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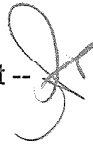
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Solubility Products and Complex Formation Equilibria in the Systems Uranyl Hydroxide and Uranyl Carbonate at 25°C and $I = 0.1$ M

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Uranyl hydroxide / Uranyl carbonate / Solubility products / Complexation

Summary

The solubility of uranyl hydroxide and uranyl carbonate and the formation constants of the complexes present in the supernatant solution were determined at 25°C in 0.1 M $NaClO_4$ solutions. The solubility products were found to be $\log K_{sp} = -22.21$ and $\log K_{sp} = -13.29$, respectively. In the pH range from 4.5 to 5.5 the hydroxo complexes $(UO_2)_2(OH)_2^{2+}$ ($\lg \beta = 22.16$), and $(UO_2)_3(OH)_5^+$ ($\lg \beta = 53.05$) were found. Under the condition $-11 < \lg(CO_3^{2-}) < -6$ three mononuclear uranyl carbonate complexes, UO_2CO_3 ($\lg \beta = 8.70$), $UO_2(CO_3)_2^{2-}$ ($\lg \beta = 16.33$), and $UO_2(CO_3)_3^{4-}$ ($\lg \beta = 23.92$) exist.

Introduction

In order to be able to estimate the risks associated with the disposal of nuclear waste it is important to have a reliable data base including the mobilities, solubilities, electrochemical potentials and stability constants of the various species that may exist under disposal conditions, and to know their behaviour towards adsorption at soil particles and leaching into environmental waters. Uranium is the major constituent of nuclear waste. The solubilities of the hydroxides and carbonates of uranium as well as their complexes in solution are of major importance and have received much attention. A number of solubility studies have been reported and in some cases the precipitates were analyzed. In the case of hydroxide the precipitate is of the composition $UO_2(OH)_2 \cdot H_2O$ in the lower pH region while at higher pH uranyl ion is precipitated as diuranate [1]. The composition of solid uranyl carbonates is more complex. Several compounds including various tricarbonates or mixed hydroxo-carbonato compounds have been suggested [2–6]. UO_2CO_3 (rutherfordine) is the solid phase in slightly acidic media.

In most cases the solubility product was calculated using literature data of the formation constants of the different complexes in solution. Unfortunately no agreement has been reached about the stoichiometry of the existing complexes, in particular in case of the hydroxide. Generally it is assumed that the monomers are of subordinate importance. UO_2OH^- only occurs in very dilute solutions ($[UO_2^{2+}] < 1$ mM) while the existence of $UO_2(OH)_2$ has not been confirmed. The principal hydrolysis products are the polymers $(UO_2)_2(OH)_2^{2+}$ at lower hydroxyl numbers and $(UO_2)_3(OH)_5^+$ or $(UO_2)_3(OH)_4^{2+}$ at hydroxyl numbers above 1.5. The compound $(UO_2)_2(OH)^{3+}$ is also suggested by several authors. In the case of uranyl carbonate the existence of the complexes UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ is well established. Some authors have suggested additional polynuclear species as well as mixed hydroxo-carbonate complexes, but agreement about their stoichiometry is virtually non-existent.

Complexation was generally studied in solutions in a pH range and at concentrations where precipitates do not occur. It is thus possible that some complexes relevant to the two-phase system have never been picked up. The aim of our investigation is a re-determination of the solubility curves. In contrast to most of the former studies of these systems we analyze our data for solubility products and formation constants for given sets of complexes at the same time.

Chemicals

Solutions containing UO_2^{2+} ions were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck p.a.). The decay products were removed on the day the experiment started by passing a solution in 9 M HCl (Merck p.a.) through Dowex 1x4 ion exchange resin (Fluka AG, 100–200 mesh, Cl-form) and eluting with 1 M HCl. The solution was evaporated to dryness and the residue redissolved in 0.1 M $HClO_4$. Solutions were standardized by titration with EDTA-solutions [7] prepared by weighing out EDTA (Merck Titriplex III, p.a., dried at 80°C for 24 hours), and by subsequent dilution in a calibrated flask.

