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Mixed Ligand Derivatives of Th(IV)—*EDTA*, —*CDTA* or —*DTPA* Chelate with Glycollic and Malic Acids

By

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With 3 Figures

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The interaction of 1 : 1 Th(IV)—*EDTA*, —*CDTA* or —*DTPA* chelate with glycollic and malic acids has been investigated potentiometrically and the formation of 1 : 1 : 1 mixed ligand chelates inferred from the potentiometric curves. The hydrolysis and dimerization constants of the binary chelates and the equilibrium constants of the ternary derivatives have been evaluated at 30 ± 1° and 35 ± 1 °C and also the thermodynamic functions, viz. ΔF^0, ΔH and ΔS.

In earlier communications from these laboratories, potentiometric studies of Th(IV)—*CDTA* or —*DTPA* chelate with monohydroxy-monocarboxylic acids[1, 2], Th(IV)—*EDTA*, —*CDTA* or —*DTPA* chelate with diamines[3, 4] and amino acids[5, 6], Th(IV)—*DTPA* chelate with hydroxy acids[7, 8] and Th(IV)—*DTPA* chelate with iminodiacetic and nitrilotriacetic acids[9] have been reported and the possibility of coordination numbers 8 to 12 for the central metal ion has been indicated. During the present investigations, pH-metric studies on the interaction of Th(IV) with *EDTA*, *CDTA* or *DTPA* in presence of an equimolar proportion of a secondary ligand such as glycollic or malic acid have been carried out and the results discussed in the present paper.

Experimental

A stock solution of metal nitrate (BDH, AR) was prepared in doubly distilled water and standardized[1]. Glycollic acid, malic acid, disodium salt of *EDTA*, cyclohexane-*trans*-1,2-diaminetetraacetic acid (*CDTA*) and diethylenetriaminepentaacetic acid (*DTPA*) used were E. Merck products. *CDTA* and *DTPA* were dissolved as the di- and tri-potassium salts resp., due to their low solubility. All the acid solutions were further checked by

potentiometric titrations using 0.1*M*-KOH solution. A Cambridge pH-meter standardized against a 0.05*M*-potassium hydrogen phthalate solution, was used for carrying out the pH-titrations at 30 ± 1° and 35 ± 1 °C.

The ionic strength of all the solutions was kept constant ($\mu = 0.1$) by using 0.1*M*-KNO_3 and low concentrations ($5.0 \times 10^{-3}M$) of the ligand and metal ion. The final volume was raised to 50 ml in each titration.

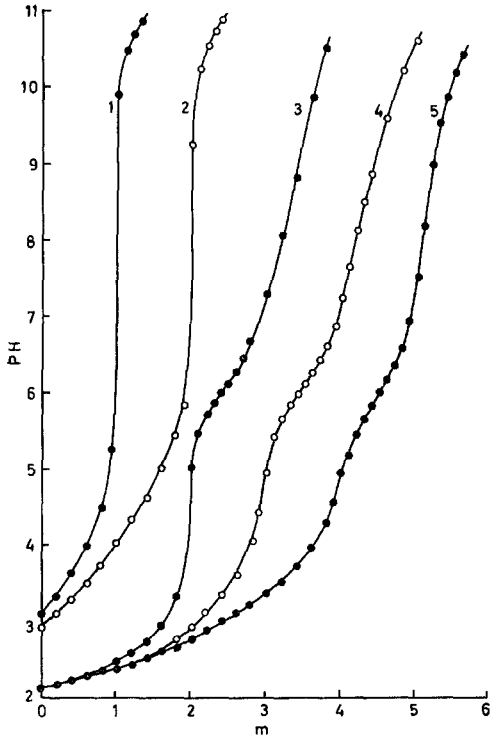


Fig. 1. Potentiometric titrations of mixed ligand system of Th(IV)—*EDTA* at 30 ± 1 °C. All solutions are $5.0 \times 10^{-3}M$ in thorium nitrate and 0.1*M* in KNO_3 at the start of titration. m = moles of alkali added per mole of the ligand or metal ion. 1. Glycollic acid; 2. Malic acid; 3. 1 : 1 Th(IV)—*EDTA*; 4. 1 : 1 : 1 Th(IV)—*EDTA*—Glycollic acid; 5. 1 : 1 : 1 Th(IV)—*EDTA*—Malic acid

The following pH-metric titrations were carried out:

System I. Th(IV)—*EDTA*—glycollic acid (Fig. 1).

