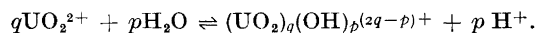# Studies on the Hydrolysis of Metal Ions

47. The Uranyl Ion in 3 M (Na)Cl Medium

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The hydrolysis equilibria of UO_2^{2+} in 3 M (Na)Cl medium have been studied at 25°C, using glass and quinhydrone electrodes. The data are given in Table 1, and the corresponding MESAK diagram in Fig. 1 of paper No. 46 in this series.[1] Table 2 gives the "best" sets of equilibrium constants obtained by LETAGROP (generalized least-square) refinement, assuming various sets of complexes, together with the corresponding standard deviation of Z. As "best" set we have chosen: log $\beta_{22} = -6.64 \pm 0.04$, log $\beta_{43} = -12.54 \pm 0.08$, log $\beta_{53} = -18.07 \pm 0.11$, log $\beta_{64} = -19.96 \pm 0.21$, log $\beta_{74} = -24.91 \pm 0.22$, where β_{pq} is the equilibrium constant of

$$qUO_2^{2+} + pH_2O \rightleftharpoons (UO_2)_q(OH)_p^{(2q-p)+} + p\,H^+.$$

For discussion see paper No. 46.[1]

The preceding paper[1] has given the background to this work which was started in September 1957. For comparison with the equilibria in 3 M (Na)ClO₄ medium, 3 M (Na)Cl-medium was chosen. In most experiments essentially the same procedure was followed as in the earlier work with sulfate medium, namely titration with alkali of an acid solution containing uranyl ion, until the first signs of precipitation.

EXPERIMENTAL

Materials and analysis

Uranium(VI)oxide, UO_3 spectroscopically pure, was heated to 800°C to remove any possible trace of ammonia, and thereby converted to U_3O_8. The weight of U_3O_8 required to give an approximately 0.30 M UO_2Cl_2 solution was warmed with a slight excess of HCl (constant-boiling), and H_2O_2 added dropwise to oxidize the U_3O_8. Water was also added from time to time and then, when all the black particles of U_3O_8 had disappeared, the solution was boiled to decompose any excess peroxide. When the solution had cooled, it was diluted to the required volume and analysed for U by precipitating the U(VI)

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as the 8-hydroxyquinoline complex, filtering it off and igniting it to U_3O_8 in a platinum crucible.[2]

The *total chloride* content of a UO_2Cl_2 solution was determined by passing a small volume of it through an ion exchange column and titrating the resultant acid with NaOH. From the stock solution of UO_2Cl_2, a solution was then made up to contain 0.100 M UO_2^{2+} and 3.00 M Cl⁻. The formal excess acidity of this solution was determined by potentiometric titration with NaOH, using a Gran plot. The result agreed well with that calculated from the quantities of U_3O_8 and HCl used in making the original solution, for instance: calc 3.1 mM, found 2.9 mM.

NaCl, Merck *p.a.* was heated for one hour at 400°C, cooled in a desiccator and tested for neutrality, which was considered satisfactory if one drop of approximately 0.100 M acid changed the color of one drop of screened methyl red in 50 ml 3 M NaCl solution (pH $6-7$).

HCl, Merck *p.a.*, was diluted and distilled in an all-glass apparatus according to the procedure given by Foulk and Hollingworth,[3] and the constant boiling fraction collected. The required weight was then diluted with water to give an approximately 1 M stock solution. The exact concentration was calculated from the composition of the constant-boiling acid (from tables) and checked by titration against $KHCO_3$ with screened methyl red as indicator. Agreement was better than 0.1 %. For use in equilibrium titrations, solid NaCl was added to the required volume of stock HCl, and the mixture diluted to give a solution approximately 0.250 M in H⁺ and 3.000 M in Cl⁻. This solution was also titrated against $KHCO_3$, both using screened methyl red as indicator and potentiometrically using a Gran extrapolation,[4] to obtain the exact equivalence point.

