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The Hydrolysis of the Uranyl Ion in Heavy Water[*1]

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The hydrolysis equilibria of the UO_2^{2+} ion in heavy water containing 3M $NaClO_4$ as an ionic medium were studied at 25°C by potentiometric titrations, employing a technique of constant-current coulometry. The deuterium-ion concentration was measured by means of a glass electrode. The most probable hydrolysis scheme chosen in the range of the total uranyl concentration from 1 to 10 mM was: $(UO_2)_2(OD)_2^{2+}-(UO_2)_3(OD)_4^{2+}-(UO_2)_3(OD)_5^{+}$; the respective stability constants were $-\log \beta_{2,2}=6.80\pm0.02$, $-\log \beta_{4,3}=14.00\pm0.07$, and $-\log \beta_{5,3}=18.63\pm0.02$. The above results reveal that the composition of the hydrolysis species in heavy water are generally the same as those in light water, while the values of the stability constants are smaller in heavy water than in light water.

In a previous paper[1)] we described the hydrolytic reaction of the beryllium ion in heavy water and concluded that the compositions of the hydrolysis species are the same in heavy water as in light water and that the values for the stability constants in heavy water are smaller than those in light water.

In this work, the hydrolytic reaction of the uranyl ion was studied, and the results obtained were compared with those in light water.

[*1] Ionic Equilibria in Heavy Water, Part IV.

[1)] H. Kakihana and M. Maeda, This Bulletin, **43**, 109 (1970).

Symbols

The symbols used are the same as those described in Part II of this series.[1]

Expermental

Reagents and Apparatus. *The reagents used* were, unless otherwise stated, prepared and analyzed as has been described in Refs. 1 and 2.

Uranyl perchlorate in heavy water was prepared by the repeated evaporation of uranyl perchlorate in light water (which had been prepared and analyzed as has been described in Ref. 3), under an infrared lamp, while adding heavy water.

NaOD solution was prepared by the electrolysis of sodium perchlorate in heavy water, using a procedure similar to that described in Ref. 4.

All the apparatuses employed were the same as those used in Refs. 1 and 2.

Experimental Procedures. The hydrolysis of the UO_2^{2+} ion was investigated by measuring the deuterium-ion concentration using a glass electrode. $NaClO_4$ was added to all the test solutions so that they contained $3\text{M}\ ClO_4^-$; the total $UO_2(II)$ concentration was maintained within the 1—10 mM range.

The deuterium-ion concentration and the generation of the deuterium ions in a test solution were measured by the use of the same cell assembly as that employed in Part II[1] of this series.

The emf of the cell at 25°C can be denoted by Eq. (1),[5] since the concentration of the deuterium ions was maintained at less than 0.01M in the present work:

$$E = E_0 + 59.15 \log d \qquad (1)$$

The potentiometric titrations were carried out as follows. First, a partially-hydrolyzed solution of the uranyl ion was made by adding the solutions T_1 and T_2 to a test solution, S. The compositions of the solutions T_1, T_2, and S were as follows;

$$T_1 = A\text{M}\ NaOD + 3\text{M}\ NaClO_4$$

$$T_2 = 2B\text{M}\ UO_2(ClO_4)_2 + X\text{M}\ DClO_4 + (3-4B-X)\text{M}\ NaClO_4$$

$$S = B\text{M}\ UO_2(ClO_4)_2 + D\text{M}\ DClO_4 + (3-2B-D)\text{M}\ NaClO_4.$$

The partially-hydrolyzed solution made thereby was kept standing overnight, while nitrogen gas was passed through the solution; the next morning no precipitate was detected in the test solution.

The partially-hydrolyzed solution was gradually acidified by generating the deuterium ions coulometrically.

During the measurements, the test solution was stirred by a stream of nitrogen gas which had been purified by leading it through heavy water and 3M $NaClO_4$ in heavy water.

All the measurements were carried out in a paraffin-oil thermostat kept at 25.00±0.01°C in a room kept by a thermostat at 25±1°C.

Results and Discussion

The values of Z and $\log d$ in each series of B, which were calculated from the potentiometric measurements by the use of Eq. (1), are represented graphically in Fig. 1.

