

LA-UR- 00-186

Approved for public release;
distribution is unlimited.

Title: Actinyl(VI) Speciation in Concentrated Sodium Chloride Solutions

Author(s): Wolfgang Runde, E-ET
Mary P. Neu, CST-18
Craig VanPelt, E-ET
Sean Reilly, CST-18
Youwen Xu, E-ET

Submitted to: For Publication in Proceedings of "NEA Workshop on Evaluation of Speciation Technology", October 26 - 28, 1999, Jaeri, Tokai, Japan

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECEIVED

OCT 04 2000

OSTI

ACTINYL(VI) SPECIATION IN CONCENTRATED SODIUM CHLORIDE SOLUTIONS

W. Runde, M.P. Neu, C. Van Pelt, S. Reilly, and Y. Xu
Chemical Science and Technology Division, Los Alamos National Laboratory,
Los Alamos, NM 87545, USA

Abstract

Thermodynamic parameters and sorption coefficients provide the fundamental database for the mathematical abstraction of environmental transport of actinides. We have been investigating the chemistry of the hexavalent actinides, U and Pu, in the solid state in concentrated salt (NaCl) solutions representative of conditions within geologic salt formations, sites for nuclear waste disposal. Chloride complexation is proven to play an important role for actinyl(VI) solubility and speciation. We investigated U(VI) and Pu(VI) equilibria with the predominant inorganic ligands hydroxide and carbonate in the presence of chloride. We used a number of spectroscopic techniques (UV-vis-NIR, Raman, FTIR, NMR, XAS) and X-ray diffraction to characterize solution species and solid phases as a function of pH, carbonate concentration, and ionic strength.

Introduction

The understanding of actinide speciation and compound stability in natural aquifer systems is the basis for developing reliable site-specific solubility predictions and transport models. Most thermodynamic data on actinide solubilities and species formation constants have been determined in dilute solutions of inert electrolytes, such as NaClO₄.¹⁻³ Natural waters, however, contain a complex mixture of inorganic and organic components that significantly affect the environmental behavior of actinides.⁴ Brines from nuclear waste repository sites in geologic salt deposits, i. e. the Waste Isolation Pilot Plant (WIPP) site in New Mexico (USA) and the Gorleben site in Niedersachsen (Germany), are highly concentrated solutions of chloride salts. Thus, for defensible risk and safety assessment calculations the understanding of actinide speciation in the presence of high chloride concentrations is crucial.

Solubility predictions for actinides in chloride solutions have been underestimated when based on thermodynamic data determined in non-interactive media.⁵ We have shown previously that chloride may replace hydration water and form actinyl(VI) chloro complexes of higher stability than those of tri-, tetra-, and pentavalent actinides.⁶ Building on those inner-sphere actinyl(VI) chloride interactions, we are studying the influence of chloride on the nature and stability of solution and solid actinyl(VI) compounds as a function of chloride concentration and pH in the presence and absence of carbonate. We are performing these studies using a variety of spectroscopic techniques (¹³C-NMR, diffuse reflectance, conventional UV-Vis-NIR absorption, FTIR, Raman, and X-ray absorption) and X-ray diffraction.

Experimental

Stock Solutions. Plutonium(VI) stock solutions were prepared by dissolving ^{239}Pu metal in 7 M HClO_4 and fuming aliquots of this solution to near dryness with concentrated HClO_4 , diluting with H_2O , then determining the total Pu concentration by liquid scintillation counting (LSC) and verifying the oxidation state purity using conventional absorbance spectrophotometry. The isotopic composition of the material was determined radioanalytically. Uranium(VI) stock solutions were prepared by dissolving uranyl nitrate (recrystallized from nitric acid) in 1 M HClO_4 . Sodium carbonate solutions were prepared by dissolving ^{13}C -enriched Na_2CO_3 (99.9% ^{13}C , Cambridge Isotopes) in known masses of distilled, deionized water.

