[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Ionization of Ethylenediaminetetraacetic Acid and its Acid Salts[1]

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RECEIVED MAY 4, 1960

The fully protonated salt of EDTA, H_6YCl_2, is prepared. Its dissociation constants at 25.0° and an ionic strength of 2.0 are $K_{H_6Y^{++}} = 0.55$ and $K_{H_5Y^+} = 0.11$. The betaine structure for H_4Y is consistent with these and the other EDTA constants, while the constants do not fit the proposed tetraacetic acid structure for H_4Y.

The four apparent ionization constants of ethylenediaminetetraacetic acid (H_4Y) have been determined by several workers.[2-4] The EDTA molecule has two additional sites available for protonation. A large increase in the solubility of EDTA and changes in its spectra below *p*H 1 were observed, which, along with the isolation of the H_6YCl_2 salt from 6 *M* HCl, is evidence that the H_5Y^+ and H_6Y^{++} species exist in strong acid solutions. The present investigation was undertaken to determine the apparent ionization constants of these species at $\mu = 2.0$ and 25.0 ± 0.1°. A knowledge of these constants is important in studying metal–EDTA chelates which are stable in strong acid solutions and in the elucidation of the mechanisms of their acid dissociation reactions. The first ionization constant of H_4Y was also determined at $\mu = 2.0$ and 25° using a titrimetric method[4b] for comparison with the H_5Y^+ and H_6Y^{++} constants. A mechanism is presented for the ionization of the H_6Y^{++} and H_5Y^+ species which accounts for the relative values of the constants and which is consistent with the mechanism proposed by Schwarzenbach[4a] for the four subsequent ionizations. An alternate mechanism for the ionization of EDTA recently proposed by Chapman[5] does not seem valid in solution.

Definition of Terms.—The symbols K_1, K_2, K_3 and K_4 used in this paper for the four apparent ionization constants of EDTA are consistent with those previously used. The symbols used for the apparent equilibrum ionization constants determined in the present work are defined as

$$H_6Y^{++} \rightleftharpoons H_5Y^+ + H^+;\ K_{H_6Y^{++}} = \frac{[H_5Y^+][H^+]}{[H_6Y^{++}]}$$

$$H_5Y^+ \rightleftharpoons H_4Y + H^+;\ K_{H_5Y^+} = \frac{[H_4Y][H^+]}{[H_5Y^+]}$$

These are concentration constants ["apparent constants"] and are not thermodynamic constants.

Experimental

The EDTA was Baker Analyzed Reagent, recrystallized from hot water three times. The stock solutions were standardized with a standard $ZnSO_4$ solution using Eriochrome Black T as an indicator.

Absorbance measurements were taken on a Beckman DU at 220 and 225 mμ with the temperature of the cell compartment maintained at 25.0 ± 0.1°. Measurements were taken with 10^{-3} *M* EDTA solutions at $\mu = 2.0$, in the $[H^+]$ range of 0.0632 to 2.00 *M*. Readings also were taken at $\mu = 4.0$ and $[H^+] = 2.00$ and 3.78 *M*. The acidity was adjusted in all cases with HCl and the ionic strength with NaCl. All flasks used were treated with Desicote to avoid contamination of the solutions by metal ions leached from the vessel walls. The spectra of solutions contained in non-treated flasks were found to change with time. All traces of metallic impurities were removed from the water used by passing it through a column of Amberlite MB-3. In the $[H^+]$ region in the vicinity of 0.15 *M* where the solubility of EDTA was exceeded, absorbance changes due to precipitation were found to be very slow. Error from this source was avoided by taking all readings immediately after the solutions were brought to temperature. This precaution was necessary for only two measurements, but the procedure was used for all solutions to avoid any possible contamination resulting from the leaching of metal ions from the glassware.

The titration data for the determination of K_1 were obtained using a Beckman G *p*H meter. The EDTA solution titrated was 9.79×10^{-4} *M* with the ionic strength adjusted to 2.0 with KCl. The temperature of the solution was maintained at 25.0 ± 0.1°.

