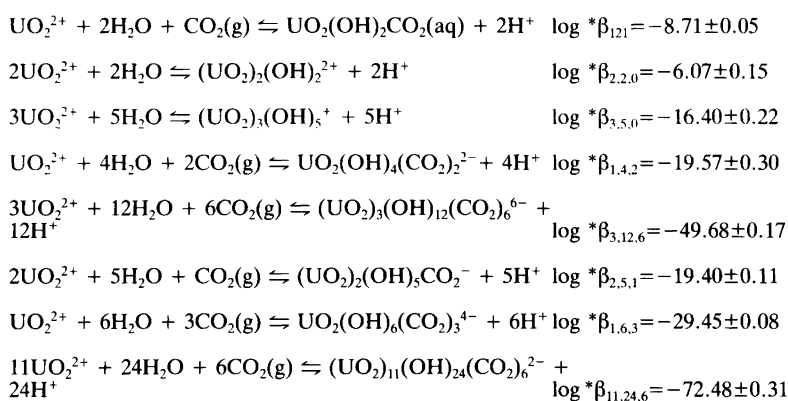# Studies on Metal Carbonate Equilibria. 22. A Coulometric Study of the Uranium(VI)–Carbonate System, the Composition of the Mixed Hydroxide Carbonate Species

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Complex formation in the uranium(VI) – H_2O – $CO_2(g)$ system has been studied at 25 °C in a 0.50 m $NaClO_4$ medium. The experimental method was potentiometry (H^+-measurements), using coulometry to change the total concentration of hydrogen ions. The $-\log [H^+]$ range covered was 3.5–5.2. The experimental data were explained using the following chemical model, where $(OH)_2CO_2^{2-} \equiv CO_3^{2-}$:

$$UO_2^{2+} + 2H_2O + CO_2(g) \rightleftharpoons UO_2(OH)_2CO_2(aq) + 2H^+ \quad \log {}^*\beta_{1,2,1} = -8.71 \pm 0.05$$

$$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+ \quad \log {}^*\beta_{2,2,0} = -6.07 \pm 0.15$$

$$3UO_2^{2+} + 5H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H^+ \quad \log {}^*\beta_{3,5,0} = -16.40 \pm 0.22$$

$$UO_2^{2+} + 4H_2O + 2CO_2(g) \rightleftharpoons UO_2(OH)_4(CO_2)_2^{2-} + 4H^+ \quad \log {}^*\beta_{1,4,2} = -19.57 \pm 0.30$$

$$3UO_2^{2+} + 12H_2O + 6CO_2(g) \rightleftharpoons (UO_2)_3(OH)_{12}(CO_2)_6^{6-} + 12H^+ \quad \log {}^*\beta_{3,12,6} = -49.68 \pm 0.17$$

$$2UO_2^{2+} + 5H_2O + CO_2(g) \rightleftharpoons (UO_2)_2(OH)_5CO_2^- + 5H^+ \quad \log {}^*\beta_{2,5,1} = -19.40 \pm 0.11$$

$$UO_2^{2+} + 6H_2O + 3CO_2(g) \rightleftharpoons UO_2(OH)_6(CO_2)_3^{4-} + 6H^+ \quad \log {}^*\beta_{1,6,3} = -29.45 \pm 0.08$$

$$11UO_2^{2+} + 24H_2O + 6CO_2(g) \rightleftharpoons (UO_2)_{11}(OH)_{24}(CO_2)_6^{2-} + 24H^+ \quad \log {}^*\beta_{11,24,6} = -72.48 \pm 0.31$$

The experimental data were fitted to the selected model by using the LETAGROP least-squares procedure. The uncertainties reported for the refined constants are 3σ, while the standard deviation in the error-carrying variable (the EMF) was 0.55 mV.
    The experiments have been made in such a way that the determination of the minor species is optimized. Previous experimental data have been reviewed in order to obtain a consistent set of equilibrium constants. A brief discussion of possible structures of the mixed uranium hydroxide–carbonate complexes is given.

There is an extensive literature on equilibria in the uranium–carbonate system. Reviews of these data have been made by Langmuir,[1] Cordfunke and O'Hare,[2] Lemire and Tremaine,[3] Robel[4] and Tripathi.[5] Some previous studies in this series[6–9] also deal with equilibria and structure of complexes in the uranium(VI) – H_2O – $CO_2(g)$ system.

The stoichiometric compositions and the equilibrium constants of the three mononuclear U(VI) carbonate complexes $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, together with the trimer $(UO_2)_3(CO_3)_6^{6-}$, are well established. The mixed U(VI) carbonate–hydroxide complexes are often minor species, and it is therefore more difficult to obtain unambiguous stoichiometries and equilibrium constants for them. Blake et al.[10] were the first to suggest the

formation of a mixed U(VI) – CO_3^{2-} – OH^- complex, $U_2O_5(CO_3)(OH)^- \equiv (UO_2)_2(CO_3)(OH)_3^-$. However, their experimental data do not seem to allow an unambiguous assignment of the stoichiometry. Ciavatta et al.[11] have suggested the formation of $(UO_2)_3(OH)_5CO_2^+$ and a large polynuclear complex, $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$. It is difficult to obtain a unique composition for complexes with a high nuclearity, hence the composition of these species in terms of coordinated carbonate and bicarbonate groups will be dealt with in the discussion. Maya[12] studied equilibria in the U(VI)–carbonate system at low partial pressures of CO_2, and found the complex $(UO_2)_2(CO_3)(OH)_3^-$ to be an important species around pH 7. Finally, Tsymbal[13] suggested the formation of $UO_2CO_3OH^-$.

