

Carbonate complexation of the uranyl(VI) ion

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Abstract

The system U(VI)/H₂O/CO₂ has been investigated by solubility measurements in 0.1 M NaClO₄ at 25 °C in equilibrium with a CO₂ atmosphere. The formation constants $\lg\beta(\text{UO}_2\text{CO}_3) = 9.23 \pm 0.04$, $\lg\beta(\text{UO}_2(\text{CO}_3)_2^{2-}) = 15.38 \pm 0.17$ and $\lg\beta(\text{UO}_2(\text{CO}_3)_3^{4-}) = 21.86 \pm 0.05$ have been evaluated. The solid phase was characterized as UO₂CO₃(s). For this phase a solubility product $\lg K_{\text{sp}}(\text{UO}_2\text{CO}_3) = -14.18 \pm 0.03$ has been obtained. An upper limit of $\lg\beta(\text{UO}_2\text{OH}^+) < 8.6$ was determined.

1. Introduction

UO₂²⁺, like most actinides, forms strong complexes with both OH⁻ and CO₃²⁻ [1]. Owing to the importance of uranium in nuclear technology, its hexavalent state in particular has been investigated intensively with respect to hydrolysis and carbonate complexation during the last half-century [2]. The majority of these contributions deals with the hydrolytic behaviour. The reaction with carbonate has been investigated by solubility [3–9], potentiometric titration [10, 11], redox measurement [12], solvent extraction [13, 14], spectroscopy [13] and ion exchange [15]. While there is uncertainty in the literature concerning the nature of the hydrolysis species, there is almost agreement that U(VI) forms UO₂(CO₃)_n⁽²⁻²ⁿ⁾ (n = 0, 1, 2, 3) complexes only. However, some authors suggest the formation of hydroxocarbonato species [10] or a polynuclear (UO₂)₃(CO₃)₆⁶⁻ species [4, 16]. Other authors [17, 18] suggest special definitions to describe the nature of the solution species, for which the reader is referred to the original publications.

In the present study, the carbonate complexation of U(VI) was investigated by solubility measurements in 0.1 M NaClO₄ solution at 25 °C, since at the time of the investigation no solubility study was available in the literature under these conditions. After termination of the experiment, results of a solubility study performed under the same conditions [3] were reported. A comparison of the results from the two studies will be given.

2. Experimental details

A solubility experiment in combination with radiochemical pH titration was carried out in a thermostatted titration vessel of volume 100 ml. An ionic strength of 0.1 M was maintained using NaClO₄ as supporting electrolyte. The solution was thermostatted to 25 ± 0.1 °C. Moistened CO₂ was bubbled through the solution continuously. A 10⁻² M ²³³U-spiked depleted U(VI) solution was introduced and U(VI) precipitated at about pH 6 by addition of 0.05 M Na₂CO₃. The solution with precipitate was left to stand under a CO₂ atmosphere for 3 weeks. The variation in uranium concentration and pH as a function of time after precipitation is given in Fig. 1.

Within the first 7 days the pH changed spontaneously to 3.3. During the following 14 days both pH and U(VI) concentration were checked repeatedly and found to

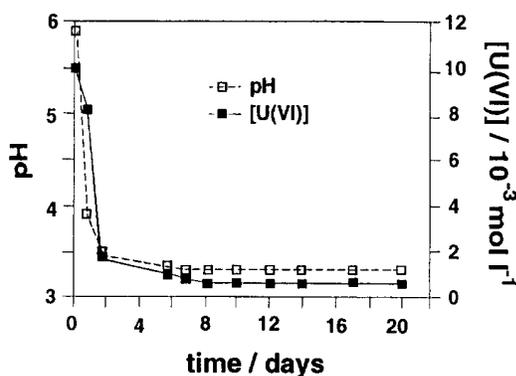
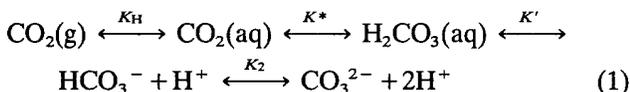


