ACTA CHEMICA SCANDINAVICA 10 (1956) 705—718

On the Complex Chemistry of the Uranyl Ion

VIII. The Complexity of Uranyl Fluoride

STEN AHRLAND, RAGNAR LARSSON and KJELL ROSENGREN

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The complexity of the uranyl fluoride system has been determined by measurements of [H+] in fluoride buffers. A perchlorate medium of ionic strength 1 M was used at a temperature 20° C. In the concentration range investigated ($C_M \leq 100$ mM; $C_A \leq 400$ mM) a strong mononuclear complex formation takes place between UO_2^{2+} and F^-, with $UO_2F_4^{2-}$ as the upper limit (Table 7). Neither polynuclear complexes, nor complexes containing HF_2^- seem to exist in this range. — The constants of the hydrogen fluoride system in the present medium were also obtained.

In the systems of complexes investigated so far, the uranyl ion is usually able to coordinate with not more than three ligands. This is the case for the acetate [1], chloroacetate [2] and glycolate [3] systems in aqueous solution and also for the nitrate systems in ketonic solvents [4]. These results are also corroborated by the existence of compounds in the solid state evidently containing groups such as $UO_2(CH_3 \cdot COO)_3^-$ and $UO_2(CO_3)_3^{4-}$ (*e. g.* Ref. [5, p. 158]).

The only exception seems to be the fluoride system, where a complex $UO_2F_4^{2-}$ has been reported in solution [6]. The same group is moreover present [7] in solid $K_3UO_2F_5$. As has already been reported [8] preliminarily, the present measurements confirm that four F^- can be taken up as ligands. In fact four should most probably be regarded as the maximum coordination number of the uranyl ion as this number would be displayed by the fluoride system on account of the high stability of the complexes and the small size of the ligand.

CALCULATION OF THE COMPLEXITY CONSTANTS FROM MEASUREMENTS OF [H+] OF FLUORIDE BUFFERS

A good method for investigating systems of strong complexes is the determination of the free ligand ion concentration [A], with subsequent calculation of the complex formation function * $\bar{n} = f([A])$. From this function the complexity constants and the composition of the system for a given value of [A] can always be calculated according to established methods [2] using the function X, here denoted X_M.

In a system like the present one where the ligand is the anion of a weak acid, [A] can be found from potentiometric measurements of $[H^+]$ in a buffer solution of the ligand and its corresponding acid. This method has also been used for the aqueous uranyl systems mentioned above. For these systems, the connection between $[H^+]$ and [A] is very simple, for the fluoride system it is somewhat more complicated owing to the peculiar property of F^- to form HF_2^- and possibly also H_2F_2 beside HF. Moreover HF_2^- may be able to form complexes with UO_2^{2+}, thus competing with the complex formation of F^-.

On the other hand no hydrolytic reactions are likely to occur under the conditions chosen for the present measurements. Those solutions which contained only little fluoride were so acid that no hydrolysis was possible and as the pH gradually rose to fairly high values, ≈ 5, with increasing concentration of fluoride, UO_2^{2+} was probably well protected by the simultaneous strong complex formation with F^- (*cf.* Ref.[1]). This was confirmed experimentally since the formation function was independent of $[H^+]$ (see p. 713).

The measurements were carried out as titrations (*cf.* Ref. [9, p. 383]). Portions of a fluoride solution were added to a certain volume of perchloric acid solution and $[H^+]$ of the resulting solution measured by means of the quinhydrone electrode. In the main series, the solutions also contained a uranyl concentration C_M, but measurements had also to be performed with solutions free from uranyl ions. As in the previous parts of this series, all solutions had a constant ionic strength $I = 1$ M, sodium perchlorate being used as the supplementary neutral salt. The temperature was also the same as before, 20° C.

The half-cell containing buffer was connected with the same reference electrode RE as used before [9]. The emf of the cell thus formed is given by

$$E = E_d + \frac{RT}{F} \ln \frac{[H^+]_0}{[H^+]} \qquad (1a)$$

In the initial perchloric acid solution before the addition of fluoride, $[H^+] = C_H$. For this special case eqn. (1 a) becomes

$$E^{(i)} = E_d^{(i)} + \frac{RT}{F} \ln \frac{[H^+]_0}{C_H} \qquad (1b)$$

Hence
$$E - E^{(i)} - E_d + E_d^{(i)} = E_H = \frac{RT}{F} \ln \frac{C_H}{[H^+]} \qquad (2)$$

As the difference of the liquid junction potentials $E_d - E_d^{(i)}$ can be estimated in separate experiments (p. 711), eqn. (2) permits the calculation of $[H^+]$ (or $C_H/[H^+]$). Hence [A] is calculated in the following way.

