whereas the accepted difference in the pK's of two ammonium groups separated by two carbon atoms is about 3 pK units.

In conclusion, then, there seems to be overwhelming evidence that the location of protons on the various species of EDTA according to Chapman is incorrect in solution, while those shown in Fig. 2 are consistent with the data.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

The Hydrolytic Behavior of Thorium(IV)-pyrocatechol-3,5-disulfonate[1]

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Potentiometric measurements are described for aqueous systems containing 4:1, 3:1, 2:1 and 1:1 moles of Tiron (disodium pyrocatechol-3,5-disulfonate) per mole of thorium(IV) salt in 0.1 M potassium nitrate solution. For ligand/metal ratios of 1.5:1 or higher the same compound is formed initially, regardless of the excess ligand present. The nature of the 1.5:1 compound is established by spectrophotometric and potentiometric studies. Extensive hydrolysis of the metal chelate takes place at all ratios of ligand to metal ion studied, but no precipitation occurs over the wide pH range investigated.

Although many studies have been made on the hydrolysis of thorium(IV) salts, few investigations have been carried out on the combination of thorium(IV) chelates with hydroxyl ions. The studies of Kraus and Holmberg[2] and of Hietanen[3,4] and Sillen[4] indicate that the reactions of the octacoördinated Th(IV) ion with hydroxyl ion are rather complex, with the formation of polynuclear complexes through hydroxo bridges. In the initiation of the present research program it was thought that the combination of the thorium(IV) ion with a sufficiently strongly bound chelating ligand would reduce both the acidity of the metal ion and the number of possible hydrolysis sites, and thus decrease both the number of hydroxyl groups bound and the extent of hydrolysis. Tiron was chosen as the ligand because of its rather considerable affinity for the thorium(IV) ion and ions of other actinide elements.

Experimental

Reagents.—Tiron, purchased from LaMotte Chemical Products Co., Baltimore, Maryland, was used to prepare an aqueous stock solution which was standardized by potentiometric titration with standard base. Reagent grade $Th(NO_3)_4 \cdot 4H_2O$, obtained from Allied Chemical and Dye Corp., N. Y., was standardized gravimetrically and used to make up a stock solution for use in potentiometric and spectrophotometric measurements.

Potentiometric Titration.—A Beckman Model GS pH meter, fitted with extension glass and calomel electrodes, was calibrated with acetic acid buffer as well as with standard HCl and NaOH to give hydrogen ion concentrations directly. Measurements were made at 25.0 ± 0.05° and the ionic strength was maintained at approximately 0.10 M by the addition of standard KNO_3 solution. Purified nitrogen was circulated through the jacketed titration cell under slight pressure to exclude carbon dioxide. In many instances equilibrium was reached very slowly, so that considerable time was required for each experimental point. All potentiometric titrations were checked by duplicate determinations.

Spectrophotometric Determination of Combining Ratios.—The method of continuous variations was applied to the determination of the formulas of the chelates formed at Tiron: Th(IV) ratios equal to or greater than 1.5. The molar ratios of Tiron to Th(IV) were varied over a wide range while maintaining [Th] + [Tiron] constant. Pyridine buffer was used to maintain the pH constant at 5.0, which is well in the inflection regions of potentiometric titration curves of compositions having a ratio of ligand to metal above 1.5. The differences of optical densities of the Tiron–Th(IV) chelate and of an equivalent amount of Tiron were determined at 305 mμ in accordance with the equation

$$\Delta = lD - l[\epsilon_1 M(l - X) + \epsilon_2 MX], \text{ where}$$

ϵ_1 = extinction coefficient of Tiron
ϵ_2 = extinction coefficient of Th(IV)
X = mole fraction of Th(IV) in initial solution
M = total initial concentrations of Th(IV) and Tiron
l = length of light path in experimental solution.
D = optical density of experimental solution

Results and Discussion

Potentiometric Measurements.—Potentiometric titrations carried out to study the action of one mole of Tiron per mole of thorium(IV) resulted in the group of curves illustrated in Fig. 1a. The total concentration of metal chelate was varied over a four-fold range, the lowest curves being obtained for the most concentrated solutions. A slight inflection was observed in all cases at an m value of 2.2-2.4, where m represents the number of moles of hydroxide added per mole of metal ion, with the highest value being obtained for the most concentrated sample. This shift in the inflection point suggests that a number of metal chelate species exist in solution simultaneously and that the relative concentration of the various species is a function of the total concentration of chelates present. There is a long sloping inflection region between m = 3.5 and 4.5, and the three curves intersect and cross over at m = 4 and at a $-\log[H^+]$ value of approximately 9.0.