Solid uranyl carbonate, UO_2CO_3, was prepared by adding saturated $NaHCO_3$ solution to the dried residue (see above) at room temperature. The residue dissolved with the evolution of CO_2 until a pale yellow precipitate was formed. The reaction vessel was then stoppered and left over night. The wet precipitate was centrifuged, washed with water several times and then analyzed by powder diffractometry (Table 1). It was identified as UO_2CO_3 by comparison with literature data [8, 9]. The X-ray diffraction pattern did not change upon drying. The dried precipitate (dried over silica gel) was also analyzed for its carbon content using a CHN-Rapid by Heraeus. The result obtained agrees with the theoretical value (calculated: 3.6%C; found; 3.1%C).

NaOH solutions were prepared weekly from Merck ampoules and protected from atmospheric CO_2 by soda lime. $HClO_4$ solutions were prepared by dilution of Merck p.a. concentrated acid, 70–72%, and standardized against standard NaOH solution. All solutions were made up to a perchlorate concentration of 0.1 M by addition of $NaClO_4 \cdot H_2O$ (Merck

p.a. >99%, used without further purification). All other chemicals were Merck p.a. grade.

Doubly distilled deionized water was used for preparing the solutions. It was boiled before use to remove all traces of CO_2.

The scintillation cocktail was Pico-Fluor 40 by Beckman.

Method

The hydrolysis experiments were conducted in sealed vessels thermostated at 25 °C. The solutions were maintained under a nitrogen atmosphere by bubbling the gas through the vessels very slowly. Before it was admitted to the vessel it passed through a sequence of wash bottles for further purification, containing 50% potassium hydroxide solution to remove carbon dioxide, distilled water, an empty bottle (used as a trap) and a solution of 0.1 M sodium perchlorate (the background electrolyte) thermostated at 25 °C. The gas was released to the atmosphere via a trap containing 0.1 M sodium perchlorate solution to prevent back diffusion.

About 20 ml of acidic solutions of known pH and uranyl ion content (concentration range 0.001 – 0.01 M) were introduced into the vessel. Different amounts of sodium hydroxide solution (ca. 0.005 M) were added under stirring to obtain solutions containing precipitates at different pH. The solutions were left to equilibrate and the pH development was monitored with time using a Metrohm pH meter (type 654) in connection with an Orion Ross electrode (81 – 62SC) filled with saturated sodium chloride solution.

For studying uranyl carbonate two different approaches were followed. In the first approach (closed system approach) solid uranyl carbonate was dissolved in different standard solutions of sodium hydrogen carbonate. The vessels were stoppered and left to equilibrate. In the second approach the solid was dissolved in solutions of different initial pH kept under a CO_2 atmosphere (open system approach). CO_2 gas was passed through bottles containing 1 M sulfuric acid, distilled water, a solution of 0.1 M sodium perchlorate and an empty bottle, before it entered the reaction vessel.

When a constant pH (± 0.02 pH units) was obtained, samples were drawn from the reaction vessels and filtered. Great care was taken to insure that during sampling and filtration the contact with air was as short as possible to avoid CO_2 contamination or loss. The samples were analyzed by liquid scintillation counting using a Beckman LS 2800 Liquid Scintillation Counter calibrated with uranium stock solutions in the concentration range from $3 \cdot 10^{-3}$ M to $1 \cdot 10^{-5}$ M, or spectrophotometrically on a Hitachi spectrophotometer model 330 via a modified method using the U(IV)-arsenazo(III) complex (645 nm) and the U(VI)-arsenazo(III) complex (650 nm) [10]. To an adequate amount of Zn powder (0.5 g Zn for 7 – 14 µg U, 0.8 g Zn for 14 – 24 µg U, 0.9 g Zn for 24 – 45 µg U) the unknown uranium solution and 5 ml 9 M HCl were added. After the zinc had dissolved, 1 ml 0.05%

ascorbic acid, 3 ml 9 M HCl, 1 ml 1 M H_2NSO_3H and 3 ml 9 M HCl were added in this order. Furthermore 1 ml of 0.06% arsenazo(III) solution and 7 ml 9 M HCl were added and the volume was made up to 25 ml with water. The spectrophotometric analysis was then carried out immediately.

Agreement between concentrations obtained by use of the two methods was within 3%.

