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Solubility of U(VI) in Highly Basic Solutions

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Summary

The solubility of U(VI) was measured in highly basic solutions ($pOHc = -\log[OH^-]$ ranges from 3 down to 0) at the ionic strength $I = 0.5-2.0$ M (M: mol dm^{-3}) over a wide range of carbonate ion concentrations $C = 1 \times 10^{-3}-0.5$ M by both oversaturation and undersaturation methods. In oversaturation experiments, the solubility of U(VI) decreased with increasing equilibration time from 1 week to 1 year, suggesting an increase in the crystallinity of the solid phase with aging. The solid phase was identified as $Na_2U_2O_7 \cdot x\,H_2O$ ($x = 3-5$) by X-ray diffraction. Undersaturation experiments conducted for 1 month with this solid phase indicated a rapid attainment of equilibrium. These data were well interpreted by considering the formation of $[UO_2(OH)_3]^-$, $[UO_2(OH)_4]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$, and the apparent equilibrium constants for $[UO_2(OH)_3]^-$ and $[UO_2(OH)_4]^{2-}$ were determined with fairly small deviations. Using the evaluated solubility product of $Na_2U_2O_7 \cdot x\,H_2O$ ($x = 3-5$), the stability constants for the above species were evaluated. The upper limit values of the stability constants of the carbonatohydroxodioxouranium(VI) complexes were also evaluated.

1. Introduction

Reliable thermoynamic stability data on complex formation of actinide ions are required to evaluate the migration of actinide elements from a deep underground repository. In a weakly acidic solution without any complexing ligands, the solubility of U(VI) is controlled by the equilibrium between its free hydrated ion and the solid. When the solution becomes weakly basic and is equilibrated with air, the solubility is greatly increased by the formation of complexes with hydroxide ion and carbonate ion. In spite that the concentration of carbonate species decrease in much more basic solutions of $pH > 12$, the highly hydrolyzed species become dominant and thus the solubility of U(VI) increases. For example, when cement containment is applied to confine transuranium elements, it requires the reliable thermodynamic constants of U(VI) hyroxide species because the cement has high basicity. The reliable stability data, however, are lacking for these hydrolyzed species, because there have been almost no experimental investigation in such highly basic solutions.

The solubility equilibria between the complex species and their solubility limiting solids are inevitably affected by the crystalline form of the solids [1, 2], stability data must be determined by experiments where both the chemical components and the crystallinity of the solids are correctly identified. Aqueous solutions of U(VI) with high *pH* conditions need rather long time to attain its equilibrium, as is the case for the Pu(IV) system [3], whereas the U(VI) system at $pH < 7$ reaches the equilibrium within 30 minutes [4]. In order to check whether the system has reached equilibrium or not, we examined an attainment of a "steady state" of the solution concentration and compared oversaturation experiments with undersaturation experiments equilibrated with the well-characterized solubility limiting solid.

The carbonate complex formation and hydrolysis reactions occur simultaneously, because the carbonate ion concentration increases with increasing *pH*. Ternary coordination compounds, presented as $[UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}$ followed by IUPAC nomenclature [5], are expected in basic solution. For U(VI), the existence of $[(UO_2)_2(CO_3)(OH)_3]^-$ [6–8] and $[UO_2(CO_3)(OH)]^-$ [9] have been suggested. In the solubility study of Np(VI), on the other hand, the formation of $[NpO_2(CO_3)(OH)_2]^{2-}$ and $[NpO_2(CO_3)_2(OH)_2]^{4-}$ have been proposed to explain the increase in the solubility with increasing carbonate ion concentration and the decrease with increasing *pH* of solutions from 12 to 13 [10–12]. These types of complexes have not been proposed in the analysis of the solubility of U(VI) because no investigations were reported for hydroxide-carbonate systems in such highly basic solutions.

The objectives of this research are thus twofold:

1) precise and accurate determination of the stability constants of hydrolyzed species of $[UO_2(OH)_3]^-$ and $[UO_2(OH)_4]^{2-}$, and

2) examination of existence of carbonatohydroxouranium(VI) ions.

2. Experimental

A stock solution of uranyl perchlorate was prepared from the uranyl nitrate hexahydrate purchased from

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Merck Co. Ltd. by a method previously described [13]. Sodium diuranate hydrate $Na_2U_2O_7 \cdot x\,H_2O$ was prepared by the following method: The uranyl nitrate hexahydrate was placed in a sealed polypropylene centrifuge tube and was dissolved in deionized water. A large excess of 10 M NaOH solution was added to the uranyl nitrate solution in a glove box filled with an inert Ar gas. The centrifuge tube was sealed and shaken at ambient temperature for 10 days. After removing the supernatant solution by decantation, the solid phase was washed with a 0.01 M NaOH solution three times also under an Ar atmosphere. The solid phase was isolated by filtering the solution through a membrane filter and dried in a vacuum desiccator for a week.

