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Chemical Speciation of Sr, Am and Cm in High Level Waste: predictive modeling of phase partitioning during tank processing

Research Objective and Results:

The objective of this project was to measure the effect of organic chelate complexation on the speciation and solubility of strontium and trivalent actinides under strongly basic, high carbonate conditions, similar to those present in the high level waste (HLW) tanks at the U.S department of energy storage sites. The research has focused on the measurement of complexation of Am (III), Cm (III) and Eu (III) with EDTA, Citrate, IDA, Oxalate (Ox), NTA and DTPA alone and with the mixtures of EDTA+ Citrate, NTA, Ox, and IDA at high ionic strength (5.0 M NaClO₄), p_H 3.60 and at temperatures ranging between 0 to 60°C. In addition, we have addressed the formation of mixed ligand complexes of Eu(III) with EDTA+citrate , NTA, Ox, CDTA+IDA, NTA and Ox and DTPA+IDA and Ox in solutions by TRLFS, NMR and EXAFS spectral studies. The fundamental data on chemical speciation and solubility has been used to develop accurate thermodynamic models, which are valid at HLW tank conditions.

NTA, IDA forms 1:1 and Ox forms both 1:1 and 1:2 complexes with Am(III), Cm(III) and Eu(III) at the temperatures of 0-60°C. The stability constants at different temperatures increase with increased temperature for all the metal ions. The positive values of ΔH and ΔS for the complexation thermodynamics reflect extensive dehydration of metal ions at such high ionic strength. TRLFS and lifetime measurements have confirmed the formation of these complexes.

With mixtures of EDTA+IDA, NTA and Ox these metal ions form ternary complexes. The stability constants of the mixed complex, β_{111} , increase with increasing temperature, with high stability constant values. The enthalpies of ternary complexation are large and positive. The NMR and EXAFS studies gave information about the binding

modes of the ligands in the formation of these complexes and TRLFS studies gave data on the total number of waters of hydration attached to the cations in the formation of these ternary complexes.

Similar studies were done on complexation with CDTA and DTPA as both binary and ternary complexation.

In addition, the sorption of Np(V)O_2^+ and U(VI)O_2^{2+} on hydroxyapatite was studied. For all these studies, the abstracts of the manuscripts submitted for publication and of those accepted for publication as well as of those already published are included in this report as are reprints of the published articles.

Publications

Complexation Thermodynamics and Structural Aspects of Actinide-Aminopolycarboxylates

G.R. Choppin, P. Thakur and J.N. Mathur, **Coord. Chem. Rev.** **250**, 936(2006)

Coordination Modes in the Formation of the Ternary Am(III), Cm(III) and Eu(III) Complexes with EDTA and NTA: TRLFS, ^{13}C NMR, EXAFS, and Thermodynamics of the Complexation

J. N. Mathur, P. Thakur, C. J. Dodge , A. J. Francis and G.R. Choppin, **Inorg. Chem** **45**, 8026 (2006)

Thermodynamics and the structural aspects of the ternary complexes of Am(III), Cm(III) and Eu(III) with Ox and EDTA+Ox.

P. Thakur, J. N. Mathur, C. J. Dodge , A. J. Francis and G.R. Choppin, **J. Chem. Soc. Dalton Trans** **4829** (2006)

Chemical Speciation of Am, Cm and Eu with EDTA at High Ionic Strength: Thermodynamics and Laser Fluorescence Spectroscopy Studies

K. Cernochova, J.N. Mathur and G.R. Choppin, **Radiochim Acta** **93**, 733 (2005)

Sorption of U(VI) species on Hydroxyapatite

P. Thakur, R.C. Moore and G.R. Choppin, **Radiochim Acta** **93**, 385 (2005)

Thermodynamics and Laser Luminescence Spectroscopy of Binary and Ternary Complexation of Am^{3+} , Cm^{3+} and Eu^{3+} with Citric Acid, and Citric Acid + EDTA at High Ionic Strength

J.N. Mathur, K. Cernochova, G.R. Choppin, **Inorg. Chim. Acta** (In press)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am^{3+} , Cm^{3+} and Eu^{3+} with IDA and EDTA+IDA

G.R. Choppin, P. Thakur and J.N. Mathur, **Inorg. Chim. Acta** (In press)

Np(V)O_2^+ sorption on Hydroxyapatite- Effect of Calcium and Phosphate anions.

