

cyclic acids, the wavelength of maximum absorption and molar extinction coefficient increase in presence of $-\text{SO}_3\text{H}$ and $-\text{CH}_3$ groups. This possibility together with lower water solubility and stronger beryllium affinity for oCA, pCA and mCA in comparison to SA makes the cresotic acids as potentially better extracting agents for Be(II) than SA.

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Some Mixed Ligand Complexes of Th(IV)*

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The stability constants of mixed ligand chelates of Th(IV) with EDTA and DTPA as primary ligands and kojic acid, Tiron, oxine and N-phenyl-N-benzoylhydroxylamine as secondary ligands have been determined. The study has revealed a coordination number of ten for Th^{4+} ion.

THOUGH the existence of mixed ligand complexes has been known for a long time, the detailed investigation of their equilibria has received attention only recently^{1,2}. In our previous communications^{3,4}

we have reported stability constant data on some mixed ligand complexes of thorium and lanthanide ions. Some further work on some more mixed ligand chelates of Th(IV) is described in this note. The primary ligands chosen were EDTA (hexadentate), diethylenetriaminepentaacetic acid (DTPA, octadentate) and triethylenetetraaminehexaacetic acid (TTHA, decadentate). The secondary ligands used were kojic acid, Tiron, oxine and N-phenyl-N-benzoylhydroxylamine (BPHA).

Thorium nitrate (Indian Rare Earths Ltd. purity >99.9%) was dissolved in 0.1M nitric acid and standardized by titration with EDTA using xylenol orange as indicator. BPHA (Koch-Light) was recrystallized from hot ethanol-water and vacuum-dried. Kojic acid (BDH, biochemical grade) was recrystallized from ethanol using animal charcoal to give buff-coloured needles. Tiron (Fluka), oxine (E. Merck GR), EDTA disodium salt (E. Merck GR), DTPA free acid (K & K Laboratories) and TTHA (Sigma Chemical Co., USA) were used as such. The primary ligands were standardized against zinc solution prepared from zinc granules (analar grade).

The experimental set-up and the method of calculation of the constants has been described previously³. Titrations for kojic acid and Tiron were carried out in an aqueous medium while those for oxine and BPHA in 20% ethanol-water medium to ensure solubility of these ligands.

Titrations were performed at 28°C and the ionic strength maintained at 0.10M by addition of KNO_3 . pH measurements were made with a Beckman model G pH meter using Beckman 40495 (0-14 pH) or a Toshniwal GA 110 (0-14 pH) glass electrode.

Titration curves for ThY-kojic acid system (where Y is the anion of the primary ligand) are depicted in Fig. 1 while the formation constants for the addition reactions of the secondary ligands are summarized in Table 1.

It is now generally recognized that elements in the fifth and subsequent periods can extend their coordination to accommodate more than six ligand atoms. Thorium ion after combination with a hexadentate ligand like EDTA is still coordinately unsaturated and can further combine with suitable secondary ligands. The present study reveals that the primary Th-EDTA complex is capable of adding on two molecules of bidentate ligands. The primary complex with the octadentate ligand (DTPA) could, however, combine only with one molecule of the

TABLE 1 — STABILITY CONSTANTS

Reagent	EDTA						DTPA log K	
	log K_1^H	log K_2^H	log K_1	log K_2	log β_2	2 log α^* (pH=5.5)		log β_2 (cond.)
Oxine	10.16	4.98	8.12	5.56	13.68	9.50	4.18	5.76
BPHA	8.88	—	7.04	4.80	11.84	6.76	5.08	5.10
Tiron	12.60†	7.60(3)	13.20(3)	7.70(3)	20.90	18.40	2.50	10.76
Kojic acid	7.81	—	6.95	5.04	11.99	4.62	7.37	4.73

$$*\alpha = 1 + K_1^H [H^+] + K_1^H K_2^H [H^+]^2$$

†Literature value.