Preparation and Characterization of U(VI) Hydrolysis Species. Aliquots of the uranyl stock solutions were diluted in solutions of 0.1, 1, 3, and 5 M NaCl solutions to yield final U(VI) concentrations of 0.1, 0.5, 1, and 10 mM. The acidic solutions were purged with argon to minimize carbonate contamination. The pH was adjusted by addition of NaOH and the solutions were allowed to equilibrate under argon atmosphere for 24 hours. The solutions were then analyzed using UV-vis, Raman, and FTIR spectroscopies.

Preparation and Characterization of Solid Actinyl(VI) Carbonates. Actinyl carbonates, AnO_2CO_3 , (An = U, Pu) were prepared by bubbling CO_2 through stirred acidic stock solutions (pH = 4) for 3 to 5 days, washing the resulting precipitate with distilled deionized water, redissolving, and repeating precipitation. For plutonium, ozone was also bubbled through the suspension for the final 2 days to re-oxidize any reduced plutonium. The resulting pale pink-tan Pu(VI) and pale yellow U(VI) solids were characterized using powder X-ray diffraction (Inel, CPS-120) and extended X-ray absorbance fine structure (EXAFS) spectroscopy. EXAFS data were recorded at Stanford Synchrotron Radiation Laboratory (SSRL): unfocused beamline 4-2, Si(220), double-crystal monochromator, 3.0 GeV, 60-100 mA.

Determination of the Thermodynamic Constant for U(VI) Bis- and Triscarbonato Equilibrium. Aliquots of the U(VI) stock solutions were added dropwise to individual 30 mM Na_2CO_3 solutions to yield a final uranium concentration of 10 mM and NaCl concentrations between 0.05 and 5 M. A small, known amount of D_2O (Cambridge Isotopes, 99.9% D) and NaCl (Baker, reagent) appropriate for the desired ionic strength were added to individual solutions. Samples were prepared with a carbonate:uranyl ratio of 3:1 to favor the formation of the monomeric triscarbonato complex. Careful titration with HClO_4 leads to the protonation of the carbonate ligand resulting in a decrease in the carbonate:uranyl ratio to 2:1. The p[H] of the resulting solutions was determined using a combination pH electrode and the calibration and ionic strength corrections described earlier.⁵ All NMR sample solutions were loaded into pyrex NMR tubes (Wilmad 5 mm o.d. 507-PP). FT ^{13}C NMR spectra were recorded on a Bruker AMX500 spectrometer with a 5 mm broadband probe operating at 125.76 MHz with ^2H field-frequency lock. The spectral reference was set for all ^{13}C NMR spectra relative to the carbonyl carbon of external acetone- d_6 set at $\delta = 206.0$.

Results and Discussion

Hydrolysis of U(VI) in Chloride Media. Uranium(VI) hydrolysis has been investigated extensively and the data reported have been evaluated recently.² Monomeric and polynuclear hydroxo species of general formulas $\text{UO}_2(\text{OH})_m^{2-m}$ ($m = 1-4$) and $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$ ($m/n = 2/2, 3/5, 4/7$) are accepted U(VI) hydrolysis species which form in the absence of carbonate. At low pH, U(VI) forms the monomeric first hydrolysis product $\text{UO}_2(\text{OH})^+$ that aggregates at high U(VI)