P. Thakur R.C. Moore and G.R. Choppin, **Radiochim Acta** (In press)

Thermodynamics and the Structure of Binary and Ternary Complexation of Am^{3+} Cm^{3+} and Eu^{3+} with DTPA and DTPA+IDA

G.R. Choppin, P. Thakur and J. N. Mathur , **Chimie** (Submitted)

Thermodynamics and Dissociation Constants of Carboxylic Acids at High Ionic Strength and Temperature

P. Thakur, J.N. Mathur, R.C. Moore and G.R. Choppin, **Inorg. Chim Acta** (Submitted)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am^{3+} , Cm^{3+} and Eu^{3+} with CDTA and CDTA+IDA

P. Thakur, J.N. Mathur and G .R. Choppin, **Inorg. Chim Acta** (submitted)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am^{3+} , Cm^{3+} and Eu^{3+} with CDTA and CDTA+NTA

P. Thakur and G.R. Choppin (**manuscript under preparation**)

Complexation thermodynamics and the structural aspects of the ternary complexes of Am(III) , Cm(III) and Eu(III) with CDTA+Ox and DTPA +Ox.

P. Thakur, C. J. Dodge , A. J. Francis and G.R. Choppin (**manuscript under preparation**)

Complexation Thermodynamics and Structural Aspects of Actinide-Aminopolycarboxylates

G.R. Choppin, P. Thakur and J.N. Mathur

Abstract

The interaction of trivalent actinides with aminopolycarboxylate ligands in aqueous solution is reviewed. The strength of complexation to form binary and ternary complexes is interpreted in terms of cationic hydration and structural effects in the interaction of metal cations with aminopolycarboxylate ligands. The trends in the enthalpies and entropies of complexation of actinide and lanthanide cations are compared and discussed in terms of those effects. The results of the spectral measurements, TRLFS, ^{13}C NMR and EXAFS, provide information on the binding modes and structural aspects of the complexation. These results reflect the progress in recent years in understanding the factors determining the complexation thermodynamics and the structural aspects of the interaction of f-element cations with aminopolycarboxylates ligands.

keywords: Actinides; Aminopolycarboxylates; complexation thermodynamics; ternary complexations; spectral aspects.

Coordination Chemistry Reviews 250, 936 (2006)

Coordination Modes in the Formation of the Ternary Am(III), Cm(III) and Eu(III) Complexes with EDTA and NTA: TRLFS, ¹³C NMR, EXAFS, and Thermodynamics of the Complexation

J. N. Mathur, P. Thakur, C. J. Dodge, A. J. Francis and G.R. Choppin

Abstract

The formation and the structure of the ternary complexes of trivalent Am, Cm and Eu with mixtures of EDTA +NTA have been studied by TRLFS, ¹³C NMR, EXAFS and two phase metal ion equilibrium distribution at 6.60 m (NaClO₄) and pCH between 3.60 to 11.50. In the ternary complexes, EDTA binds via four carboxylates and two nitrogens, while the binding of the NTA varies with the hydrogen ion concentration, pCH and the concentration ratios of the metal ion and the ligand. When the concentration ratios of the metal to ligand is low (1:1:1-1:1:2), two ternary complexes M(EDTA)(NTAH)³⁻ and M(EDTA)(NTA)⁴⁻ are formed at pCH ca. 9.00 in which NTA binds via three carboxylates, via two carboxylates and one nitrogen or via two carboxylates and a H₂O. At higher ratios (1:1:20 and 1:10:10) and pCH's of ca. 9.00 and 11.50, one ternary complex M(EDTA)(NTA)⁴⁻ is formed in which NTA binds via three carboxylates and not via nitrogen. The two phase equilibrium distribution studies at tracer concentrations of Am, Cm, and Eu have also confirmed the formation of the ternary complex M(EDTA)(NTA)⁴⁻ at temperatures between 0-60°C. The stability constants (logβ₁₁₁) for these metal ions increase with increasing temperature. The endothermic enthalpy and positive entropy indicated a significant effect of cation dehydration in the formation of the ternary complexes at high ionic strength.

