

Studies on the Hydrolysis of Metal Ions

59. The Uranyl Ion in Magnesium Nitrate Medium

ULLA SCHEDIN and MINA FRYDMAN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

and

Nuclear Chemistry Division, Research Institute of National Defence, Sundbyberg 4, Sweden

The hydrolysis equilibria of uranyl ions in 3 M (Mg)NO₃ and 5 M (Mg)NO₃ have been studied at 25°C using a glass electrode. The data are given in Tables 1 and 2 and Fig. 6.

Around 30 species $(p,q) = (\text{UO}_2)_q(\text{OH})_p^{(2q-p)+}$ were tried in the LETAGROP "species selector". The rejected ones are given in Tables 3 and 4.

The "best" set of complexes chosen were (2,2), (5,3), and (1,1). Their equilibrium constants were, in 5 M (Mg)NO₃, $\log \beta_{2,2} = -6.52 \pm 0.02$, $\log \beta_{5,3} = -17.76 \pm 0.02$, $\log \beta_{1,1} = -5.53 \pm 0.25$, and in 3 M (Mg)NO₃, $\log \beta_{2,2} = -6.34 \pm 0.03$, $\log \beta_{5,3} = -17.37 \pm 0.04$, $\log \beta_{1,1} = -5.38$ (max. -5.14), where $\beta_{p,q}$ is the equilibrium constant of $q\text{UO}_2^{2+} + p\text{H}_2\text{O} = (\text{UO}_2)_q(\text{OH})_p^{(2q-p)+} + p\text{H}^+$.

For future work on plutonium, a titration assembly was needed that used only a few milliliters and could be safely handled in a glove box. Several assemblies (Figs. 1-4) were developed and tested on the present system. Fig. 5 shows the good agreement between a $Z(\log h)_B$ curve obtained in the "deciliter apparatus" and the corresponding curve obtained with the "milliliter assembly" of Fig. 1a in a glove box.

Earlier investigations on the hydrolysis of the uranyl ion are surveyed in a preceding paper.¹ Whereas there were some differences between the minor species, the (2,2) species occurred in all ionic media with the anions Cl⁻, SO₄²⁻, ClO₄⁻ and NO₃⁻.

The only earlier work in nitrate medium from this laboratory is a study in 1 M (K)NO₃. We found it desirable to make further investigations in nitrate media, partly because of their practical importance. As media 1.5 M Mg(NO₃)₂ and 2.5 M Mg(NO₃)₂ were chosen and the solutions were made to contain 3 M (Mg)NO₃ and 5 M (Mg)NO₃. The positive ion Mg²⁺ was selected because it is

probable that the change in the activity factors would be least if the uranyl ion was exchanged against an ion of the same charge.

This work was also a preparation for investigations on the plutonium system and, as only small quantities of Pu would be available, included development and testing of a smaller titration assembly. After some experience had been gained, an apparatus was built which worked with only a few milliliters and was easy to handle in a glove box.

EXPERIMENTAL

Reagents

Magnesium nitrate stock solutions were prepared from once or twice recrystallized $\text{Mg}(\text{NO}_3)_2$, Merck *p.a.* Three different stock solutions were used; no significant difference was obtained in the experimental data $Z(\log h)$. The Mg content was determined by passing the solution through a H^+ -saturated cation exchanger and titrating the H^+ ions set free with standardized NaOH. The reproducibility was within $\pm 0.15\%$. Sometimes Mg was also analyzed by the pyrophosphate method. Good agreement, within $\pm < 0.15\%$, was always obtained between the two methods.

The uranyl nitrate used was $\text{UO}_2(\text{NO}_3)_2$, Fluka *p.a.* It was recrystallized once. It was standardized by igniting at 950°C and weighing as U_3O_8 . It was also precipitated with oxine, ignited to U_3O_8 and weighed. The two methods gave the same result within 0.2% .

Since it was impractical to add the slightly soluble $\text{Mg}(\text{OH})_2$ from a buret, hydrolyzed uranyl nitrate solutions were instead prepared by shaking with an OH^- saturated anion exchanger. The Cl^- in the ion exchanger was first removed in a column by passing HNO_3 , until no precipitation of AgCl occurred when Ag^+ was added to the eluate. The resin was then carefully washed with boiled, distilled water and saturated with NaOH still in the same column. The alkaline solutions were always treated under N_2 to avoid carbonate formation.

Nitric acid was made by dilution of HNO_3 , Merck *p.a.* It was standardized against recrystallized KHCO_3 and checked against standardized NaOH. The agreement was within $\pm 0.05\%$.

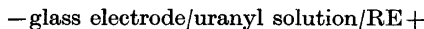
Sodium hydroxide was prepared as a 50% solution from solid NaOH, Merck *p.a.* Na_2CO_3 was removed by filtering through a G4 Jena glass filter. The solution was diluted with boiled water in N_2 atmosphere. It was standardized against recrystallized hydrazine sulfate.

The distilled water was always boiled to expel CO_2 .

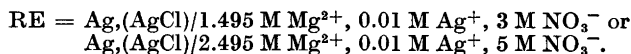
N_2 gas was taken from a cylinder and freed from acidic and alkaline impurities by passing through 10% NaOH and 10% H_2SO_4 . It was finally saturated with H_2O vapor by bubbling through water and ionic medium.

