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URANIUM(IV) SOLUBILITY AND HYDROLYSIS CONSTANTS UNDER REDUCED CONDITIONS

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Abstract

The solubility of $\text{UO}_2(\text{s})$ was examined in dilute NaCl solutions at room temperature and in the pH range from 2 to 12. Dissolution equilibrium showed good agreements between the data obtained by oversaturation and undersaturation experiments.

The dissolution reactions that control the solubility of U[IV] are estimated as $\text{UO}_2(\text{s}) + 4\text{H}^+ \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0$. The log K at zero ionic strength are yielded 0.34 ± 0.4 and -8.7 ± 0.4 , respectively. The hydrolysis constant ($\log \beta_{1,1}$) is calculated -9.0 ± 0.5 for the hydrolysis reaction of $\text{U}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0 + 4\text{H}^+$. Contribution of the other uranium species to the solubility are of minor importance.

The crystallization of the precipitations of $\text{UO}_2(\text{s})$ progressed gradually in the oversaturation experiments. Nevertheless the progress of crystallization had little effect on the solubility.

Introduction

Prediction of the aqueous behavior of uranium is an important matter for the safety assessments of radioactive waste isolation. The thermochemical data of U[IV] is one of key data for the prediction of uranium behavior, because the valence of uranium is predicted tetravalent under the assumed redox condition in a deep groundwater.

The solubility of U[IV] has been studied by many authors, however the reported data vary over several orders of magnitude[1-9]. The differences in the reported data are probably based on the difference of keeping of redox potential, because U[IV] is readily oxidized to U[VI] in the presence of O_2 . In this study, we have measured the solubility of $\text{UO}_2(\text{s})$ and have estimated the hydrolysis constants. The valence of uranium was maintained as tetravalent by using sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) and solvent extraction in a prepurified Ar atmosphere.

Methods

To eliminate the oxidation of U[IV] to U[VI], all experiments were conducted in a glovebox with prepurified Ar atmosphere (above 99.99% Ar, under one part per million of O_2). Water used was distilled water thoroughly sparged with high-purified Ar.

Reagents

U[IV] stock solution was prepared by electrolytic reduction from uranium nitrate solution. Uranium nitrate solution ($\sim 0.1\text{M}$ of U and 3N HNO_3) with 0.1M hydrazine was electrolyzed (5A, 5V, Ti catalyst) for 2 hours continuously. Just before the experiment, U[IV] stock solution was treated 3 times by solvent extraction with 10% TBP- CCl_4 repeatedly to eliminate the remained U[VI] in the stock solution. Ratio of U[VI] to U[IV] was below 0.001%. It was measured by gravimetric analysis of U[VI] coprecipitation with fluorine.

The $\text{UO}_2(\text{s})$ sample was prepared by reduction of ammonium diuranate (ADU , $(\text{NH}_4)_2\text{U}_2\text{O}_7$). The reduction procedure was the roasting at 650°C for 2 hours in mixed gas (H_2 50%, N_2 50%) atmosphere. X-ray diffraction pattern of $\text{UO}_2(\text{s})$ sample is given in Figure 3. The diffraction peaks were very sharp and the $\text{UO}_2(\text{s})$ sample was identified as crystalline.

NaOH solution for pH adjustment was prepared by using a new bottle of super grade NaOH . The NaOH solution was treated with 7% excess BaCl_2 to lower the dissolved carbonate through BaCO_3 precipitation. This procedure is similar with that of Rai et al.[1].

Experimental Procedure

In the case of oversaturation experiments, each sample was prepared by 1ml U[IV] stock solution and 29ml deoxygenated distilled water containing 0.01M hydrosulfite sodium ($\text{Na}_2\text{S}_2\text{O}_4$) in a 50ml glass vial. The uranium concentration of the sample was approximately 0.003M.

In the case of undersaturation experiments, approximately 30mg of $\text{UO}_2(\text{s})$ powder was added into 30ml of 0.01M $\text{Na}_2\text{S}_2\text{O}_4$ solution prepared by deoxygenated distilled water.

The following operations were the same in both of the oversaturation and the undersaturation experiments.

Ionic strength of each sample was adjusted to 0.1 by adding NaClO_4 . The pH value of the sample was adjusted to a range between approximately pH 2 and 12 by adding HClO_4 or carbonate-free NaOH . Upon pH adjustment in oversaturation experiments, precipitates of U[IV] hydroxide were observed in all samples. The vials were sealed and continuously shaken at room temperature (25°C) during aging term.