Inorganic Chemistry 45, 8026 (2006)

Thermodynamics and the structural aspects of the ternary complexes of Am(III), Cm(III) and Eu(III) with Ox and EDTA+Ox

P. Thakur, J. N. Mathur, C J. Dodge , A. J. Francis and G .R. Choppin

Abstract

The stability constants and the associated thermodynamic parameters of formation of the binary and the ternary complexes of Am^{3+} , Cm^{3+} and Eu^{3+} were determined by using solvent extraction to measure the variation in the distribution coefficient with temperature (0-60°C) for aqueous solutions of $I=6.60 \text{ m}$ (NaClO_4). The formation of ternary complexes is favored by both the enthalpy (exothermic) and the entropy (positive) values. ^{13}C NMR, TRLFS and EXAFS spectral data reflected the coordination modes in the ternary complexes. In the formation of the ternary complexes, the coordination number of EDTA changes from 6 in the binary $\text{M}(\text{EDTA})$ to 5 and 4 in the ternary complexes $\text{M}(\text{EDTA})(\text{Ox})^{3-}$ and $\text{M}(\text{EDTA})(\text{Ox})_2^{5-}$, respectively.

Journal Chemical Society, Dalton Transactions 4829 (2006)

Chemical Speciation of Am, Cm and Eu with EDTA at High Ionic Strength: Thermodynamics and Laser Fluorescence Spectroscopy Studies

K. Cernochova, J.N. Mathur, G.R. Choppin

Abstract

The complexation of Am^{3+} , Cm^{3+} and Eu^{3+} with EDTA has been studied at an ionic strength of $6.60 \text{ mol}\cdot\text{kg}^{-1}$ (NaClO_4) and pH 3.60 in the temperature range of 0 to 60°C with a solvent extraction technique. The complex $\text{M}(\text{EDTA})^-$ was formed with stability constant values ($\log \beta_{101}$) at 25°C between 15.9 and 16.1 which increased with increasing temperature. The complex formation enthalpies have been obtained from the temperature dependence of the stability constants. The large positive enthalpy and entropy changes are attributed to the considerably reduced water activity at such high ionic strength resulting in large positive contributions from the dehydration of the trivalent metal ions as compared to the smaller negative contributions from the M^{3+} - EDTA^{4-} bonding interaction. The nature of the species of the EuEDTA complex formed at $6.60 \text{ mol}\cdot\text{kg}^{-1}$ (NaClO_4) and $\text{pH} \geq 3.60$ was studied by time-resolved laser fluorescence spectroscopy and lifetime measurements. Between pH 3.60 and 7.0, $\text{Eu}(\text{EDTA})(\text{H}_2\text{O})_3^-$ was formed while at pH 9.0, $\text{Eu}(\text{OH})(\text{EDTA})(\text{H}_2\text{O})_2^{2-}$ was present.

Radiochim Acta 93, 733 (2005)

Sorption of U(VI) species on Hydroxyapatite

P. Thakur, R.C. Moore and G.R. Choppin

Abstract

The sorption of uranyl (UO_2^{2+}) cations to hydroxyapatite was studied as a function of the amount of sorbent, ionic strength, U(VI) concentration, pH and temperature. The rate of uranyl sorption on hydroxyapatite decreased with increased uranyl concentrations. The amount sorbed decreased with increased ionic strength and increased with pH to a maximum at 7-8. The sorption data for UO_2^{2+} were fitted well by the Freundlich and Dubinin-Radushkevich (D-R) isotherms. The anions Cl^- , NO_3^- , SO_4^{2-} and CH_3COO^- decreased the sorption of uranium on hydroxyapatite while $\text{S}_2\text{O}_3^{2-}$ slightly increased it. The sorbed uranium was desorbed by 0.10 M and 1.00 M solutions of HCl and HNO_3 .

The thermodynamic parameters for the sorption of UO_2^{2+} were measured at temperatures of 298, 313, 323 and 333 K. The temperature dependence confirmed an endothermic heat of sorption. The activation energy for the sorption process was calculated to be $+2.75 \pm 0.02$ kJ/mol.

