Studies on the Hydrolysis of Metal Ions

32. The Uranyl Ion, UO_2^{2+} , in Na_2SO_4 Medium

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The hydrolysis of UO_2^{2+} has been studied in a 1.5 M (sodium)-sulfate medium at 25°C by electrometric titration using glass electrodes. The total uranium concentration ranged between 0.0003 and 0.04 M. Special studies were made on similar cells without uranyl or with uranyl at acidities giving negligible hydrolysis. The results make it reasonable to assume $K(\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}) \approx 0.4$ M and to neglect $\text{Na}^+ - \text{SO}_4^{2-}$ complexing. $K(\text{Na}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NaSO}_4^-)$ is estimated to be $\leq 0.13 \text{ M}^{-1}$. The average number of sulfate groups bound per uranyl group was found to lie between 2 and 3 with a probable value of about 2.9. The sulfate groups of the uranyl sulfate complexes seem to have somewhat lower affinity for protons than the free sulfate ions.

The present data indicate the formation of "core + links" complexes of the general formula $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$. "Direct analysis" indicates that at least the first four complexes, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_4(\text{OH})_6^{2+}$, $(\text{UO}_2)_5(\text{OH})_8^{2+}$, exist.

If only these are assumed to exist, the best values for the equilibrium constants k_n of the reaction, $(n+1)\text{UO}_2^{2+} + 2n\text{H}_2\text{O} \rightleftharpoons \text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+} + 2n\text{H}^+$, are $\log k_1 = -8.17$, $\log k_2 = -16.20$, $\log k_3 = -24.51$ and $\log k_4 = -32.14$. The data were also well explained by theory "IIIc"¹, assuming an infinite series of complexes with $\log k_n = -(7.66n + \log n! + 0.52)$, thus $\log k_1 = -8.18$, $\log k_2 = -16.15$, $\log k_3 = -24.29$ and $\log k_4 = -32.56$.

Some years ago, the hydrolysis of the ion UO_2^{2+} in a perchlorate medium was studied by Ahrland *et al.*²⁻³. The hydrolysis products were found to be polynuclear and of a "core + links" type, $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$. The data were best explained with an unlimited mechanism, assuming the formation of complexes with all integral values for n , "hypothesis III"¹. With this approximation of the real mechanism, the equilibrium constant for the first reaction,

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$\text{UO}_2^{2+} + 2\text{H}_2\text{O} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2(\text{OH})_2\text{UO}_2^{2+} + 2\text{H}^+$, was found to be $k_1 = 10^{-6.05 \pm 0.10}$ and for all following reactions, $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+} + 2\text{H}_2\text{O} + \text{UO}_2^{2+} \rightleftharpoons \text{UO}_2((\text{OH})_2\text{UO}_2)_{n+1}^{2+} + 2\text{H}^+$, the constants were $k = 10^{-6.35 \pm 0.1}$.

It was considered valuable to study the hydrolysis of UO_2^{2+} in other ionic media and for this investigation 1.5 M Na_2SO_4 was chosen.

SYMBOLS

In general, the symbols are those used in the previous papers of this series. $b = [\text{UO}_2^{2+}]$, concentration of free UO_2^{2+} ; B = total concentration of U(VI); $c = [\text{SO}_4^{2-}]$; C = total concentration of sulfate (4); E = measured emf in mV (2); $E_0 = E + 59.16 \log h - E_j$ (2); E_j = liquid junction potential (2); $E' = E + 59.16 \log H$ (5); E'_0 , defined by (6); F , defined by (12); $g(u) = \sum k_n u^n$ (10), (9); $h = [\text{H}^+]$; H = total analytical excess concentration of hydrogen ions, assuming no hydrolysis (3); k_n = equilibrium constant for $(n+1) \text{UO}_2^{2+} + 2n\text{H}_2\text{O} \rightleftharpoons \text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+} + 2n\text{H}^+$ (10); k, k_0 = constants in "hypothesis IIIc": $k_n = k_0 k^n (n!)^{-1}$ (17); K = dissociation constant of HSO_4^- (3); K_1 = complex formation constant of MgSO_4 (44); n = number of links per "core + links" complex; $\bar{n}$ = average number of links per complex (11); $\bar{n}_s$ = average number of sulfate groups bound per uranyl group (4); $u = h^{-2}b$ (9), (8b); $v_{1/2}$ = value of v for $y = 1/2$ (19); $w = k_1^{-1}k_2u$ (15); $x = \log B - 2 \log h$ (7); $x_{1/2}$ = value of x for $y = 1/2$ (18); $y = Z/2$ (7); Z = average number of OH bound per UO_2^{2+} (1); $\alpha = k_1 k_2^{-2} k_3$ (13).

Concentrations and equilibrium constants are expressed in M (mole l⁻¹) as a rule, but in the text and headings the convenient unit mM is sometimes used.

As usual, all species may, in addition to the formula as written, contain a certain number of medium ions and solvent molecules.

METHOD OF MEASUREMENT

This study of the hydrolysis of uranium(VI) in sulfate solution was made as a series of potentiometric titrations at 25°C. All solutions were made 1.5 M in sulfate by the addition of sodium sulfate. This was done in order to make possible the use of concentrations instead of activities in the formulas for emf and equilibrium constants.

In each titration, the total uranyl concentration, B , was kept constant while H , the analytical concentration of H^+ , was varied. The free concentration of H^+ , h , was measured with a glass electrode. The average number of hydroxyl groups bound per uranyl group, Z , was calculated from

$$Z = (h + [\text{HSO}_4^-] - H)/B \quad (1)$$

The data could then be plotted in the form $Z(\log h)_B$.