Procedure

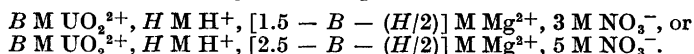
All experiments were carried out as potentiometric titrations with a glass electrode and an Ag,AgCl electrode as a reference electrode (RE). The cell was:



where



In each titration the total uranyl concentration (B) was kept constant but the analytical H^+ excess (which was often negative) was different in the titration vessel and in the buret. The solutions had the general composition:



To check that the measurements corresponded to equilibrium, titrations were made in both directions, adding an acidic uranyl solution to a hydrolyzed uranyl solution or *vice versa*. Most of the titrations started with the hydrolyzed solution in the titration vessel as it was possible to reach a higher Z value without precipitation in this way.

With Nernst's formula it was possible to calculate the concentration of free H^+ (h) in each point:

$$E = E_0 + E_j + 59.16 \log h$$

Following Biedermann and Sillén² it was assumed that $E_j = jh$, where j is a constant which could be determined in solutions not containing uranium. Then E_0 could be determined from that part of the titration where no hydrolysis occurred. First a Gran³ plot was made to get a better value of H . This was then used to plot $E_0 + E_j$ versus h , which gave E_0 .

Apparatus. General

The ordinary apparatus often used at this institute, in this paper called the "deciliter apparatus", consisted of the following parts: a five-necked flask provided with a glass-electrode (Beckman 40498), a reference half-cell (a Wilhelm bridge⁴), gas inlet and gas outlet (for mixing by nitrogen bubbling). The initial volume was usually $v_0 = 35$ ml. The additions were made from an ordinary 20 ml buret, calibrated with water. It was placed in a room thermostated to $25 \pm 1.5^\circ\text{C}$ and the flask and most of the Wilhelm bridge were inserted in a paraffin oil thermostat at $25 \pm 0.05^\circ\text{C}$. The emf was measured with a Radiometer pHM4 valve potentiometer calibrated against a Cambridge Vernier Potentiometer.

For the investigations on Pu, where only small amounts of material would be available, some parts of the titration assembly had to be changed in order to meet the following requirements if possible:

1. It should work with a few milliliters of equilibrium solution with the same accuracy as the "deciliter apparatus".
2. It should be easy and safe to handle in a glove box.

Naturally the titration vessel had to be reduced in size, and the first types tried are shown in Fig. 1a (type A) and Fig. 1b (type B). Later a commercially available one, the Ingold Universal Titration Vessel 605 (type C) was mostly used (Fig. 2). A was

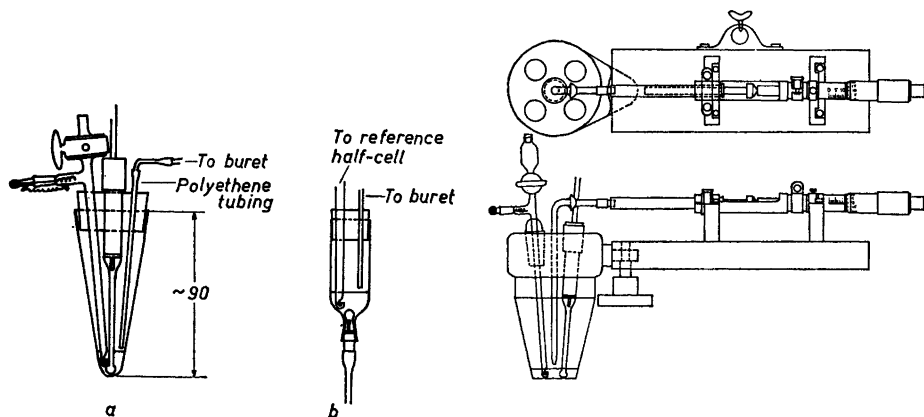


Fig. 1. a). Titration assembly (vessel of type A) used in many of the uranyl experiments using at least 2 ml. b). Smallest titration vessel (type B) using only 1 ml.

Fig. 2. The titration assembly (vessel of type C) used in the glove box.

simply a conical glass vessel with a rubber stopper. B was a straight glass tube with a rubber stopper and a glass joint at the bottom for the glass electrode. C was a conical glass vessel onto which a screw cap fitted. The cap had five holes for B14 joints. The smallest titration volume for A was 2 ml, for B 1 ml and for C 5 ml. A and C were used with a semimicro glass electrode Radiometer G222C and B with Radiometer G265C. A was used both in the oil thermostat and in the glove box, B only in the oil thermostat and C only in the glove box.

In the first experiments using small volumes, the reference half-cell used was the ordinary Wilhelm bridge⁴ with its bent capillary dipping into the small equilibrium solution contained in A or B. The whole assembly was inserted into the paraffin oil thermostat. The Wilhelm bridge was, however, a bit less accurately thermostated than usual. As these titration vessels were shorter than the "deciliter one" the oil level had to be lower to prevent leakage of oil into the vessel. No reproducible $Z(\log h)_B$ curves could be obtained using this assembly.

We soon understood that the explanation might be that solution was pumped in and out through the capillary junction, whenever the temperature fluctuated slightly. The volume of the Wilhelm bridge was about 100 ml, and if its temperature was increased by 0.1°C, the volume increase would be 0.03 ml, which means more than 1% of the total volume of the titration vessel.

To avoid this trouble another type of reference half-cell was constructed (Fig. 3a). It had no salt bridge and the total volume was about 5 ml. In use, the upper part of the reference half-cell stuck out into the air above the oil surface. One might have feared that the temperature of the reference electrode would have fluctuated somewhat, but no such effect was observed.

During the Pu work we later found it necessary to have a reference half-cell with a salt bridge, but still a small volume, and the one in Fig. 3b was provided. The volume of the cell in contact with the equilibrium solution was about 5 ml. In the cell in Fig. 3b, ionic medium was contained in the left-hand part and the tube with the bent capillary, which dipped into the titration solution. In the right-hand part was the reference electrode. The four-way stopcock with only one V bore made it easy to renew the solution in each part. It was also possible to renew the liquid junction during a titration by passing the solution to the right or left through the four-way stopcock and out through the waste tube. The spherical joint was inserted to make the cell a little flexible and avoid damage.