After aging term, the pH and Eh values were measured and each sample was filtered by using ultra filter (Millipore co. TGC-1) of 10000 molecular-weight cutoffs. The filtered solutions were adjusted to pH 2 by HClO_4 and were treated by solvent extraction with 10% TBP-CCl_4 to eliminate the effect of U[VI] . Solid samples were washed by deoxygenated water. The pH of deoxygenated water was adjusted to the sample pH before use.

Measurements

The pH values were measured with a combination-glass electrode (Yokokawa Electrical co. PH-82). Concentrations of uranium were measured by using fluorescence spectrum analyzer (Shimazu Production co. RF-5000) and inductively coupled plasma mass spectroscopy (ICP-MS, Seiko Electronic Industry co. SPQ-8000A-1). The detection limit of uranium was $2 \times 10^{-11}\text{M}$ by ICP-MS analyzer. The crystallization of precipitates were analyzed by using X-ray diffraction meter (MAC Science co. MXP-1) with $\text{Cu-K}\alpha$ radiation.

Results and Discussion

Figure 1 shows the aqueous uranium concentration observed after different aging terms in the oversaturation and the undersaturation experiments. The data obtained by both experiments show good agreements. It suggests that the dissolution reactions of uranium are the same in the both experiments. The dissolution reaction reached a equilibrium state after 14 days of the oversaturation experiments because the value and the scatter of data converged. In pH below 2 the uranium concentration decreases approximately 4 order of magnitude for each unit increase of pH. In pH above 3 the uranium concentrations are essentially independent on pH.

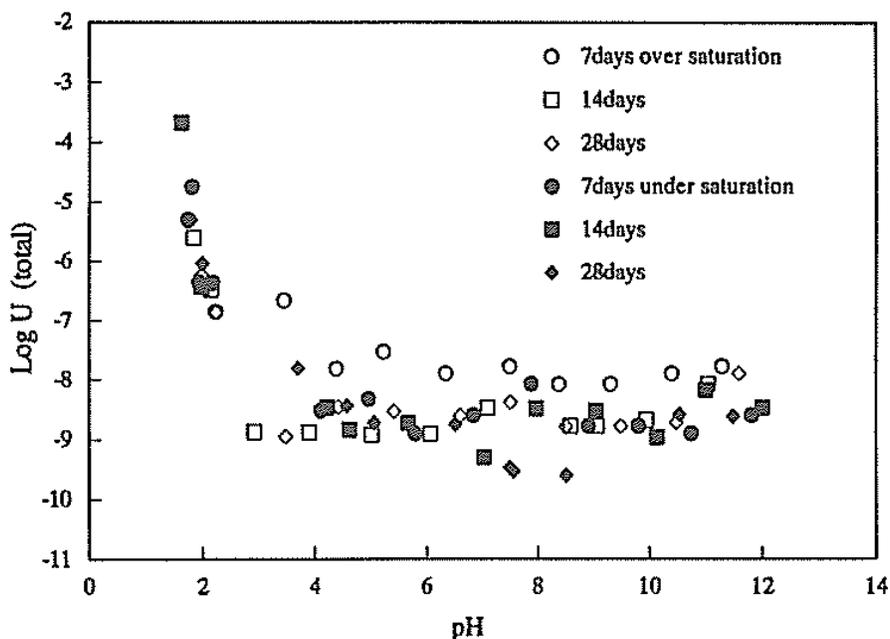


Figure 1. Concentrations of U[IV] at different aging terms in the oversaturation and the undersaturation experiments as a function of pH.

Figure 2 gives a comparison of the solubility data obtained in this study with literature data. Data of this study are 4~6 order of magnitude lower than the results for the solubility of $UO_2(am)$ at room temperature reported by Bruno et al. [2], 0.5~2 order of magnitude lower than the results by Rai et al. [1]. However the tendency of solubility data in this study is very similar to those of Rai et al.

