

Equilibrium Ultrafiltration of Hydrolyzed Thorium(IV) Solutions

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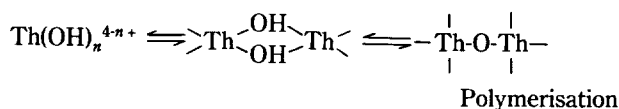
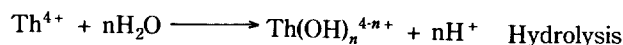
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The polymeric species formed on the hydrolysis of Th(IV) from solubility experiments of ThO₂ in 0.1M NaClO₄ and Th(OH)₄ in 0.5M NaClO₄ were removed by ultrafiltration using 1 nm ultrafilters. The resultant equilibrium concentrations of mono-hydroxy Th(IV) species in solutions between pH 1.5 to 13 were measured by the NAA method. From these data solubility product of thorium dioxide and the stability constants of mono-hydroxy Th(IV) were determined. The values obtained were $\log K_{sp} -50.76 \pm 0.08$, $\log \beta_{1,1} 12.42 \pm 0.02$, $\log \beta_{1,2} 22.46 \pm 0.15$, $\log \beta_{1,3} 34.36 \pm 0.07$, $\log \beta_{1,4} 42.58 \pm 0.08$, which are in good agreement with the values given in the literature. In addition, several dimeric species, Th₂(OH)₂⁶⁺, Th₂(OH)₃⁵⁺ and Th₂(OH)₄⁴⁺ have been identified.

Introduction

For over a decade, researchers in the field have known that polymeric species are formed when Th(IV) hydrolyzes. The hydrolysis and polymerisation chemistry of Th(IV) have attracted much research interest in recent years because of its interference in nuclear fuel ion-exchange and extraction schemes, and its migration behaviour as radionuclide in the environment. Thorium can be used as nuclear fuel and the aquatic chemistry of Th(IV) is very similar to Pu(IV) and U(IV) (ionic radius is 1.0 Å in comparison to Pu⁴⁺ and U⁴⁺ which have 0.90 and 0.93 Å). The polymerisation of Th(IV) ordinarily follows closely after its hydrolysis such that two reactions are difficult to separate¹. However, in concept two reactions can be treated separately as shown in Equation 1.



Equation 1. Hydrolysis and Polymerisation of Th(IV)

The nature of the dissolved Th(IV) species in aquatic media can be determined by either direct or indirect methods². The indirect method of using thermodynamic data has major limitations due to the lack of sufficient data. However, the presence of Th(IV) hydrous polymers render it prohibitively difficult to apply any one direct analytical method to the study of these phenomena. The solubility product can only be at best estimated in the presence of polymeric species, leading to further uncertainties. The solubility product has been calculated from available thermodynamic data (NBS, private communication). The stability constants $\beta_{1,1}$ and $\beta_{1,2}$ of mono-hydroxy species of Th(IV) were determined using potentiometric methods^{3,4}. The other constant, $\beta_{1,3}$ and $\beta_{1,4}$ were estimated from solubility of ThO₂⁵ at pH greater than 4.5.

Research on Th(IV) hydrous polymers were conducted using a variety of methods including potentiometry^{3,7}, ultracentrifugation⁸, light scattering⁹ and X-ray scattering¹⁰. The summary of this work is given in 'The hydrolysis of cations' by Baes and Mesmer¹¹.

Recently, a scheme that incorporates particle size separa-

tion by ultrafiltration has been used to separate mono-hydroxy metal ion species from polymeric species for analysis¹². The object of this study is to use such a scheme to directly determine the solubility product and stability constants of mono-hydroxy Th(IV) species from solubility of ThO₂ and Th(OH)₄ in aquatic media.

Materials

Great care was taken to prepare reagents to be free of dissolved carbon dioxide gas and carbonate.

Water. A double deionized water was refluxed in a quartz refluxing vessel under bleeding helium atmosphere for 3 to 4 hours prior to usage. The pH of 0.1M sodium perchlorate solution prepared with this water was 6.8 ± 0.3 .

Perchloric Acid. Perchloric acid was prepared by diluting the concentrated acid (Merck analysis grade, 70%) with water in an inert gas box.