Fig. 1. Variation in uranium concentration and pH as a function of time after precipitation of U(VI) from 0.1 M NaClO₄ in equilibrium with CO₂ atmosphere.

remain unchanged within experimental error. After this time the pH of the solution was varied stepwise by the addition of small aliquots of either 0.1 M HClO₄ or 0.05 M Na₂CO₃ in the pH range 3.0–6.2. A steady state was usually attained, from both supersaturation and undersaturation, within 1–3 days. The U(VI) concentration was measured when the adjusted pH had stabilized for a certain period of time (2–3 days). The total duration of the experiment was about 7 months.

Phase separation was achieved by ultrafiltration through 220 nm pore size. U(VI) concentrations were measured as a function of pH/lg[CO₃²⁻] by liquid scintillation counting (LSC) (Tricarb 300, Packard Co.) of the ²³³U α activity. The spike was checked by α and γ spectrometry to ascertain that neither α-decaying nor γ-decaying daughters of ²³³U will add a contribution of more than 0.5% to the counting window of the ²³³U α activity in the LSC. The α-counting efficiency of the counting device was determined experimentally and an efficiency of 99.64 ± 0.74% was found by calibration with a ²⁴¹Am standard (Amersham Co.).

Combination glass electrodes (Orion Co.) were used for pH measurement after calibration against four standard buffer solutions in the pH range 1.7–10.0. A precision of ±0.02 pH units was found. Carbonate concentrations were calculated from measured pH values via



$$\lg[\text{CO}_3^{2-}] = \sum \lg K + \lg p_{\text{CO}_2} + 2\text{pH} \quad (2)$$

with $\sum \lg K = \lg(K_H K^* K' K_2) = -17.62 \pm 0.07$ [19]. These data were rechecked later and $\sum \lg K = -17.65 \pm 0.09$ was obtained [20].

Solid phases were characterized indirectly using unspiked uranium by differential thermal analysis (DTA) with simultaneous thermogravimetry (TGA) and X-ray powder diffraction. For DTA–TGA about 15–25 mg of air-dried solid phase have been used.

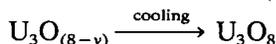
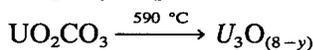
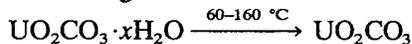
3. Results and discussion

3.1. Characterization of the solid phase

The chemical state of the solid phase has been investigated using unspiked U(VI) as reference. Precipitates were produced and kept for present conditions at pH 3.5, 4.2 and 6.1 at 24 ± 2 °C. For each pH, samples of the solid phases have been characterized after 2, 5, 8 and 16 weeks. During this time the pH remained unchanged within 0.08 pH units and neither X-ray powder diffraction patterns nor DTA/TGA analysis revealed significant changes in the state of the solid phases. A typical X-ray powder pattern of the

greenish-yellow compounds produced by precipitation from aqueous solution in equilibrium with a CO₂ atmosphere is compared in Table 1 with that given for UO₂CO₃(s) (rutherfordine) in the literature [21].

Experimental results from DTA–TGA were found to be in agreement with the following transformations:



Since the loss of water between 60 and 160 °C did not result in a significant signal in the DTA curve, it was interpreted as adsorbed water with a contribution of 0.6–0.9 formula units in the air-dried samples. Highly crystalline, greenish-black U₃O₈(s) has been identified as the final product by its X-ray powder pattern. The loss of oxygen by heating above 800 °C is a well-known feature of U₃O₈(s) [22]. During cooling, oxygen is replaced rapidly and U₃O₈(s) is commonly used as the weighing form for the gravimetric determination of uranium [23]. The samples have also been characterized by PAS and Fourier transform IR–photoacoustic spectroscopy (FTIR–PAS). Results have already been given elsewhere [5].

