Final Report

The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species"

Award Register No. 15023
9/10/02 – 9/14/06

During this contract period, a number of papers were published. The papers prior to this report have been reported in earlier annual reports. This final report covers the 2005 & 2006 publications which have been published as well as the last few which have been submitted, but are still under review for acceptance for publication. The titles and Abstracts of the papers are presented in Section A, and the full published papers in Section B.

Section A.
Abstracts of Published and Submitted Papers

Complexation / speciation studies of Ni^{2+} ion with ortho silicic acid in perchlorate media

P. N. Pathak and G. R. Choppin

Department of Chemistry and Bio-chemistry, The Florida State University, Tallahassee, FL-32306, USA

(Received May 17, 2005)

Abstract

The complexation behavior of Ni^{2+} with *ortho*-silicic acid (*o*-SA) has been studied as a function of ionic strength (I) from 0.20 to 1.00M ($NaClO_4$) at pcH 4.55±0.05 and 25°C by a solvent extraction technique with bis(2-ethylhexyl) phosphoric acid (HDEHP) as the extractant. The stoichiometry of the extracted species was determined to be $Ni(DEHP)_2(HDEHP)_2$. Ni^{2+} forms a 1:1 complex, $Ni(OSi(OH)_3)^+$, as the predominant species with concentrations of 1.00×10^{-3} to 1.00×10^{-2}M *o*-SA. The stability constant (log β_1) values for $Ni(OSi(OH)_3)^+$ complex formation decrease with increased ionic strength. These values have been fitted with the extended Debye-Huckel expression to obtain the value of log $\beta_1 = 6.34 \pm 0.03$ at I = 0.00M. The data allowed the calculation of speciation of the Ni^{2+}- silicate system as a function of ionic strength.

Complexation Studies of Co^{2+} ion with Orthosilicic Acid

P. N. Pathak and G. R. Choppin

Department of Chemistry and Bio-chemistry, The Florida State University, Tallahassee, FL-32306, USA

(Received June 6, 2005)

Abstract

The complexation behavior of Co^{2+} with *ortho*-silicic acid (*o*-SA) has been studied as a function of ionic strength (I) from 0.20 to 1.00M ($NaClO_4$) at pH 4.96±0.03 and 25°C by a solvent extraction technique with bis(2-ethylhexyl) phosphoric acid (HDEHP) as the extractant. The stoichiometry of the extracted species was determined to be $Co(DEHP)_2(HDEHP)_2$. Co^{2+} forms a 1:1 complex, $CoOSi(OH)_3^+$, as the predominant species with *o*-SA concentrations of 3.00×10^{-4} to 4.00×10^{-3}M. The stability constant (log β_1) values for $CoOSi(OH)_3^+$ complex decrease with increase in ionic strength. These values were fitted with the extended Debye-Huckel expression to obtain the value of log β_1 at I = 0.00M. The effect of aging time of the *o*-SA solution on log β_1 values for $CoOSi(OH)_3^+$ complex was investigated and compared with those of the $UO_2OSi(OH)_3^+$ complex.

Sorption Studies of europium(III) on hydrous silica

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL-32306, USA

(Received September 22, 2005)

Abstract

Sorption behavior of europium, Eu^{3+}, on $SiO_2.xH_2O$ (silica gel) has been investigated as a function of time, the amount of silica gel, Eu^{3+} concentration, the ionic strength, and pH (in absence and in presence of carbonate). The sorption data were fitted to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. The sorption capacity of silica gel was determined to be in the range 2.62-8.00($\times 10^{-7}$) mol/g at pH 5.30±0.05 and 0.20M $NaClO_4$. The mean energy of sorption was calculated to be 13.50±0.05 kJ/mol from the D-R isotherm, suggesting the involvement of ion exchange reactions in the sorption process. Sorption of Eu^{3+} decreased with increased ionic strength. A gradual decrease in pH with increased ionic strength supports the involvement of an ion exchange mechanism in the sorption process. The diffusion coefficient of Eu^{3+} ion on silica gel was calculated as $3.98(\pm 0.12)\times 10^{-13} m^2 s^{-1}$ under the particle diffusion-controlled conditions.

