Uranium(IV) Hydrolysis Constants and Solubility Product of UO₂·xH₂O(am)

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The solubility of $UO_2 \cdot xH_2O$ was examined in dilute solutions at room temperature and in the pH range from 2 to 12. Iron powder and Eu^{2+} were used to effectively eliminate O_2 and to maintain reducing conditions so as to minimize the possibility of oxidation of U(IV) to U(VI) during the experiments. The $UO_2 \cdot xH_2O$ was found to be amorphous to X-rays, and its solubility, especially at pH values >4, was found to be 3–4 orders of magnitude lower than previously reported. A thermodynamic analysis of our solubility data yielded a log K at zero ionic strength of 3.5 ± 0.8 for the solubility reaction $UO_2 \cdot xH_2O(am) + 3H^+ \rightleftharpoons UOH^{3+} + (x + 1)H_2O$. A recalculation of the first hydrolysis constant from spectrophotometric data reported in the literature in conjunction with our solubility data yielded a log K at zero ionic strength of −0.50 ± 0.03 for the reaction $U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$ and a log K of −52.0 ± 0.8 for the reaction $UO_2 \cdot xH_2O(am) \rightleftharpoons U^{4+} + 4OH^- + (x - 2)H_2O$. These values are consistent with both the reliable solubility and spectrophotometric data and the thermodynamic properties of other actinides. Although from our data it was not possible to obtain precise values of constants (K_{1n}) for other hydrolysis reactions, $U^{4+} + nH_2O \rightleftharpoons U(OH)_n^{4-n} + nH^+$, the upper limits that can be calculated for log K_{12} through log K_{15} (<−4.0, <−8.0, <−12.0, and <−26, respectively) are several orders of magnitude lower than those previously reported.

Introduction

Uranium chemistry has been studied for several decades. However, the key fundamental thermochemical data required to predict the aqueous behavior of U(IV) are at best estimated, at worst inaccurate or missing. For example, reported solubilities and solubility products of amorphous UO_2 vary over several orders of magnitude.[1-5] Except for the value of the first hydrolysis constant,[6,7] no credible experimental values for hydrolysis constants are available. The hydrolysis constants that are generally accepted and widely quoted[8,9] are based on questionable extrapolation schemes from limited and unreliable data[10] for amorphous UO_2 solubility. Ryan and Rai[3] have discussed in detail the uncertainties in these currently available values for hydrolysis constants.

The general lack of data and the poor quality of the data available can be attributed to the absence of rigid controls on important analytical and experimental variables and to the difficulties of studying UO_2. For example, the equilibrium potential of the U(IV)/U(VI) couple is very low, and O_2 is a strong and rapid oxidant for U(IV): oxidation increases with increasing pH, and at pH 2 and O_2 levels the same as those in the air, oxidation takes only a few minutes.[11] Therefore, keeping redox potentials very low (O_2 fugacities < 10^{-65}) is absolutely critical for maintaining uranium as U(IV) during experiments. However, studies of amorphous UO_2 solubility by Gayer and Leider[10] and Galkin and Stepanova[12] were conducted under highly alkaline conditions and at O_2 fugacities ranging between about $10^{-0.7}$ and 10^{-5}. Ryan and Rai[3] conducted similar experiments but carried them out in the presence of highly reducing agents such as $Na_2S_2O_4$ and obtained solubilities approximately 3.5 orders of magnitude lower than those obtained by the earlier workers. Apparently, the very high solubilities of amorphous UO_2 reported by the earlier authors

were caused by inadequate controls on redox potential, which resulted in the oxidation of U(IV) to U(VI).

Because reliable U(IV) hydrolysis constants are unavailable, the UO_2 solubilities reported by Gayer and Leider,[10] Galkin and Stepanova,[12] and Ryan and Rai[3] for highly alkaline conditions in which U(IV) is almost entirely hydrolyzed cannot be used to calculate the solubility product of UO_2. Recognizing this problem, Bruno et al.[2] conducted solubility experiments over a pH range from about 2 to 10, using H_2 gas as the reductant and Pd as the catalyst. However, the solubilities they measured at pH values greater than 4 were about as high as those obtained by Gayer and Leider[10] and by Galkin and Stepanova.[12] These results indicate that Bruno et al.[2] were not successful in effectively controlling the oxidation state of uranium. Bruno et al.[2] claimed that the difference between their results and those obtained by Ryan and Rai[3] was based on differences in the crystallinity of the solid phases.