NaOH solution, approximately 1 M, was made by dilution under nitrogen, from a saturated solution of NaOH Merck *p.a.*, which was centrifuged before use to remove Na_2CO_3. The diluted solution was standardised against the standard HCl and then a solution with approximately 0.125 M OH⁻ and 3.000 M Cl⁻ was made by adding solid NaCl to the required volume of NaOH solution and diluting to the mark. This solution was then standardized against Merck p.a. hydrazine sulfate with screened methyl red as indicator, and checked against the standardized HCl. The agreement between the two standardisations was 0.1 %. The solutions containing NaOH were stored under nitrogen in polythene bottles fitted with rubber stoppers carrying polythene tubes. Portions of the stock solutions were blown out with purified nitrogen as required.

Quinhydrone, Merck *p.a.*, was recrystallized twice from water under nitrogen and dried over silica gel in a nitrogen atmosphere.

All the water used was doubly distilled and, when necessary, boiled to remove dissolved CO_2.

N_2 gas from a cylinder was washed by bubbling through 10 % H_2SO_4 and 10 % NaOH and then presaturated with water vapor by bubbling through two washbottles each containing 3 M NaCl.

Apparatus and experimental details

The work was carried out in a room thermostated at 25°C, and the measurements were made in a paraffin oil thermostat at 25°C $\pm$ 0.05°C or better.

All pipets, burets and flasks were calibrated at 25°C using water and 3.000 M NaCl. The density of the latter solution was measured using a pycnometer and found to be 1.111_4 g/ml at 25°C. (Interpolation of Wasastjerna's values [5] gave 1.1120 g/ml).

While the liquid was allowed to drip slowly, no difference was found in the volumes of water and solutions delivered from the burets. Some of the pipets, however, delivered 0.1 % less solution than water. All volumes were corrected to *in vacuo*.

The (equilibrium) uranyl solutions studied had the general composition; B M UO_2^{2+}, H M H⁺, $(3-2B-H)$ M Na⁺, 3 M Cl⁻.

The cells were of the following types (RE = Ag, AgCl|3 M NaCl|):

RE|uranyl solution + quinhydrone|Pt or RE|uranyl solution|glass electrode.

The salt bridge was of the usual "Wilhelm" type.[6] The Ag, AgCl electrodes were made by the method of Brown.[7] A Beckman 40498 glass electrode was used in conjunction with a Radiometer PHM3 valve potentiometer; with a quinhydrone electrode, a Leeds and Northtrup type K3 potentiometer was used.

Nitrogen bubbling. In titrations with the glass electrode, N_2 gas was bubbled constantly at a slow rate through the solution. This served both as a stirrer and to exclude CO_2 from the system. With quinhydrone, however, a steady slight drift in potential occurred, probably because of the evaporation of quinone. So, in the quinhydrone titrations, N_2-bubbling was discontinued, after an initial saturation with N_2, and stirring was performed manually.

Solutions containing quinhydrone became progressively darker in color on standing. Even with stirring an increase in the darkening could be observed on each addition of alkali, and so the quinhydrone check titrations were carried out preferably where only acid solutions were added.

Two types of titrations were carried out. In one, "constant B titration", the total uranyl concentration, B, was kept constant but Z and $\log h$ were varied by adding acid or alkali. In the other type, "constant Z titrations", calculated amounts of a partly hydrolysed uranyl chloride solution were added, successively, to a 3 M NaCl solution. Finally, a measured excess of acid was added, for checking E_0 and H.

