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# Studies on the Hydrolysis of Metal Ions

## X. The Hydrolysis of the Uranyl Ion, $UO_2^{2+}$

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Some five years ago, one of us (Ahrland [1]) published an investigation on the hydrolysis of the ion $UO_2^{2+}$. Uranyl solutions of various initial concentrations were titrated with $OH^-$, and the hydrogen ion concentration was measured with quinhydrone or glass electrodes at various points during the titration. The equilibria were studied at 20° C in 1 C $NaClO_4$ medium.

The data were more accurate and covered a wider concentration range than any published before. They showed quite obviously that the uranyl ion $UO_2^{2+}$ does not attract protons even at the highest acidities studied, and that the splitting off of protons at low acidities is connected with the formation of mainly polynuclear complexes.

In the meantime, mathematical methods for dealing with polynuclear complexes have been published (ABI[2], ABII[3]), and applied to the hydrolysis of a number of ions (parts VIII[4] and IX[5] of this series). We thought it would be interesting to apply these methods to the data for $UO_2^{2+}$ in order to see whether they could throw light on the mechanism of its hydrolysis.

### Formula of the complexes

We shall use the same notation as in previous parts of this series; $h$ = hydrogen ion concentration $[H^+]$; $M$ = total (analytical) concentration of uranyl ion, free or bound in complexes; $Z$ = average number of $H^+$ set free (or $OH^-$ bound) per uranyl group. (The symbols in the original paper [1] were $[H^+]$ for $h$, $C_M$ for $M$, and $\bar{n}$ for $Z$.)

Ahrland's data can be expressed in the form $Z(h, M)$ — each titration gives $Z$ values for a number of sets $(h, M)$. Since $M$ varied in each titration, one cannot simply measure the distances between curves $Z(\log h)_M$, as described in (VIII, 14 and following). However, by picking out a few values it was found by very rough calculations that the value for $t$ in (VIII, 14 and 15) is probably 2 for $UO_2^{2+}$.

$$t = 2 \qquad (1)$$

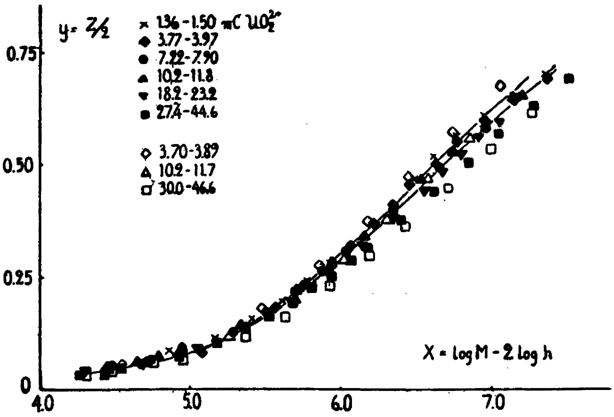

***Fig. 1.** Points, Ahrland's data on the hydrolysis of $UO_2^{2+}$, reduced to the form y(x); symbols see the figure. "Best curves": I (lower curve) equal weight to all points; II (upper curve) giving low weight to points for high concentrations. Points with open symbols (last three in list) were obtained with glass electrode, the others with quinhydrone electrode.*

To test this value, we have plotted $Z$ or rather

$$y = \frac{Z}{2} \tag{2}$$

as a function of

$$x = \log M - 2 \log h \tag{3}$$

As seen from Fig. 1, with this choice of coordinates the data for a wide range of concentrations seem to fall upon a single curve $y(x)$. The largest deviations are for the very highest $M$ values, around 30—40 mC. They may be due either to deviations in the activity factors or to a small error in the determination of free acid ("$C_H$"), which was not so accurate for the highest $M$, with the method chosen. If one considers that the range in log $M$ is almost 1.6, it is easily understood that other reasonable values for $t$, such as 1, 1.5, 2.5, or 3, would give a systematic spread of the data $y(x)$.

