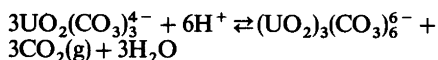


## Dioxouranium(VI) Carbonate Complexes in Neutral and Alkaline Solutions

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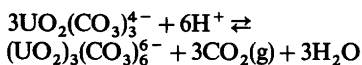
Spectrophotometric measurements in uranium(VI) solutions at  $[U(VI)] \leq 0.03$  M, combined with a potentiometric determination of the hydrogen ion concentration with a glass electrode have been explained by assuming the formation of  $UO_2(CO_3)_3^{4-}$  only, in the  $\log [H^+]$  range  $-12 < \log [H^+] < -7$ . In addition, the equilibrium constant  $\log K = 41.5 \pm 0.1$  of the previously studied equilibrium<sup>1</sup>



has been confirmed. The molar absorption coefficients  $\epsilon_1$  for the mononuclear and  $\epsilon_2$  for the threenuclear species have been determined at two different wavelengths:  $\epsilon_1^{445} = 23.6 \pm 0.2$ ,  $\epsilon_2^{445} = 44.8 \pm 0.4$ ,  $\epsilon_1^{459} = 16.9 \pm 0.2$ ,  $\epsilon_2^{459} = 29.9 \pm 0.4$  cm<sup>-1</sup> M<sup>-1</sup>. No evidence has been found for the formation of mixed species  $(UO_2)_r(OH)_q(CO_3)_r$ , throughout the acidity range investigated. In more alkaline solutions ( $[H^+] < 10^{-12}$  M) the formation of a yellow solid, probably consisting of U(VI) oxides, was observed. All measurements were made at 25 °C in a 3 M (Na)ClO<sub>4</sub> medium.

The equilibria between  $UO_2^{2+}$ ,  $H_2O$  and  $CO_2(g)$  at 25 °C in a 3 M NaClO<sub>4</sub> medium have been previously<sup>1</sup> studied at acidities ranging from  $[H^+] \approx 10^{-5}$  M to  $[H^+] \approx 10^{-7}$  M by determining  $[HCO_3^-]$  with a glass electrode.

The data could be explained by assuming the equilibrium



with the equilibrium constant  $\log K = 41.5 \pm 0.1$ . The upper limit  $[H^+] \approx 10^{-5}$  M was imposed by

the formation of solid U(VI) carbonates, whereas at  $[H^+] < 10^{-7}$  M, the concentration of the bound carbonate becomes a small number compared to the analytical as well as to the free concentration of  $HCO_3^-$ . The error in the concentration of bound carbonate which strongly depends upon the difference between these two quantities will thus increase with decreasing  $[H^+]$ , making it impossible to ascertain whether any other species than  $UO_2(CO_3)_3^{4-}$  is formed in alkaline solutions or not.

The aim of the present study is to extend the investigation on the complex formation between  $UO_2^{2+}$ ,  $CO_2(g)$  and  $H_2O$  to the lowest attainable acidities in order to find out the composition of the species formed, particularly whether ternary complexes  $(UO_2)_p(OH)_q(CO_3)_r$  are formed or not.

It is well known that the absorption spectrum of uranium(VI) changes as a result of complex formation and spectrophotometric techniques have also been used in some previous studies of the uranium(VI) carbonate system.<sup>2,3</sup>

We have undertaken to study the equilibria between  $UO_2^{2+}$ ,  $CO_2(g)$  and  $H_2O$  in the range  $-12 < \log [H^+] < -5$  by measuring the optical absorbance,  $A$ , and the free hydrogen ion concentration,  $h$ , in solutions of several levels of uranium(VI) concentration,  $B$ , at various acidities. The measurements were carried out at 25 °C in a 3 M (Na)ClO<sub>4</sub> medium.

