 mm.; $\mu = 0.50$; $-\log [H^+] = 8.50$. Optical densities plotted are only $1/10$ actual value. All solutions 0.10 M in KNO_3 .

These correspond to theoretical values of $(\partial \log T_M / \partial \log [H^+])_Z$ (equation 9) of 1.60, 1.44 and 1.45, respectively. Of these values the latter two are far removed from the 1.80 ± 0.06 result observed experimentally. In addition these complexes would

TABLE I

PREDICTED INFLECTION POINTS FOR GENERAL REACTION
 $(n + 1)M + (n + 1)H_2A \rightleftharpoons MA(M[OH]_iA)_n + (nt + i(n + 1))H^+$ FOR VARIOUS VALUES OF n , i AND t

n	$i = 1$ $t = 1$	$i = 1$ $t = 2$	$i = 2$ $t = 1$	$i = 2$ $t = 2$
0	1.00	1.00	2.00	2.00
1	1.50	2.00	2.50	3.00
2	1.67	2.33	2.67*	3.33
3	1.75	2.50	2.75	3.50
4	1.80	2.60*	2.80	3.60
5	1.83	2.67*	2.83	3.67
6	1.86	2.71	2.86	3.71
7	1.88	2.75	2.88	3.75
8	1.89	2.78	2.89	3.78
∞	2.00	3.00	3.00	4.00

require that only one phenolic group would dissociate a proton upon chelate formation. Studies on the cupric¹⁸ and vanadyl¹⁹ chelates of Tiron having formation constants of $10^{14.6}$ and $10^{17.2}$, respectively, show that both protons are dissociated at low pH values although it is possible that intermediate complexes of the MHA type exist at very low pH . The fact that qualitative

(18) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiäinen, *THIS JOURNAL*, **79**, 3036 (1957).

(19) S. Chaberek, Jr., R. L. Gustafson, R. C. Courtney and A. E. Martell, *ibid.*, **81**, 515 (1959).

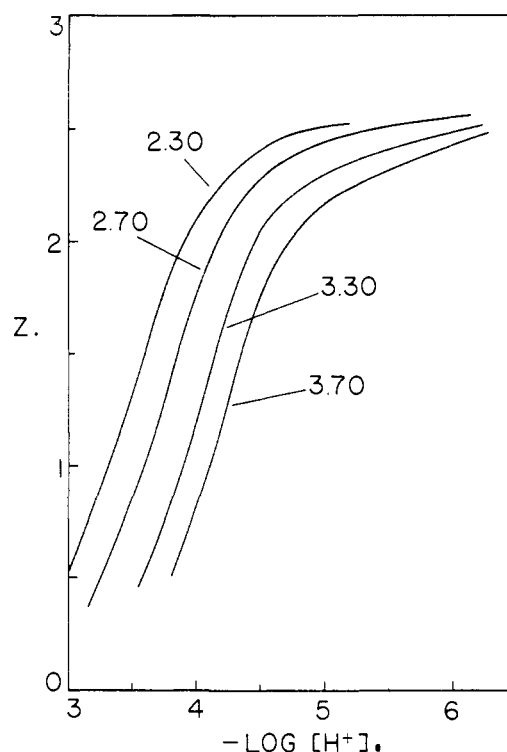
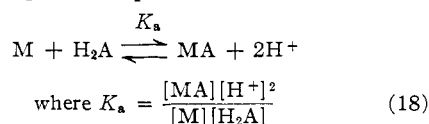


Fig. 7.—Plot of Z vs. $-\log [H^+]$ for 1:1 uranyl-Tiron chelates at various concentrations. Numbers on graph refer to $-\log T_M$; $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3).

experiments have shown that uranyl-Tiron complexes are intermediate in stability between those of cupric and vanadyl ion strongly suggests that both of the phenolic hydrogens also are dissociated initially in the present case. Hence in the calculation, it is assumed that the complex present at pH 5.3 is $[MA(M[OH]A)_2]$.