Bruno et al.[4] also studied the solubility products of amorphous and crystalline UO_2 and obtained log K_{sp} values of −55.5 and −57.6, respectively. These K_{sp} values and the difference between the two values are both inconsistent with the known properties of other tetravalent actinides,[5] which show much lower values for the crystalline material and much larger differences between the crystalline and the amorphous materials. Therefore, we conducted experiments with amorphous UO_2 in the pH range 2–12 and in the presence of inorganic reductants (Fe and Eu^{2+}) that are effective in maintaining very low oxidation/reduction potentials. The experiments were conducted (1) in the low-pH region, where a reliable value for the first hydrolysis constant is available, so that the K_{sp} could be calculated, and (2) in the high-pH region, so that hydrolysis constants higher than the first could be calculated, Ryan and Rai's[3] data pertaining to the solubility of amorphous UO_2 could be verified, and an upper limit on the solubility could be set.

Methods and Materials

Because U(IV) is readily oxidized to U(VI) in the presence of O_2, several precautions were taken to minimize oxidation during preparation of the U(IV) stock solution and during the equilibrations. These precautions included (1) preparing the concentrated U(IV) stock solution in approximately 2 M HCl [in which U(IV) is relatively stable], storing it under N_2 in a sealed container, and treating it with uranium metal immediately before use to ensure the absence of U(V) and U(VI); (2) conducting the experiments in low-redox-potential solutions with a calculated O_2 content reduced to <10^{-75} atm by prior equilibrations with Fe powder; (3) conducting the experiments in the presence of Eu^{2+} or Fe powder to maintain very low O_2 fugacities; (4) filling the sample tubes nearly to capacity to minimize gas space; (5) sealing the sample tubes during equilibrations and sealing the ion-specific electrodes into the sample containers during measurements to avoid O_2 diffusion; and (6) conducting the experiments in a glovebox with a N_2 atmosphere.

Reagents. In all cases, water was deaerated by boiling, thorough sparging with N_2 (99.99%), and equilibrating with 325-mesh Fe powder obtained from Alfa Products. The dissolved-O_2 content of the Fe-

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equilibrated water was estimated from the measured redox potential and previous experimental studies[13] to be $<10^{-75}$ atm, a value many orders of magnitude lower than the 10^{-6} atm generally achievable by sparging with a prepurified inert gas such as N_2.

A NaOH stock solution was prepared in a N_2 atmosphere, by using the deaerated water, from a new bottle of reagent-grade pellets of NaOH. The stock was treated with about 7% excess $BaCl_2$ to lower the dissolved carbonate through $BaCO_3$ precipitation.

Uranium(IV) stock solution was prepared by dissolving Hanford reactor-grade uranium metal in 12 M HCl (initially while the solution was cooled and finally while it was heated to 100 °C). The hot solution was centrifuged while slow H_2 evolution was still occurring from black residues. The solution ($\sim$500 g of U(IV)/L and $\sim$2 M HCl) was then filtered through a 250-nm Millipore Solvinert filter (Millipore Corp., Bedford, MA) and stored under N_2 in a sealed container. The spectrophotometric analysis of the stock solution revealed the presence of U(IV) and the absence of measurable amounts of other uranium oxidation states. To eliminate any oxidized uranium species that might have been present in undetectable amounts, the stock solution was treated with uranium metal prior to each use.

Solid $EuCl_2$ was prepared from Eu_2O_3 of $>$99.9% purity (relative to other rare earths) obtained from American Potash and Chemical Corp. Fifteen grams of the Eu_2O_3 was placed in a fused-SiO_2 furnace-reaction tube, the exit line of which went through an empty trap and then a concentrated H_2SO_4 bubbler to prevent back-diffusion of O_2 or H_2O vapor. The reaction tube was flushed with moisture-free He. The furnace was preheated with He flow for about 1 h, and a considerable amount of moisture was driven off. An appreciable portion of the moisture condensed downstream in the reaction tube and was driven out with a heat gun. Carbon tetrachloride was then added to the He gas stream, and the temperature was raised to 500 °C. Chlorination proceeded well, as evidenced by the conversion from white Eu_2O_3 to yellow $EuCl_3$. After 2 h, the temperature was raised to 550 °C for 5 h more. The He was then replaced with 6% H_2 in He to reduce $EuCl_3$ to $EuCl_2$. Reduction (color change from yellow to white) appeared to be fairly rapid, and the temperature was raised to 560 °C after 1 h, to 630 °C after another 0.5 h, and to 660 °C after 45 min more. It was maintained at 660 °C for 3 h. The $EuCl_2$ was stored under N_2 in a desiccator until used.

