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Initial Assessment of Hydrous Thorium(IV) Solubility and Speciation in Geological Environments: An Experimental Approach in Presence of Organic Ligands

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Data on the hydrolysis of Thorium(IV) and solubility of ThO_2 in presence of organic ligands are of critical importance to the safe disposal and treatment of high-level nuclear waste. Such data are required to predict reliably thorium behaviour in high-level waste repositories where organic anions may be present. In addition, Th(IV) is considered to be a chemical analogue of tetravalent actinides such as Pu(IV). To establish the effect of pH and organic ligands on the hydrolysis of Th(IV), experiments on the solubility of hydrous ThO_2 in aqueous solution at room temperature were performed, covering a wide range of pH (pH = 3-12) in 0.1 molal $NaNO_3$ solutions. Experiments also were conducted in the presence of citrate, oxalate and EDTA with a concentration range of 100-500 μmol. The solubility of ThO_2 decreases with increase of pH (pH 3 to 6) and remains near the detection limit of ICP-MS (10^{-9}-10^{-10} M) in the range pH 6-12. These values are in accordance with data in the literature. The solubility of ThO_2 does not appear to be a sensitive function of the concentration of the investigated organic ligands at any given pH providing the fact that bulk of organic ligands is potentially absorbed by ThO_2 solid phase. Thorium concentrations obtained from unfiltered and filtered samples showed almost an order of magnitude variation in molal concentration indicating a significant amount of colloid formation.

Key Words: Thorium oxide, Solubility, Organic ligands, Dissolution.

INTRODUCTION

Uncontrolled large amounts of thorium may be found near hazardous waste sites and high-level nuclear waste tanks systems at locations such as Hanford (Washington) and Savannah river (South Carolina). Also, significant quantity of naturally occurring thorium may be hosted in geological formations where it can be freely available by the leaching of the country rock. Moreover, there has been a growing interest in using thorium as an alternative fuel for nuclear power reactor systems. Recent studies of the performance of thorium-based fuels report that these fuels can be used to reduce concerns related to potential proliferation of nuclear weapons and disposal of the current uranium dioxide fuel waste[1]. Furthermore, ThO_2 is thermodynamically more stable since UO_2 can be oxidized to form various higher oxides including U_4O_9, U_3O_7, U_2O_5, U_3O_8 or UO_3, which they are more soluble than UO_2 and hence may pose more risk to the environment near waste repositories[2]. Because several reactor concepts based on thorium fuel cycles are under consideration[3], it is important to have thermodynamic data to predict how such fuel and its waste form will behave in the environment. While the solubility of thorium oxide has been studied periodically over the last few decades, quantitative data on ThO_2 solubility in the presence of organic ligands are scarce. The object of this research was to measure ThO_2 (s) solubility with respect to pH and study complexation of thorium in the presence of organic ligands (EDTA, oxalate and citrate).

The solubilities of both amorphous and crystalline thorium compounds as a function of pH have been studied extensively by several groups and thorium concentrations determined at various conditions[4-8] but there is little information on ThO_2 solubility in the presence of organic ligands in the literature. Although thorium solubility and speciation in geological environments are dominated by complexation with inorganic ligands[9-13] some organic ligands with strong chelating properties may increase the solubility and therefore the mobility of thorium and other actinides in near-surface waste sites[14,15].

This paper examines the effect of pH and organic ligands (EDTA, citrate and oxalate) on the solubility of hydrous, amorphous ThO_2 in aqueous solutions at room temperature at 0.1 M ionic strength.

EXPERIMENTAL

All materials used in the experiments were reagent grade and all solutions were prepared by weight, employing 18 MΩ cm^{-1} deionized water. Sodium nitrate (purity 99.98 %) was supplied by Baker and nitric acid (trace-metal grade) was supplied by Johnson Matthey Aesar. Commercially available thorium(IV) nitrate hydrate (purity 99 %) in powder form was purchased from Sigma-Aldrich and used for the synthesis[16] of ThO_2.

Solid product

The solid ThO_2 was characterized before and after experiments by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), using a Jeol 6100 scanning electron microscope with elemental analysis and image capture software by Roentec. The initial ThO_2 was found to persist throughout the experiments and no new phases were observed.