If all complexes which are mentioned above are considered as possibly existing, C_H can be written as

$$C_H = [H^+] + [HA] + [HA_2] + 2[H_2A_2] + \sum_{q=1}^{Q} q\ [M(HA_2)_q]$$

---

* Unless stated otherwise, the same symbols are used as in the previous parts I—VII of this series.

where A = F^- and M = UO_2^{2+}. Introducing

$$[HA] = \delta_1[H^+][A] \qquad (3) \qquad\qquad [HA_2] = \delta_2[H^+][A]^2 \qquad (4)$$

$$[H_2A_2] = \delta_2''[H^+]^2[A]^2 \qquad (5) \qquad [M(HA_2)_q] = \eta_q[M][H^+]^q[A]^{2q} \qquad (6)$$

we obtain

$$C_H/[H^+] = 1 + \delta_1[A] + \delta_2[A]^2 + 2[H^+]\delta_2''[A]^2 + [M]\sum_{q=1}^{Q} q \cdot \eta_q [H^+]^{q-1}[A]^{2q} \qquad (7)$$

The function experimentally determined from eqn. (2) thus generally depends upon [A], [H^+] and [M]. If complexes containing HF_2^- do not exist in perceptible amounts, then the function will be independent of [M], and [A] can be calculated from eqn. (7) provided the constants δ are known.

Still more complicated complexes could be conceived, *e. g.* mixed complexes containing both F^- and HF_2^- as ligands, or polynuclear HF_2^--complexes. But this would introduce no new variable and therefore no further essential complication. The function (7) may thus be regarded as the general case.

If on the other hand values of [A] are calculated from eqn. (7) on the assumption that HF_2-complexes do not exist and they in fact do, then the computed values of [A] will be in error. However, the error will decrease as [M] (i. e. C_M) decreases and will finally disappear when $C_M \rightarrow 0$. It should therefore in any case be possible to obtain the right values of [A] by a method of extrapolation.

From the values of [A] found, the corresponding values of the ligand number of the metal ion $\bar{n}_M$, *i. e.* the complex formation function of the UO_2^{2+}—F^- system, are calculated according to

$$\bar{n}_M = \frac{C_A - [A] - \bar{n}_H \cdot C_H}{C_M} \qquad (8)$$

where $\bar{n}_H$ is the ligand number of the hydrogen ion. This quantity, defined as the mean number of fluoride ions bound by each hydrogen ion is generally given by:

$$\bar{n}_H = \frac{\delta_1[A] + 2\delta_2[A]^2 + 2[H^+]\delta_2''[A]^2 + 2[M]\sum_{q=1}^{Q} q \cdot \eta_q\,[H^+]^{q-1}[A]^{2q}}{1 + \delta_1[A] + \delta_2[A]^2 + 2[H^+]\delta_2''[A]^2 + [M]\sum_{q=1}^{Q} q \cdot \eta_q\,[H^+]^{q-1}[A]^{2q}} \qquad (9)$$

Thus the same condition applies to the calculation of $\bar{n}_H$ from eqn. (9) as to that of [A] from eqn. (7): if no HF_2^--complexes exist $\bar{n}_H$ may be calculated directly, if on the contrary such complexes exist, eqn. (9) gives the correct values of $\bar{n}_H$ when $C_M \rightarrow 0$. When [A] and $\bar{n}_H$ are known, $\bar{n}_M$ can be calculated from (8).

Therefore, if no HF_2^--complexes exist, all values of C_M will give the correct complex formation function, and if such complexes really do exist the correct values can in any case be calculated when $C_M \rightarrow 0$. In such a case however, we will find the complex formation function dependent on C_M when formally calculated on the assumption that $\eta = 0$.