The buret was usually an Agla Micrometer Buret, capacity 0.5 ml, from Burroughs Wellcome and Co. (Fig. 2). It was calibrated with water for the total volume. The mean

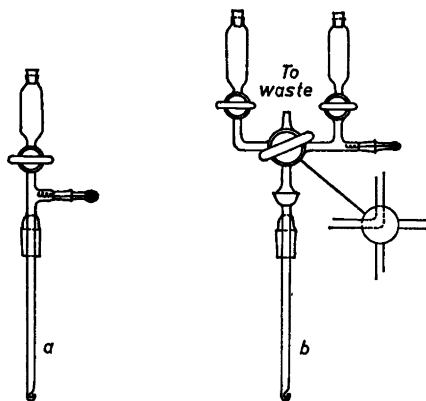


Fig. 3. Reference half-cells, a) without salt bridge, b) with a salt bridge.

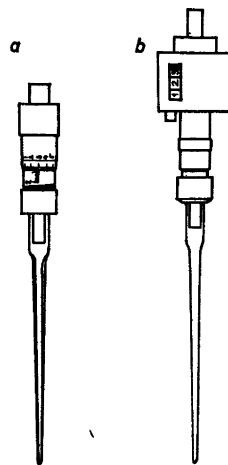


Fig. 4. Burets, a) made by RGI in all glass and plastics. b) Manostat Digi-Pet.

of four such calibrations was 0.4997 ± 0.0002 ml. Two other types of burets were also tried, both working in the same way as the Agla buret with a plunger and a screw from which the additions were read. The first was made by RGI Inc. in glass and plastics, capacity 2 ml (Fig. 4a). It was calibrated with mercury and the error was about 1% of the added volume. The other was from Manostat Corp., capacity 0.1 or 1 ml and was provided with a direct reading digital counter (Fig. 4b).

There were some problems connected with the use of the Agla buret. If the tip of the buret was inserted into the equilibrium solution during a titration, the emf was found to creep for hours, probably due to diffusion of ions in the junction. Therefore we always placed the end of the tip just above the surface of the solution. The last drop was swept away, when the solution was vigorously mixed.

It was found that the plunger of the syringe could move downwards by its own weight, when it was placed vertically. If it was placed horizontally, on the other hand, the glass tip was easily broken when the apparatus was assembled. So, when used together with titration vessel A or B, the glass tip of the Agla buret was exchanged for a thin, rather stiff, and non-breakable polyethylene tubing with inner diameter about 1 mm.

In the uranyl experiments the tip was inserted through a hole in the rubber stopper so that gas could still pass out through the hole. During the Pu titrations in vessel C it became necessary to have the vessel completely closed. So a glass tip was used and made to fit exactly to the hole in the stopper. We tried to join the tip and the syringe with a tubing (inner diameter about 3 mm and length about 150 mm) to get flexibility, but sometimes we got errors corresponding to several per cent of the volume added, probably because the volume contained would change every time the tubing was touched. The problem was solved by mounting the cap of vessel C and the Agla buret on the same plate of plexiglas (Fig. 2). The tip and the syringe were joined by a spherical glass joint, which gave some flexibility.

When the titration assembly was used in the glove box, the temperature of the whole box was kept constant at 25°C. To achieve this a contact thermometer was placed near the entrance of a fan (Philips, HK 4250 G). The heating coil in the fan was changed to give only about 20 W and connected to the contact thermometer over a relay. In front of the outlet of the fan a cooling pipe with water was placed. The fan and the cooling pipe were situated near the bottom of the box, while at the top there was another fan. Calibrated thermometers were placed at three points. The temperature difference was less than 1°C between top and bottom and the temperature was constant within 0.2°C near the titration vessel.

To test a new small titration assembly, titrations were first made on the uranyl system in the "deciliter apparatus" and then repeated in the small one first in the oil thermostat outside the glove box, and then in the glove box, and the agreement was studied. During these tests we have found that the smallest assemblies using 1 or 2 ml consisting of vessel B or A, provided with any one of the reference half-cells in Fig. 3 and the Agla buret, seems to be as accurate as the "deciliter" one and very suitable for studies on *e.g.* extremely expensive materials. Fig. 5 shows the good agreement, better than 0.005 Z units, between the $Z(\log h)_{B=20}$ curves obtained in the "deciliter" apparatus ($v_0 = 35$ ml) in the oil thermostat and in the small assembly shown in Fig. 1a placed in the glove box ($v_0 = 2$ ml).

For our Pu experiments, which had to be performed in the glove box, these assemblies had however some disadvantages. They were rather difficult to handle with big gloves: it was easy to break some of the glass parts, and broken glass is a hazard in glove boxes. The parts were not standardized and thus difficult to replace. Besides type B was a bit difficult to clean with its greased joint at the bottom. As we later found we could afford to use somewhat larger volumes of Pu solutions than we had initially thought, the titration assembly in Fig. 3 proved to be the most suitable for our purpose. It was very easy to handle with the gloves, every part could easily be replaced, the volume was not too big ($v_0 = 5$ ml), the vessel could be made completely tight and the additions from the Agla buret were easily read.