Radiochim Acta 93, 385 (2005)

Thermodynamics and Laser Luminescence Spectroscopy of Binary and Ternary Complexation of Am³⁺, Cm³⁺ and Eu³⁺ with Citric Acid, and Citric Acid + EDTA at High Ionic Strength

J.N. Mathur, K. Cernochova, G.R. Choppin

Abstract

The binary complexation of Am³⁺, Cm³⁺ and Eu³⁺ with citrate has been studied at I= 6.60 m (NaClO₄), pCH=3.60 and in the temperatures range of 0 to 60°C employing a solvent extraction technique with di-(2-ethylhexyl)phosphoric acid/heptane. Two complexes, MCit and MCit₂³⁻, were formed at all temperatures. For the three metal ions, the log β₁₀₁ was between 5.9 to 6.2 and log β₁₀₂ between 10.2 to 10.6 at 25°C. The thermodynamic parameters for the Am-Cit system have been calculated from the temperature dependence of the β₁₀₁ and β₁₀₂ values. Positive enthalpy and entropy values for the formation of both complexes are interpreted as due to the contributions from the dehydration of the metal ions exceeding the exothermic cation-anion pairing. The formation of the ternary complex M(EDTA)(Cit)⁴⁻ (M = Cm and Eu) was measured to have large stability constants (log β₁₁₁ between 20.9-24.4) at 25° and 60°C. Time resolved laser luminescence spectroscopy and lifetime measurement data validated the nature of the complexes of Eu(III) formed in the presence of Cit and EDTA+Cit in 6.60 m (NaClO₄) solution.

Inorg. Chim Acta (In press)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am³⁺, Cm³⁺ and Eu³⁺ with IDA and EDTA+IDA

G.R. Choppin, P. Thakur and J.N. Mathur

Abstract

The stability and the associated thermodynamic parameters of the binary and the ternary complexes of trivalent Am, Cm, and Eu with IDA and with EDTA+IDA, were determined by using a solvent extraction technique for aqueous solutions of $I = 6.60$ m (NaClO_4) at temperatures of 0-60°C. The endothermic enthalpy and the positive entropy reflect the significant effect of dehydration in the formation of these complexes at high ionic strength. TRLFS and NMR (^1H and ^{13}C) data helped to establish the structure of the ternary complexes in solution. In the ternary complex $\text{M}(\text{EDTA})(\text{IDA})^{3-}$, EDTA binds via four carboxylates and two nitrogens, and IDA via two carboxylates and one nitrogen to the central Eu^{3+} .

Inorg Chim Acta (In press)

Np(V)O₂⁺ sorption on Hydroxyapatite- Effect of Calcium and Phosphate anions.

P. Thakur R.C. Moore and G.R. Choppin

Abstract

The sorption of NpO₂⁺ on hydroxyapatite from aqueous solution was studied as a function of the amount of sorbent, initial NpO₂⁺ concentration, ionic strength and pH. The hydroxyapatite was characterized by SEM, EDS, XRD, FT-IR and ICP-MS analysis. At ionic strengths of 0.10 to 5.00 M NaClO₄, the sorption increased with increased pH to a maximum between pH 8-8.5, then decreased as the pH further increased.

The kinetics of NpO₂⁺ sorption on hydroxyapatite followed Lagergren first order kinetics. The temperature dependence of sorption was small, in the range of 273-283K, and increased more sharply at higher temperatures, 298-333K. The heat of sorption of NpO₂⁺ was endothermic while the free energy values were exothermic due to a large positive entropy. The activation energy for the sorption process was calculated to be 29.52±1.2 kJ/mole. The effect of calcium and phosphate on NpO₂⁺ sorption was studied as a function of concentration and pH.