The cell used was

— glass electrode | solution S | SE +
SE, the reference electrode, was

SE = Ag, AgCl | 10 mM Ag₂SO₄, 1 490 mM Na₂SO₄ | 1 500 mM Na₂SO₄

Solution S had the composition

S = B mM UO₂SO₄, H/2 mM H₂SO₄, (1 500 — B — H/2) mM Na₂SO₄

For the cell used, the measured emf may be written

$$E = E_0 - 59.16 \log h + E_j \quad (2)$$

From the definitions it follows:

$$h[\text{SO}_4^{2-}] = K[\text{HSO}_4^-]; H = h + [\text{HSO}_4^-] - BZ \quad (3)$$

and

$$C = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + \bar{n}_s B \quad (4)$$

We will introduce the quantity E' defined by

$$E' = E + 59.16 \log H \quad (5)$$

In the Appendix, equations are treated which are identical with (1) — (5) except that BZ is neglected, so, in the final result (30), H should strictly speaking be replaced by $(H + BZ)$. Moreover, the limiting value for $[\text{SO}_4^{2-}]$ at low acidities, c_0 , is $(C - \bar{n}_s B)$ and not C . According to (30), for $H \ll C$, E' (H) approximates to a straight line which (for H , or rather $H + BZ$, $\rightarrow 0$) extrapolates to

$$E'_0 = E_0 + 59.16 \log [1 + (C - \bar{n}_s B) K^{-1}] \quad (6)$$

The experimental record, E' versus H for constant B , gave straight lines for intermediate concentrations where the hydrolysis was negligible (Fig. 9). These lines gave E'_0 by extrapolation and, from this quantity, E_0 was calculated using eqn. (6). The values $K = 0.4$ M and $\bar{n}_s = 2.9$ were used (see Appendix). Since the hydrolysis of the uranyl ion took place at pH > 3, no correction in E for the liquid junction potential was needed.

Reagents and Analysis

Uranyl sulfate was prepared from an especially pure UO₃ sample obtained from AB Atomenergi, Stockholm. After ignition to U₃O₈ at 850°C, a weighed amount was dissolved in an equivalent amount of sulfuric acid by the aid of H₂O₂ (Merck p.a.). After boiling, the solution was diluted with water to an exactly known volume. The concentration of uranium was checked by ignition to U₃O₈ and the sulfate concentration was checked by passing a sample through a hydrogen-saturated cation exchanger and titrating with NaOH.

Sodium sulfate. The p.a. quality of Merck was recrystallized from water several times and dried in an oven to constant weight.

Sulfuric acid solutions were prepared from the p.a. quality of Merck and standardized against standard NaOH.

Sodium hydroxide. A 50 % solution was prepared from the E.K.A. product. Dilute solutions were prepared from water or sodium sulfate solutions and 50 % NaOH, filtered through a Jena G 4 filter. The alkaline solutions were standardized against recrystallized hydrazine sulfate (Merck p.a.).

Silver sulfate solution was prepared from the p.a. quality of Baker without purification.

Water. Deaerated distilled water was always used.

Apparatus

The apparatus was of the type generally used for studying hydrolysis mechanisms in this institute⁴.

Two glass electrodes were used, one Radiometer G 102 BK and one Jena 9006 gaf.

The silver-silver chloride electrode was prepared according to Brown⁵.

A valve potentiometer, Radiometer PHM 3 ik, was used for the emf measurements and the emf values were read to 0.1 mV.

Agitation in the titration vessel was arranged by bubbling nitrogen gas through the solution, and, in addition, swirling after each addition from the burets. The nitrogen was purified by washing with 10 % NaOH and 10 % H₂SO₄. Before entering the titration vessel, the gas was saturated with water by passing it through two wash bottles containing 1.5 M sodium sulfate.

Procedure

The measurements were made in a room thermostated to $25 \pm 1^\circ\text{C}$ with the cell in an oil thermostat set at $25.0 \pm 0.1^\circ\text{C}$.

The procedure may be best described by giving, as an example, one of the titrations with $B = 40$ mM.

The following solutions were used

A = 40 mM UO₂SO₄, 1 460 mM Na₂SO₄

B = 40 mM UO₂SO₄, 75 mM H₂SO₄, 1 385 mM Na₂SO₄

C = 80 mM UO₂SO₄, 1 420 mM Na₂SO₄

D = 188.3 mM NaOH, 1 500 mM Na₂SO₄

At the start of the titration, 50 ml of A and 5 ml of B were put into the titration vessel. Equal amounts of C and D were added from burets at intervals and the emfs were record-

Table 1. A titration with $B = 40$ mM

$$E_0 = 108.1 - 59.16 \log \left(1 + \frac{1.5 - 0.04 \times 2.9}{0.4} \right) = 69.7 \text{ mV}$$

v_A ml	v_B ml	v_C ml	v_D ml	H $\text{M} \times 10^3$	E mV	E' mV	$-\log h$	h $\text{M} \times 10^3$	Z
50.00	5.00			13.64	218.4	108.0			
		2.00	2.00	6.34	238.2	108.1	2.848	1.42	0.000
		3.00	3.00	3.05	255.9		3.147	0.713	0.003
		4.01	4.00	-0.081	287.7		3.684	0.207	0.025
		6.01	6.00	-5.683	320.1		4.232	0.059	0.149
		8.00	8.00	-10.65	329.7		4.394	0.040	0.271
		11.00	11.00	-17.16	337.8		4.531	0.029	0.432
		13.00	13.00	-20.96	341.8		4.599	0.025	0.527
		15.00	15.00	-24.41	345.3		4.658	0.022	0.613
		18.00	18.00	-29.00	349.8		4.734	0.018	0.727
		21.00	21.00	-33.03	353.8		4.802	0.016	0.828
		24.00	24.00	-36.59	357.5		4.864	0.014	0.916
		29.02	29.00	-41.72	363.5		4.966	0.011	1.044
		34.00	34.00	-45.95	369.3		5.064	0.009	1.150
	15.00			-31.22	351.9		4.770	0.017	0.783
	30.00			-12.85	332.7		4.445	0.036	0.325
	42.60			-0.076	288.2		3.693	0.203	0.025
	55.00			10.68	224.7	108.1	2.620	2.40	0.000
	90.00			34.13	194.7	107.9			

Table 2. Data Z ($\log h$) at various total concentrations of uranyl ion, B .

