Mixed Ligand Derivatives of 1:1 Th(IV)–DTPA Chelate with Some Hydroxy Acids(II)

O. P. Pachauri and J. P. Tandon

Chemical Laboratories, University of Rajasthan, Jaipur-302004, India
(Z. Naturforsch. 30b, 751–754 [1975]; received April 7/May 21, 1975)

Mixed Ligand Derivatives, Formation Constants

Studies of the interaction between 1:1 Th(IV)–DTPA chelate (where DTPA = diethyl­
etriaminopentaacetic acid) with certain bidentate ligands, such as salicylic acid (SA),
5-sulphosalicylic acid (SSA) and 8-hydroxy quinoline-5-sulphonic acid (HQSA) have been
carried out potentiometrically. The nature of the titration curves indicates that the
bidentate ligand is added stepwise to the initially formed metal diethyl­netriaminopenta­
acetate. The formation constants (log $K_{MAB}$) of the resulting 1:1:1 mixed ligand derivatives
have been determined at $30 \pm 1 \, ^\circ\mathrm{C}$ and $\mu = 0.1$ (KNO$_3$). The order of stability in terms of
the secondary ligand has been found to be SA > SSA > HQSA.

In an earlier communication$^1$ from these laboratories, equilibrium studies have been reported for
the formation of a few 1:1:1 mixed ligand complexes in Th(IV)-DTPA-hydroxy acid systems
(where hydroxy acid = Tiron, CS or PY). In these derivatives, the possibility of ten-fold coordination
for the central metal ion has been indicated. The expanded coordination number of Th(IV) has been
proposed$^2$–3 and suggested by several workers$^4$. It was, therefore, considered of interest to carry out
equilibrium studies of the metal diethylenetriamine
pentacacetate in presence of some hydroxy acids, such as SA, SSA, and HQSA with the view to see
the possibility of increased coordination number and determining the stability constants of the
resulting biligand complexes.

* Abbreviations

DTPA: Diethylenetriaminopentaacetic acid,
SA: salicylic acid,
SSA: 5-sulphosalicylic acid,
HQSA: 8-hydroxy quinoline-5-sulphonic acid,
Tiron: disodium-1,2-dihydroxybenzene-3,5-
disulphonate,
CS: chromotropic acid salt or disodium-1,8-
dihydroxynaphthalene-3,6-disulphonate,
PY: pyrocatechol.

Requests for reprints should be sent to Prof. Dr.
J. P. Tandon, Reader in Chemistry, Univ. of Raja­
stan, Jaipur, India.

Experimental

A stock solution of metal nitrate (BDH Anal­aR)
was prepared and standardized as described pre­vi­ously.$^5$ Salicylic acid, 5-sulpho salicylic acid
(BDH, AR) and 8-hydroxy quinoline-5-sulphonic acid
(prepared and recrystallized several times with
doubly distilled water) were used and their purity
was checked by potentiometric titrations. Diethyl­netriaminopentaacetic acid (DTPA) was used in
the form of its tripotassium salt and HQSA as
monopotassium salt due to their low solubility in
water. The pH-titrations were carried out at
$30 \pm 1 \, ^\circ\mathrm{C}$ with a Cambridge pH-meter, which was
standardized against 0.05 M potassium hydrogen
phthalate solution.

The following potentiometric titrations were
carried out:

1. 10 ml (0.025 M) hydroxy acid.
2. 10 ml (0.025 M) thorium nitrate + 10 ml (0.025 M)
   tripotassium salt of DTPA [Th(IV)–DTPA; 1:1].
3. 10 ml (0.025 M) thorium nitrate + 10 ml (0.025 M)
   tripotassium salt of DTPA + 10 ml (0.025 M)
   hydroxy acid [Th(IV)–DTPA-hydroxy acid;
   1:1:1].

The ionic strength (\( \mu = 0.1 \)) of all the solutions
was kept constant by using potassium nitrate and
low concentrations of ligand and the metal ion.
The final volume was raised to 50 ml in each
titrination.