Diffraction pattern obtained from the synthesized ThO_2 did not match the crystalline ThO_2 pattern. The pattern is somewhere between amorphous ThO_2 (am) and microcrystalline $ThO_2 \cdot xH_2O$ (mcr) (Fig. 1). This was planned since well crystalline ThO_2 is well known for its highly insoluble character that would not allow to complete this research in a reasonable time-scale due to the slow kinetics of dissolution of crystalline ThO_2.

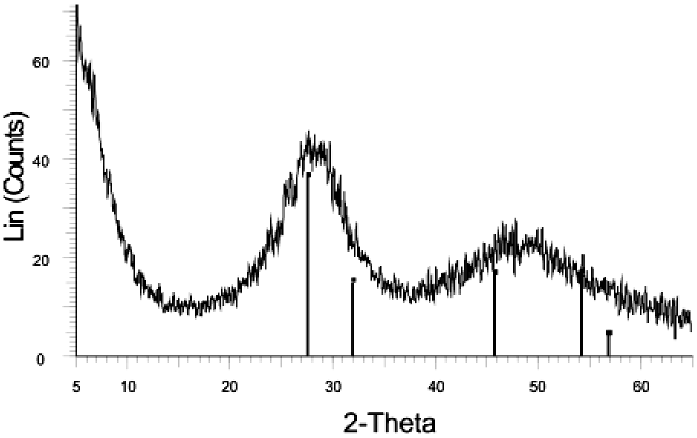


Fig. 1. X-ray diffraction pattern for the amorphous ThO_2 phase. The bold straight lines represent peaks for solid ThO_2, Thorianite (syn)

Sampling

The experiments were designed to investigate the effect of organic ligands (citrate, EDTA and oxalate: 100-500 μmol) and pH at room temperature in 0.1 M $NaNO_3$ solutions. Experimental solutions were prepared at fixed pH and a constant ionic strength of 0.1 M by dissolving weighed amounts of $NaNO_3$ in HNO_3 solution. Solutions for pH-dependence experiments were prepared by the addition of diluted NaOH to get the necessary pH. For each experiment, 2-3 g of ThO_2(s) and 100 mL of the desired solution were loaded into 120 mL sterile polypropylene bottles. All experiments were conducted on a bench-top shaker at room temperature (23 ± 2°C).

In this study, pH was measured on the concentration scale as the pH_m $(-\log m_{H^+})$ of room-temperature experimental solutions was measured *in situ* using a radiometer Copenhagen PHM 84 meter employing a ross combination glass electrode. Electrodes were calibrated against standards prepared at the same ionic strength as the experiments in order to minimize errors due to differences in liquid-junction potentials and activity coefficients.

Sampling was performed at regular intervals to check the evolution of pH and thorium concentration. Before sampling, the solid was permitted to settle for about 5-10 d to help separate solution from the suspension (Fig. 2).

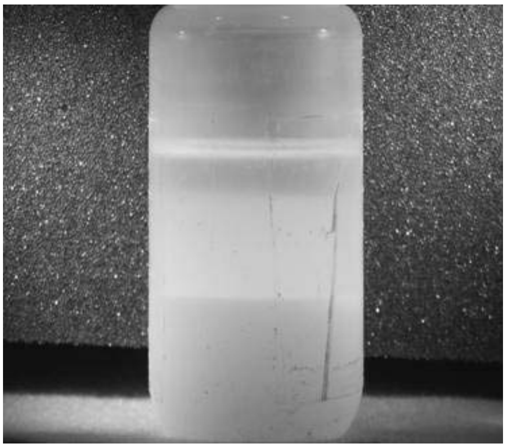


Fig. 2. Picture of suspended ThO_2 phase. Before sampling, the solid was permitted to settle for about 5-10 d to distinctively separate solution from the suspension

Aliquots of samples were collected and centrifuged at 6000 rpm for 25 min. The solution (15 mL) was withdrawn and filtered through Amicon Centricon-30 filters (30,000 MW cutoff) by Millipore corporation. The filtered samples were acidified to 2 % with trace metal grade nitric acid to insure that all thorium remained in solution until analysis. After sampling, the shaker was turned on again until the next sampling. Total thorium concentrations were determined initially by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using an axial-view torch (Perkin Elmer Optima 3000 XL) in the Department of Geological Sciences, University of Idaho (USA). Samples with very low concentrations (near the detection limits of ICP-AES) were analyzed for Th at the Washington State University ICP-MS laboratory using a Hewlett-Packard Model 4500 Inductively Coupled Plasma- mass spectrometer (ICP-MS). Calibration standards for each analysis were made from certified Th standard acquired from Fisher Scientific. Sets of 3-5 different concentrations of standards were used to establish a calibration curve. Blanks and standards of known concentrations were run periodically throughout the analyses for quality-control. Total organic ligands and potential metal complexes in solutions were checked before and after experiments by Micromass Quattro II mass spectrometer (Altrincham, England) equipped with an electrospray ionization probe, two quadrupole analyzers and a hexapole collision cell (Fig. 3).

