

Mixed Ligand Chelates of Th(IV) with EDTA & CDTA as Primary Ligands & Glycine, *dl*- α -Alanine & Phenylalanine as Secondary Ligands

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pH-titrations of the reaction mixtures containing thorium nitrate, EDTA or CDTA and an amino acid (glycine, *-dl*-alanine or phenylalanine), in equimolar concentrations, indicate the formation of 1:1:1 mixed ligand derivatives. Their formation constants, $\log K_{MAB}^{MA}$, at $30 \pm 1^\circ$ and $\mu = 0.1M$ (KNO_3) have been calculated. The order of stabilities in terms of primary ligand has been found to be EDTA > CDTA and in terms of secondary ligand as Gly > α -Aln > PhAln.

MARTELL and coworkers¹ have studied the interaction of Th(IV) ion with EDTA and cyclohexane-1,2-diamine tetraacetic acid (CDTA) potentiometrically and showed that both the hexadentate chelating agents occupy six of the eight coordination sites of the metal ion. Later on, these workers as well as others^{2,3} prepared ternary complexes by reacting the above chelates with bidentate ligands. It was therefore, considered worthwhile to investigate potentiometrically mixed ligand chelates of Th(IV) with EDTA or CDTA as primary ligands and amino acids like glycine, *dl*- α -alanine or phenylalanine as secondary ligands. In an earlier communication⁴ from our laboratories, similar studies on the system Th(IV)-CDTA-hydroxy acid, have been reported.

Materials and Methods

Stock solution of thorium nitrate was prepared and standardized as described previously⁴. Solutions of the disodium salt of EDTA, dipotassium salt of CDTA, glycine (purified), *dl*- α -alanine (α (Aln) and phenylalanine (Ph-Aln) were prepared in distilled water. All the acid solutions were standardized by potentiometric titrations against 0.1M KOH. The ionic strength of all the reaction mixtures was kept constant ($\mu = 0.1M$) using 0.1M potassium nitrate and low concentrations ($5 \times 10^{-3}M$) of the ligands and metal ions.

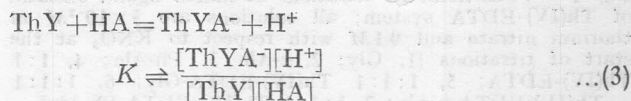
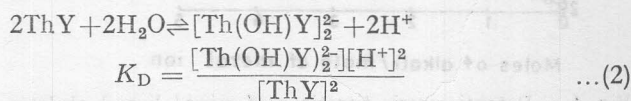
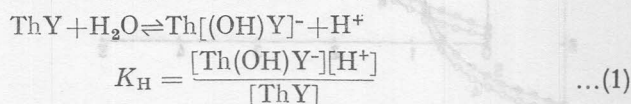
Results and Discussion

Martell *et al.*¹ reported the occurrence of a buffer region at $pH > 5.5$ in the potentiometric titration curve of 1:1 Th(IV)-EDTA system against alkali. This was ascribed to the hydrolysis of normal 1:1 Th(IV)-EDTA chelate, followed by the formation of a binuclear diolated derivative. The values of hydrolysis and dimerization constants calculated using the method employed by earlier workers¹ were found to be 11.0×10^{-8} and 1.0×10^{-10} respectively. The hydrolysis and dimerization constants of Th(IV)-CDTA system at $30 \pm 1^\circ$ have been reported earlier⁴.

The dissociation constants of amino acids were taken from the literature⁵. The mixed ligand

formation constants ($\log K_{MAB}^{MA}$) were calculated by the method of Thompson and Loraas⁶.

The solution equilibria in the upper buffer region of the potentiometric curves of 1:1 Th-EDTA or CDTA are given by Eqs. (1)-(3).



where Y^{4-} represents anion of EDTA or CDTA and HA, the molecule of an amino acid. $\text{Th}(\text{OH})\text{Y}^-$ represents the monohydroxo derivative, $[\text{Th}(\text{OH})\text{Y}]_2^{2-}$ the binuclear diolated chelate and ThYA^- the mixed species.

If T_M represents the total concentration of all metal species, T_A that of various ligand species and T_{OH} that of alkali added to the solution during the titration, the following equilibria (Eqs. 4 and 5) are obtained.

$$T_M = [\text{ThY}] + [\text{Th}(\text{OH})\text{Y}^-] + 2[\text{Th}(\text{OH})\text{Y}]_2^{2-} + [\text{ThYA}^-] \quad \dots(4)$$

$$T_{OH} + [\text{H}^+] - [\text{OH}^-] = [\text{Th}(\text{OH})\text{Y}^-] + 2[\text{Th}(\text{OH})\text{Y}]_2^{2-} + [\text{ThYA}^-] \quad \dots(5)$$

Since T_{OH} represents the total concentration of the alkali added after the formation of 1:1 Th(IV)-EDTA or CDTA chelate, Eq. 5 can be rewritten in the form of Eq. 6.

