

Studies on Metal Carbonate Complexes. 19. Complex Formation in the Th(IV)–H₂O– CO₂(g) System*

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Hydroxide and carbonate are two of the most important ligands in most groundwater systems. To a large extent they determine the solubility of sparingly soluble solids like metal oxides or oxide hydrates, and the speciation of the soluble metal complexes. In previous parts of this series we have described equilibria and structures of a number of metal–hydroxide–carbonate systems. This is a short communication of some recent equilibrium studies on the Th(IV)–H₂O–CO₂ system.

There is extensive literature on Th(IV) hydrolysis [1–3] (and references cited therein). Quite a few

different stoichiometries have been proposed, which seem to cluster round the polynuclear complexes: Th₂(OH)₂²⁺, Th₄(OH)₈⁸⁺, Th₆(OH)₁₄¹⁰⁺, together with the mononuclear ThOH and Th(OH)₄(aq). There is no evidence for anionic hydroxide complexes. One reason for the large number of chemical models proposed might be the experimental shortcomings due to the use of NaHCO₃ or NaOH as titrants, see for example ref. 4. Our study involves both the binary Th(IV)–H₂O and the ternary Th(IV)–H₂O–CO₂(g) system. The only previous information on Th(IV) carbonate complexes are from crystal structure determinations [5, 6], where a mononuclear complex Th(CO₃)₅⁶⁻ was identified. A complex of the same stoichiometry is formed by U(IV), see for example Part 4 of this series [7]. No quantitative information is available on the formation of Th(IV) carbonate complexes at pH < 10.

Experimental

The equilibria in the Th(IV)–H₂O–CO₂(g) system were studied in constant 3.0 M (NaClO₄ aqueous medium, at *T* = 25 °C, by means of the potentiometric technique. In each titration Th(IV) and *P*(CO₂) were kept constant. The total metal concentration range studied was Th(IV): 0.54(0.24 at

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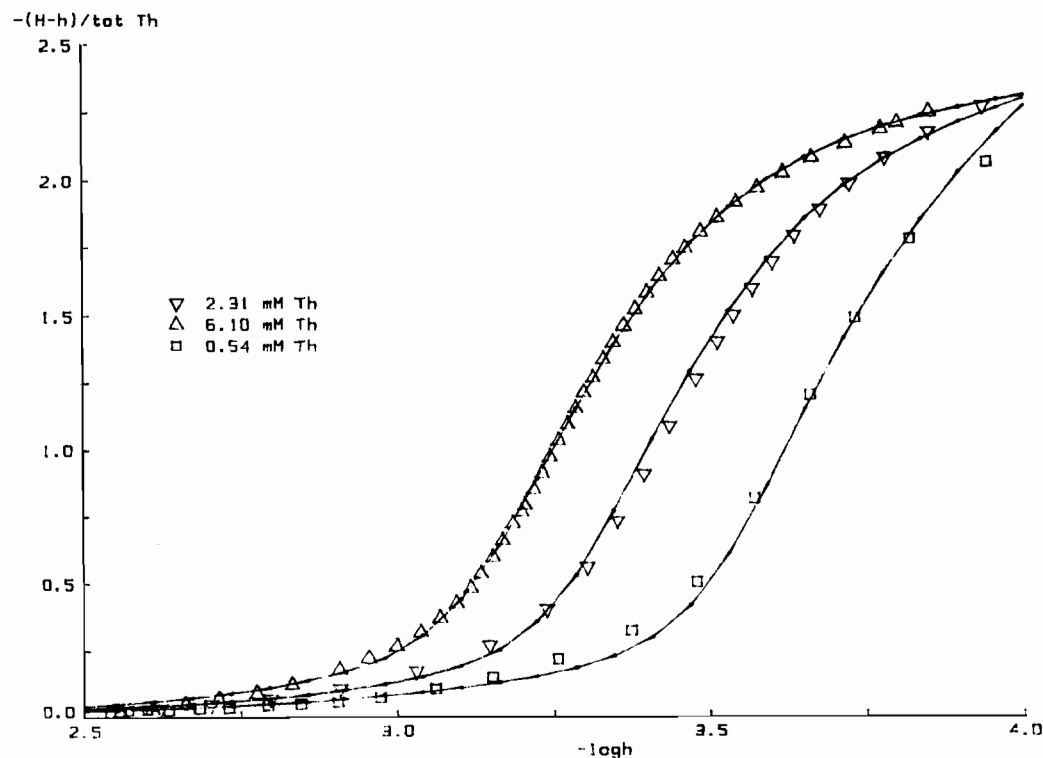


Fig. 1. Experimental and theoretical curves for the experiments at *P*(CO₂) = 0 atm.

