

**A Potentiometric Study of Some Ligand
Amino Acid Chelates of Thorium and Zirconium: EDTA
Aspartic Acid/Glutamic Acid System**

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Summary: Mixed ligand 1:1:1 chelates of Th(IV) and Zr(IV) containing EDTA as primary ligand and amino acids such as aspartic acid and glutamic acid as secondary ligands, have been studied potentiometrically, and their stability constants $\log K_{MLA}$ are reported. The mixed complexes formed are $[Th(EDTA)A]^{2-}$ and $[Zr(EDTA)(OH)A]^{3-}$ respectively (where A = aspartate or glutamate anions) and Th(IV) forms stronger chelate than Zr(IV).

Introduction

Martell [1-2] et al. pointed out that maximum co-ordination number of Th(IV) and Zr(IV) is normally eight, whereas EDTA can occupy a most six co-ordination positions, thus leaving two positions free for hydrolysis, olation and polymerization reactions. They further observed that when the chelates of these metals, formed with such polydentate ligands as EDTA, HEDTA, CDTA, NTA etc. combine with some other secondary ligand (monodentate, bidentate etc.) to form mixed ligand chelates, they become much more resistant to hydrolysis etc. Earlier Tiwari and Srivastava [3] also studied some mixed ligand amino acid chelates of thorium. In the present study, some mixed ligand systems of thorium and zirconium have been potentiometrically investigated, and their stability constants are reported. EDTA has been used as a primary ligand, and aspartic and glutamic acids as secondary ligands.

Experimental

The solutions of the reagents were prepared in double distilled water free from carbon dioxide and standardized by appropriate standard methods. pH titration were carried out employing Leeds and Northrup pH meter, in a double walled pyrex glass vessel with a sealed on water jacket at 25°C. Purified nitrogen was bubbled through the solution mixtures to exclude carbon dioxide both before and during the titrations.

Various mixtures containing the metal ion, the primary ligand and the secondary ligand in the molar ratio of 1:1:1 (MLA) were prepared and titrated with carbonate-free standard sodium hydroxide solution. For comparison similar titrations were carried out for simple 1:1 metal chelate systems as well, involving both EDTA (L) and secondary ligands (A). All the solutions also contained a fixed amount of free acid (2 equivalents of $HClO_4$) and the

ionic strength was kept at 0.1M with sodium-perchlorate. Stability constants for the mixed chelates (K_{MLA} values) were calculated as described by Ozer [4], and Singh and Srivastava [5].

Typical pH titration curves for the mixed ligand systems [Th(IV) - EDTA - aspartic acid] and [Th(IV) - EDTA - glutamic acid] are given in figs. 1 and 2. A titration curve for a sample 1:1 Th - EDTA (ML) chelate, reveals two inflexions at $a = 6$ (pH range 4 - 6), (all titration mixtures contain 2 equivalents of free $HClO_4$, and EDTA was added in the form of H_4Y) and $a = 7$ (pH range 7 - 8) respectively. The first inflexion corresponds to the formation of the 1:1 Th-EDTA chelate, whereas between $a = 6$ to $a = 7$, one more base is added to form its hydroxochelate, which may further dimerize to form olated dinuclear [6] thorium chelate. In the MA system also the inflexion appears at $a \approx 6$, but in this system precipitation starts right from pH ≈ 4.5 onward.

The MLA titration curves for mixed ligand systems, however, do not show any inflexion at $a=6$, but an inflexion is observed at $a=7$ (pH 6) with both secondary ligands, aspartic and glutamic acids. Further beyond $a=7$, these curves also show a buffer region at lower pH values than the corresponding theoretical composite [2,4] curves, and thus the formation of the mixed chelates is inferred.

Moreover, these solutions remain clear throughout, and there is even no drifting of pH values right upto pH 10, whereas the ML titrations show a drift in pH values above pH 8, and in the MA titrations (simple 1:1 chelates with secondary ligands)

precipitation starts from pH 4.5 onwards.

Similarly pH titration curves for the mixed ligand chelate systems of [Zr(IV) - EDTA - aspartic acid] and [Zr(IV) - EDTA - glutamic acid] are given in figs. 3 and 4 respectively.