Calculations

In aqueous solutions metal ions can form numerous complexes with hydroxide or carbonate ions. The formation of complexes can be represented by the following equation

$$pM^{n+} + qOH^- + zCO_3^{2-}$$
$$\leftrightarrow [M_p(OH)_q(CO_3)_z]^{(pn-q-2z)+}.$$
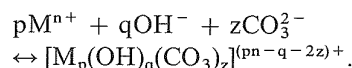
The stability constant β_{pqz} of the complex is defined as

$$\beta_{pqz} = \frac{[M_p(OH)_q(CO_3)_z]^{(pn-q-2z)+}}{[M^{n+}]^p[OH^-]^q[CO_3^{2-}]^z}.$$

In this equation $[M^{n+}]$ can be expressed by the mass balance equation

$$[M^{n+}] = [M]_t - \sum_p p\beta_{pqz}[M^{n+}]^p[OH^-]^q[CO_3^{2-}]^z$$

where $[M]_t$ is the analytical concentration of the metal ion in solution. In the presence of a precipitate the free metal concentration $[M^{n+}]$ is determined by the solubility product K_{sp},

$$K_{sp} = [M^{n+}]^r[OH^-]^x \quad \text{or}$$
$$K_{sp} = [M^{n+}]^t[CO_3^{2-}]^y.$$

In this equation r and t represent the number of metal ions in the precipitate while x and y represent the number of hydroxide or carbonate ions, respectively.

$[OH^-]$ can be measured via pH. In the closed system approach the concentration of free carbonate ion, $[CO_3^{2-}]$, can be calculated from the total amount of carbonate in solution, c_T, and the protonation constants of carbonic acid, K_1 and K_2, by

$$[CO_3^{2-}] = c_T \cdot K_1 \cdot K_2/([H]^2 + K_1 \cdot [H] + K_1 \cdot K_2).$$

In the open system approach the concentration of CO_3^{2-} can be calculated from pH, the partial pressure of CO_2, $p(CO_2)$, in the system, and the protonation constants via

$$[CO_3^{2-}] = (K_H \cdot K_1 \cdot K_2)p(CO_2)/[H]^2$$

where K_H refers to the equilibrium between dissolved and gaseous CO_2. The values used for K_1, K_2, and $K_H \cdot K_1 \cdot K_2$ were $\log K_1 = -10.003$, $\log K_2 = -6.207$, and $\log(K_H \cdot K_1 \cdot K_2) = -17.64$ at an ionic strength of $I = 0.1$ M [11].

We have thus substituted all the free concentrations and have obtained $[M]_t$ as a function of the solubility product and the formation constants. In

order to optimize the parameters β_{pqz} and K_{sp} for a given set of complexes the simplex algorithm [12] was used to minimize the sum of squares v^2,

$$v^2 = \sum_j (([M]_{j(calc)} - [M]_{j(exp)})/\sigma_j)^2$$

where j is the number of data points and σ_j is the statistical error of each data point.

The refinements were repeated several times with different starting values for the constants in order to ensure that the absolute minimum had been found.

The error of each parameter was estimated by re-calculating the constants from 15 files where a random error (max. 5%) was added to the uranium concentrations. We quote the average of the difference between our original value and the values obtained from the random error data files as the error of our constants.

Results and discussion

Uranium hydroxide

Precipitation from uranium solutions (ca. $5 \cdot 10^{-3}$ mol/l) starts at a pH of about 4.3. Equilibration times varied between 3 to 14 days. No systematic dependence on pH was observed. In some cases the pH was already constant while the concentration of uranium still decreased. This may be due to various effects acting simultaneously. One of them may be the change of an amorphous precipitate into a crystalline compound or the change of the structure of such a compound, e.g., dehydration or a different modification. A second effect may be the formation of colloids, in particular because a large amount of colloid formation has been reported for the analogous Pu(VI) hydroxide. A third possibility may be the adsorption of uranium compounds at the precipitate or at container walls, which happens very slowly. We observed that if a lot of precipitate was present in our reaction vessel the analytical uranium concentration tends to be slightly lower than in the samples containing only a small amount of precipitate. The fact that high uranium values were more frequently found in the lower pH region may point to the existence of supersaturated solutions. In this case precipitation in these solutions would happen very rapidly which, on the other hand, never occured. Finally the size of the solid particles may increase with time. This could be ruled out because filtering solutions through filters of different pore size (2 nm, 10 nm, 220 nm, 450 nm) showed that the uranium concentrations obtained remained unchanged. On account of the fact that adsorption at the precipitate and colloid formation lead to low uranium values in solution while incomplete crystallization leads to high values, all samples for which these effects were observed were discarded.