Calculations

In view of the very high stability of the Th(IV)–
DTPA chelate (log$K \gg 27$ at $25 \, ^\circ\mathrm{C}$)$^9$, it is
assumed that in the reaction mixture of equimolar proportions of metal nitrate and DTPA, all the thorium ions are completely transformed into normal 1:1 chelate. However, on addition of the secondary ligand, the analysis of pH-metric titration data indicates the formation of 1:1:1 ternary derivatives in the upper buffer region of the titration curves (curves 5-7, Fig. 1).

\[
\text{Th}Y^- + \text{H}_2\text{O} \rightleftharpoons \text{Th(OH)Y}^{2-} + \text{H}^+ \\
\text{and } K_H = \frac{[\text{Th(OH)Y}^{2-}][\text{H}^+]}{[\text{ThY}^-]} \quad (1)
\]

where \( Y^{2-} \) represents diethylenetriamine pentaacetate anion, Th\( Y^- \) the normal 1:1 complex, Th\( Y^{2-} \) monohydroxo derivative; and for a mixed system:

\[
\text{Th}Y^- + \text{HA}^- \rightleftharpoons \text{ThYA}^{3-} + \text{H}^+
\]

where HA\(^{-} \) represents the anion of a dibasic acid SA. The hydrogen ion of the carboxylic group of SA was found to be displaced before the occurrence of the second buffer region in the titration curve (curve 5, Fig. 1).

The equilibrium constant \( K \) of the above reaction may be defined as:

\[
K = \frac{[\text{ThYA}^{3-}][\text{H}^+]}{[\text{ThY}^-][\text{HA}^-]} \quad (2)
\]

If \( T_M \) represents the total concentration of all the metal species, \( T_A \) that of various ligand species and \( T_{OH} \) be the concentration of the alkali added to the solution during the titration, then from the material balance the following equations can be given:

\[
T_M = [\text{ThY}^-] + [\text{Th(OH)Y}^{2-}] + [\text{ThYA}^{3-}] \quad (3)
\]

\[
T_{OH} + [\text{H}^+] - [\text{OH}^-] = [\text{Th(OH)Y}^{2-}] + [\text{ThYA}^{3-}] \quad (4)
\]

Since \( T_{OH} \) represents the total concentration of the alkali added after 1:1 complex formation, equation (4) becomes:

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

where "\( m \)" is the mole of alkali added per mole of the metal ion and

\[
T_A = [\text{HA}^-] + [\text{ThYA}^{3-}] \quad (6)
\]

The elimination of [Th\( \text{YA}^{3-} \)] and [Th\( \text{(OH)Y}^{2-} \)] between (3) and (5) gives:

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

Equating equations (3) and (6) we get:

\[
[\text{HA}^-] = [\text{ThY}^-] + [\text{Th(OH)Y}^{2-}] \quad (8)
\]

After calculating the value of [Th\( Y^- \)], the equilibrium concentration of Th\( (OH)Y^{2-} \) can be determined from equation (1) and that of Th\( \text{YA}^{3-} \)-mixed species from equation (3).
Substituting the equilibrium concentrations of different species in equation (2), the equilibrium constant $K_1$ can be determined.

For the ternary systems involving HQSA (a dibasic acid) and SSA (a tribasic acid) as the secondary ligand, the similar expressions may be given. In the former case, one hydrogen ion of HQSA has already been neutralized by using its monopotassium salt, while two hydrogen ions are displaced from SSA during the titration before the occurrence of the upper buffer region (curve 6).

**Formation constant of 1:1:1 chelates:** The formation constant $K_{MAB}$ of the 1:1:1 chelate may be defined by:

$$K_{MAB} = \frac{[ThY^3-][A^2-]}{[ThY^-][A*-]}$$

If $K_2$ be the second dissociation constant of the ligand, we may have:

$$K_{MAB} = \frac{K}{K_2}$$

where $K$ is the equilibrium constant defined by equation (2).

**Results and Discussion**

Curves 1–3 (Fig. 1) represent the potentiometric titrations of SA, SSA and HQSA, respectively. A sharp inflexion at $m = 1$ in the case of SA and HQSA corresponds to the neutralization of one proton from each acid. Due to the displacement of two hydrogen ions, a well defined inflexion at $m = 2$ is exhibited in the case of SSA.