We may then conclude that, with good approximation, all complexes present in considerable amounts can be written in the form (*cf.* ABI[2], 16—19, 25—26, VIII[4], 15):

$$UO_2((OH)_2UO_2)_n^{2+} \tag{4a}$$

or, which is equivalent,

$$UO_2(OUO_2)_n^{2+} \tag{4b}$$

For structural reasons to be given below we find (4a) more probable. For the sake of brevity we shall, however, use the shorter (4b) in most of our equations.

### Direct analysis of $y(x)$ curve

When the general formula (4) of the complexes has been established, the next questions are which complexes (which values for $n$ in 4) occur and what are the equilibrium constants for the formation of these complexes.

As was demonstrated in ABII[3] and exemplified in part IX[5], the data $y(x)$ can be used directly for obtaining a power series $g(u)$, the coefficients of which are equilibrium constants $k_n$ for the formation of the various complexes (10 below). From $g(u)$ one may then calculate $\bar{n}$, the average number of "links" per complex at any point of the $y(x)$ curve. We have (ABII[3], 14, 15, 73)

$$\log(1+g) = \int_{-\infty}^{x} y\,dx + \log(1—y) + y\log e \tag{5}$$

$$\log u = x—y\log e—\int_{-\infty}^{x} y\,dx \tag{6}$$

$$\frac{\mathrm{d}\log g}{\mathrm{d}\log u} = \bar{n} = \frac{\Sigma nc_n}{\Sigma c_n} \tag{7}$$

The variables $u$ and $g$ are (VIII, 31, 32; ABII, 2, 3, 3a):

$$u = mh^{-t} = [\mathrm{UO}_2^{2+}]\ h^{-2} \tag{8}$$

$$g = f(u) = \Sigma\ k_n u^n \tag{9}$$

and $k_n$ is the equilibrium constant for the reaction:

$$(n+1)\mathrm{UO}_2^{2+} + n\ \mathrm{H_2O} \rightleftharpoons \mathrm{UO_2(OUO_2)}_n^{2+} + 2\ n\ \mathrm{H}^+;\ \text{equil. const.} = k_n \tag{10}$$

For the calculations, a "best" curve $y(x)$ was drawn in two different ways, either: I) giving equal weight to the data for all $M$ values or II) giving less weight to the very highest concentrations (Fig. 1); the latter seems preferable,

Table 1 gives the values for $\log(1+g)$ and $\log u$ obtained from (5) and (6) assuming the residue integral

$$\delta = \int_{-\infty}^{4.4} y\ \mathrm{d}x \tag{11}$$

to be zero.

Fig. 2 shows $\bar{n}$ as a function of $x$, using curve I with three values for $\delta$ and curve II with one $\delta$ value. The first part of the curve, for $x$ less than about 6, is seen to be very sensitive to the choice of $\delta$. It may be noted that the initial decrease in $\bar{n}(x)$ cannot be real because of the law of mass action. Moreover, the lowest possible value for $\bar{n}$ should be 1, since $\bar{n}$ is the average number of $\mathrm{OUO_2}$ "links" per complex, and the uncomplexed ions $\mathrm{UO}_2^{2+}$ are not counted in the average (7). Since the first part of $\bar{n}(x)$ is also very sensitive to the way the "best" curve $y(x)$ is drawn through the experimental points, no great weight should be placed on its irregular behavior.

*Table 1. Points from "best curves" I and II, and primary values for "direct analysis".*