The solubility of uranyl hydroxide was measured in the pH region 4.5 – 5.5. In this region the precipitate consists of $UO_2(OH)_2 \cdot H_2O$ (or $UO_3 \cdot 2H_2O$). This

Table 1. X-ray diffraction data of our precipitates

X-ray powder diffractograms were recorded on an automatic powder diffractometer Phillips PW 1700 (Cu-K_α, graphite monochromator, variable slit). The relative intensities I/I_{max} of the peaks may differ from values reported in literature because of the use of a variable divergence slit. This results in a drop of the intensities of peaks at low angles, i.e. high d.

X-ray diffraction lines of $UO_2(OH)_2 \cdot H_2O$ (d in Å (1Å = 10^{-1} nm); I/I_{max} in %)
(7.316;99),(3.681;59),(3.583;77),(3.504;42),(3.223;100),
(3.167;50),(2.565;46),(2.084;11),(2.040;33),(2.008;33),(1.965;27).

X-ray diffraction lines of UO_2CO_3 (d in Å (1Å = 10^{-1} nm); I/I_{max} in %)
(4.670;60),(4.320;85),(3.881;73),(3.210;100),(2.640;75),
(2.510;16),(2.431;36),(2.329;22),(2.155;25),(2.130;31),(2.060;97),
(1.937;27),(1.910;52),(1.884;33).

Table 2. Solubility data of uranyl hydroxide and uranyl carbonate

Solubility data of $UO_2(OH)_2 \cdot H_2O$ (pH; lg[analytical uranium conc.])

(4.36;−2.51),(4.40;−2.43),(4.44;−2.50),(4.45;−2.66),(4.53;
−2.81),(4.53;−2.86),(4.55;−2.78),(4.56;−2.85),(4.61;
−2.96),(4.65;−2.85),(4.71;−3.04),(4.72;−3.13),(4.80;
−3.23),(4.89;−3.40),(4.92;−3.29),(5.02;−3.47),(5.03;
−3.38),(5.16;−4.05),(5.18;−3.97),(5.20;−3.85),(5.24;
−3.98),(5.30;−4.13),(5.48;−4.41),(5.51;−4.36),(5.71;−4.54).

Solubility data of UO_2CO_3 (pH, lg[CO_3^{2-}], lg[analytical uranium conc.])

(3.63;−10.38;−2.98),(3.90;−9.84;−2.91),(3.94;−9.76;
−3.48),(4.18;−9.28;−3.96),(4.19;−9.26;−3.94),(4.19;−9.25;
−3.98),(4.24;−9.15;−3.40),(4.27;−9.10;−4.00),(4.28;−9.08;
−4.00),(4.33;−8.99;−4.07),(4.34;−8.96;−4.04),(4.34;−8.96;
−4.10),(4.39;−8.86;−4.23),(4.46;−8.72;−4.31),(4.55;−8.54;
−4.42),(4.79;−8.06;−4.35),(4.81;−8.02;−4.29),(4.83;−7.98;
−4.28),(4.90;−7.84;−4.24),(5.04;−7.56;−3.95),(5.05;−7.54;
−4.14),(5.41;−6.82;−2.61),(5.47;−6.70;−2.78)

fact was confirmed by analyzing the centrifuged and dried precipitates by X-ray powder diffractometry, followed by comparison with literature [9]. A typical spectrum is listed in Table 1. Above pH = 5.5 the solid phase starts to change and ultimately becomes uranyl diuranate (in agreement with literature [1]).

The solubility data are listed in Table 2 and the solubility curve is shown in Fig. 1. The solubility drops sharply with increasing pH. If there were no complexes in the solution the solubility curve would follow a straight line with a slope of −2. We can indeed draw such a line with a slope of about −1.8, indicating some complex formation.

