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Thorium(IV) Hydrous Oxide Solubility

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The hydrolysis of thorium(IV) has received a considerable amount of study,^{1,2} but the agreement between some of the individual workers apparently is poor. Most of this work has been carried out at pH values below about 4.5 although one solubility study³ has been carried out in the pH range 3.4-7.0. From this work,³ solubility product values for hydrous ThO₂ and hydrolysis constants for formation of Th(OH)₃⁺ and Th(OH)₄⁰(aq) were reported.^{1,3} The minimum solubility of active (hydrous) ThO₂ due to formation of Th(OH)₄⁰(aq) was proposed to be 10^{-6.3} M, and the minimum solubility of fully crystalline ThO₂ (above pH 6) has been proposed¹ to be 10^{-9.6} M.

Recently, the formation constant and free energy of formation of the Th(OH)₅⁻ ion have been estimated⁴ from reported¹ values of formation constants for the Th(OH)₃⁺, Th(OH)₂²⁺, Th(OH)₃⁺, and Th(OH)₄⁰(aq) complexes. On the basis of currently accepted thermochemical data⁵⁻⁷ for ThO₂ and for water and OH⁻ ion, the reported⁴ value for Th(OH)₅⁻ would indicate a totally unreasonable solubility of ThO₂(c) of 0.4 M at unit OH⁻ activity. Similar amphoteric behavior and formation constant values of U(IV),^{1,4,8-11} Np(IV),^{10,11} and Pu(IV)^{1,4,9-11} have been proposed for formation of the M(OH)₅⁻ ion and in the case of U and Pu the M(OH)₆²⁻ ions.⁴ All of the tetravalent actinides can be expected to show qualitatively similar hydrolysis behavior with the extent of hydrolysis, as reflected by the hydrolysis constants, increasing with increasing atomic number and decreasing ionic radius. As with the radius change,¹² the degree of hydrolysis might be expected to change most rapidly with the first members of the series.

We have recently measured the solubilities of uranium¹³ and neptunium¹⁴ in alkaline solutions under reducing conditions and found no convincing evidence of measurable amphoteric behavior, thereby placing much lower limits on formation constants for anionic species of U(IV) and Np(IV) than those reported. It is very difficult to maintain U in the reduced (tetravalent) state under high-pH conditions and somewhat less difficult in the case of neptunium. Thorium is exclusively tetravalent, and thus its hydrolytic properties at high pH are easier to determine. This work reports results of a study of the solubility of amorphous, hydrous ThO₂ over the pH range 3.5-14.2.

Experimental Section

Reagents. Baker reagent grade Th(NO₃)₄·5H₂O, Eastman 10% tetraethylammonium hydroxide, and Cerac High Purity grade LiOH were used. The LiOH was analyzed for Si by an ion-coupled plasma spectroscopy method and was found to contain 64 μmol of Si/mol of LiOH. All other chemicals were reagent grade. The carbonate concentrations of the tetraethylammonium hydroxide and a stock solution of the LiOH

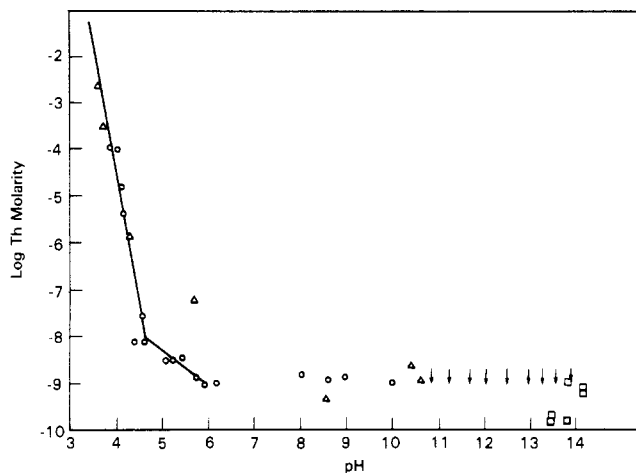


Figure 1. Measured solubilities of thorium(IV) hydrous oxide as a function of pH. Triangles represent series 1 (tetraethylammonium) samples in which a counting signal was actually observed for the activation product of Th even if very near background. Arrow tips represent the detection limits on tetraethylammonium hydroxide (series 1) samples for which no activation product signal above background was actually observed. Squares denote LiOH samples, and circles represent series 3 samples ($\mu = 0.1$ with NaClO₄).