Experimental Procedure. All experiments were conducted in a glovebox with a prepurified N_2 atmosphere (99.99% N_2, with a few parts per million of oxygen). In most of the experiments, solubility was approached from oversaturation to avoid oxidation of the solid during washing. These experiments were conducted in 50-mL glass centrifuge tubes containing 35 mL of deoxygenated deionized water, with or without 100 mg of Fe powder or 0.05 g of $EuCl_2$, to which aliquots of U(IV) stock containing approximately 15–60 mg of uranium were added. The pH values of these samples were adjusted to a range between approximately pH 2 and 12 by using HCl or carbonate-free NaOH. Upon pH adjustment, precipitates of U(IV) hydroxide (represented here as $UO_2 \cdot xH_2O$) were observed in all of the tubes. The tubes were sealed and continuously shaken at room temperature ($\sim$21 ± 2 °C). Periodically, the pH values were measured and aqueous and solid aliquots were withdrawn for analyses. As much as possible, the studies were confined to short time frames (days) to obtain the solubility of amorphous $UO_2 \cdot xH_2O$ and to avoid possible complications caused by the precipitates becoming crystalline over long equilibration periods.

To check the approach to equilibrium from the undersaturation direction, the pH values of the samples that had been equilibrated from the oversaturation direction were adjusted from about 3.5 to about 2.6. The samples were then treated in a manner similar to that described above.

The ionic strength in our solutions was fairly constant, averaging 0.05 ± 0.01 in all solutions below pH 4 except the two solutions with the highest total soluble U concentrations (log [U] = -2.08 and -2.09), where the ionic strengths were 0.115 and 0.093, respectively.

The data interpretations were done by using a coupled nonlinear least-squares and chemical equilibrium program (NONLIN, developed by A. R. Felmy). In the NONLIN program, the actual quantity minimized was the standard deviation defined as

$$\sigma = \left(\frac{\sum\limits_{i=1}^{N} [f(x)]^2}{N} \right)^{1/2}$$

where N is the total number of data points and $f(x)$ is given by the phase

Table I. Uranium Concentrations in a Solution Successively Filtered through Different Filters (0.0018 μm)

filter no.	log [U][a]	remarks
1	-3.52	aliquot 1 filtrate
	-3.58	aliquot 2 filtrate
2	-3.57	filtration of filter 1, aliquot 1 filtrate
3	-3.63	filtration of filter 2 filtrate

[a] [U] is in mol/L.

equilibrium condition as $f(x) = \mu_{solid} - \mu_{solution}$. For $UO_2 \cdot xH_2O(am)$ this condition gives

$$f(x) = \mu^{\circ}_{UO_2 \cdot xH_2O(am)} - (\mu_{U^{4+}} + 4\mu_{OH^-})$$

Measurements. The pH values were measured with a combination-glass electrode calibrated against pH buffers.

Because of the inadequacy of centrifugation alone,[14] Amicon type F-25 Centriflo membrane cones (Amicon Corp., Lexington, MA) with effective 25 000 molecular-weight cutoffs and approximately 0.0018-μm pore sizes were used to effectively separate solids from solutions. Pretreatment steps[15] consisted of (1) washing and equilibrating the filters with deionized waters adjusted to the pH values of the samples, to avoid precipitation or dissolution of the solid phase caused by a change in the pH during filtration, and (2) passing a small aliquot of the sample through the filters (this filtrate was discarded), to saturate any possible adsorption sites on the filters and filtration containers. The efficacy of these filter treatment procedures for separating $PuO_2 \cdot xH_2O$ from solution had been tested previously,[15] and the treatment was found to be reliable. The similarity of uranium concentrations in a solution successively filtered through different 0.0018-μm filters (Table I) shows a lack of significant adsorption by the filters and further attests to the fact that the filters can be successfully used to separate $UO_2 \cdot xH_2O$ from solution.

The sealed tubes were centrifuged at about 1800g, and an aliquot was withdrawn for filtration. The filtrates were analyzed as follows: for uranium, by laser-induced fluorescence, using a Scintrex Model UA-3 uranium analyzer and the known-additions technique;[16,17] for other cations, such as Na, Fe, and Eu, by inductively coupled plasma spectroscopy; for anions such as Cl, by ion chromatography. Because the UA-3 analyzer is sensitive only to U(VI), the aqueous uranium samples were ozonated to convert all U(IV) to U(VI) prior to analysis. The uranium analysis method was tested and found to be free of interference from the levels of NaCl present in the aqueous samples. The acidic solutions containing millimolar uranium concentrations were analyzed for U(IV) concentration by spectrophotometry. The crystallinity of the precipitates was determined by using an X-ray diffractometer that used Cu K_α radiation.