concentrations to form the dimeric species $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$. The absorbance maximum of the dimer is observed at 421 nm (421.8 nm⁷) in NaClO_4 solutions, independent of the electrolyte concentration. The molar absorbance of this complex ($79 \pm 5 \text{ L Mol}^{-1} \text{ cm}^{-1}$) is an order of magnitude greater than that of the uncomplexed UO_2^{2+} ion ($7.9 \pm 0.3 \text{ L Mol}^{-1} \text{ cm}^{-1}$). Addition of NaCl results in a significant change in the absorption spectra of the UO_2^{2+} ion although the shift of the absorption maxima of up to 10 nm is far smaller than those of strong U(VI) complexes, such as the 30 nm shift observed upon carbonate complexation.⁸ The maximum absorbance of UO_2^{2+} in NaClO_4 (413 nm) is shifted to 423 nm in 5 M NaCl (Figure 1).⁶ With increasing pH, the formation of the U(VI) hydroxo species is indicated by a significant absorbance increase. However, while the shape of the spectrum is very similar to that observed in NaClO_4 (absorbance maximum at 421 nm) the maximum absorbance is shifted to 425 nm. These findings were confirmed by results obtained from Raman and FTIR studies. The Raman (873 cm^{-1}) and FTIR (961 cm^{-1}) bands of the uncomplexed UO_2^{2+} ion are shifted in 5 M NaCl due to chloride complexation by about 10 wavenumbers to 862 cm^{-1} and 951 cm^{-1} , respectively (Figure 2). While Raman and FTIR bands of the dimeric hydroxo species in NaClO_4 appear at 852 and 941 cm^{-1} , respectively, the corresponding bands cannot be observed in NaCl solutions. However, additional peaks appear in 5 M NaCl at 837 and 922 cm^{-1} , respectively, at higher p[H]. These bands match the Raman (839 cm^{-1}) and FTIR (924 cm^{-1}) signals of the trimeric $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ observed in NaClO_4 . These spectroscopic results suggest that the stability of $(\text{UO}_2)_2(\text{OH})_2^{2+}$ is decreased significantly in the presence of chloride, such that this species is not observed spectroscopically. Clearly, the speciation of uranyl(VI) is different in concentrated chloride solutions than it is in perchlorate solutions. One explanation for the differences is the formation of mixed U(VI) chloro-hydroxo complexes; however, we have no direct evidence for such mixed ligand species. Currently, we are continuing this work, including determining formation constants for the hydroxide species formed in concentrated chloride solution which we have described qualitatively here.

Figures 1 and 2

Characterization of Solid AnO_2CO_3 . The actinyl(VI) carbonates, UO_2CO_3 and PuO_2CO_3 , were precipitated from solutions (pH 4) saturated with 100% CO_2 . The XRD powder patterns of both solids agree well with each other and with those previously reported.^{9,10} To determine the local coordination environments of the actinides we measured the EXAFS spectra of each solid (Figure 4). The actinyl An=O distances were determined to be 1.76 for U and 1.74 for Pu. The equatorial An- OCO_2 bond distances are very similar to those in $\text{UO}_2(\text{CO}_3)_3^{4-}$ and in $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, i.e. 2.45 Å for An-- OCO_2 with the carbonate coordinated in a bidentate fashion.¹¹ The Fourier transform moduli show the An---An distance of 4.2 Å, consistent with the Pmmn structure reported.¹²

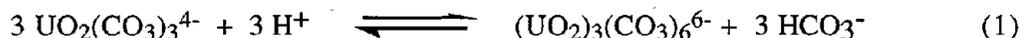
Figure 3

Given the large range of solubility products reported for U(VI) and Pu(VI) hydroxide phases, the correlated stability range of $\text{AnO}_2\text{CO}_3(\text{s})$ is unclear. The $\text{AnO}_2\text{CO}_3(\text{s})$ stability depends mainly on the CO_2 partial pressure and the pH, which together determine the carbonate concentration in solution, and the ionic strength. Lowering the CO_2 partial pressure from 1 atm (pH 4) to $10^{-3.5}$ atm favors the

transformation of $\text{AnO}_2\text{CO}_3(\text{s})$ to a $\text{An}(\text{VI})$ hydroxide or oxide phase. In 5 M NaCl, $\text{UO}_2\text{CO}_3(\text{s})$ transformed into a crystalline phase with significantly different Bragg reflections than the starting material. The powder pattern of the new phase compares well with that reported for the sodium uranate, $\text{Na}_2\text{U}_7\text{O}_{22}$.¹³ At lower ionic strength, the crystallinity of the final solid is lower and broad Bragg reflections match those of $\text{UO}_2(\text{OH})_2$. Plutonium(VI) reacts sensitively to changes in ionic strength and radionuclide inventory. At low ionic strength, $\text{Pu}(\text{VI})$ is found to be reduced within days to increasing fractions of polymeric $\text{Pu}(\text{IV})$ hydroxide and PuO_2^+ . The pale pink-tan plutonyl solid is found to be stable for only weeks under these conditions. However, in concentrated NaCl, chloride complexation and radiolysis stabilize plutonium in the hexavalent oxidation state. Radiolytically produced chlorine and hypochlorite have been reported to be responsible for creating an oxidizing medium.¹⁴ While chloride appears to stabilize $\text{Pu}(\text{VI})$, it does not affect the composition of the carbonate solid precipitated from concentrated NaCl solutions.

