Final Report

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

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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

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(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 pH 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 1.00x10\(^{-5}\) to 1.00x10\(^{-2}\)M o-SA. The stability constant (log \(\beta_1\)) 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±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

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(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 3.00x10\(^{-4}\) to 4.00x10\(^{-2}\)M. The stability constant (log \(\beta_1\)) 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 \(\beta_1\) at I = 0.00M. The effect of aging time of the o-SA solution on log \(\beta_1\) values for CoOSi(OH)\(_3\))\(^+\) complex was investigated and compared with those of the UO\(_2\)OSi(OH)\(_3\))\(^+\) complex.
Sorption Studies of europium(III) on hydrous silica

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(Received September 22, 2005)

Abstract

Sorption behavior of europium, Eu$^{3+}$, on SiO$_2$.xH$_2$O (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($\times 10^{-3}$) 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(±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

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(Received December 13, 2006)

Abstract

Batch sorption experiments of cesium, Cs$^+$, on SiO$_2$.xH$_2$O (silica gel) have been conducted with variable times of equilibration, amounts of silica gel (0.10-1.00 g), cesium concentrations (5.00$\times 10^{-6}$-2.40$\times 10^{-3}$ 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(±0.86)$\times 10^{-11}$ m$^2$sec$^{-1}$ under particle diffusion-controlled conditions. The sorption rate was 3.94(±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

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(Received October 20, 2005)

Abstract

Sorption of nickel, Ni²⁺, on SiO₂·xH₂O (silica gel) has been studied as a function of time, amount of silica gel (0.10-1.00 g), nickel concentration (5.00x10⁻⁶ -1.20x10⁻⁵ M), ionic strength (0.20-1.40 M NaClO₄), pH (6.50 to 8.50), and temperature (273-318 K). From kinetic data, the diffusion coefficient of Ni²⁺ ion was calculated to be 1.28(±0.07)x10⁻¹¹ m² sec⁻¹ under particle diffusion-controlled conditions. The sorption rate was determined as 3.79(±0.35)x10⁻³ sec⁻¹ at 298 K, pH 8.40 in 0.20 M (NaClO₄). 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 NaClO₄) to 16.12(±0.37)% (1.40 M NaClO₄) at pH (initial) 8.50(±0.05). A gradual decrease in pH with increased ionic strength suggests an ion exchange mechanism. Sorption of Ni²⁺ on silica gel increased with temperature indicating an endothermic enthalpy. The effect of different ligands such as fluoride, carbonate, phosphate and oxalate on Ni²⁺ sorption on silica gel was studied.

Thermodynamic study of metal silicate complexation in perchlorate media

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(Received August 18, 2005)

Abstract

The thermodynamic parameters of formation of the α-silicate complexes of UO₂²⁺, Cm³⁺ and Eu³⁺ have been measured in the temperature range 5 – 45°C in an aqueous medium of 0.20M (NaClO₄) ionic strength. Solvent extraction with bis(2-ethylhexyl) phosphoric acid (HDEHP) was used to measure the stability constant (log βₜ) 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

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

Abstract

Sorption of Co²⁺ on SiO₂ ·xH₂O (silica gel) has been investigated as a function of time, amount of silica gel (0.10-1.00 g), cobalt concentration (5.00x10⁻⁵ -1.20x10⁻⁷ M), ionic strength (0.20-1.40 M NaClO₄), pH (-6.80-10.80), and temperature (273-318 K). Based on kinetic studies, the diffusion coefficient of Co²⁺ ion was calculated to be 6.86(±0.44) x 10⁻¹² m²/sec⁻¹ under particle diffusion-controlled conditions. The sorption rate was determined to be 2.61(±0.19) x 10⁻¹⁸ cm²/sec at 298 K, pH 6.70(±0.05) and 0.20 M NaClO₄ 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 Co²⁺ by an ion exchange mechanism. Effect of different ligands such as CO₃²⁻, F⁻, H₂PO₄⁻ and C₂O₄²⁻ on the sorption of Co²⁺ 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 Am³⁺ Cations on Suspended Silicate: Effects of pH, Ionic Strength, Complexing Anions, Humic Acid and Metal Ions