$B = 0.040$ M. Z , $-\log h$: (R) 0.000, 2.620 (b); 0.000, 2.848; 0.003, 3.147; 0.025, 3.684; 0.025, 3.693 (b); 0.149, 4.232; 0.271, 4.394; 0.325, 4.445 (b); 0.432, 4.531; 0.527, 4.599; 0.613, 4.658; 0.727, 4.734; 0.783, 4.770 (b); 0.828, 4.802; 0.916, 4.864; 1.044, 4.966; 1.150, 5.064 — (J) 0.024, 3.657; 0.180, 4.279; 0.328, 4.445; 0.518, 4.594; 0.674, 4.700; 0.807, 4.788; 0.920, 4.869; 1.047, 4.971; 1.177, 5.092; 1.284, 5.211; 1.373, 5.333; 1.448, 5.459.

$B = 0.020$ M. Z , $-\log h$: (R) 0.000, 2.920; 0.003, 3.233; 0.030, 3.950; 0.083, 4.247; 0.143, 4.391; 0.262, 4.545; 0.376, 4.646; 0.688, 4.856; 0.875, 4.981; 1.040, 5.114; 1.194, 5.258; 1.268, 5.339; 1.339, 5.432 — (J) 0.027, 3.913; 0.353, 4.623; 0.652, 4.829; 0.913, 5.008; 1.142, 5.198; 1.345, 5.434.

$B = 0.010$ M. Z , $-\log h$: (R) -0.002 , 2.909; 0.028, 4.180; 0.039, 4.265; 0.086, 4.447; 0.205, 4.649; 0.376, 4.802; 0.542, 4.916; 0.704, 5.022; 0.859, 5.127; 1.007, 5.237; 1.151, 5.364; 1.290, 5.516; 1.358, 5.605; 1.425, 5.708 — (J) 0.031, 4.150; 0.124, 4.517; 0.229, 4.667; 0.368, 4.791; 0.504, 4.887; 0.636, 4.973; 0.764, 5.058; 0.889, 5.142; 1.010, 5.235; 1.157, 5.367; 1.298, 5.524; 1.438, 5.729.

$B = 0.005$ M. Z , $-\log h$: (R) -0.006 , 3.511; -0.006 , 3.869; 0.061, 4.537; 0.372, 4.948; 0.683, 5.156; 0.986, 5.362; 1.278, 5.643 — (J) 0.037, 4.363; 0.139, 4.696; 0.256, 4.846; 0.363, 4.938; 0.471, 5.014; 0.676, 5.147; 0.867, 5.274; 1.049, 5.409; 1.214, 5.560 — (J) 0.039, 4.375; 0.166, 4.740; 0.308, 4.890; 0.449, 4.997; 0.590, 5.090; 0.729, 5.178; 0.866, 5.271; 1.001, 5.370; 1.134, 5.489; 1.265, 5.627; 1.394, 5.803.

$B = 0.0025$ M. Z , $-\log h$: (R) -0.009 , 3.800; 0.342, 5.081; 0.488, 5.184; 0.630, 5.276; 0.771, 5.367; 0.908, 5.460; 1.042, 5.565; 1.173, 5.685; 1.302, 5.828; 1.430, 6.008 — (J) 0.045, 4.625; 0.126, 4.848; 0.264, 5.015; 0.380, 5.110; 0.495, 5.186; 0.719, 5.328; 0.935, 5.477; 1.144, 5.651; 1.346, 5.877 — (J) 0.047, 4.588; 0.137, 4.857; 0.242, 4.985; 0.458, 5.157; 0.673, 5.294; 0.887, 5.433; 1.098, 5.595; 1.308, 5.813.

$B = 0.00125$ M. Z , $-\log h$: (J) -0.001 , 4.081 (b); 0.020, 4.513 (b); 0.059, 4.786; 0.085, 4.875 (b); 0.109, 4.938; 0.120, 4.960 (b); 0.159, 5.026 (b); 0.166, 5.039; 0.284, 5.169; 0.398, 5.261; 0.505, 5.333; 0.588, 5.384 (b); 0.607, 5.396; 0.704, 5.458; 0.881, 5.572; 1.041, 5.683 — (J) 0.059, 4.784; 0.202, 5.083; 0.365, 5.233; 0.529, 5.343; 0.693, 5.448; 0.846, 5.553; 1.015, 5.670; 1.174, 5.800; 1.330, 5.976; 1.485, 6.200.

$B = 0.00063$ M. Z , $-\log h$: (J) 0.074, 4.968; 0.187, 5.203; 0.317, 5.337; 0.447, 5.433; 0.573, 5.518; 0.698, 5.596; 0.818, 5.672; 0.935, 5.744; 1.048, 5.829; 1.156, 5.922; 1.263, 6.032.

$B = 0.00031$ M. Z , $-\log h$: (J) 0.093, 5.151; 0.180, 5.325; 0.338, 5.491; 0.504, 5.607; 0.722, 5.743; 0.937, 5.883; 1.148, 6.045; 1.353, 6.258.

(b) indicates backtitration data

(R) ((J)) the titration has been performed with the Radiometer (Jena) electrode.

ed. At the end of the titration, the hydrolysis was reversed by adding portions of B from a buret in order to make sure that the equilibria were completely reversible. The titration data will be found in Table 1.

In some instances, especially for the lower concentrations, only A, C, and D type solutions were used and E_0 was determined separately in a solution of known H value.

Fig. 1. Experimental data plotted as $Z (-\log h)_B$. Curves calculated assuming "mechanism IIIc" ($k_0 = 0.30$, $\log k = -7.66$).