Radiochim Acta (In press)

Thermodynamics and the Structure of Binary and Ternary Complexation of Am³⁺, Cm³⁺ and Eu³⁺ with DTPA and DTPA+IDA

G.R. Choppin, P. Thakur and J. N. Mathur

Abstract

The formation, their stability and the thermodynamic parameters of the binary complexation of Am³⁺, Cm³⁺ and Eu³⁺ with DTPA and of the ternary complexation of DTPA + IDA were studied in aqueous solutions of I=6.60 m (NaClO₄) and temperatures of 0-60°C by solvent extraction technique. The stability constants of these complexes increased with increasing temperature. Positive enthalpy and the large entropy values for the binary and the ternary complexation indicated significant effect of cation dehydration at such high ionic strengths. TRLFS and NMR (¹H and ¹³C) data provided insight into the structure of the ternary complexes in solution. In the binary, MDTPA²⁻ complex, M³⁺ binds via five carboxylates and three nitrogens, while in the ternary complex M(DTPA)(IDA)⁴⁻, DTPA retains all of its eight coordination sites with IDA binds weakly via one of its carboxylates.

Chimie (Submitted)

Thermodynamics and Dissociation Constants of Carboxylic Acids at High Ionic Strength and Temperature

P. Thakur, J.N. Mathur, R.C. Moore and G.R. Choppin

Abstract

Dissociation constants (pK_a) of oxalic, iminodiacetic, citric, nitrilotriacetic, ethylenediaminetetraacetic, 1,2 dicyclohexyl ethylenediaminetetraacetic and diethylenetriaminepentaacetic acid have been determined potentiometrically using a glass electrode at an ionic strength of 6.60 m (NaClO_4) and temperatures of 0 to 60°C. The constants of iminodiacetic, nitrilotriacetic and diethylenetriaminepentaacetic acid were measured at 25°C at ionic strengths from 0.30 to 6.60 m (NaClO_4). The thermodynamic parameters for the dissociation of these carboxylic acids were derived from the temperature dependence of the dissociation constants. The Specific Ion Interaction Theory (SIT) and the parabolic model successfully described the ionic strength dependencies of the pK_a values. The variation of the pK_a values at high ionic strengths as a function of the type and concentration of supporting electrolyte is discussed and compared with literature data.

Inorg. Chim. Acta (Submitted)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am³⁺, Cm³⁺ and Eu³⁺ with CDTA and CDTA+IDA

P. Thakur, J.N. Mathur and G .R. Choppin

Abstract

The stability constants and the associated thermodynamic parameters of the formation of the binary complexes of trivalent Am³⁺, Cm³⁺ and Eu³⁺ with CDTA and of their ternary complexes with CDTA+IDA, were determined by a solvent extraction technique in aqueous solutions of I=6.60 m (NaClO₄) at temperatures of 0-60°C. The endothermic enthalpy and the positive entropy values reflect the significant effects of cation dehydration and of the rigidity of the ligand structure in the formation of these complexes. TRLFS and NMR (¹H and ¹³C) data provided information on the structure of the ternary complexes in solution. The size and rigidity of CDTA affect the binding mode of IDA in the complexation of M(CDTA)(IDA)(H₂O)³⁻ and M(CDTA)(IDA)³⁻ in which IDA has a bidentate coordination mode in the former and a tridentate coordination mode in the latter.

Inorg Chim Acta (Submitted)

Complexation thermodynamics and the structure of the binary and the ternary complexes of Am³⁺, Cm³⁺ and Eu³⁺ with CDTA and CDTA+NTA

P. Thakur and G.R. Choppin

Abstract

The stability constants and thermodynamic parameters of the formation of the binary complexes of Am³⁺, Cm³⁺ and Eu³⁺ with CDTA and of their ternary complexes with CDTA+NTA, were determined by a solvent extraction technique in aqueous solutions of I = 6.60 m (NaClO₄) over a temperature range of 0-60°C. The cation dehydration and the rigid structure of CDTA both contribute to the endothermic enthalpies of complexation of the binary M(CDTA)⁻ and ternary M(CDTA)(NTA)⁴⁻. The TRLFS and NMR (¹H and ¹³C) spectral studies gave insight into the hydration number and the binding modes of the ligands in these complexes. In the binary, M(CDTA)⁻, the metal binds via four carboxylates and two nitrogens. In the ternary complex, M(CDTA)(NTA)⁴⁻, CDTA again binds via the same six coordination sites while NTA binding via three donor groups for 9-coordinated lanthanides. For eight coordinated lanthanides usually hexadentate CDTA become pentadentate, while NTA binds via three donor sites. In high ionic strengths, these complexes can be significant in separation processes.

Inorg Chim Acta (manuscript under preparation)