

Project 86753
The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration
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RESULTS TO DATE: *Please also see emailed Progress Report to Roland Hirsch.

Research Objectives:

The objective of this research project is to develop the necessary thermodynamic data, including aqueous phase stability constants and Pitzer ion-interaction parameters, to predict the changes in the aqueous phase chemistry that occur when high ionic strength, highly basic tank wastes enter the vadose zone.

Research Progress and Implications:

Polymerization Behavior of Silicic Acid

The presence of considerable amounts of silicic acid in natural waters may be a cause for the migration of radionuclides into natural waters and the environment from waste depository sites. This has stimulated interest in studying the complexation behavior of silicate with the radionuclides likely to be present at the disposal sites of wastes from treatment processes of nuclear weapons and nuclear reactor fuel. As a consequence, stability constants of the complexes of 5f element cations and silicate anions may be necessary parameters in modeling the behavior of actinides in the environment of waste disposal sites. Experiments were carried out on the polymerization of silicic acid to better understand its behavior under different experimental conditions of pH, temperature, silicic acid concentrations and aging time. The effect of pH on the change in o-silicic acid concentration for various aging times in solutions having an initial concentration of o-Si(OH)₄ of 0.025M in a medium of fixed ionic strength of 0.2M (NaClO₄) at 25C was measured. The rate of polymerization was slow at low and high pH, reaching a maximum in the range of pH 6-8. The rate of polymerization was found to increase with temperature and aging times and the data was consistent with second order kinetics. The values of the polymerization rate constant (k) at different temperatures were found to decrease with temperature from 10-25C, then increased in the 25-60C temperature range. Such a pattern in the behavior of the rate constants of the polymerization reaction of silicic acid indicates two different mechanisms.

The experimental data on the degree of polymerization (P) of silicic acid against aging time (tag) at varying initial concentration of silicic acid [(SA)_i] at constant pH and temperature has been measured for use in developing a mathematical equation correlating P with tag and (SA)_i which allows prediction of the degree of polymerization of silicic acid at different aging times and different initial silicic acid concentrations.

This polymerization data is being analyzed to fit it with a thermodynamic model using the Pitzer equations reported by Felmy, et al. [1].

U(VI) interaction with o-silicate:

The results on polymerization of silicic acid have provided the conditions for its complexation study with metal ions. Experiments were carried out on complexation behavior of UO₂²⁺ ion with silicic acid from 0.2M NaClO₄ using a solvent extraction technique employing di-2-ethyl hexyl phosphoric acid, (DEHPA, H₂A₂ in dimer form) in heptane. In the lower pH range (1.0 - 2.0), the data was consistent with the stoichiometry of the extracted species as [UO₂(A₂H)] in the organic phase. However, in the higher pH

range (2.50 to 5.0), the slope of log D (distribution ratio) vs pH was less than 1, the D values increased with increased pH and the material balance of activity of ^{233}U had an experimental error limit of < 3%. In the presence of silicic acid, the extraction of $\text{UO}_2(2+)$ ion increased to pH 4.0 and then decreased as the pH increased to 5.0. The D values in presence of silicic acid were found to be smaller than the D values for the extraction of $\text{UO}_2(2+)$ ion in the absence of silicic acid. The experimental results obtained at a pH values of 3.5, 4.0 & 4.4 and $I = 0.2\text{M NaClO}_4$ for varying concentrations of silicic acid (0.025 to 0.075M, freshly prepared from $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) indicated the formation of the 1:1 complex; i.e, $\text{UO}_2\text{OSi}(\text{OH})_3+$. The stability constant values were found to be the same irrespective of pH. Formation of a second complex was observed with the aged (3-5hrs.) silicic acid solutions (>0.05M).

Based on the presence of appreciable concentrations of silicic acid in natural water systems, the magnitude of these constants indicate that in mildly acidic to neutral natural waters, complexation by silicate can be an important factor in the speciation of the uranyl ions.

This research is being conducted by Dr. Dhruva Kumar Singh.

Eu (III) interaction with silicic acid: Europium silicate interaction is being studied from 0.2M NaClO_4 solution at pH of 3.50 and 25C using a solvent extraction technique employing HDEHP as extractant. In the range of 0.001 to 0.01M silicic acid, the data indicated the formation of 1: 1 complex with the 1:1 log stability constant equal to 7.96.

This research is being conducted by Dr. Poonam Thakur.

References: 1. A.R.Felmy, H. Cho, J.M. Rustad and M.J.Mason, (2001). Journal of Solution Chemistry, Vol.30, No. 6, Pages. 509-525.

DELIVERABLES:

Mansuscripts:

(1)Study on Polymerization Behaviour of Silicic Acid, *Geochimica et Cosmochimica Acta* (submitted).

(2)Complexation Study of Uranyl(VI) with Ortho Silicate,*Radiochimica Acta* (to be submitted).

Other products (Presentations) delivered:

(1) "Study on the role of silicate complexes in the migration of radionuclides in environment" presented at the 226th Am. Chem. Soc. meeting in New York, September 2003 in the Division of Nuclear Chemistry and Technology.

(2) "Speciation of UO_2^{2+} and Am^{3+} Ions with Silicic Acid in Aqueous Medium" accepted for presentation in the 227th Am. Chem. Soc. National Meeting scheduled to be held at Anaheim, California on March 28 - April 1, 2004.