As has been repeatedly pointed out before, even the true complex formation curve is dependent upon C_M, if polynuclear complexes exist[10, 11, 9]. Therefore if the function is found to depend upon C_M there may be two different reasons. On the other hand if it is found to be independent of C_M we may safely conclude that neither complexes of HF_2^- nor polynuclear ones exist as it is most improbable that these two factors would just compensate each other over the whole ranges of [A] and C_M used.

The constants δ necessary for the calculation of [A] and $\bar{n}_H$ are determined by separate titration series with solutions containing no uranyl ions. The symbols referring to those are denoted by primes in the following. For a solution of the same C_H as above, the emf, E_H', corresponding to E_H of eqn. (2) is given by

$$E'—E^{(i)} — E_d' + E_d^{(i)} = E_H' = \frac{RT}{F} \ln \frac{C_H}{[H^+]'} \qquad (10)$$

In this case we obtain

$$C_H/[H^+]' = 1 + \delta_1[A]' + \delta_2([A]')^2 + 2[H^+]'\delta_2''([A]')^2 \qquad (11)$$

The function $C_H/[H^+]'$ determined experimentally is thus generally dependent upon $[A]'$ and $[H^+]'$. If however H_2F_2 does not exist in the solution, $C_H/[H^+]'$ will be a function of $[A]'$ only. In any case, this will be true when $C_H \rightarrow 0$ and, consequently, $[H^+] \rightarrow 0$. Thus the limiting function will be

$$\lim_{C_H \rightarrow 0} C_H/[H^+]' = 1 + \delta_1[A]' + \delta_2([A]')^2 = X_H \qquad (12)$$

When corresponding values of $(C_H/(H^+]')_{C_H=0}$ and $[A]'$ are known δ_1 and δ_2 can be calculated from eqn. (12) (*cf.* Ref.[2, p. 787]).

The determination of the limiting function (12) is carried out by the Fronaeus' method[11 p. 18], *i. e.* corresponding values of E_H' and C_A for series of different values of C_H are plotted and the resulting family of curves is cut at a number of values of E_H'. The corresponding values of C_H and C_A thus found are now plotted with E_H' as parameter. The resulting lines when extrapolated to $C_H = 0$ give $C_A = [A]'$ corresponding to $(C_H/[H^+]')_{C_H=0}$ for each line. Moreover, this value of $(A]'$ will remain constant along the line of constant E_H' (*i. e.* constant $C_H/[H^+]'$) if H_2F_2 does not exist, as seen from eqns. (10) and (11). The ligand number $\bar{n}_H'$ of these solutions free from uranyl ions is, according to the definition of p. 707 given by the formula

$$\bar{n}_H' = (C_A — [A]')/C_H \qquad (13)$$

and if H_2F_2 does not exist it is connected with $[A]'$ according to (*cf.* eqn. (9))

$$\bar{n}_H' = \frac{\delta_1[A]' + 2\delta_2([A]')^2}{1 + \delta_1[A]' + \delta_2([A]')^2} \qquad (14)$$

Therefore $\bar{n}_H'$ is constant too along a line of constant $[A]'$. The C_A, C_H lines of constant E_H' will therefore in such a case be straight ones with the slope $k_E = \bar{n}_H'$, as evident from eqn. (13).

If on the other hand H_2F_2 really exists in perceptible amounts then neither $[A]'$ nor $\bar{n}_H'$ are constant along a line of constant E_H'. The slope k_E will then not be $\bar{n}_H'$, but another quantity $< \bar{n}_H'$ (*cf.* Fronæus[11, p. 21]). A comparison between the values of $\bar{n}_H'$ calculated from eqn. (14) using the values of δ_1 and δ_2 found from eqn. (12) and the slope k_E of the C_A, C_H lines will therefore reveal if H_2F_2 really does exist. In fact it does not, and in the following calculations of $\bar{n}_M = f([A])$ the terms referring to this complex are therefore omitted.

It is however necessary to exercise some care when using the values of δ_1 and δ_2 so found for calculating [A] in the way described on p. 707. Unfortunately, δ_1 and δ_2 vary perceptibly as the medium is altered by the exchange of perchlorate for fluoride. The values of δ_1 and δ_2 found apply to a perchlorate medium, and are therefore not sufficiently exact when C_A is high, especially as [A] must be determined as precisely as possible at high C_A on account of the gradual decrease of the difference C_A—[A] relative to [A] which always makes the computation of high values of $\bar{n}_M$ rather uncertain (*cf.* Refs.[1, 3]).