In order to calculate the solubility product and the stability constants of the complexes different models were considered. The following complexes have been suggested in the literature [4, 13 – 21]: UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_2(OH)^{3+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, $(UO_2)_4(OH)_6^{2+}$, and

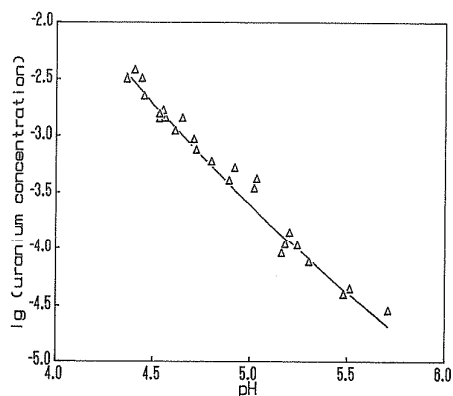**Fig. 1.** Experimental (triangles) and theoretical (line) solubility curve of $UO_2(OH)_2 \cdot H_2O$ at 25°C and $I = 0.1$ M.

$(UO_2)_4(OH)_7^+$. All these complexes and several combinations thereof were used as input to our refinements. In addition, complexes of the form $UO_2(OH)_n^{(2-n)+}$ were also considered. It turns out that the refinements are relatively insensitive to the choice of complexes and their formation constants because complexation is only a minor effect compared to the solubility equilibrium. Several models fitted the data equally well. For these models speciation plots were drawn using our refined stability constants. Only those models were taken into further consideration for which all the complexes assumed contained more than 5% of the total amount of dissolved uranium. Complexes with less than 5% were considered to be a consequence of the accumulation of experimental errors, and were discarded. From the statistical point of view it is still impossible to decide which of the remaining models is the best description of our system. In particular models containing highly polymerized species gave fits not significantly different from those obtained by assuming only mononuclear complexes, or mixtures of mononuclear and polynuclear species. We thus performed some spectrophotometric measurements of solutions just before the onset of precipitation and of solutions at a pH just above the point where precipitation begins. The spectra show a similar pattern, namely two prominent peaks at 420 and 428 nm. Before the onset of precipitation the peak at 420 nm is the major peak, while the peak at 428 nm is slightly lower. The relative intensities change as precipitation sets in. We can nevertheless conclude that the speciation has not changed drastically in the two cases. Earlier potentiometric and also spectrophotometric measurements in solutions without precipitates have been interpreted in terms of the complexes $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ (Table 3), so it seems reasonable to assume the presence of these species. We do indeed expect a large amount of polymerized species in our saturated solutions. Inclusion of further polymers into our refinements is possible, but does not lead to any improvement of the fit.

The solubility products and the stability constants obtained from our data are listed in Table 3 together with some selected literature data. The agreement of the stability constants with literature is very satisfactory with respect to the computational difficulties that occurred. It turned out that the minimum of the sum of squares lies in a very flat region so that refinements with vastly different starting values (up to $\pm 10^5$) all converge with identical sum of squares, but yield different values for the thermodynamic constants. The differences of $\lg \beta$ (e.g., ± 1 for β_{22}) exceed the errors calculated for the constants by the random error approach (± 0.03 for β_{22}). The value of the solubility product, however, falls within the estimated error range. We can thus be confident about our solubility product, but the values of our stability constants should be treated as estimates rather than final values.

Uranyl carbonate

Equilibration times varied between 3 and 14 days for both the closed system approach and the open system approach. With the open system approach equilibration times tended to decrease with decreasing pH whereas no systematics could be observed with the closed system approach. The composition of the precipitate was investigated using C-14 marked carbonate and X-ray analysis. The precipitate changes from UO_2CO_3 to a mixed uranyl-hydroxo-carbonate at pH > 6.5 and to uranyl hydroxide or sodium diuranate at pH > 8. Apparently different transition states occur, but none of them was characterized in detail. Our solubility curve covers the region $3 < pH < 6$ and $-11 < \lg[CO_3^{2-}] < -6$ where UO_2CO_3 is the solid phase.

Filtration experiments did not show any significant differences between filters of different pore size (2 − 800 nm). We therefore used filters of 450 nm pore size for our analyses.

The solubility curves obtained by both methods agree, but the data points obtained by the closed system approach show a large spread. This is probably caused by small losses of carbonate as CO_2 during the experiments and during sample preparation. In addition the determination of the total amount of carbonate in solution via liquid scintillation counting is problematic in the presence of uranium. Quench effects occur, the size of which depends on the uranium concentration. We therefore only used the data obtained by the open system approach in our calculations (Table 2).