1. 10 ml (0.025*M*) glycollic acid (curve 1).

2. 10 ml (0.025*M*) thorium nitrate + 10 ml (0.025*M*) *EDTA* [Th(IV)—*EDTA*; 1 : 1] (curve 3).

3. 10 ml (0.025*M*) thorium nitrate + 10 ml (0.025*M*)—*EDTA* + 10 ml (0.025*M*)—glycollic acid [Th(IV)—*EDTA*—glycollic acid; 1 : 1 : 1] (curve 4).

Similar sets of solutions were titrated for the systems Th(IV)—*EDTA*—malic acid (Fig. 1), Th(IV)—*CDTA*—glycollic or malic acid and Th(IV)—*DTPA*—glycollic or malic acid.

Results and Discussion

Martell et al.[10] reported the hydrolysis of normal 1 : 1 Th(IV)—*EDTA* or —*CDTA* chelate followed by dimerization reactions, whereas Th(IV)—*DTPA* undergoes only hydrolysis. The hydrolysis and dimeriza-

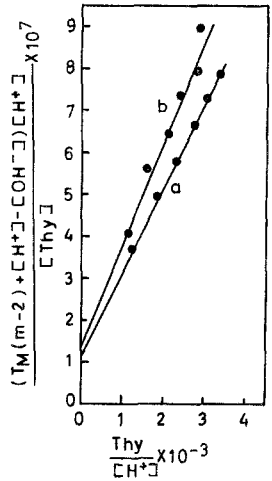


Fig. 2. The dimer formation of monohydroxo derivative of Th(IV)—*EDTA* chelate at a) 30 °C and b) 35 °C

tion constants of these reactions at 30 ± 1 °C have been reported earlier[1, 6, 7] and the dimerization constants as calculated at 35 ± 1 °C (Figs. 2 and 3) are about 1 percent less.

Methods similar to those employed by *Thompson* and *Loraas*[11] were used for the calculations of the equilibrium constants of the ternary derivatives.

The values of the thermodynamic functions viz. ΔF^0, ΔH and ΔS were calculated at 35 °C. The free energy change (ΔF^0) and the values (ΔH) are given by the following equations:

$$\Delta F^0 = -RT \ln K$$

$$\Delta H = \frac{RT_1T_2 (\ln K_2 - \ln K_1)}{T_2 - T_1}$$

In Fig. 1, curves 1 and 2 represent the potentiometric titrations of glycollic and malic acids exhibiting well defined inflexions at $m = 1$ and $m = 2$, resp. (m = moles of alkali added per mole of the ligand or metal ion). The curves indicate that only carboxylic hydrogen of these acids dissociates in acid solutions and the hydroxy hydrogen remains unaffected.

Curve 3 represents the potentiometric titration of an equimolar mixture of thorium nitrate and *EDTA*, *CDTA* or *DTPA* in Fig. 1.