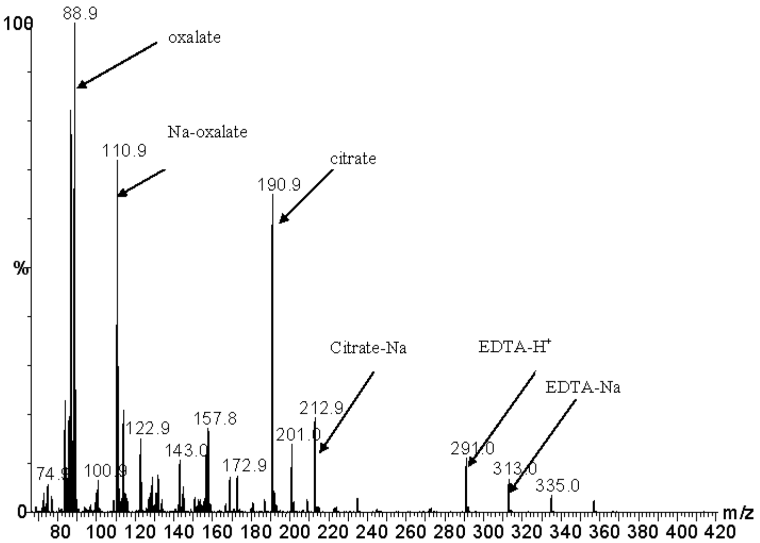


Fig. 3. Mass spectra of organic ligands and nitrate medium

RESULTS AND DISCUSSION

Preliminary analyses of replicate samples taken as a function of time showed that thorium concentration attained a constant value in 2-3 weeks at any pH range, which is consistent with reports in the literature that thermodynamic equilibrium for amorphous thorium oxide dissolution usually is obtained within a month or less[8,17]. However, concentrations obtained in the near-neutral and alkaline pH region fail to give any useful kinetic data because all the samples appear to be about the same concentration near the detection limit of the instrument (ICP-MS). In any case, thorium oxide was reacted with the experimental solution for a period of one month to be consistent with previous work.

The solubility of ThO_2 is shown in Table-1 and plotted in (Figs. 4a-c) and (Figs. 5a-c). The results of the experiments show that solubility is notably low, especially in the pH range encountered in geological environments.

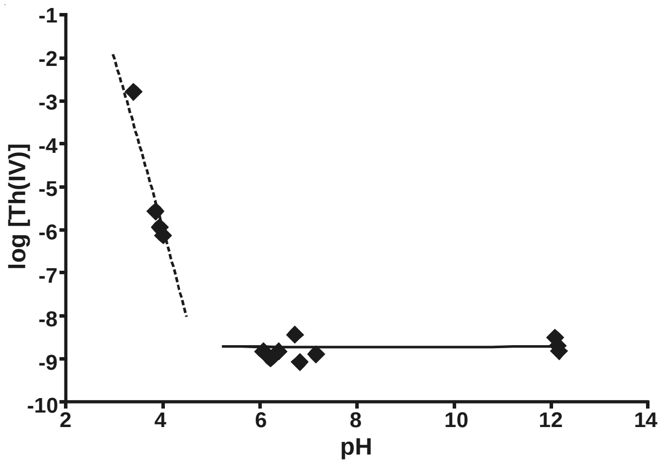
Fig. 4 shows solubility data for solutions for 100-500 μmol kg^{-1} each of citrate, EDTA and oxalate, as a function of pH. Over the range investigated, ThO_2 solubility is strongly dependent on pH in the acidic region while it is very weakly dependent on pH in the neutral to alkaline region. In the absence of organic ligands, the solubility of ThO_2 may be described in terms of reactions of the following type (assuming the concentrations are too low for the formation of polynuclear species):

$$ThO_2 + (4\text{-}n)H^+ \rightleftharpoons Th(OH)_n^{4-n} + (2\text{-}n)H_2O \qquad (1)$$