Results and Discussion

The aqueous uranium concentrations observed at different times, in the presence of different reductants, and by being approached from both the oversaturation and undersaturation directions are similar (Figure 1), indicating that the concentrations are at equilibrium. Between pH 2 and 4, the uranium concentration decreases approximately 3 orders of magnitude for each unit increase in pH, whereas the concentration is essentially independent of pH above pH 4. As in the results of Ryan and Rai,[3] there is no evidence of amphoteric behavior, although there is a little more scatter in the data around pH 11, especially in experiments conducted in deaerated water only, without Fe powder. This scatter may have resulted from the incomplete elimination or inadvertent readmission of dissolved O_2, because the scatter disappeared, at short equilibration times, when the experiments were conducted in the presence of Fe powder.

The 3 order of magnitude decrease in uranium concentration observed for each unit increase in pH in the low-pH region is drastically different from the results reported by Bruno et al.[2] for the solubility of $UO_2 \cdot xH_2O(am)$ at room temperature (Figure 2). Their uranium concentrations decreased 1 order of magnitude, rather than 3 orders of magnitude, for each unit increase in pH.

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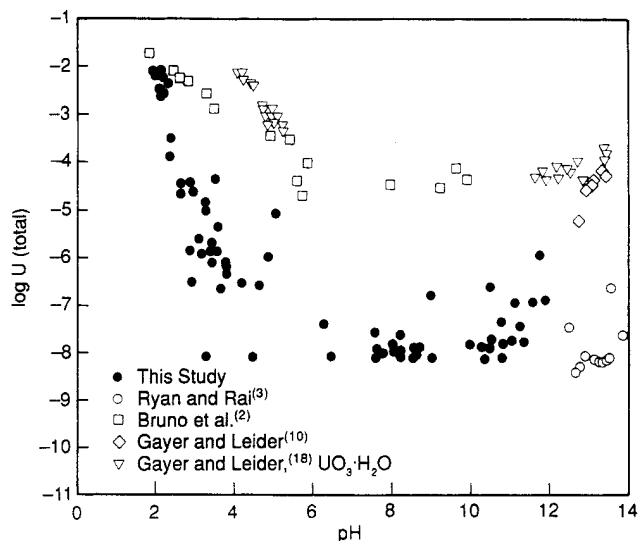(15) Rai, Dhanpat. *Radiochim. Acta* **1984**, *35*, 97–106.
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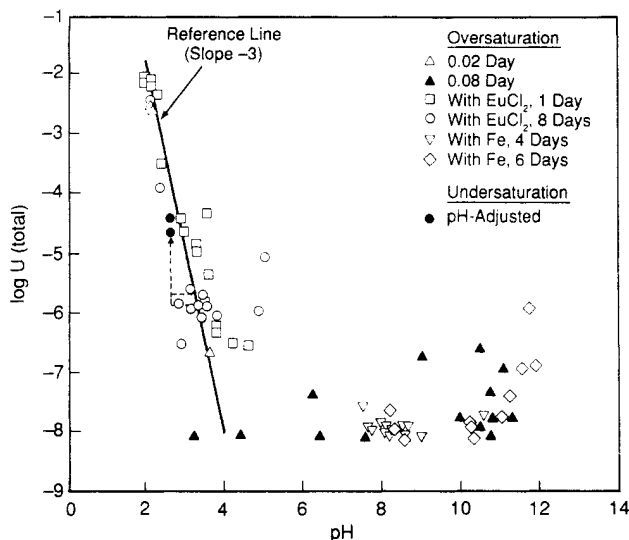
Figure 1. Uranium concentrations in 0.0018-μm filtrates from $UO_2 \cdot xH_2O$(am) suspensions, in deoxygenated water with and without the presence of metallic Fe or $EuCl_2$ as reductants, that were equilibrated for different periods.


Figure 2. Comparison of aqueous U concentrations in equilibrium with $UO_2 \cdot xH_2O$(am) obtained in this study (data from Figure 1) with those obtained by Ryan and Rai,[3] Bruno et al.,[2] and Gayer and Leider.[10] Also plotted are solubility data for $UO_3 \cdot H_2O$ from Gayer and Leider.[18]

Also, the solubilities we observed at higher pH values (Figure 2) are about 3.5 orders of magnitude lower than those observed by Bruno et al.,[2] Gayer and Leider,[10] and Galkin and Stepanova.[12] The $UO_2 \cdot xH_2O$ used in this study (Figure 3) shows an X-ray diffraction pattern similar to that of the solid in Bruno et al.'s[2] study, and both materials are amorphous. The solubility data of Gayer and Leider[10] and of Galkin and Stepanova[12] are reportedly for the amorphous phase as well. Therefore, these differences in solubility must result from differences in experimental or analytical variables.