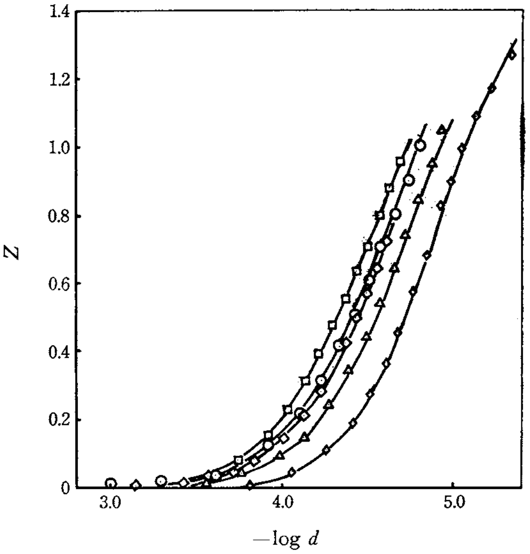

Fig. 1. Average number, Z, of OD bound per UO_2, as a function of $\log d$. Drawn curves were calculated with the stability constants given in Table 2.

B
□ 9.0506 mM
○ 6.177
◇ 5.231
△ 2.971
◆ 1.227

The experimental data were analyzed by a graphical method and by computer calculations.

First, the hydrolysis data were submitted to graphical analysis in order to obtain some preliminary information on the composition of the hydrolysis species formed; then, on the basis of the information thus obtained, computer analysis was made in order to evaluate the most probable hydrolysis scheme and the stability constants of the species formed.

1) The Evaluation of the Composition of the Hydrolysis Products by Graphical Analysis. In order to ascertain the mean composition of the polynuclear species formed, *i. e.*, $\bar{p}$ and $\bar{q}$, the general integration method presented by Sillén[6] was employed. The results of the calculations are

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[2] H. Kakihana and M. Maeda, This Bulletin, **42**, 1458 (1969).

[3] S. Hietanen, B. R. L. Row and L. G. Sillén, *Acta Chem. Scand.*, **17**, 2735 (1963).

[4] H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).

[5] H. Kakihana, M. Maeda and T. Amaya, This Bulletin, **43**, No. 5 (1970), in press.

[6] L. G. Sillén, *Acta Chem. Scand.*, **15**, 1981 (1961).

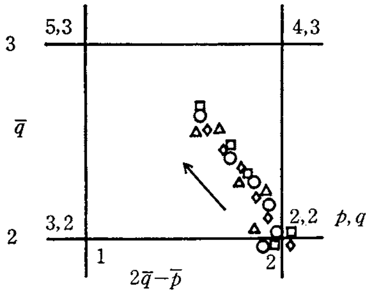

Fig. 2. Average composition of the hydrolysis species in the form of $\bar{q}$ *vs.* $(2\bar{q}-\bar{p})$.
Direction of an arrow corresponds to the increase in Z. Symbols are the same as those in Fig. 1.

shown in Fig. 2 as $\bar{q}$ *vs.* $(2\bar{q}-\bar{p})$.[7] From this figure, it may be seen that the (2,2) species exists at low Z values, while the (5,3) species may be present at high Z values, judging from the directions of the plots.

2) The Evaluation of the Composition and the Stability Constants of the Hydrolysis Products by Computer Analysis. The generalized, least-squares method was, with the help of an electronic computer (HITAC 5020), used to determine the most probable hydrolysis scheme containing the lowest number of species which would suffice to account for the experimental data and for the stability constants of the species formed. The least-squares calculations on the electronic computer were carried out using same procedure as that described in Ref. 1.

Several combinations of the hydrolysis species were attempted by starting with the species which had been suggested by the graphical analysis of the present work and by the investigations previously made by several researchers[8] in light water with the ClO_4^- anion. The results of the computations for several combinations of these species are shown in Table 1.