It appears logical that the chelated uranyl ion should be less susceptible to hydrolysis than the aquo ion, which itself hydrolyzes only slightly below pH 3.5. Therefore, the assumption is made that the initial reaction is that of chelate formation alone according to the equation



Other pertinent equations are

$$T_M = [MA] + [M] + 2[M(OH)_2M] \quad (19)$$

$$T_A = [MA] + [H_2A] \quad (20)$$

$$T_{OH} + [H^+] = 2[MA] + 2[M(OH)_2M] \quad (21)$$

Combination of the above expressions yields the relationship for $[M]$

$$[M] = \frac{-b \pm \sqrt{b^2 - 4c}}{2} \quad (22)$$

$$b = [H^+]^2/K_2$$

$$c = [H^+]^2(T_{OH} + [H^+] - 2T_M)/2K_2$$

Once $[M]$ is determined, the values of $[MA]$ and $[H_2A]$ readily are calculated.

Calculation of K_a gave essentially constant values in the range $m = 0$ to 1.5 for solutions containing

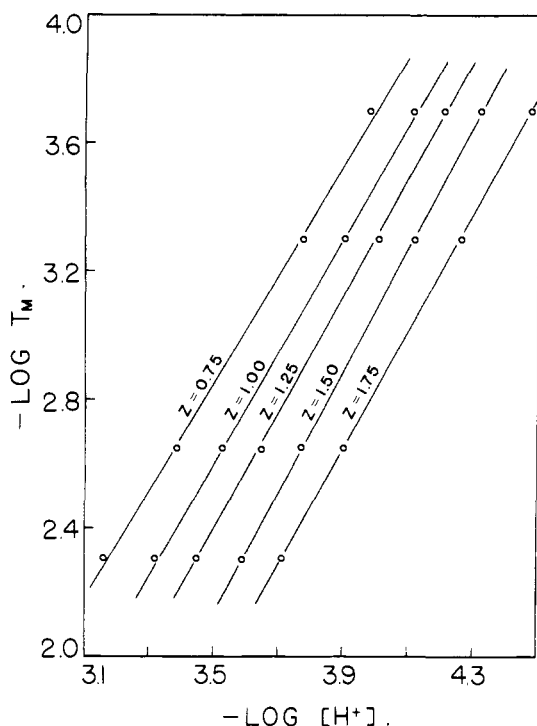


Fig. 8.—Plot of $-\log T_M$ vs. $-\log [H^+]$ at constant Z based on data shown in Fig. 7.

either 1:1 or 2:1 ratios of ligand to uranyl ion as shown in Table II. The value of $K_a = 10^{-4.20}$ corresponds to a value of $K_{MA} = \frac{K_a}{K_e K_f} = 10^{15.88}$ for the reaction $M + A \rightleftharpoons MA$, where K_e and K_f are the first and second dissociation constants of Tiron. These values were found to be $10^{-7.60}$ and $10^{-12.48}$, respectively, in good agreement with the values of $10^{-7.66}$ and $10^{-12.6}$ obtained by Schwarzenbach and Willi²⁰ at $t = 20.0^\circ$ and $\mu = 0.1$.

T_A/T_M	T_M	pK_a
1	5×10^{-3}	4.05 ± 0.01
1	2×10^{-3}	$4.17 \pm .01$
1	5×10^{-4}	$4.30 \pm .02$
2	5×10^{-3}	$4.20 \pm .01$
2	2×10^{-3}	$4.30 \pm .02$
Average value		$4.20 \pm .08$

It will be noticed in Table II that for the 1:1 systems there is a definite trend toward higher values of K_a as the concentration of metal chelate is increased. This leads to the possibility that polynuclear chelates are being formed to some extent. Ultracentrifugation measurements²¹ have shown that interaction of 1:1.5 ratios of Th(IV) to Tiron results in the formation of binuclear chelates, even in pH regions where no hydrolysis of the metal ion is believed to take place. This leads to the belief that polymerization takes place *via* bridging by the phenolic oxygen atoms of Tiron.

