

## Mixed Ligand Derivatives of Th-EDTA Chelate with some Monhydroxy – Mono-carboxylic Acids

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With 3 Figures

### Abstract

Interaction of the 1:1 Th-EDTA diaquo chelate with lactic, mandelic, o-hydroxy naphthoic acids has been investigated by the potentiometric technique. Formation of the mixed ligand chelate derivatives was indicated above pH 5.5. Equilibrium constants of the reactions have been determined.

### Introduction

In view of the strong chelation of metal ions with polyaminopoly carboxylic acids, recently<sup>1-4</sup>) there has been considerable interest in the study of the mixed ligand derivatives of the chelate compounds in which some of the coordination positions of the metal atom remain unfilled by the polydentate ligand. In the Th-EDTA chelate, for example<sup>5</sup>), the EDTA molecule satisfies six coordination positions of the metal atom. A bidentate ligand may, thus, have a tendency to bind the chelate. It was, therefore, considered of interest to study the interaction of the Th-EDTA chelate compound with some monhydroxy-mono-carboxylic acids, viz., mandelic, lactic and o-hydroxynaphthoic acids, which act as bidentate ligands. Attempts were also made to determine equilibrium constants of the reactions.

### Materials and Methods

Thorium nitrate,  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , disodium salt of EDTA,  $\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2 \cdot 2\text{H}_2\text{O}$  and lactic acid were of B.D.H., Analar quality. Mandelic acid was

<sup>1</sup>) L. C. THOMPSON and J. A. LORAAS, *Inorg. Chem.* **2**, 89 (1963).

<sup>2</sup>) B. I. INTORRE and A. E. MARTELL, *J. Amer. chem. Soc.* **82**, 358 (1960).

<sup>3</sup>) W. B. SCHAAP and D. L. McMASTERS, *ibid.* **83**, 4699 (1961).

<sup>4</sup>) G. H. CAREY, R. BOGUCKI and A. E. MARTELL, *Inorg. Chem.* **3**, 1288 (1964).

<sup>5</sup>) R. BOGUCKI and A. E. MARTELL, *J. Amer. chem. Soc.* **80**, 4170 (1958).

purified by recrystallisation. The *o*-hydroxynaphthoic acids were purified as described earlier<sup>6</sup>).

A stock solution of thorium nitrate was standardized gravimetrically by precipitation with ammonium hydroxide and subsequent ignition to ThO<sub>2</sub>. The acid solutions were standardized by potentiometric titrations with standard alkali solution. Standardization of KOH solution was effected by titration against a standard potassium hydrogen phthalate solution.

pH measurements were carried out with a Cambridge pH Meter, standardized against a 0.05 M solution of potassium hydrogen phthalate, at room temperature ( $25 \pm 1^\circ\text{C}$ ).

The experimental method consisted of potentiometric titrations of 1:1 reaction mixtures of thorium nitrate and disodium salt of EDTA with caustic potash (0.1 M) in the absence and presence of the hydroxy carboxylic acid used as a second ligand. The ionic strength was maintained relatively constant by using a medium containing 0.1 M KNO<sub>3</sub> and low concentrations of ligand and the metal ions.

#### Calculation of Equilibrium Constants

In view of the high stability of the Th-EDTA chelate ( $\log k_{\text{Th-EDTA}} = 23.2$ )<sup>7</sup>), it was assumed that in the reaction mixture of equimolar concentration of thorium nitrate and EDTA, all the metal ions were completely transformed into the 1:1 chelate. Analysis of the potentiometric titration data indicated formation of the mixed ligand chelates in the upper buffer region of the curves (Figs. 1 and 2).

Occurrence of a buffer region above pH 5.5, in potentiometric titration curve of 1:1 thorium nitrate — EDTA system with KOH, has been reported by BOGUCKI, et al.<sup>5</sup>), to be due to the hydrolysis of the Th-EDTA chelate followed by a dimerization reaction. Hydrolysis and dimerization constants of these reactions were reported to be  $9.12 \times 10^{-8}$  and  $1.51 \times 10^{-10}$  respectively. For correcting concentrations of the mixed ligand chelates, calculated at various points of the titration curves, the above constants were determined (Fig. 3) by the method of the earlier workers<sup>5</sup>), under the experimental conditions used in the present investigation. The values of these constants were found to be  $8.50 \times 10^{-8}$  and  $1.09 \times 10^{-10}$  respectively, which are in close agreement with reported values<sup>5</sup>).

<sup>6</sup>) R. P. AGARWAL and R. C. MEHROTRA, *Ind. J. Chem.* **2**, 138 (1964).

<sup>7</sup>) G. SCHWARZENBACH, R. GUT and G. ANDEREGG, *Helv. chim. Acta* **37**, 937 (1954).