Sample solutions were prepared in sealed polypropylene tubes. The stock solution of uranyl perchlorate (for the oversaturation experiments) or the sodium diuranate (for the undersaturation experiments) was added so as to adjust the U(VI) concentration to be 10^{-2} M, *i.e.* larger than the U(VI) solubility in the region of interests. To adjust hydroxide ion concentration, total carbonate ion concentration and ionic strength, NaOH, $NaHCO_3$ and $NaClO_4$ (Wako Pure Chemical Industries, Ltd.) of analytical grade, respectively, were used without further purification. The sample solutions were shaken at 25±1 °C for a certain period to attain equilibrium. The concentration of dissolved U(VI) was defined as the concentration of U(VI) contained in the solution filtrated through the membrane filter (Millipore Co. Ltd., NMWL 10^5) because the concentration of U(VI) in the filtrated solutions were independent of the pore sizes of the filters. The concentrations of U(VI), [U], and total carbonate ions, C, were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) HP4500 (Hewlett Packard Co. Ltd.) and Total Organic Carbon Analyzer TOC-5000A (Shimadzu Corp.), respectively. All treatments were conducted under an Ar gas atmosphere to exclude contamination by CO_2 contained in air.

The hydroxide ion concentrations, $[OH^-] = 10^{-pOHc}$, of the test solutions with three different ionic strengths (I = 0.5, 1.0, 2.0 M) were determined using a cell with a glass electrode and a reference electrode:

$$\text{test solution (ionic strength} = I)$$

$$|\ I\ \text{M NaClO}_4,\ 3.3\ \text{M NaCl}\ |\ \text{AgCl, Ag}\,. \qquad (1)$$

The electrode with I M $NaClO_4$ electrolyte was calibrated against a solution with I M $NaClO_4$, and was used in the test solution with the same electrolyte concentration. The emf of the cell has linear relationship with the logarithm of the hydrogen ion concentration as:

$$E = E^0 + \frac{RT}{F}\ln a_{OH^-} + E_j$$

$$= E^{0*} + \frac{RT}{F}\ln[OH^-] + E_j\,, \qquad (2)$$

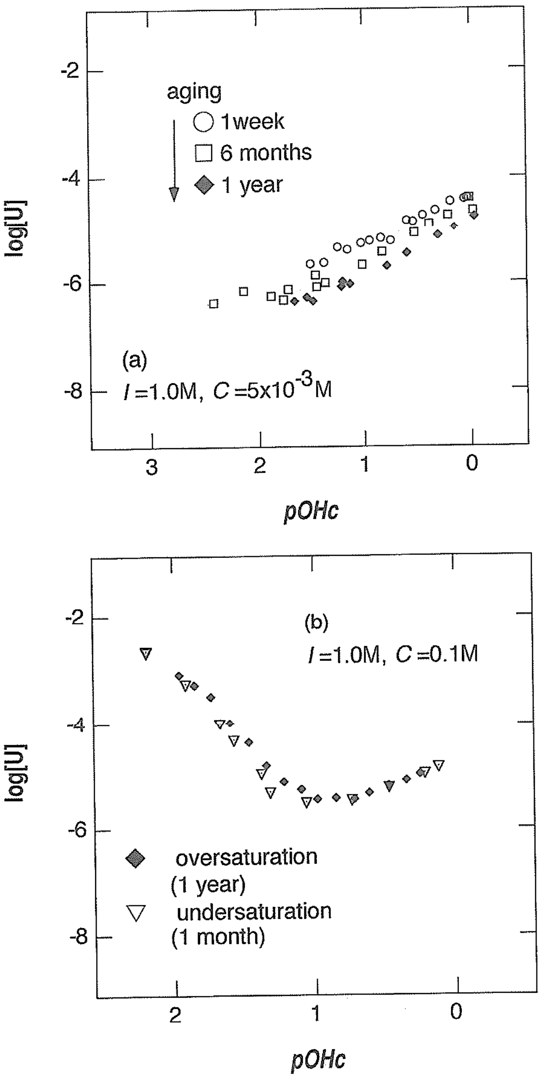

Fig. 1. Comparison of U(VI) concentrations obtained in our study at I = 1.0 M (a) U(VI) concentration of the oversaturation samples aged for 1 week (○), 6 months (□) and 1 year (◆). (b) U(VI) concentration of the oversaturation samples aged for 1 year (◆) and the undersaturation samples aged for 1 month (▽).

where E^0 and E^{0*} are constants, a_{OH^-} is the activity of the hydroxyl ion, and E_j is the liquid junction potential. The electrode with I M $NaClO_4$ was calibrated by determining the $E^{0*} + E_j$ by the Gran plot [14] in the same concentration of electrolyte.

The identification of solid phases was performed by X-ray Powder Diffraction (XPD) method.