(20) G. Schwarzenbach and A. Willi, *Helv. Chim. Acta*, **34**, 528 (1951).

(21) R. L. Gustafson and A. E. Martell, to be published.

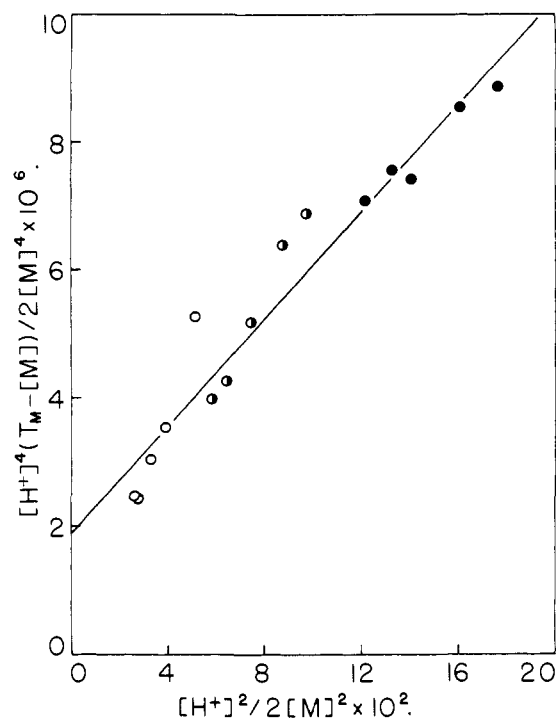
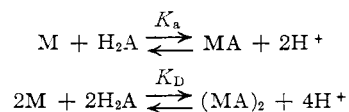


Fig. 9.—Plot of $[H^+]^4(T_M - [M])/2[M]^4$ vs. $[H^+]^2/2[M]^2$ for the 1:1 $UO_2(VI)$ -Tiron system in the pH range 2.8-4.0: \circ , $T_M = 5 \times 10^{-3} M$; \bullet , $T_M = 2 \times 10^{-3} M$; \bullet , $T_M = 5 \times 10^{-4} M$.

If it is assumed that the only two reactions taking place in the first part of the lower region are

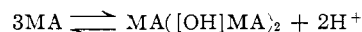


it may be shown using equations similar to (19), (20) and (21) (but assuming that the concentration of $M[OH]_2M$ is negligible) that

$$K_D + \frac{[H^+]^2}{2[M]^2} K_a = \frac{[H^+]^4(T_M - [M])}{2[M]^4} \quad (23)$$

Hence a plot of $[H^+]^4(T_M - [M])/2[M]^4$ as ordinate vs. $[H^+]^2/2[M]^2$ as abscissa should produce a straight line of slope K_a having an intercept equal to K_D if MA and $(MA)_2$ are the only chelate species present in solution. As is illustrated in Fig. 9 the best straight line gives a value of $pK_a = 4.38$ and $pK_D = 5.72$, the former value comparing with $pK_a = 4.20$ for the case where the possibility of the presence of the dimer was not considered. It is clear that the plot is not actually linear, however, suggesting that although some $(MA)_2$ may be present, other chelate species such as MHA and M_2HA_2 may also exist in solution. The inclusion of two more parameters for these species would result in a very complex algebraic expression containing four unknowns in one equation and any attempt at solution of such a system seems unwarranted in the present case.

Hydrolysis of the Uranyl-Tiron Chelate.—As a first approximation it was assumed that the polymerization reaction proceeds in a single step.



where

$$K_b = \frac{[\text{MA}(\text{OH})\text{MA}]_2[\text{H}^+]^2}{[\text{MA}]^3} \quad (24)$$