The solution equilibria in the upper buffer region of the titration curves may be defined by the equations:

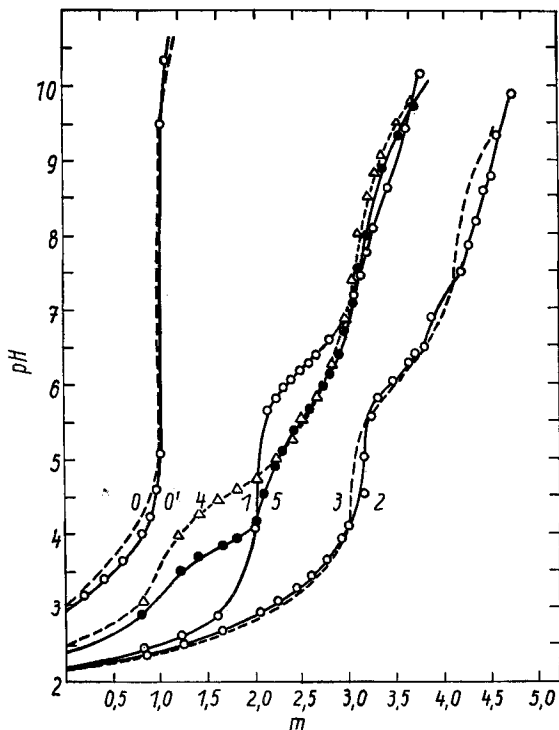
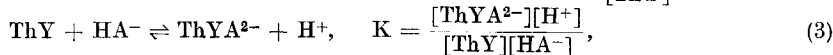
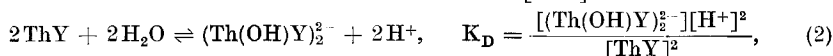
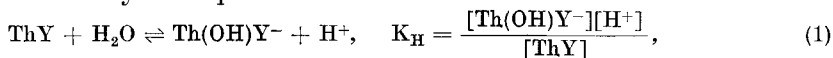


Fig. 1. Potentiometric titrations of 1:1 Th-EDTA systems ( $5 \cdot 10^{-3}$  M) in presence and absence of the hydroxycarboxylic acids in aqueous medium: 1, 1:1 Th-EDTA; 2, 1:1:1 Th-EDTA-Lactic acid; 3, 1:1:1 Th-EDTA-Mandelic acid; 4, 1:1:1 Th-EDTA-1-hydroxy-2-naphthoate (potassium salt); 5, Th-EDTA-2-hydroxy-3-naphthoate potassium salt). Curves O and O' represent potentiometric titrations of lactic and mandelic acid solutions ( $5 \cdot 10^{-3}$  M) with KOH.  $m$  = moles of KOH added per mole of the ligand.  $\mu = 0$ . 1M ( $\text{KNO}_3$ ).

where  $\text{Y}^{4-}$  represents ethylenediaminetetra acetate anion and  $\text{HA}^-$  represents anion of the dibasic acid  $\text{H}_2\text{A}$ , used as a bidentate ligand. The strongly acidic carboxylic hydrogen of  $\text{H}_2\text{A}$  was found to be neutralized before the occurrence of the upper buffer region in the titration curves. In writing formulae of the chelate species, water molecules of hydration were omitted for the sake of simplicity.

If  $T_M$  represents total concentration of all the metal species present in a 1:1:1 Th-EDTA- $\text{H}_2\text{A}$  system and if "m" be the moles of base added per mole of the metal salts, then

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

$$(m - 3) T_M + [\text{H}^+] - [\text{OH}^-] = [\text{Th(OH)Y}^-] + 2[(\text{Th(OH)Y})_2^{2-}] + [\text{ThYA}^{2-}], \quad (5)$$

$$T_M = [\text{HA}^-] + [\text{ThYA}^{2-}]. \quad (6)$$

Fig. 2. Potentiometric titrations of 1:1 Th-EDTA systems ( $5 \cdot 10^{-3}$  M) in presence and absence of the hydroxy naphthoic acids in 50% alcoholic medium: 1, 1:1 Th-EDTA; 2, 1:1:1 Th-EDTA-1-hydroxy-2-naphthoic acid; 3, 1:1:1 Th-EDTA-2-hydroxy-3-naphthoic acid. Curves O and O' represent potentiometric titrations of 1-hydroxy-2-naphthonic and 2-hydroxy-3-naphthonic acid solutions ( $5 \cdot 10^{-3}$  M) with KOH.  $m$  = moles of base added per mole of the ligand.  $\mu$  = O. IM ( $\text{KNO}_3$ ).