### NOTATIONS

$h$	= concentration of $H^+$
$H$	= analytical concentration excess of $H^+$ over $H_2O$ , $CO_2$ and $UO_2^{2+}$
$b$	= concentration of $UO_2^{2+}$

- $B$  = total concentration of U(VI)  
 $a$  =  $P_{\text{CO}_2}$  = partial pressure of  $\text{CO}_2(\text{g})$  at equilibrium =  
 = atmospheric pressure - vapour pressure of water in 3 M  $\text{NaClO}_4$  (= 0.0276 atm at 25 °C)  
 $A$  = optical absorbance per cm cell length  
 $\epsilon_1$  = molar absorption coefficient of  $\text{UO}_2(\text{CO}_3)_3^{4-}$  in  $\text{cm}^{-1} \text{M}^{-1}$   
 $\epsilon_2$  = molar absorption coefficient of  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  in  $\text{cm}^{-1} \text{M}^{-1}$   
 $\beta_{1,6,3}$  = equilibrium constant for  $\text{UO}_2^{2+} + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-} + 6\text{H}^+$   
 $\beta_{3,12,6}$  = equilibrium constant for  $3\text{UO}_2^{2+} + 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 12\text{H}^+$   
 $K$  =  $\beta_{3,12,6}\beta_{1,6,3}^{-3}$  = equilibrium constant for  $3\text{UO}_2(\text{CO}_3)_3^{4-} + 6\text{H}^+ \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$

## EXPERIMENTAL

### Materials and analysis

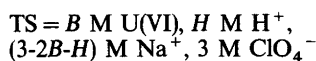
Sodium Carbonate solutions made from the Merck p.a. product were analyzed with standard  $\text{HClO}_4$ .

The preparations of uranium(VI) perchlorate, perchloric acid, sodium hydrogen carbonate, sodium perchlorate, silver perchlorate and sodium hydroxide solutions as well as the details on the equilibration of the test solutions with  $\text{CO}_2(\text{g})$  are described in a previous paper.<sup>1</sup>

**Equipment.** The absorbance,  $A$ , was measured with a precision of 0.002 absorbance units using a Hitachi 200 Spectrophotometer. Quartz cuvettes of 1 and 5 cm optical path lengths were used. The emf measurements were carried out as previously described.<sup>1</sup>

**Experimental technique.** The experiments were carried out as titrations where  $B$  was held constant while  $H$  was varied. In solutions where  $-7 < \log h < -5$ , the partial pressure of  $\text{CO}_2(\text{g})$ ,  $a$ , was kept constant by passing a stream of  $\text{CO}_2(\text{g})$  through the test solution.

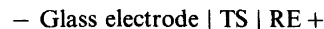
The test solutions had the general composition



The  $B$  range investigated,  $3 \times 10^{-3} \text{ M} \leq B \leq 3 \times 10^{-2} \text{ M}$ , corresponds to that of the previous study.<sup>1</sup> The lowest acidity value  $-\log h \approx 12$ , was

determined by the incipient formation of a yellow solid, presumably uranium(VI) oxides, however no chemical analysis has been made.

The highest acidity,  $-\log h \approx 5$  was imposed by the formation of  $\text{UO}_2\text{CO}_3(\text{s})$ . The concentration of the free hydrogen ion,  $h$ , was determined by means of the cell



where  $\text{RE} = 3 \text{ M NaClO}_4 \mid 0.01 \text{ M AgClO}_4, 2.99 \text{ M NaClO}_4 \mid \text{AgCl, Ag}$

The emf of the cell in mV at 25 °C is expressed by eqn. (1), where  $E^\circ$  is a constant,  $f_{\text{H}^+}$  is the activity

$$E = E^\circ - 59.15 \log h - 59.16 \log f_{\text{H}^+} + E_j \quad (1)$$

coefficient of  $\text{H}^+$  and  $E_j$  the liquid junction potential between TS and 3 M  $\text{NaClO}_4$ . On the basis of the specific interaction theory,<sup>4-6</sup>  $f_{\text{H}^+}$  is expected to be practically constant in the solutions studied. Only minor variations in  $E_j$  take place as the composition of TS is changed. Corrections for the variations of  $E_j - 59.16 \log f_{\text{H}^+}$  with  $[\text{Na}^+]$  have been evaluated experimentally,<sup>1</sup> eqn. (2),  $E^\circ$  in

$$E_j - 59.16 \log f_{\text{H}^+} = 7.2 \Delta[\text{Na}^+] \quad (2)$$

(1) was determined as described before.<sup>1</sup> The absorbance  $A$ , of TS was measured at two different wavelengths ( $\lambda = 445 \text{ nm}$  and  $459 \text{ nm}$ ) by using a double beam spectrophotometer with 3 M  $\text{NaClO}_4$  as the reference solution.

From the spectrophotometric and emf data the function

$$\log \frac{A}{B} (-\log h)_{B,\lambda}$$

was obtained. This function forms the basis of the following mathematical analysis of the equilibrium data.