DATA AND RESULTS

Formula of the complexes

The data were first calculated* (Tab. 2) and plotted in the form $Z(\log h)_B$, see Fig. 1. The curves for different values of B do not coincide but are nearly parallel with a nearly constant spacing of $0.15 \log h$ units. Since the concentrations have a constant ratio of 2, $\Delta \log B = 0.30$ and thus $(\Delta \log B / \Delta \log h)_Z = 2$, which implies that polynuclear species of the formula $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$ are formed in the hydrolysis process⁶. The data were therefore plotted in a diagram with

$$y = Z/2; x = \log B - 2 \log h \quad (7)$$

From Fig. 2, it is seen that the points fall on practically the same curve (however there are systematic but small divergences for B values of 1.25 mM and lower). One can thus conclude that the main hydrolysis products are polynuclear with the formula given above.

The next step is to deduce which complexes occur and the equilibrium constants for the formation of these complexes.

* As seen, e.g. from the data in Table 1 and eqn. (6), the value for E_0 depends on the value assumed for K . A reasonable shift of K will, however, only shift the $\log h$ scale by a constant, and not affect the Z values. The conclusions on the species found will thus not be affected, though the equilibrium constants will be shifted, as given by eqns. (21) and (22).

Fig. 2. Experimental data plotted as $y(x)$. Full drawn curve calculated assuming "mechanism IIIc" ($k_0 = 0.30$, $\log k = -7.66$). Broken curve calculated assuming the existence of only the first four complexes ($\log k_1 = -8.17$; $\log k_2 = -16.20$; $\log k_3 = -24.51$; $\log k_4 = -32.14$).

Direct analysis of the $y(x)$ curve

A smooth curve was drawn through the data $y(x)$ with no weight given to the points for $B = 1.25$ mM and lower.

The analysis of this curve was performed according to AB II¹. The function $g(u)$ is calculated from the data by means of the following equations

$$\log(1 + g) = \int_{-\infty}^x y \, dx + \log(1 - y) + y \log e \quad (8a)$$

$$\log u = x - y \log e - \int_{-\infty}^x y \, dx \quad (8b)$$

The variables u and g are

$$u = bh^{-2} = [\text{UO}_2^{2+}]h^{-2} \quad (9)$$

$$g = \sum k_n u^n = k_1 u + k_2 u^2 + \dots \quad (10)$$

Thus, $g(u)$ is a power series, the coefficients of which are equilibrium constants k_n for the formation of the complexes.

From the $g(u)$ data, we can calculate the average number of links per complex

$$\bar{n} = \frac{d \log g}{d \log u} = \frac{y}{1 - y - F^{-1}} \quad (11)$$

Fig. 3. $\bar{n}$ (eqn. 11) as a function of $\log u$.

where

$$\log F = y \log e + \int_{-\infty}^x y \, dx \quad (12)$$

From Fig. 3 where $\bar{n}(\log u)$ is plotted, $\bar{n}$ is seen to start at about 1.0 and rise uniformly to a value of 3.1 for the highest $\log u$ value. This would imply that complexes with more than three "links" are formed.

Neglecting, for the moment, this result and assuming that only the first three complexes exist, we may write

$$gu^{-1}k_1^{-1} = 1 + k_2k_1^{-1}u + k_3k_1^{-1}u^2 = 1 + w + aw^2 \quad (13)$$

$$\log(1 + w + aw^2) = \log gu^{-1} - \log k_1 \quad (14)$$

$$\log w = \log u + \log k_2 - \log k_1 \quad (15)$$

A family of normalized curves, $\log(1 + w + aw^2)$ versus $\log w$, was compared with the experimental curve, $\log gu^{-1}$ versus $\log u$, and an attempt was made to fit them together. An acceptable fit was obtained for low values of g ; at the highest g values, there were deviations so that the existence of at least a fourth complex had to be considered.

From the position of best fitting, it was estimated that $\log k_1 = -8.17 \pm 0.01$ and $\log k_2 = -16.20 \pm 0.05$.

Rewriting eqn. (10) and assuming the existence of four complexes, we obtain

$$(gu^{-1} - k_1 - k_2u)u^{-2} = k_3 + k_4u \quad (16)$$

A family of curves, $(gu^{-1} - k_1 - k_2u)u^{-2}$ versus u , was calculated for various sets of values for k_1 and k_2 . The best straight lines were obtained with the two sets given in Fig. 4. From the intercepts and slopes of the lines, it is possible to obtain k_3 and k_4 .

Fig. 4. $(gu^{-1} - k_1 - k_2u)u^{-2}$ (eqn. 16) as a function of u . Dots calculated from experimental values assuming $\log k_1 = -8.17$, $\log k_2 = -16.22$. Open circles calculated from the same experimental values assuming $\log k_1 = -8.18$; $\log k_2 = -16.17$.

By means of this direct analysis of the curve $y(x)$, an acceptable fit can be obtained with $\log k_1 = -8.17 \pm 0.01$, $\log k_2 = -16.20 \pm 0.03$, $\log k_3 = -24.51 \pm 0.09$ and $\log k_4 = -32.14 \pm 0.02$.

Testing of simple mechanisms

The $y(x)$ curve was independently compared with curves calculated for various simple mechanisms discussed in AB II (hypotheses II, III a, b, and c). A good fit was obtained with only one of them, namely hypothesis III c. In this hypothesis, it is assumed that complexes with all values of n are formed and that the equilibrium constant, k_n , is given by

$$k_n = k_0 k^n (n!)^{-1} \quad (17)$$

which means that the formation of higher complexes becomes increasingly difficult.

k_0 may be obtained from the comparison discussed above and k from the following equation

$$\log k = \log 2 + k_0 v_{1/2}^2 e^{v_{1/2}} - x_{1/2} \quad (18)$$

where $v_{1/2}$ is taken from the equation

$$e^{v_{1/2}} (v_{1/2} - 1) = k_0^{-1} \quad (19)$$

and $x_{1/2}$ is the value of x for $y = 1/2$.