| | Curve I | | | Curve II | | |
|---|---|---|---|---|---|---|
| $x$ | $y$ | $\log u + \delta$ | $\log(1+g)-\delta$ | $y$ | $\log u + \delta$ | $\log(1+g)-\delta$ |
| 4.4 | 0.039 | 4.3831 | −0.0004 | 0.040 | 4.3826 | −0.0003 |
| 4.6 | 0.050 | 4.5694 | 0.0083 | 0.050 | 4.5693 | 0.0084 |
| 4.8 | 0.062 | 4.7530 | 0.0192 | 0.062 | 4.7529 | 0.0193 |
| 5.0 | 0.080 | 4.9310 | 0.0328 | 0.080 | 4.9309 | 0.0329 |
| 5.2 | 0.106 | 5.1011 | 0.0502 | 0.106 | 5.1010 | 0.0503 |
| 5.4 | 0.141 | 5.2612 | 0.0728 | 0.145 | 5.2589 | 0.0730 |
| 5.6 | 0.180 | 5.4121 | 0.1017 | 0.186 | 5.4080 | 0.1026 |
| 5.8 | 0.230 | 5.5494 | 0.1317 | 0.240 | 5.5420 | 0.1388 |
| 6.0 | 0.285 | 5.6740 | 0.1803 | 0.300 | 5.6619 | 0.1832 |
| 6.2 | 0.346 | 5.7844 | 0.2312 | 0.364 | 5.7677 | 0.2357 |
| 6.4 | 0.410 | 5.8810 | 0.2898 | 0.430 | 5.8597 | 0.2962 |
| 6.6 | 0.471 | 5.9665 | 0.3569 | 0.493 | 5.9400 | 0.3650 |
| 6.8 | 0.530 | 6.0407 | 0.4314 | 0.553 | 6.0093 | 0.4410 |
| 7.0 | 0.588 | 6.1037 | 0.5112 | 0.614 | 6.0661 | 0.5205 |
| 7.2 | 0.646 | 6.1551 | 0.5939 | 0.668 | 6.1145 | 0.6066 |
| 7.4 | 0.696 | 6.1992 | 0.6837 | | | |

The $\bar{n}(x)$ curve for $x$ values higher than 6 is almost independent of the choice of $\delta$. The "best" $y(x)$ curves I and II lead to $\bar{n}(x)$ curves which are only slightly shifted, and have the same general shape. The curve is seen to rise rather uniformly, without any "shelf", and has attained values of about $\bar{n} = 2.5$ at the end of the experimental range. There is no sign that the curve will bend off before $\bar{n} = 3$.

We may conclude that the complex with $n = 1$, $(UO_2)_2O^{2+}$, predominates at the lowest degree of hydrolysis, and that larger complexes are certainly formed, at least one with $n$ not less than 3.

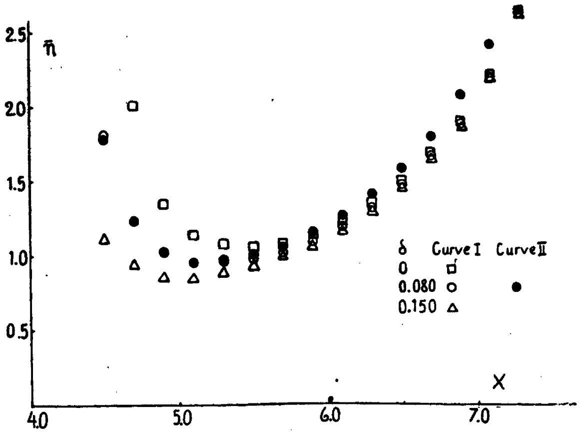

*Fig. 2. Average number of links per complex, $\bar{n}$, calculated by direct analysis of $y(x)$ curve. Open symbols: from curve I with $\delta = 0$ (□). 0.080 (○), and 0.150 (△). Black dots ●; from curve II, $\delta = 0.080$.*