Kinetic and thermodynamic studies on cesium(I) sorption on hydrous silica

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University,

(Received December 13, 2006)

Abstract

Batch sorption experiments of cesium, Cs^+, on $SiO_2.xH_2O$ (silica gel) have been conducted with variable times of equilibration, amounts of silica gel (0.10-1.00 g), cesium concentrations (5.00×10^{-5} -2.40×10^{-3} M), ionic strengths (0.20-1.40 M $NaClO_4$), pH's (2.50 to 7.70), and temperatures (273 to 333 K). The diffusion coefficient of Cs^+ ion was calculated to be $9.19(\pm 0.86)\times 10^{-11}$ $m^2 sec^{-1}$ under particle diffusion-controlled conditions. The sorption rate was $3.94(\pm 0.65)\times 10^{-3}$ sec^{-1} at 298 K, pH 7.70(±0.05) in 0.20 M $NaClO_4$. The sorption data fits the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. Cesium sorption on 0.20 g silica gel decreased with ionic strength from 40.42(±0.34)% in 0.20 M $NaClO_4$ to 6.35(±0.40)% in 1.40 M $NaClO_4$, at $pH_{(initial)}$ 8.20(±0.05). A gradual decrease in pH with increased ionic strength is consistent with a cation exchange mechanism. Sorption of Cs^+ on silica gel decreased with increased temperature, indicating an exothermic enthalpy. The presence of anions such as fluoride, carbonate, phosphate and oxalate in the aqueous medium did not influence the cesium sorption profile.

Nickel(II) sorption on hydrous silica: A kinetic and thermodynamic study

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL-32306, USA

(Received October 20, 2005)

Abstract

Sorption of nickel, Ni^{2+}, on $SiO_2.xH_2O$ (silica gel) has been studied as a function of time, amount of silica gel (0.10-1.00 g), nickel concentration (5.00×10^{-5} -1.20×10^{-3} M), ionic strength (0.20-1.40 M $NaClO_4$), pH (6.50 to 8.50), and temperature (273-318 K). From kinetic data, the diffusion coefficient of Ni^{2+} ion was calculated to be $1.28(\pm 0.07) \times 10^{-11}$ $m^2 sec^{-1}$ under particle diffusion-controlled conditions. The sorption rate was determined as $3.79(\pm 0.35) \times 10^{-3}$ sec^{-1} at 298 K, pH 8.40 in 0.20 M ($NaClO_4$). The sorption data were fitted to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. Nickel sorption on 0.20 g silica gel decreased with ionic strength from 77.70(±0.70)% (0.20 M $NaClO_4$) to 16.12(±0.37)% (1.40 M $NaClO_4$) at pH (initial) 8.50(±0.05). A gradual decrease in pH with increased ionic strength suggests an ion exchange mechanism. Sorption of Ni^{2+} on silica gel increased with temperature indicating an endothermic enthalpy. The effect of different ligands such as fluoride, carbonate, phosphate and oxalate on Ni^{2+} sorption on silica gel was studied.

Thermodynamic study of metal silicate complexation in perchlorate media

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(Received August 18, 2005)

Abstract

The thermodynamic parameters of formation of the *o*-silicate complexes of UO_2^{2+}, Cm^{3+} and Eu^{3+} have been measured in the temperature range 5 – 45°C in an aqueous medium of 0.20M ($NaClO_4$) ionic strength. Solvent extraction with bis(2-ethylhexyl) phosphoric acid (HDEHP) was used to measure the stability constant (log β_1) values of the silicate complexes as a function of temperature to obtain the enthalpies and entropies of complexation. The complexation reactions are entropy driven and opposed by the enthalpy. These thermodynamic values are consistent with the formation of an inner sphere complex.