3. Results and discussion

3.1 Aging and solid phase

Aqueous U(VI) concentrations in I = 0.5, 1.0 and 2.0 M solutions of the oversaturation experiments decreased with increasing standing time from 1 week to 1 year as indicated in Fig. 1(a) for I = 1.0 M. After 1 year for I = 1.0 M and after 6 month for I = 0.5 M,

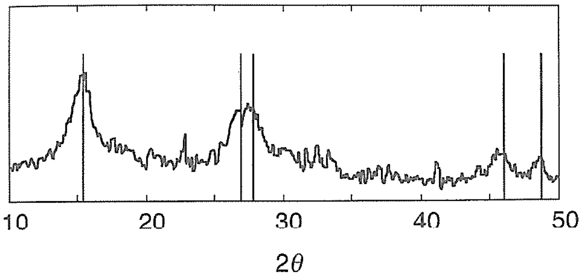

Fig. 2. X-ray powder diffraction diagram obtained with Cu $K\alpha$ for the solid compound precipitated in the oversaturation sample aged for a week at *pOHc* 1−2, compared with the data of sodium diuranate hydrate from ASTM No. 18-1436.

they were found to be unchanged. This suggests that equilibrium is attained within a period from 6 months to 1 year.

In order to determine if the sample had certainly reached to its equilibrium or not, undersaturation experiments were also necessary. Some researchers avoid the precipitation of sodium uranate by using tetraalkylammonium hydroxide and tetraalkylammonium salts to adjust alkalinity and ionic strength, respectively [15]. We took an another approach and carried out the oversaturation experiment as follows. After the solutions of which *pOHc* ranged from 0.5 to 2 were aged for 1 week, the solid phase was collected from the sample solutions and dried in air. Based on the result of XPD (Fig. 2), the solid phase precipitated in the oversaturation experiments was identified as sodium diuranate hydrate $Na_2U_2O_7 \cdot x\,H_2O$ ($x = 3-5$) based on the reference data ASTM No. 18-1436. Thus, we included this well-identified compound as a solubility limiting solid phase in the undersaturation experiments.

The results of the oversaturation experiments aged for 1 year and the undersaturation experiments aged for 1 month ($C = 0.1$ M for all) are shown in Fig. 1(b). According to the figure, the aqueous U(VI) concentrations equilibrated with the $Na_2U_2O_7 \cdot x\,H_2O$ solid phase are almost the same as the U(VI) concentration in the oversaturation sample aged for 1 year.

Based on these results, the following conclusion is drawn: (a) The solubility limiting solid phase for the undersaturation experiments was correctly selected. (b) In spite of the fact that the attainment of equilibrium is fairly slow in strong basic solutions, aging for 6 months to 1 year is enough for the oversaturation experiments, and the aging of 1 month is enough for the undersaturation experiments.

3.2 Calculation of the equilibrium constants

Table 1 is the list of the values of [U], *C* and *pOHc* of all the samples in undersaturation experiments. There are three series of experiments: the dependency on *pOHc* at *C* in the 10^{-3} M order (run: A05U, A10U, A20U) and at *C* in the 10^{-1} M order (run: B05U, B10U, B20U), and the dependency on *C* (run: C05U, C10U, C20U).

The formation of $[UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}$ was characterized by an apparent equilibrium constant K' for the reaction (3) assuming the solubility limiting solid phase to be $Na_2U_2O_7 \cdot x\,H_2O$.

$$\begin{aligned}0.5\,Na_2U_2O_7 \cdot x\,H_2O + (q-3)\,OH^- + p\,CO_3^{2-} \\ \rightleftharpoons [UO_2(CO_3)_p(OH)_q]^{(2-2p-q)} + Na^+ \\ + (0.5\,x - 1.5)\,H_2O \quad (x = 3-5)\,.\end{aligned} \tag{3}$$

The apparent equilibrium constant K' is thus defined as

$$K' = \frac{[[UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}][Na^+]}{[OH^-]^{(q-3)}[CO_3^{2-}]^p}\,. \tag{4}$$

In the basic solutions examined in the present work, anionic hydrolyzed species and carbonate complexes are expected to be major species. It is known that the average number of coordinated hydroxo ligand per uranyl hydrolyzed molecule, $\bar{n}$, increases with increasing $[OH^-]$ to reach $\bar{n} = 3-4$ at *pH* 13 [16]. No hydrolyzed species with $\bar{n} > 4$ has been reported so far. A polymeric hydrolyzed species $[(UO_2)_3(OH)_7]^-$ ($\bar{n} = 2.33$) has been widely investigated as one of the major species in the region around *pH* 8−9 but almost no contribution is expected at $pOHc < 3$ from the stability constant [17]. No other polymeric hydrolyzed species with $\bar{n} > 2.33$ has been reported [1, 2, 9, 18]. Based on the present knowledge, it can be expected that the species of which contributions are important at *pOHc* 0−3 are $[UO_2(OH)_4]^{2-}$ and $[UO_2(OH)_3]^-$. Thus the U(VI) concentrations obtained in the range of *pOHc* 2.5−0.0 were analyzed by assuming predominant contribution of the species $[UO_2(OH)_4]^{2-}$, $[UO_2(OH)_3]^-$ and $[UO_2(CO_3)_3]^{4-}$, described as

$$\begin{aligned}[U] = [[UO_2(CO_3)_3]^{4-}] + [[UO_2(OH)_3]^-] \\ + [[UO_2(OH)_4]^{2-}]\,.\end{aligned} \tag{5}$$