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Abstract

Sorption of tracer Am³⁺ to silicate particles was studied as a function of pH (4 to 9) and of ionic strength (0.20 M to 1.50 M (NaClO₄ at 298 K. The sorption increased with increased pH from 4 to 6 above which saturation was observed. The insensitivity of Am³⁺ 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 humic acid, on Am³⁺ sorption were investigated. Synergistic enhancement in Am³⁺ sorption was observed in the presence of phosphate (4 ≤ pH ≤ 7) and acetate (4 ≤ pH ≤ 5) ligands at 0.20 M (NaClO₄). The presence of the other ligands inhibited Am³⁺ sorption in the order: EDTA > citrate > oxalate > carbonate. Am³⁺ sorption in the presence of HA (25.00 mg/L) increased in the pH range of 4.0 to 5.5, then decreased. Increased ionic strength enhanced Am³⁺ sorption in the presence of 25.00 mg/L HA for 4 ≤ pH ≤ 9. The sorption increased in the presence of a mixture of HA (25.00 mg/L) and phosphate (1.00 x 10⁻³ M) as compared to that of HA (25.00 mg/L) alone. The presence of Fe³⁺ (1.00x10⁻³ M) enhanced Am³⁺ sorption at pH ~ 4 but suppressed it from pH of 5 to 9; 1.00 x 10⁻⁴ M of Ca²⁺ and of UO₂²⁺ 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

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

Abstract

Sorption of NpO$_2^+$ on silicate (10.00 g/L) particles dispersed in sodium perchlorate media was studied as a function of pH and ionic strength at 298 K. The sorption increased with increased pH in the range of 6.5 to 9.2, above which saturation was observed. An increase in ionic strength from 0.20 M (NaClO$_4$) increased the NpO$_2^+$ sorption, which then decreased at 1.50 M (NaClO$_4$) for 7 < pH < 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 < pH < 8) and humic acid (6.5 < pH < 8.8). This behavior was attributed to the formation of ternary NpO$_2^+$/silicate/ligand complexes. The effects of Ca(II) (1.00 x 10$^{-3}$ M) and Eu(III) (1.00 x 10$^{-4}$ and 1.00 x 10$^{-5}$ M) ions on NpO$_2^+$ sorption to suspended silicate were also investigated.

Polymerization and complexation behavior of silicic acid: a review

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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 silica: 
A TRLFS study for ternary complex formation

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(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 NaClO₄ 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 NpO₂⁺ ion in perchlorate media

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(Submitted: J. Radiochemica Acta)

Abstract

Complexation behavior of NpO₂⁺ with ortho-silicic acid (o-SA) has been studied at ionic strengths (I) from 0.10 to 1.00 M (NaClO₄) 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 β₁) for the 1:1 complex, NpO₂(OSi(OH)₃), were found to decrease with increase in ionic strength of the aqueous phase [6.83±0.01 at I=0.10 M 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 Am³⁺, Eu³⁺, UO₂²⁺, PuO₂²⁺, Np⁴⁺, Ni²⁺, and Co²⁺. The speciation of NpO₂⁺-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

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Abstract

Sorption of uranyl ion, UO$_2^{2+}$, on silicate particles (3.00 g/L) was studied in sodium perchlorate solution as a function of pH 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, ethylenediamine and humic acid in the pH 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)

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(Submitted: Radiochimica Acta)

Abstract

The effects of ionic strength and of ethylenediaminetetraacetic acid (EDTA) on the sorption of uranyl ion, UO$_2^{2+}$, to SiO$_2$·H$_2$O (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$_4$ ~ 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 ≥1.00 M NaClO$_4$. 
Polymerization study of o-Si(OH)₄ and complexation with Am(II), Eu(III) and Cm(III)

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Abstract

The formation of 1:1 complexes of Am³⁺, Cm³⁺, and Eu³⁺ with ortho-silicate, o-OSi(OH)₄, at pH 3.50 in ionic strengths of 0.20 to 1.00 M (NaClO₄ was studied by solvent extraction with di-(2-ethylhexyl) phosphoric acid (HDEHP) in heptane as extractant. The stability constant (log β values decrease with increased ionic strength from 0.20 to 1.00 M (NaClO₄ for silicic acid concentrations from 0.002 to 0.02 M. The extended Debye—Huckel 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 min) had no effect on the stability constant of these metal ions for 0.002-0.02 M silicic acid at pH 3.50 and 1= 0.20 M (NaClO₄ The fraction of polymeric silicic acid present in solutions of 0.20 to 4.50 M NaClO₄ solutions at pH 3.0 to 10.0, T=0-60°C and aging time = 5 to 300 min. was measured for determination of the silicon-molydate 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,

Complexation Studies of Co\(^{2+}\) ion with Orthosilicic Acid,

Sorption Studies of europium(III) on hydrous silica,

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

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

Thermodynamic study of metal silicate complexation in perchlorate media

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\(^{13}\) Cations on Suspended Silicate: Effects of pH, Ionic Strength, Complexing Anions, Humic Acid and Metal Ions

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