$$T_M(m-2) + [\text{H}^+] - [\text{OH}^-] = [\text{Th}(\text{OH})\text{Y}^-] + 2[\text{Th}(\text{OH})\text{Y}]_2^{2-} + [\text{ThYA}^-] \quad \dots(6)$$

where m = the mole of alkali added per mole of the ligand or metal ion, and $T_A = [\text{HA}] + [\text{ThYA}^-]$. Combining Eqs. (4) and (6) we get Eq. (7).

$$[\text{ThY}] = T_M(3-m) - [\text{H}^+] + [\text{OH}^-] \quad \dots(7)$$

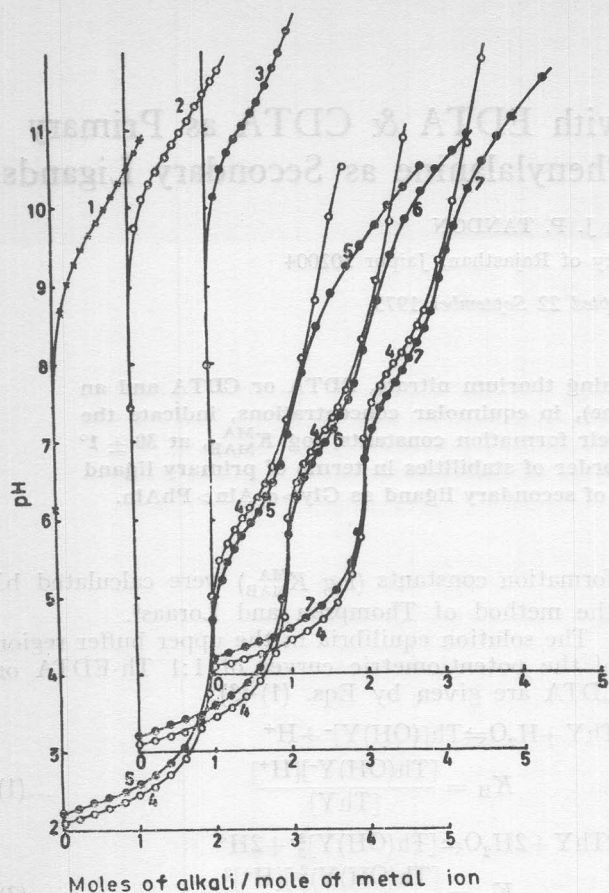


Fig. 1 — Potentiometric titrations of mixed ligand chelates of Th(IV)-EDTA system; all solutions are $5 \times 10^{-3}M$ in thorium nitrate and $0.1M$ with respect to KNO_3 at the start of titrations [1, Gly; 2, α -Aln; 3, Ph-Aln; 4, 1:1 Th(IV)-EDTA; 5, 1:1:1 Th(IV)-EDTA-Gly; 6, 1:1:1 Th(IV)-EDTA- α -Aln; 7, 1:1:1 Th(IV)-EDTA-Ph-Aln]

For the hydrolysis of 1:1 Th(IV)-EDTA chelate, the combination of Eqs. (1) and (2) with usual electroneutrality relations yields Eq. 8.

$$\frac{(T_M(m-2) + [H^+] - [OH^-])[H^+]}{[ThY]} = K_H + 2K_D \frac{[ThY]}{[H^+]} \quad \dots(8)$$

where $[ThY] = T_M(3-m) - [H^+] + [OH^-]$. $T_M(m-2)$ is the total concentration of the alkali added beyond the formation of the normal diaquo chelate, ThY. A

plot of $\frac{(T_M(m-2) + [H^+] - [OH^-])[H^+]}{[ThY]}$ against $\frac{[ThY]}{[H^+]}$ is

linear with a slope $2K_D$ and intercept K_H at $\frac{[ThY]}{[H^+]} = 0$.

After determining the concentration of ThY from Eq. (7), and since $T_M = T_A$, the equilibrium concentrations of other species involved in Eq. (3) can be calculated algebraically from Eqs. (4) and (6), and relation $T_A = [HA] + [ThYA^-]$ and the value of equilibrium constant K of the mixed system.

The formation constant K_{MAB}^{MA} of the 1:1:1 chelate

may be defined as:

$$K_{MAB}^{MA} = \frac{[ThYA^-]}{[ThY][A^-]} \quad \dots(9)$$

If K_1 represents the dissociation constant of amino acid, it may be shown that:

$$K_{MAB}^{MA} = \frac{K}{K_1} \quad \dots(10)$$

where K represents the equilibrium constant defined by Eq. (3).