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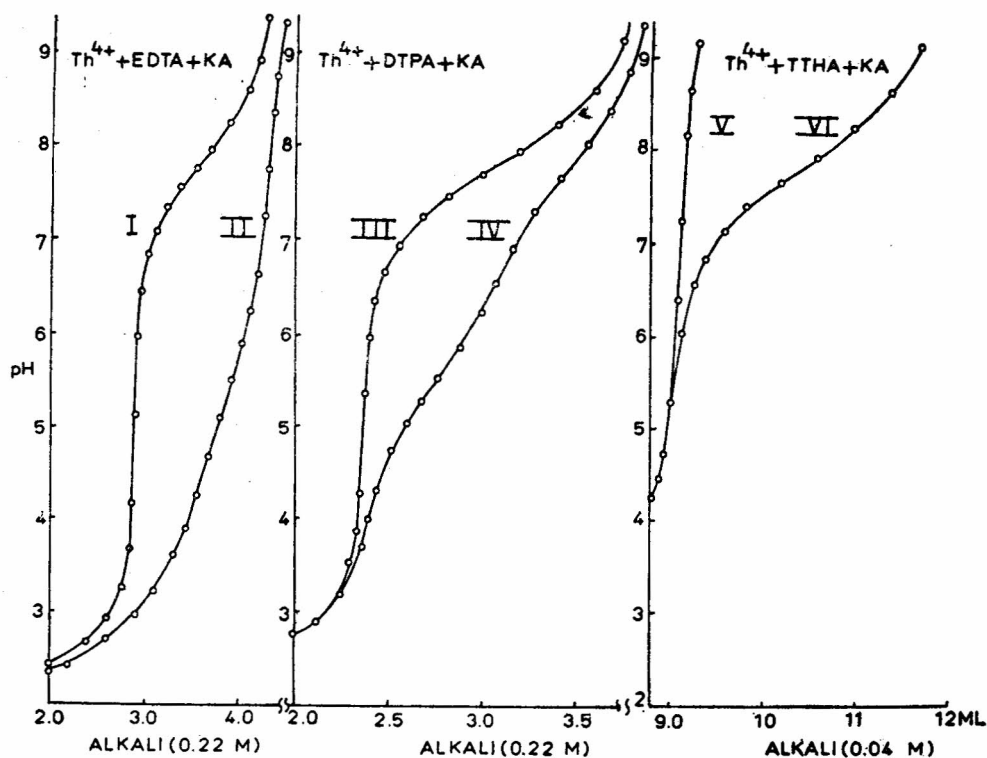
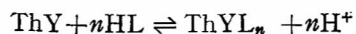


Fig. 1—Titration curves for ThY-kojic acid system (Y=anion of the primary ligand) [(I), equivalent free acid+kojic acid; (II), Th⁴⁺ (5 ml of 0.03M)+EDTA (disodium salt)+kojic acid (1:1:2); (III), equivalent free acid+kojic acid; (IV), Th⁴⁺ (5 ml of 0.03M)+DTPA (trisodium salt)+kojic acid (1:1:2); (V), Th⁴⁺ (5 ml of 0.012M)+TTHA (1:1); (VI), same as in (V)+kojic acid (1:1:2); eq. free acid = free acid in Th⁴⁺ solution+acid liberated during complex formation with EDTA]

bidentate ligand thus indicating a tenfold coordination for the Th⁴⁺ ion. This finding has been further confirmed by lack of residual affinity for secondary ligands when the decadentate TTHA acted as the primary ligand.

The reaction leading to the formation of mixed ligand chelates can be one of addition or partial substitution, i.e. the secondary ligand displacing some of the groups of the multidentate primary ligand and thus maintaining the initial coordination number. In such a situation, the carboxyl groups set free, because of their high proton affinity, would immediately take up protons from the system and disturb the proton balance as represented by the reaction



where Y and L are the anions of the primary and secondary ligands respectively. The sharp and appropriate inflexions in the titration curves in the presence of secondary ligands, however, show complete titration of equivalent protons as depicted in the above reaction, thus confirming that the mixed ligand chelates are formed by reactions of the additive type and that the Th⁴⁺ ion is capable of extending its coordination (up to ten) to accommodate secondary ligand atoms.

In the Th⁴⁺-EDTA-Tiron system reported earlier, the mixed ligand chelate was found to reach a composition of 1:1:2. For the Th⁴⁺-DTPA-Tiron system, the present study has revealed attachment of only one Tiron molecule with primary Th⁴⁺-DTPA complex. Further, the stabilities of mixed ligand chelates is greater when EDTA is the primary

ligand. This is expected since, in this case, the secondary ligand would be approaching a neutral primary complex in contrast to a uninegatively charged Th-DTPA ion.

Among the secondary ligands Tiron, by virtue of two phenolate oxygens suitably positioned to give a five-membered chelate ring structure, shows the highest stability. During the sequential titration of thorium and rare earths with EDTA using xylol orange as indicator, it was found that after the initial titration of Th⁴⁺ at pH \approx 2.5, subsequent raising of pH to 5.5 leads to a pink colouration due to the formation of a mixed chelate Th-EDTA-XO making the subsequent titration of rare earth impossible. Addition of kojic acid, in spite of its intrinsic lower affinity compared to Tiron, was found to be useful in preventing the formation of the pink-coloured mixed chelate. The use of kojic acid and EDTA in a sequential determination of thorium and rare earths has been described separately⁵. The successful use of kojic acid is due to its higher conditional stability constant⁶ under the conditions of the experiment (pH = 5.5).

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