Ineffective controls on redox potential, inadequate techniques for separating solids from solutions, and higher analytical detection limits for uranium will all result in higher apparent solubilities. We surmise that the higher solubilities of $UO_2 \cdot xH_2O$ observed by Bruno et al.[2] and others are probably a result of inadequate control of the oxidation state of uranium, especially at higher pH values, for the following reasons: (1) the solubilities we observed in this study are lower than those observed by others, including Bruno et al.;[2] (2) Fe powder and Eu^{2+}, which react readily with dissolved O_2, were used in our experiments; (3) our solubility results at higher pH values are low, like those obtained by Ryan and Rai[3] using $Na_2S_2O_4$ to maintain very low dissolved-O_2 fu-
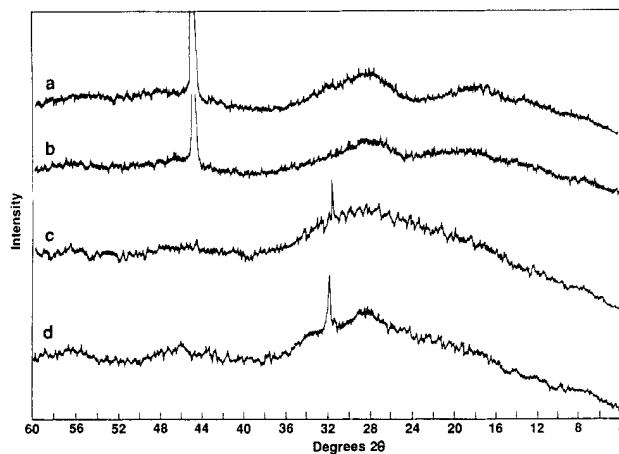
Figure 3. Tracings of X-ray diffraction patterns from solids separated from $UO_2 \cdot xH_2O$ suspensions equilibrated for different times (a and b for 6 days, c and d for 2 h) and at different pH values: (a) pH 11.7, precipitate from deoxygenated H_2O + Fe powder; (b) pH 8.2, precipitate from deoxygenated H_2O + Fe powder; (c) pH 6.4, precipitate from deoxygenated H_2O; (d) pH 3.3, precipitate from deoxygenated H_2O. None of the sharp peaks observed are for UO_2(c). Peaks around 2θ = 45° are for metallic Fe. The lack of UO_2(c) peaks and the broad hump around $2\theta = 28°$, where the most intense peak for UO_2(c) would be expected, are indications that the precipitates are amorphous $UO_2 \cdot xH_2O$.
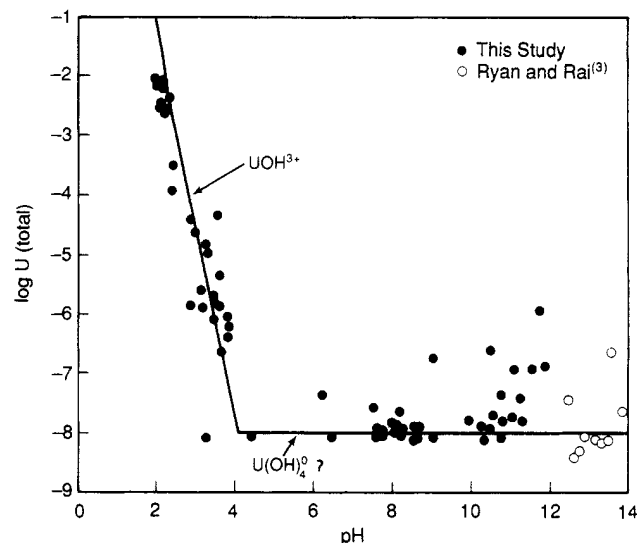
Figure 4. Aqueous U concentrations in equilibrium with $UO_2 \cdot xH_2O$(am). The solid lines are best-fit lines to data and correspond to $UO_2 \cdot xH_2O$(am) + $3H^+ \rightleftharpoons UOH^{3+}$ + $(x + 1)H_2O$ and $UO_2 \cdot xH_2O$(am) $\rightleftharpoons U(OH)_4^0$ + $(x - 2)H_2O$.

gacities (Figures 2 and 4); (4) our U(IV) solubilities are qualitatively similar to the solubilities of Np(IV),[13] which is less readily oxidized than U(IV), and of Th(IV),[19] which cannot be oxidized.