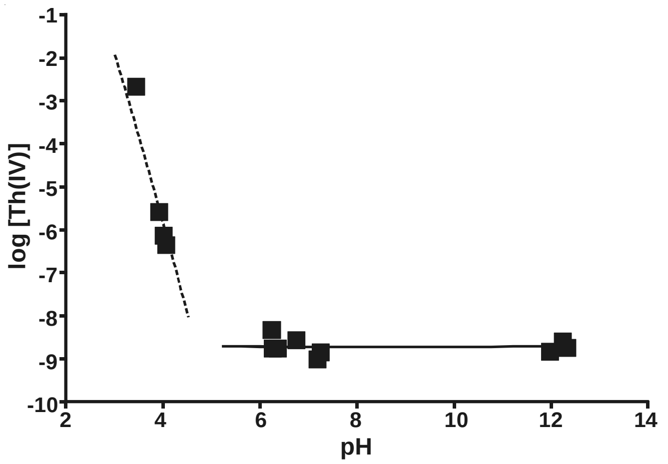
TABLE-1
EQUILIBRIUM SUMMARY OF EXPERIMENTAL RESULTS FROM ThO_2 (am) SOLUBILITY IN 0.1 M $NaNO_3$-HNO_3 MEDIA AT 23°C

Sample No.	Organic ligand	pH	Th-Concentration (mol/Kg H_2O)
Th-0.1-pH3	Ligand-free	3.39	2.14E-03
Th-0.1-c1	Citrate-100 µmol	3.39	2.08E-03
Th-0.1-c2	Citrate-200 µmol	3.41	1.86E-03
Th-0.1-c5	Citrate-500 µmol	3.40	1.86E-03
Th-0.1-o1	Oxalate-100 µmol	3.43	1.96E-03
Th-0.1-o2	Oxalate-200 µmol	3.41	1.98E-03
Th-0.1-o5	Oxalate-500 µmol	3.37	2.09E-03
Th-0.1-e1	EDTA-100 µmol	3.41	2.01E-03
Th-0.1-e2	EDTA-200 µmol	3.42	1.90E-03
Th-0.1-e5	EDTA-500 µmol	3.43	2.00E-03
Th-0.1-pH4	Ligand-free	4.07	8.55E-07
Th-0.1-c1	Citrate-100 µmol	3.85	3.19E-06
Th-0.1-c2	Citrate-200 µmol	3.99	9.90E-07
Th-0.1-c5	Citrate-500 µmol	3.94	1.36E-06
Th-0.1-o1	Oxalate-100 µmol	4.12	1.36E-07
Th-0.1-o2	Oxalate-200 µmol	4.05	2.80E-07
Th-0.1-o5	Oxalate-500 µmol	3.91	1.45E-06
Th-0.1-e1	EDTA-100 µmol	3.99	7.21E-07
Th-0.1-e2	EDTA-200 µmol	3.89	2.48E-06
Th-0.1-e5	EDTA-500 µmol	4.04	4.48E-07
Th-0.1-pH6	Ligand-free	5.34	4.31E-09
Th-0.1-c1	Citrate-100 µmol	6.07	1.87E-09
Th-0.1-c2	Citrate-200 µmol	6.37	1.70E-09
Th-0.1-c5	Citrate-500 µmol	6.23	1.33E-09
Th-0.1-o1	Oxalate-100 µmol	6.22	1.17E-09
Th-0.1-o2	Oxalate-200 µmol	5.98	8.20E-10
Th-0.1-o5	Oxalate-500 µmol	5.98	9.01E-10
Th-0.1-e1	EDTA-100 µmol	6.22	1.79E-09
Th-0.1-e2	EDTA-200 µmol	6.34	1.70E-09
Th-0.1-e5	EDTA-500 µmol	6.23	4.31E-09
Th-0.1-pH7	Ligand-free	7.10	N.D
Th-0.1-c1	Citrate-100 µmol	6.72	4.38E-09
Th-0.1-c2	Citrate-200 µmol	7.14	1.63E-09
Th-0.1-c5	Citrate-500 µmol	6.83	1.04E-09
Th-0.1-o1	Oxalate-100 µmol	7.20	3.22E-08
Th-0.1-o2	Oxalate-200 µmol	7.41	8.89E-09
Th-0.1-o5	Oxalate-500 µmol	7.06	2.49E-09
Th-0.1-e1	EDTA-100 µmol	7.20	1.24E-09
Th-0.1-e2	EDTA-200 µmol	7.16	9.90E-10
Th-0.1-e5	EDTA-500 µmol	6.73	2.68E-09

