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Thorium Citrate Complexes, their Composition, Structure and Behavior

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The complex compounds which exist in heterogeneous as well as homogeneous systems of thorium and citrate in acid, neutral and alkaline solutions were studied. The phenomena observed may be accounted for as follows. A soluble complex of the composition $[\text{Th}_2\text{Ci}_3]$ is formed in water solution ($p\text{H} \sim 3.0$). In 50% alcoholic solution a soluble complex of the composition $[\text{ThCi}_2]$ is obtained ($p\text{H} \sim 3.0$). The insoluble compound has the composition $[\text{ThCi}]_n$ and is soluble quantitatively in an excess of sodium citrate. At high $p\text{H}$'s, the soluble $[\text{Th}_2\text{Ci}_3]$ is probably transformed into $[\text{Th}_2\text{Ci}'_3]^{4-}$. The insoluble $[\text{ThCi}]_n$ is soluble in sodium hydroxide ($p\text{H} \sim 8.0$).

Citrate complexes of the rare earths have been studied in recent years, especially in connection with the various methods used to separate these elements from one another, either in analytical or in commercial quantities.¹ The properties of these complexes, however, have not been fully investigated. It was therefore our purpose to study the above complexes without reference to their application to special branches of chemistry, but rather as a continuation of our studies of the complexes of oxyacids.² In this study of thorium all calculations were based on molar ratios of thorium to citrate. With the help of "heterometric"³ and other physico-chemical measurements we were able to determine the solubility, composition and behavior of the various compounds existing in the solid state and in solution.

As the following experimental material shows, the reactions taking place between thorium and citrate in solution are the result of the formation of only a few complex compounds. Special attention was given to the influence of alkali on these complexes. In all cases, equations were formulated which conform with the stoichiometric course of the reactions measured.

Experimental

Reagents and Solutions.—The stock solutions of thorium nitrate and sodium citrate used throughout this investigation were prepared by weighing the salts $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (Baker C.P.) and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Baker C.P. Analyzed). Solutions of the required concentrations were then prepared from the stock solutions by dilution.

(1) Yu. M. Telmachev, *C. A.*, **40**, 3682⁵ (1946); T. Moeller and G. K. Schweitzer, *Anal. Chem.*, **20**, 1201 (1948); T. Moeller, G. K. Schweitzer and D. D. Starr, *Chem. Revs.*, **42**, 63 (1948); M. Haisinsky and Y. Jeng-Tsong, *Anal. Chem. Acta*, **3**, 422 (1949); J. Schubert and H. Wallace, Jr., *J. Biol. Chem.*, **183**, 157 (1950); R. A. Day, Jr., and R. W. Stoughton, *THIS JOURNAL*, **72**, 5662 (1950); W. J. Blaedel and H. V. Malmstadt, *Anal. Chem.*, **23**, 471 (1951); M. Venkataramanah, T. K. Stayanarayanmurthy and Bh. S. V. Raghava Rao, *C. A.*, **45**, 1909f (1951); B. R. Lakshmana Rao and Bh. S. V. Raghava Rao, *ibid.*, **45**, 2365g (1951); D. S. N. Murthy and Bh. S. V. Raghava Rao, *ibid.*, **45**, 2365i (1951); B. R. Lakshmana Rao and Bh. S. V. Raghava Rao, *ibid.*, **45**, 6962g (1951); T. K. S. Murthy, B. R. Lakshmana Rao, *ibid.*, **45**, 6963a (1951); C. J. Rodden and J. C. Warf, *ibid.*, **45**, 7466i (1951).

(2) M. Bobtelsky and L. Bobtelsky-Chaikin, *Comptes rend.*, **203**, S72 (1936); M. Bobtelsky and M. Rappaport, *ibid.*, **205**, 234 (1937); M. Bobtelsky and B. Kirson, *ibid.*, **208**, 1577 (1939); M. Bobtelsky and A. E. Simchen, *ibid.*, **208**, 1646 (1939); M. Bobtelsky and J. Jordan, *THIS JOURNAL*, **67**, 1824 (1945); *ibid.*, **69**, 2286 (1947); M. Bobtelsky and A. E. Simchen, *ibid.*, **64**, 454 (1942); M. Bobtelsky and C. Heitner, *Bull. soc. chim.*, **18**, 494 (1951); **18**, 502 (1951); **19**, 358 (1952); **20**, 938 (1952); **20**, 943 (1952).