## TREATMENT OF THE DATA AND RESULTS

The primary data  $A(B, H, a, \lambda)$  and  $E(B, H, a)$ , recalculated in the form of  $\log \frac{A}{B} (-\log h)_{B,\lambda}$ , are graphically represented (dots) in Figs. 1 and 2 for two different wavelengths.\* By analyzing eqn. (5)

\* The primary data are obtainable from the authors on request.

one notices that this function affords some of the advantages of the formation curve  $^7 \bar{n}(-\log h)$ , for instance, to predict the presence of polynuclear species. Furthermore, (*vide infra*) the function can be directly compared to model curves  $^8$  to ascertain the composition of the solution.

In order to simplify the calculations, the data from the acidity range  $10^{-5}$  to  $10^{-7}$  M, in which  $a$  ( $=0.98$  atm) was kept constant, were first considered.

From the previous study,<sup>1</sup> we know that only two uranium(VI) species  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  are present in this range. Hence we may write eqns. (3) and (4), where  $^*\beta_1$  and  $^*\beta_2$

$$B = ^*\beta_1 b h^{-6} + 3^*\beta_2 b^3 h^{-12} \quad (3)$$

$$A = \varepsilon_1 ^*\beta_1 b h^{-6} + \varepsilon_2 ^*\beta_2 b^3 h^{-12} \quad (4)$$

indicate  $\beta_{1,6,3} a^3$  and  $\beta_{3,12,6} a^6$ , respectively, and  $A$  refers to an optical path length of 1 cm at a given wavelength.

From (3) and (4) we obtain eqn. (5)

$$\log \frac{A}{B} = \log \varepsilon_1 + \log \frac{^*\beta_1 b h^{-6} + \frac{\varepsilon_2}{\varepsilon_1} ^*\beta_2 b^3 h^{-12}}{^*\beta_1 b h^{-6} + 3^*\beta_2 b^3 h^{-12}} \quad (5)$$

Introduction of the normalized  $^8$  variables

$$u = ^*\beta_1 b h^{-6} \text{ and } v = ^*\beta_2 b^3 h^{-12} \quad (6)$$

into (5) yields eqn. (7), where  $L = \varepsilon_2/\varepsilon_1$ .

$$\log \frac{A}{B} = \log \varepsilon_1 + \log \frac{u + Lv}{u + 3v} = \log \varepsilon_1 + Y \quad (7)$$

Furthermore, from (6) we get eqn. (8), where  $^*K = ^*\beta_2 ^*\beta_1^{-3} = K a^{-3}$

$$-\log h = \frac{1}{2} \log u - \frac{1}{6} \log v + \frac{1}{6} \log \frac{^*\beta_2}{^*\beta_1^3} = X + \frac{1}{6} \log ^*K \quad (8)$$

From the normalized form of  $B$

$$B = u + 3v \quad (9)$$

obtained by introducing (6) in (3), the function  $u = u(v)_B$  can be tabulated for every experimental  $B$

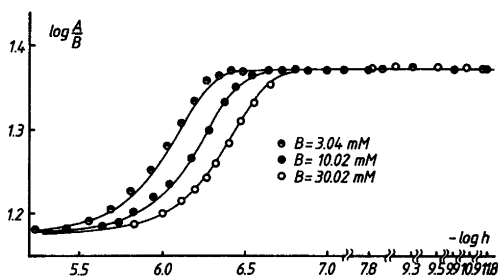


Fig. 1. Data (dots)  $\log \frac{A}{B}$  as a function of  $-\log h$  for three levels of  $B$  at  $\lambda=445$  nm and model curves  $Y(X)$  (full lines) constructed with  $L=1.90$ . From the position of best fit,  $\log ^*K=41.5 \pm 0.1$ ,  $\varepsilon_1=23.6 \pm 0.2$  and  $\varepsilon_2=44.8 \pm 0.4 \text{ cm}^{-1} \text{ M}^{-1}$  are deduced.

value. Thus, the normalized  $^8$  projection maps  $Y(X)$  can be obtained for various values of  $L$ .

A comparison between the experimental plot  $\log \frac{A}{B}(-\log h)_{B,\lambda}$  and its normalized form  $Y(X)_L$  is made by displacing the maps along the coordinates. If the chemical model is correct, a position of best fit will be found for the proper value of  $L$  which allows the evaluation of  $\frac{1}{6} \log K$  and  $\log \varepsilon_1$  as the differences of the coordinates.  $\varepsilon_2$  is obtained from the value of  $L$  which gives the best fit.

