

Experimental measurements of the solubility of ThO₂ in NaNO₃ solutions: Hydrolysis of Th(IV) and complexation by organic ligands

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To establish the effect of pH and organic ligands on the hydrolysis of Th(IV), experiments on the solubility of ThO₂ were designed at room temperature, over a wide range of pH (pH = 3.0 to 10.0) in 0.1 molal NaNO₃ solutions. Experiments also were conducted in the presence of citrate, EDTA and oxalate with a concentration range 100 to 500 μmol. Data on the hydrolysis of Th(IV) and solubility of the ThO₂ in the presence of organic ligands are of critical importance to the safe disposal and treatment of high-level nuclear waste. Such data are required to reliably predict thorium behavior in high-level waste repositories where organic anions may be present. In addition, Th(IV) is considered to be a chemical analogue of other tetravalent actinides such as Pu(IV).

ThO₂ was synthesized from Th(NO₃)₄·5H₂O by the method of Östhols et al. (1994). The solid ThO₂ was then characterized by powder X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), before the experiments. According to the XRD data, our ThO₂ yielded diffraction patterns in between the amorphous and microcrystalline states.

Approach to equilibrium was from supersaturation. Aliquots of samples were periodically collected at various pH and centrifuged at 6000rpm for 25 minutes. Amicon Centricon-30 filters (30,000 MW cutoff) by Millipore corporation were used to determine the thorium concentration in the aqueous phase. Solubilities obtained at pH 3 in the presence of organic ligands are:

	citrate	EDTA	oxalate
100μM	2.08E-03	2.01E-03	1.96E-03
200μM	1.86E-03	1.90E-03	1.98E-03

The solubility of ThO₂ does not appear to be a sensitive function of the concentration of the investigated organic ligands at pH = 3.0. 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. Experiments involving organic ligands at higher concentrations and pH are still in progress.