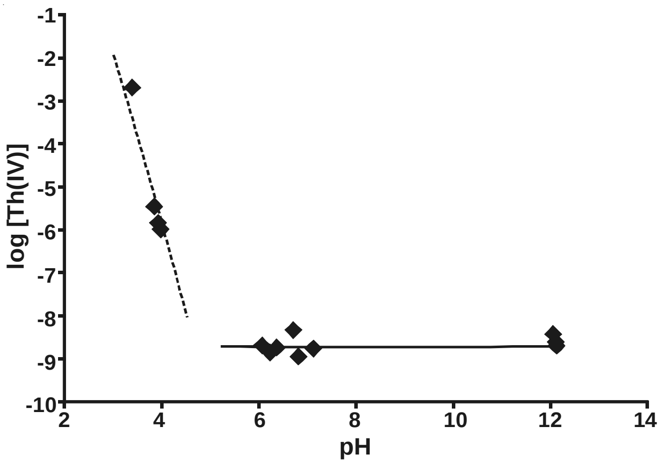
Sample No.	Organic ligand	pH	Th-Concentration (mol/Kg H_2O)
Th-0.1-pH12	Ligand-free	12.29	9.09E-09
Th-0.1-c1	Citrate-100 µmol	12.06	3.67E-09
Th-0.1-c2	Citrate-200 µmol	12.12	2.36E-09
Th-0.1-c5	Citrate-500 µmol	12.14	1.98E-09
Th-0.1-o1	Oxalate-100 µmol	12.22	1.33E-09
Th-0.1-o2	Oxalate-200 µmol	12.14	1.58E-09
Th-0.1-o5	Oxalate-500 µmol	12.07	1.61E-09
Th-0.1-e1	EDTA-100 µmol	12.28	1.73E-09
Th-0.1-e2	EDTA-200 µmol	11.95	1.48E-09
Th-0.1-e5	EDTA-500 µmol	12.19	2.29E-09



(A)

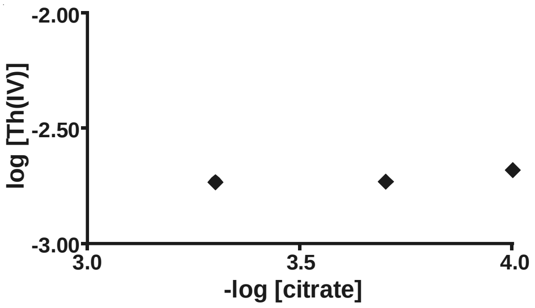


(B)

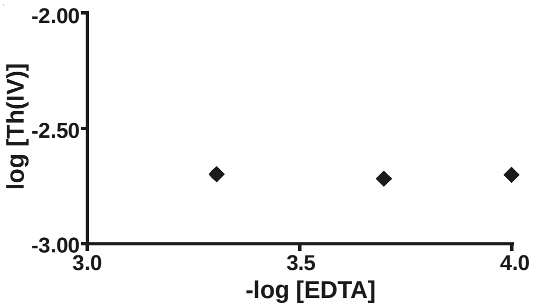


(C)

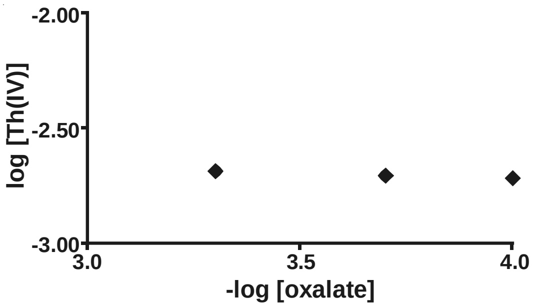
Fig. 4. Plots of log [Th(IV)] *vs.* pH for 0.1 mol/kg $NaNO_3$ solutions in equilibrium with solid ThO_2 at 23°C. Experimental data represented by the triangles, squares and diamonds are depicted for solutions with 100, 200 and 500 µmol/kg of (A) citrate, (B) EDTA and (C) oxalate. The dotted lines represent fits to slope -4 and to slope 0 to illustrate how close the experimental data conform to these slopes



(A)



(B)



(C)

Fig. 5. Plots of ThO_2 solubility dependence on organic ligands at pH3 for solutions with 100, 200 and 500 µmol/kg of (A) citrate, (B) EDTA and (C) oxalate. The effects of organic ligands on solubility appear to be insignificant at this pH implying that Th must be hydrolyzed to a substantial degree