Therefore high values of [A] should be calculated using values of δ valid at these [A]. It is however not necessary to carry out a formal calculation of these values, instead [A] may be found by an appropiate modification of the method used previously[1–3] for simple acid systems.

From eqns. (10) and (2) the difference E_A is given by

$$E_H' - E_H = E_A = \frac{RT}{F} \ln \frac{[\mathrm{H}^+]}{[\mathrm{H}^+]'} \tag{15}$$

Combining eqns. (15) and (4) and setting $[\mathrm{HA}_2]/[\mathrm{HA}_2]' = \alpha_2/\alpha_2'$ ($\alpha_2 = [\mathrm{HA}_2]/C_H$ and $\alpha_2' = [\mathrm{HA}_2]'/C_H$, *cf.*[2]) we obtain

$$2\ln \frac{[\mathrm{A}]'}{[\mathrm{A}]} = \frac{E_A}{RT/F} + \ln \frac{\alpha_2'}{\alpha_2} \tag{16}$$

Combining eqns. (15) and (3) we obtain analogously

$$\ln \frac{[\mathrm{A}]'}{[\mathrm{A}]} = \frac{E_A}{RT/F} - \ln \frac{\alpha_1}{\alpha_1'} \tag{17}$$

where $\alpha_1 = [\mathrm{HA}]/C_H$ and $\alpha_1' = [\mathrm{HA}]'/C_H$. At high values of [A], $[\mathrm{H}^+]$ is negligible compared with [HA] and $[\mathrm{HA}_2]$. Therefore

$$\alpha_1 + \alpha_2 = 1 \tag{18}$$

Moreover the following connection exists (*cf.* eqn. (14))

$$\alpha_1 + 2\alpha_2 = \bar{n}_H \tag{19}$$

Hence $\alpha_2 = \bar{n}_H - 1$ and $\alpha_1 = 2 - \bar{n}_H$ which when combined with eqns. (16) and (17) give

$$2\ln \frac{[\mathrm{A}]'}{[\mathrm{A}]} = \frac{E_A}{RT/F} + \ln \frac{\bar{n}_H' - 1}{\bar{n}_H - 1} \tag{20}$$

and

$$\ln \frac{[\mathrm{A}]'}{[\mathrm{A}]} = \frac{E_A}{RT/F} - \ln \frac{2 - \bar{n}_H}{2 - \bar{n}_H'} \tag{21}$$

Hence [A] can be calculated by a series of approximations utilizing the fact that $[A]' = C_A - \bar{n}_H' \cdot C_H \approx C_A$ at high values of C_A. A sufficiently good value of [A]$'$ can therefore be found by successive approximations using values of $\bar{n}_H'$ obtained from eqn. (14) with the values of δ calculated previously. As [A] is not too far from [A]$'$, $\bar{n}_H \approx \bar{n}_H'$ and an approximate value of [A] can thus be calculated from eqn. (20) (if $\bar{n}_H' > 1.5$) or eqn. (21) (if $\bar{n}_H' < 1.5$). From this value of [A] a better value of $\bar{n}_H$ is obtained. Inserted in eqns. (20) or (21) the new $\bar{n}_H$will yield a better value of [A] and so by successive approximations the true value of [A] will finally be found.

In practice all values of [A] are first calculated according to the method first mentioned and then, starting with highest ones, recalculated by the more laborious method of E_A using eqns. (20) and (21) until this method gives a value of [A] identical with that found from δ_1 and δ_2.

EXPERIMENTAL

Chemicals: Uranyl perchlorate was prepared as before [9]. Its purity was proved by the fact that the solution had an extinction curve identical to that of the carefully purified preparation used before. The exact concentration of the stock solution (C_M = 334 mM) was determined cerimetrically.