Apparatus in the uranyl experiments

The uranyl experiments were made either in the "deciliter" apparatus or in the small titration assembly shown in Fig 1a. In 3 M (Mg)NO₃ at least one titration at each B value

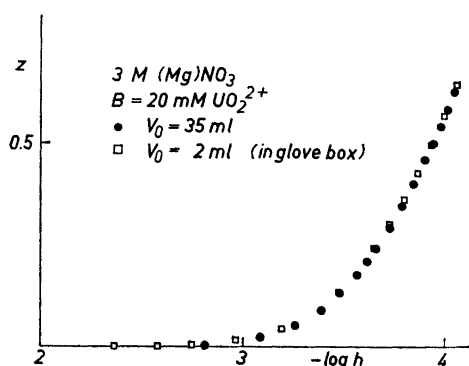


Fig. 5. Hydrolysis of 20 mM uranyl solution in 3 M (Mg)NO₃. Full points are measured in the "deciliter apparatus" with $v_0 = 35$ ml. Open squares are measured in the small assembly in Fig. 2a ($v_0 = 5$ ml) in a glove box.

was made in the "deciliter" apparatus and some of them were repeated in the small assembly. In 5 M (Mg)NO₃ all the curves were obtained in the small apparatus. The vessel was always placed in the oil thermostat, except during the testing experiments in the glove box, which are not included in Table 1 or Fig. 6a. The data in 5 M (Mg)NO₃ seemed to be a little more accurate than the others, and the small titration assembly obviously worked very satisfactorily.

DATA

The experimental data are collected in Tables 1 and 2 and shown in Fig. 6 as $Z = f(-\log h)_B$. The total concentration values B were the following: 2, 5, 10, 20, 50, and 100 mM. Each curve corresponds to at least two titrations.

Table 1. Hydrolysis of uranyl ion in 3 M (Mg)NO₃. The experimental data (Z , $-\log h$)_B are given and for the points used in the LETAGROP calculations also $1000(Z_{\text{calc}} - Z_{\text{obs}})$ using the "best" set of equilibrium constants and δZ .

$B = 0.002$ M. 3.259, 0.001, +1; 3.391, 0.009, 0; 3.566, 0.012; 3.646, 0.022; 3.577, 0.025, +3; 3.683, 0.042, +3; 3.766, 0.047; 3.788, 0.068, +3; 3.845, 0.071; 3.888, 0.101, +3; 3.916, 0.102; 3.992, 0.138; 3.977, 0.140, +3; 4.057, 0.180; 4.057, 0.186, +2; 4.129, 0.228; 4.126, 0.236, -1; 4.195, 0.282; 4.194, 0.290, -2; 4.256, 0.344; 4.258, 0.346, +1; 4.315, 0.409, -4; 4.319, 0.413; 4.373, 0.474, -2; 4.383, 0.496; 4.427, 0.543, -4; 4.446, 0.581; 4.481, 0.616, -4; 4.476, 0.630; 4.513, 0.683; 4.533, 0.693, -7; 4.591, 0.775, -3; 4.650, 0.862, -2; 4.721, 0.954, +11;

$B = 0.005$ M. 2.913, 0.001, -6; 3.055, 0.003, -4; 3.254, 0.013, -3; 3.284, 0.015; 3.369, 0.033; 3.506, 0.045, -2; 3.724, 0.109, -1; 3.749, 0.121; 3.887, 0.194, -1; 3.915, 0.220; 4.014, 0.287; 4.027, 0.294, +3; 4.072, 0.343; 4.149, 0.407, +6; 4.202, 0.473; 4.259, 0.534, +4; 4.287, 0.570; 4.315, 0.613; 4.365, 0.670, +6; 4.361, 0.674; 4.425, 0.757; 4.522, 0.885; 4.533, 0.906;

$B = 0.010$ M. 2.865, 0.002, -9; 2.882, 0.002; 2.985, 0.008, -11; 3.105, 0.012; 3.132, 0.018, -12; 3.296, 0.036, -10; 3.360, 0.044; 3.443, 0.064, -8; 3.555, 0.099; 3.561, 0.101, -6; 3.659, 0.143, -4; 3.698, 0.165; 3.742, 0.188, -2; 3.815, 0.238; 3.817, 0.238, -1; 3.883, 0.290, -1; 3.913, 0.318; 3.952, 0.345, +4; 4.003, 0.402; 4.016, 0.016, 0.404, +7; 4.075, 0.465, +8; 4.136, 0.531, +11; 4.195, 0.601, +12; 4.260, 0.675, +22;

$B = 0.020$ M. 2.525, 0.002, 0; 2.757, 0.002; 2.610, 0.003; 2.709, 0.003; 2.696, 0.004, +1; 2.844, 0.006; 2.784, 0.007; 2.855, 0.007; 2.767, 0.009; 2.861, 0.010; 2.929, 0.011; 2.929, 0.014, +1; 3.003, 0.017; 3.012, 0.017; 3.085, 0.021; 3.073, 0.029; 3.103, 0.034; 3.149, 0.036; 3.171, 0.040; 3.186, 0.043, +1; 3.203, 0.046; 3.250, 0.057; 3.276, 0.060; 3.323, 0.078; 3.358, 0.088; 3.370, 0.089, +1; 3.340, 0.090; 3.435, 0.108; 3.433, 0.118; 3.485,

0.142; 3.504, 0.144, +2; 3.490, 0.146; 3.521, 0.153; 3.492, 0.156; 3.538, 0.162; 3.534, 0.173; 3.593, 0.192; 3.578, 0.201; 3.607, 0.204, +1; 3.610, 0.227; 3.646, 0.227; 3.649, 0.235; 3.626, 0.238; 3.686, 0.258; 3.700, 0.267, +3; 3.722, 0.286; 3.710, 0.289; 3.705, 0.304; 3.749, 0.311; 3.754, 0.314; 3.778, 0.333; 3.784, 0.334, +4; 3.800, 0.354; 3.812; 0.364; 3.803, 0.372; 3.820, 0.372; 3.790, 0.381; 3.839, 0.389; 3.859, 0.407, -2; 3.865, 0.416; 3.894, 0.460; 3.867, 0.462; 3.915, 0.470; 3.933, 0.482, -4; 3.965, 0.526; 3.982, 0.546; 4.009, 0.563, -3; 4.018, 0.585; 4.070, 0.646; 4.082, 0.648, -4; 4.067, 0.655; 4.158, 0.737, 0;