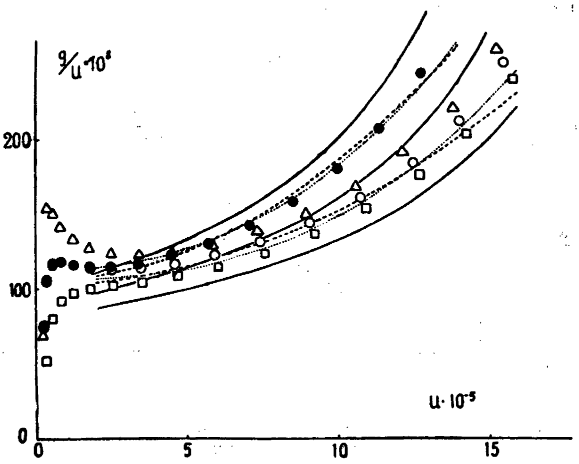

*Fig. 3. Points: function $gu^{-1}$, calculated by direct analysis of $y(x)$ curve, symbols as in Fig. 2. Full-drawn curves: hypothesis IIIa, $k_0 = 2$, $\log k = -6.40$ (lower), $-6.35$ (middle), $-6.30$ (upper). Broken curves: $\log k_1 = -5.99$, $\log k_3 = -18.30$ (lower); $\log k_1 = -5.98$, $\log k_3 = -18.10$ (upper). Dotted curves: $\log k_1 = -5.975$, $\log k_3 = -18.64$, $\log k_4 = -24.70$ (lower), $\log k_1 = -5.95$, $\log k_3 = -18.30$, $\log k_4 = -24.70$ (upper).*

## Limited series of complexes

In order to find possible values for the constant $k_n$ we have plotted $gu^{-1}$ as a function of $u$, as obtained by direct analysis of the $y(x)$ curves (Fig. 3, same symbols as in Fig. 2). According to (9) we should have

$$gu^{-1} = \Sigma k_n u^{n-1} = k_1 + k_2 u + k_3 u^2 + k_4 u^3 + \ldots \tag{12}$$

We have tried to fit the empirical points in Fig. 3 with polynomials containing only a few members. For instance, the points obtained from curve I with $\delta = 0.080$ fit rather well with (12) assuming either of the sets:

$k_1 = 10^{-5.99}$; $k_2 = 0$; $k_3 = 10^{-18.30}$; $k_4 = 0$ (broken)
or $k_1 = 10^{-5.975}$; $k_2 = 0$; $k_3 = 10^{-18.64}$; $k_4 = 10^{-24.70}$ (dotted)

With these sets one obtains the lower broken and dotted curves in Fig. 3. On the other hand, a good fit with the points from curve II with $\delta = 0.080$ is obtained for

$k_1 = 10^{-5.98}$; $k_2 = 0$; $k_3 = 10^{-18.10}$; $k_4 = 0$ (broken)
or $k_1 = 10^{-5.95}$; $k_2 = 0$; $k_3 = 10^{-18.30}$; $k_4 = 10^{-24.70}$ (dotted)

As seen from Fig. 3 the upward trend of the experimental data at the highest $x$ indicates that there are terms of higher degree in (12) which have been neglected.

Fig. 4 shows the $y(x)$ curves calculated with these sets of constants — the differences are seen to be within the limits of experimental error. However,

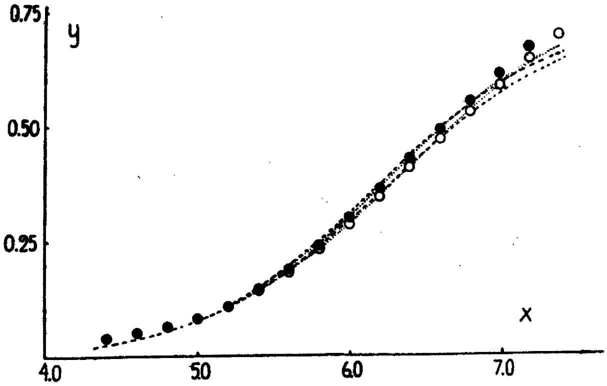

*Fig. 4. Diagram y(x). Points from best curves I (circles) and II (dots). Curves: calculated with limited polynomials, symbols as in Fig. 3.*

the experimental points for high $y$ possess an upward trend relative to the curves calculated using polynomials with no higher constants than $k_3$ or $k_4$.