1:1:1 Th(IV)-EDTA-amino acid systems — The pH-metric titrations of Gly, α -Aln and Ph-Aln exhibit very poor inflexions (Fig. 1) due to the formation of the zwitter ion and migration of the proton of the carboxylic group to the nitrogen atom of the amino group, which ionizes slowly at higher pH. $H_3N^+ - CH_2COO^- + OH^- \rightleftharpoons H_2N - CH_2COO^- + H_2O$ ($0 < m < 1$)

The titration of the solutions containing equimolar proportions of thorium nitrate and disodium salt of EDTA gives inflexions at $m = 2$ and $m = 3$, where m is the volume of alkali added. The first inflexion corresponds to the neutralization of the two protons from EDTA molecule giving the normal hydrated 1:1 Th(IV)-EDTA chelate. Occurrence of a second buffer region has been reported to be due to the hydrolysis and dimerization of 1:1 chelate.

In the potentiometric titrations of 1:1:1 Th(IV)-EDTA-Gly, α -Aln and -Ph-Aln systems two inflexions at $m = 2$ and $m = 3$ are observed. In the lower buffer region, 1:1 Th(IV)-EDTA complex is completely formed prior to the addition of the secondary ligands. Further addition of alkali neutralizes the proton liberated from the amino acid resulting in an inflexion at $m = 3$. A lower buffer region between $m = 2$ and $m = 3$ in these cases compared with the curve representing the titration of Th(IV) + disodium salt of EDTA, clearly indicates the formation of 1:1:1 ternary complex.

1:1:1 Th(IV)-CDTA-amino acid systems — Potentiometric titration curves of the systems containing equimolar ratios of Th(IV), CDTA and one of the amino acids were found to be almost similar to the curves representing analogous EDTA systems. However, in these cases the upper buffer region, where mixed derivative is being formed, occurs at a higher pH.

A comparison of the formation constants, $\log K_{MAB}^{MA}$, listed in Table 1 indicates that the order of stability of the ternary complexes in terms of the

TABLE 1 — FORMATION CONSTANTS OF THE MIXED LIGAND CHELATES

[Temp. = $30 \pm 1^\circ$, $\mu = 0.1M$ (KNO_3)]

System	$\log K_{MAB}^{MA}$
Th(IV)-EDTA-Gly	6.06 ± 0.05
Th(IV)-EDTA- α -Aln	5.90 ± 0.01
Th(IV)-EDTA-PhAln	5.56 ± 0.04
Th(IV)-CDTA-Gly	5.16 ± 0.02
Th(IV)-CDTA- α -Aln	5.07 ± 0.04
Th(IV)-CDTA-Ph-Aln	4.81 ± 0.04

primary ligand is EDTA > CDTA and in terms of the secondary ligand is Gly > α -Aln > Ph-Aln. The higher stabilities of the mixed ligand chelates of EDTA over the analogous CDTA derivatives may be explained on the basis of the lower stabilities of the binary chelates of the former¹.

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Some substituted benzene-sulphonic acids such as methanedic acid, ethanedic acid, 2-amino-1,3-benzenedic acid and 3-amino-1,3-benzenedic acid have been used for the spectrophotometric determination of Os(VI) and Os(VIII). Out of these, only ethanedic acid and 2-amino-1,3-benzenedic acid are suitable for the spectrophotometric determination of Os(VI) and Os(VIII). Ethanedic acid is most suitable as in this case complete development of colour is observed within 10 to 15 min and in the acidic range 2.5 to 3.5. A large number of cations have been found to interfere. However, the interference of these ions can be avoided by prior distribution of osmium as OsO₄.

In our earlier communications^{2,3} we have reported some interesting effects that are produced due to introduction of non-coordinating substituents on organic reagents in addition to the chelating groups and successfully used these for spectrophotometric determination of some metal ions.

Neither benzene-sulphonic acid nor salicylic acid give colour reaction with Os(VIII). However, the aromatic compounds containing both amino (-NH₂) and sulphinate (-SO₂H) groups in the benzene ring give colour reactions with Os(VIII). The use of salicylanilic acid (2-aminobenzenesulphonic acid) as a spectrophotometric reagent for the determination of Os(VI) and Os(VIII) has been investigated earlier by Majumdar and Sen Gupta.⁴

In continuation of these studies, the efficacy of using methanedic acid (2-aminobenzenesulphonic acid), ethanedic acid (2-amino-1,3-benzenedic acid), 2-amino-1,3-benzenedic acid for the spectrophotometric determination of Os(VI) and Os(VIII) has been investigated. As a natural curiosity, this study is expected to throw light on the effect produced by changing the position of coordinating group, viz. amino group and/or introducing a non-coordinating methyl group in salicylanilic acid.

Since Os(VI) did not react with these reagents, studies were carried out for the determination of Os(VI) and Os(VIII).

Methanedic acid gave a red colour with both Os(VI) and Os(VIII), the λ_{max} being at 490 nm. Although an intense colour developed immediately, its intensity went on increasing with time even after 24 hr. On prolonged standing the colour changed to reddish black with a shift in λ_{max} . The conditional variations such as those of reagent concentration, acidity and temperature showed no positive effect on the above colour reaction. This methanedic acid proved to be a total failure for the spectrophotometric determination of osmium. Ethanedic acid on the other hand was an effective reagent for both