At pH <2, where uranium concentrations are high and the oxidation state can be analytically determined, both our results and those of Bruno et al.[2] show that uranium is present as U(IV), and our solubilities are also similar to theirs (Figure 2). Bruno et al.[2] assumed that uranium was present as U(IV) in their solutions at pH values >2 and supported their conclusions by showing that their solubility is similar to the solubilities observed by Gayer and Leider[10] and Galkin and Stepanova.[12] However, because these earlier researchers did not use any reductant to remove O_2 and because effective O_2 fugacities of $<10^{-65}$ atm (calculated from standard potentials) are required to maintain uranium in the tetravalent state, it is likely that the dominant aqueous species in their equilibrating solutions, with O_2 fugacities ranging between approximately $10^{-0.7}$ and 10^{-5} atm, was U(VI). For this reason, and because the solubilities of hydrous hexavalent uranium oxide (actually sodium polyuranates of somewhat indefinite composition) reported earlier by Gayer and Leider[18] are

similar to the solubilities reported by Bruno et al.,[2] it appears unlikely that Bruno et al. were able to maintain uranium in the tetravalent state. Bruno et al.[2] ignored Ryan and Rai's[3] criticism of Gayer and Leider's[10] data, erroneously discounting Ryan and Rai's[3] lower solubility data by hypothesizing that the data were for a more crystalline solid. Our data clearly show that the $UO_2 \cdot xH_2O(am)$ used in our study is similar to the solid used by Bruno et al.,[2] and our measured solubilities are similar to those obtained by Ryan and Rai,[3] further emphasizing that the solid in Ryan and Rai's[3] study must also have been amorphous and that the differences between the solubilities measured in this study and those measured by Bruno et al.[2] most likely result from ineffective control of redox potentials by Bruno et al.[2]

Although we were unable to directly determine the uranium oxidation state in aqueous solutions with pH values >2.3, the presence of slopes <−2 when log uranium is plotted against pH suggests that we were successful in maintaining uranium in the U(IV) state. Had oxidation taken place, the slopes should have been ≥−2 as a result of either the oxidation of a fixed amount of U(IV) or the dissolution of a U(VI) solid, such as $UO_3 \cdot H_2O$ or something approximating $Na_2U_2O_7 \cdot xH_2O$, that may form from the oxidation product. However, the scatter in our data may result from the partial oxidation of U(IV) to U(VI) in some of the samples. The solubility data in acid solutions (Figure 1) indicate an approximate slope of −3 versus the measured pH. This slope is a strong indication that the predominant reaction occurring in this pH region is

$$UO_2 \cdot xH_2O(am) + 3H^+ \rightleftharpoons UOH^{3+} + (x+1)H_2O \quad (1)$$

Utilizing a coupled nonlinear least-squares and chemical equilibrium program (NONLIN) that we developed, we calculated the equilibrium constant for reaction 1 from selected data shown in Figure 4 (27 points out of a total of 32, with obvious outliers discarded) for 1- and 8-day equilibration periods. This analysis yields a log K at zero ionic strength for reaction 1 of +3.5 ± 0.8.

To obtain a reliable value for the solubility product of $UO_2 \cdot xH_2O(am)$ from these data, an accurate value for the first hydrolysis constant for U(IV) is needed. Only three experimental determinations of the first hydrolysis constant of U(IV) have been made. Hietanen[20] performed electromotive-force measurements of U(IV) hydrolysis at high total U(IV) concentrations using 3 M $NaClO_4$ as the background electrolyte. Extrapolation of his data to dilute solutions is complicated by the possible formation of polynuclear species and the oxidation of U(IV) to U(VI), which would appear to be unavoidable in his solutions, as well as by the fact that only one concentration of $NaClO_4$ was studied. The most definitive data on the first monomeric hydrolysis product of U(IV) are the spectrophotometric data of Kraus and Nelson,[6] taken in both chloride and perchlorate media. These data, for ionic strengths of 0.02–2.0 M at relatively low total U(IV) concentrations (~0.001 M), are consistent with the later spectrophotometric work of Sullivan and Hindman[7] in 2 M $NaClO_4$. We have recalculated the data of Kraus and Nelson[6] utilizing the comprehensive ion-interaction model of Pitzer[21] and co-workers. Making the reasonable assumption in these calculations that ion-interaction parameters for $Th^{4+}-Cl^-$ [22] apply to $U^{4+}-Cl^-$, and again utilizing the nonlinear least-squares program NONLIN, we refitted the concentration constants of Kraus and Nelson[6] in chloride media. These calculations yield a log K value of −0.50 ± 0.03 for the reaction

$$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+ \quad (2)$$
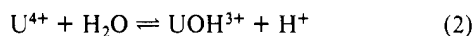
and Pitzer ion-interaction parameters for $UOH^{3+}-Cl^-$ of $\beta^0 = 0.17$, $\beta^1 = 6.2$, and $C^\phi = 0.03$. Our calculated log K value of −0.50