were determined by BaCO₃ precipitation, and sufficient strontium nitrate was added to the tetraethylammonium stock solution to make it 3×10^{-3} M in excess Sr²⁺ and to the LiOH stock solution to make it 8.5×10^{-4} M in excess Sr²⁺ after SrCO₃ precipitation. Acidimetric titration showed the tetraethylammonium stock solution to be 0.673 M OH⁻ and the LiOH stock solution to be 1.530 M OH⁻, and these stock solutions were maintained under argon. A 100 g/L Th stock solution in 0.1 M HNO₃ was prepared.

General Procedure. Solutions (20 mL) (series 1) of tetraethylammonium hydroxide above pH 12 were prepared by calculated dilution of the stock solution. To each solution was added 50 μL of the thorium stock solution (5 mg of Th). All solutions (20 mL) below pH 12 were prepared by adding 50 μL of the Th stock solution to water followed immediately by addition of tetraethylammonium hydroxide to the desired pH if above pH 9. For desired pH values below 9, the solutions were brought to pH 9-10 with tetraethylammonium hydroxide, causing immediate precipitation, and were brought back immediately to the desired pH with 0.1 M HNO₃. Six solutions (series 2) in the [OH⁻] range 0.28-1.38 M were prepared from the LiOH stock solution and 1.00 mL of Th stock solution (100 mg of Th). At this Th concentration, the Th/Si ratio in these samples varied from 235 to 935, and thus it is strongly felt that Si impurity cannot affect the results. An additional 17 solutions (series 3) were prepared in the pH range 3.5-10 in which 0.625 mL of the Th stock solution (62.5 mg of Th) was added to water that was then made basic with carbonate-free NaOH. The precipitated hydrous ThO₂ was washed with water and made up to 17 mL of 0.1 M NaClO₄ and the desired pH with hydrochloric acid or NaOH solution. Solution makeup was done under an Ar cover flow or in an inert-atmosphere box. Solutions were immediately sealed; series 1 and 2 were shaken for 25-27 days and series 3 was shaken for 7 days at 25 °C.

Solutions were centrifuged in the sealed containers for from 1 to 4 h at 1000 G. This removed any detectable Tyndall effect from most of the high-pH samples but not from the lower pH solutions. Ten-milliliter portions of the centrifuged series 1 and 2 solutions were then filtered at 60-psi pressure through 13-mm-diameter Nuclepore Ultrafilters, Type F, No. 1F7257, having mol wt 20000 cutoff for globular proteins (~2-μm pore size). Series 3 solutions were filtered through Amicon CF 25 conical centrifuge filters having mol wt 25000 (for globular proteins) cutoff. Filtration times varied from 20 min to 3 h in proportion to the extent of the Tyndall effect observable after centrifugation. The pH values of the unfiltered portions of the solutions were determined at the time of sampling for those solutions having pH ≤ 12, while those above 12 were calculated from the measured OH⁻ concentration.

Analyses. Thorium analyses on the filtered series 1 and 2 solutions were done by neutron activation. Samples, along with Th standards and a USGS GSP-1 standard, were irradiated at $\sim 6 \times 10^{12}$ neutrons cm⁻² s⁻¹ for 14 h. Samples were counted on a normal Ge(Li) counting system and on a coincidence and anticoincidence Ge(Li)-NaI(Tl) system. Approximately 4 weeks' delay between irradiation and counting was necessary to allow for decay of ²⁴Na ($t_{1/2} = 15$ h) and ⁸²Br ($t_{1/2} = 36$ h). Bromine is a possible expected impurity in tetraethylammonium hy-

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droxide on the basis of its method of manufacture and indeed could be detected turbidimetrically by Ag^+ precipitation. After decay of these impurities, Compton scattering from ^{85}Sr ($t_{1/2} = 65$ days) and ^{65}Zn ($t_{1/2} = 240$ days) in the tetraethylammonium hydroxide solutions increased the background, preventing increase of the sensitivity for the Th activation product, ^{233}Pa ($t_{1/2} = 27$ days), with the coincidence-anticoincidence system. The Sr was, of course, added to remove carbonate, but the Zn was an unsuspected impurity in the tetraethylammonium hydroxide. Thorium analyses on the filtered and acidified series 3 solutions and blanks to which no Th was added were done by inductively coupled plasma mass spectroscopy.