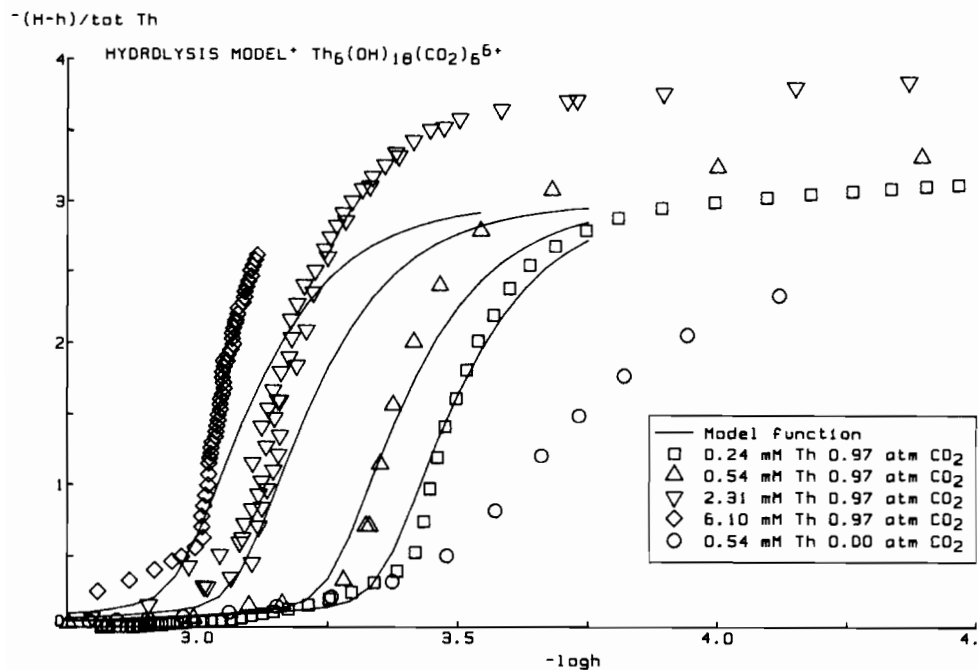
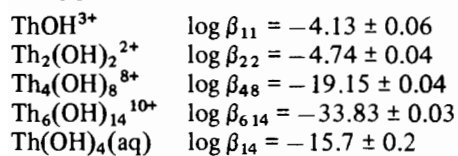


Fig. 2. Experimental and theoretical curves for the experiments performed at $P(\text{CO}_2) = 0.97$ atm. A titration obtained in the absence of CO_2 is included for the sake of comparison.

$P(\text{CO}_2) > 0$)—6.1 mM. The partial pressure ranged from 0 to 0.97 atm. The total acidity of the test solutions was varied by a coulometric titration technique. This technique was chosen in order to minimize the risk of local precipitation and because of its high accuracy [4].

Results

The results obtained at $P(\text{CO}_2) = 0$ (Fig. 1) can be explained by taking into account the formation of the following hydrolysis complexes with the $\log \beta_{pq}$ values:



For $P(\text{CO}_2) > 0$ (Fig. 2) no definitive chemical model can yet be presented. At low metal concentration the data can be partially explained by the formation of mixed hexanuclear oligomers. The nuclearity of the mixed complexes increases rapidly with the metal concentration.

Discussion

Our hydrolysis data indicates the formation of the complexes $\text{Th}_4(\text{OH})_8^{8+}$ and $\text{Th}_6(\text{OH})_{14}^{10+}$,

while the previously proposed species $\text{Th}_4(\text{OH})_{12}^{4+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$ can be ruled out. The stoichiometry of $\text{Th}_6(\text{OH})_{14}^{10+}$ is supported by the X-ray studies of Johansson *et al.* [8, 9] where $\text{Th}_6(\text{OH})_{14}^{10+}$ consists of three face sharing tetrahedra of Th_4 where the central tetrahedron has an oxide in the centre and the two other oxides (or $-\text{OH}$) outside the three remaining faces, see for example the structure of $\text{Pb}_6\text{O}(\text{OH})_6$ [10]. By using e.m.f. techniques only we cannot distinguish between 2OH^- and O^{2-} . Hence, $\text{Th}_6(\text{OH})_{14}^{10+}$ may contain either coordinated oxide ions or coordinate hydroxide ions. The 'limiting species' may be $\text{Th}_6(\text{O})(\text{OH})_6(\text{OH})_6^{10+}$ and $\text{Th}_6(\text{O})(\text{O})_6^{10+}$ with 6OH^- or 6O^{2-} outside the triangular faces, see for example Fig. 3.