As k_0 was seen to be about 0.3, k_0 values of 0.29, 0.30 and 0.31 were tried and gu^{-1} was calculated from

$$gu^{-1} = k_0 u^{-1} (e^{ku} - 1) \quad (20)$$

Fig. 5. gu^{-1} (eqn. 20) as a function of u . Solid lines calculated with "IIIc", $\log k = -7.66$ and $k_0 = 0.31$ (upper), 0.30 (middle) and 0.29 (lower line). Broken curve calculated with only four complexes, constants like in Fig. 2.

and plotted against u . From the comparison in Fig. 5 with experimental points, it is seen that $k_0 = 0.30$ gives the best fit.

With $\log k = -7.66 \pm 0.01$, $\log k_0 = -0.52 \pm 0.01$ and $\log k_n = -(7.66n + \log n! + 0.52)$, the following constants were calculated for the "IIIc" approximation. $\log k_1 = -8.18$, $\log k_2 = -16.15$, $\log k_3 = -24.29$, $\log k_4 = -32.56$. If "IIIc" was the real mechanism, the mean deviations would be $\pm 0.01(n+1)$.

The $y(x)$ curves calculated from III c and from direct analysis are given in Fig. 2 and are seen to practically coincide except for the highest x values. Here, the experimental determinations favor hypothesis III c or a limited series with more than four complexes.

If in the future, a more reliable value K' for K is found, it will be quite easy to calculate better values k'_n for the constants k_n . From (3), (4) and the equation

$$k_n = \frac{[\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}][\text{H}^+]^{2n}}{[\text{UO}_2^{2+}]^{n+1}} \quad (21)$$

we get

$$\log k'_n = \log k_n + 2n \log \left(\frac{K'(C + K - \bar{n}_s B)}{K(C + K' - \bar{n}_s B)} \right) \quad (22)$$

Fig. 6. $\log B$ as a function of x for Z values 0.1 to 1.4. Circles: experimental points. The lines are calculated assuming "mechanism IIIc" ($k_0 = 0.30$, $\log k = -7.66$).

where the correction term $\bar{n}_s B$ is of minor importance. When B varies from 0 to 0.04 M, the change in $\log k_4$ is only 0.01.

Deviations from the "core + links" mechanism

In Fig. 6, the experimental results are plotted as $\log B(x)_Z$. It is seen that there are systematic deviations from the "core + links" curve. These deviations may be explained in several ways:

a) It was assumed that besides the main complexes, $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$, there is also present the mononuclear species UO_2OH^+ or the dinuclear complex $(\text{UO}_2)_2\text{OH}^{3+}$. These assumptions were tested with methods outlined in AB IV⁷ but none of them could explain the deviations nor could a combination of the assumptions be satisfactorily applied. As indicated by the recent work of Hietanen and Dunsmore, there may also be larger complexes containing more OH than the "core + links" formulas.

b) One may suspect the uncertainty in K (the dissociation constant of HSO_4^-) to be responsible for the deviations. However, a change in the value of K within the possible limits merely moves the $Z(\log h)_B$ curves along the $(-\log h)$ axis without changing the form of the curves or the spacing between them.

c) A third possible explanation is the presence of impurities in the sodium sulfate. In the preliminary titrations, the p.a. product of Merck was used without purification. It was not possible, however, to get stable potentials in titrations with the lower uranium concentrations, thus indicating slow hydrolysis and precipitation reactions. After several recrystallisations, stable and reversible potentials were obtained for even the lowest uranium concentrations. However, the titration curves (Fig. 1) for the lower concentrations (≤ 2.5 mM) moved to the right the more purified the sodium sulfate became, i.e. the deviations became smaller. Thus, the deviations from the "core + links" mechanism may partly be attributable to the presence of impurities still left in the sodium sulfate. The question must, however, be left open for the time being.

Supersaturation of the solutions

The titrations were in general continued until the potentials became unstable, indicating that precipitation had started. This happened when Z had reached values around 1.4. However, precipitation did occur at much lower Z values if the solutions were left overnight. This means that a great number of the measurements have probably been made in supersaturated solutions. However, as pointed out by Biedermann and Schindler⁸, a true picture of the hydrolysis equilibria in the clear solution will still be obtained provided the rate of precipitation is negligible compared with that of the hydrolysis.

COMMENTS

The data obtained in this investigation indicate that the hydrolysis of the uranyl ion in a sulfate medium gives the same type of products, $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$, as in a perchlorate medium. The range of hydrolysis, however, lies about one pH unit higher for the sulfate medium. This is explained by the rather strong complex formation between uranyl and sulfate ions ($\bar{n}_s = 2.9$) in 1.5 M sodium sulfate.

It is interesting to note that probably all basic uranyl sulfates described in literature can be written as containing groups $\text{UO}_2((\text{OH})_2\text{UO}_2)_n^{2+}$, e.g.

Zippeite ⁹	$\text{UO}_2((\text{OH})_2\text{UO}_2)_1\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Synthetic compound ¹⁰	$\text{UO}_2((\text{OH})_2\text{UO}_2)_2\text{SO}_4$
"	$\text{UO}_2((\text{OH})_2\text{UO}_2)_3\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Johannite ⁹	$\text{CuUO}_2((\text{OH})_2\text{UO}_2)_1(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Uranopilite ⁹	$\text{UO}_2((\text{OH})_2\text{UO}_2)_5\text{SO}_4 \cdot 12\text{H}_2\text{O}$

In addition, there seems to be evidence for the existence of the compound $(\text{NH}_4)_6\text{UO}_2((\text{OH})_2\text{UO}_2)_7(\text{SO}_4)_4$ ¹¹.

APPENDIX

Liquid junction potential and sulfate complexing

General equations. For the cell
 — glass electrode | H M H^+ , B M UO_2^{2+} , $(2C-H-2B)$ M Na^+ , C M SO_4^{2-} |
 or Pt, H_2
 | C M Na_2SO_4 | 0.02 M Ag^+ , $(2C - 0.02)$ M Na^+ , C M SO_4^{2-} | $AgCl$, Ag^+ we may write

$$E = E_0 - RTF^{-1} \ln h + E_j \quad (23)$$

Introducing

$$E' = E + RTF^{-1} \ln H \quad (24)$$

we get

$$E' = E_0 + RTF^{-1} \ln (Hh^{-1}) + E_j \quad (25)$$

We shall first consider cells where $B = 0$, thus no uranyl is present.