$B = 0.050 M$. 2.160, 0.002; 2.387, 0.002; 2.562, 0.004, +16; 2.926, 0.036; 2.956, 0.037, +14; 3.189, 0.097, +11; 3.248, 0.121; 3.336, 0.165, +8; 3.430, 0.220; 3.455, 0.239, +6; 3.517, 0.275; 3.555, 0.316, +3; 3.642, 0.386; 3.649, 0.398, 0; 3.692, 0.440, -4; 3.704, 0.448; 3.737, 0.485, -6; 3.763, 0.504; 3.783, 0.530, -7; 3.831, 0.576; 3.827, 0.576, -8; 3.864, 0.614; 3.871, 0.624, -11; 3.918, 0.673, -9; 3.960, 0.723, -12; 4.009, 0.775, -9; 4.058, 0.828, -4; 4.088, 0.862; 4.107, 0.883, -1;

$B = 0.100 M$. 2.227, 0.001, +28; 2.085, 0.002; 2.356, 0.005; 2.508, 0.011; 2.599, 0.015, +26; 2.645, 0.022; 2.760, 0.035; 2.871, 0.055, +21; 2.875, 0.056; 2.959, 0.078; 3.020, 0.100; 3.033, 0.103, +18; 3.103, 0.133; 3.146, 0.156, +13; 3.154, 0.159; 3.200, 0.182; 3.236, 0.210, +9; 3.298, 0.245; 3.322, 0.265, +10; 3.353, 0.289; 3.390, 0.323, +3; 3.404, 0.327; 3.441, 0.361; 3.457, 0.383, -3; 3.475, 0.390; 3.506, 0.417; 3.518, 0.444, -13; 3.584, 0.506, -16; 3.647, 0.572, -24; 3.709, 0.639, -32; 3.772, 0.707, -39;

Table 2. Hydrolysis of uranyl ion in 5 M (Mg)NO₃. The experimental data (Z , $-\log h$)_B are given and for the points used in the LETAGROP calculations also $1000(Z_{\text{calc}} - Z_{\text{obs}})$ using the "best" set of equilibrium constants and δZ .

$B = 0.002 M$. 3.421, 0.005, +2; 3.553, 0.012; 3.710, 0.029, +6; 3.710, 0.031; 3.864, 0.062; 3.923, 0.079, +5; 4.001, 0.109; 3.997, 0.110, +1; 4.069, 0.143, +1; 4.111, 0.167; 4.131, 0.180, -1; 4.192, 0.219, 0; 4.212, 0.232; 4.246, 0.260, -1; 4.297, 0.304, -1; 4.331, 0.334; 4.373, 0.382, -4; 4.403, 0.415; 4.446, 0.465, -4; 4.473, 0.500; 4.517, 0.555, -2; 4.547, 0.592; 4.584, 0.651, -2; 4.594, 0.704; 4.653, 0.753, 0; 4.657, 0.753;

$B = 0.005 M$. 3.218, 0.007; 3.433, 0.017; 3.651, 0.052, +4; 3.658, 0.054; 3.778, 0.086; 3.822, 0.108, +4; 3.855, 0.123; 3.930, 0.164; 3.945, 0.175, -1; 3.998, 0.207; 4.057, 0.248, -3; 4.060, 0.252; 4.092, 0.279, 0; 4.153, 0.332; 4.180, 0.362, -3; 4.241, 0.418; 4.265, 0.450, -1; 4.317, 0.510; 4.342, 0.544, -2; 4.395, 0.608; 4.417, 0.645, -3; 4.466, 0.710, +1; 4.471, 0.714;

$B = 0.010 M$. 3.041, 0.004; 3.047, 0.011, -4; 3.380, 0.034; 3.389, 0.041, -5; 3.511, 0.064, -3; 3.641, 0.098; 3.647, 0.106, -3; 3.719, 0.137, -3; 3.808, 0.179; 3.871, 0.222, +1; 3.938, 0.268; 3.989, 0.314, 0; 4.052, 0.364; 4.096, 0.413, +3; 4.148, 0.467; 4.190, 0.520, -1; 4.244, 0.577; 4.287, 0.633, +7; 4.341, 0.695; 4.342, 0.705, +8;

$B = 0.020 M$. 2.762, 0.011, 0; 2.963, 0.016; 3.091, 0.028, -2; 3.291, 0.052; 3.379, 0.074, -2; 3.506, 0.110; 3.565, 0.137, +1; 3.649, 0.178; 3.692, 0.207, +1; 3.766, 0.252; 3.801, 0.283, +2; 3.864, 0.331; 3.898, 0.364, +3; 3.952, 0.415; 3.984, 0.450, 0; 4.040, 0.505; 4.072, 0.543, +1; 4.123, 0.601; 4.156, 0.641, +2; 4.201, 0.704, -5; 4.207, 0.704;