Experimental conditions are not always optimized for the determination of minor species, and we have undertaken this study in order to obtain additional experimental

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[†] This is part of the Ph.D. thesis of B. L. at the RIT.

information that will allow us to obtain a more unambiguous assignment of the composition of some minor species. A proposed stoichiometry should, of course, also be compatible with the known coordination chemistry both of the ligands and of U(VI). For this reason we will also make some proposals for the structures.

The experiments have been carried out at 25 °C in a 0.50 m sodium perchlorate medium. They are optimized for a study of the minor species which are formed in the $-\log$ [H$^+$] range studied.

Experimental

Chemicals used. Stock solutions of $UO_2(ClO_4)_2$ and $NaClO_4$ were prepared and analyzed as described before.[6] The CO_2 gas and the CO_2/N_2 gas mixtures used in the experiments were washed and conditioned by passing them through solutions containing first 10 % H_2SO_4 and then 0.50 M $NaClO_4$ solutions.

Experimental method. The experiments were performed as coulometric titrations[14] in a thermostatted air box at 25.00 ± 0.01 °C. The initial test solution was prepared with $-\log$ [H$^+$] slightly above 7. Care was taken to ensure that no precipitation of $UO_2CO_3(s)$ occurred. The coulometric titrations were then made by increasing the hydrogen ion concentration of the test solution. By using low currents, ca. 1 mA, we could decrease the hydrogen ion concentration slowly, thus avoiding a local decrease of pH, which could result in the precipitation of $UO_2CO_3(s)$. It was not possible to use coulometry to decrease the hydrogen ion concentration [because of reduction of U(VI) to U(IV)]. For more experimental details, see Ref. 14. The [H$^+$] concentration was measured using a glass electrode and a double-junction Ag,AgCl reference electrode, both from Metrohm. The E_0 value of the electrode was obtained by carrying out a Gran titration. Two different U(VI) total concentrations, 1.00 and 0.20 mM, were studied at two different partial pressures, 0.97 and 0.30 atm, respectively. The experimental data are given in Table 1.

Data analysis. The data in Table 1 were used to test different chemical models (see Table 3 later). The first chemical model involving the species (1,2,1; 2,2,0; 3,5,0; 1,4,2; 3,12,6; 1,6,3) results in a large standard deviation in the error-carrying variable. We then included the species $(UO_2)_2(OH)_5CO_2^-$, which significantly reduced both the standard deviation in the EMF and the error square sum. Addition of the species $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$ gave an additional improvement of the chemical model. Both the total acidity and the measured EMF were used as error-carrying variables. The results of the two minimization procedures differ: when the total acidity was used as the error-carrying variable the equilibrium constant for the 11-nuclear complex was zero, while the constant was well-defined when minimizing the EMF. In a coulometric method it is natural to use the EMF as the error-carrying

Table 1. Experimental data given as $-\log$ [H$^+$], $H_{tot}/10^3$ m, $P_{CO_2}/$atm. $H_{tot} = $ [H$^+$]$-$[HCO$_3^-$]-2[CO$_3^{2-}$]$-$[OH$^-$]$-$
$\Sigma[(UO_2)_p(OH)_q(CO_2)_r]$.

Series 1: $[UO_2^{2+}]_{tot} = 0.000196$ m

5.199,$-4.603,0.979$; 5.175,$-4.365,0.979$; 5.150,$-4.127,0.979$;
5.122,$-3.889,0.979$; 5.093,$-3.651,0.979$; 5.062,$-3.413,0.979$;
5.030,$-3.175,0.979$; 4.995,$-2.937,0.978$; 4.957,$-2.699,0.978$;
4.915,$-2.461,0.978$; 4.868,$-2.223,0.978$; 4.834,$-2.069,0.977$;
4.798,$-1.915,0.977$; 4.759,$-1.761,0.977$; 4.716,$-1.606,0.977$;
4.668,$-1.451,0.977$; 4.616,$-1.297,0.977$; 4.557,$-1.142,0.977$;
4.495,$-0.988,0.977$; 4.422,$-0.834,0.977$; 4.343,$-0.680,0.976$;
4.248,$-0.517,0.976$; 4.140,$-0.363,0.976$