Kinetics and thermodynamics of cobalt(II) sorption on hydrous silica

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry,The Florida State University, Tallahassee, FL-32306, USA

(*Accepted for publication in J. Radioanal. Nucl. Chem.)

Abstract

Sorption of Co^{2+} on $SiO_2.xH_2O$ (silica gel) has been investigated as a function of time, amount of silica gel (0.10-1.00g), cobalt concentration (5.00×10^{-5} -1.20×10^{-3} M), ionic strength (0.20-1.40 M $NaClO_4$), pH (~6.80-10.80), and temperature (273-318 K). Based on kinetic studies, the diffusion coefficient of Co^{2+} ion was calculated to be $6.86(\pm0.44)\times10^{-12}$ m^2sec^{-1} under particle diffusion-controlled conditions. The sorption rate was determined to be $2.61(\pm0.19)\times10^{-3}$ sec^{-1} at 298 K, pH 6.70(±0.05) and 0.20 M $NaClO_4$ using the Lagergren equation. The sorption data were fitted to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. Cobalt sorption decreased with increased ionic strength. A gradual decrease in pH with increased ionic strength supported the sorption of Co^{2+} by an ion exchange mechanism. Effect of different ligands such as CO_3^{2-}, F^-, $H_2PO_4^-$ and $C_2O_4^{2-}$ on the sorption of Co^{2+} was studied in the pH range 6.50 to 8.50. Temperature variation experiments gave an endothermic enthalpy for sorption of cobalt on silica gel which becomes more spontaneous as the temperature increases.

Sorption of Am^{+3} Cations on Suspended Silicate: Effects of pH, Ionic Strength, Complexing Anions, Humic Acid and Metal Ions

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(*Submitted: Inorg. Chim. Acta)

Abstract

Sorption of tracer Am^{+3} to silicate particles was studied as a function of pcH (4 to 9) and of ionic strength (0.20 M to 1.50 M ($NaClO_4$ at 298 K. The sorption increased with increased pcH from 4 to 6 above which saturation was observed. The insensitivity of Am^{+3} sorption to increased ionic strength indicates inner-sphere complexation with the surface silicate sites. The effects of different complexing anions such as carbonate, acetate, oxalate, phosphate, citrate, EDTA and hunfic acid, on Am^{+3} sorption were investigated. Synergistic enhancement in Am^{+3} sorption was observed in the presence of phosphate ($4 \leq$ pcH ≤ 7) and acetate ($4 \leq$ pciH ≤ 5) ligands at 0.20 M ($NaClO_4$) The presence of the other ligands inhibited Am^{+3} sorption in the order: EDTA > citrate> oxalate> carbonate. Am^{+3} sorption in the presence of HA (25.00 mglL) increased in the pcH range of 4.0 to 5.5, then decreased. Increased ionic strength enhanced Am^{+3} sorption in the presence of 25.00 mg/L HA for $4 \leq$ pcH ≤ 9. The sorption increased in the presence of a mixture of HA (25.00 mg/L) and phosphate ($1 .00 \times 19^{-3}$ M) as compared to that of HA (25.00 mg/L) alone. The presence of Fe^{3+} ($1 .00\times10^{-3}$ M) enhanced Am^{+3} sorption at pcH ~ 4 but suppressed it from pcH of 5 to 9; $1 .00 \times 10^{-4}$ M of Ca^{2+} and of UO_2^{2+} ions had no effect on the sorption profile.

Sorption of Neptunyl(V) Cations on Suspended Silicate: Effects of pH, Ionic Strength, Complexing Anions, Humic Acid, and Metal Ions

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(Submitted: J. Radioanal. Nucl. Chem.)