Stability of the Trimeric Species, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, as a Function of NaCl.

Based on NMR, EXAFS and single X-ray crystal diffraction studies the trimeric species has been unequivocally characterized¹¹ and proven to exist in solution when $\text{U}(\text{VI})$ and carbonate concentrations are both in the millimolar range. However, its stability and relevance in solid-liquid phase equilibrium studies is still questionable. We studied the stability of $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ in 0.05 – 5 m NaCl solutions by using ^{13}C NMR spectroscopy. This technique allows the identification of the $\text{U}(\text{VI})$ carbonate species involved in the solution equilibrium via their chemical shifts and the $\text{U}(\text{VI})$ species concentration ratio by integrating the resonances corresponding to each species at each pH. Using the known $\text{U}(\text{VI})$ concentrations, measured $\text{p}[\text{H}]$, and calculated bicarbonate concentrations, we calculated the apparent equilibrium constant relating the two species at each NaCl concentration according to Eq. (1)



Since the trimeric species is so highly charged, we anticipated a large effect of the NaCl concentration on the equilibrium between these two species. Indeed, the equilibrium constant is dependent on NaCl concentration; an example of the changes observed at a given pH as a function of ionic strength (Table 1). The values determined for the equilibrium constant range from $\log K'_{\text{eq}} = 20.9 \pm 0.2$ with no NaCl in solution to 18.7 ± 0.2 in 5.0 m NaCl. The greatest changes occur for NaCl concentrations up to 1.4 m; the apparent stability constant varies little when NaCl concentrations are higher than 2 m.

Table 1. Apparent Equilibrium Constants for the First Protonation Step of $\text{UO}_2(\text{CO}_3)_3^{4-}$ as a Function of NaCl Concentrations.

[NaCl] (m)	$\log K'_{\text{eq}}$	[NaCl] (m)	$\log K'_{\text{eq}}$
0.000	20.9 ± 0.2	2.15	18.6 ± 0.2
0.496	19.7 ± 0.1	2.45	18.5 ± 0.2
0.597	19.5 ± 0.2	2.75	18.7 ± 0.1
0.938	19.2 ± 0.2	2.98	18.6 ± 0.2
0.998	19.1 ± 0.3	3.37	18.7 ± 0.1
1.380	18.8 ± 0.2	4.78	18.6 ± 0.2
2.000	18.6 ± 0.2	4.95	18.6 ± 0.1
2.036	18.7 ± 0.1	5.02	18.7 ± 0.1

Figure 4

Solubility data of uranyl in carbonate media have been interpreted with the formation of only monomeric species, $\text{UO}_2(\text{CO}_3)_m^{2-2m}$ where $m = 1 - 3$.² In these studies the solutions were prepared by addition of acid to the uranyl carbonate solutions to form the trimeric species without precipitation (undersaturation conditions). The solubility of $\text{UO}_2\text{CO}_3(\text{s})$ increases at $[\text{CO}_3^{2-}]$ higher than 10^{-8} M due to the formation of anionic U(VI) carbonate complexes. Under conditions where the biscarbonato complex is stable we observe a large scattering in the U(VI) solubility data depending on whether the experiment is performed from undersaturation or oversaturation. Starting the solubility experiment from the alkaline side, similar to the sample preparation for the NMR studies, allows for the stabilization of U(VI) in solution by formation of the more soluble trimeric compound. Undersaturation experiments prohibit large U(VI) concentration and favor the formation of the monomeric species $\text{UO}_2(\text{CO}_3)_2^{2-}$. Figure 5 shows the UV-Vis absorbance of U(VI) in carbonate solution taken from an oversaturation experiment compared with those of the pure trimeric species and a synthetic solution with predominantly $\text{UO}_2(\text{CO}_3)_3^{4-}$. The solution from the solubility experiment clearly matches the absorbance features of $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ and differs significantly from those corresponding to $\text{UO}_2(\text{CO}_3)_3^{4-}$. These findings were confirmed by ¹³C NMR studies. Thus far we found only the monomeric species in solution when solubility experiments are performed from undersaturation.