Series 2: $[UO_2^{2+}]_{tot} = 0.000196$ m

5.724,$-4.895,0.292$; 5.701,$-4.657,0.292$; 5.676,$-4.419,0.292$;
5.649,$-4.181,0.292$; 5.621,$-3.943,0.292$; 5.591,$-3.704,0.292$;
5.559,$-3.466,0.292$; 5.524,$-2.989,0.291$; 5.441,$-2.718,0.291$;
5.413,$-2.564,0.291$; 5.384,$-2.410,0.291$; 5.352,$-2.255,0.291$;
5.319,$-2.101,0.291$; 5.283,$-1.946,0.291$; 5.244,$-1.792,0.291$;
5.200,$-1.633,0.291$; 5.151,$-1.479,0.291$; 5.095,$-1.324,0.291$;
5.031,$-1.170,0.291$; 4.951,$-1.004,0.291$; 4.864,$-0.849,0.291$;
4.764,$-0.695,0.292$; 4.647,$-0.541,0.292$; 4.511,$-0.386,0.292$;
4.347,$-0.232,0.292$; 4.135,$-0.077,0.292$; 3.859,$-0.773,0.292$

Series 3: $[UO_2^{2+}]_{tot} = 0.001$ m

5.513,$-5.898,0.292$; 5.459,$-5.452,0.292$; 5.407,$-5.005,0.292$;
5.366,$-4.559,0.291$; 5.308,$-4.070,0.291$; 5.231,$-3.624,0.290$;
5.118,$-3.177,0.290$; 4.943,$-2.683,0.289$; 4.749,$-2.237,0.289$;
4.610,$-1.791,0.290$; 4.502,$-1.344,0.290$; 4.363,$-0.897,0.291$;
4.155,$-0.451,0.291$

Series 4: $[UO_2^{2+}]_{tot} = 0.001$ m

5.121,$-6.590,0.972$; 5.076,$-6.143,0.971$; 5.034,$-5.696,0.971$;
4.990,$-5.249,0.970$; 4.942,$-4.803,0.970$; 4.887,$-4.316,0.970$;
4.825,$-3.852,0.970$; 4.759,$-3.405,0.970$; 4.659,$-2.862,0.970$;
4.554,$-2.405,0.970$; 4.436,$-1.940,0.970$; 4.314,$-1.477,0.970$;
4.184,$-1.030,0.969$; 3.772,$-0.137,0.965$

variable. Our results indicate, however, that it is difficult to obtain unambiguous information about the large polynuclear complex. The final chemical model is given in Table 2, where the values estimated in a recent review of uranium thermodynamics[17] are also reported.

In all minimizations the equilibrium constant for the reaction $CO_2(g) + H_2O \rightleftharpoons HCO_3^- + H^+$ was optimized, and we obtained $\log *\beta_{0,1,1} = -7.606\pm0.004$, in close agreement with the accepted literature value[17] of $\log *\beta_{0,1,1} = -7.607$. This indicates the absence of systematic experimental errors in this study.

Results and discussion

The results in Table 2 confirm the formation of the same major species as previously identified by other investigators. However, the precision of the present study is much higher than the previous ones in the same pH region. This is indicated by the standard deviation in the error-carrying variable (the measured EMF), which is ±0.55 mV in this

Table 2. Equilibrium constants for the complexes formed in the U(VI) – H_2O – $CO_2(g)$ system at 25 °C. The stoichiometry and the equilibrium reactions refer to the reactions $pUO_2^{2+} + qH_2O + rCO_2(g) \rightleftharpoons (UO_2)_p(OH)_q(CO_2)_r + qH^+$, where $OHCO_2^- \equiv HCO_3^-$ and $(OH)_2CO_2^{2-} \equiv CO_3^{2-}$.

Reaction	$-\log {}^*\beta_{pqr}{}^a$	$-\log {}^*\beta_{pqr}{}^b$
$UO_2^{2+} + 2H_2O + CO_2(g) \rightleftharpoons UO_2(OH)_2CO_2 + 2H^+$	8.71 ± 0.05	8.73 ± 0.60
$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$	6.07 ± 0.15	6.01 ± 0.05
$3UO_2^{2+} + 3H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H^+$	16.40 ± 0.22	16.52 ± 0.16
$UO_2^{2+} + 4H_2O + 2CO_2(g) \rightleftharpoons UO_2(OH)_4(CO_2)_2^{2-} + 4H^+$	19.57 ± 0.30	18.7 ± 0.11
$3UO_2^{2+} + 12H_2O + 6CO_2(g) \rightleftharpoons (UO_2)_3(OH)_{12}(CO_2)_6 + 12H^+$	49.68 ± 0.17	49.2 ± 1.1
$11UO_2^{2+} + 24H_2O + 6CO_2(g) \rightleftharpoons (UO_2)_{11}(OH)_{24}(CO_2)_6^{2-} + 24H^+$	72.48 ± 0.31	73.3 ± 2.5
$2UO_2^{2+} + 5H_2O + CO_2(g) \rightleftharpoons (UO_2)_2(OH)_5CO_2^- + 5H^+$	19.40 ± 0.11	18.63 ± 0.14^c
		18.90 ± 0.10^d
$UO_2^{2+} + 6H_2O + 3CO_2(g) \rightleftharpoons UO_2(OH)_6(CO_2)_3^{4-} + 6H^+$	29.45 ± 0.08	29.71 ± 0.18