A combination glass electrode calibrated with pH 4, 7, and 10 buffers was used for pH measurement.

Results

The solubility of Th(IV) as a function of solution pH is shown in Figure 1. The values shown can be considered to be the solubility of amorphous (hydrous) ThO_2 since electron diffraction studies¹⁵ of aging of hydrous ThO_2 at 25 °C show no crystallinity at the time period (25–27 days) or less of the present solubility study. Solubilities in tetraethylammonium hydroxide (series 1) in the pH region 10–14 are essentially all at or below the detection limit of about 10^{-9} M. Measured values in LiOH solutions (series 2) in the pH range 13.4–14.2 were in the 10^{-10} – 10^{-9} M Th range. These values appear to represent true Th measurements in the neutron activation analysis, but whether they represent true solubilities is not certain since the points are limited in number and two values that were duplicates vary from each other by a factor of 6.6. Since solubilities in this region were approached from the supersaturated side, the values can all be considered upper limits. These results show that the soluble neutral species, $\text{Th}(\text{OH})_4^0(\text{aq})$, cannot contribute to total thorium solubility to an extent exceeding 2×10^{-10} or at the absolute highest 10^{-9} M. This contradicts the results of Nabivanets and Kudritskaya,³ who reported a value of 4.8×10^{-7} M for the pH-independent concentration of this species in equilibrium with amorphous ThO_2 . This difference probably indicates that their value is a background level in either their solids-liquid separation technique or their analytical technique. The data indicate that amphoteric species do not contribute to Th solubility of $>10^{-9}$ M at pH 14, but whether the values measured in LiOH are due to amphoteric species at all is not certain.

At pH values between 5.5 and 11, measured Th values were obtained for both series 1 and 3 samples, but all series 3 values in this range are within a factor of 1.6 of the average blank values so they can be considered to be at background. For the series 1 samples in this range, only one at pH 5.7 is significantly above background, and it appears to be a flier. In this region, solubility was approached from undersaturation in most samples, and in the two lowest pH points of Figure 1, the volume of solids visibly decreased in the first hour of equilibration. In the lowest pH sample only a Tyndall effect remained. It is clear, however, that in the pH 3.6–4.7 region, the average slope is somewhat greater than 4. The fact that the slope is greater than 4 may be at least partially due to the presence of some polynuclear species, at least at the higher Th concentration, low-pH end of this region. Because of the difficulty of accurately determining slopes greater than 4 and because of possible complications due to a small pH-dependent anion-exchange capacity of hydrous ThO_2 ,^{16,17} no attempt is made here to interpret this slope. This steep slope over about 5.5 orders of magnitude in aqueous Th concentration does point to mononuclear hydrolyzed Th ions not being dominant solution species at least up to pH 4.5. Between pH 4.5 and 6 a lower slope (≤ 1) is observed, but since it is based entirely on three points that are only a factor of 3 above background, we do not attempt to interpret it. Baes and Mesmer,¹ in reviewing several prior studies, have given formation constants for such polynuclear species. It should

be noted that other values have since been published² but that the hydrolysis scheme should decrease the slope to less than 4. Using the values given by Baes and Mesmer,¹ we can show that polynuclear species will not be significant at pH 4.0 and 1.5×10^{-5} M Th (the solubility at that pH for series 1 solutions). The solubility product of the amorphous ThO_2 in the present work can be determined from these numbers. Neglecting mononuclear complexes and activity coefficients would give an apparent $\log K_{sp} = -44.8$ for the reaction