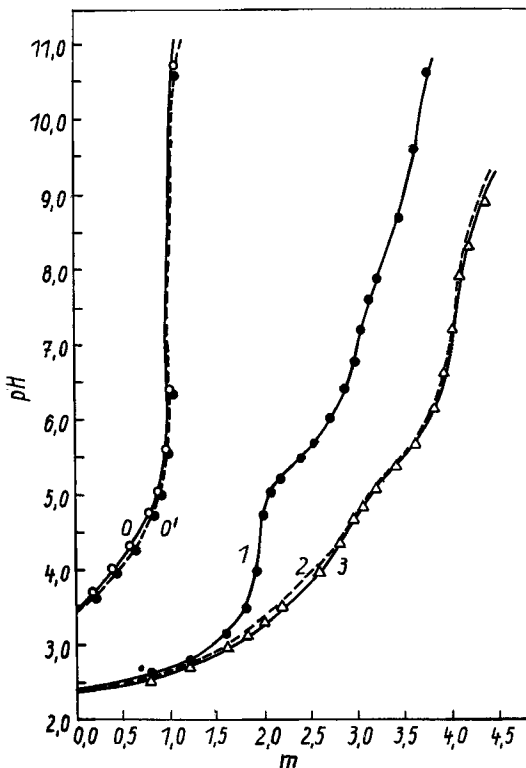
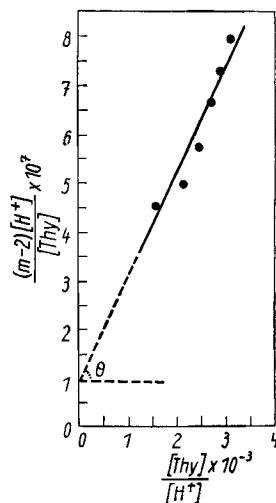


Fig. 3. Graphical demonstration of hydrolysis and dimerization of 1:1 Th-EDTA chelate, Thy.  $m$  = moles of KOH added per mole of the metal ion.

$$K_H = \frac{(m - 2)[H^+]}{[ThY]} \left( \text{at } \frac{[ThY]}{[H^+]} = 0 \right)$$

$$= 8.5 \cdot 10^{-8}$$

$$K_D = 1/2 \Theta = 1.09 \cdot 10^{-10}$$



Elimination of  $[\text{ThYA}^{2-}]$  between equations 4 and 5 gives:

$$[\text{ThY}] = (4 - m) T_M - [\text{H}^+] + [\text{OH}^-]. \quad (7)$$

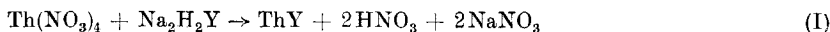
After determining the equilibrium concentration of the diaquo chelate,  $\text{ThY}$ , the concentrations  $[\text{Th}(\text{OH})\text{Y}^-]$  and  $[(\text{Th}(\text{OH})\text{Y})_2^{2-}]$  may be calculated from equations (1) and (2) respectively. The concentrations  $[\text{ThYA}^{2-}]$  and  $[\text{HA}^-]$  may then be determined easily.

## Results and Discussion

Comparison of the potentiometric titration curves (Figs. 1 and 2) of the 1:1 Th-EDTA system, in absence and presence of a bidentate ligand, showed considerable lowering of the upper buffer region of the later, indicating formation of mixed ligand chelate species in solution. A detailed analysis of the potentiometric titration data and the values of equilibrium constants for the interaction of the 1:1 Th-EDTA chelate with the bidentate ligands studies are given below:

### 1:1:1 Th-EDTA-Lactic acid and 1:1:1 Th-EDTA-Mandelic acid systems

Similar nature of the potentiometric titration curves of these systems with KOH indicated similarity of reactions in both the cases. Curve 1 (Fig. 1) for the potentiometric titration of the reaction mixture containing equimolar concentration of thorium nitrate and disodium salt ( $\text{Na}_2\text{H}_2\text{Y}$ ) of EDTA with KOH, exhibits inflexions at  $m = 2$  and  $m = 3$ . The lower buffer region in this curve can be explained<sup>8)</sup> on the basis of the neutralization of two equivalents of nitric acid liberated by the reaction:



occurrence of the upper buffer region in the curve has been reported to be due to the hydrolysis and dimerization of the diaquo chelate,  $\text{ThY}$ , as represented by equations (1) and (2) respectively.

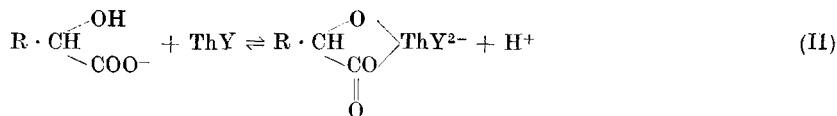
Occurrence of a sharp inflexion at one equivalent of KOH in the potentiometric titration curves of lactic and mandelic acids (curves 0 and 0') indicate that only carboxylic hydrogen of these acids dissociates in acid solutions and the hydroxy hydrogen remains unaffected under the experimental conditions.