^{a}From this study. ^{b}Values as given by the NEA review[17] recalculated to $I = 0.5$ m $NaClO_4$. ^{c}Value as given by Maya[12] recalculated to $I = 0.5$ m $NaClO_4$. ^{d}Value as given by Table 3, Maya model 3, recalculated to $I = 0.5$ m $NaClO_4$.

study, as compared to, e.g. ± 2.4 mV in the study of Maya.[12] The numerical values of the equilibrium constant can be compared if corrections are made for differences in the ionic media used in these studies. Such corrections were made by using the specific ion interaction theory.[16] The agreement between these data and the ones selected by the OECD/NEA expert team on uranium[17] is excellent for all species except $UO_2(CO_3)_2^{2+}$, where our data indicate a smaller equilibrium constant than previously reported. The NEA values given in Table 2 have been recalculated to $I =$

Fig. 1. Species distribution diagrams in the U(VI) – H_2O – $CO_2(g)$ system at 25 °C. (a) Refers to our titration series 3 (Table 1), while (b) corresponds to the conditions used by Maya,[12] with $\log_{10}(P_{CO_2}/\text{atm}) = -2.554$.

0.50 m using the specific ion interaction theory and the interaction coefficients selected by the NEA review. The stoichiometries of two species, $(UO_2)_2(CO_3)(OH)_3^-$ and $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$, were also confirmed. However, the stoichiometry of the large polynuclear complex is not uniquely defined, [the uncertainties in the stoichiometric coefficients for CO_2 (or CO_3^{2-}) and OH^- are ± 1], while the nuclearity is much better defined.

The discrepancy found for $\log {}^*\beta_{1,4,2}$ is probably a result of the neglect of the species $(UO_2)_2(OH)_3CO_3^-$ in many previous investigations. Both $UO_2(CO_3)_2^{2-}$ and $(UO_2)_2(CO_3)(OH)_3^-$ are formed in approximately the same P_{CO_2} vs. $-\log [H^+]$ range [Fig. 1(a)], and the neglect of $UO_2(CO_3)(OH)_3^-$ results in a concentration that is too large (and in a value of the formation constant that is too high) for $UO_2(CO_3)_2^{2-}$. The refinement of model 1 confirms this reasoning: the value of $\log {}^*\beta_{1,4,2}$ is larger here (and in agreement with the NEA value) than in the final model. Bidoglio *et al.*[18] made a thermal-lensing spectrophotometric investigation of the equilibrium $UO_2(CO_3)_2^{2-} + CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$, where the concentration of uranium(VI) was kept very low (4×10^{-6} M) and consequently the formation of $(UO_2)_3(CO_3)_6^{6-}$ and $(UO_2)_2(CO_3)(OH)_3^-$ was suppressed. The resulting equilibrium constant from this study, in combination with the well-known equilibrium constants for the reactions $UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$ and $CO_3^{2-} + 2H^+ \rightleftharpoons CO_2(g) + H_2O$ in 0.5 M $NaClO_4$, gives, for the reaction $UO_2^{2+} + 4H_2O + CO_2(g) \rightleftharpoons UO_2(OH)_4(CO_2)_2^{2-}$, $\log {}^*\beta_{1,4,2} = -19.09 \pm 0.21$, which also indicates that the formation constant for the complex $UO_2(OH)_4CO_2^{2-}$ [$\equiv UO_2(CO_3)_2^{2-}$] is overestimated in previous studies (Table 2; the NEA value).

Previous experimental studies. As mentioned in the introduction, previous investigators have proposed several different chemical models for the equilibria in the U(VI) – H_2O – $CO_2(g)$ system. These models will now be discussed in order to decide if there are any inconsistencies in the experimental information.

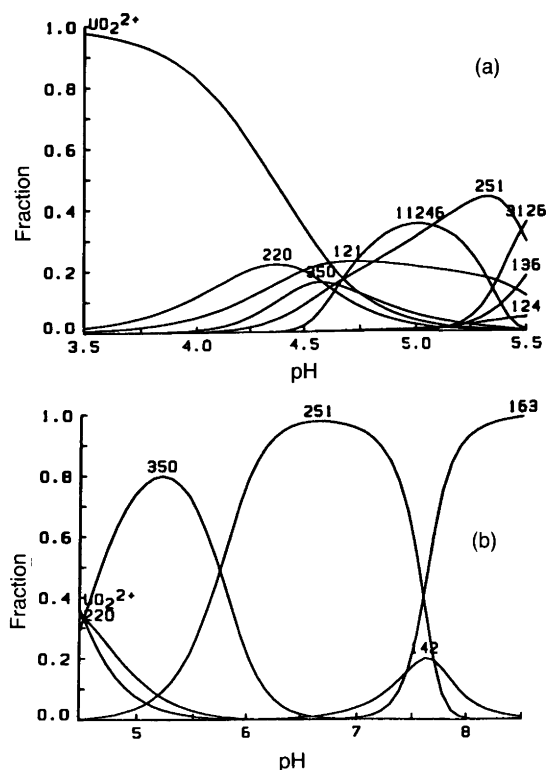Tsymbal[13] studied the U(VI) carbonate system in 0.1 M