Sodium Hydroxide. The commercially available carbonate free sodium hydroxide (Baker Chemical, Delut it No. 4869) was diluted to appropriate concentration in inert gas box for usage.

Thorium Dioxide. Thorium nitrate (Merck analysis grade) solution and ammonium oxalate (Merck analysis grade) were mixed to produce thorium oxalate precipitate which was filtered and dried. This powder was heated at 700°C for 48 hours under a flushed helium gas atmosphere and kept in the inert gas box for use.

Thorium Hydroxide. The fresh thorium hydroxide was prepared by adding carbonate free sodium hydroxide solution to thorium nitrate solution under helium atmosphere. The white precipitate was filtered and washed three times with water prior to use.

Experimental Methods

ThO₂-solubility experiment. By mixing 0.1M NaClO₄, 0.1M NaOH and 0.1M HClO₄ solutions in appropriate quantities, 45 blank solutions having different pH from 1.5 to 13 were prepared. Some 0.2g of ThO₂ was placed into each of the glass vials with teflon caps (pierce, No. 13075) and polyethylene bottles (Sahlberg, 303/50), and 40 ml of blank solution was added to each of these samples. These samples were kept in darkness in an inert gas box with occasional

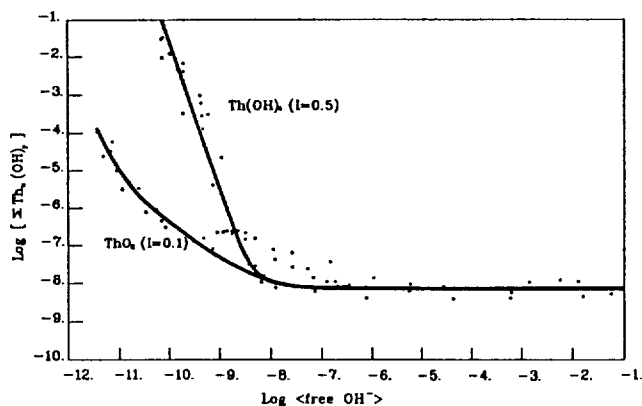


Figure 1. Solubility of ThO_2 and Th(OH)_4 at 18°C .

shaking for one year. The pH of the samples was adjusted from time to time by adding acid or base solutions.

Th(OH)_4 -Solubility Experiment. Some 70g of freshly precipitated Th(OH)_4 and 500 ml of 0.5M NaClO_4 solution was placed in a 2 L Duran three neck flask and stirred continuously with a magnetic stirrer under helium atmosphere. The initial pH of this solution was 8.0. The pH of the solution was adjusted in ± 0.5 increments by adding 0.5M HClO_4 or 0.5M NaOH . After continuous stirring for one day, the solution was allowed to settle for 1hr. A sample of 5.0 ml was carefully removed for the analysis. The procedure was repeated for the duration of two months.

Ultrafiltration. The samples from each of the two experiments were initially filtered using $0.45\ \mu\text{m}$ sartorius filter. They were filtered again using sartorius 5KD (Type SM 14529, 13 mm diameter) prior to analysis.

pH Measurement. The Orion Ross glass electrode and Metrohm Hensau pH meter (Type E 500) was used exclusively.

Chemical Analysis. The dissolved thorium content was analyzed by neutron activation analysis in the FRM reactor (Forschungs reactor Munich) at the position with neutron flux of $2 \times 10^{13}\text{n/sec}$. The samples from acidic solutions, 200-300 μl of the solution was dripped onto a folded filtered paper using 100 μl micropipette, dried and sealed in clean polyethylene bag prior to activation. The samples from neutral or basic solutions, 1000 μl of the solution was placed into a suprasil quartz tube (Hereaus, 8 mm diameter) dried and sealed and activated for 20 hours. The daughter product of Th-232 , Pa-233 with the characteristic gamma line at 311 KeV was analyzed by gamma spectroscopy.