The ML titration curve for Zr - EDTA chelate shows an inflexion at $a = 4$ (pH ~ 4) and then another at $a = 5$ (pH ~ 6), which correspond respectively to the formation of normal Zr - EDTA chelate, and the hydroxochelate, which may further undergo olation and polymerization reactions. Finally above pH 9.0 precipitation of hydrous zirconium oxide occurs. In the MA titration curves, an inflexion is observed at $a = 4$, indicating the formation of the simple 1:1 chelate, but from pH 5 onwards, precipitation starts.

But the MLA titration curves for mixed ligand systems of zirconium do not show any inflexion at $a = 4$, but show well marked inflexions at $a = 6$ (pH 6). With aspartic acid however, a slight inflexion at $a = 5$ is also observed. Further, initially the solutions are slightly cloudy, but from pH 6 onwards they become perfectly clear, and remain so right upto pH 10, after which slight turbidity appears. Beyond $a = 6$, the MLA curves also show a buffer region at lower pH values than corresponding composite curves. Thus the formation of the mixed chelates is inferred.

It is concluded that ordinarily Th - EDTA chelate takes up one more base to form the hydroxochelate, which may further dimerize, but in presence of a secondary ligand (aspartic or glutamic acid) it combines with aspartate or glutamate ions to form a mixed chelate.

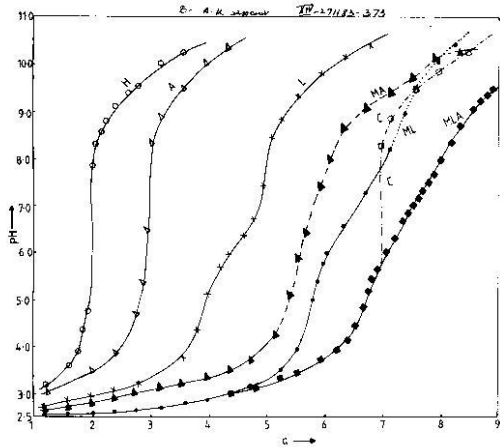


Fig. 1 Titration curves for Th(IV) (EDTA) Aspartic acid system. H-0.002M HClO₄, A-Aspartic acid, L-EDTA, C-Composite curve. MA-1:1 Molar ratio of Th(IV) to Aspartic acid. ML-1:1 Molar ratio of Th(IV) to EDTA. MLA-1:1:1 Molar ratio of Th(IV), EDTA and Aspartic acid. All ligand concentrations=0.001M. --- Indicates precipitation. Indicates drifting of pH values.

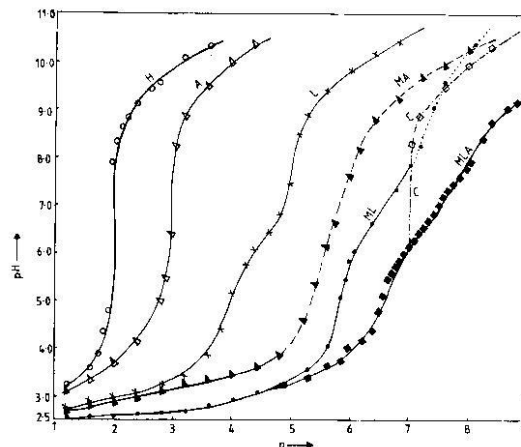


Fig. 2 Titration curves for Th(IV) (EDTA) Glutamic acid system. H-0.002M HClO₄, A-Glutamic acid, L-EDTA, C-Composite curve. MA-1:1 Molar ratio of Th(IV) to Glutamic acid. ML-1:1 Molar ratio of Th(IV) to EDTA. MLA-1:1:1 Molar ratio of Th(IV) EDTA and Glutamic acid. All ligand concentrations=0.001M. --- Indicates precipitation. Indicates drifting of pH values.