The undersaturation data listed in Table 1 were used to compute the apparent equilibrium constants K'. The numerical computations of K' were performed by the non-linear least-squares fitting to minimize the sum of the squared deviations $\sum(\log[U]_{obsd.} - \log[U]_{calcd.})^2$, dealing with both dependency on *pOHc* (run: A05U, B05U, A10U, B10U, A20U, B20U) and *C* (run: C05U, C10U, C20U) simultaneously for a given ionic strength. The determined values of $\log K'$ are listed in Table 2. The errors immanent in the measured parameters are evaluated as $(\sigma_{\log[U]})^2 = 9.2\times10^{-4}$, $(\sigma_{\log C})^2 = 1.6\times10^{-5}$ and $(\sigma_{pHc})^2 = 4.4\times10^{-4}$ in the region of the measurements.

Fig. 3 shows the experimental U(VI) concentrations and the solubility curves calculated based on the $\log K'$ values listed in Table 2. The three species included in the calculation show the *pOHc* dependen-

Table 1. Experimental data for the system U(VI)/CO_3^{2-}/OH^- at 25°C

condition:	I=0.5M								
run:	A05U			B05U			C05U		
period:	3 month			4 month			4 month		
	pOHc	*C*	[U]	*pOHc*	*C*	[U]	*pOHc*	*C*	[U]
	2.75	2.67E-03	3.43E-07	1.85	1.43E-01	8.27E-04	0.78	1.20E-01	6.21E-06
	2.56	2.54E-03	5.50E-07	1.72	1.27E-01	3.48E-04	0.78	1.92E-01	5.76E-06
	2.37	2.90E-03	4.57E 07	1.61	1.46E-01	1.88E-04	0.78	1.14E-01	4.66E-06
	2.43	2.72E-03	2.62E-07	1.47	1.21E-01	4.01E-05	0.78	8.53E-02	4.77E-06
	2.13	2.79E-03	2.72E-07	1.36	1.30E-01	1.75E-05	0.78	8.06E-02	3.20E-06
	1.93	2.58E-03	3.49E-07	1.20	1.41E-01	7.29E-06	0.78	5.47E-02	3.13E-06
	1.80	2.99E-03	4.61E-07	1.11	1.44E-01	5.72E-06	0.78	5.48E-02	3.47E-06
	1.68	2.71E-03	4.82E-07	0.99	1.23E-01	4.46E-06	0.79	3.10E-02	2.54E-06
	1.50	2.61E-03	6.66E-07	0.87	1.24E-01	3.79E-06	0.79	1.68E-02	2.61E-06
	1.44	2.97E-03	7.90E-07	0.75	1.15E-01	4.29E-06	0.79	1.77E-02	2.42E-06
	1.30	2.75E-03	8.78E-07	0.63	1.14E-01	6.35E-06	0.79	7.00E-03	3.47E-06
	1.17	3.17E-03	1.18E-06	0.52	1.27E-01	7.71E-06	0.78	6.70E-03	2.59E-06
	0.98	2.59E-03	2.45E-06	0.42	1.36E-01	9.46E-06	0.78	4.60E-03	2.26E-06
	0.84	3.07E-03	2.43E-06	0.30	1.02E-01	1.27E-05	0.78	3.60E-03	2.29E-06
	0.77	2.82E-03	3.08E-06						
	0.61	2.78E-03	4.54E-06						
	0.46	3.20E-03	6.93E-06						
	0.30	3.00E-03	9.19E-06						
	0.25	2.88E-03	1.28E-05						
average		2.83E-03			1.28E-01		0.78		
condition:	I=1.0M								
run:	A10U			B10U			C10U		
period:	3 month			6 month			6 month		
	pOHc	*C*	[U]	*pOHc*	*C*	[U]	*pOHc*	*C*	[U]
	2.50	2.19E-03	1.41E-07	2.02	1.21E-01	1.09E-03	0.97	1.62E-01	5.33E-06
	2.73	1.77E-03	2.19E-07	1.93	1.43E-01	6.63E-04	0.94	1.41E-01	2.99E-06
	2.40	2.20E-03	1.60E-07	1.83	1.37E-01	3.65E-04	0.95	7.40E-02	1.95E-06
	2.37	1.87E-03	1.18E-07	1.68	1.16E-01	1.15E-04	0.96	6.62E-02	1.78E-06
	2.23	2.00E-03	1.50E-07	1.55	1.28E-01	5.03E-05	0.97	4.20E-02	1.58E-06
	2.14	1.99E-03	2.52E-07	1.40	1.12E-01	1.77E-05	0.95	2.96E-02	2.06E-06
	1.90	2.18E-03	2.04E-07	1.28	1.23E-01	8.52E-06	0.95	2.10E-02	1.15E 06
	1.77	2.52E-03	3.19E-07	1.14	1.35E-01	5.42E-06	0.95	1.66E-02	1.29E-06
	1.59	2.55E-03	3.23E-07	1.02	1.31E-01	3.20E-06	0.95	1.24E-02	1.28E-06
	1.52	2.44E-03	4.21E-07	0.88	1.45E-01	3.34E-06	0.95	9.63E-03	1.22E-06
	1.41	2.69E-03	5.29E-07	0.78	1.24E-01	3.54E-06	0.95	7.92E-03	1.83E-06
	1.29	2.22E-03	6.04E-07	0.62	1.28E-01	4.49E-06	0.94	7.39E-03	1.33E-06
	1.15	2.21E-03	9.09E-07	0.49	1.28E-01	5.79E-06	0.94	6.17E-03	1.26E-06
	1.02	3.18E-03	1.13E-06	0.39	1.32E-01	7.18E-06			
	0.95	2.52E-03	1.32E-06	0.29	1.57E-01	9.97E-06			
	0.83	2.80E-03	1.77E-06						
	0.68	4.04E-03	2.65E-06						
	0.55	2.79E-03	3.69E-06						
	0.44	2.73E-03	4.67E-06						
average		2.46E-03			1.30E-01		0.95		
condition:	I=2.0M								
run:	A20U			B20U			C20U		
period:	1 month			1 month			1 month		
	pOHc	*C*	[U]	*pOHc*	*C*	[U]	*pOHc*	*C*	[U]
	2.49	3.56E-03	5.89E-07	2.07	1.12E-01	4.01E-04	0.98	1.76E-01	3.77E-06
	2.48	3.53E-03	3.16E-07	1.63	1.13E-01	2.13E-05	0.98	1.64E-01	3.14E-06
	2.19	3.73E-03	5.84E-07	1.53	1.09E-01	8.28E-06	1.00	1.40E-01	3.54E-06
	1.94	4.08E-03	1.06E-06	1.38	1.09E-01	5.79E-06	0.98	9.03E-02	2.45E-06
	1.76	3.88E-03	8.75E-07	1.28	1.08E-01	3.88E-06	1.00	7.10E-02	2.02E-06
	1.55	3.94E-03	1.22E-06	1.16	1.33E-01	2.75E-06	0.98	2.26E-02	1.68E-06
	1.32	4.02E-03	1.77E-06	1.04	1.31E-01	2.46E-06	0.97	2.41E-02	1.90E-06
	1.13	4.02E-03	1.56E-06	0.91	1.07E-01	2.91E-06	1.00	2.01E-02	1.96E-06
	0.89	3.96E-03	1.97E-06	0.80	9.80E-02	5.29E-06	0.98	1.59E-02	2.19E-06
	0.66	3.99E-03	3.57E-06	0.69	1.10E-01	3.71E-06	0.99	1.37E-02	1.74E-06
	0.49	3.88E-03	4.93E-06	0.55	1.26E-01	4.42E-06	0.99	1.15E-02	2.32E-06
	0.35	4.01E-03	7.55E-06	0.45	1.27E-01	6.13E-06	0.99	7.00E-03	1.99E-06
	0.14	4.05E-03	1.23E-05	0.35	1.23E-01	8.14E-06	0.99	7.10E-03	1.57E-06
							0.96	6.30E-03	1.39E-06
average		3.89E-03			1.16E-01		0.99		