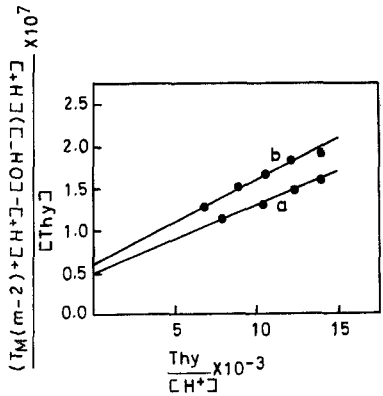


Fig. 3. The dimer formation of monohydroxo derivative of Th(IV)—*CDTA* chelate at a) 30 °C and b) 35 °C

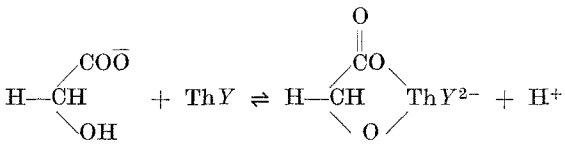
This curve gives a sharp inflexion at $m = 2$ due to the neutralization of two protons from each acid molecule and indicates the formation of a normal hydrated 1 : 1 Th(IV)—*EDTA*, —*CDTA* or —*DTPA* chelate.

Occurance of another buffer region at pH > 5.5 and pH > 6 in the case of 1 : 1 Th(IV)—*EDTA* and 1 : 1 Th(IV)—*CDTA* systems, resp., has been reported to be due to the hydrolysis of these binary complexes, which follow a binuclear olation[10].

A second buffer region observed at higher pH($\approx$ 8) in the case of 1 : 1 Th(IV)—*DTPA* system has been ascribed to the hydrolysis of the normal 1 : 1 chelate without undergoing a dimerization reaction[10].

Curve 4 represents the potentiometric titration of Th(IV)—*EDTA*—glycollic acid, Th(IV)—*CDTA*—glycollic acid and Th(IV)—*DTPA*—glycollic acid in equimolar concentrations (Fig. 1). An inflexion at $m = 3$ in each case may be ascribed to the neutralization of two protons from the hexadentate *EDTA*, *CDTA* or octadentate *DTPA* and one from the bidentate glycollic acid molecule. Comparision of the upper buffer region of

curve 4 with that of curve 3 shows a considerable lowering indicating the interaction of the 1 : 1 Th(IV)—*EDTA*, —*CDTA* or —*DTPA* chelate with glycollic acid. The reaction may be indicated as:



where Y^{4-} represents the *EDTA* or *CDTA* anion. In this reaction, the hydrogen of the hydroxy group of glycollic acid becomes more labile and acidic by the donation of a pair of electrons from the hydroxy oxygen atom and forms a mixed ligand complex. Thus the lowering in the upper buffer region of curve 4 (Fig. 1) as compared to curve 3 (Fig. 1) is a direct measure of the above type of chelation. The calculated values of equilibrium constants ($-\log K$) of these mixed systems are given in Table 1.

Table 1. *Equilibrium Constants of the Mixed Ligand Chelates.* $\mu = 0.1$ (KNO_3)

System	Equilibrium constant ($-\log K$) $t = 30 \pm 1$ °C	$t = 35 \pm 1$ °C
Th(IV)—*EDTA*—glycollic acid	4.62 ± 0.03	4.64 ± 0.02
Th(IV)—*EDTA*—malic acid	3.87 ± 0.06	3.90 ± 0.04
Th(IV)—*CDTA*—glycollic acid	5.70 ± 0.05	5.83 ± 0.08
Th(IV)—*CDTA*—malic acid	4.72 ± 0.04	4.79 ± 0.06
Th(IV)—*DTPA*—glycollic acid	6.42 ± 0.01	6.48 ± 0.03
Th(IV)—*DTPA*—malic acid	5.89 ± 0.02	5.93 ± 0.02

In case of the formation of 1 : 1 : 1 Th(IV)—*EDTA*, —*CDTA* or —*DTPA*—malic acid chelate, a similar explanation may be given. In these cases, as indicated by the curve 5 (Fig. 1), an inflexion appears at $m = 4$ due to the presence of two carboxylic groups in malic acid molecule. The equilibrium constants of these ternary derivatives are also listed in Table 1.