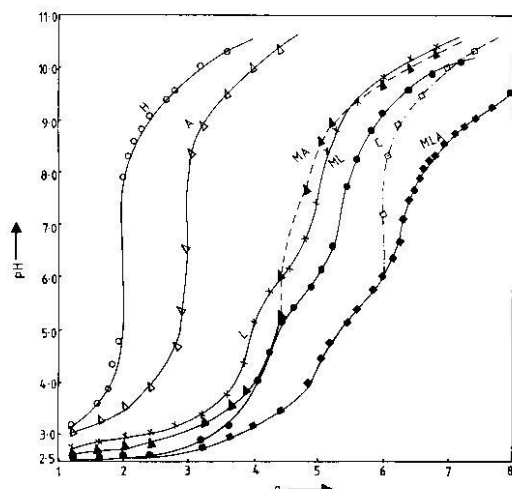


Fig. 3 Titration curves for Zr(IV) (EDTA) Aspartic acid system. H-0.002M HClO₄, A-Aspartic acid, L-EDTA. MA-1:1 Molar ratio of Zr(IV) to Aspartic acid. ML-1:1 Molar ratio of Zr(IV) to EDTA. MLA-1:1:1 Molar ratio of Zr(IV), EDTA and Aspartic acid. C-Composite curve. All ligand concentrations=0.001M. --- Indicates precipitation. Indicates drifting of pH values.

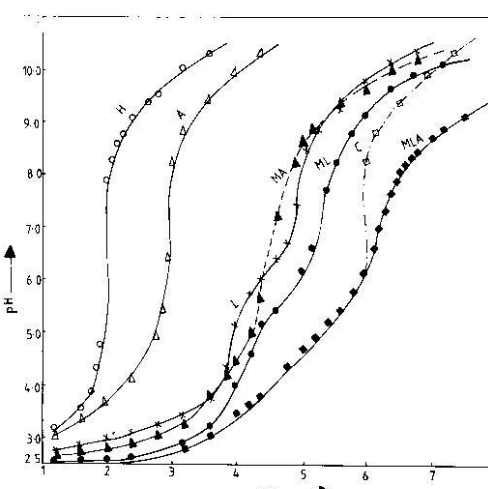
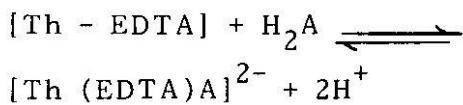
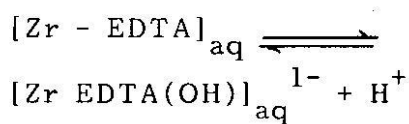


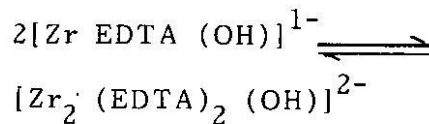
Fig. 4 Titration curves for Zr(IV) (EDTA) Glutamic acid system. H-0.002M HClO₄, A-Glutamic acid, L-EDTA. MA-1:1 Molar ratio of Zr(IV) to Glutamic acid. ML-1:1 Molar ratio of Zr(IV) to EDTA. MLA-1:1:1 Molar ratio of Zr(IV) EDTA and Glutamic acid. C-Composite curve. All ligand concentrations=0.001M. --- Indicates precipitation. Indicates drifting of pH values.



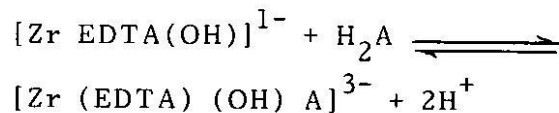
With Zr(IV), however, the normal Zr - EDTA chelate is first hydrolyzed to form the hydroxochelate, which combines with the secondary ligands to form the mixed chelates



ordinarily



but in presence of secondary ligands



The stability constants of the mixed ligand chelates (at 25°C 0.1M NaClO₄), calculated [5] in terms of the secondary ligand A, are reported as:-

Table 1: Stability constants of Mixed Ligand Amino Acid Chelates of Thorium and Zirconium

Primary Ligand	Secondary Ligand	Th(IV) $\log K_{MLA}$	Zr(IV) $\log K_{M(OH)A}$
EDTA	Aspartic acid	5.89±0.05	5.06±0.04
EDTA	Glutamic acid	5.81±0.04	4.88±0.66

References

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