Equilibrium. No difference was found in the results if the titrations were performed in the opposite direction. Constant B titrations were started from a fairly acid region, where it was presumed that no hydrolysis occurred, and continued until a point was reached when precipitation began. This was shown by the fact that the emf began to be unsteady, and to creep in a direction that corresponded to a continually increasing acidity of the solution. Several titrations were reversed at some point before the expected point of precipitation; acid was then added instead of alkali. No difference in the $Z(\log h)_B$ graphs was observed in titrations in the other direction, so it was concluded that equilibrium was reached after each addition during the titration, as long as no precipitation had appeared.
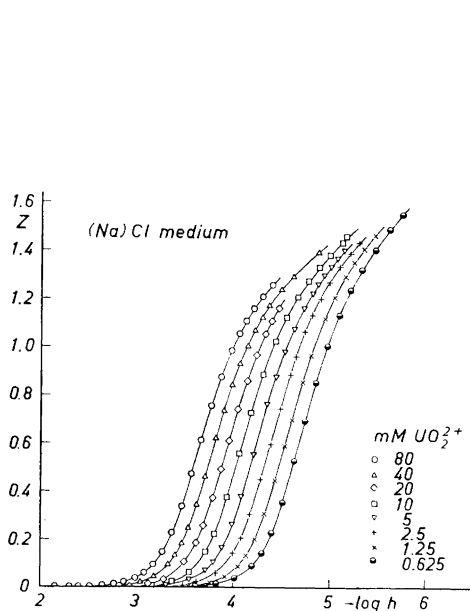

Fig. 1. Hydrolysis of uranyl ion in 3 M (Na)Cl medium $Z(\log h)_B$. Points: experimental data at various B values. Smooth curves drawn through data, for calculated curves, see Fig. 3.
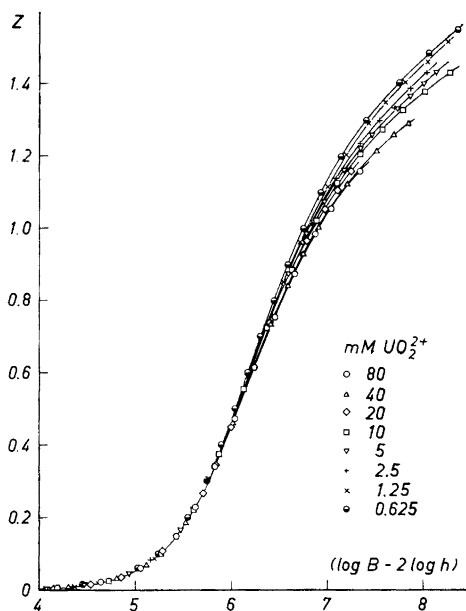
Fig. 2. Data in Fig. 1, shifted along the horizontal axis to Z *versus* $(\log B - 2 \log h)$. Some almost coinciding points have been suppressed for clarity.

Table 1. Hydrolysis of uranyl ion in 3 M Na(Cl) medium. Experimental data ($-\log h$, Z, $1000(Z_{calc}-Z)$), at various uranyl concentrations. Z_{calc} calculated with final set of equilibrium constants.

$B = 0.080$ M. 2.156, 0.000; 2.307, 0.001; 2.402, 0.002; 2.514, 0.004; 2.644, 0.007; 2.762, 0.013; 2.868, 0.022; 2.983, 0.037; 3.075, 0.060; 3.169, 0.094, $\pm$ 0; 3.262, 0.147, $\pm$ 0; 3.360, 0.228, + 1; 3.462, 0.338, + 6; 3.564, 0.472, + 7; 3.666, 0.615, + 6; 3.773, 0.754, + 9; 3.875, 0.874, + 10; 3.983, 0.984, + 8; 4.065, 1.054, + 8; 4.137, 1.108, + 6; 4.216, 1.159, + 6; 4.308, 1.209, + 6; 4.410, 1.257, + 5;

$B = 0.040$ M. 2.496, 0.000; 2.572, 0.001; 2.655, 0.003; 2.780, 0.005; 2.852, 0.009; 2.947, 0.015; 3.031, 0.022; 3.101, 0.032; 3.176, 0.047; 3.255, 0.068; 3.322, 0.095; 3.393, 0.133, + 1; 3.462, 0.185, $\pm$ 0; 3.531, 0.248, + 2; 3.618, 0.345, + 6; 3.705, 0.461, + 6; 3.820, 0.620, + 7; 3.902, 0.734, + 4; 3.990, 0.841, + 5; 4.070, 0.929, + 5; 4.150, 1.003; 4.226, 1.068, + 7; 4.302, 1.123, + 8; 4.375, 1.171, + 6; 4.455, 1.215, + 7; 4.500, 1.239; 4.545, 1.261, + 6; 4.596, 1.282; 4.622, 1.292, + 8; 4.889, 1.393, + 9.