Figure 5

Conclusions

We have shown that actinyl(VI) ions may form inner-sphere complexes with chloride. In brines relevant to nuclear waste repositories in geologic salt formations the dissolved chloride concentration is such that the mono-, bis- and perhaps the trischloro complexes are important. Uranyl(VI) hydrolysis reactions are more complicated and the dimeric hydroxo complex appears to be less stable in NaCl solutions. Plutonium(VI) is more stable towards reduction in highly concentrated chloride solutions than in perchlorate or dilute chloride solutions. In contrast, at low ionic strength the solubility of $\text{PuO}_2\text{CO}_3(\text{s})$ can be determined only after relatively short times of solid-liquid phase equilibration due to the redox instability of Pu(VI) and reduction to Pu(IV) colloid and Pu(V) in solution. Increasing NaCl concentrations favor the stability of the U(VI) triscarbonato complex with respect to formation of the trimeric $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, consistent with the trend observed in sodium perchlorate.^{4,7} Data from the NEA review of uranium thermodynamics yield an equilibrium constant for Eq. (1) of $\log K^\circ = 17.8$ ² and Allen, *et al.*¹¹ reported $\log K' = 18.1 \pm 0.5$ in 2.5 m NaClO_4 ; for comparison, we have determined $\log K' = 18.5$ in 2.5 m NaCl. We observed that the formation of the $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ clearly depends on the details of sample preparation and its formation has to be considered in solubility experiments performed from oversaturation at $[\text{CO}_3^{2-}] \geq 10^{-8}$ M.

Acknowledgments

EXAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) in collaboration with Steve D. Conradson, Materials Science and Technology Division, Los Alamos National Laboratory. SSRL is supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. Full details of the EXAFS data and analysis will be reported elsewhere. This work was supported by the Waste Isolation Pilot Plant, under Contract No. AN-1756 with Sandia National Laboratory and by Los Alamos National Laboratory Directed

Research Development and the Nuclear Materials Stabilization Task Group, EM-66 of the U.S. D.O.E.

References

- (1) Silva, R. J.; Bidoglio, G.; Rand, M. H.; Robouch, P. B.; Wanner, H.; Puigdomenech, I. *Chemical Thermodynamics of Americium*; Elsevier: New York, 1995; Vol. 2.
- (2) Grenthe, I.; Fuger, J.; Konings, R. J. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; North-Holland Elsevier Science Publishers b.V.: Amsterdam, 1992; Vol. 1.
- (3) Fuger, J.; Khodakovsky, I. L.; Serfeyeva, E. I.; Medvedev, V. A.; Navratil, J. D. *Part 12. The Actinide Aqueous Inorganic Complexes*; IAEA: Vienna, 1992.
- (4) Choppin, G. R.; Du, M. *Radiochim. Acta* **1992**, *58/59*, 101-104.
- (5) Runde, W.; Neu, M. P.; Clark, D. L. *Geochim. Cosmochim. Acta* **1996**, *60*, 2065-2073.
- (6) Runde, W.; Neu, M. P.; Conradson, S. D.; Clark, D. L.; Palmer, P. D.; Reilly, S. D.; Scott, B. L.; Tait, C. D. In *Materials Research Society Symposium*; Boston, MA, 1996; pp 693-703.
- (7) Meinrath, G. *J. All. Comp.* **1998**, *275-277*, 777-781.
- (8) Cinneide, S., O.; Scanlan, J. P.; Hynes, M. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013.
- (9) Navratil, J. D.; Bramlet, H. I. *J. Inorg. Nucl. Chem.* **1978**, *35*, 157.
- (10) Pashalidis, I.; Runde, W.; Kim, J. I. *Radiochim. Acta* **1993**, *61*, 141.
- (11) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelman, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797-4807.
- (12) Clark, J. R.; Christ, C. L. *Am. Min.* **1957**, *41*, 844.
- (13) JCPDS 5-132 and Wamser et al. *J. Am. Chem. Soc.* **1952**, *74*, 1022.
- (14) Büppelmann, K.; Kim, J. I.; Lierse, C. *Radiochim. Acta* **1988**, *44/45*, 65.