The excess of perchloric acid in the present preparation was determined potentiometrically. A sample of the stock solution, suitably diluted, was titrated with a perchloric acid solution, and $[H^+]$ of the solutions thus obtained was measured by means of a quinhydrone electrode connected with the usual reference electrode RE of $[H^+]_0$ = 10.06 mM. As I = 1 M throughout the cell $[H^+]$ can be calculated directly from the emfs measured provided a correction is applied for the liquid junction potentials between solutions of different $[H^+]$ (*cf.* p. 711). The differences between the values of $[H^+]$ thus found and those stoichiometrically calculated from the amounts of perchloric acid added will give the acid content of the uranyl salt, provided the hydrolysis of the uranyl ion is negligible. This is the case [9] when $[H^+] > 10$ mM and in fact a constant difference = 8.3 ± 0.3 mM was found in the present titration where the value of $[H^+]$ measured increased from 8.2 to 67.2 mM while C_M was kept constant = 33.4 mM. The amount of free acid in the stock solution is thus 83 mM. This method of determining free acid in the presence of the fairly acidic uranyl ion is much more satisfactory than the method of potentiometric titration with alkali used previously.

Perchloric acid was of analytical grade and *sodium perchlorate*, Ciba *purum*, was purified and tested as described before [9].

Sodium fluoride: First a preparation "Bakers analyzed", lot No 3593, was used. A stock solution with C_A = 600 mM and I = 1 M was prepared. Such a solution should have pH ≈ 8.4. The present one contained excess alkali and perchloric acid was therefore added until phenolphtalein was decolourized. The solution was kept in a polythene bottle where its pH remained constant. (The pH soon rose perceptibly when the solution came into contact with glass.) During the measurement the fluoride solution had to be added from a glass burette. The titrations therefore had to be completed within about two hours; during this time no perceptible increase of pH had occurred. By use of this stock solution series of titrations with C_H = 5, 10, 15, and 25 mM, with no uranyl ions present, were first performed in order to investigate the hydrogen fluoride system. After that three uranyl ion titrations were carried out with C_M' = 10 mM, C_H = 10 mM; C_M' = 25 mM, C_H = 10 mM; and C_M' = 25 mM, C_H = 25 mM respectively * yielding three sets of values of the formation function $\bar{n}_M = f([A])$.

At this stage it became desirable to extend the search for polynuclear complexes by using higher values of [M]. Another preparation of sodium fluoride "Baker analyzed", lot No. 5093, had then to be used. As a check, the uranyl free titrations of C_H = 10 and

---

* C_M' = initial value of C_M in a series of measurements (*cf.* p. 711).

25 mM were repeated with a stock solution of this preparation. In spite of the fact that this solution did not contain any free alkali, as shown by its pH, perceptibly higher values of E_H were found than before, especially for the lower value of C_H = 10 mM. The difference became greater with increasing C_A, finally reaching ≈ 3.5 mV for C_H = 10 mM. Evidently the presence of a base much stronger than F^- must be suspected but on the other hand it cannot be very strong as shown by the pH of the solution. A potentiometric titration of the fluoride stock solution also revealed that it possessed a buffering region around pH 7. The amount of the foreign base could be estimated as ≈ 0.4 mole %. This prompted us to investigate a sample left of the first stock solution, and we found that it also contained the same basic impurity but in only about half the amount. It could therefore be assumed that E_H and hence the constants of the hydrogen fluoride system are slightly in error as determined by use of the first stock solution. The figures of the uranyl system on the other hand should not be much affected as they are calculated from the difference between two series of measurements of the same C_H, one with and the other without uranyl ions, which both ought to contain the same error in their emfs.

The foreign basic substance is evidently connected with the hydrolysis of the fluosilicate, present as an impurity in the fluoride preparations. It should however be possible to remove its influence by repressing this hydrolysis in advance. In fact the titration curve of the stock solution shows a minimum of buffer capacity at pH ≈ 6.3. An adjustment of pH to this value will therefore prevent further consumption of H^+ by the fluosilicate, while F^- is still left unaffected by H^+.

When the check titrations of C_H = 10 and 25 mM were repeated with such a solution, E_H had in fact decreased and moreover to a value lower than that found with the first stock solution, as could be expected. This difference is at most only 2 mV and the new constants of the hydrogen fluoride system are therefore only slightly different from those previously determined. Series of measurements were then made with uranyl solutions of C_M = 50 and 100 mM, both having C_H = 25 mM. As expected the formation function $\bar{n}_M$ = f ([A]) hence obtained does not deviate essentially from that found by the previous measurements (*cf.* p. 713).