To confirm the existence of the H_6Y^{++} species in strong acid solutions, a sample of EDTA was crystallized from a 6 *M* HCl solution and analyzed for C, H and Cl.

TABLE I

MICROANALYTICAL DATA FOR EDTA CRYSTALLIZED FROM 6 *M* HCl

Element	Theor. % assuming H_6YCl_2	Exptl. %
Carbon	32.89	33.23
Hydrogen	4.94	5.09
Chlorine	19.41	19.37

TABLE II

TITRATION DATA FOR CALCULATION OF K_1[a]

*p*H	Equiv. base	Y_T
3.14	0.340	6.30×10^{-4} M
3.30	0.870	6.52×10^{-4} M
3.42	1.147	6.04×10^{-4} M

[a] K_1 found = 2.0×10^{-3}.

The value of K_1 was found to be 2.0×10^{-3} at $\mu = 2.0$ and 25.0° using a titrimetric method.[4b] The concentration of H_3Y^- in the $[H^+]$ range when absorbance measurements were taken is thus very small, and it was assumed that K_1 could be neglected in the derivation of the equation used to calculate $K_{H_6Y^{++}}$ and $K_{H_5Y^+}$. From $Y_T = [H_4Y] + [H_5Y^+] + [H_6Y^{++}]$ and $A = \epsilon_4 [H_4Y] + \epsilon_5[H_5Y^+] + \epsilon_6 [H_6Y^{++}]$ this equation can be derived.

$$K_{H_5Y^+}\left(\frac{10^3A - \epsilon_4}{[H^+]}\right) + \frac{1}{K_{H_6Y^{++}}}(10^3A\ [H^+] - \epsilon_6[H^+]) - \epsilon_5 = -10^3A$$

where $Y_T = 1.00 \times 10^{-3}$, A = absorbance in a 1.00 cm. cell, ϵ_4, ϵ_5 and ϵ_6 = molar extinction coefficients of H_4Y, H_5Y^+ and H_6Y^{++}, respectively.

The approximate value of ϵ_4 was obtained by assuming that the absorbance at $[H^+] = 0.0632$ *M* was due to H_4Y only. Since at $\mu = 4.0$ the absorbance readings at $[H^+] =$ 2.00 and 3.78 *M* were practically the same, it was assumed

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research and Development Command, under contract No. AF 49(638)-60. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] F. Carini and A. Martell, THIS JOURNAL, **74**, 5745 (1952).

[3] M. J. Cabell, A.E.R.E. Report C/R 813, Ministry of Supply, Harwell, Berks, England (1951).

[4] (a) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947); (b) G. Schwarzenbach, A. Willi and R. O. Bach, *ibid.*, **30**, 1316 (1947).

[5] D. Chapman, *J. Chem. Soc.*, 1766 (1955).

TABLE III

DISSOCIATION CONSTANTS OF THE ACID SALTS OF EDTA

λ	$K_{H_6Y^{++}}$	$K_{H_5Y^+}$	ϵ_4	ϵ_5	ϵ_6
220	0.515	0.121	226	358	92
225	0.593	0.107	193	232	60
Av.	0.55	0.11			

the absorbance was due to H_6Y^{++} only, and ϵ_6 was calculated from this value. Increasing the ionic strength apparently represses the ionization of H_6Y^{++}. This leaves three unknowns, $K_{H_6Y^{++}}$, $K_{H_5Y^+}$ and ϵ_5, which were determined by solving the above equation simultaneously with absorbance values at three different hydrogen ion concentrations taken from the curve of absorbance *vs.* $-\log [H^+]$. A second approximation using these values of $K_{H_6Y^{++}}$, $K_{H_5Y^+}$ and ϵ_5 gave a better value for ϵ_4 and the same value for ϵ_6 at absorbances at $[H^+] = 0.0632$ and 2.00 *M*, respectively. Further approximations were carried out until ϵ_4, $K_{H_6Y^{++}}$ and $K_{H_5Y^+}$ were essentially constant. The absorbance *vs.* $-\log [H^+]$ curve calculated from these constants fitted the experimental curve closely as seen in Fig. 1.