$NaClO_4$ from pH 3 to pH 7 by means of the EMF technique. The potentiometric measurements seem carefully made, and precautions were taken to standardize the glass electrode and to control the liquid junction potentials. The experiments were made as titrations in which acid was added to a solution of known total concentration of uranium, $0.5 < U(VI) < 5$ mM, and carbonate, $3 <$ total carbonate < 30 mM. The total concentration was kept constant by working in a closed system in which there is a continuous increase of the partial pressure of CO_2 as CO_3^{2-} and HCO_3^- are transformed into $CO_2(g)$. There is a risk of precipitation of $UO_2CO_3(s)$ around pH 5, but no mention of the formation of a precipitate was given by the author. Tsymbal explained his data by assuming the formation of the complexes $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2-(CO_3)_3^{4-}$, and the ternary species $UO_2CO_3OH^-$. We have tested Tsymbal's data against different chemical models (Table 3). The tests were made by a least-squares analysis of Tsymbal's experimental data, using the program LE-TAGROP DISTR to describe the two-phase system (gas + solution) studied. The error-carrying variable was the total concentration of H^+ in the system. It would have been preferable to use the EMF, but this was not possible in the subroutine available to us. In the initial refinements we found it difficult to obtain convergence; there was also a strong correlation between the species $UO_2CO_3(aq)$ and $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$. The data indicated the presence of a systematic error in the total acidity of the uraninium(VI) stock solution used by Tsymbal. He reported the total acidity to be zero in this solution, while we found that a ratio $H/U = 0.20$ gave a much better fit of the experimental data, and a very much lower error-square sum; this refinement is denoted "Tsymbal model 3" in Table 3. The indicated error is surprisingly large, and one can therefore not exclude some other systematic error in the experiments. Such an error must be present in Tsymbal's hydrolysis data, as discussed by Tripathi.[5] The hydroxide complexes are minor species under the experimental conditions used. Hence, the least-squares refinements are not very sensitive to the values of $^*\beta_{2,2,0}$ and $^*\beta_{3,5,0}$. We make the following findings.

(a) The equilibrium constants of the carbonate complexes are not strongly dependent on the equilibrium constants of the hydroxide complexes, because these species are present in fairly low concentrations in the test solutions in most of the investigated $-\log[H^+]$ range.

(b) There are significant amounts of $(UO_2)_3(CO_3)_6^{6-}$ formed. Tsymbal's data thus confirm the studies in Refs. 6 and 7. The equilibrium constant $\log_{10} K = 54.4\pm0.1$ for the reaction $3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-}$ is in fair agreement with the value of Grenthe et al.,[7] $\log_{10} K = 54.2$, recalculated to 0.1 M $NaClO_4$.

(c) The agreement between the chemical model and the experimental data is improved if the large polynuclear complex proposed by Ciavatta et al.[11] is included. As only small amounts of this complex are formed, the model selection is not very sensitive to this species (Table 3).

Table 3. Least-squares analysis of different chemical models using previously published experimental data from Tsymbal,[13] Ciavatta et al.[11] and Maya[12] and data from the present investigation. Note that the refinements of Tsymbal's data use equilibrium constants of the type

$$pUO_2^{2+} + qH_2O + rCO_3^{2-} \rightleftharpoons (UO_2)_p(OH)_q(CO_3)_r + qH^+,$$
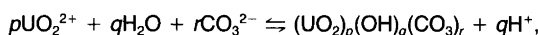
while the data of Ciavatta et al., the data of Maya and the data from the present investigation refer to equilibrium constants of the type

$$pUO_2^{2+} + qH_2O + rCO_2(g) \rightleftharpoons (UO_2^{2+})_p(OH)_q(CO_2)_r + qH^+.$$
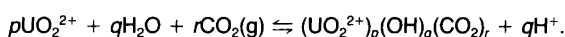
The constants with $\pm$ error given are the ones optimized in the minimization. The errors given are three standard deviations (3σ).