Apparatus: The electrode vessel used for the fluoride buffers was made from methacrylate plastic (»plexiglas»). The stems of the electrodes, the burette tips and other parts which might come into contact with these solutions were also made from plastic (»perspex» tubing). These plastics are completely resistant towards the solutions used. The plexiglas especially has a good transparancy and both are moreover easily worked. The solutions are mixed by a stream of nitrogen gas free from oxygen [9], and the gas inlet tube could also be used to remove the last drop from the burette tips.

Procedure: To a known volume of a solution of known C_M and C_H present in the electrode vessel initially fluoride stock solution was added from one burette and perchloric acid was added from another, in order to keep C_H of the buffer constant during the titration. In the later measurements, the acid solution of the second burette also contained uranyl ions so as to keep also C_M constant. This is not necessary but simplifies the calculations somewhat.

The potentials measured were reproducible within ±0.2 mV and they attained their final values almost at once.

MEASUREMENTS

The solutions are so acid at the outset that perceptible liquid junction potentials must exist. Approximately these potentials are determined merely by $[H^+]$. They may therefore be determined by separate titrations of 1 M

Table 1. The liquid junction potential E_d *as a function of* E. $[H^+]_0$ = *10 mM.*

E mV	>40	30	20	10	0	−10	−20	−30
E_d mV	−0.6	−0.5	−0.3	−0.2	0	0.3	0.9	1.7
$[H^+]$ mM	<2.0	3.0	4.5	6.7	10	15	23	35

sodium perchlorate with a perchloric acid solution. The difference between the emfs found and those calculated stoichiometrically are considered to be liquid junction potentials, the activity conditions assumed to be constant as usual. In Table 1, smoothed values of E_d (or E_d') for some round E (or E') are tabulated together with the corresponding values of [H$^+$]. From these figures all resulting liquid junction potentials for the calculation of E_H (or E_H') are easily found (*cf.* eqns. (2) and (10)).

The measurements of the hydrogen fluoride system then performed are tabulated in Table 2 A for the first fluoride preparation and in Table 2 B for the second one. The C_H, C_A function of Table 2 A are straight lines, the slopes of which agree fairly well with the ligand number $\bar{n}_H'$ calculated from (14) Fig. 1. In fact k_E is for some reason even a little higher than $\bar{n}_H'$. Thus H_2F_2 does not exist at the concentrations used here. The constants found are slightly higher for the first preparation than for the second one. For δ_1, the

Table 2. The complexity constants of the hydrogen fluoride system.

C_H mM	25	15	10	5	0	X_H	X_{1H} M^{-1}	X_{2H} M^{-2}	k_E
E_H mV	C_A mM				$C_A = [A]$				
A. First fluoride preparation $\delta_1 = 870 \pm 30$ M^{-1} $\delta_2 = 3\,300 \pm 300$ M^{-2}									
25	18.4	12.1	8.7	5.2	1.95	2.69	870		0.66
40	25.5	17.1	13.0	8.7	4.4	4.88	880		0.85
55	32.8	23:2	18.4	13.6	8.7	8.84	900	3 500	0.96
70	42.4	31.9	26.7	21.2	15.9	15.95	940	4 400	1.06
85	57.2	45.8	40.3	34.8	29.2	29.0	960	3 100	1.11
100	80.5	67.7	61.8	56.2	49.8	52.5	1 035	3 300	1.22
110	103.3	89.5	83.5	76.8	70.1	78.1	1 100	3 300	1.35
120	132.0	118.5	111.2	104.4	97.3	115.7	1 180	3 200	1.60
130	172.0	155.7	147.2	138.5	130.0	171.9	1 320	3 500	
140	222	204	196	185	177	256	1 440	3 200	
150	287	265	257	242	234	380	1 620	3 200	
B. Second fluoride preparation $\delta_1 = 850 \pm 30$ M^{-1} $\delta_2 = 2\,600 \pm 300$ M^{-2}									
50	31.2		16.7		7.0	7.25	890		0.97
70	43.7		27.6		16.9	15.95	890		1.07
90	65.9		48.4		36.7	35.4	940	2 460	1.17
100	83.5		65.2		53.0	52.5	970	2 260	1.22
110	107.3		87.6		74.5	78.1	1 040	2 550	1.31
120	138.4		117.3		103.2	115.7	1 120	2 620	1.41
130	179.4		155.8		140.1	171.9	1 220	2 650	1.57
140	232.5		207		190	256	1 350	2 640	
150	298		271		253	380	1 500	2 570	
155	339		309		289	464	1 600	2 600	
160	389		355		332	564	1 700	2 560	