Combining

$$h [SO_4^{2-}] = K [HSO_4^-] \quad (26)$$

and

$$H = h + [HSO_4^-] \quad (27)$$

we get

$$E' = E_0 + RTF^{-1} \ln (1 + K^{-1} c) + E_j \quad (28)$$

where

$$c = [SO_4^{2-}] \quad (29)$$

For values of H which are not too large, we may write (c_0 is the value for c when $H = 0$)

$$E' = E_0 + RTF^{-1} \ln(1 + c_0 K^{-1}) + H(dE'/dH)_{H=0} \quad (30)$$

By differentiating (28) we find

$$(dE'/dH)_{H=0} = RTF^{-1} (K + c_0)^{-1} (dc/dH)_{H=0} + (dE_j/dH)_{H=0} \quad (31)$$

Na_2SO_4 medium; $Na^+ - SO_4^{2-}$ complexing neglected

Assuming $B = 0$ and no complex formation between Na^+ and SO_4^{2-} we have

$$c = C - [HSO_4^-] \quad (32)$$

Combining (26), (27) and (32) gives

$$c^2 + c(K + H - C) - KC = 0 \quad (33)$$

We differentiate with respect to the variables c and H which gives an expression for dc/dH . This is simplified for small H values where we may set $H \approx 0$ and $c \approx c_0 = C$

$$(dc/dH)_{H=0} = -C(C + K)^{-1} \quad (34)$$

E_j may be written according to Henderson's formula

$$E_j = RTF^{-1} (D'' - D') (S'' - S')^{-1} \ln(S''/S') \quad (35)$$

where

$$D = (\sum c_i l_i)_{\text{cations}} - (\sum c_i l_i)_{\text{anions}} \quad (36)$$

$$S = (\sum c_i z_i l_i)_{\text{cations}} + (\sum c_i |z_i| l_i)_{\text{anions}} \quad (37)$$

c_i is the concentration of an ion, l_i its equivalent conductance and z_i its charge. Further, ' indicates the solution which faces the positive pole of the cell and '' the solution which faces the negative pole.

From (26), (27) and (32), we get

$$h = HK(C + K)^{-1} \quad (38)$$

By insertion of (36), (37), and (38) into (35) we get (39)

$$E_j = \frac{RT[K(l_H - l_{Na}) + C(l_{SO_4} - l_{HSO_4} - l_{Na})]}{F[K(l_H - l_{Na}) + C(l_{HSO_4} - 2l_{SO_4} - l_{Na})]} \ln \left(1 + \frac{HK(l_H - l_{Na}) + HC(l_{HSO_4} - 2l_{SO_4} - l_{Na})}{2C(C + K)A_{Na_2SO_4}} \right)$$

Transforming the "ln" expression into a series and using only the first term and differentiating E_j with respect to H , we find

$$(dE_j/dH)_{H=0} = \frac{RT}{F} \frac{K(l_H - l_{Na}) + C(l_{SO_4} - l_{HSO_4} - l_{Na})}{2C(C + K)A_{Na_2SO_4}} \quad (40)$$

Insertion into (30) gives

$$E' = E_0 + RTF^{-1} \ln(1 + CK^{-1}) + H(dE'/dH)_{H=0} \quad (41)$$

where

$$(dE'/dH)_{H=0} = \frac{RT}{F(C + K)} \left(\frac{K(l_H - l_{Na}) + C(l_{SO_4} - l_{HSO_4} - l_{Na})}{2CA_{Na_2SO_4}} - \frac{C}{C + K} \right) \quad (42)$$

In Fig. 7, the experimental results $E'(H)$ of a number of titrations are given. As is expected from (42), a straight line is obtained (the lowest line in Fig. 7). From the slope, we find $dE'/dH = -7.7 \text{ mV M}^{-1}$ (see Fig. 11).

To determine K from the experimental data $E(H)$, values would have been required for l_H , l_{SO_4} , l_{HSO_4} and l_{Na} in 1.5 M Na_2SO_4 at 25°C. Such values are, however, not available with the required accuracy. If the rather vague estimates which can be made about them are put into (42), the result is that K is of the order of 0.1 — 0.5 M.

In Fig. 8, the values of Baes¹² and Young *et al.*¹³ are given for K in H_2SO_4 , NH_4HSO_4 , $NaHSO_4$ and Na_2SO_4 at various concentrations and 25°C. These

Fig. 7. E' (eqn. 24) as a function of H . Open circles: 1 M MgSO_4 (glass electrode). Dots: 1.5 M MgSO_4 (glass electrode). Triangles: 1.5 M Na_2SO_4 (glass electrode). Squares: 1.5 M Na_2SO_4 (hydrogen electrode).

values are based on Raman data. The diagram indicates that K is about 0.4 M in 1.5 M Na_2SO_4 .

As will be shown below, applying (55) gives a maximum value, $K \leq 0.5$ M.

Fig. 8. Plot of K against C , sulfate concentration^{12,13}. Dots: H_2SO_4 . Open circles: NaHSO_4 . Triangles: NH_4HSO_4 . Squares: Na_2SO_4 .

In conclusion, we can therefore state that $K \approx 0.4$ M in 1.5 M Na_2SO_4 at 25°C.

Inserting $K = 0.4$ M and $dE'/dH = -7.7$ mV $^{-1}$ into (31) we obtain $dE_j/dH = 3.0$ mV M $^{-1}$ and by the aid of (38) we find $dE_j/dh = 14$ mV M $^{-1}$, which is nearly the same values as for 3 M NaClO_4 .