From these results, rutherfordine UO₂CO₃(s) is assumed as the equilibrium solid phase in the ²³³U-spiked U(VI) solution under a CO₂ atmosphere. In the pH range 3.5–6.2 in equilibrium with a CO₂ atmosphere, rutherfordine is reported as the solubility-limiting solid phase from 25 to 200 °C in 0.02 M NaClO₄/NaCl solutions [6] and in NaClO₄ solutions up to 3 M at 25 °C [4].

TABLE 1. Comparison of X-ray data of the solid precipitated from 0.1 M NaClO₄ at 25 °C under CO₂ atmosphere with literature data for UO₂CO₃(s) (rutherfordine) [21]

This work <i>d</i> (pm)	Intensity ^a	Reference 21 <i>d</i> (pm)	<i>I/I</i> ₀
465	s	461	100
431	s	430	70
389	m	392	30
321	m	323	40
264	m	264	25
260.8	vw	260	6
250.4	vw	251.2	10
243.1	w	242.0	15
231.8	m	230.9	20
215.3	w	215.6	10
205.9	w	206.2	20
193.9	w	195.3	4
191.3	w	192.6	15
187.8	w	187.9	10
174.3	w	174.6	6
		172.3	4
170.0	vw	170.1	4

^as, strong; m, medium; w, weak; vw, very weak.

3.2. Solubility study

The solubility data have been interpreted via

$$[U(VI)]_t = K_{sp}(UO_2CO_3)[CO_3^{2-}]^{-1}(1 + \sum \beta_n [CO_3^{2-}]^n) \quad (3)$$

with $[U(VI)]_t$ giving the measured total U(VI) concentration, $K_{sp}(UO_2CO_3) = [UO_2^{2+}][CO_3^{2-}]$, $\beta_n = [UO_2(CO_3)_n]^{(2-2n)} [UO_2^{2+}]^{-1} [CO_3^{2-}]^{-n}$ and square brackets denoting concentrations.

Figure 2(a) gives the experimental data, the calculated solubility curve together with the calculated absolute concentrations of each species as a function of pH and free carbonate concentration. The shaded area represents 3σ uncertainty.

The solubility is usually approached from both undersaturated and supersaturated solution. However, at about pH 6 an unusually slow equilibration of the system was observed from supersaturation. While steady state conditions were usually established within a few days, the supersaturated system in the pH region 5.8–6.2 did not attain a steady state within up to 3 weeks. Open circles give the solubility measured after 1 week

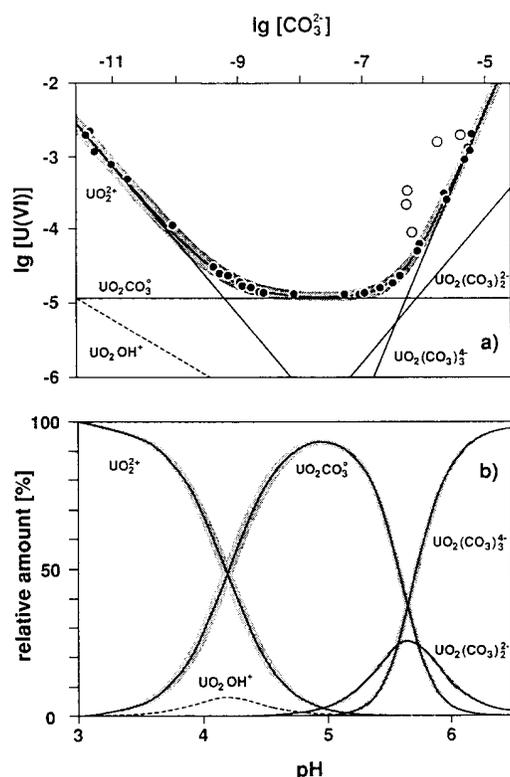


Fig. 2. (a) Solubility of $UO_2CO_3(s)$ as a function of pH and carbonate concentration in 0.1 M perchlorate solution at 25 °C in equilibrium with CO_2 atmosphere. The shaded area represents the 3σ error limit. Open circles represent a non-equilibrium state of the system upon precipitation from supersaturated solution. (b) Relative amount of U(VI) species as a function of pH and carbonate concentration.