TABLE 1. THE ERROR SQUARE SUMS AND THE VALUES OF THE STABILITY CONSTANTS FOR THE SCHEMES CHOSEN

$\beta_{1,1}$ $\times 10^7$	$\beta_{2,2}$ $\times 10^7$	$\beta_{4,3}$ $\times 10^{14}$	$\beta_{5,3}$ $\times 10^{19}$	$\beta_{6,4}$ $\times 10^{22}$	U $\times 10^2$
—	1.89	—	3.14	—	1.72
17.8	1.71	—	3.16	—	1.70
—	1.58	1.02	2.32	—	1.27
8.26	1.33	1.56	1.95	—	1.73
—	1.58	0.969	2.29	1.46	1.30

The (2,2) - (4,3) - (5,3) species scheme had the least error-square sum and the least systematic errors of the schemes chosen; also, it showed a satisfactory agreement with the experimental data. It is shown in Fig. 1 as solid lines superimposed on the experimental data. The (2,2) - (4,3) - (5,3) - (6,4) species scheme, which had the second least error-square sum, gave rise to slight larger systematic errors than the (2,2) - (4,3) - (5,3) species scheme at higher Z values.

In the present work, no further attempt was made to search for new species other than those listed in Table 1.

From the results described above, it was concluded that the present experimental data in heavy water could be explained by assuming the (2,2) - (4,3) - (5,3) species scheme within the limits of experimental error.

The final values for the stability constants for the system of heavy water are listed in Table 2, together with those for the system of light water described by Dunsmore, Hietanen, and Sillén.[7]

3) Distribution of the Species. The distribution of the hydrolysis species in heavy water and in light water, calculated at the total uranyl concentration of 10 mM, and assuming the values of the stability constants in Table 2, is represented graphically in Fig. 3. There is a general shift toward less hydrolysis in heavy water at a given pH. The dominance of the (2,2) and (5,3) species in the accessible pH region is apparent in both heavy water and light water.

TABLE 2. THE VALUES FOR THE STABILITY CONSTANTS OF THE HYDROLYSIS SPECIES OF THE BERYLLIUM ION IN HEAVY WATER AND IN LIGHT WATER CONTAINING 3M $NaClO_4$ AS AN IONIC MEDIUM

	Present work* (in heavy water)	Ref. 7** (in light water)
$-\log\beta_{2,2}$	6.80±0.02	6.04±0.02
$-\log\beta_{4,3}$	14.00±0.07	13.21(>12.97)
$-\log\beta_{5,3}$	18.63±0.02	16.53±0.03
$-\log\beta_{1,1}$	—	6.10(>5.86)

* The uncertainties of the constants were estimated by multiplying by three the standard deviations.

** Range with up to 0.1M UO_2^{2+}

In the present work, it has been found that the compositions of the species formed in heavy water, *i.e.*, $(UO_2)_2(OD)_2^{2+}$, $(UO_2)_3(OD)_4^{2+}$, and $(UO_2)_3(OD)_5^+$, are generally the same as those in light water, although the (1,1) species or of the (6,4) species, which had previously been found, was not found in the present heavy water - system. It has also been found that the values of the stability

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[7] H. S. Dunsmore, S. Hietanen and L. G. Sillén, *ibid.*, **17**, 2644 (1963).

[8] "Stability Constants," ed. by L. G. Sillén and A. E. Martell, The Chemical Society, London (1964).

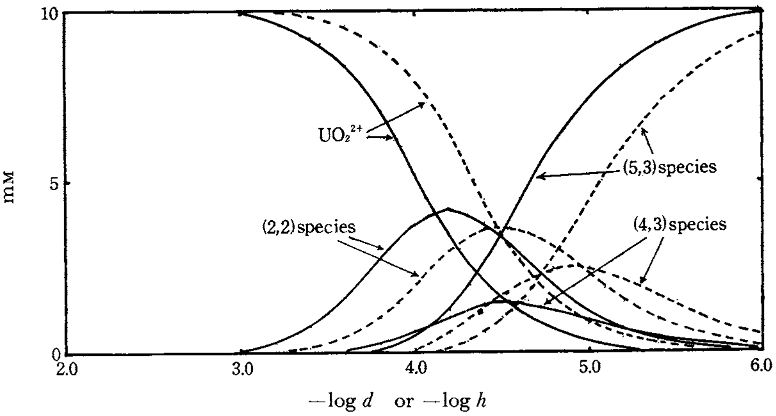

Fig. 3. The calculated distribution of the hydrolysis species in heavy water and in light water at the total uranyl concentration of 10 mM.
Dashed curves denote the distribution of the species in heavy water and full curves the distribution in light water.

constants of the hydrolysis products in heavy water are smaller than those in light water; this tendency is in agreement with that of the beryllium ion.[1])

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