(3) M. Bobtelsky and B. Graus, *An. chim. Acta*, **9**, 163 (1953); M. Bobtelsky and I. Bar-Gadda, *Bull. soc. chim.*, **20**, 276 (1953); **20**, 382 (1953); **20**, 687 (1953); **20**, 819 (1953); M. Bobtelsky and I. Bar-Gadda, *An. chim. Acta*, **9**, 168 (1953); M. Bobtelsky and I. Weltwart, *ibid.*, **9**, 281 (1953); **9**, 37 (1953).

Apparatus and Procedure.—The apparatus used and the procedure followed were the same as in a previous report.⁴ The heterometric measurements were carried out at room temperature (18–27°).

Results and Discussion

Heterometric Measurements.—Figures 1 and 2 show the composition and results of heterometric titrations carried out in water solution. At first a saturated solution is obtained, following which a difficultly soluble salt of the empirical composition $[\text{ThCi}]_n \downarrow$ is precipitated (Fig. 1, curves 1 and 2). The first point of maximum density is reached exactly at the molar ratio of 1[Th]:1[Ci]. The complete redissolving of the precipitate is obtained in both cases exactly at the molar ratio of 2[Th]:3[Ci] (= $[\text{Th}_2\text{Ci}_3]$). In the reverse titrations (Fig. 2), the point of initial precipitation lies at the molar ratio of 2[Th]:3[Ci], and the first maximum point at 1[Th]:1[Ci] (= $[\text{ThCi}]$). The latter may be formulated as $\text{Th}[\text{Th}_2\text{Ci}_3] \downarrow$. This salt dissolves slowly in excess thorium. The nature of the last reaction is not clear.

Similar titrations were carried out in 50% alcoholic solution (Figs. 3 and 4). The first maximum density point is reached at the molar ratio of 1[Th]:1[Ci]. The point of complete redissolving is obtained in curves 2 and 3 by extrapolation at the approximate ratio 1[Th]:2[Ci]. In the reverse titrations (Fig. 4) in all four cases, the point of initial precipitation lies at the molar ratio of 1[Th]:2[Ci] (= $[\text{ThCi}_2]$) and the first maximum point at the ratio of 1[Th]:1[Ci] (= $\text{Th}[\text{ThCi}_2] \downarrow$). An excess of thorium is of no further influence.

As to the critical points obtained in the figures (the points of *initial* and *maximum* precipitation and the point of *complete solution*) the following may be said: the first maximum point is always associated with a reaction involving precipitation which is completed at this point. In many cases this point may even be used as an analytical end-point.³ The point of complete solution corresponds here to the point of initial precipitation in the reverse titrations. These points, which are independent of the concentrations of the reactants, indicate the end of complex formation.

The differences in the nature of the curves obtained (*i.e.*, between Figs. 1 and 2, and between Figs. 3 and 4) are caused partly by the difference in medium and by the slight solubility of $[\text{ThCi}]_n$ in excess thorium.

The different molar ratios at which the initial precipitation occurs in the two solvents may be

(4) M. Bobtelsky and B. Graus, *THIS JOURNAL*, **75**, 4172 (1953).