One can thus get a fair agreement assuming $k_2 = 0$. However we consider this fact as fortuitous.

## Simple unlimited mechanisms

We have also compared the empirical $y(x)$ with curves calculated assuming the various mechanisms discussed in ABII. As could be expected already from the $\bar{n}$ curves, no mechanism involving a single complex (hypothesis II) gave an acceptable fit.

With the unlimited mechanisms, on the other hand, a reasonable fit was obtained with IIIa, $k_0 \approx 2$, $\log k = -6.35 \pm 0.10$. With either IIIb ($k_0 \approx 3 \rightarrow 4$) or IIIc ($k_0 \approx 0.5 \rightarrow 1.0$) the points for $y < 0.5$ could be made to agree, whereas the higher $y$ deviated.

Mechanism IIIa would involve $k_n = k_0 k^n$. Thus we would have the equilibrium constant for the initial reaction:

$$\mathrm{UO_2^{2+} + H_2O + UO_2^{2+} \rightleftharpoons UO_2OUO_2^{2+} + 2\ H^+};\ kk_0 = 10^{-6.05 \pm 0.1} \quad (13)$$

and the constants for all following reactions would be equal:

$$\mathrm{UO_2(OUO_2)_n^{2+} + H_2O + UO_2^{2+} \rightleftharpoons UO_2(OUO_2)_{n+1}^{2+} + 2\ H^+};\ k = 10^{-6.35 \pm 0.1} \quad (13a)$$

Fig. 3 gives, as full-drawn curves, $gu^{-1}$ calculated with IIIa, $k_0 = 2$ assuming $\log k = -6.30$, $-6.35$ or $-6.40$. The fit with any set of empirical points could be further improved by small adjustments of $k_0$ and $k$. However, we think this would mean no gain in real accuracy.

The $y(x)$ curves calculated with IIIa and the same $k$ and $k_0$ values are given in Figs. 5 and 6. The agreement is satisfactory. The small deviation at the lowest values of $y$ is not serious. In this range the solution is

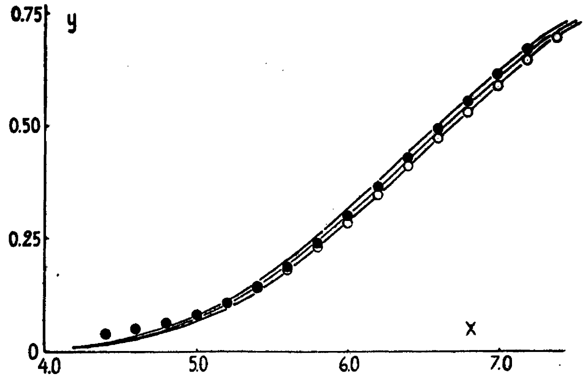

*Fig. 5. Diagram y(x). Points from "best curves" I (circles), II (dots). Curves: calculated for mechanism IIIa with $k_0 = 2$ and $\log k = -6.30$ (upper), $-6.35$, and $-6.40$ (lower).*

fairly acidic, and $y$ is less accurate partly because it is the difference between two large quantities, partly because of the liquid junction potential.

One can thus obtain a reasonable agreement with the experimental data assuming either a limited number of complexes $UO_2(OUO_2)_n^{2+}$, or an unlimited series of such complexes.

However, it seems hard to understand why Nature should form only the complexes with $n = 1$ and 3, or 1, 3 and 4 in the series (4) and then abruptly break the series at $n = 3$ or 4. To us it seems more plausible that the series goes on to high $n$, and that an extension of the experimental range would give