Table 2. Summary for the logarithm of apparent equilibrium constants (log K') and the equilibrium constants extrapolated to $I_m =$ 0 m (log K'^{0}) and ion interaction coefficients with sodium ion (ε(species, Na^+)) for the U(VI) carbonate, hydroxyl complexes at 25±1 °C based on the Equilibrium (3). The errors indicate the 95% confidence level[a]

Species	log K'			log K'^{0}	$\Delta\varepsilon$[a]	ε(species,Na^+)[b]
	I = 0.5 M	I = 1.0 M	I = 2.0 M			
$[UO_2(OH)_3]^-$	−7.28±0.37	−7.45±0.38	−6.04±0.11	−8.31±0.41	−0.82±0.20	−0.83±0.20
$[UO_2(OH)_4]^{2}$	−5.05±0.06	−4.87±0.04	−4.50±0.14	−5.85±0.08	−0.16±0.08	−0.13±0.08
$[UO_2(CO_3)_3]^{4-}$	−6.66±0.10	−6.37±0.07	−6.48±0.06	−7.85±0.10	0.21±0.06	−0.07±0.11

[a] $\Delta\varepsilon$ is defined as in Eq. (9).
[b] The values are calculated by using $\varepsilon(OH^-,Na^+)$ = 0.04±0.01, $\varepsilon(CO_3^{2-},Na^+)$ = 0.05±0.03, $\varepsilon(Na^+,ClO_4^-)$ = 0.01±0.01 [17].