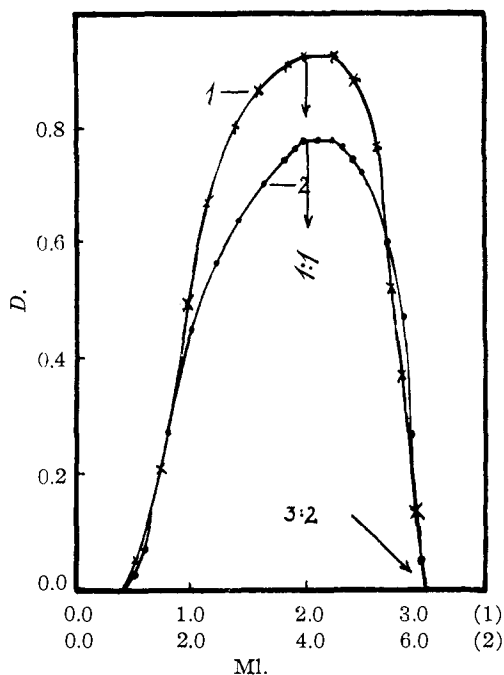


Fig. 1.—(1) 2 cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ + 8 cc. H_2O + x cc. 0.1 M Na_3Ci ; (2) 4 cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ + 16 cc. H_2O + x cc. 0.1 M Na_3Ci .

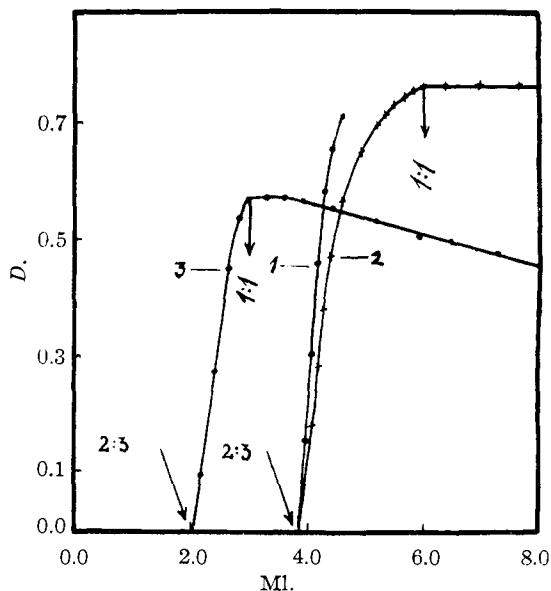


Fig. 2.—(1) 6 cc. 0.1 M Na_3Ci + 14 cc. H_2O + x cc. 0.1 M $\text{Th}(\text{NO}_3)_4$; (2) 6 cc. 0.05 M Na_3Ci + 14 cc. H_2O + x cc. 0.05 M $\text{Th}(\text{NO}_3)_4$; (3) 3 cc. 0.05 M Na_3Ci + 17 cc. H_2O + x cc. 0.05 M $\text{Th}(\text{NO}_3)_4$.

explained by the different solubilities of the products obtained. The reactions which take place in the solution may be formulated as

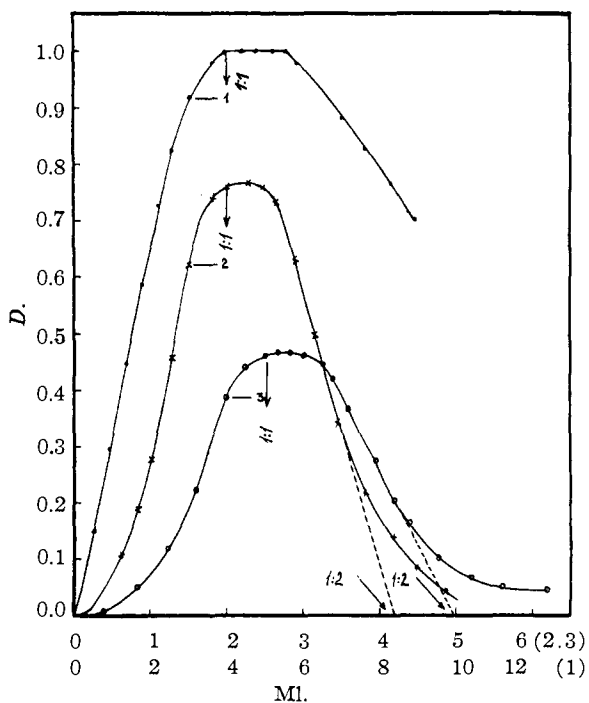
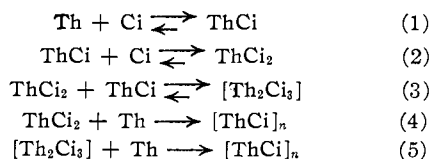