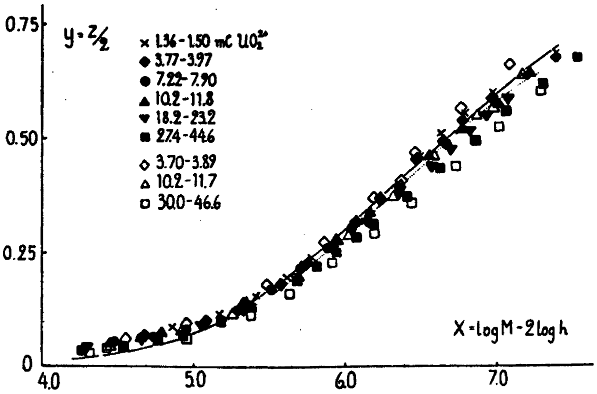

*Fig. 6. Diagram y(x). All experimental points, symbols as in Fig. 1. Full-drawn curve: calculated for mechanism IIIa, $k_0 = 2$ and $\log k = -6.35$. Dotted curve: calculated with $\log k_1 = -5.975$, $\log k_3 = -18.64$, $\log k_4 = -24.70$.*

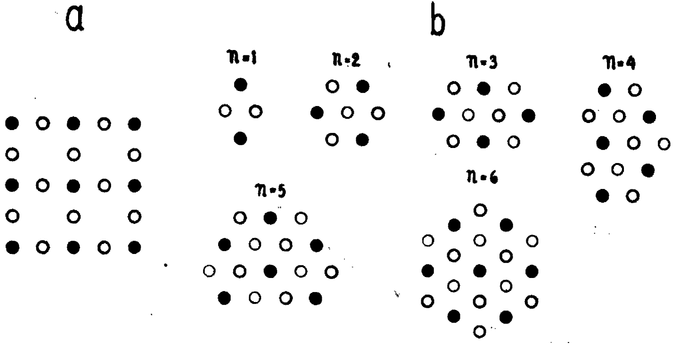

*Fig. 7. Slightly idealized structure of uranyl-hydroxide (or -oxide) sheets: a) coordination* $UO_2 - 4\,OH, OH - 2\,UO_2$, *b) coordination* $UO_2 - 6\,OH, OH - 3\,UO_2$. *Possible structures of complexes* $UO_2((OH)_2UO_2)_n^{2+}$ *with n = 1 to 6 are shown as increasing fragments of a sheet. Black circles = uranyl groups with U in the plane of the paper and the two uranyl O (not shown here) above and below, perpendicular to the paper. Circles = oxygen atoms a) in the plane of the paper b) above (thick) and below (thin) the plane of the paper.*

still higher $\bar{n}$ values. Also a consideration of possible structures of the complexes (4) gives little indication as to why a few $n$ values should be preferred to all others (See below).

## Comparison with other data

The formation of the complex $(UO_2)_2O^{2+}$ has been indicated by Faucherre[6] and Sutton[7]. Our equilibrium constant, $k_1 = 10^{-6.05}$ for ionic strength $I = 1.0$, may be compared with Faucherre's: $10^{-5.97}$ for $I = 0.60$ and $10^{-5.72}$ for $I = 0.06$. Sutton also found evidence for the complex $U_3O_8^{2+}$ and gave $k_1 = 10^{-5.94}$ for $I = 0.1$ and $k_2 = 10^{-12.9}$ (compare $k_2 = 10^{-12.4}$ with mechanism IIIa). He also proposed complexes like $U_3O_8(OH)_i^{2-i}$ (with $i = 1, 2, 3, 4$, and 5) but, unlike us, found no evidence for complexes with more than three U. — It would be interesting to have data obtained with a constant ionic medium and a wide range of $M$ and $Z$ also from the alkaline range, where uranium forms anions, according to Sutton.

## Structure of the complexes

The equilibrium data have indicated that the general formula of the hydrolysis products of $UO_2^{2+}$ can be described by the formula (4), $UO_2((OH)_2UO_2)_n^{2+}$, or $UO_2(OUO_2)_n^{2+}$. From X-ray investigations, several crystal structures are known where $UO_2^{2+}$ groups are joined by $O^{2-}$ or $OH^-$ groups to form sheets.