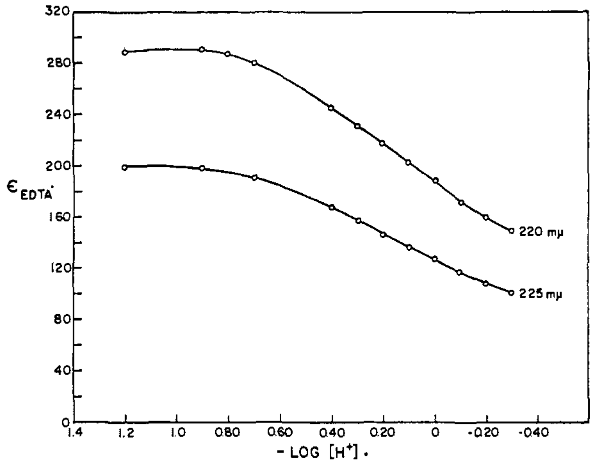


Fig. 1.—Molar absorptivity of EDTA as a function of $[H^+]$ at $\mu = 2.0$ and 25.0°; points are experimental and curve is calculated from values of $K_{H_6Y^{+2}}$, $K_{H_5Y^+}$, ϵ_4, ϵ_5 and ϵ_6 in Table III.

Discussion

The proposed mechanism for the ionization of H_6Y^{++} and H_5Y^+, together with that proposed by Schwarzenbach[4a] for the four subsequent ionizations, are given in Fig. 2.

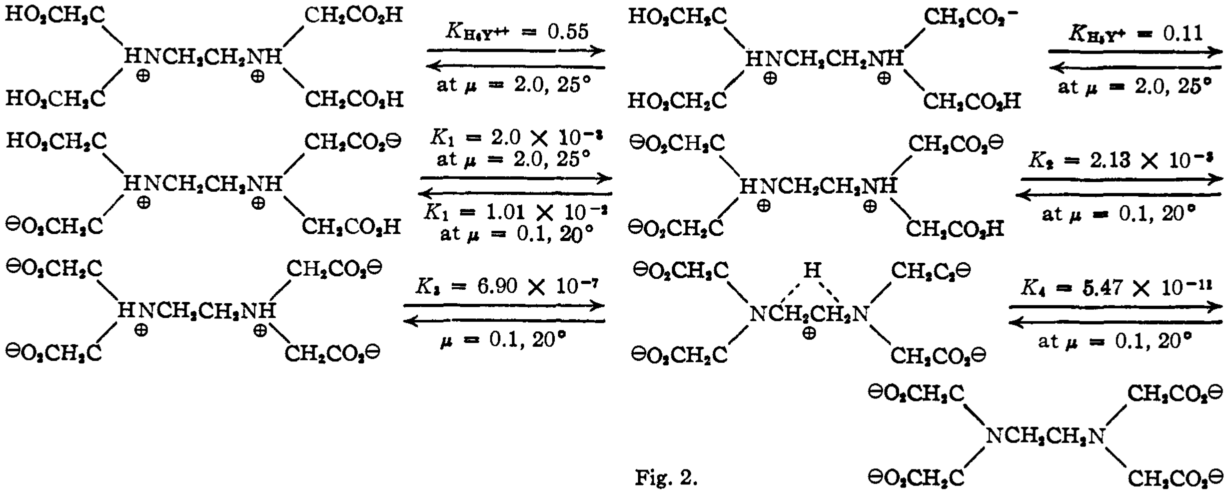
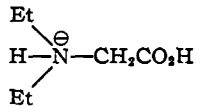


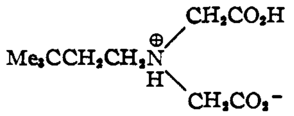
Fig. 2.