Fig. 3.—(1) 4 cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ + 1 cc. H_2O + 5 cc. alc. + x cc. 0.1 M Na_3Ci 50% alc.; (2) 2 cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ + 3 cc. H_2O + 5 cc. alc. + x cc. 0.1 M Na_3Ci 50% alc.; (3) 5 cc. 0.05 M $\text{Th}(\text{NO}_3)_4$ + 5 cc. H_2O + 10 cc. alc. + x cc. 0.1 M Na_3Ci 50% alc.

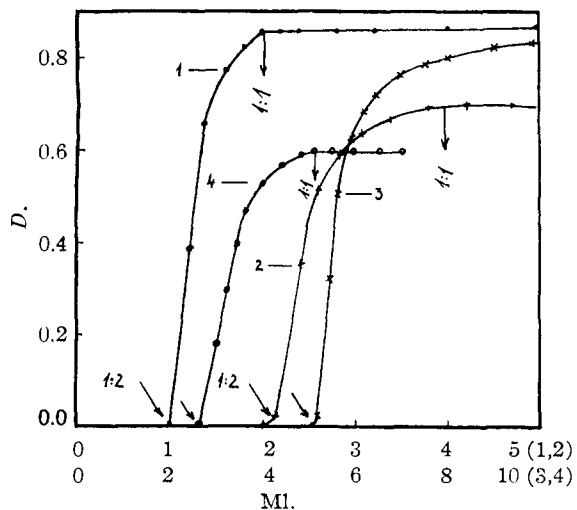


Fig. 4.—(1) 2 cc. 0.1 M Na_3Ci + 3 cc. H_2O + 5 cc. alc. + x cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ 50% alc.; (2) 4 cc. 0.1 M Na_3Ci + 6 cc. H_2O + 10 cc. alc. + x cc. 0.1 M $\text{Th}(\text{NO}_3)_4$ 50% alc.; (3) 5 cc. 0.1 M Na_3Ci + 5 cc. H_2O + 10 cc. alc. + x cc. 0.05 M $\text{Th}(\text{NO}_3)_4$ 50% alc.; (4) 5 cc. 0.05 M Na_3Ci + 5 cc. H_2O + 10 cc. alc. + x cc. 0.05 M $\text{Th}(\text{NO}_3)_4$ 50% alc.

These equations of course constitute a working hypothesis only, and are not necessarily the only ones which can explain the observed facts.

What occurs subsequently depends on the solubility of the different products in the particular solvent used. In 50% alcohol the reaction may stop with the formation of $[\text{ThCi}_2]$ and the precipitation of an insoluble compound which follows.

On the other hand, in water solution a further reaction occurs, and only after the complete formation of $[\text{Th}_2\text{Ci}_3]$ is an insoluble compound formed.

The behavior of the compounds obtained, and especially of $[\text{ThCi}]_n \downarrow$, toward alkali, is as follows: the addition of sodium hydroxide (even a concentrated solution) to the soluble citrate complex has no measurable effect. The addition of sodium hydroxide solution has no effect on the density of a suspension of $[\text{ThCi}]_n \downarrow$ until approximately one equivalent of hydroxide per mole of citrate or thorium has been added. An excess of sodium hydroxide dissolves the precipitate rapidly. Ammonia has the same effect as sodium hydroxide.