Series 1 data are used here since this same series (same hydrous oxide aging time etc.) extends to the very high pH range. It should be apparent from Figure 1 that essentially the same result is obtained from series 3 results in the pH 3.9–4.3 range, where solubilities are low enough to minimize polynuclear species in solution but are high enough to provide good analytical accuracy. If the hydrolysis constants of Baes and Mesmer¹ for formation of $\text{Th}(\text{OH})_3^{3+}$ and $\text{Th}(\text{OH})_2^{2+}$ are correct, $\log K_{sp}$ would become more negative by 0.7 and the activity coefficient correction for our ionic strength of ~ 0.005 would make $\log K_{sp}$ more negative by an additional 0.4, giving a value of $\log K_{sp} = -45.9$. There is some reason, in addition to the >4 slope in Figure 1, to question whether the use of the Baes and Mesmer values of the two formation constants, particularly the second, is completely valid. As we show below, the values for $\text{Th}(\text{OH})_4^0(\text{aq})$ and $\text{Th}(\text{OH})_5^-$ are very much smaller than the proposed values. If one does accept the unproven concept proposed by Baes and Mesmer¹ as well as by Barnum⁴ that there is a continuous linear progression in differences in the logarithms of formation constants, the value reported for $\text{Th}(\text{OH})_2^{2+}$ would appear too high. Nevertheless, this should not produce an error of more than about 0.5 in $\log K_{sp}$. (It should also be noted that even if the hydrolysis scheme of Brown et al.² were used, our data would give $\log K_{sp} = -46.3$.) For comparison, a value of $\log K_{sp} = -46.6$ was calculated by Baes and Mesmer¹ for the amorphous ThO_2 in the work of Nabivanets and Kudritskaya.³

The log (solubility product) of fully crystalline ThO_2 , eq 1 with $\text{ThO}_2(\text{c})$ replacing $\text{ThO}_2(\text{am})$, calculated¹⁸ from accepted thermochemical data^{5–7} for $\text{ThO}_2(\text{c})$ ($\Delta G_f^\circ = -1168.8$ kJ mol⁻¹) and Th^{4+} ($\Delta G_f^\circ = -704.6$ kJ mol⁻¹), is $\log K_{sp} = -54.14$. This value is considerably lower than the value of -49.4 reported by Baes and Mesmer¹ to have been calculated from thermochemical data, and the source of their data is unclear. It also is considerably lower than the reported value of -49.7 based on solubility measurements of Baes et al.,¹⁹ and it appears very unlikely on the basis of the electron diffraction data of Prasad et al.¹⁵ that their ThO_2 approached from supersaturation could be completely and fully crystalline in the time frame of their experiments. It must be emphasized that measured solubilities will always be controlled by any trace of less than fully crystalline material present. On the basis of the difference between K_{sp} for $\text{ThO}_2(\text{c})$ from thermochemical data and the value for our $\text{ThO}_2(\text{am})$, we obtain a difference of 47.1 kJ mol⁻¹ between the free energies of formation of these oxides. This agrees reasonably well with a free energy difference of 41.4 kJ mol⁻¹ between our value for $\text{PuO}_2(\text{am})$ ^{18,20} and the thermochemical value for $\text{PuO}_2(\text{c})$ ^{5,6} and a free energy difference of 52.5 kJ mol⁻¹ between the value for $\text{NpO}_2(\text{am})$ ¹⁴ and the thermochemical value for $\text{NpO}_2(\text{c})$.^{5,6}

The data of Figure 1 give $\log K_{55} \leq -9.0$ for the reaction



From the free energy of formation (-1121.7 kJ mol⁻¹) of $\text{ThO}_2(\text{am})$ determined from the K_{sp} data above, a value of $\Delta G_f^\circ \geq -1702.1$ kJ mol⁻¹ for $\text{Th}(\text{OH})_5^-$ is obtained. This value, along with the free energy of formation of Th^{4+} cited above, leads to $\log \beta_5^* \leq -33.1$ for the reaction



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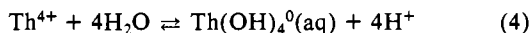
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Similarly, from the data of Figure 1, a value of $\Delta G_f^\circ \geq -1540.7$ kJ mol⁻¹ for Th(OH)₄⁰(aq) and a value of $\log \beta_4^* \leq -19.7$ are obtained for the reaction