Table II. Comparison of Uranium Concentrations Measured with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and with a Scintrex Model UA-3 Uranium Analyzer

	log [U][a]			log [U][a]	
pH	ICP-MS	UA-3	pH	ICP-MS	UA-3
7.72	−8.15	−8.00	10.25	−8.01	−7.86
7.98	−7.97	−7.86	11.04	−7.86	−7.73
8.18	−8.20	−7.62	11.73	−5.98	−5.92
8.53	−8.28	−8.10			

[a] [U] is in mol/L.

is in good agreement with the −0.65 value from Baes and Mesmer's[8] extrapolation and the value of −0.68 from Kraus and Nelson.[6]

From reaction 2 with a log K value of −0.50 and from reaction 1, a log K_{sp}, at zero ionic strength, of −52.0 ± 0.8 was calculated for the reaction

$$UO_2 \cdot xH_2O \rightleftharpoons U^{4+} + 4OH^- + (x-2)H_2O \quad (3)$$

This value agrees well with the value of −52.6 estimated by Rai et al.[5] from the linear relationship between the experimental log K_{sp} values of thorium(IV), neptunium(IV), and plutonium(IV) hydrous oxides and the inverse square of the M^{4+} ionic radii. Thus our final model, which includes log $K = -0.50$ for reaction 2 and log $K_{sp} = -52.0$ and the Pitzer ion-interaction parameters for $UOH^{3+}-Cl^-$, (1) reproduces the spectrophotometric data of Kraus and Nelson,[6] (2) reproduces the solubility data for the hydrolysis of U(IV) at low concentration and pH values <4 [from this study, and from the work of Bruno et al.[2] for solutions in which the aqueous species was definitely shown to be U(IV)], and (3) is consistent with the thermochemical properties of other actinides.

Uranium concentrations at pH values >4 are around 10^{-8} M, our approximate detection limit for the laser-induced fluorescence method. Although a large number of data points from this study and from Ryan and Rai[3] are around 10^{-8} M, a fair number of samples (especially between pH 10 and 12) show higher uranium concentrations (Figure 4). Other than the possible oxidation of U(IV) to U(VI), there are no explanations for the higher concentrations. Therefore, the low values (~10^{-8} M) obtained must be considered to be the solubility of $UO_2 \cdot xH_2O(am)$. To determine whether the values around 10^{-8} M are an artifact of the detection limit, several samples were analyzed by inductively coupled plasma mass spectroscopy, which has detection limits of about 10^{-12} M. These analyses (Table II) confirm that the measured uranium concentrations are real. Methods are currently not available to accurately check the oxidation state of aqueous uranium at these low concentrations. If one assumes that the uranium is present as U(IV), then the log K for the reaction

$$UO_2 \cdot xH_2O(am) \rightleftharpoons U(OH)_4^0 + (x-2)H_2O \quad (4)$$
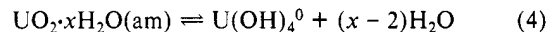
is approximately −8.0. If, on the other hand, uranium is present as U(VI), which may be the case, then the log K value of −8.0 is an upper limit for reaction 4. In any case, as shown in Figure 2, the measured solubilities for $UO_2 \cdot xH_2O(am)$ throughout the pH range between 4 and 14 are 3–4 orders of magnitude lower than reported previously.[2,10,12] As pointed out earlier, we surmise that the reason for the higher solubilities reported previously is the inability to control the redox state of uranium: Gayer and Leider[10] made no attempt; Galkin and Stepanova[12] purged with Ar, but even prepurified Ar or N_2 contains tens of parts per million of O_2, whereas O_2 fugacities less than about 10^{-65} are needed to keep uranium in the U(IV) state.

From our data, it is not possible to obtain precise values of constants (K_{1n}) for other hydrolysis reactions

$$U^{4+} + nH_2O \rightleftharpoons U(OH)_n^{4-n} + nH^+ \quad (5)$$
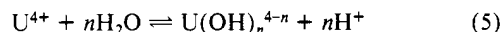
However, if it is assumed that $U(OH)_2^{2+}$ and $U(OH)_3^+$ become dominant species at pH 4, where measured U concentrations are approximately 10^{-8} M (Figure 4), and that $U(OH)_5^-$, if it exists, becomes dominant at pH 14, then the upper limits on log K_{12}, log K_{13}, and log K_{15} are <−4.0, <−8.0, and <−26, respectively.