Other pertinent equations are

$$K_4 = \frac{[\text{M}(\text{OH})_2\text{M}]_3[\text{H}^+]^6}{[\text{M}]^4} \quad (25)$$

$$T_M = 3[\text{MA}(\text{OH})\text{MA}]_2 + [\text{MA}] + [\text{M}] + 2[\text{M}(\text{OH})_2\text{M}] + 4[\text{M}(\text{OH})_2\text{M}]_3 \quad (26)$$

$$T_A = 3[\text{MA}(\text{OH})\text{MA}]_2 + [\text{MA}] + [\text{H}_2\text{A}] \quad (27)$$

$$T_{\text{OH}} + [\text{H}^+] = 8[\text{MA}(\text{OH})\text{MA}]_2 + 2[\text{MA}] + 2[\text{M}(\text{OH})_2\text{M}] + 6[\text{M}(\text{OH})_2\text{M}]_3 \quad (28)$$

To add an extra expression allowing for the formation of $[\text{MA}(\text{OH})\text{MA}]$, which seems to be a likely intermediate, would be to create a situation involving nine unknowns with eight equations. Although such situations may be handled easily in some cases, the complexity of some of the terms involved is such that the more rigorous approach is impractical. Combination of equations 13, 18 and 24-28 gives an equation in $[\text{M}]$ which may be solved by successive approximations

$$3 \left(T_{\text{OH}} + [\text{H}^+] - 2 T_M + \frac{2K_2[\text{M}]^2}{[\text{H}^+]^2} + \frac{2K_4[\text{M}]^4}{[\text{H}^+]^6} - 2[\text{M}] \right) = 2 \left(T_A - \frac{2K_2[\text{M}]^2}{[\text{H}^+]^2} - [\text{M}] - \frac{K_a[\text{M}]}{[\text{H}^+]^2} \left[\frac{2K_2[\text{M}]^2}{[\text{H}^+]^2} + [\text{M}] \right] \right) \quad (29)$$

Once the value of $[\text{M}]$ has been determined, the other terms may be calculated with little difficulty. Values of pK_b have been calculated from data at $T_M = 5 \times 10^{-3}$ and 2×10^{-3} in the range $m = 1.5-2.5$ and are listed in Table III. An average value of 3.05 ± 0.04 has been obtained from data

TABLE III

VALUES OF pK_b CALCULATED ACCORDING TO EQUATION 24

$-\log [\text{H}^+]$	T_M	pK_b
3.73	5×10^{-3}	3.06
3.78	5×10^{-3}	3.11
3.82	5×10^{-3}	3.09
3.89	5×10^{-3}	3.05
3.96	5×10^{-3}	2.97
4.05	5×10^{-3}	2.98
4.19	5×10^{-3}	3.05
4.34	5×10^{-3}	3.09
3.84	2×10^{-3}	2.57
3.92	2×10^{-3}	2.50
4.02	2×10^{-3}	2.50
4.15	2×10^{-3}	2.54
4.33	2×10^{-3}	2.65

where $T_M = 5 \times 10^{-3}$, whereas data where $T_M = 2 \times 10^{-3}$ yielded $pK_b = 2.55 \pm 0.05$. In this connection it should be pointed out that the values of pK_a used in calculation of pK_b were those obtained from the same titration curve; *i.e.*, the values of $pK_a = 4.05$ and 4.17 were used in calculating pK_b at metal ion concentrations of 5×10^{-3} and $2 \times 10^{-3} M$, respectively. This variation in pK_a would be expected to produce a large deviation in K_b since K_a appears as the third power in the equation

$$K_b = \frac{[\text{MA}(\text{OH})\text{MA}]_2[\text{H}^+]^2}{K_a^3[\text{M}]^3[\text{H}_2\text{A}]^3} \quad (30)$$