At low CO_3^{2-} concentrations the solubility drops with increasing CO_3^{2-} concentration. If there were no uranyl carbonate complexes in the solution we would expect a straight line with a slope of -1. Using only the first 4 data points we indeed calculated a slope of -1. As the carbonate concentration increases, the solubility curve flattens due to the appearance of uranyl carbonate complexes and eventually rises again

Table 3. Solubility product K_{sp} of $UO_2(OH)_2 \cdot H_2O$ and logarithms of the formation constants $\beta_{pq} = [(UO_2)_p(OH)_q]/([UO_2]^p[OH]^q)$ for the uranyl-hydroxide complexes at 25°C

Medium	pK_{sp}	$\lg\beta_{11}$	$\lg\beta_{21}$	$\lg\beta_{22}$	$\lg\beta_{35}$	$\lg\beta_{34}$		Ref.
→0	21.96	—	—	—	—	—		[22]
	19.82	—	—	—	—	—		[22]
	23.74	—	—	—	—	—		[22]
	22.70	—	—	—	—	—		[22]
	23.00	—	—	—	—	—		[22]
→0, 20°C	17.22	—	—	—	—	—		[22]
0.2 M NH$_4$NO$_3$	21.74	—	—	—	—	—		[22]
0.1 M KNO$_3$	—	7.9	—	22.16	—	—	$\lg\beta_{46}=66.4$	[13]
0.1 M KNO$_3$	—	8.5	—	22.11	53.59	43.69	$\lg\beta_{47}=37.69$	[14]
0.1 M NaClO$_4$	—	—	11.8	21.91	—	—		[15]
0.1 M NaClO$_4$	—	9.61	11.78	21.91	54.36	—	$\lg\beta_{37}=73.97$	[4]
0.1 M NaClO$_4$	22.21	—	—	22.16	53.05	—		[*]
0.5 M KNO$_3$	—	8.3	—	22.08	53.78	—		[16]
0.5 M NaClO$_4$	—	—	10.19	21.97	53.22	42.83		[17]
1 M KNO$_3$	—	—	9.8	22.04	53.79	43.2		[18]
1 M NaClO$_4$	—	9.2	—	21.90	53.26	—		[19]
1 M NaClO$_4$	—	—	—	22.06	53.59	—		[20]
1 M NaClO$_4$	—	—	10.34	22.98	—	—		[21]
1 M NaCl	—	8.4	—	21.80	53.04	43.33		[19]

* This study; estimated errors: pK_{sp}: ±0.01, $\lg\beta_{22}$: ±0.03, $\lg\beta_{35}$: ±0.04.

Table 4. Solubility product K_{sp} of UO_2CO_3 and logarithms of the formation constants $\beta_{pqr} = [(UO_2)_p(OH)_q(CO_3)_z]/([UO_2]^p[OH]^q[CO_3]^z)$ for the uranyl-hydroxide-carbonate complexes at 25°C

Medium	pK_{sp}	$\lg\beta_{101}$	$\lg\beta_{102}$	$\lg\beta_{103}$		Ref.
	14.15					[24]
	14.26					[25]
0	—	9.87	16.7	—		[26]
→0	—	—	14.6	18.3		[27]
0.0003 M	—	10.09	—	—		[28]
0.1 M NaClO$_4$	13.29	8.70	16.33	23.92		[*]
0.1 M NaClO$_4$	—	—	16.15	21.81		
$2UO_2^{2+} + CO_2 + 4H_2O \rightarrow (UO_2)_2(OH)_3(CO_3) + 5H^+$ $\log\beta = -18.63$						[23]
0.1 M NaNO$_3$	—	9.0	16.22	21.70		[29]
0.1 M NaNO$_3$	—	—	—	21.54 (20°C)		[30]
0.1 M NaClO$_4$	—	—	16.16	21.57		[4]
0.1 M NaClO$_4$	—	—	—	K3=4.7		[31]
0.2 M NH$_4$NO$_3$	—	—	15.57	20.7		[32]
0.5 M NaClO$_4$	13.21	8.3	15.36	21.46	$\lg\beta_{306}=53.7$	[33]
1 M NH$_4$Cl	—	—	—	22.8		[34]
3 M NaClO$_4$	13.94	8.3	16.2	22.61	$\lg\beta_{306}=56.2$	[33]
3 M NaClO$_4$	—	9.02	—	—		
$3UO_2^{2+} + CO_2 + 4H_2O \rightarrow (UO_2)_3(OH)_3(CO_3)^+ + 5H^+$ $\log\beta = -16.34$						
$11UO_2^{2+} + 6CO_2 + 18H_2O \rightarrow (UO_2)_{11}(OH)_{12}(CO_3)_6^{2-} + 24H^+$ $\log\beta = -72.0$						[35]
3 M NaClO$_4$	$3UO_2(CO_3)_3^{4-} + 6H^+ \rightarrow (UO_2)_3(CO_3)_6^{6-} + 3CO_2(g) + 3H_2O$ $\log\beta - -41.5$					[21]
3 M NaClO$_4$	$3UO_2(CO_3)_3^{4-} + 3CO_2(g) + 3H_2O \rightarrow (UO_2)_3(CO_3)_6^{6-} + 6HCO_3^-$ $\log\beta = -6.43$					[36]