$B = 0.020$ M. 2.723, 0.000; 2.813, 0.002; 2.921, 0.004; 3.038, 0.010; 3.115, 0.015; 3.188, 0.022; 3.277, 0.035; 3.366, 0.055; 3.490, 0.107, $-$3; 3.560, 0.148; 3.614, 0.187, $\pm$ 0; 3.688, 0.258, $\pm$ 0; 3.785, 0.373, $\pm$ 0; 3.871, 0.491, $-$1; 3.956, 0.609, $\pm$ 0; 3.983, 0.643, + 4; 4.049, 0.740, $-$4; 4.144, 0.858, $-$4; 4.240, 0.966, $-$7; 4.334, 1.053, $-$6; 4.400, 1.108, $-$7; 4.473, 1.160, $-$7.

$B = 0.010$ M. 2.899, $-$0.001; 3.064, + 0.002; 3.158, 0.008; 3.268, 0.013; 3.364, 0.024; 3.451, 0.038; 3.547, 0.062; 3.636, 0.100, + 1; 3.713, 0.147, $\pm$ 0; 3.805, 0.223, + 1; 3.935, 0.374, $\pm$ 0; 4.065, 0.554, $-$1; 4.185, 0.725, $-$4; 4.312, 0.885, $-$5; 4.440, 1.021, $-$6; 4.554, 1.123, $-$9; 4.672, 1.207, $-$9; 4.787, 1.275, $-$7; 4.893, 1.329, $-$6; 5.006, 1.380, $-$4; 5.137, 1.432, $\pm$ 0; 5.175, 1.457, $-$10.

$B = 0.005$ M. 2.940, 0.000; 3.011, 0.001; 3.094, 0.003; 3.190, 0.005; 3.302, 0.010; 3.385, 0.014; 3.466, 0.022; 3.546, 0.032; 3.618, 0.045; 3.716, 0.071; 3.794, 0.105, $\pm$ 0; 3.886, 0.165, $-$1; 3.992, 0.262, + 1; 4.085, 0.378, $-$3; 4.212, 0.552, $\pm$ 0; 4.355, 0.760, $-$8; 4.446, 0.875, $-$7; 4.538, 0.979, $-$7; 4.634, 1.074, $-$7; 4.738, 1.161, $-$7; 4.822, 1.222; 4.883, 1.260, $-$5; 4.947, 1.297; 5.018, 1.333, $\pm$ 0; 5.083, 1.367, $\pm$ 0; 5.154, 1.401, $\pm$ 0; 5.217, 1.433, $-$3.

$B = 0.0025$ M. 3.232, 0.000; 3.323, 0.002; 3.472, 0.009; 3.618, 0.023; 3.823, 0.060; 4.002, 0.144, $-$4; 4.081, 0.208, $-$6; 4.174, 0.305, $-$5; 4.283, 0.449, $-$7; 4.390, 0.595, + 1; 4.491, 0.744, $-$4; 4.596, 0.884, $-$7; 4.652, 0.960, $-$16; 4.746, 1.062, $-$17; 4.822, 1.133, $-$17; 4.906, 1.202, $-$15; 4.999, 1.269, $-$14; 5.105, 1.335, $-$11; 5.217, 1.390, $-$3; 5.301, 1.433, $-$4;

$B = 0.00125$ M. 3.447, 0.001, 3.535, 0.003, 3.637, 0.010, 3.756, 0.018, 3.838, 0.029, 3.918, 0.044, 3.988, 0.064, 4.052, 0.086; 4.136, 0.132, $-$2; 4.227, 0.200, $-$1; 4.327, 0.306, $-$1; 4.432, 0.443, $-$1; 4.531, 0.588, + 1; 4.610, 0.694, + 11; 4.720, 0.852, + 5; 4.807, 0.962, + 2; 4.951, 1.116, + 1; 5.051, 1.205, + 1; 5.166, 1.292, + 2; 5.255, 1.350, + 2; 5.358, 1.406, + 6; 5.472, 1.463, + 6.