$B = 0.050 M$. 2.567, 0.004; 2.775, 0.012; 2.971, 0.030; 2.978, 0.031, -2; 3.130, 0.055, -2; 3.166, 0.063; 3.238, 0.084, -3; 3.271, 0.092; 3.328, 0.114, 0; 3.348, 0.123; 3.401, 0.146, +1; 3.462, 0.178; 3.502, 0.203, +1; 3.560, 0.237; 3.592, 0.264, +2; 3.644, 0.300; 3.671, 0.328, 0; 3.722, 0.366; 3.750, 0.397, 0; 3.796, 0.438; 3.823, 0.470, -4; 3.876, 0.514; 3.901, 0.547, -2; 3.950, 0.594; 3.977, 0.630, -3; 4.031, 0.680; 4.026, 0.683, 0;

$B = 0.100 M$. 2.348, 0.003; 2.308, 0.005, 0; 2.755, 0.025; 2.865, 0.039, -5; 3.022, 0.069; 3.085, 0.086, -5; 3.178, 0.120; 3.225, 0.139, -5; 3.296, 0.175; 3.338, 0.196, -1; 3.394, 0.235; 3.428, 0.257, -2; 3.482, 0.298; 3.519, 0.321, +3; 3.565, 0.365; 3.602, 0.390, +4; 3.644, 0.436; 3.678, 0.463, 0; 3.720, 0.512; 3.761, 0.540, +3; 3.801, 0.592; 3.842, 0.623, +1; 3.896, 0.675, +6; 3.888, 0.679;

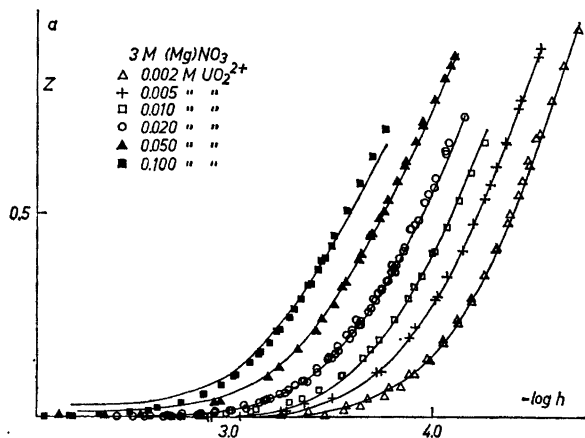


Fig. 6 a. Hydrolysis of uranyl ion in 3 M (Mg)NO₃. Points are experimental data $Z(\log h)_B$ and curves are calculated with the "best" set of constants and δZ .

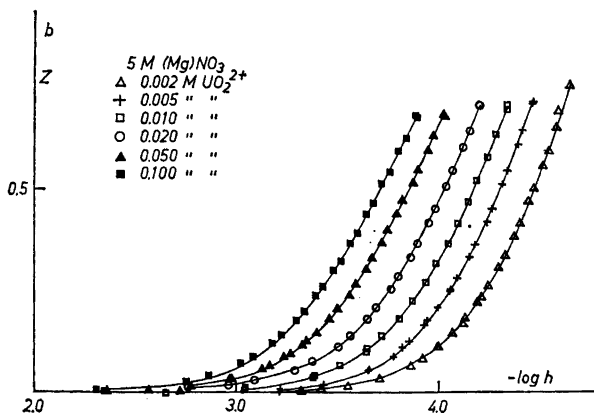


Fig. 6 b. Hydrolysis of uranyl ion in 5 M (Mg)NO₃. Points are experimental data $Z(\log h)_B$ and curves are calculated with the "best" set of constants and δZ .

The points are experimental data and the full drawn curves are calculated with the "best" set of constants below. For $B = 5 \text{ mM}$ in 3 M (Mg)NO₃, where very many titrations were made to test the small assemblies, only those made in the "deciliter" apparatus are included.

TREATMENT OF DATA

From the titration curves in Fig. 6 it is obvious that there must be polynuclear complexes. The average composition (\bar{p}, \bar{q}) was calculated with the general integration method⁵ by the computer program MESAK. The only

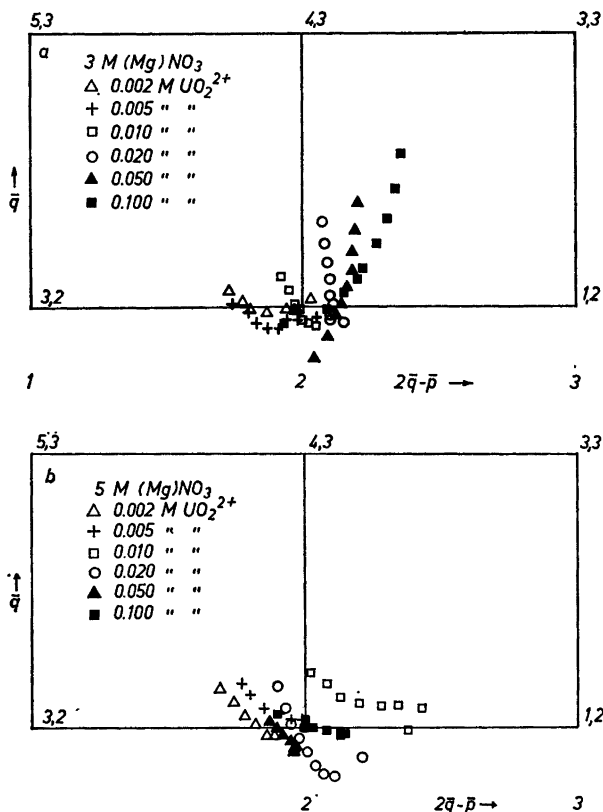


Fig. 7. Hydrolysis of uranyl ion in, a) 3 M (Mg)NO₃, b) 5 M (Mg)NO₃. Average composition of complexes as \bar{q} versus $(2\bar{q} - \bar{p})$, calculated by the MESAK program directly from data.

assumptions needed were that the law of mass action was valid and the data accurate. One titration at each B was used for the calculations. The result is seen in Fig. 7 as \bar{q} versus $(2\bar{q} - \bar{p})$. The main complex is obviously (2,2).