TABLE I

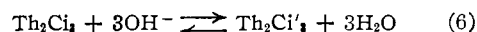
General composition: a cc. $0.1 M \text{Na}_3\text{Ci} + b$ cc. $0.1 M \text{NaOH} + (20 - a - b)$ cc. $\text{H}_2\text{O} + x$ cc. $0.1 M \text{Th}(\text{NO}_3)_4$

Na ₃ Ci cc. (1)	NaOH cc. (2)	Thorium measured, cc.		(4) - (3)	Soluble thorium, cc., calculated as				Addnl. Th for pptn. of [Th ₂ Ci ₃] + Th ₂ Ci ₃ ' cc. (10)
		At begin of pre-cip. (3)	At end of pre-cip. (4)		Th-Ci' + (5)	Th-Ci ₂ ' (6)	Th-Ci ₂ ' (7)	Th-Ci ₂ ' (8)	
3	3	2.25	3.25	1.0	3.0	3.0	2.0	1.5	1.0
6	3	4.2	6.0	1.8	5.0	4.5	4.0	3.0	2.0
5	5	3.75	5.5	1.75	5.0	5.0	3.3	2.5	1.7
5	4	3.6	5.2	1.6	4.7	4.5	3.3	2.5	1.7
5	3	3.6	5.2	1.6	4.3	4.0	3.3	2.5	1.7
4	4	3.0	4.4	1.4	4.0	4.0	2.7	2.0	1.3
4	2	2.8	4.1	1.3	3.3	3.0	2.7	2.0	1.3
5	3	2.5	4.75	2.25	4.3	4.0	3.3	2.5	1.7
6	3	2.5	5.8	3.3	5.0	4.5	4.0	3.0	2.0

A series of titrations were carried out by the addition of $\text{Th}(\text{NO}_3)_4$ to mixtures of citrate and sodium hydroxide. In all cases, a clear solution is obtained first. At a certain point, which depends on the composition, an initial precipitation occurs and the density rises until the first maximum point; it then remains constant. Stoichiometric calculations were made, on the basis of these two critical points, for the reactions which may occur in solution, and the results are compiled in Table I. These calculations are based on the assumption that the sodium hydroxide acts on the thorium citrate complex, resulting in a soluble citrate complex compound in which the hydrogen of the hydroxy group is quantitatively neutralized (= Ci'). The free citrate remaining in solution then forms, on further addition of thorium, the regular soluble complex without the participation of sodium hydroxide. If we compare the measured values with those calculated, we find that it is the values of columns 3 and 8, and again those of columns 5 and 10, which are in closest agreement. This means that in strongly alkaline solutions either the complex $[\text{Th}_2\text{Ci}_3]$ or $[\text{Th}_2\text{Ci}_3']$ is present. The assumption that a soluble compound $[\text{ThCi}']$ exists in solution is not confirmed by the results of our calculations. The final precipitate (compare columns 5 and 10) is the thorium salt $[\text{ThCi}]_n$ (= $\text{Th}[\text{Th}_2\text{Ci}_3]$ or $\text{Th}[\text{Th}_2\text{Ci}_3']$). Only in the presence of 50% alcohol is the complex $[\text{ThCi}_2]$ or $[\text{ThCi}_2']$ detected, which, on the further addition of thorium, results in an insoluble salt $[\text{ThCi}]_n$. Although these titrations do not prove that the citrate is transformed by neutralization to Ci' in the

presence of sodium hydroxide, the $p\text{H}$ curve (see Fig. 5, curve 1) shows that such a neutralization does indeed occur in these solutions.

$p\text{H}$ Measurements.—On the gradual addition of sodium citrate to the thorium solution the $p\text{H}$ decreases until a complete precipitation of the $[\text{ThCi}]_n$ is obtained at $p\text{H} \sim 1.8$. On continued addition of citrate, the salt $[\text{ThCi}]_n$ dissolves, giving $[\text{Th}_2\text{Ci}_3]$, and the $p\text{H}$ rises somewhat ($p\text{H} \sim 3$). Excess sodium citrate acts as a buffer and the $p\text{H}$ rises slowly. Figure 5 shows $p\text{H}$ titrations carried out in the presence of sodium hydroxide. Curve 1 shows a titration of a solution containing the complex $[\text{Th}_2\text{Ci}_3]$ (and free sodium citrate). This curve, recalling a regular curve of neutralization of an acid, is very instructive. The inflection occurs at $p\text{H} \sim 8$. For complete neutralization 1.5 equivalents of sodium hydroxide per atom of thorium, or 3 equivalents per 2 atoms of thorium are required. The reaction occurring in solution may be written as