difference is within the experimental error, but for δ_2 it is just beyond. For reasons mentioned above the second set is thought to be the best one. As the series with the two preparations were so close together, measurements with the second one were confined to the two values of C_H already mentioned. The values of k_E obtained from the lines through the two points at each E_H agree however tolerably well with the $\bar{n}_H'$ calculated from δ_1 and δ_2, Fig. 1. — For the same medium Sundén [12] has found $\delta_1 = 840$ M^{-1} and $\delta_2 \approx 1700$ M^{-2}.

The three uranyl series performed with the first stock solution are tabulated in Tables 3 and 4. Table 3 contains the series of the same $C_H = 10.17$ mM having $C_M = 10$ and 25 mM at the outset. The formation functions, shown in Fig. 2, coincide completely within the experimental errors (which are most marked at high [A], *cf.* p. 709). This proves that neither polynuclear complexes nor complexes containing HF_2 exist in the solutions measured (*cf.* p. 708). Table 4 contains the series of $C_H = 25.43$ mM, $C_M = 25$ mM. The formation function found coincides with those already obtained, Fig. 2, thus proving that no noticeable hydrolysis exists in the solutions [1].

The two uranyl titrations performed with the second stock solution have both $C_H = 25.00$ mM. They are tabulated in Table 5 and the values of $\bar{n}_M$ and [A] are plotted in Fig. 2. The formation function of $C_M = 50$ mM coincides very well with that of lower C_M. Perhaps a slight deviation downwards could be traced for the very lowest values of [A]. For the series of $C_M = 100$ mM a deviation for low [A] is quite perceptible, but nevertheless the coincidence is complete for this series also as soon as [A] > 0.2 mM.

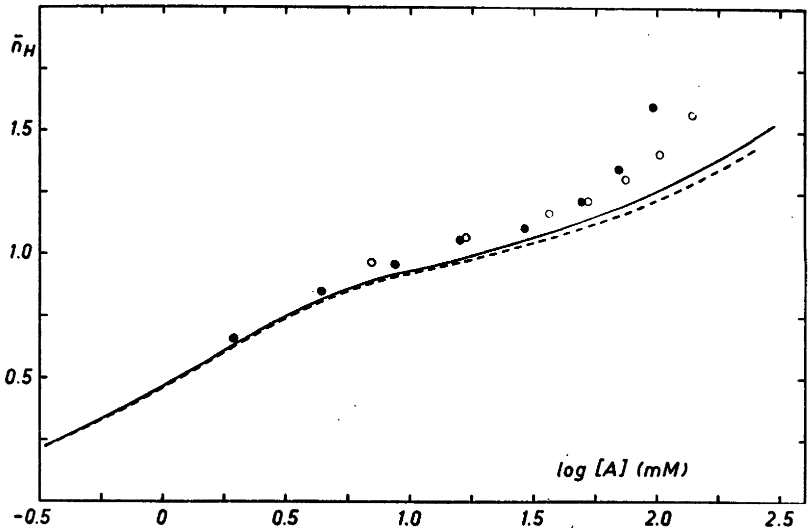

Fig. 1 Complex formation function of the hydrogen fluoride system. —

Curves calculated from (14) with the values of δ_1 and δ_2 found, circles obtained from the slopes k_E of the C_H, C_A-lines of constant E_H'. First fluoride preparation: fulldrawn curve and filled circles; second preparation: dashed curve and open circles.

This deviation at high C_M cannot be attributed to a formation of polynuclear complexes as this would cause the formation curve to move upwards instead of downwards as here (*cf.* Refs.[9, 11, p. 16]). The most probable explanation is a considerable change in the activity conditions caused by the high uranyl concentration since the uranyl salt is responsible for 1/3 of the ionic strength of the solution. Alternatively a small change in the liquid junction potentials might be the cause. E_H is < 3.5 mV in this region and a quite small systematic error in the emf measured will therefore have a very marked effect.