Data and model	Complexes (p,q,r)	$-\log {}^*\beta_{pqr}$	Standard deviation in the error-carrying variable
Tsymbal original model	2,2,0	6.09	
	3,5,0	15.64	
	1,0,2	-16.18 ± 0.06[a]	
	1,0,3	-21.57 ± 0.02[a]	
	1,1,1	-4.10 ± 0.02[a]	
Tsymbal model 1	2,2,0	6.05	0.0202 mM H_T[b]
	3,5,0	16.24	
	1,0,1	-9.02 ± 0.18	
	1,0,2	-16.4 ± 0.1	
	1,0,3	-21.8 ± 0.2	
	3,0,6	-54.9 ± 0.1	
Tsymbal model 2	2,2,0	5.70	0.0195 mM H_T[b]
	3,5,0	15.60	
	1,0,1	-9.3 ± 0.2	
	1,0,2	-16.1 ± 0.2	
	1,0,3	-21.3 ± 0.3	
	3,0,6	-55.0 ± 0.2	
	11,12,6	-34.7 ± 0.2	
Tsymbal model 3	2,2,0	5.70	0.0137 mM H_T[b]
	3,5,0	15.6	
	1,0,1	-9.5 ± 0.2	
	1,0,2	-16.0 ± 0.2	
	1,0,3	-21.3 ± 0.3	
	3,0,6	-54.4 ± 0.1	
	11,12,6	-32.9 ± 0.5	
Ciavatta et al. original model	2,2,0	6.02 ± 0.01	0.444 mV
	3,5,0	16.73 ± 0.07	
	1,2,1	9.00 ± 0.01	
	11,24,6	72.0 ± 0.1	
	3,5,1	16.5 ± 0.1	
Ciavatta et al. without 3,5,1	2,2,0	6.01 ± 0.01	0.473 mV
	3,5,0	16.59 ± 0.06	
	1,2,1	8.99 ± 0.02	
	11,24,6	71.9 ± 0.1	
Ciavatta et al. 3,5,1 replaced with 2,5,1	2,2,0	5.99 ± 0.01	0.444 mV
	3,5,0	16.68 ± 0.07	
	1,2,1	9.01 ± 0.01	
	11,24,6	72.0 ± 0.1	
	2,5,1	20.2 ± 0.2	

contd.

Table 3 (contd.)

Data and model	Complexes (p,q,r)	$-\log {}^*\beta_{pqr}$	Standard deviation in the error-carrying variable
Ciavatta *et al.* 3,5,1 replaced with 1,3,1	2,2,0 3,5,0 1,2,1 11,24,6 1,3,1	6.00±0.01 16.60±0.03 9.02±0.02 71.9±0.1 14.7±0.2	0.456 mV
Ciavatta *et al.* original model +2,5,1	2,2,0 3,5,0 1,2,1 3,5,1 11,24,6 2,5,1	6.01±0.01 16.87±0.09 9.03±0.01 16.35±0.08 72.14±0.14 20.1±0.1	0.392 mV
Maya model 1; only 2,5,1 optimized	0,1,1 2,2,0 3,5,0 1,2,1 1,4,2 3,12,6 1,6,3 2,5,1	7.62±0.06[c] 5.89±0.05[c] 16.19±0.13[c] 8.65±0.64[c] 18.88±0.11[c] 51.17±1.3[c] 30.91±0.16[c] 18.83±0.10	6.3 mV
Maya model 2; same as model 1 except that both (0,1,1) and (2,5,1) are optimized	0,1,1 2,5,1	7.85±0.09 18.87±0.11	3.4 mV
Maya model 3; same as model 1 except that (0,1,1), (2,5,1) and (1,6,3) are optimized	0,1,1 2,5,1 1,6,3	7.78±0.06 18.90±0.10 31.19±0.19	2.95 mV
This work basic model; all constants optimized	1,2,1 2,2,0 3,5,0 1,4,2 3,12,6 1,6,3	8.61±0.08 6.05[d] 16.12±0.27 18.74±0.11 49.91[d] 29.77±0.33	1.22 mV
This work basic model+ (2,5,1); all constants optimized	1,2,1 2,2,0 3,5,0 1,4,2 3,12,6 1,6,3 2,5,1	8.73±0.05 6.12±0.20 16.26±0.25 19.54[d] 49.78±0.21 29.37±0.09 29.26±0.07	0.62 mV
This work basic model+ (2,5,1) and (11,24,6); all constants optimized	1,2,1 2,2,0 3,5,0 1,4,2 3,12,6 1,6,3 2,5,1 11,24,6	8.71±0.05 6.07±0.15 16.40±0.22 19.57±0.30 49.68±0.17 29.45±0.08 19.40±0.11 72.48±0.31	0.55

[a]The errors indicated are given by Tsymbal.[13] [b]H_T is the total acidity. [c]Values given by NEA[17] recalculated to $I = 0.1$ M $NaClO_4$. [d]Maximum value; given by the least-squares program.

(d) No significant amounts of $(UO_2)_2(CO_3)(OH)_3^-$ and $(UO_2)_3(OH)_5(CO_2)^+$ are formed under the experimental conditions used by Tsymbal; hence his data cannot be used to verify or reject these species.

(e) The formation of $UO_2CO_3OH^-$ could not be confirmed.