FIGURE CAPTIONS

Figure 1: UV-vis absorbance spectra of U(VI) in 5 M NaClO₄ (left) and 5 M NaCl (right) as function of pH.

Figure 2: FTIR (left) and Raman (right) spectra of U(VI) in 5 M NaCl as function of p[H].

Figure 3. EXAFS of UO₂CO₃ and PuO₂CO₃. The Fourier transform amplitude for each solid is shown. The shells of neighboring scatterers which comprise the fit to the data are based upon an idealized Pmmn structure and are plotted here with negative intensity.

Figure 4. ¹³C NMR spectra of 10 mM uranyl carbonate at [H⁺] = 10⁻⁸ M as a function of sodium chloride.

Figure 5. Absorbance spectra of U(VI) solution derived from a solubility experiment ([NaCl] = 2m, pH 5.7 and 1 atm CO₂ partial pressure) and of known uranyl carbonate species.

Figures

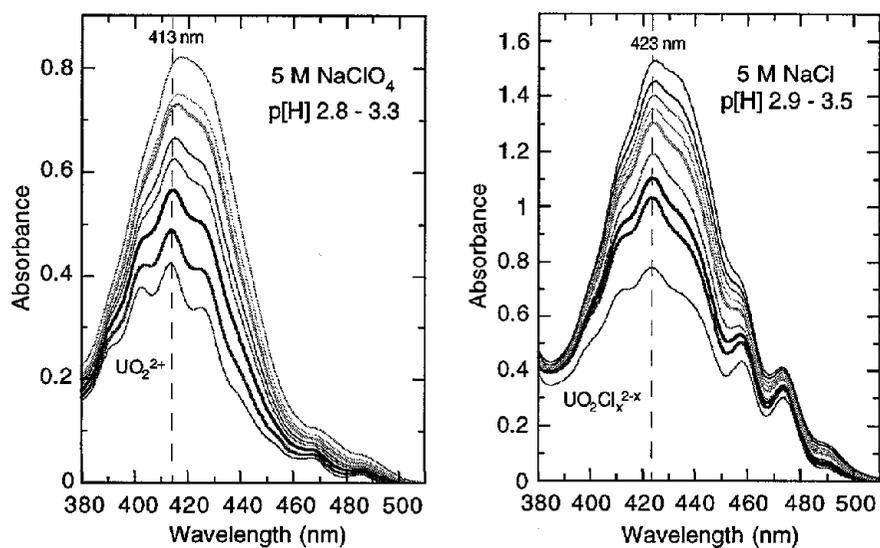


Figure 1: UV-vis absorbance spectra of U(VI) in 5 M NaClO₄ (left) and 5 M NaCl (right) as function of pH.

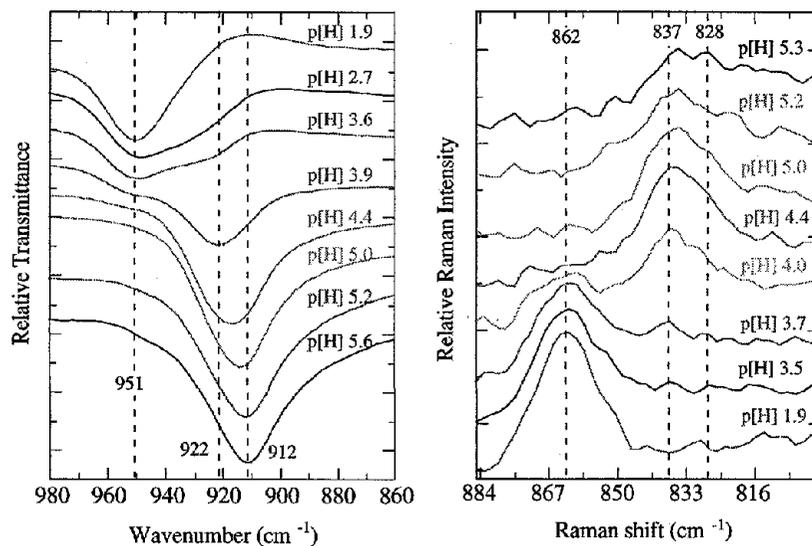


Figure 2: FTIR (left) and Raman (right) spectra of U(VI) in 5 M NaCl as function of p[H].