These values result in calculated solubilities of ThO₂(c) of $\leq 1.2 \times 10^{-18}$ M as the pH-independent species, Th(OH)₄⁰(aq), and $\leq 6 \times 10^{-18}$ M at pH 14 as the Th(OH)₅⁻ ion. In contrast, Baes and Mesmer¹ propose a pH-independent minimum ThO₂(c) solubility as Th(OH)₄⁰(aq) of 2.5×10^{-10} M, and Barnum's⁴ data for Th(OH)₅⁻ yield a ThO₂(c) solubility of 0.4 M at pH 14. This error of a factor of $\geq 6.6 \times 10^{16}$ in solubility is much greater than Barnum's claimed accuracy in his formation constants of about a factor of 3.⁴ Such inaccuracies put in extreme doubt the validity of Barnum's⁴ and Baes and Mesmer's¹ proposed linear or near-linear extrapolation of differences in logarithms of hydrolysis constants or free energies of formation of mononuclear hydrolytic species.

We have now placed limits on the logarithms of formation constants ($\log \beta_5^*$) of Th(OH)₅⁻, U(OH)₅⁻, and Np(OH)₅⁻ of ≤ -33.1 , ≤ -22.7 ,¹³ and ≤ -24.7 ,¹⁴ respectively. The formation constant of Pu(OH)₅⁻ has been reported in several recent publications,^{1,4,9-11,21} and a value of $\log \beta_5^* = -15.0$ is usually given.^{1,4,9-11} Such a value, when combined with ΔG_f° for Pu⁴⁺ of -481.6 kJ mol⁻¹²² and a value of $\log K_{sp} = -56.85$ for amorphous

PuO₂,^{18,20} would lead to a solubility of PuO₂(am) of >0.01 M at pH 14. Kim et al.²¹ have actually shown calculated solubilities at pH 14 considerably in excess of 1 M Pu(IV). Such values are preposterous in terms of the long known fact that Pu(IV) is quantitatively precipitated by excess alkali, and such formation constants should not be published. It is not possible to extrapolate our limit values for Th, U, and Np to Pu as a function of ionic radii precisely because they are only upper limits. It is, however, reasonable, on the basis of known chemical behavior in other systems, to expect that the $\log \beta_5^*$ value for Pu(OH)₅⁻ would be no more than about 2 log units more positive than that for Np(OH)₅⁻. This would place $\log \beta_5^* \leq -22.7$ for Pu(OH)₅⁻ and would yield a PuO₂(am) solubility as Pu(IV) of $\leq 2.3 \times 10^{-10}$ M at pH 14. In view of the oxidation-state-control problem with Pu(IV) under alkaline conditions, such a value would be difficult to reliably verify. In fact, it is very probable that a pH region exists in which Pu(IV) is never the dominant solution oxidation state regardless of redox potential. This region may extend as low as pH 4 and as high as pH 14. On the basis of this work, we feel that no conclusive evidence of any amphoteric behavior of any tetravalent actinide in aqueous solutions has been published.

In conclusion, a value of $\log K_{sp} = -45.9 \pm 0.5$ for ThO₂·xH₂O was obtained from these data. The results set upper limits for $\log \beta_5^* \leq -33.1$ for the reaction $\text{Th}^{4+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_5^- + 5\text{H}^+$ and for $\log \beta_4^* \leq -19.7$ for the reaction $\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_4^0(\text{aq}) + 4\text{H}^+$.

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Registry No. ThO₂, 1314-20-1; LiOH, 1310-65-2; tetraethylammonium hydroxide, 77-98-5.

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Additions and Corrections

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Randolph P. Thummel,* Francois Lefoulon, and James D. Korp: Polyaza Cavity-Shaped Molecules. 12. Ruthenium(II) Complexes of 3,3'-Annulated 2,2'-Bipyridine: Synthesis, Properties, and Structure.

Pages 2370–2376. The correct space group for complex **4d** is $P\bar{1}$ and not $P1$ as given on p 2370, abstract, line 7; p 2374, paragraph 3, line 1; and p 2375, Table VII, line 3. The Laue symmetry for **4d** is $\bar{1}$ and not 1 as given on p 2375, paragraph 4, line 6.—Randolph P. Thummel