A family of titration curves for solutions containing two moles of Tiron per mole of thorium ion are shown in Fig. 1b. In all cases a steep inflection was observed at an m value of 3.0, and all of the curves intersect and cross over at the point where 5.5 moles of base have been added per mole of metal ion. Since sharp inflections at m = 3 are observed regardless of the excess of ligand employed (see Figs. 1c and 1d), it appears that a single chelate species is present in this region. Also, titration curves in Fig. 1a do not have the sharp inflection as observed in Figs. 1b, 1c and 1d. This difference indicates that the compound formed contains more than one mole of ligand per gram-ion of metal.

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[1] This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1823.

[2] K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[3] S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

[4] S. Hietanen and L. G. Sillen, *ibid.*, **8**, 1607 (1954).

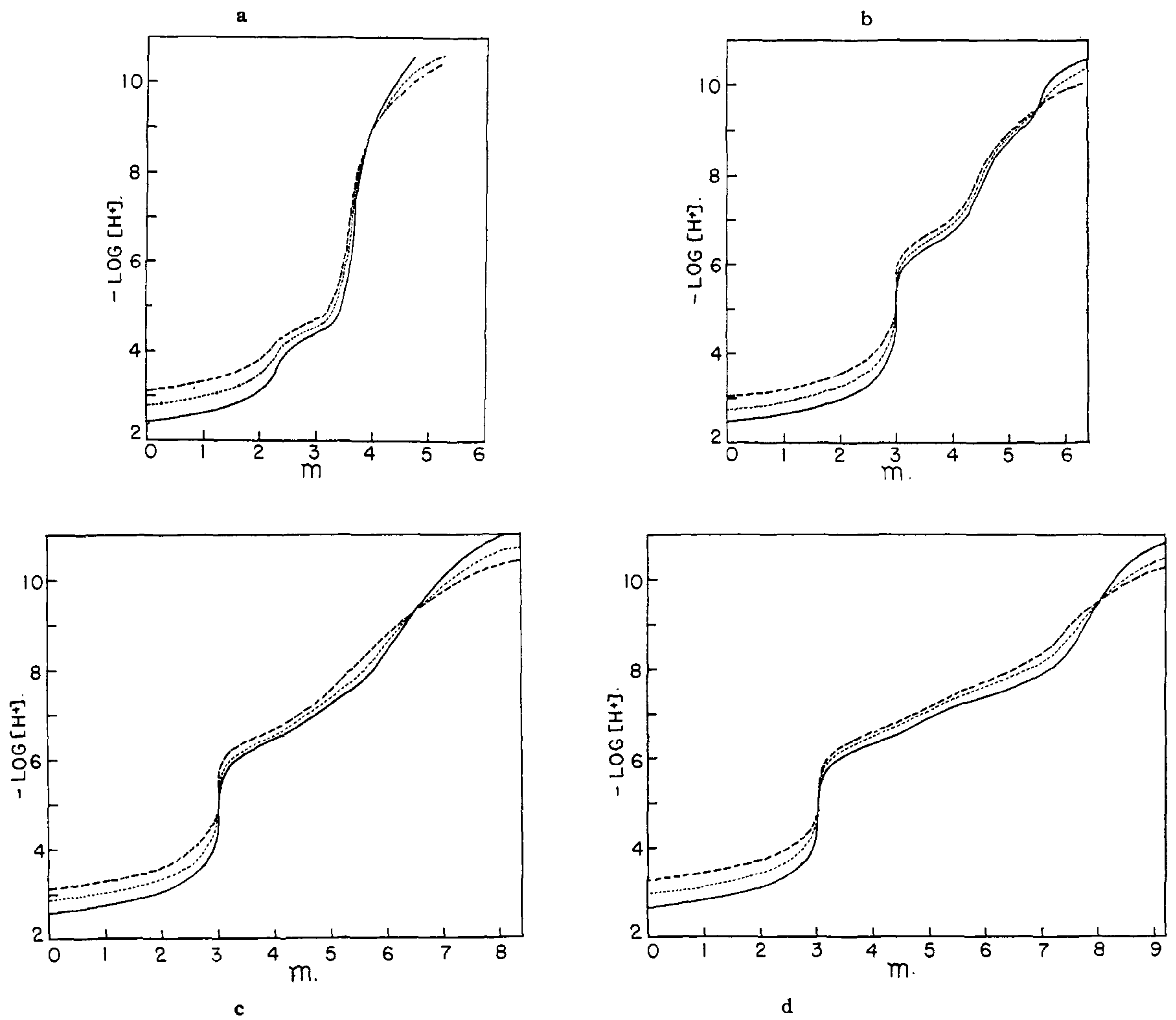

Fig. 1.—(a) Titration curves of 1:1 Tiron–thorium(IV) chelates: m = moles of base added per mole of metal ion —— A, T_A = molar concentration of ligand = 2.45×10^{-3} M; — B, $T_A = 1.23 \times 10^{-3}$ M; - - - C, $T_A = 6.15 \times 10^{-4}$ M. (b) Titration curves of 2:1 Tiron–thorium(IV) chelates: A, $T_A = 3.27 \times 10^{-3}$ M; B, $T_A = 1.63 \times 10^{-3}$ M; C, $T_A = 8.14 \times 10^{-4}$ M. (c) Titration curves of 3:1 Tiron–thorium(IV) chelates: A, $T_A = 3.69 \times 10^{-3}$ M; B, $T_A = 1.84 \times 10^{-3}$ M; $T_A = 9.21 \times 10^{-4}$ M. (d) Titration curves of 4:1 Tiron–thorium chelates: A, $T_A = 3.86 \times 10^{-3}$ M; B, $T_A = 1.93 \times 10^{-3}$ M; C, $T_A = 9.64 \times 10^{-4}$ M.