MgSO_4 medium; $\text{Mg}^{2+} - \text{SO}_4^{2-}$ complexing neglected

In Fig. 7, the data $E'(H)$ are given not only for 1.5 M Na_2SO_4 but also for 1' and 1.5 M MgSO_4 . For all these solutions, we obtained approximately straight lines with the difference that dE'/dH is positive for MgSO_4 and negative for Na_2SO_4 .

In the same way as for Na_2SO_4 an expression can be deduced for dE'/dH at low H -values.

$$(dE'/dH)_{H=0} = \frac{RT}{F(C+K)} \left(\frac{K(l_H - 0.5 l_{\text{Mg}}) + C(l_{\text{SO}_4} - l_{\text{HSO}_4} - 0.5 l_{\text{Mg}})}{2C A_{\text{MgSO}_4}} - \frac{C}{C+K} \right) \quad (43)$$

Some tentative calculations show that, in order to make dE'/dH positive with MgSO_4 , either K must have a value several times greater than that for 1.5 M Na_2SO_4 , which seems improbable, or some species must be assumed which we have neglected.

Complexes $\text{MgSO}_4(\text{NaSO}_4^-)$ in the media

Let us assume that magnesium and sulfate ions form a complex with each other. We can then no longer set $c_0 = C$ as was done in the derivation of (42) and (43).

In (31), which is still valid, the last term, $(dE_j/dH)_{H=0}$ is likely to be positive. We shall derive expressions for $(dc/dH)_{H=0}$, starting with MgSO_4 , and then show how $(dE'/dH)_{H=0}$ can have opposite signs for MgSO_4 and Na_2SO_4 .

We define the equilibrium constant K_1 as follows:

$$[\text{MgSO}_4] = [\text{Mg}^{2+}] [\text{SO}_4^{2-}] K_1 = [\text{Mg}^{2+}] c K_1 \quad (44)$$

We then have

$$[\text{H}^+]_{\text{tot}} + hK^{-1}(K+c) = H \quad (45)$$

$$[\text{Mg}^{2+}]_{\text{tot}} = [\text{Mg}^{2+}](1 + cK_1) = C - 0.5H \quad (46)$$

$$[\text{SO}_4^{2-}]_{\text{tot}} = c(1 + hK^{-1} + [\text{Mg}^{2+}]K_1) = C \quad (47)$$

Eliminating $[\text{Mg}^{2+}]$ and h , we get

$$c + Hc(K+c)^{-1} + cK_1(1+cK_1)^{-1}(C-0.5H) = C \quad (48)$$

We now differentiate with respect to the variables c and H which gives an expression for dc/dH . This is simplified for small H values where we may set $[\text{Mg}^{2+}] \approx c \approx c_0$ and (cf. 47) $C \approx c_0 + c_0^2 K_1$ (49)

$$\left(\frac{dc}{dH} \right)_{H=0} = -c_0 \frac{2 - K_1(K - c_0)}{2(K + c_0)(1 + 2c_0 K_1)} \quad (50)$$

It is possible to eliminate c_0 from (50) using (49). The resulting equation, however, seems more complicated than (49) and (50) taken together.

In the case of Na_2SO_4 , we get in the same way

$$(dc/dH)_{H=0} = -c_0 \frac{1 - KK_1}{(K + c_0)(1 + 2c_0K_1 + CK_1)} \quad (51)$$

where in this case K_1 is the formation constant of NaSO_4^- .

For 1.5 M Na_2SO_4 , $dE'/dH = -7.7 \text{ mV M}^{-1}$. By combining literature data for equivalent conductances and transference numbers, the following probable values of equivalent conductance have been estimated: $l_{\text{H}} = 230$, $l_{\text{Na}} = 14$, $l_{\text{SO}_4} = 24$ and $l_{\text{HSO}_4} = 14$. It is found from (40), by insertion of these values, that $(dE_j/dH)_{H=0}$ will be positive as long as $K > 0.03$. By changing the values above by 20 % and combining these values in the most unfavourable manner, it is further found that $(dE_j/dH)_{H=0}$ will be positive as long as $K > 0.14$. It thus seems quite plausible to assume $(dE_j/dH)_{H=0} \geq 0$. It then follows from (31) (with $K = 0.4 \text{ M}$) that $K_1 < 0.13 \text{ M}^{-1}$ and $c_0 > 1.1 \text{ M}$.

In the case of MgSO_4 , it is seen from (50) that dc/dH will be positive if K_1 is sufficiently large. To make dE'/dH positive, it is not necessary that the first term in dE'/dH should be positive. It is sufficient that its absolute value is $< dE_j/dH$ since dE_j/dH is probably positive.

For dilute solutions ($C \rightarrow 0$) experimental values for K_1 are given in the literature¹⁴: for MgSO_4 $K_1 \approx 200 \text{ M}^{-1}$ and for NaSO_4^- $K_1 \approx 5 \text{ M}^{-1}$. For strong solutions no experimental values could be found, but an estimate can be made, using the similarity between simple 2—2-sulfates pointed out by Leden¹⁶. For CdSO_4 also, $K_1 \approx 200 \text{ M}^{-1}$ at extreme dilution but¹⁶ in 3 M NaClO_4 it is $\approx 7 \text{ M}^{-1}$. It is then fair to assume that in 1.5 M sulfate media K_1 (MgSO_4) is of the order of ten whereas K_1 (NaSO_4^-) is much lower. The formation constant for MgSO_4 , using the same E_j as for Na_2SO_4 and with eqns. (31) and (50), gives K_1 of the order of 100. This indicates that the complex formation is considerable; exactly for this reason the contribution from the liquid junction potential will probably be greater which will decrease the value for K_1 . The order of ten seems quite reasonable.