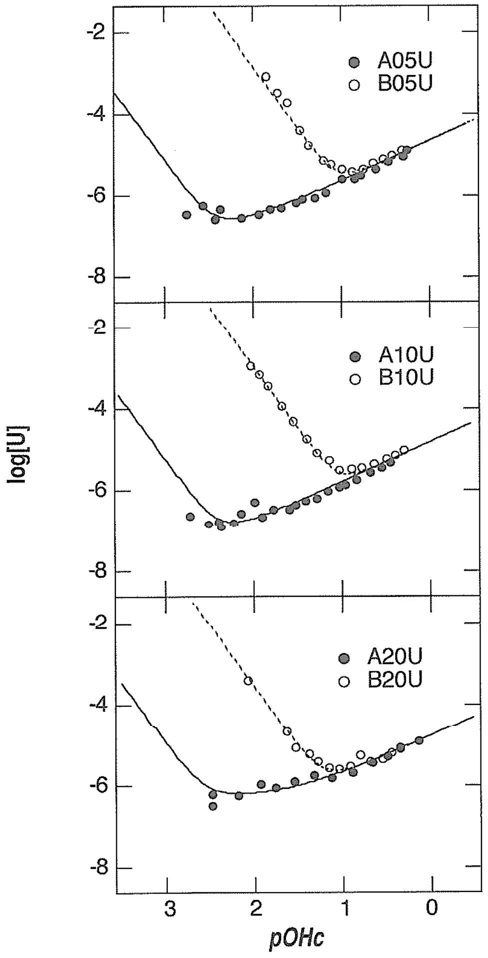

Fig. 3. Experimental and calculated solubilities of U(VI) as a function of *pOHc* at I = 0.5, 1.0, 2.0 M. Circles are experimental values and lines are calculated values with the present model parameters.

cies in Fig. 3 as $\dfrac{\partial \log[U]}{\partial\, pOHc} = +3$ for $[UO_2(CO_3)_3]^{4-}$, 0 for $[UO_2(OH)_3]^-$ and −1 for $[UO_2(OH)_4]^{2-}$. Thus the requirements of the solubility experiment for the precise determination of the thermodynamic data for $[UO_2(OH)_4]^{2-}$ and $[UO_2(OH)_3]^-$ are withdrawn as (i) the measurements under the condition of very low concentration of carbonate ion and (ii) the measurements at high concentration of hydroxide ion less than $pOHc < 2$. Our present experiments fulfill both requirements.

3.3 Comparison of the results with the literature data

The ionic strength corrections were made before the comparison of the present results with the literature data. The apparent equilibrium constants extrapolated to the condition where the ion strength is zero (K'^{0}) are determined by using the specific ion interaction they (S.I.T.) [17, 19−22]. It has an equation representing ionic strength dependence valid for up to I = 3.5 M [23]. For the apparent equilibrium constant (4), the S.I.T. presentation is described as;

$$\log K' - \Delta z^2 D = \log K'^{0} - \Delta\varepsilon I_m\,, \tag{6}$$

$$D = \frac{0.5091\, I_m^{0.5}}{1 + 1.5\, I_m^{0.5}}\,, \tag{7}$$

$$\Delta z^2 = (2 - 2p - q)^2 + 1 + (3 - q) - 4p\,, \tag{8}$$

$$\begin{aligned}\Delta\varepsilon = {} & \varepsilon([UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}, Na^+) \\ & + (3-q)\varepsilon(OH^-,Na^+) + \varepsilon(Na^+,ClO_4^-) \\ & - p\varepsilon(CO_3^{2-},Na^+)\,,\end{aligned} \tag{9}$$

where I_m m (m: mol kg^{-1}) is the molality of the sodium perchlorate dissolved in the medium. The calculated equilibrium constants of U(VI) carbonate and hydroxide complexes at I_m = 0 m (*i.e.*, I = 0 M) and 25±1 °C are estimated in Fig. 4, and summarized in Table 2. The values of the ion interaction coefficients for negatively charged species ε(species, Na^+) are also obtained and tabulated in Table 2.

It is convenient to compare our results with the literature data in terms of the stability constants β^0 at the ionic strength of zero which is given by:

$$UO_2^{2+} + p\, CO_3^{2-} + q\, OH^- \rightleftharpoons [UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}\,, \tag{10}$$

$$\beta^0 = \frac{a_{[UO_2(CO_3)_p(OH)_q]^{(2-2p-q)}}}{(a_{UO_2^{2+}})\,(a_{CO_3^{2-}})^p (a_{OH^-})^q}\,. \tag{11}$$