$B = 0.000625$ M. 3.393, 0.000; 3.504, 0.001; 3.610, 0.006; 3.712, 0.008; 3.828, 0.017; 3.920, 0.024; 4.016, 0.039; 4.112, 0.061; 4.196, 0.090; 4.301, 0.144; 4.401, 0.228; 4.513, 0.355, $-$1; 4.634, 0.526, + 1; 4.745, 0.691, + 3; 4.856, 0.850, + 3; 4.978, 1.003, + 6; 5.099, 1.130, + 10; 5.219, 1.236, + 13; 5.335, 1.321, + 17; 5.477, 1.404, + 23; 5.629, 1.485, + 17; 5.760, 1.550, + 4; 5.858, 1.613, $-$28.

In titrations with a quinhydrone electrode, a slight drift in emf towards alkalinity was noticed immediately after the start of hydrolysis but was not detectable for higher Z values. This drift was also shown by the glass electrode, and only when quinhydrone was present in the solution. It is therefore presumed that there is a slight reaction between the hydrolysed uranyl ion and quinhydrone, and so all titrations using quinhydrone were carried out as quickly as possible.

DATA

The measured emf of the cell can be written

$$E = E_0 - 59.155 \log h + E_j \tag{1}$$

Biedermann and Sillén [8] have found that the liquid junction potential, E_j, can be taken as proportional to h. By titrations with solutions not containing uranium we found $E_j = 18 \, h$ mV. E was corrected for E_j where E_j was significant.

For each separate "titration", E_0 was determined from eqn. (1), using the section of the titration where the hydrolysis was negligible. E_0 remained fairly constant, within about 0.1 mV from day to day. The primary data, (E, H, B), were used to calculate $\log h$ and Z, and then the family of curves, $Z (\log h)_B$ was drawn. Selected points are given in Fig. 1, and the complete data are given in Table 1.

Several titrations were carried out at each of the concentrations 80, 40, 20, 10, 5, 2.5, 1.25, and 0.625 mM UO_2^{2+} and the agreement between the curves was better than 0.01 $\log h$ unit; therefore, in general, only every third point, (sometimes every second point), is shown in the graphs. For the final refinement with LETAGROP 120 points were selected at random, as uniformly as possible distributed over the whole experimental range. These points are seen in Fig. 3.

TREATMENT OF DATA

It is obvious from Fig. 1 that polynuclear complexes are formed, and that the curves are nearly parallel, with the spacing $(\partial \log B / \partial \log h)_Z = 0.5$ which indicates (p, q) complexes of the "core and links" formula $(2n, n + 1)$. If these had been the only complexes present, a shift of coordinate to $X = \log B - 2 \log h$ would make all points $Z(X)$ coincide. They do so, practically, at low Z and low B values; however in the upper part there are significant deviations (Fig. 2).

The data were now treated by the general integration method [9] which makes no other assumption than that the law of mass action is valid and that the data are accurate. The resulting MESAK diagram, Fig. 1a in the preceding paper,[1] gives the average composition of the complex in the form $\bar{q}$ versus $(2\bar{q} - \bar{p})$, for three different concentrations. The conclusion is that the (2,2) complex must exist, and also (5,3) or (7,4), and that (4,3) or (6,4) are indicated strongly.

Next, for various combinations of complexes, the values for the equilibrium constants were sought to give the "best" fit with the data, as indicated by the minimum value of $U = \Sigma(Z_{calc} - Z_{obs})$.[2] Our program LETAGROP [10,11] allows
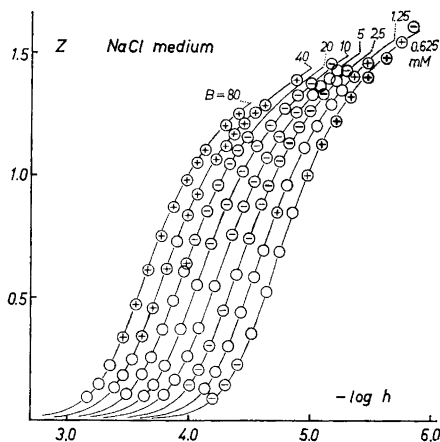
Fig. 3. Diagram $Z(\log h)_B$. Curves: calculated with equilibrium constants given in text. Points: 120 experimental points chosen for the LETAGROP treatment. Sign in circle indicates direction and magnitude of the deviation of Z_{calc} from the experimental value (thick if deviation $> 1.5\,\sigma$, thin if between $0.5\,\sigma$ and $1.5\,\sigma$).