The figures show the fit obtained between the experimental data (dots)  $\log \frac{A}{B}(-\log h)_{B,\lambda}$  for three levels of  $B$  (3, 10 and 30 mM) at two different

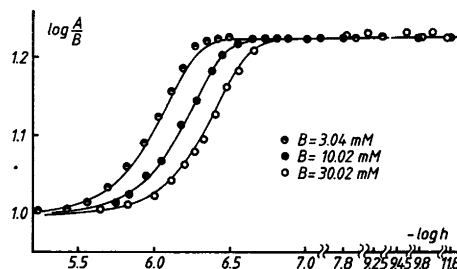


Fig. 2. Data (dots)  $\log \frac{A}{B}$  as a function of  $-\log h$  for three levels of  $B$ , at  $\lambda=459$  nm and model curves  $Y(X)$  (full lines) constructed with  $L=1.77$ . From the position of best fit,  $\log ^*K=41.5 \pm 0.1$ ,  $\varepsilon_1=16.9 \pm 0.2$  and  $\varepsilon_2=29.9 \pm 0.4 \text{ cm}^{-1} \text{ M}^{-1}$  are deduced.

wavelengths ( $\lambda = 445$  nm, Fig. 1 and  $\lambda = 459$  nm, Fig. 2).

The model functions (full lines)  $Y(X)_L$  have been calculated with  $L = 1.90$  (Fig. 1) and  $L = 1.77$  (Fig. 2).

One also observes that the fit between the experimental and the theoretical maps is good in the range  $-12 < \log h < 7$  too, even though eqns. (3) to (9) have been derived for data obtained at constant  $a$ . This indicates that the terms in (5) which account for the polynuclear species tend to zero when  $\log h < -7$ . Consequently  $\log \frac{A}{B} = \log \varepsilon_1$ , independent of  $a$ . The attainment of a "plateau" for the  $\log \frac{A}{B}(-\log h)$  function at  $-12 < \log h < -7$ , indicates that no other species than  $\text{UO}_2(\text{CO}_3)_3^{4-}$  is formed in measurable amounts at these acidities.

From the comparison of the maps, the following results have been obtained:

$$\log K \simeq \log *K = 41.5 \pm 0.1, \varepsilon_1^{445} = 23.6 \pm 0.2, \varepsilon_2^{445} = 44.8 \pm 0.4, \varepsilon_1^{459} = 16.9 \pm 0.2 \text{ and } \varepsilon_2^{459} = 29.9 \pm 0.4 \text{ cm}^{-1} \text{ M}^{-1}.$$

The uncertainties have been evaluated from the limiting positions of the maps which still gave an acceptable fit, thus they have to be considered as maximum deviations. Our molar absorption coefficients at  $\lambda = 445$  and  $459$  nm for the  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  complex may be compared (see Table 1) with those reported by Bullwinkel<sup>2</sup> and Scanlan<sup>3</sup> by multiplying their values by three as these authors assumed the complex to be mononuclear  $\text{UO}_2(\text{CO}_3)_2^{2-}$ . The agreement between our values and Bullwinkel's is excellent. This is not the case for the molar absorption coefficients reported by Scanlan. In our opinion, the deviations observed between Scanlan's results and ours may be due to the slow attainment of the equilibrium in the reaction between  $\text{UO}_2\text{CO}_3(\text{s})$ ,  $\text{NaHCO}_3$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}$  which was used to

prepare the solution supposedly containing  $\text{UO}_2(\text{CO}_3)_2^{2-}$ . In the light of the present work and our preceding one,<sup>1</sup> his solutions also contained  $\text{UO}_2(\text{CO}_3)_3^{4-}$ .

It is worthwhile to note that, with our method of calculations, no previous knowledge of the molar absorption coefficients of the complexes is required.

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Table 1. Molar absorption coefficients of  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  in  $\text{cm}^{-1} \text{ M}^{-1}$ .

$\lambda$ (nm)	Obtained in this work	Recalculated from the data obtained by	
		Bullwinkel <sup>2</sup>	Scanlan <sup>3</sup>
445	$44.8 \pm 0.4$	~ 45	~ 33
459	$29.9 \pm 0.4$	30.0	22.5