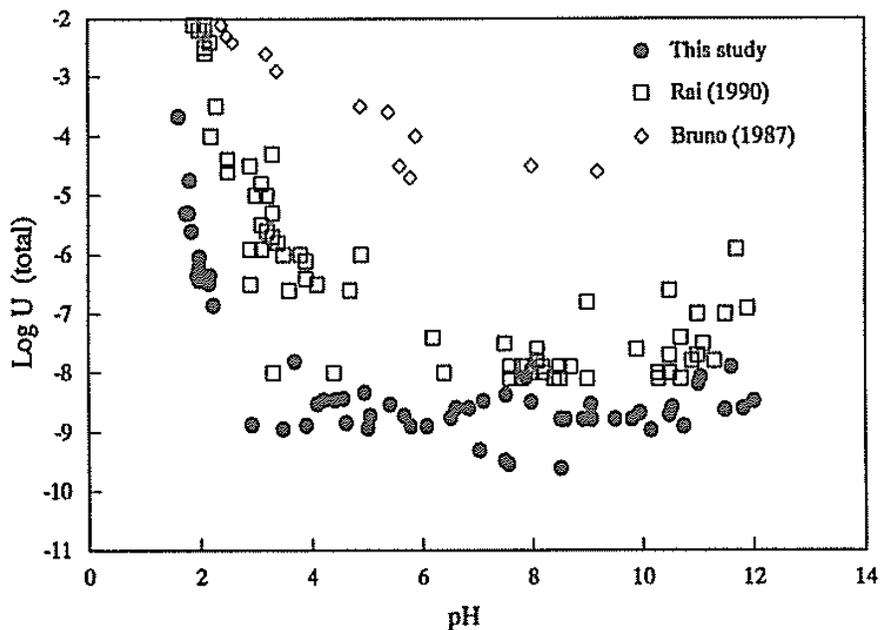


Figure 2. Comparison of solubility data obtained in this study with literature data.

Figure 3 shows the diffraction patterns of precipitations in the oversaturation experiments of pH 4~7. The diffraction peaks became stronger and sharper with the aging time. In pH above 4, precipitates obtained in the oversaturation experiments in each aging term were identified as $\text{UO}_2(\text{s})$ by X-ray diffraction pattern. In pH below 4, the diffraction patterns were no clear. The XRD results in pH above 4 suggests that the crystallization of the precipitates are progressing in the experiments. Nevertheless the concentrations of U[IV] are independent on the aging terms. The progress of crystallization had little effect on the solubility.

In the undersaturation experiments, the crystallization of solid phase was not changed from initial form of $\text{UO}_2(\text{s})$ in all pH range during aging terms.

In pH below 2, the solubilities of U[IV] indicate slop of approximately -4 versus pH. The dominant reaction in this pH region is estimated as follows,



In pH above 2, the solubilities are constantly around 10^{-9} M and independent on pH. The dominant reaction in this pH region is estimated as follows,



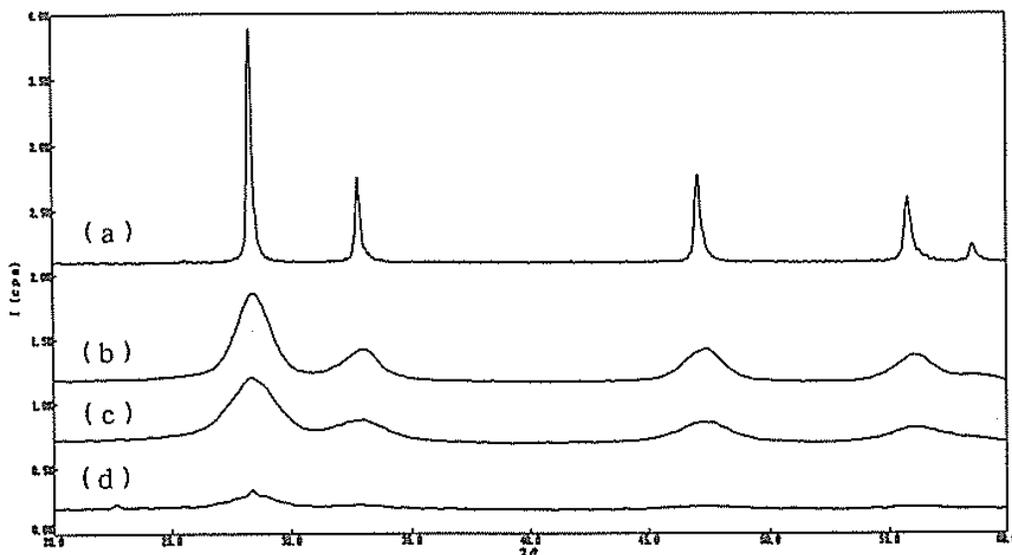


Figure 3. X-ray diffraction patterns of $\text{UO}_2(\text{s})$ precipitations at different aging terms in oversaturation experiments. (a) $\text{UO}_2(\text{s})$ sample used in undersaturation experiments; (b) pH 4.4 at 7 days; (c) pH 5.0 at 14 days; (d) pH 4.4 at 28 days.