The complex $[\text{Th}_2\text{Ci}_3]$ behaves as an acid (e.g., acetic acid) with a $pK = 4.6$. The result obtained is of special interest in that the solution contains thorium and citrate in the proportion 1[Th]:2[Ci], while the complex obtained has a composition 2[Th]:3[Ci] (= $[\text{Th}_2\text{Ci}_3']$). During the neutralization of $[\text{Th}_2\text{Ci}_3]$ to $[\text{Th}_2\text{Ci}_3']$, the $p\text{H}$ of the solution increases from 4 to 8.

Curve 2 is a plot of results of a $p\text{H}$ titration of a water suspension of $[\text{ThCi}]_n$ with sodium hydroxide solution. The titration of the heterogeneous system proceeds slowly, and the $p\text{H}$ values for the latter part of the curve are obtained only after waiting a considerable time, while the precipitate is dissolving, for the readings to become constant. The curve shows two $p\text{H}$ inflection points. The first point occurs at $p\text{H} \geq 4.0$, after one equivalent of sodium hydroxide has been added per mole of thorium citrate. On further addition of hydroxide, the suspension gradually redissolves, and a clear solution is obtained after approximately a second equivalent of hydroxide has been added. The second $p\text{H}$ inflection then occurs at $p\text{H} \sim 7.5$. Although the results of curve 2 are more complicated, it is interesting to note that the higher $p\text{H}$ inflection points in both curves lie at nearly the same $p\text{H}$ (7.5–8).

Conductometric Measurements.—Figure 6 shows the results of the reactions between thorium and citrate (which as far as we know have not been investigated conductometrically). The results obtained are interesting, as they correspond in general to the heterometric results. The curves show two critical points, one maximum and one minimum, at approximately the same molar ratios as in the heterometric curves. In both titrations, maximum conductivity is obtained at the point of complete formation of $[\text{ThCi}]_n$, corresponding to the point of lowest $p\text{H}$ in such titrations. Similar titrations were made in 50% alcoholic solutions. The breaks were obtained at the same molar ratios as in Fig. 6.

On the basis of the experimental results obtained, the following may be said about the structure of the

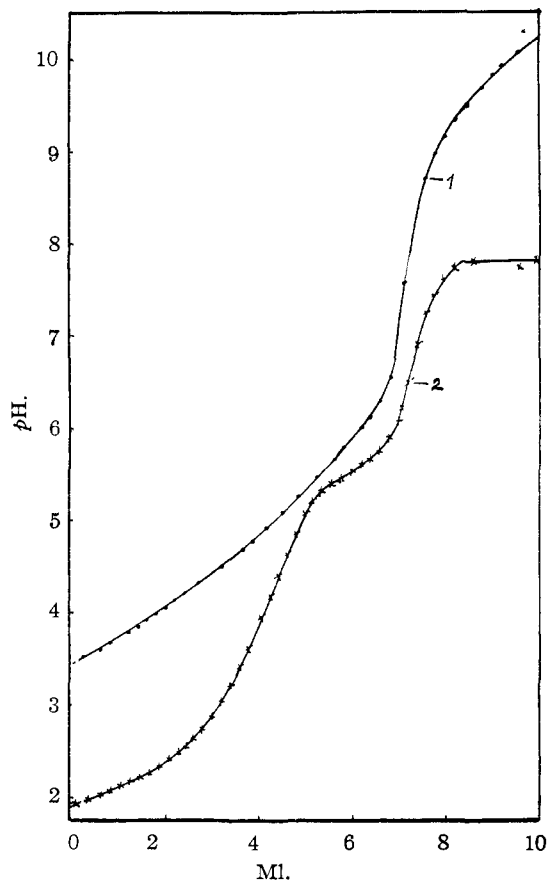


Fig. 5.—(1) 5 cc. 0.1 M Th(NO₃)₄ + 10 cc. H₂O + 5 cc. 0.2 M Na₃Ci + x cc. 0.1 M NaOH; (2) 4 cc. 0.1 M Th(NO₃)₄ + 4 cc. 0.1 M Na₃Ci + 12 cc. H₂O + x cc. 0.1 M NaOH.