Ciavatta *et al.*[11] also used the EMF technique to study the U(VI)–carbonate system. This study is optimized for the determination of hydroxide complexes and UO_2CO_3(aq), and cannot therefore be used to test the formation of other species, with the exception of the large polynuclear complex. However, noticeable amounts of this complex are only present in a few test solutions at the highest $-\log [H^+]$ values investigated [Fig. 1(a)]. This is the concentration range where precipitation may occur. We assume that Ciavatta *et al.* would have observed the formation of a precipitate, and conclude that the complex proposed by them is not an artifact. This conclusion is supported by the additional experimental work and the reinterpretations reported in the present study (Table 3). The ternary complex
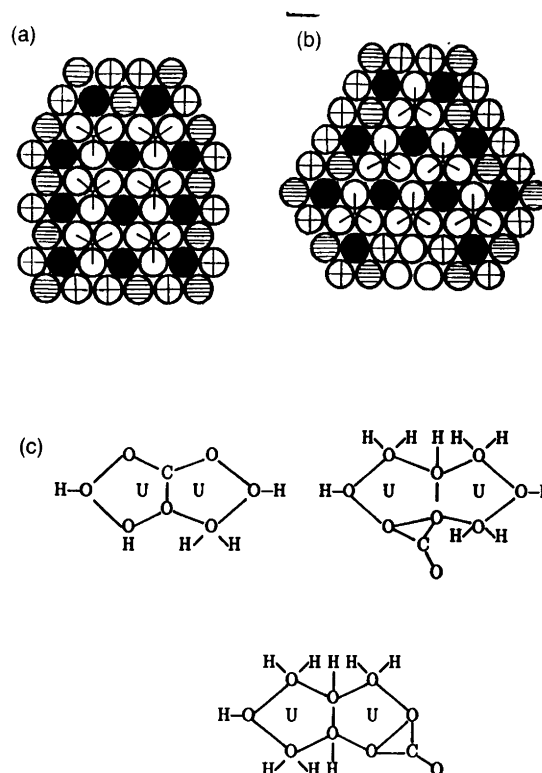

Fig. 2. (a) A model of $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$ based on the rutherfordine structure. The complex is planar with the black uranyl groups perpendicular to the plane formed by the ligands [CO_3^{2-}, OH^- (striped), and H_2O (crossed)]. The two inner U(VI) ions have six-coordination in the plane, while the external ones may be either five- or six-coordinated. (b) A structure of the same complex based on the known $(UO_2)_3(CO_3)_6^{6-}$ structure.[8] The symbols have the same significance as in the previous model. (c) The three possible models for $(UO_2)_2(CO_3)(OH)_3^-$, where the ligands form a plane perpendicular to the two uranyl ions.

$(UO_2)_3(OH)_5(CO_2)^+ \equiv (UO_2)_3(O)(OH)_2(HCO_3)^+$ proposed by Ciavatta et al. has a maximum concentration that constitutes, at most, of 5 % of the total concentration of uranium. Hence, the formation of this complex, although chemically resonable, cf. Bruno et al.,[19] cannot be considered as proven.

Maya[12] used an EMF method for the study of the U(VI)–carbonate system at low partial pressures of CO_2, $3 \times 10^{-4} < P_{CO_2} < 10^{-2}$ atm, $5 < -\log[H^+] < 8.5$, and $10^{-3} < U(VI) < 2 \times 10^{-3}$ M. This is a precise study: however, the author reports a rather large drift in the measured potentials, about 1 mV h^{-1}. This fact may be an explanation of the large standard deviation (2.4 mV) in the error-carrying variable in the least-squares refinement. Our experience indicates that the time for equilibrium between the gas phase and solution is long (hours) at low partial pressures of CO_2. Hence, the test solutions might not quite have attained equilibrium in Maya's study. Another indicator of a small systematic error in this study is offered by the experimental value of the equilibrium constant for the protonation reaction $CO_2(g) + H_2O \leftrightarrows CO_3^{2-} + 2H^+$, which is equal to $\log_{10} {}^*\beta_{0,1,2} = -17.67 \pm 0.03$, as compared to the value calculated from the CODATA Gibbs energies of formation of reactants and products, and the SIT procedure for ionic strength corrections, $\log_{10} {}^*\beta_{0,1,2} = -17.52 \pm 0.05$. A refinement of the equilibrium constant for the reaction $CO_2(g) + H_2O \leftrightarrows HCO_3^- + H^+$ (Table 3, models 2 and 3) also indicates the presence of a small systematic error in Maya's study. There is no doubt that these data identify a ternary complex of the composition $(UO_2)_2(CO_3)(OH)_3^-$, one that is predominant over a rather broad pH range [Fig. 1(b)]. Additional experimental studies of Maya et al.[20] confirm that a predominant complex, with a composition differing from the other main species $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, is formed. We have reanalyzed the data that are reported by Maya[12] and confirm his chemical model, but with equilibrium constants that differ somewhat from those proposed in the original publication (Table 3).