As in the 2:1 titration, the titrations of 3:1 and 4:1 Tiron–thorium systems illustrated in Figs. 1c and 1d are characterized by long, sloping buffer regions which terminate in a slight inflection which is more pronounced at the higher concentrations. The decrease in pH of these buffer systems with increasing metal (and chelate) concentration indicates the possibility of olation reactions which result in the formation of polynuclear metal chelate compounds. Such reactions may occur with further participation of the ligand in metal chelate formation beyond the formation of the initial metal chelate at $m = 3$. That the latter is the case is indicated in the stoichiometry of the titration curves, since the buffer regions of the 3:1 and 4:1 systems would be much shorter if the reactions taking place merely involve olation of the metal chelate formed initially plus titration of the excess ligand present.

Because of the characteristic differences between the 1:1 and 2:1 curves illustrated in Figs. 1a and 1b, a series of titrations were carried out at a number of ratios of ligand to metal between 1:1 and 2:1. The results of this study are given in Fig. 2. In the lower buffer region the 1.5:1, 1.6:1 and 2:1 curves are practically identical, and the inflections occur at $m = 3$, as is the case for higher ratios of ligand to metal. The slight shifts in the inflection at $m = 3$ would be expected since the concentration of excess ligand varies in each case. Between the ligand-metal ratios of 1:1 and 1.5:1, the curves are unique for each ratio and show an extension of the weak inflection of the 1:1 curve to higher m values as well as an upward shift of the second buffer region. Since the curves obtained for ligand to metal ratios between 1:1 and 1.5:1 cannot be derived by adding up abscissas of the 1:1 and 1.5:1 titrations, it is apparent that the composition of