To find the complexes and their equilibrium constants our computer program LETAGROP⁶⁻⁹ was used. With various combinations of complexes we searched for that set of equilibrium constants $\beta_{p,q}$ that gave the lowest value on the error square sum $U = \sum w(Z_{\text{calc}} - Z_{\text{obs}})^2$. The program allowed weighting (w), but there seemed to be no reason to put different weights on the points in this case ($w = 1$).

The complexes found in earlier investigations were tried first, and next some of the surrounding species. Fig. 8 shows the (p,q) values tried, altogether around 30.

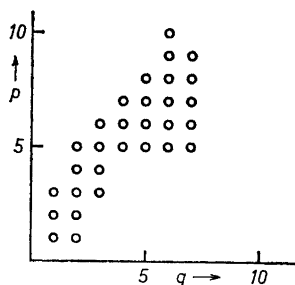


Fig. 8. Hydrolysis of uranyl ion in 3 M (Mg)NO₃ and 5 M (Mg)NO₃. (p, q) values tried in the LETAGROP calculations using the "species selector".

To get a rapid investigation of all these complexes we used a "species selector". This means that besides the probable main complexes and their equilibrium constants, the computer is given some new ones. These are now

Table 3. Hydrolysis of uranyl ion in 3 M (Mg)NO₃. Maximum values of $\log(\beta + 3\sigma)$ for rejected complexes in the LETAGROP calculations using the "species selector".

p	q	$\log(\beta + 3\sigma)$	p	q	$\log(\beta + 3\sigma)$
1	1	- 6.06	5	5	- 14.11
3	1	- 16*	7	5	- 22.53
1	2	- 3.80	5	6	- 10.81
3	2	- 11.66	6	6	- 16.60
4	2	- 14.65	7	6	- 20.04
5	2	- 19.77	8	6	- 24.56
3	3	- 10*	9	6	- 28.84
4	3	- 13.74	10	6	- 33.02
6	3	- 25*	6	7	- 15.38
5	4	- 15.33	7	7	- 18.89
7	4	- 24.28	9	7	- 26.44

* For these constants [$\beta + 3\sigma(\beta)$] came out negative:

$$\beta_{3,1} \pm \sigma(\beta_{3,1}) = (-5.2 \pm 1.5) \times 10^{-16}$$

$$\beta_{3,3} \pm \sigma(\beta_{3,3}) = (-2.5 \pm 0.8) \times 10^{-10}$$

$$\beta_{6,3} \pm \sigma(\beta_{6,3}) = (-9.9 \pm 2.6) \times 10^{-24}$$

added in turn one after another, and the $\beta_{p,q}$ of the new complex is varied alone at first to get a better value, and then together with the old ones. The calculation gives the values of the $\beta_{p,q}$, that give a minimum in U , together with their standard deviations $\sigma(\beta_{p,q})$. A complex is rejected if the quotient β/σ is smaller than a given value "sigfak", which was set to 1. The complexes not accepted are given in Tables 3 and 4, together with their "maximum" value, $\log(\beta + 3\sigma)$. In 5 M (Mg)NO₃ only the three species (2,2), (5,3), and (1,1) were left at the end of these calculations. The value of $\sigma(Z)$ also seemed fairly reasonable with respect to the experimental errors. In 3 M (Mg)NO₃ we obtained the same main complexes (2,2) and (5,3), but six other complexes were also left, some of which looked suspect.

Table 4. Hydrolysis of uranyl ion in 5 M (Mg)NO₃. Maximum values of $\log(\beta + 3\sigma)$ for rejected complexes in the LETAGROP calculations using the "species selector".

p	q	$\log(\beta + 3\sigma)$	p	q	$\log(\beta + 3\sigma)$
2	1	-10.72	7	5	-23.45
3	1	-15.66	8	5	-27.40
1	2	-4.02	5	6	-14.20
3	2	-12.13	6	6	-18.12
4	2	-17.17	7	6	-22.21
5	2	-22.05	8	6	-25.98
3	3	-10.29	9	6	-30.06
4	3	-14.24	10	6	-33.88
6	3	-23.54	5	7	-12.55
5	4	-16.92	6	7	-16.72
6	4	-20.89	7	7	-20.64
7	4	-24.77	8	7	-24.55
5	5	-15.58	9	7	-28.50
6	5	-19.49			

We found it reasonable to assume that we had a systematic error (*e.g.* in the analysis), which could be expressed as a constant correction δZ , different in each set of data (each titration). Thus δZ was treated in the usual way of a LETAGROP calculation. We could have the stability constants $\beta_{p,q}$ fixed and only vary δZ (TAGE) or vary both the $\beta_{p,q}$ and δZ at the same time (KOKS). For 5 M (Mg)NO₃ this procedure just gave a lower value for $\sigma(Z)$ but the same complexes (2,2), (5,3), and (1,1). With 3 M (Mg)NO₃ we also got a lower $\sigma(Z)$, but no further complexes were rejected. We found, however, that the error square sum U for the set with the highest concentration of B was considerably higher than the others, see Fig. 9. This may be due to changes in the activity factors when such a great part of the positive ions in the medium is exchanged by uranyl ions. So we excluded the set with the highest concentration and repeated the calculation. After that we had only four complexes left (2,2), (5,3), (6,4), and (2,1) and the rejected complexes are in Table 5.