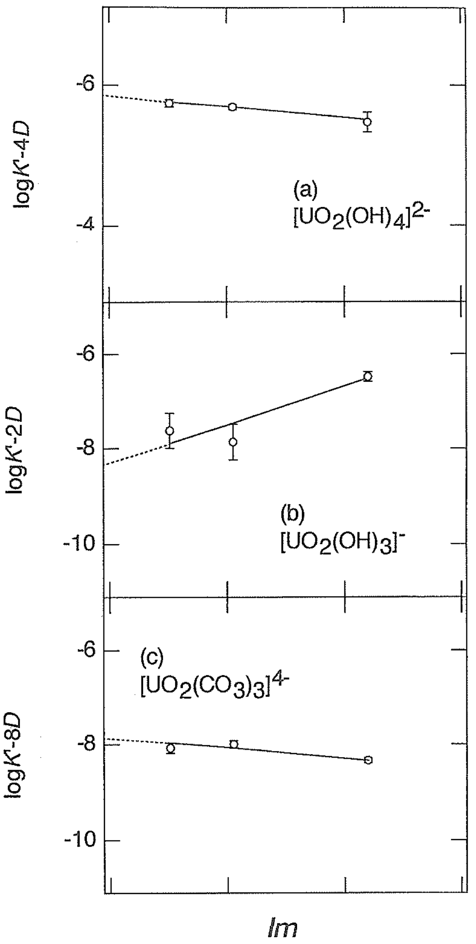

Fig. 4. Calculations of the equilibrium constants extrapolated to I_m = 0 m according to S.I.T. The open circles are the experimental data, the lines are the results of the least-squared fitting procedure based on Eq. (6) and the dotted lines are extrapolations. D is the Debye-Hückel term as expressed as in Eq. (7).

Thus the stability constants β^0 can be evaluated by combining the solubility product of the solid compound $Na_2U_2O_7 \cdot x\,H_2O$ with the apparent equilibrium constant K'^0 for reaction (3),

$$\log\beta^0 = \log K'^0 - \log K^0_{\mathrm{sp(hyd)}}, \qquad (12)$$

where $K^0_{\mathrm{sp(hyd)}}$ is the solubility product of the solubility limiting solid phase, $Na_2U_2O_7 \cdot x\,H_2O$. However, the solubility product of reaction (13), $K^0_{\mathrm{sp(hyd)}}$, is not available at present.

$$0.5\,Na_2U_2O_7 \cdot x\,H_2O \rightleftharpoons UO_2^{2+} + Na^+ + 3\,OH^- + (0.5\,x-1.5)\,H_2O \; (x = 3-5)\,. \qquad (13)$$

In the present study, the solubility product $K^0_{\mathrm{sp(hyd)}}$ is then evaluated by taking the literature value of $\log\beta^0$ for $[UO_2(CO_3)_3]^{4-}$. Among the literature values for $[UO_2(CO_3)_3]^{4-}$, the value of Grenthe *et al.* has been determined carefully and given to be 21.60±0.05 with a fair accuracy. By using this value, the value of $\log K^0_{\mathrm{sp(hyd)}}$ is obtained to be −29.45±1.04.

The obtained value for $Na_2U_2O_7 \cdot x\,H_2O$ may be compared with that of the solubility product for the solid phase of $Na_2U_2O_7$(cr) as in reaction (14).

$$0.5\,Na_2U_2O_7(\mathrm{cr}) + 1.5\,H_2O \rightleftharpoons UO_2^{2+} + Na^+ + 3\,OH^-\,. \qquad (14)$$

Using the thermodynamic data cited in Ref. [17], the molar Gibbs free energy of formation ΔG_f^0 of $Na_2U_2O_7$(cr) is calculated to be −175.273±2.672 kJ mol^{-1} and the solubility product is calculated to be $\log K^0_{\mathrm{sp(cr)}} = -28.09 \pm 0.47$. A definite difference between both values may be found and attributed to different solid phases.

The values of $\log\beta^0$ for the other species of $[UO_2(OH)_4]^{2-}$ and $[UO_2(OH)_3]^-$ are determined based on the presently obtained value of $\log K^0_{\mathrm{sp(hyd)}}$ (Table 3). The value for $[UO_2(OH)_4]^{2-}$ was first determined experimentally in the present study. The species $[UO_2(OH)_4]^{2-}$ appears only in highly basic solutions and it is necessary to check attainment of the equilibrium. A value of $\log K'^0_{\mathrm{(hyd)}} = -5.85 \pm 0.08$ was determined after the aging for more than 6 months. The mean value is higher than the value evaluated in Ref. [17] and the standard deviation becomes very small. This species has been considered once in potentiometric study [16], but is is not clearly stated whether the equilibrium was attained with certainty. In the present study, the good linearity of the specific ion interaction correlation as can be seen in Fig. 4 yields fairly small standard deviations for the two values of $\log K'^0_{\mathrm{(hyd)}}$ and ε. Thus the equilibrium constant determined in the present work seems much more reliable than the equilibrium constants reported in their work. The value of $\varepsilon([UO_2(OH)_4]^{2-}, Na^+)$ is determined as −0.16±0.06 in this work for the first time.