This mechanism can be supported by comparing the ratios of ionization constants of various acids[6] whose ionization steps are known with the ratios of the ionization constants of EDTA and by considering the statistical and the electrical effect upon these ratios.

The very large K_1/K_4 ratio of 1.85×10^8, indicating that the ionizing group in HY^{-3} is much more basic than in H_4Y, is consistent with Schwarzenbach's proposal that the former ionization involves an ammonium group and the latter a carboxylic acid group. Two other similar systems are


$\mathrm{H{-}\overset{\oplus}{N}(Et)_2{-}CH_2CO_2H}$

and


$\mathrm{Me_3CCH_2CH_2\overset{\oplus}{N}H(CH_2CO_2H)(CH_2CO_2^-)}$

where $K_1/K_2 = 2.7 \times 10^3$ and 0.7×10^3, respectively. Here the first ionizing proton obviously comes from a carboxyl group and the second from an ammonium group.

The experimental K_1/K_2 ratio of 4.74, which is in general agreement with the statistically predicted ratio of 2.67 used by Schwarzenbach, indicates that the proton ionizing from H_3Y^- is approximately equivalent to that ionizing from H_4Y. These two ionizations must involve the two carboxylic acid groups on opposite ends of the molecule. The statistical ratio of 2.67 assumes four equivalent sites (carboxylate groups) for protonation and two equivalent carboxylic acids for ionization. A better statistical approximation gives a ratio of 4.0 assuming interaction between the carboxylic acid and carboxylate group at the same end of the molecule. The K_1/K_2 ratio lends support to the proposal that both nitrogens are positively charged. A positively charged nitrogen separated from a

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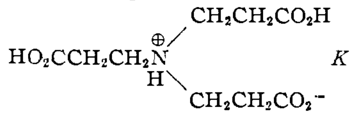
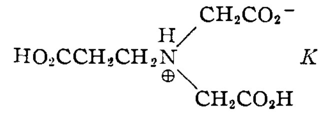
[6] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part I, Organic Ligands," The Chemical Society, London (1957).

carboxylic acid group by only one methylene group will enhance the ionization of the carboxylic acid group. The validity of this statement can be seen from these examples



$K_1/K_2 = 3.72$

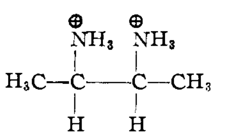
where the carboxylic acid groups are equidistant from the positively charged nitrogen, and



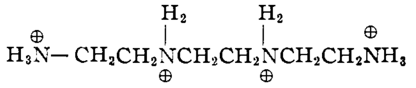
$K_1/K_2 = 43$

where one of the carboxylic acid groups is separated from the positively charged nitrogen by two methylene groups, the other by only one. Therefore the latter ionizes more readily than the former. This effect can be seen by the larger K_1/K_2 ratio. In the case of EDTA, since the ionizing (carboxylic acid) groups in H_4Y and H_3Y^- are equivalent as shown by the K_1/K_2 ratio, both nitrogens must be positively charged in order that the effect on the ionization of each carboxylic acid group be the same.

The K_3/K_4 ratio of 1.26×10^3 compares favorably to that of other systems which involve the ionization of 2 ammonium groups separated by 2 carbon atoms. Two examples are



$K_1/K_2 = 1.23 \times 10^3$



$K_1/K_2 = 2.24 \times 10^3$

The ratio of $K_{H_6Y^{++}}/K_{H_5Y^+}$ should be similar to the K_1/K_2 ratio, as in both cases the ionization of carboxylic acid groups on opposite ends of the EDTA molecule are involved, and the statistically predicted ratio is the same in both cases. The experimental ratios of $K_{H_6Y^{++}}/K_{H_5Y^+} = 5.0$ and $K_1/K_2 = 4.74$ are in good agreement.