different compounds which were established in this work. The insoluble [ThCi]_n is most probably a neutral salt of the composition Th[Th₂Ci₃]. A similar salt is obtained with cerous (see subsequent reports). Therefore, the hypothesis is made that thorium acts as the trivalent [ThOH]³⁺ ion, and that a complex compound is obtained which may be formulated as

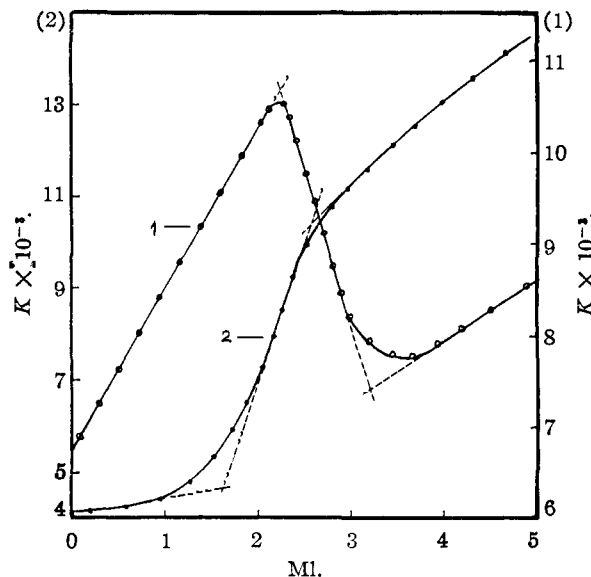
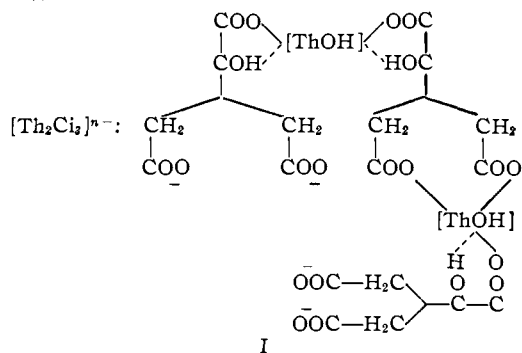
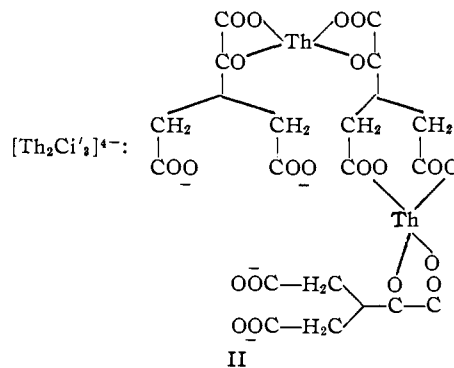


Fig. 6.—(1) 5 cc. 0.1 M Th(NO₃)₄ + 45 cc. H₂O + x cc. 0.2 M Na₃Ci; (2) 5 cc. 0.1 M Na₃Ci + 45 cc. H₂O + x cc. 0.2 M Th(NO₃)₄.

The insoluble [ThCi]_n could then be formulated as [ThOH] [(ThOH)₂Ci₃], and the anion complex as [(ThOH)₂Ci₃]³⁻. Formula I even takes into consideration the fact that Th₂Ci₃ is composed of [ThCi₂] + [ThCi], according to reaction 3.

As to the complex which exists at high pH's, we must conclude on the basis of our previous investigations (for example, Pb²⁺, Ce³⁺, etc.) that [Th₂Ci₃]⁴⁻ is a very stable covalent complex (it is not decomposed even by a considerable excess of sodium hydroxide), which may be formulated as



An equilibrium exists between the above forms, according to equation 6. Nothing certain can be said as to the extent to which the free carboxylic groups (= CH₂COO⁻) are bound to the central thorium atom.

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