In the crystal structure of $BaUO_2O_2$ (Samson and Sillén[8]), the coordination is $UO_2$—4 O, O—2 $UO_2$; in $CaUO_2O_2$ (Zachariasen[9]), we have $UO_2$—6 O, O—3 $UO_2$. These and a number of other metal uranyl oxides studied by

Zachariasen and coworkers were prepared from melts. Sheets with a coordination $UO_2$—4 OH, OH—2 $UO_2$ or $UO_2$—6 OH, OH—3 $UO_2$ have also been found in uranyl hydroxides prepared from aqueous solutions and studied in this laboratory.

One can imagine complexes of formula $UO_2(OUO_2)_n^{2+}$ as fragments of sheets with coordination $UO_2$—4 O, O—2 $UO_2$, or complexes $UO_2((OH)_2UO_2)_n^{2+}$ as fragments of sheets with coordination $UO_2$—6 OH, OH—3 $UO_2$ (Fig. 7). The latter structure seems to us to be more plausible because first it gives a more compact structure and second it would give a direct connection between the structure of the complexes and the structure of uranyl hydroxides which can be precipitated by increasing the pH of uranyl solutions.

Of course, we would not claim that no other complexes are found than those of the series (4). However, since it gives a good approximation to the equilibrium data in the range studied, and is easy to combine with the structure data, we hope that the mechanism proposed will contain some essential features of the process.

## SUMMARY

Ahrland's data[1] on the hydrolysis of $UO_2^{2+}$ in 1 C $NaClO_4$ medium at 20° C have been recalculated using methods for treating polynuclear complexes which have since been published[2-4]. It was found that the data can be explained assuming that all complexes formed in appreciable amounts can be written in the form (4), $UO_2((OH)_2UO_2)_n^{2+}$, or, which is equivalent, $UO_2(OUO_2)_n^{2+}$. This follows from the fact that $Z$ (the number of $H^+$ split off per $UO_2^{2+}$) is, within the experimental error, a function of the single variable $x = \log M - 2 \log h$. No certain indication of mononuclear complexes could be found

A direct analysis of the $y(x)$ curve — $y = \frac{1}{2} Z$ — showed that several complexes with different $n$ are formed. A reasonable agreement with the experimental data could be obtained either by limited mechanisms, assuming complexes with $n = 1 \rightarrow 3$ or $1 \rightarrow 4$, or with an unlimited mechanism, assuming that complexes with all integral values for $n$ are formed. The authors are inclined to prefer the latter type of explanation.

A quite good approximation to the experimental data is obtained by the very simple assumption that the equilibrium constant for the first reaction: $UO_2^{2+} + H_2O + UO_2^{2+} \rightleftharpoons (UO_2)_2O^{2+} + 2\ H^+$ is $10^{-6.05\pm0.1}$, and that the equilibrium constants for all the following reactions: $UO_2(OUO_2)_n^{2+} + H_2O + {} + UO_2 \rightleftharpoons UO_2(OUO_2)_{n+1}^{2+} + 2\ H^+$ is $10^{-6.35\pm0.1}$.

In view of X-ray evidence on the structure of compounds that may be precipitated from uranyl solutions, it seems reasonable that the complexes are sheet-like, probably with double OH bridges (Fig. 7b). The most correct formula would thus be $UO_2((OH)_2UO_2)_n^{2+}$.

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## REFERENCES

1. Ahrland, S. *Acta Chem. Scand.* **3** (1949) 374.
2. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 299 (= ABI).
3. Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 318 (= ABII).
4. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1607 (= Part VIII).
5. Hietanen, S. *Acta Chem. Scand.* **8** (1954) 1626 (= Part IX).
6. Faucherre, J. *Compt. rend.* **227** (1948) 1367.
7. Sutton, J. *J. Chem. Soc.* **1949** S 275.
8. Samson, S. and Sillén, L. G. *Arkiv Kemi, Mineral. Geol.* **25 A** (1947) No. 21.
9. Zachariasen, W. H. *Acta Cryst.* **1** (1948) 281.

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