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

O. P. PACHAURI & J. P. TANDON
Department of Chemistry, University of Rajasthan, Jaipur 302004

Received 7 June 1975; accepted 22 September 1975

pH-titrations of the reaction mixtures containing thorium nitrate, EDTA or CDTA and an amino acid (glycine, dl-α-alanine or phenylalanine), in equimolar concentrations, indicate the formation of 1:1:1 mixed ligand derivatives. Their formation constants, log \( K_{MAB}^{1} \) at 30 ± 1°C and \( \mu = 0.1M \) (KNO₃) 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 coworkers have studied the interaction of Th(IV) ion with EDTA and cyclohexane-1,2-diamine tetraaoetic 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 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 communication 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 previously. Solutions of the disodium salt of EDTA, dipotassium salt of CDTA, glycine (purified), dl-α-alanine (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. 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 workers were found to be 11.0 \( \times 10^{-8} \) and 1.0 \( \times 10^{-10} \) respectively. The hydrolysis and dimerization constants of Th(IV)-CDTA system at 30 ± 1°C have been reported earlier.

The dissociation constants of amino acids were taken from the literature. The mixed ligand formation constants (log \( K_{MAB}^{1} \)) were calculated by the method of Thompson and Loraas.

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).

\[
\begin{align*}
\text{ThY} + \text{H}_2\text{O} & \rightleftharpoons \text{Th}[(\text{OH})\text{Y}]^- + \text{H}^+ \\
K_H &= \frac{[\text{Th}(\text{OH})\text{Y}]^-}{[\text{ThY}]} \quad (1)
\end{align*}
\]

\[
2\text{ThY} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Th}(\text{OH})\text{Y}]_2^2^- + 2\text{H}^+ \\
K_D &= \frac{[\text{Th}(\text{OH})\text{Y}]_2^2^-}{[\text{ThY}]^2} \quad (2)
\]

\[
\text{ThY} + \text{HA} = \text{Th}\text{YA}^- + \text{H}^+ \\
K &= \frac{[\text{Th} \text{YA}^-]}{[\text{ThY}][\text{HA}]} \quad (3)
\]

where \( \text{Y}^- \) represents anion of EDTA or CDTA and HA, the molecule of an amino acid. Th(OH)Y represents the monohydroxido derivative, [Th(OH)Y]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.

\[
\begin{align*}
T_M &= [\text{ThY}] + [\text{Th}((\text{OH})\text{Y})] + 2([\text{Th}((\text{OH})\text{Y})])^2^- + [\text{Th} \text{YA}^-] \quad (4)
\end{align*}
\]

\[
\begin{align*}
T_{OH} + [\text{H}^+] - [\text{OH}^-] &= [\text{Th}((\text{OH})\text{Y})] + 2([\text{Th}((\text{OH})\text{Y})])^2^- + [\text{Th} \text{YA}^-] \quad (5)
\end{align*}
\]

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.

\[
\begin{align*}
T_M(m-2) + [\text{H}^+] - [\text{OH}^-] &= [\text{Th}((\text{OH})\text{Y})] + 2([\text{Th}((\text{OH})\text{Y})])^2^- + [\text{Th} \text{YA}^-] \quad (6)
\end{align*}
\]

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

\[
[\text{ThY}] = T_M(3-m) - [\text{H}^+] + [\text{OH}^-] \quad (7)
\]
may be defined as:

\[ K_{\text{MA}} = \frac{[\text{ThY}]}{[\text{ThY}][\text{A}]} \]  \hspace{1cm} (9)

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

\[ K'_{\text{MA}} = \frac{K}{K_1} \]  \hspace{1cm} (10)

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

1:1:1 \( \text{Th(IV)} \)-EDTA-amino acid systems — The \( \phi \)H-metric titrations of Gly, \( \alpha \)-Aln and Ph-Aln exhibit very poor inflexions (Fig. 1) due to the formation of zwitter ion and migration of the proton of the carboxylic group to the nitrogen atom of the amino group, which ionizes slowly at higher \( \phi \)H.

\[ \text{H}_3\text{N}^+-\text{CH}_2\text{COO}^- + \text{OH}^- \rightarrow \text{H}_2\text{N}^- - \text{CH}_2\text{COO}^- + \text{H}_2\text{O} \]

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 the EDTA molecule giving the normal hydrated 1:1 \( \text{Th(IV)} \)-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 \( \text{Th(IV)} \)-EDTA-Gly, \( \alpha \)-Aln and -Ph-Aln systems two inflexions at \( m = 2 \) and \( m = 3 \) are observed. In the lower buffer region, 1:1 \( \text{Th(IV)} \)-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 \( \text{Th(IV)} \) + disodium salt of EDTA, clearly indicates the formation of 1:1:1 ternary complex.

1:1:1 \( \text{Th(IV)} \)-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 \( \phi \)H.

A comparison of the formation constants, \( \log K'_{\text{MA}} \), listed in Table 1 indicates that the order of stability of the ternary complexes in terms of the

<table>
<thead>
<tr>
<th>System</th>
<th>( \log K'_{\text{MA}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Th(IV)} )-EDTA-Gly</td>
<td>6.06 ± 0.03</td>
</tr>
<tr>
<td>( \text{Th(IV)} )-EDTA-( \alpha )-Aln</td>
<td>5.90 ± 0.01</td>
</tr>
<tr>
<td>( \text{Th(IV)} )-EDTA-Ph-Aln</td>
<td>5.56 ± 0.04</td>
</tr>
<tr>
<td>( \text{Th(IV)} )-CDTA-( \alpha )-Aln</td>
<td>5.16 ± 0.02</td>
</tr>
<tr>
<td>( \text{Th(IV)} )-CDTA-Ph-Aln</td>
<td>5.07 ± 0.04</td>
</tr>
<tr>
<td>( \text{Th(IV)} )-CDTA-Ph-Aln</td>
<td>4.81 ± 0.04</td>
</tr>
</tbody>
</table>

Table 1 — FormationConstants of the Mixed Ligand Chelates
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 former.

Acknowledgement

The authors thank Prof. R. C. Mehrotra and Prof. K. C. Joshi for laboratory facilities and the authorities of N.R.E.C. College, Khurja, for encouragement.

References