a weighting of the points, but no reason was seen not to give the points equal weight. The combination [(2,2), (4,3), (5,3)] gave an acceptable agreement over a considerable part of the experimental range but systematic deviations at higher Z. Introducing (6,4) and (7,4) gave an improved fit, as shown by the decreasing values for $\sigma(Z)$ in Table 2.

Table 2 gives a summary of our calculations with LETAGROP. The upper half gives the primary results. For the first set of species, the logarithms of the β_{pq} were varied; for the two following, the values for the β, or their ratio to β_{22} or β_{22}^2, were used as variable constants. The results are quoted with the standard deviation σ given by the computer. The difference between the programs should not influence the values of β_{pq} at the minimum.

In the lower half of Table 2, the same results have been made uniform to give $\log \beta_{pq}$, and $3\sigma(\log \beta_{pq})$, which corresponds to 99.7 % confidence intervals. Instead of the error square sum, Table 2 gives $1000\,\sigma(Z)$ (σ^2 is proportional to U). From our knowledge of the experimental errors we might expect $\sigma(Z)$ to be around 0.010; it comes out as 0.012 for the first combination, and as 0.0075 for the "best" one. The introduction of more complexes does not

Table 2. Hydrolysis of uranyl ion in 3 M (Na)Cl medium. LETAGROP results. Upper half: primary results with σ, lower half: $\log \beta$, with 3σ.

$\log \beta_{22}$	$\log \beta_{43}$	$\log \beta_{53}$			$1000\,\sigma(Z)$
-6.657 ± 0.014	-12.535 ± 0.007	-17.793 ± 0.011	—	—	11.7
$10^7\,\beta_{22}$	$10^6\beta_{43}/\beta_{22}$	$10^{12}\beta_{53}/\beta_{22}$	$10^7\beta_{64}/\beta_{22}^2$	$10^{12}\beta_{74}/\beta_{22}^2$	
2.218 ± 0.048	1.288 ± 0.039	6.986 ± 0.187	82.54 ± 14.69	—	11.1
2.282 ± 0.069	1.280 ± 0.062	3.757 ± 0.301	2.085 ± 0.312	2.340 ± 0.323	7.5
$\log \beta_{22}$	$\log \beta_{43}$	$\log \beta_{53}$	$\log \beta_{64}$	$\log \beta_{74}$	
-6.657 ± 0.042	-12.535 ± 0.021	-17.793 ± 0.033	—	—	11.7
-6.654 ± 0.028	-12.544 ± 0.048	-17.810 ± 0.045	-18.391 ± 0.242	—	11.1
-6.642 ± 0.040	-12.535 ± 0.075	-18.067 ± 0.112	-19.964 ± 0.212	-24.914 ± 0.220	7.5

affect the constants β_{22} and β_{43} for the two main complexes very much, but it seems that in explaining the data, the (5,3) complex can to a certain extent be replaced by the (7,4) complex.

We shall prefer the last combination, since it gives a much lower error square sum, and suggest the following "best" set of equilibrium constants:

$\log \beta_{22} = -\ 6.64 \pm 0.04$, $\log \beta_{43} = -12.54 \pm 0.08$, $\log \beta_{53} = -18.07 \pm 0.11$, $\log \beta_{64} = -19.96 \pm 0.21$, $\log \beta_{74} = -24.91 \pm 0.22$

Fig. 3 shows the experimental points used in the LETAGROP calculation, and the curves calculated with the equilibrium constants finally chosen. The deviations are also indicated in Table 1. In Fig. 3, thin or thick plus or minus signs indicate the sign and magnitude of the difference between calculated and experimental Z values.

For comparison with work in other media and for acknowledgements, the reader is referred to the introductory paper (part 46).[1]

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