The experimental data in the presence of CO_2 clearly indicates the formation of very stable $\text{Th}(\text{IV})-\text{OH}-\text{HCO}_3/\text{CO}_3$ complexes of high nuclearity. At the lowest metal concentration and $P(\text{CO}_2) = 1$ atm we have tried to explain our data with the complex

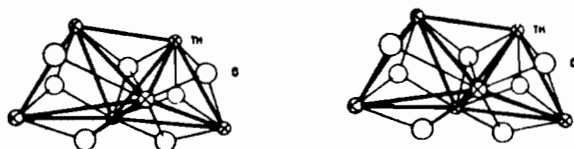


Fig. 3. Tentative structures for the $\text{Th}_6(\text{OH})_{14}^{10+}$ complex according to ref. 9.

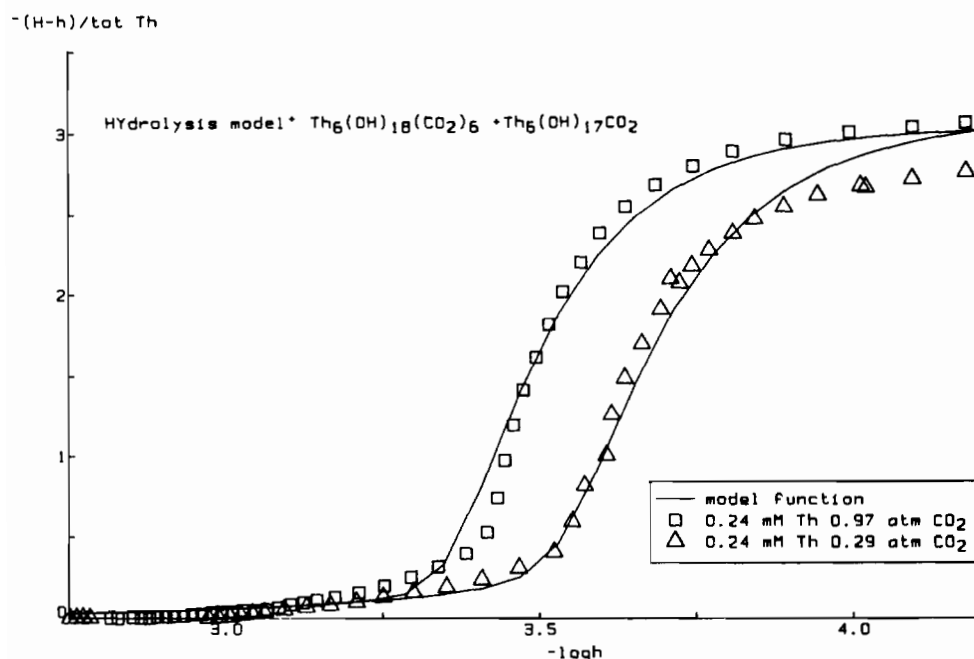


Fig. 4. Experimental and model curves for the experiments performed with $[\text{Th(IV)}] = 0.24 \text{ mM}$, at $P(\text{CO}_2)$: 0.3 and 0.97 atm.

$\text{Th}_6(\text{OH})_{18}(\text{CO}_2)_6^{6+}$. At $P(\text{CO}_2) = 0.3 \text{ atm}$ with the complex $\text{Th}_6(\text{OH})_{17}\text{CO}_2^{7+}$, see Fig. 4. These complexes fit into the same structural type as the hexanuclear hydrolysis complex, the only difference being that six(one) of the oxygens on the faces are replaced by six(one) bidentately bonded carbonato groups.

These results indicate that CO_2 could increase the solubility and consequently the mobility of thorium in natural waters with $\text{pH} < 7$.

References

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