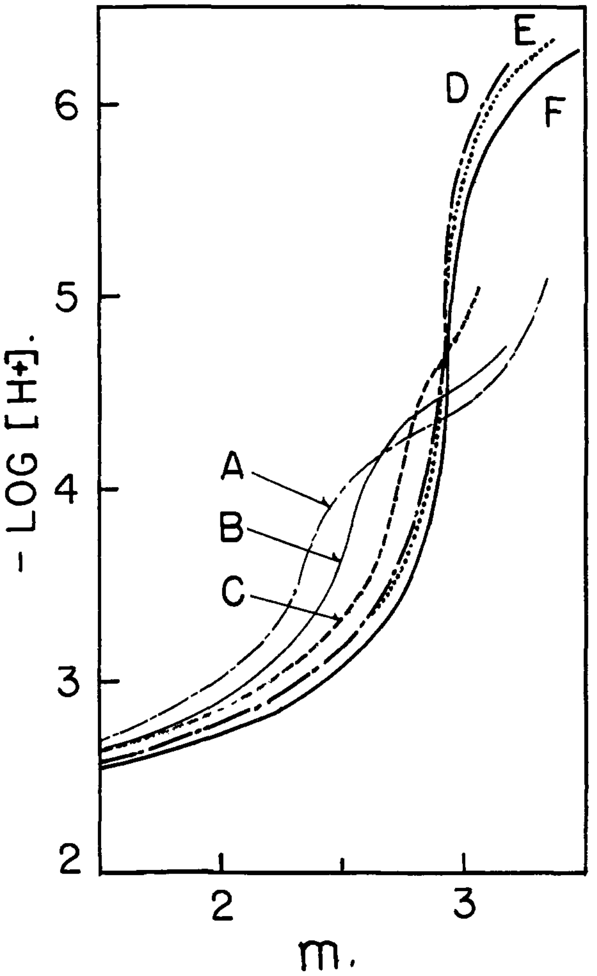

Fig. 2.—Potentiometric titration of Tiron-Th(IV) chelates at ligand:metal ratios of: A, 1.0; B, 1.2; C, 1.4; D, 1.6; E, 1.8; F, 2.0; $[Th^{+4}] = 2.5 \times 10^{-3}$ M; m = moles of base added per mole of metal ion.

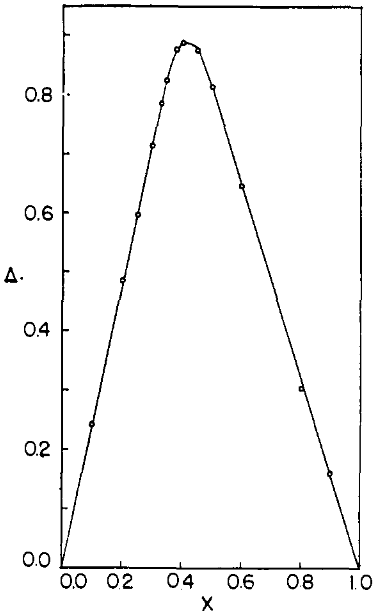

Fig. 3.—Continuous variations plot of optical density difference *vs.* mole fraction of Th(IV) at $[Th^{+4}]$ + [Tiron] = 2.577×10^{-4} M and $-\log [H^+] = 5.0$ (X = mole fraction of Th(IV); Δ = optical density increment resulting from complex formation).

the metal chelates formed varies continually as the ligand:metal ratio is increased up to 1.5:1. The potentiometric titrations clearly show, however, that when sufficient ligand is present, a unique metal chelate compound having 1.5 moles of Tiron per gram-ion of Th(IV) is formed below *p*H 5.

Spectrophotometric Studies.—The spectrophotometric determination of the combining ratios of Tiron and Th(IV) at *p*H 5.0 by the method of continuous variations, illustrated in Fig. 3, provides further evidence for the formation of the 1.5:1 chelate compound. The peak of the plot of optical density, which occurs at a mole fraction [Th]/([Th] + [Tiron]) of 0.4, indicates a combining ratio of 1.5 Tiron per metal ion. In addition, the absorption measurements at 320 mμ suggest that at ligand/metal ratios of 1:1 or less, only one species, the 1:1 chelate compound, is formed. This conclusion is based on the fact that with increasing mole fraction the slope of the line changes at 0.5 and the optical density varies in a linear manner beyond that point.