Results and Discussion

Thorium is found in nature only as tetravalent cations. Since the dissolution of Th(IV) in aqueous solutions results in the formation of three categories of dissolved species, monomeric, polymeric and colloidal species, different values of solubility are obtained depending on the method of phase separation. By the ultrafiltration using filters of different pore sizes, species down to 1 nm can be removed disparately from the solution. With the use of 1 nm filters, polymeric Th(IV) species were removed from thorium solutions from ThO_2 and Th(OH)_4 solubility experiments. The use of glass vials and polyethylene bottles produced no appreciable difference to the results. The ThO_2 -solubility experiment was

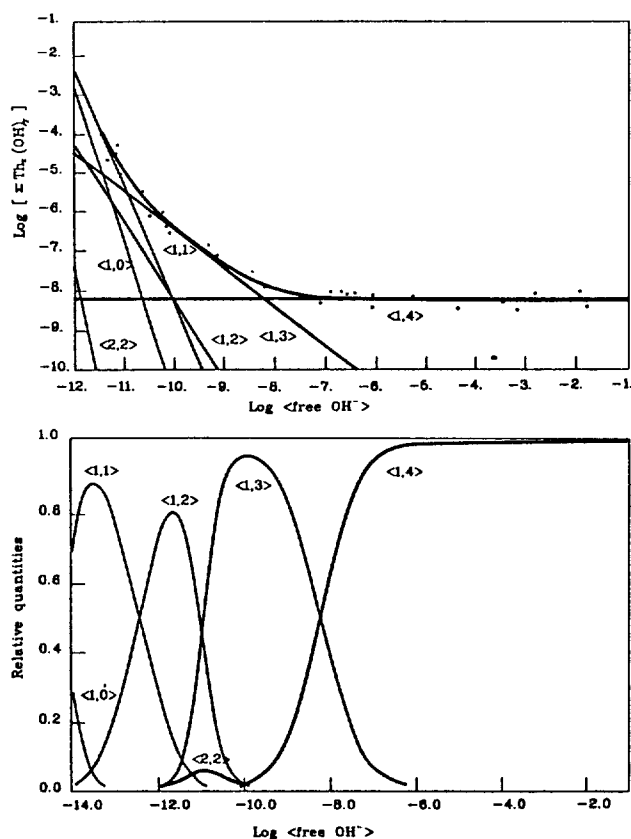


Figure 2. Distribution of hydrolysis products from ThO_2 solubility experiment at $I = 0.1$ and 18°C .

conducted at the solution ionic strength of 0.1. However, due to larger total dissolved thorium species, the Th(OH)_4 -solubility experiment was measured at the higher solution ionic strength of 0.5. The results are shown in Figure 1.

Although these two experiments were conducted at different ionic strengths, the identical solubility behaviours were observed in the neutral and basic media. However, in the acidic media solubility data from Th(OH)_4 was higher than that for ThO_2 . The results seem to suggest that not all polymeric species were removed by ultrafiltration.

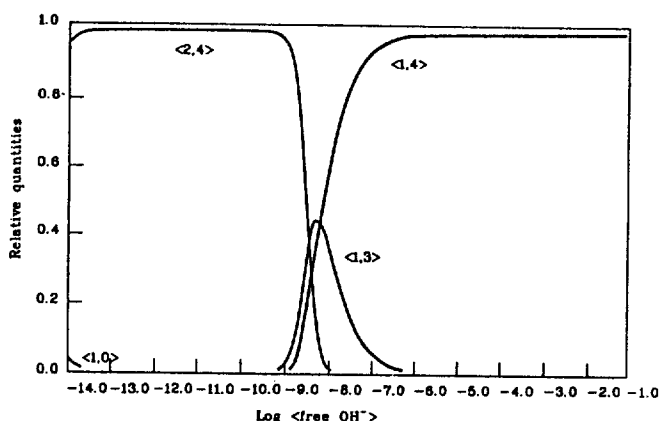
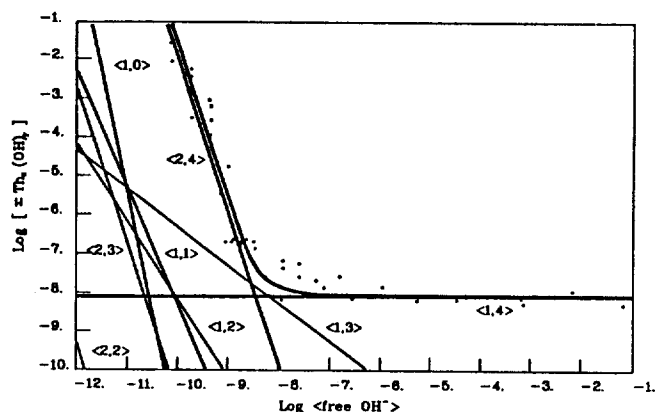
The results in Figure 2 show the distribution of hydrolysis products from the ThO_2 solubility experiment. Starting with the values given in the literature, the values of K_{sp} and stability constants were varied in small increments to achieve the best possible curve fitting using the linear least square curve fit technique. The best possible curve fit was achieved only when hydrolyzed Th(IV) dimer terms were included.