Table 5. Hydrolysis of uranyl ion in 3 M (Mg)NO₃. Maximum values of $\log(\beta + 3\sigma)$ of rejected complexes in the LETAGROP calculations using TAGE and KOKS and excluding the set with $B = 100$ mM.

p	q	$\log(\beta + 3\sigma)$
6	5	-17.48
8	5	-27.22
5	7	-10.99
8	7	-21.87

DISCUSSION

According to the calculations there seems to be little doubt about the main species (2,2) and (5,3), which came out with well-defined equilibrium constants in both media. This is also in accordance with earlier investigations at this

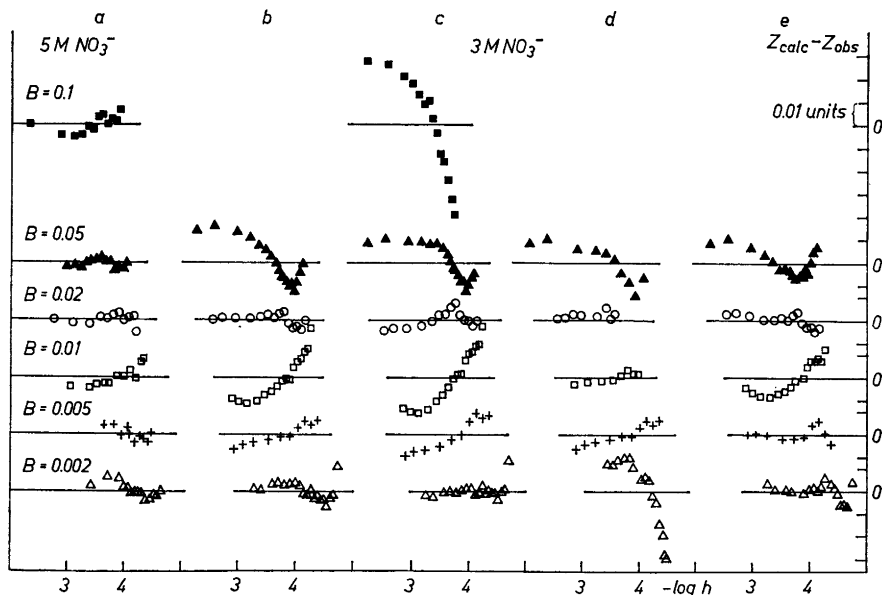


Fig. 9. Hydrolysis of uranyl ion in $\text{Mg}(\text{NO}_3)_2$ medium. ($Z_{\text{calc}} - Z_{\text{obs}}$) versus $\log h$ for the different B values assuming δZ and different complexes, which gave the following "best" values for the $\beta_{p,q}$ (exception is d, where we used the "best" $\beta_{p,q}$ we got in b) instead. a) $\log \beta_{1,1} = -5.53$, $\log \beta_{2,2} = -6.52$, $\log \beta_{5,3} = -17.76$ in 5 M $(\text{Mg})\text{NO}_3$. b) $\log \beta_{1,1} = -5.38$, $\log \beta_{2,2} = -6.34$, $\log \beta_{5,3} = -17.37$ in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM excluded. c) $\log \beta_{1,1} = -5.53$, $\log \beta_{2,2} = -6.31$, $\log \beta_{5,3} = -17.36$ in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM included. d) $\log \beta_{1,1} = -5.38$, $\log \beta_{2,2} = -6.34$, $\log \beta_{5,3} = -17.37$ in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM excluded. Here we used other sets of data (other titrations) but the "best" values of $\beta_{p,q}$ we got in b) and thus only varied δZ . e) $\log \beta_{2,1} = -9.99$, $\log \beta_{2,2} = -6.33$, $\log \beta_{5,3} = -17.73$, $\log \beta_{6,4} = -19.77$ with $B = 100$ mM excluded.

institute and elsewhere. In 5 M $(\text{Mg})\text{NO}_3$ there also seems to be some evidence for (1,1). In Fig. 9 we have plotted ($Z_{\text{calc}} - Z_{\text{obs}}$) versus $\log h$ for the different B values using the "best" values for the $\beta_{p,q}$ (except in d) and δZ assuming

- (2,2), (5,3), and (1,1) in 5 M $(\text{Mg})\text{NO}_3$.
- (2,2), (5,3), and (1,1) in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM excluded.
- (2,2), (5,3), and (1,1) in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM included.
- (2,2), (5,3), and (1,1) in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM excluded and using other sets of data (other titrations) but the same values of the constants as in b).
- (2,2), (5,3), (6,4), and (2,1) in 3 M $(\text{Mg})\text{NO}_3$ with $B = 100$ mM excluded.

From this diagram it is obvious that the best fit in 3 M NO_3^- is given with the species (2,2), (5,3), (6,4), and (2,1). It is, however, doubtful that we should have different species in the same type of medium. As the set (2,2), (5,3), and (1,1) fit almost as well as (2,2), (5,3), (6,4), and (2,1) in 3 M $(\text{Mg})\text{NO}_3$ and the former set of species is indicated by the data for 5 M $(\text{Mg})\text{NO}_3$, the former set seems slightly preferable. However, $\beta_{1,1}$ is not very well-defined in 3 M NO_3^- .

The data used in Fig. 9d gave rather high $|\delta Z|$ values for the lowest uranyl concentration, and this bad fit may be due to some experimental error.

Thus our "best" set of species and their equilibrium constants with their standard deviations are:

Medium	$\log \beta_{1,1}$	$\log \beta_{2,2}$	$\log \beta_{5,3}$	1000 (σZ)
5 M NO_3^-	-5.53 ± 0.25	-6.52 ± 0.02	-17.76 ± 0.02	3.4
3 M NO_3^-	-5.38 (max -5.14)	-6.34 ± 0.04	-17.37 ± 0.04	7.0

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