The complex formation between uranyl and sulfate ions in 1.5 M Na_2SO_4

When uranyl ions are present in the solutions under non-hydrolyzing conditions and $\bar{n}_s$ is the average number of sulfate groups bound per uranyl group, we have

$$c = C - \bar{n}_s B - [\text{HSO}_4^-] - [\text{NaSO}_4^-] \quad (52)$$

Let us first neglect $[\text{NaSO}_4^-]$. Combining eqns. (25), (26), (27), and (52) we get

$$E' = E_0 + RTF^{-1} \ln(1 + (C - [\text{HSO}_4^-] - \bar{n}_s B)K^{-1}) + E_j. \quad (52 \text{ a})$$

When $H \rightarrow 0$, $[\text{HSO}_4^-] \rightarrow 0$ and we obtain

$$E'_0 = E_0 + RTF^{-1} \ln(1 + (C - \bar{n}_s B)K^{-1}) \quad (6)$$

We define

$$\Delta E = E'_{B=0, H=0} - E'_{B=B, H=0} \quad (53)$$

Fig. 9. E' as a function of H . Open circles: $B = 0$. Dots: $B = 5$ mM. Open triangles: $B = 20$ mM. Black triangles: $B = 30$ mM. Open squares: $B = 40$ mM. Black squares: $B = 50$ mM. The figures in the plot indicate the number of points with the same values.

The lines are calculated according to the method of least squares.

From (53) and (6), it follows that

$$\bar{n}_s = B^{-1}(K + C)(1 - e^{-\Delta EF/RT}) \quad (54)$$

The experimental plot, $E'(H)$, gives straight lines for constant B , Fig. 9. By extrapolation to $H = 0$, we get E'_0 .

From Fig. 10, it is seen that, for $B = 0$, we have

$$\bar{n}_s(C + K)^{-1} = 1.6 \pm 0.1 \quad (55)$$

which indicates that the value for $\bar{n}_s$ in 1.5 M Na_2SO_4 is ≈ 3.0 (with $K = 0.4$). Since no evidence has been found for complexes with more than three SO_4^{2-} per UO_2^{2+} , we may assume that $\bar{n}_s$ must have a value not greater than 3.0 and (55) then gives that $K \leq 0.5$ M in 1.5 M Na_2SO_4 .

Fig. 10. $\bar{n}_s(C + K)^{-1}$ (eqn. 54) as a function of B .

If we assume the existence of NaSO_4^- , we get

$$\bar{n}_s = B^{-1}(K + c_0)(1 - e^{-\Delta EF/RT}) \quad (56)$$

$\bar{n}_s$ will thus become lower. For the probable maximum value of $K_1 = 0.13 \text{ M}^{-1}$ (see above), we have $c_0 \approx 1.1 \text{ M}$ which gives by inserting into (56) that $\bar{n}_s$ is between 2.3 and 2.6. Assuming a maximum value of 3.0 for $\bar{n}_s$ gives $K \leq 0.9$.

In conclusion, it may be stated that there are on an average between 2 and 3 sulfate groups bound per uranyl group in 1.5 M Na_2SO_4 , with a probable value of nearly 3. It may be noted that a calculation of $\bar{n}_s$ by means of Ahrlund's¹⁵ values for 1 M NaClO_4 gives a value of 2.9.

The proton affinity of uranyl sulfate complexes

When protons are brought into solutions containing uranyl and sulfate ions, the protons can combine both with the free sulfate ions and with the sulfate groups in the uranyl sulfate complexes. In the following an attempt is made to determine the extent of the second mechanism.

The equilibrium constant for the dissociation of protons from the bisulfate groups formed with the uranyl sulfate complexes is supposed to be constant and is designed by L . We then have

$$C = c(1 + hK^{-1}) + \bar{n}_s B \quad (57)$$

$$H = h + hcK^{-1} + \bar{n}_s B \frac{h}{h + L} \quad (58)$$

Inserting eqn. (58) into

$$E' = E_0 + RTF^{-1} \ln(Hh^{-1}) + E_j \quad (25)$$

and differentiating we get

$$\begin{aligned} (dE'/dH)_{H=0} = RTF^{-1} & (K + C - \bar{n}_s B + \bar{n}_s BKL^{-1})^{-1} (dc/dH)_{H=0} + \\ & + (dE_j/dH)_{H=0} \end{aligned} \quad (59)$$

By combining (57) and (58) we get after differentiating

$$(dc/dH)_{H=0} = - \frac{C - \bar{n}_s B}{C - \bar{n}_s B + K + \bar{n}_s BKL^{-1}} \quad (60)$$

Fig. 11. $-\frac{dE'}{dH}$ (eqn. 61) as a function of B . Upper line: $L^{-1} = 0$. Lowest line: $L = K$.

Inserting this into (4) gives

$$(dE'/dH)_{H=0} = -RTF^{-1} \frac{C - \bar{n}B}{(C + K - \bar{n}_s B + \bar{n}_s BKL^{-1})^2} + (dE_j/dH)_{H=0} \quad (61)$$

First we will assume that no protons combine with the sulfate groups linked to the uranyl ions, *i.e.*, $L^{-1} = 0$.

$$(dE'/dH)_{H=0} = -RTF^{-1} \frac{C - \bar{n}_s B}{(C + K - \bar{n}_s B)^2} + (dE_j/dH)_{H=0} \quad (61 a)$$

Inserting $C = 1.5$, $K = 0.4$ and $\bar{n}_s = 2.9$ we find that $(dE'/dH)_{H=0}$ will diminish with 0.6 mV M^{-1} when B rises from 0 to 0.05 M .

Second it will be assumed that $L = K$, *i.e.*, $KL^{-1} = 1$.

$$(dE'/dH)_{H=0} = -RTF^{-1} \left(\frac{C - \bar{n}_s B}{(C + K)^2} \right) + (dE_j/dH)_{H=0} \quad (61 b)$$

In this case the slope will rise with 1.0 mVM^{-1} when B rises from 0 to 0.05 M .

From the results given in Fig. 11 we can conclude that $0 < L^{-1} < K^{-1}$, *i.e.*, the protons probably do combine with the sulfate groups attached to the uranyl ions, but not as easily as with the free sulfate ions.

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