Reaction mixture containing 1:1 molar ratio of Th(IV) to tri potassium salt of DTPA gives a steep inflexion at $m = 2$ (curve 4) due to the displacement of two hydrogen ions from DTPA indicating the formation of a normal 1:1 diaquo chelate in the lower buffer region. A second buffer region, which corresponds to the hydrolysis of the 1:1 Th(IV)-DTPA chelate is observed at higher pH between $m = 2$ and $m = 3$.

Curve 5 (Fig. 1) exhibits the titration of 1:1:1 Th(IV)-DTPA-SA system resulting in two inflexions. The first inflexion at $m = 3$ indicates the titration of two free hydrogen ions neutralized from 1:1 Th(IV)-DTPA complex and the third one from SA. In the second buffer region between $m = 2$ and $m = 3$, the proton of the phenolic group of SA molecule is displaced showing the formation of 1:1:1 mixed derivative.

Curve 6 (Fig. 1) represents the titration of 1:1:1 Th(IV)-DTPA-SSA system exhibiting inflexions at $m = 4$ and $m = 5$. The first inflexion corresponds to the simultaneous neutralization of two protons, one each from 1:1 Th(IV)-DTPA complex and SSA molecule. Between $m = 4$ and $m = 5$, the final proton from SSA molecule is displaced resulting in the formation of 1:1:1 ternary complex.

The initially lower pH in the Th(IV)-DTPA-SA (curve 5) and Th(IV)-DTPA-SSA (curve 6) systems in comparison to the corresponding theoretical composite curves (drawn by adding the horizontal distance of the secondary ligand curve to the 1:1 Th(IV)-DTPA curve at the same pH) (curves 8 and 9) is due to the ionization of one proton from SA and two protons from SSA respectively. The lower pH relative to theoretical composite curves (curves 8 and 9) between $m = 2$ and $m = 3$ in the case of SA and $m = 4$ and $m = 5$ in the case of SSA indicates that 1:1:1 mixed complexes are formed in these upper regions.

In the case of 1:1:1 Th(IV)-DTPA-HQSA (curve 7, Fig. 1), two inflexions at $m = 2$ and $m = 3$ are observed. In the lower buffer region, 1:1 Th(IV)-DTPA complex is formed prior to the addition of the secondary ligand. Further addition of alkali neutralized the proton liberated from the phenolic groups of HQSA molecule resulting in an inflexion at $m = 3$. The lowering of the buffer-region between $m = 2$ and $m = 3$ relative to the theoretical composite curve (curve 10, Fig. 1) clearly shows the formation of 1:1:1 mixed derivative.

**Table I. Formation constants of the mixed ligand chelates ($t = 30 \pm 1 ^{\circ}C, \mu = 0.1 (KNO_3)$).**

<table>
<thead>
<tr>
<th>System</th>
<th>$\log K_{MAB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(IV)-DTPA-SA</td>
<td>8.32 $\pm$ 0.06</td>
</tr>
<tr>
<td>Th(IV)-DTPA-SSA</td>
<td>6.72 $\pm$ 0.05</td>
</tr>
<tr>
<td>Th(IV)-DTPA-HQSA</td>
<td>5.09 $\pm$ 0.07</td>
</tr>
</tbody>
</table>

**Formation constants of the mixed ligand chelates:** A comparison of the formation constants given in Table I indicates that the order of stability of the ternary derivatives in terms of the secondary ligand is SA > SSA > HQSA. The presence of sulphonate...
group in SSA and HQSA molecule decreases their basicity and this results in the lowering of the stability of their ternary complexes. Steric factor may also be responsible for the poor complexing power of HQSA.

We are thankful to Prof. R. C. Mehrotra and Prof. K. C. Joshi for providing the necessary facilities. Thanks are also due to the authorities of N.R.E.C. College, Khurja (U.P.) for the necessary encouragement.

2 T. A. Bohigian (Jr.) and A. E. Martell, Inorg. Chem. 4, 1264 [1965].