Abstract

Sorption of NpO_2^+ on silicate (10.00 gIL) particles dispersed in sodium perchiorate media was studied as a function of pcH and ionic strength at 298 K. The sorption increased with increased pcH in the range of ~ 6.5 to 9.2, above which saturation was observed. An increase in ionic strength from 0.20 M to 1.00 M ($NaClO_4$) increased the NpO_2+ sorption, which then decreased at 1.50 M ($NaClO_4$) for 7 < pcH < 8.5. The effects of different types of ligands on the sorption of NpO_2^+ to suspended silicate were investigated. The types of ligands included: (i) inorganic anions (fluoride, carbonate, phosphate) (ii) N-donors (ethylenediamine, 1,10 phenanthroline) (iii) carboxylic acids (oxalic acid, citric acid, iminodiacetic acid, ethylenediaminetetraacetic acid) and (iv) humic acid. A synergistic enhancement in sorption to the suspended silicate was observed for phosphate, oxalate, ethylenediaminetetraacetic acid, ethylenediamine, 1,10 phenanthroline (5 < pcH < 8) and humic acid (6.5 < pcH < 8.8). This behavior was attributed to the formation of ternary NpO_2^+ /silicate/ligand complexes. The effects of Ca(II) ($I.00 \times 10^{-3}$ M) and Eu(III) (1.00×10^{-4} and $I .00 \times 10^{-3}$ M) ions on NpO_2^+ sorption to suspended silicate were also investigated.

Polymerization and complexation behavior of silicic acid:a review

G. R. Choppin, N. Pathak and P. Thakur

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

Abstract

The role of dissolved silica (silicic acid) in the migration of radionuclides has been of interest for several decades. Studies have shown that the interaction of silicic acid with the metal cations is complicated due to a tendency to polymerize which is dependent on pH, ionic strength, temperature, etc. of the system. While polymerization of silicic acid has been studied in detail, uncertainty remains on the effect of these changes on cations in environmental systems. The nature and the role of silicate species in the environmental behavior of cationic radionuclides is the focus of this review. The interaction of metal cations such as UO_2^{2+} Eu^{3+} Cm^{3+} and Cu^{2+} with polymeric silica is discussed. The effects of different experimental parameters (e.g., pH, ionic: strength, temperature, acids, fluoride and hydroxyl anions, organic compounds, etc.) on the polymerization behavior of silicic acid are reviewed. Monomeric silicic, acid is most stable at ca. pH 2 and most unstable at pH 7-8. Polymerization increases with increased ionic strength, temperature, and the aging time of the silicic acid solutions. Hydroxyl and fluoride ions catalyze the polymerization of silicic acid. The presence of metal ions, (e.g., aluminium, beryllium, thorium and iron) inhibits the polymerization process through complexation with hydroxyl and fluoride ions.

Effect of complexing anions on europium sorption on suspended sifica: A TRLFS study for ternary complex formation

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(Submitted: Radiochimica Acta)

Abstract

The sorption of europium, Eu(III), on suspended silica was studied in perchlorate media under varying concentrations of Eu(III) and silica, at pH 4 to 8, and ionic strength from 0.20 to 1.40 M $NaClO_4$ at 298 K. The complexing anions, carbonate, acetate, citrate, oxalate, phosphate and EDTA, affected the sorption of Eu(III). A synergistic enhancement in the sorption of Eu(III) was observed for oxalate and phosphate ligands. Other anions suppressed the sorption in the order: acetate <carbonate < citrate < EDTA. The results of TRLFS studies were consistent with ternary Eu/silica/ligand complexation for oxalate and phosphate anions.

Silicate complexation of NpO_2^+ ion in perchlorate media

P. N. Pathak and G. R. Choppin

Department of Chemistry and Bio-chemistry, The Florida State University, Tallahassee, FL-32306, USA

(Submitted: J. Radiochimica Acta)

Abstract

Complexation behavior of NpO_2^+ with *ortho*-silicic acid (*o*-SA) has been studied at ionic strengths (I) from 0.10 to 1.00 M ($NaClO_4$) at pcH 3.68±0.08 and 25°C using solvent extraction with bis-(2-ethylhexyl) phosphoric acid (HDEHP) as the extractant. The stability constant value (log β_1) for the 1:1 complex, $Np0_2(OSi(OH)_3)$, were found to decrease with increase in ionic strength of the aqueous phase [6.83±0.01 at I=0.10M to 6.51±0.02 at I=1.00 M]. These values have been fitted with the extended Debye-Huck expression and compared with similar values of complexation of the metal ions Am^{3+}, Eu^{3+}, UO_2^{2+}, $Pu0_2^{2+}$, Np^{4+}, Ni^{2+}, and Co^{2+}. The speciation of NpO_2^+ -*o*-silicate/carbonate system has been calculated as a function of pcH under ground water conditions.