of equilibration. Each of these datum points was attained from supersaturation from one point at the higher concentration to the datum point at the lower concentration upon addition of 0.1 M $HClO_4$. A detailed investigation of this phenomenon is still required. The solubility behaviour of U(VI) in the pH range 5.8–6.2 is therefore investigated only from undersaturation.

Special attention was directed to the pH range 4.0–4.5 in order to detect a possible contribution of the UO_2OH^+ species. Each datum point was determined in triplicate and several days were allowed between each measurement. No significant contribution of the UO_2OH^+ species could be derived from the solubility data. As an upper limit, $lg\beta(UO_2OH^+) < 8.6$ was calculated.

Figure 2(b) presents the relative amount of each species, including UO_2OH^+ . This species is taken into account by $lg\beta(UO_2OH^+) = 8.04 \pm 0.08$ [24]. The shaded areas again account for 3σ uncertainty. UO_2OH^+ is not included in the calculation of uncertainties, since its formation constant is not derived from this study but taken from the literature. The species $(UO_2)_3(OH)_5^+$ with $lg\beta_{35} = 52.71 \pm 0.16$ [10] and $(UO_2)_2(OH)_2^{2+}$ with $lg\beta_{22} = 21.67 \pm 0.37$ [10] have also been included in the calculations, resulting in contributions of less than 0.8%.

Error limits have been calculated using two different algorithms [25]: the bootstrap algorithm and jack-knife analysis. The derived mean values and standard deviations are given in Table 2. The calculated mean values are in good agreement for the two methods. The same holds for the calculated σ values, except for the error calculated for $lg\beta_2$. The highest uncertainties from Table 2 were attributed to the derived formation constants.

In Table 3 a comparison of the present data with data available in the general literature is given. The literature data have been critically discussed in a recent review [26], except for the very recent data from ref. 3. Since the method and conditions of the study reported in ref. 3 are the same as in the present work, a direct comparison can be made. Considerable differences can be found between the constants derived from the two studies. The solubility products and formation constants $lg\beta_2$ differ by about one order of magnitude and $lg\beta_3$ by more than two orders of magnitude. The formation constant $lg\beta_3 = 23.92 \pm 0.03$ in ref. 3 is one of the highest values suggested for this constant at present. Data given

TABLE 2. Results of statistical analysis of experimental data

method	lgK_{sp}	$lg\beta_1$	$lg\beta_2$	$lg\beta_3$
Jack-knife	-14.18 ± 0.03	9.23 ± 0.04	15.38 ± 0.17	21.86 ± 0.05
Bootstrap	-14.18 ± 0.02	9.23 ± 0.03	15.36 ± 0.11	21.86 ± 0.04

TABLE 3. Comparison of present data with experimental data available in literature