Slopes of straight lines fit to plots of log m_{Th} *vs.* pH (Fig. 4) are *ca.* -4 at the acidic region and near 0 at neutral and alkaline region for experiments conducted at constant ionic strength (I = 0.1) implying that the dominant Th species should be Th^{4+} and $Th(OH)_4^0$ as follows:

$$ThO_2 + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O \quad (2)$$

$$ThO_2 + 2H_2O \rightleftharpoons Th(OH)_{4(aq)} \quad (3)$$

The pH-dependence of ThO_2 solubility in the solutions containing organic ligands is very similar to that obtained in the absence of organic ligands. This could indicate that the predominant dissolved Th species in the organic ligand-bearing solutions are bound by several hydroxide ions in addition to an organic ligand. In other words, the species are likely to be highly hydrolyzed and of the form $Th(OH)_nL_m^q$, where L is one of the organic ligands and q is the overall charge on the complex.

Fig. 5 shows the different plots of ThO_2 solubility in the presence of various organic ligands from 100-500 µmol kg^{-1} concentrations at constant pH (pH = 3). The effects of organic ligands including EDTA, citrate and oxalate on solubility appear to be insignificant at this pH. This further suggests that Th must be hydrolyzed to a substantial degree. Also, no free ligand or metal complexes were observed in the samples taken from the selected runs. This implies that organic ligands were strongly adsorbed onto the solid material.

The results are consistent with literature data at 0.1 M ionic strength for ThO_2 (am) oxide in the acidic pH region where the Th^{4+} is the predominant aqueous specie and the slope of a straight line *ca.* -4 was confirmed (Fig. 6). Slight differences can be attributed degree of crystallinity in the starting material. It has been observed that at low pH, the solubility of

ThO_2 strongly depends on the crystallinity of the solid. Indeed, differences in the solubility of several orders of magnitude have been found between freshly precipitated amorphous and well-crystalline solids . In more alkaline solutions, all the data available in the literature[4,8] as well as this work have been limited by the capabilities of the analytical instruments available. The solubilities of both amorphous and crystalline Th oxide data measured in the laboratory at pH > 6 have been found in the range of 10^{-7} M > [Th] > 10^{-10} M. Therefore, it may be safe to assume that the solubility of Th oxide is independent of bulk crystallinity of the starting material in this pH range.

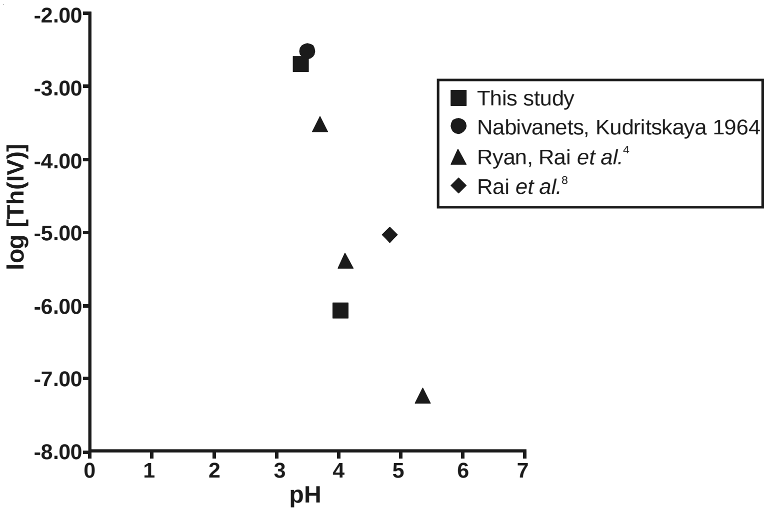


Fig. 6. Plots of the comparison of present study results with literature data at 0.1 m ionic strength for ThO_2(am) oxide in the acidic pH region

Conclusion

In summary, the results of the present study confirm the strong dependence of amorphous Th oxide solubility on pH in acidic conditions. The solubility of ThO_2 does not show any significant dependence on the concentration of the investigated organic ligands to derive consequential thermodynamic data. The reason that there are no thorium organic complexes inferred in this study is due to the fact that the total ligand concentration in solution could be less than for the overall designs of the experiments because of adsorptive losses. Therefore, higher concentrations of organic ligands should be employed in future experimental studies to fully investigate the effects of these ligands on the Th speciation and mobility in geological environments.

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