By using the values for the constants ${}^*\beta_{0,1,1}$, ${}^*\beta_{0,2,1}$, ${}^*\beta_{3,5,0}$, ${}^*\beta_{2,2,0}$, ${}^*\beta_{1,4,2}$, ${}^*\beta_{3,12,6}$ and ${}^*\beta_{1,6,3}$ selected by the NEA review and recalculated to $I = 0.1$ M $NaClO_4$, and refining the equilibrium constant for the formation of $(UO_2)_2(CO_3)(OH)_3^-$, we obtained $\log_{10} {}^*\beta_{2,5,1} = -18.83 \pm 0.10$, as compared to the value $\log_{10} {}^*\beta_{2,5,1} = -18.63 \pm 0.08$ reported by Maya. The resulting standard deviation in the measured potential is ± 6.3 mV. A refinement of ${}^*\beta_{2,5,1}$, together with ${}^*\beta_{0,1,1}$, gives $\log_{10} {}^*\beta_{2,5,1} = -18.87 \pm 0.11$ and $\log_{10} {}^*\beta_{0,1,1} = -7.854 \pm 0.089$. The standard deviation decreases to ± 3.4 mV and the error-square sum by factor of four, as compared to the first case. The value of $\log_{10} {}^*\beta_{0,1,1}$ is 0.2 units lower than reported by Maya.[12] The uncertainties found in our reinterpretation are larger than those reported by Maya. However, his calculations may have been based on more experimental material than that reported in the publication. Differences in the least-squares procedure may also contribute to these differences. A distribution diagram

[Fig. 1(c)] shows that $(UO_2)_2CO_3(OH)_3^-$ is a predominant complex in the range $6 < -\log[H^+] < 7.5$ under the experimental conditions used by Maya. There is thus no doubt as to the composition of this species, even if the equilibrium constant does not have the highest precision.

Our own experimental data in 0.5 m $NaClO_4$ confirm the formation of both $(UO_2)_2CO_3(OH)_3^-$ and the large polynuclear complex. Our data indicate that the equilibrium constant for the first complex is somewhat smaller than the value reported by Maya; at the same time the overall precision in the experiment is much higher, and the standard deviation in the measured potential is ± 0.55 mV. The equilibrium constant for the large polynuclear complex is in good agreement with the value proposed by Ciavatta et al.,[11] recalculated to the same ionic strength. However, the relative amounts of this complex are larger in our study, up to a maximum of 35 % of U_{tot}, than in that of Ciavatta et al.[11]

The neutral complex $UO_2CO_3(aq)$ exists in approximately the same pH region as the large polynuclear complex. The value of the equilibrium constant is close to that reported by Grenthe et al.[7] in a solubility study. If precipitation had occurred in the EMF study this would affect the equilibrium constants for both the neutral and the large polynuclear complexes. This is obviously not the case for the neutral complex, which in turn indicates that the large polynuclear species is not an experimental artifact. In Tables 2 and 3 we have listed the equilibrium constants obtained in this study, together with our reinterpretations of previously published data. The agreement is by-and-large good.

Structural implications of the proposed stoichiometries. By performing the experimental studies at several different and constant partial pressures of $CO_2(g)$ the three-component system U(VI) – H_2O–$CO_2(g)$ can be transformed into a two-component problem.[6] As a result of this it is not possible to decide if CO_2 is bonded as HCO_3^- and/or CO_3^{2-} in the complexes. In order to obtain such knowledge additional chemical information is necessary. Such information may be provided by spectroscopic techniques (Raman–IR[19] or NMR[9,10]), or other structure methods, e.g. large-angle X-ray scattering.[9] Indirect information based on known structural features of the ligand and central ion and/or the magnitude of the binding constants of various ligands may also be used. The structures of the ions $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$ are well established.[9,21] However, no structural information is available on the other species. The large polynuclear complex poses a special problem, because it is necessary to verify whether the stoichiometry is at all resonable before accepting its existence. Figs. 2(a) and 2(b) illustrate two possible structures for such a complex. The models in Fig. 2 contain structural features that are well established both for the ligands and for U(VI). The packing and the bridging properties of the carbonate in Fig. 2(a) are similar to those found in the rutherfordine structure.[9] U(VI) has five or six coordinated oxygens in the

equatorial plane, perpendicular to the O–U–O axis. The proposed model results in the stoichiometry $(UO_2)_{11}$-$(CO_3)_6(OH)_{12}(H_2O)_{4-13}{}^{2-}$. Fig. 2(b) contains structure elements that are found[9] in $(UO_2)_3(CO_3)_6{}^{6-}$. The most satisfying model from structural point of view has the stoichiometry $(UO_2)_{11}(CO_3)_6(OH)_{12}(H_2O)_{8-16}{}^{2-}$. The variations in the water composition depend on whether the coordination number of the "external" U(VI) is five or six. From a structural point of view both the proposed stoichiometries are reasonable. In order to obtain an unambiguous structure (and stoichiometry) it is necessary to obtain additional chemical information. Because of solubility constraints, and the simultaneous presence of several complexes, it is not straightforward to use NMR methods, which we previously have found to be a very powerful tool. Three different structures [Fig. 2(c)] seem possible for $(UO_2)_2(CO_3)(OH)_3{}^{-}$. They might be distinguished by using C^{13} and O^{17} NMR; however, it is difficult to prepare solutions of sufficiently high concentration owing to precipitation of $UO_2CO_3(s)$.

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