Reference	Method ^a	lg β_1	lg β_2	lg β_3	lg K_{sp}	Conditions
This work	Sol	9.23±0.04	15.38±0.17	21.86±0.05	-14.18±0.03	0.1 M NaClO ₄ , 25 °C
3	Sol	8.70±0.04	16.33±0.07	23.92±0.03	-13.29±0.01	0.1 M NaClO ₄ , 25 °C
5	Sol				-13.89±0.11	0.1 M NaClO ₄ , 24 °C
4	Sol	9.5±0.2	16.6±0.2	21.3±0.2	-14.4±0.1	I=0
		8.3±0.1	15.36±0.15	21.46±0.15	-13.21±0.06	0.5 M NaClO ₄ , 25 °C
		8.3±0.1	16.20±0.15	22.61±0.15	-13.94±0.06	3 M NaClO ₄ , 25 °C
12	Pot			24		3 M NaClO ₄ , 25 °C
10	Tit		16.15±0.29	21.81±0.05		0.1 M NaClO ₄ , 25 °C
13	Ext/Sp		16.22	5.47 ^b		0.1 M NaNO ₃ , 20 °C
14	Ext			21.54±0.03		0.1 M NaNO ₃ , 20 °C
6	Sol	9.87	16.7		-14.26	I=0, 25 °C
11	Tit	4.1±0.2	16.17±0.06	21.57±0.03		0.1 M NaClO ₄ , 25 °C
15	IE			7.00±0.04 ^b		0.5 M NaNO ₃
7	Sol		15.57	20.70		0.2 M NH ₄ NO ₃ , RT ^c
8	Sol			22.77±0.2		1 M NH ₄ Cl, 25 °C
9	Sol			3.52 ^b		NaCl-Na ₂ SO ₄ , 24 °C

^aSol, solubility; Pot, redox measurement; Tit, potentiometric titration; Ext, solvent extraction; Sp, spectroscopy; IE, ion exchange.

^bData given as stepwise constant.

^cRT, room temperature.

TABLE 4. Experimental data

pH	lg[U(VI)]	lg[CO ₃ ²⁻]
3.08	-2.71	-11.46
3.11	-2.66	-11.40
3.15	-2.94	-11.32
3.17	-2.93	-11.28
3.28	-3.12	-11.06
3.41	-3.32	-10.80
3.77	-3.95	-10.08
4.10	-4.50	-9.42
4.15	-4.60	-9.32
4.15	-4.61	-9.32
4.22	-4.63	-9.18
4.31	-4.71	-9.00
4.33	-4.76	-8.96
4.40	-4.79	-8.82
4.47	-4.84	-8.68
4.50	-4.86	-8.62
4.75	-4.89	-8.12
5.16	-4.89	-7.30
5.28	-4.88	-7.06
5.33	-4.86	-6.96
5.55	-4.72	-6.52
5.61	-4.62	-6.40
5.75	-4.29	-6.12
5.77	-4.19	-6.08
5.97	-3.52	-5.68
5.98	-3.58	-5.66
6.13	-3.04	-5.36
6.16	-2.88	-5.30
6.17	-2.92	-5.28
6.19	-2.68	-5.24

in the literature for lg β_3 are quite consistent. For 0.1 M solutions lg β_3 varies in a narrow range between 21.54±0.03 [14] and 21.81±0.05 [10]. The formation constant lg β_3 derived from the present data is obtained

from undersaturated solution only, but with lg β_3 = 21.86±0.05, this value is in good agreement with the literature.

The present solubility product lg K_{sp} (UO₂CO₃) = -14.18±0.05 is in reasonable agreement with the previously determined value of -13.89±0.11 [5].

4. Conclusions

The solid-liquid phase equilibrium of hexavalent uranium has been investigated in 0.1 M NaClO₄ solution at 25±0.1 °C in equilibrium with a CO₂ atmosphere. The formation constants lg β_1 = 9.23±0.04, lg β_2 = 15.38±0.17 and lg β_3 = 21.86±0.05 have been evaluated from the solubility data. UO₂CO₃(s) was characterized indirectly as the equilibrium solid phase. A solubility product lg K_{sp} (UO₂CO₃) = -14.18±0.03 was determined. Comparison of the present data with a solubility study [3] reported in the literature for the same conditions has shown considerable discrepancy, especially in the solubility product and the formation constant evaluated for the tricarbonato complex of U(VI). From the available data, clear reasons for these discrepancies cannot be given. In future work, solubility studies will be combined with spectroscopic speciation of the aqueous phase to clarify whether such inconsistencies might result from different solution species of U(VI) or from differences in the state of the U(VI) solid phase.

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