The experimental value of -50.76 was obtained for $\log K_{sp}$ of ThO_2 . This seems to be low in comparison to the theoretical estimation given in the literature. The cause may either be due to the uncertainty associated with the free energy of formation of ThO_2 or that ThO_2 may react with water to produce $\text{ThO}_2 \cdot n\text{H}_2\text{O}$, which must be of a different energy state than original ThO_2 .

The solubility product is an indispensable primary quantity for the accurate determination of hydrolysis constants, especially from solubility experiments. Its uncertainty is directly transferred to the hydrolysis constants. As a result the calculated values of stability constants of hydrolyzed Th(IV) species were some 5% larger than that given in the literature.

Table 1. Stability Constants of Thorium(IV) Hydrolysis Products from ThO₂ Solubility Experiment, at 18°C (*I* = 0.1)

species	Log β calculated	Log β literature (11)
Th(OH) ₁ ³⁺	12.42 ± 0.02	11.40
Th(OH) ₂ ²⁺	22.46 ± 0.15	21.75
Th(OH) ₃ ⁺	34.36 ± 0.07	31.26
Th(OH) ₄	42.58 ± 0.08	41.06
Th ₂ (OH) ₂ ⁶⁺	22.11 ± 0.10	21.11

**Figure 3.** Distribution of hydrolysis products from Th(OH)₄ solubility experiment at *I* = 0.5 and 18°C.

In the solubility experiment of Th(OH)₄, addition of the acid to the basic solution containing precipitated Th(OH)₄ and base to the acidic thorium solution produced the identical solubility curve. A careful observation showed that when a base was added to acidic thorium solution, a localized high basicity resulted in the formation of white precipitous Th(OH)₄ which redissolved quickly on stirring. The results are shown in Figure 3.

The experimental value of the log *K_{sp}* of Th(OH)₄ is -50.52 ± 0.08, very similar to the value derived from ThO₂ experiment. In addition the stability constants of mono-hydroxy Th(IV) species from this experiment, as shown in Table 2, are almost identical to those from the ThO₂ experiment. The apparent reason for the higher thorium concentration in the acidic solutions seems to be the presence of dimeric species in much greater abundance, the dominant one be-

Table 2. The Stability Constants of Th(IV) Hydrolysis Products from Th(OH)₄ Solubility Experiment at 18°C (*I* = 0.5)

Species	Log β experimental	Log β literature (11)
Th(OH) ₁ ³⁺	12.58 ± 0.02	11.56
Th(OH) ₂ ²⁺	22.33 ± 0.15	21.62
Th(OH) ₃ ⁺	34.42 ± 0.07	31.42
Th(OH) ₄	42.76 ± 0.08	41.32
Th ₂ (OH) ₂ ⁶⁺	30.05 ± 0.04	20.58
Th ₂ (OH) ₃ ⁵⁺	32.21 ± 0.11	
Th ₂ (OH) ₄ ⁴⁺	59.07 ± 0.04	

ing Th₂(OH)₄⁴⁺.

The reason for the presence of much larger quantities of dimeric species from the Th(OH)₄ solubility experiment is not clearly understood. One possible explanation is that fresh Th(OH)₄ has a three dimensional array of bridged hydroxy structure which can be easily broken down in acid media to form supersaturated thorium solutions containing many dimeric, trimeric and other polymeric species.

Conclusion

The equilibrium ultrafiltration has been shown to be a useful method in disparately removing all polymeric species larger than dimers from thorium solutions. The analysis of the resultant solution provided experimental verification of the existence of mono-hydroxy Th(IV) species. Furthermore, it has shown renewed promise for the speciation of polynuclear species by computation on experimental curves derived from solubility experiments.

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