For $[UO_2(OH)_3]^-$, $\log K'^0_{\mathrm{(hyd)}}$ is determined as −8.31±0.41, which is substantially lower than the value presumed by Sandino *et al.* [1]. They have examined the species $[UO_2(OH)_3]^-$ in the region of *pH* 6−9 and a value of $\log K'^0_{\mathrm{hyd}} = -6.65 \pm 0.78$ is evaluated from their $\log\beta^0$ value. Such large solubilities expected from the large $\log K'^0_{\mathrm{(hyd)}}$ value were not observed in this study. The difference between our value and the data reviewed by Grenthe is as large as 1.66. This species requires further investigations to settle this large discrepancies. The ion interaction parameter $\varepsilon([UO_2(OH)_3]^-, Na^+)$ is calculated as −0.82±0.20.

The stability constants $\log\beta^0$ are also calculated by using the Eq. (12) and the $\log K'^0_{\mathrm{(hyd)}}$ value obtained in this study as listed in Table 3.

There have been several reports on the carbonatohydroxo complexes for neptunium(VI) since the report first appeared in 1971 [10] (Table 4). However, there have been remained a question why such species having moderately large stability constants have not been observed for uranium(VI). The upper limit values of the stability constants for $[UO_2(CO_3)(OH)_2]^{2-}$ and $[UO_2(CO_3)_2(OH)_2]^{4-}$ are calculated by a rough maximum estimation which made the concentration of one

Table 3. Comparison of the apparent equilibrium constants $\log K'^{0}$ and the stability constants β^{0} extrapolated to $I_m = 0$ m for the U(VI) carbonate, hydroxyl, and carbonatohydroxo complexes at 25±1 °C[a]

Species	$\log K'^{0}_{(\mathrm{hyd})}$	$\log K'^{0}_{(\mathrm{cr})}$	$\log \beta^{0}$	Ref.
$[UO_2(OH)_3]^-$	-8.31 ± 0.41		21.14 ± 0.79[b]	this work
	-6.65 ± 0.78[d]	-5.29 ± 0.62[c]	22.8 ± 0.4	[17]
$[UO_2(OH)_4]^{2-}$	-5.85 ± 0.08		23.60 ± 0.68[b]	this work
	-6 ± 2[d]	-5 ± 2[c]	23 ± 2	[17]
$[UO_2(CO_3)_3]^{4-}$	-7.85 ± 0.10		21.60 ± 0.68[b]	this work
	-7.85 ± 0.67[d]	-6.49 ± 0.47[c]	21.60 ± 0.05	[17]

[a] The errors indicated the 95% confidence level.
[b] Calculated from the K'^{0} and $K^{0}_{\mathrm{sp(hyd)}}$ values.
[c] Calculated from the $\log \beta^{0}$ and $K^{0}_{\mathrm{sp(cr)}}$ values.
[d] Calculated from the $\log \beta^{0}$ and $K^{0}_{\mathrm{sp(hyd)}}$ values.

Table 4. Comparison of the estimated upper limit value for carbonatohydroxo complexes for U(VI) with the reported value for Np(VI)

Species	$\log \beta$[a]	I(M)	Method[c]	Ref.
$[NpO_2(CO_3)(OH)_2]^{2-}$	23.32	n.s.[b]	sol.	[10]
	20.21 ± 0.15	0.1	sol., spec.	[11]
	20.11 ± 0.23	0.1	sol., spec.	[12]
$[NpO_2(CO_3)_2(OH)_2]^{4-}$	26.28	0.1	sol.	[24]
	<21.61	0.1	sol., spec.	[11]
$[UO_2(CO_3)(OH)_2]^{2-}$	<22.6[d]	0.5	sol.	this work
$[UO_2(CO_3)_2(OH)_2]^{4-}$	<23.5[d]	0.5	sol.	this work

[a] The value of $\log \beta$ at a certain ionic strength. The errors indicated the 95% confidence level.
[b] n.s.: not specified.
[c] sol.: solubility experiment, spec.: spectroscopic measurement.
[d] Same as b) in Table 3.

of these species alone reach to the minimum of the solubility curve. The estimated values for carbonatohydroxouranium(VI) species are included in Table 4.

4. Conclusions

The apparent equilibrium constants of $[UO_2(OH)_3]^-$, $[UO_2(OH)_4]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$ with solid phase $Na_2U_2O_7$ at $I = 0$ M were determined from the solubility data obtained in undersaturation experiments. The equilibrium constant for $[UO_2(OH)_4]^{2-}$ was first determined experimentally in the present work. The equilibrium constant for $[UO_2(OH)_3]$ was first determined in highly basic solutions, which revealed $[UO_2(OH)_3]^-$ concentration 1−2 orders lower than expected from the literature data. The attainment of the equilibrium was certified by both observing the end of the decrease in the solubility with time and comparing the solubilities in the oversaturation samples with the solubilities in the undersaturation samples. The period of the equilibrium attainment was very long more than 6 months for the oversaturation samples. The solubility product of the solid phase $Na_2U_2O_7 \cdot x\,H_2O$ was evaluated. Using the value, the stability constants for the above species were determined. The upper limit values of the stability constants of the carbonatohydroxcodioxouranium(VI) complexes were also evaluated.

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