Lower buffer region of the curve 2 (Fig. 1), for the potentiometric titration of 1:1:1 Th-EDTA-Lactic acid system, is a composite of the lower buffer region of the curve 1 for the titration of Th-EDTA system and the curve 0 for the titration of lactic acid with KOH. First inflexion point in the curve 2 thus appears at  $m = 3$ , two equivalent of alkali being con-

<sup>8)</sup> R. P. AGARWAL and R. C. MEHROTRA, (Unpublished work).

sumed in the neutralization of acid liberated by virtue of the reaction (I) and one mole used up in the neutralization of lactic acid. Lower part of the curve 3, for the 1:1:1 Th-EDTA-Mandelic acid system, may be explained in a similar manner.

Comparison of the upper buffer region of curve 1 (Fig. 1) with that of curves 2 and 3, shows a considerable lowering, above a pH of about 5.5, in the latter cases indicating the interaction of the diaquo 1:1 Th-EDTA chelate with the  $\alpha$ -hydroxy carboxylic acids. The reaction may be represented as:



where R represents a methyl or a phenyl group. By the donation of a lone pair of electrons from the hydroxy oxygen atom of the ligand, the hydrogen of the —OH group becomes more labile and acidic. Lowering in the upper buffer regions in curves 2 and 3, thus, is a direct measure of the above type of chelation. Attempts were, therefore, made to determine equilibrium constants of the reactions. These constants calculated at various points of titration curves of lactate and mandelate systems are listed in tables 1 and 2 respectively.

Table 1  
Equilibrium constants in Th-EDTA-Lactic acid system

KOH (ml.)	8.2	8.4	8.6	9.0	9.2	9.4
pH	5.79	5.91	6.02	6.25	6.39	6.53
pK	4.492	4.520	4.519	4.586	4.458	4.565

Mean value of pK = 4.523

Table 2  
Equilibrium constants in Th-EDTA-Mandelic acid system

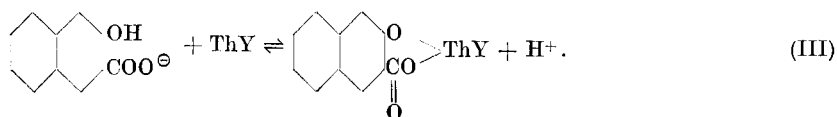
KOH (ml.)	8.2	8.4	8.6	8.8	9.0	9.2	9.4
pH	5.70	5.83	5.95	6.06	6.18	6.31	6.47
pK	4.025	4.025	4.031	3.980	3.983	3.960	3.972

Mean value of pK = 3.996

Comparison of the pK values in tables 1 and 2 and titration curves of the systems indicated that mandelic acid acts as a stronger chelating agent than lactic acid in the formation of the mixed ligand derivatives.

### Th-EDTA-1-hydroxy-2-naphthoic acid and Th-EDTA-2-hydroxy-3-naphthoic acid systems

The lower buffer region in the curves 4 and 5 (Fig. 1) for 1:1 thorium nitrate-EDTA system in the presence of one mole of potassium salts of 1-hydroxy-2-naphthoic and 2-hydroxy-3-naphthoic acids respectively, are above the first buffer region of the curve 1. This is probably due to the insolubility of the *o*-hydroxy naphthoic acids. This has been confirmed by the actual isolation of the acids from the reaction mixtures. Similar potentiometric titration (Fig. 2) in 50% alcoholic medium in which the acids were soluble, supported the above conclusion. As in lactate and mandelate systems in these cases also, lowering of the upper buffer region may be taken as a measure of the mixed ligand chelate formation. The reaction may be represented as:



Equilibrium constants for the interaction of Th-EDTA chelate with both the *o*-hydroxy-naphthoic acids were found to be almost the same. The pK values of one system are, therefore, only given (Table 3):

Table 3  
Equilibrium constants in Th-EDTA-1-Hydroxy-2-Naphthoic acid system

KOH (ml.)	6.0	6.2	6.4	6.6	6.8	7.0
pH	5.32	5.50	5.67	5.85	6.05	6.27
pK	2.972	2.969	2.964	2.925	2.965	2.911

Mean value of pK = 2.951

Comparison of the pK values listed in tables 1, 2 and 3 indicated that *o*-hydroxy naphthoic acids form stronger chelates as compared to the  $\alpha$ -hydroxy carboxylic acids.

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