* This study; estimated errors: pK_{sp}: ±0.01, $\lg\beta_{101}$: ±0.04, $\lg\beta_{102}$: ±0.07, $\lg\beta_{103}$: ±0.03.

as the coordination number of the uranyl ion increases.

In order to calculate the solubility product and stability constants data analysis was carried out with different models consisting of combinations of the following species that have been suggested in the literature [4, 21, 23–36]: UO_2CO_3, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_2CO_3(OH)_3^-$, and $(UO_2)_3CO_3(OH)_3^+$. Complexes with hydrogen carbonate ions have been shown not to exist [33] and

therefore were not taken into consideration. It turned out that the best refinements were found for the model consisting of the complexes UO_2CO_3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$. Stability constants for the other complexes suggested above could be refined together with those for the three monomers, but their inclusion did not lead to any improvement of the fit. In addition, speciation plots showed that the concentrations of these complexes were negligibly small. The stability constants obtained for these complexes are thus
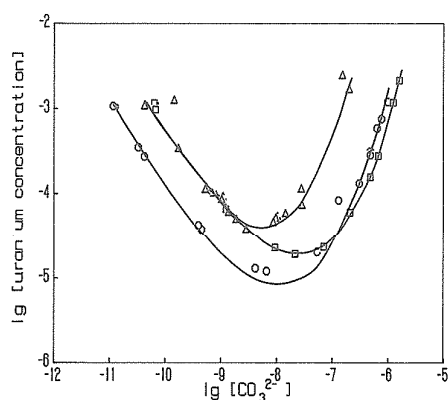
Fig. 2. Experimental (symbols) and theoretical (lines) solubility curves of UO_2CO_3 at 25°C and $I=0.1$ M (triangles, this work), $I=0.5$ M (squares, [33]), and $I=3$ M (circles, [33]).

considered to be "error absorbers" with no chemical meaning and were excluded from the models.

In contrast to the uranium-hydroxide system no mathematical problems occurred. The stability constants obtained by using different starting values all fall within the range determined by our error estimation.

Agreement between the values obtained here for the solubility product and stability constants and values reported in literature (Table 4) is satisfactory. The value obtained for the solubility product at $I=0.1$ M lies between those reported at $I=0.5$ M and $I=3$ M [33]. This is expected due to the dependence of the solubility product on the activity coefficients. This behaviour is not, however, found for the values of the stability constants as a consequence of the different models chosen by different researchers to describe their data.

In Fig. 2 our experimental and theoretical solubility curve is displayed together with two curves obtained at higher ionic strengths [33]. At low carbonate concentration ($lg[CO_3^{2-}]<-9$) the solubility curves at the different ionic strengths are almost parallel lines. In this region complex formation is weak and the solubility curve is mainly determined by the solubility product. At higher carbonate concentration complex formation becomes more important and the curves differ from each other due to the different speciation and different degree of complexation. At $I=0.1$ M a larger amount of carbonate is bound per uranyl ion than at the other ionic strengths. The major complex at high carbonate concentrations is $UO_2(CO_3)_3^{4-}$. At $I=0.5$ M and $I=3$ M $UO_2(CO_3)_3^{4-}$ also becomes the major complex, but $(UO_2)_3(CO_3)_6^{6-}$ is an important competitor. It has been indicated [33] that the formation of $(UO_2)_3(CO_3)_6^{6-}$ is favoured at higher ionic strengths due to the possible stabilization of the complex by ions of the background electrolyte. This is probably the reason why this complex has not been found to occur in our study at $I=0.1$ M.

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