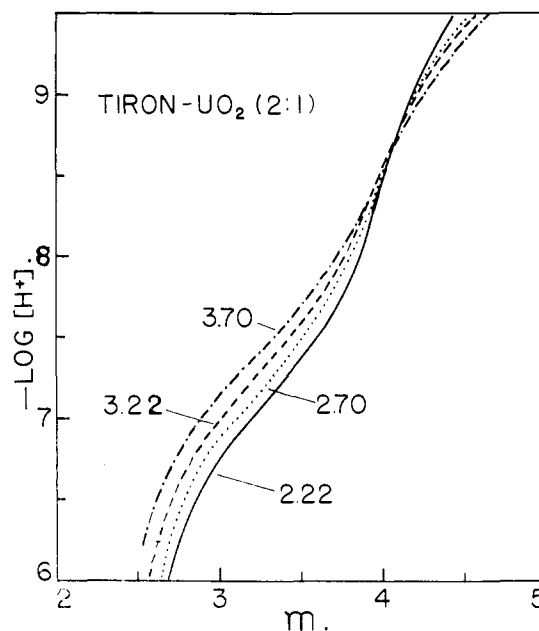
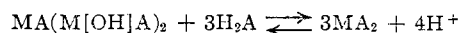


Fig. 10.—Plot of potentiometric titration data obtained for solutions containing a 2:1 ratio of Tiron to uranyl ion. Numbers on curve refer to $-\log T_M$; $t = 25.0^\circ$; $\mu = 0.1$ (KNO_3); m = number of moles of KOH added per mole of metal ion.

Also an error of $0.05 pK_b$ unit is produced by an error of only $0.01 pH$ unit. By the use of average constants of $pK_a = 4.13$ and $pK_b = 2.80$, the experimental data may be reproduced within an average deviation of $\pm 0.03 pH$ unit. The introduction of an arbitrary constant for the reaction corresponding to the formation of $[\text{MA}(\text{OH})\text{MA}]$ resulted in a divergence of the calculated values of K_b , suggesting that the concentration of the binuclear chelate species is small relative to that of the ternuclear form throughout the course of the titration.

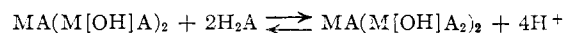
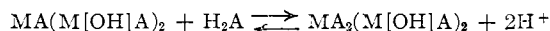
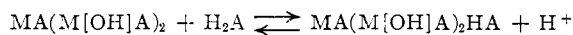
Interaction of the Ternuclear 1:1 Chelate with Additional Tiron.—In Fig. 10 are illustrated a series of titration curves for solutions containing 2:1 ratios of ligand to metal ion. The curves cross at an inflection region where m has a value of approximately 4. A similar family of curves obtained for solutions containing a 7:3 ratio of ligand to uranyl ion showed an inflection and cross-over at $m = 4^{1/3}$. A plot of T_M vs. $-\log[\text{H}^+]$ of the data of Fig. 10 produced values of $(\partial \log T_M / \partial \log [\text{H}^+])$ of approximately 4, suggesting that more than a single reaction was taking place. Calculations of expected values of $(\partial \log T_M / \partial \log [\text{H}^+])$ for reasonable hypothetical reactions lead in nearly every case to values of 2 or less. However, it is possible that combinations of various reactions might produce high values of the slope. As a simple example, if a monohydroxo chelate has only a slight tendency to form polymeric species, there would be virtually no displacement of the buffer regions of the titration curves, thus producing a very slight change in $-\log[\text{H}^+]$ per change in the metal ion concentration. In the limiting case where all curves are superimposed, the value of $(\partial \log T_M / \partial \log [\text{H}^+])$ would be infinity.

The simplest possible reaction which might be imagined is the interaction of three additional moles of Tiron with the ternuclear complex to form three moles of a 2:1 mononuclear complex. Such a reaction appears to be impossible on the basis of the results of the continuous variations experiments illustrated in Fig. 5 where the presence of a complex containing a 7:3 ratio of Tiron to uranyl ion is indicated. Nevertheless, calculations were attempted on the basis of the assumption that the reaction