Sorption of Uranyl(VI) Cations on Suspended Silicate: Effects of N-donors Ligands, Carboxylic Acids, Humic Acid, Metal Ions and Organic Cosolvents

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(Submitted: Radiochimica Acta)

Abstract

Sorption of uranyl ion, UO_2^{2+} on silicate particles (3.00 gIL) was studied in sodium perchiorate solution as a function of pcH and ionic strength at 298 K. The effects of different ligand types (e.g. N-donors, carboxylic acids, humic acid) on the uranyl sorption were investigated. A synergistic enhancement in uranyl sorption was observed in the presence of the N-donor ligands such as 1,10 phenanthroline, ethylenecliamine and humic acid in the pcH range 3 to 4. Carboxylic acids inhibited the sorption in the order: citric acid> malonic acid> nitrilotriacetic acid> iminodiacetic acid> sulfosalicylic acid > succinic acid > glycolic acid. The presence of organic cosolvents such as dimethylsulfoxide, glycerol and tetrahydrofuran had no significant influence on the uranyl sorption profile. Uranyl sorption decreased marginally in the presence of $1.00x10^{-3}$ M Eu(III).

Sorption of uranyl ion on hydrous silica: effects of ionic strength and ethylenediaminetetraacetic acid (edta)

P. N. Pathak and G. R. Choppin

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, FL-32306, USA

(Submitted: Radiochimica Acta)

Abstract

The effects of ionic strength and of ethylenediaminetetraacetic acid (EDTA) on the sorption of uranyl ion, UO_2^{2+} to $Si0_2xH_2O$ (silica gel) were investigated. It was observed that pH and the ions present in the supporting electrolytes influence the ionic strength effects. The presence of different sodium salts in the concentration range (0.20 to 1.40 M) suppressed the sorption of UO_2^{2+} in the order: $NaNO_3 < NaClO_4 < NaCl < NaOCOCH_3 < NaSO_4$ (pH 2.75(±0.05)), while the presence of perchlorate salts of Li^+, Na^+ and Ca^{2+} (0.20 to 1.40 M) promoted the sorption of UO_2^{2+} on silica gel in the order: $LiClO_4 \sim NaClO_4 < Ca(ClO_4)_2$ at pH 2.80(±0.05). The ionic strength effect on UO_2^{2+} sorption was studied in presence of EDTA ($0-1.00x10^{-3}$ M) in the pH range 2.90 to 5.57. The sorption data and speciation calculation suggest negligible complexation of UO_2^{2+} with EDTA at $I \geq 1.00$ M $NaC1O_4$

Polymerization study of o-$Si(OH)_4$ and complexation with Am(II), Eu(III) and Cm(III)

P. Thakur, D.K. Singh and G. R. Choppin

Department of Chemistry & Biochemistry, The Florida State University, Tallahassee, FL- 32306, USA

(Submitted: Inorg. Chim. Acta)