It should be noted that in case of 1 : 1 : 1 Th(IV)—*EDTA* or *CDTA*—glycollic acid mixed complex, the metal ion shows its usual 8 coordination number, whereas in 1 : 1 : 1 Th(IV)—*EDTA* or *CDTA*—malic acid system, the coordination number seems to be extended to 9. Similary, for the mixed chelate formed with octadentate *DTPA* and glycollic acid there are 10 possible coordinating centres present, while with malic acid the number may be 11. It therefore,

indicates that the Th(IV) ion may possess 10 and 11 coordination number in the resulting ternary complexes.

A comparision of equilibrium constants listed in Table 1 indicates that malic acid forms stronger chelates than glycollic acid. The order of stability of the ternary chelates in terms of primary ligand is found to be $EDTA > CDTA > DTPA$. This is in accordance with the stability of binary complexes, which follow the order:

$$DTPA > CDTA > EDTA^{10}.$$

ΔF^0, ΔH and ΔS values are reported in Table 2.

Table 2. *Values of Thermodynamic Functions for Equilibrium Reactions of Mixed Chelates and Hydrolysis and Dimerization Reactions of Binary* Th(IV) *Chelates at 35 °C*

Reaction	ΔF^0 (kcal/mole)	Δ H (kcal/mole)	Δ S (cal/mole/degree)
	Th(IV)—*EDTA*		
^{K}Th(IV)—*EDTA*—glycollic acid	+ 6.55	— 1.71	— 26.81
^{K}Th(IV)—*EDTA*—malic acid	+ 5.51	— 2.57	— 26.23
^{K}Th(OH)*Y*	+ 9.70	+ 7.70	— 6.49
^{K}[Th(OH)*Y*]$_2$	+ 14.01	+ 6.84	— 23.28
	Th(IV)—*CDTA*		
^{K}Th(IV)—*CDTA*—glycollic acid	+ 8.23	— 11.12	— 62.82
^{K}Th(IV)—*CDTA*—malic acid	+ 6.76	— 5.99	— 41.39
^{K}Th(OH)*Y*	+ 10.20	+ 6.84	— 10.91
^{K}[Th(OH)*Y*]$_2$	+ 15.95	+ 8.555	— 24.01
	Th(IV)—*DTPA*		
^{K}Th(IV)—*DTPA*—glycollic acid	+ 9.15	— 5.13	— 46.36
^{K}Th(IV)—*DTPA*—malic acid	+ 8.37	— 3.42	— 38.27
^{K}Th(OH)*Y*	+ 12.12	+ 5.13	— 22.70

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References

[1] *O. P. Pachauri* and *J. P. Tandon*, Bull. Acad. Polon. Sci. **22**, 981 (1974).
[2] *O. P. Pachauri* and *J. P. Tandon*, Mh. Chem. **107**, 83 (1976).
[3] *O. P. Pachauri* and *J. P. Tandon*, Acta. Chim. Hung. **86**, 39 (1975).
[4] *O. P. Pachauri* and *J. P. Tandon*, Indian J. Chem. (in press).

[5] *O. P. Pachauri* and *J. P. Tandon*, Bull. Acad. Polon. Sci. **24,** 7 (1976).
[6] *O. P. Pachauri* and *J. P. Tandon*, Indian J. Chem. (in press).
[7] *O. P. Pachauri* and *J. P. Tandon*, J. Inorg. Nucl. Chem. **37**, 2321 (1975).
[8] *O. P. Pachauri* and *J. P. Tandon*, Z. Naturforsch. **30 b**, 751 (1975).
[9] *O. P. Pachauri* and *J. P. Tandon*, Zh. Obsh. Khim. (in press).
[10] *R. F. Bogucki* and *A. E. Martell*, J. Amer. Chem. Soc. **80**, 4170 (1958).
[11] *L. C. Thompson* and *J. A. Loraas*, Inorg. Chem. **2**, 89 (1963).

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