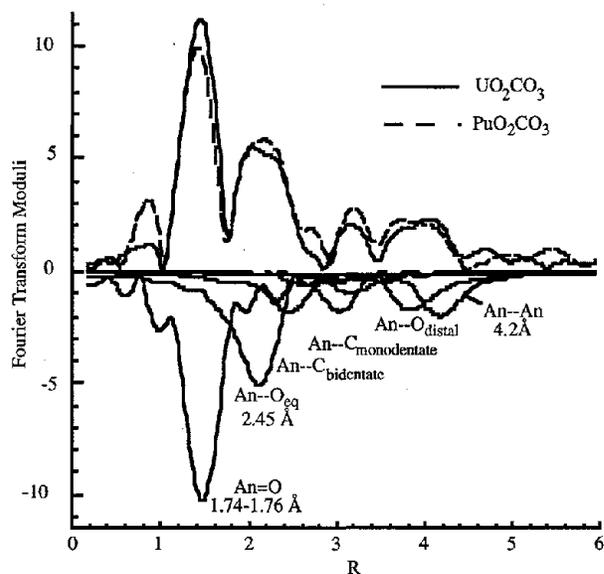


Figure 3. EXAFS of UO_2CO_3 and PuO_2CO_3 . The Fourier transform amplitude for each solid is shown. The shells of neighboring scatterers which comprise the fit to the data are based upon an idealized Pmmn structure and are plotted here with negative intensity.

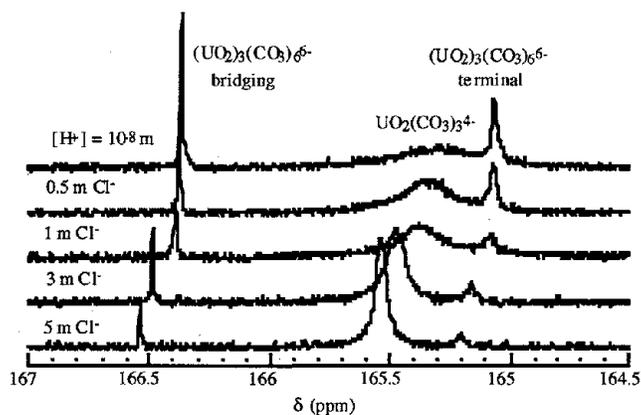


Figure 4. ^{13}C NMR spectra of 10 mM uranyl carbonate at $[\text{H}^+] = 10^{-8}$ M as a function of sodium chloride.

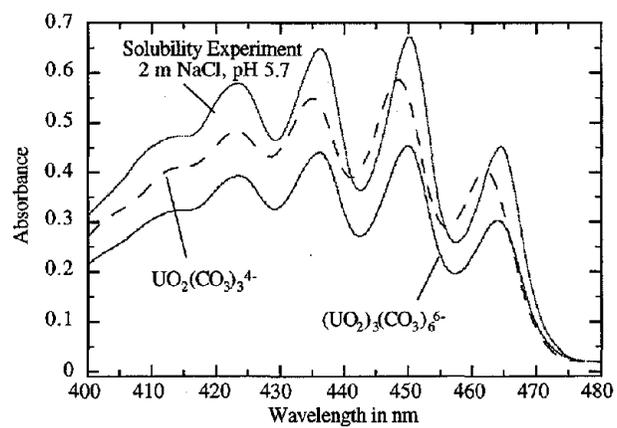


Figure 5. Absorbance spectra of U(VI) solution derived from a solubility experiment ($[\text{NaCl}] = 2\text{m}$, pH 5.7 and 1 atm CO_2 partial pressure) and of known uranyl carbonate species.