Abstract

The formation of 1:1 complexes of Am^{3+}, Cm^{3+}, and Eu^{3+} with ortho- silicate, o-OSi(OH)f, at pcH 3.50 in ionic strengths of 0.20 tol .00 M (NaC1O was studied by solvent extraction with di-(2-ethylhexyl) phosphoric acid (HDEHP) in heptane as extractant. The stability constant (log j values decrease with increased ionic strength from 0.20 to 1.00 M (NaClO for silicic acid concentrations from 0.002 to 0.02 M. The extended Debye—Huckle expression was used to analyze these values of the log values to calculate the stability constants at 1=0 (IV!). Increasing the concentration of silicic acid above 0.02 M increased the amount of M extracted into the organic phase, contrary to the trend usually observed for increased ligand concentration in solvent extraction. This reversed trend is likely due to the extraction of cationic species of silicic acid by HDEHP. Aging time (60 to 300 mm) had no effect on the stability constant of these metal ions for 0.002-0.02 M silicic acid at pcH 3.50 and 1= 0.20 M (NaClO The fraction of polymeric silicic acid present in solutions of 0.20 to 4.50 M $NaClO_4$ solutions at pcH 3.0 to 10.0, T=0-60°C and aging time = 5 to 300 min. was measured for determination of the siliconmolydate reactions to ascertain the proper conditions to study metal + o – silicate complexation.

Section B.

Published Papers

Publications

Complexation / speciation studies of Ni^{2+} ion with ortho silicic acid
in perchlorate media,
P. N. Pathak and G. R. Choppin, **J. Radioanalyt. and Nucl. Chem., 267, No. 1; 175-182 (2006)**

Complexation Studies of Co^{2+} ion with Orthosilicic Acid,
P. N. Pathak and G. R. Choppin, **J. Radioanal. Nucl. Chem., 267, No. 2; 309 -314 (2006)**

Sorption Studies of europium(III) on hydrous silica,
P. N. Pathak and G. R. Choppin, **J. Radioanal. Nucl. Chem., 270, No. 2; 277-283, (2006)**

Kinetic and thermodynamic studies on cesium(I) sorption on hydrous silica,
P. N. Pathak and G. R. Choppin, **J. Radioanal Nucl. Chem., 270, No. 2; 299-305 (2006)**

Nickel(II) sorption on hydrous silica: A kinetic and thermodynamic study,
P. N. Pathak and G. R. Choppin, **J. Radioanal Nucl. Chem., Vol. 268, No.3; 467-473 (2006)**

Thermodynamic study of metal silicate complexation in perchlorate media
P. N. Pathak and G. R. Choppin, **Radiochim. Acta 94, 81-86 (2006)**

Kinetics and thermodynamics of cobalt(II) sorption on hydrous silica
P. N. Pathak and G. R. Choppin, **accepted for publication in J. Radioanal. Nucl. Chem.**

Sorption of Am^{+3} Cations on Suspended Silicate: Effects of pH, Ionic Strength,
Complexing Anions, Humic Acid and Metal Ions
P. N. Pathak and G. R. Choppin, **(submitted: Inorg. Chim. Acta)**

Sorption of Neptunyl(V) Cations on Suspended Silicate: Effects of pH, Ionic
Strength, Complexing Anions, Humic Acid, and Metal Ions
P. N. Pathak and G. R. Choppin, (submitted: J. Radioanal. Nucl. Chem.)

Polymerization and complexation behavior of silicic acid:a review
G. R. Choppin, N. Pathak and P. Thakur

Effect of complexing anions on europium sorption on suspended sifica:
A TRLFS study for ternary complex formation
P. N. Pathak and G. R. Choppin, **(submitted: Radiochimica Acta)**

Silicate complexation of NpO_2^+ ion in perchlorate media
P. N. Pathak and G. R. Choppin, **(submitted: J. Radiochimica Acta)**

Sorption of Uranyl(VI) Cations on Suspended Silicate: Effects of N-donors Ligands, Carboxylic Acids, Humic Acid, Metal Ions and Organic Cosolvents
P. N. Pathak and G. R. Choppin, **(submitted: Radiochimica Acta)**

Sorption of uranyl ion on hydrous silica: effects of ionic strength and ethylenediaminetetraacetic acid (edta)
P. N. Pathak and G. R. Choppin, **(submitted: Radiochimica Acta)**

Polymerization study of o-$Si(OH)_4$ and complexation with Am(II), Eu(III) and Cm(III)
P. Thakur, D.K. Singh and G. R. Choppin, **(submitted: Inorg. Chim. Acta)**