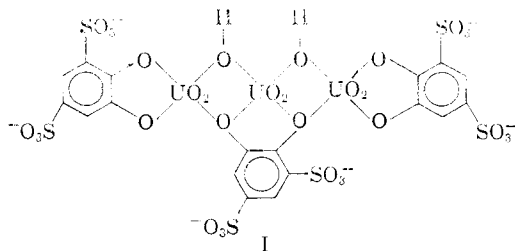


takes place. Steadily decreasing values of K with an increase in m were obtained, showing that this reaction does not proceed in a single step. This effect, however, does not eliminate the possibility of an over-all reaction of the above type, as it would still be possible for the depolymerization reaction to occur in two or more steps. If this were the case, the over-simplification made above would result in a drift of calculated values, as was observed. In addition to the drift in the equilibrium constant, further evidence against the formation of a simple mononuclear 2:1 chelate may be found in the spectrophotometric data described above. In addition, investigation of the uranyl 8-hydroxyquinoline-5-sulfonate system has shown²² that the 2:1 chelate undergoes extensive hydrolysis above pH 5. It would seem therefore that the existence of a mononuclear 2:1 uranyl-Tiron chelate at pH 8.5 would be unlikely, despite the greater stability of the Tiron chelates over those of 8-hydroxyquinoline-5-sulfonate.

Consideration has been given to several other possible reactions which might occur in the initial part of the second buffer region above $m = 2.67$, such as



Of these, only the second gave reasonable agreement with the experimental data, as shown in Table IV. The self-consistency of the dissociation constants obtained over a reasonably wide range of concentration and pH suggests that the initial reaction takes place between the ternuclear complex and a single mole of Tiron. If the ternuclear complex is visualized as



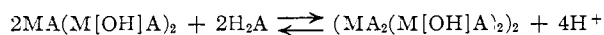
(22) C. Richard, R. L. Gustafson and A. E. Martell, *THIS JOURNAL*, **81**, 1033 (1959).

TABLE IV
EQUILIBRIUM CONSTANTS FOR THE REACTION
 $MA(M[OH]A)_2 + H_2A \rightleftharpoons MA_2(M[OH]A)_2 + 2H^+$

T_M	$-\log [H^+]$	pK
5×10^{-3}	6.37	10.96
5×10^{-3}	6.62	11.10
5×10^{-3}	6.80	11.17
5×10^{-3}	6.96	11.20
5×10^{-3}	7.10	11.15
5×10^{-3}	7.26	11.25
1.5×10^{-3}	6.75	11.00
1.5×10^{-3}	6.92	11.05
1.5×10^{-3}	7.07	11.07
1.5×10^{-3}	7.23	11.11
1.5×10^{-3}	7.37	11.05

Average $pK = 11.12 \pm 0.06$

where the oxygen donors from one Tiron molecule may or may not form bridges in the same manner as do the hydroxo groups, it seems quite possible that the incorporation of an additional mole of Tiron might cause the polymer shown above to close into a cyclic arrangement with the fourth Tiron molecule acting as a bridge between the terminal uranyl groups. The fact that equilibrium is attained very slowly in the second buffer region also suggests that some type of polymerization or depolymerization reaction is taking place, rather than simply the addition of Tiron molecules to the existing ternuclear species. Consideration of the reaction



where two ternuclear units are considered to be linked together by Tiron bridges, resulted in widely divergent values of the calculated equilibrium constants.

The remainder of the titration curve beyond $m = 3.3$ closely resembles that of the free ligand, indicating little or no affinity of the complex for additional Tiron groups. However, the spectrophotometric data show that interaction does take place resulting in the incorporation of one ligand molecule per uranyl ion such that ultimately a 7:3 complex is obtained. Since Tiron dissociates but a single proton below pH 8.5, it may function either as a monodentate ligand by coordination of the phenolate anion or may actually form a weak chelate ring.

Some interaction of the complex with hydroxyl ion is indicated above pH 8.5. No attempt has been made to analyze the data in this high pH range but it is probable that partial displacement of Tiron molecules by hydroxyl ions takes place. This is indicated by the fact that the optical densities of chelates containing more than one mole of Tiron per gram ion of uranyl salt steadily decrease as the pH is raised above pH 8.5. No appearance of a solid phase was observed even in the most alkaline range studied.

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