Figure 4 shows the activities of U[IV] without 7 days data in oversaturation experiments. The activities of U[IV] are calculated from the solubility data by Davies activity correction equation[10] which is described as follows.

Davies equation ;

$$\log \gamma = -A \left[|Z_+ Z_-| \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right] \quad (3)$$

A : constant (0.51 at 25°C)

Z_+ : electric charge

I : ionic strength

Ionic strength

$$I = 1/2 \sum Z_i \cdot C_i \quad (4)$$

Z_i : number of electric charge of species i

C_i : concentration of species i

The equilibrium constant ($\log K_1$) at zero ionic strength for equation(1) in pH below 2 is calculated by means of least-squares fitting of U[IV] activity and pH. $\log K_1$ is estimated 0.34 ± 0.4 . The equilibrium constant ($\log K_2$) for equation(2) in pH above 2 is estimated -8.7 ± 0.4 by the same procedure. These values are several orders of magnitude lower than the literature data[1-5].

The hydrolysis constant ($\log \beta_{1,4}$) is calculated -9.0 ± 0.5 for the reaction of $\text{U}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0 + 4\text{H}^+$ by using $\log K_1$ and $\log K_2$.

Contribution of the other uranium species (UOH^{3+} , $\text{U}(\text{OH})_2^{2+}$, $\text{U}(\text{OH})_3^+$ and $\text{U}(\text{OH})_4^-$) to the solubility are estimated of minor importance.

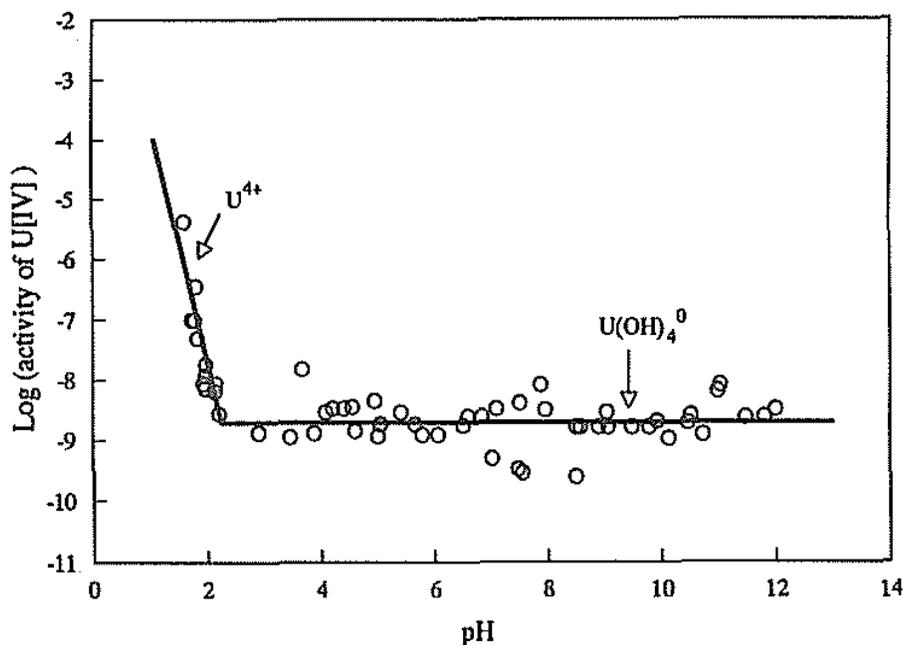


Figure 4. Calculated activity of U[IV] species as a function of pH. Lines are best-fit lines for the reactions of $\text{UO}_2(\text{s}) + 4\text{H}^+ \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0$.

Conclusion

The dominant dissolution reactions that control the solubility of U[IV] are identified as $\text{UO}_2(\text{s}) + 4\text{H}^+ \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0$. The log K_s of each reaction at zero ionic strength are yielded 0.34 ± 0.4 and -8.7 ± 0.4 , respectively. The hydrolysis constant ($\log \beta_{14}$) is calculated -9.0 ± 0.5 for the hydrolysis reaction $\text{U}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{U}(\text{OH})_4^0 + 4\text{H}^+$. Contribution of the other uranium species to the solubility are of minor importance. These values are several orders of magnitude lower than those of previously reported.

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