The experimental $K_{H_5Y^+}/K_1$ ratio of 55 is larger than the statistically predicted ratio of 2.25. This may be explained by an electrostatic effect or possibly by hydrogen bonding. Since in the case of H_5Y^+ and H_4Y both protons can be considered to be ionizing from the same end of the molecule, and since the charges on one end of the molecule appear to have little effect on the ionization of the other, as shown by the K_1/K_2 and $K_{H_6Y^{++}}/K_{H_5Y^+}$ ratios, only half of the molecule need be considered. This may be compared to β-methylglutaric acid where the K_1/K_2 ratio is 92. However, when the statistical factor of 4 is removed, the ratio becomes 23. When the statistical factor of 2.25 is removed from the $K_{H_5Y^+}/K_1$ ratio of 55, this ratio becomes 24.5, which is in close agreement with that of β-methylglutaric acid. Greenspan[7] explains the large increase of K_1/K_2 ratio of β-methylglutaric acid over that of the unsubstituted glutaric acid as due the increase in the tendency of the long chain acid to coil, bringing the carboxyl groups closer together. This would increase the electrostatic effect as predicted by the Bjerrum[8] equation or the more accurate relationship derived by Westheimer and Kirkwood[9] by decreasing the distance between negatively charged carboxylates. It would also make hydrogen bonding more favorable. McDaniel and Brown[10] have suggested that hydrogen bonding may explain high K_1/K_2 ratios for dibasic acids. Westheimer and Benfey[11] have shown that the effect of hydrogen bonding on these ratios is small compared to the electrostatic effect, except for some substituted dibasic acids.

An alternate mode of ionization for EDTA has been proposed by Chapman[5] based on the infrared spectra of EDTA and its di- and tetrasodium salts. The mechanism is shown in Fig. 3.

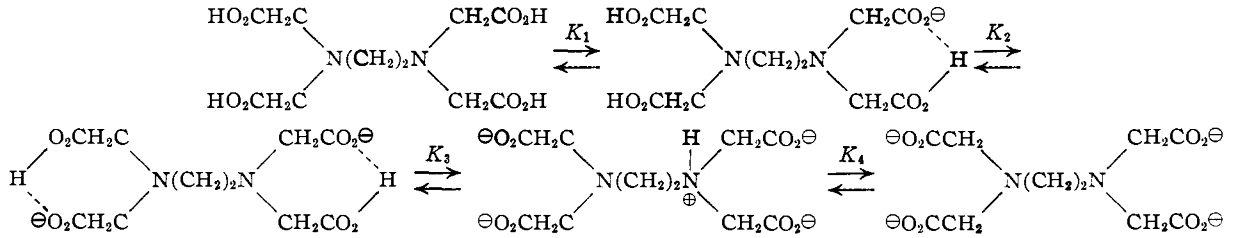


Fig. 3.

Chapman bases this mechanism on two facts: (1) The infrared spectrum of solid H_4Y does not show an ionized carboxyl group as would be expected if the molecule had a betaine structure. (2) The spectrum of solid Na_2H_2Y shows the presence of un-ionized carboxylic acid groups. The structure of the molecule in the solid state and in solution may be different but if so it is an unusual shift. Chapman argues against the betaine structure in H_4Y by saying that the nitrogens are too close together to be both positively charged and that in HY^{-3} the proton has migrated to the nitrogen as now the possibility of two positive charges on neighboring nitrogen atoms does not occur. This, however, does not explain why at least one nitrogen cannot be positively charged in H_4Y. According to Chapman's mechanism, the protons ionizing from H_6Y^{++} and H_5Y^+ would have to come off the two nitrogens. The observed difference between $pK_{H_6Y^{++}}$ and $pK_{H_5Y^+}$ is 0.69.

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[7] J. Greenspan, *Chem. Revs.*, **12**, 353 (1933).

[8] N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

[9] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

[10] D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953).

[11] F. H. Westheimer and D. T. Benfey, THIS JOURNAL, **78**, 5309 (1956).

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]

BY YUKITO MURAKAMI AND ARTHUR E. MARTELL

RECEIVED FEBRUARY 26, 1960

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. Silien, *ibid.*, **8**, 1607 (1954).