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The value of log K_{14} from reactions 5 and 6 is <-12.0. Even though these values of log K_{1n} are not precise, they are several orders of magnitude lower than the values generally accepted[8] (log K_{12} through log K_{15} of -2.6, -5.8, -10.3, and -16.0, respectively), recently reported[2] (log K_{13} and log K_{14} of -1.1 and -5.4, respectively), or used in thermodynamic equilibrium codes such as EQ3NR[23] (log K_{12} through log K_{15} of -2.25, -4.88, -8.53, and -16.5, respectively).

In conclusion, the solubility of amorphous $UO_2 \cdot xH_2O$, especially at pH values >4, was found to be 3–4 orders of magnitude lower than previously reported.[2,10,12] This difference results primarily from the inability of previous workers to maintain reducing conditions. The measured values for solubility product and the U(IV) first hydrolysis constant are consistent with the reliable solubility and spectrophotometric data and with the properties of other tetravalent actinides. The measured upper-limit values for the equilibrium constants for the formation of $U(OH)_2{}^{2+}$, $U(OH)_3{}^+$, $U(OH)_4{}^0$, and $U(OH)_5{}^-$ are several orders of magnitude lower than those previously reported.[2,8,23]

Registry No. U, 7440-61-1; $UO_2 \cdot xH_2O$, 19961-12-7.

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Open-Chain Polyamine Ligands with More Rigid Double Connecting Bridges. Study of Their Metal Ion Selectivities by Molecular Mechanics Calculation, Crystallography, and Thermodynamics

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Ligands with two N-(2-aminoethyl), N-(3-aminopropyl), or N-acetate pendant groups on piperazine (PIP), homopiperazine (HPIP), or 1,5-diazacyclooctane (DACO) are described. Protonation and formation constants of some of the complexes of these ligands with Cu(II), Ni(II), Zn(II), Cd(II), Pb(II), Ca(II), Sr(II), and Ba(II) are determined. Electronic spectra of the complexes with Cu(II) and low-spin Ni(II) are reported. It is shown that (A) doubly bridged open-chain polyamines have metal ion size selectivity patterns that resemble those of isomeric tetraaza macrocycles and (B) ligand field (LF) strengths of doubly bridged open-chain polyamines are similar to those of isomeric tetraaza macrocycles. Point A suggests that size selectivity is controlled by chelate ring size rather than macrocyclic ring size, and point B indicates that LF strength is controlled by donor atom basicity along the series primary $<$ secondary $<$ tertiary if there are no large differences in steric distortions of the M–N bonds. log K_1 values of complexes of doubly bridged open-chain polyamine ligands are lower than those of tetraaza macrocycles. This is attributed to low levels of preorganization in the doubly bridged open-chain polyamine free ligand, where there is a large increase in strain energy on altering the ligand from its lowest energy conformer to that required for complex formation. The crystal structure of [Ni(BAP-HP)](ClO$_4$)$_2$ is reported (BAP-HP = 1,4-bis(3-aminopropyl)-1,4-diazacycloheptane). Crystal data: $C_{11}H_{26}Cl_2N_4O_8Ni$, monoclinic, space group $P2_1/n$, $a = 9.008$ (8) Å, $b = 14.251$ (3) Å, and $c = 14.490$ (4) Å, $\beta = 98.09$ (5)°, $Z = 4$, $V = 1841.6$ Å^3, $d_m = 1.710$ g·cm^{-3}, $d_c = 1.702$ g·cm^{-3}. The final conventional R factor was 0.0603. Molecular mechanics (MM) calculations showed that the rigidity of doubly bridged open-chain tetraamines in their complexes was slightly less than that of tetraaza macrocycles.

Introduction

An important idea in the chemistry of more structurally elaborate ligands is *preorganization*,[1] i.e. that the free ligand is already in the correct conformation for complexing a metal ion. With highly preorganized ligands there may even be a drop in strain energy (U) on complex formation.[2,3] More sharply defined metal ion size requirements of highly preorganized ligands lead to enhanced metal ion size-match selectivity; i.e., the ligand complexes more strongly with metal ions that better match the ligand size requirements. This is best seen in spherands[2] (Figure 1), which can selectively extract the tiny amounts of Li$^+$ ion present in AR KOH, since the Li$^+$ ion matches the size requirements of the spherand, whereas K$^+$ does not.[2] Recent work[4,5] has shown

how higher levels of preorganization may be achieved for tetraaza macrocycles by double bridging a pair of nitrogen donor atoms, giving sharper metal ion size selectivity, in the ligand B-12-aneN$_4$, seen in Figure 1. The high levels of preorganization due to the piperazine bridge between adjacent nitrogens result in very slow rates of metalation and demetalation, as is found with all highly preorganized ligands.

Molecular mechanics (MM) calculations[6,7] show that the size selectivity of tetraaza macrocycles is mainly controlled by the size

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