Thus a mononuclear complex formation between UO_2^{2+} and F^- is the only reaction involving UO_2^{2+} which takes place in the present solutions. From the bend of the complex formation curve towards $\bar{n}_M = 4$ it is plain that $UO_2F_4^{2-}$ is the upper limit of this complex formation, at least within the range investigated here ($[A] < 300$ mM).

From the complex formation function thus found the complexity constants were calculated [2], Table 6. As $\bar{n}_M/[A]$ increases very rapidly for low [A] a finite value $[A]_0 = 0.04$ mM was chosen as the lower limit of integration when $X_M([A])$ was computed. The values of β found are given in Table 7 together with the ligand number and the composition of the system calculated [2] for some values of [A]. The formation curve thus found is introduced in Fig. 2 (fulldrawn). As seen it fits the experimental points very well *.

Table 7 also contains the consecutive constants [3] b and the ratios b_n/b_{n+1}. Especially the first and third ratios have unusually high values [3, 10, 11] indicating a remarkable stability of the first and third complexes. Consequently the maximum values of α_1 and α_3 (at $\bar{n}_M = 1$ and 3) are unusually high. High values of b_n/b_{n+1} seems to be a common feature of many strong fluoride systems, (for ref. see [13]) but it is quite contrary to that displayed by other uranyl systems [3], especially the acetate.

COMPARISON WITH PREVIOUS WORK

The strong complexity of uranyl fluoride was recognized during the early work on atomic energy but the first quantitative investigation is due to Kraus [14], who found $\beta_1 = 2.1 \times 10^4$ M^{-1} by an ion exchange method in an ionic medium not stated. The spectrophotometric work of Blake, Lowrie and Brown [6] gave $\beta_1 \approx 3 \times 10^5$ M^{-1} and moreover evidence was found for $UO_2F_4^{2-}$, with a value of $\beta_4 \approx 10^8$ M^{-4}. The method used was not very accurate nor was a constant ionic medium maintained. The results are therefore very approximate, and the authors themselves give the uncertainty as one power of ten. Day and Powers [15] have investigated the fluoride complexes in perchlorate medium at several temperatures and ionic strengths by means of TTA-extraction. Owing to the strong complexity a conveniently measurable partition was obtained only for low C_A. Only the first constant $[UO_2F^+][H^+]/[UO_2^{2+}][HF]$ can therefore be computed. For 20° C, $I = 1$ M a value ≈ 34 is found by inter-

---

* The values of β given here deviate slightly from those of the preliminary note [8]. It has been found that the formation curve obtained from the present values gives a somewhat better fit to the experimental points than did the curve from the previous ones.

Table 3. Determination of $\bar{n}_M$ *as a function of* $[A]$ *for* $C_M = 10$ *and 25 mM,* $C_H = 10.17$ *mM.*

C_M' mM	10					25				
$E^{(i)}$ mV	0.0					0.1				
C_A mM	C_M mM	E_H mV	X_H	[A] mM	$\bar{n}_M$	C_M mC	E_H mV	X_H	[A] mM	$\bar{n}_M$
8.83	9.81	1.3	1.053	0.061	0.843	24.5	0.3	1.012	0.014	0.355
17.3	9.62	6.9	1.314	0.361	1.51	24.05	1.0	1.040	0.046	0.73
25.5	9.44	17.6	2.007	1.15	2.04	23.6	2.4	1.100	0.115	1.04
33.4	9.27	32.9	3.68	3.05	2.47	23.15	5.3	1.234	0.269	1.35
40.9	9.10	48.8	6.89	6.60	2.79	22.75	9.4	1.451	0.518	1.63
55.9	8.78	71.6	17.05	17.3	3.18	21.95	22.7	2.456	1.66	2.17
75.0	8.33	90.4	35.8	36.0	3.35	20.65	50.8	7.47	7.24	2.84
104.0	7.70	106.9	68.7	64.4	3.58	19.25	84.5	28.4	28.5	3.36
128.6	7.14	116.9	101.5	90.5	3.57	17.85	101.3	55.3	53.4	3.56
168.7	6.25	129.3	167.0	133.1	3.54	15.6	119.6	114.0	99.2	3.64
200.0	5.56	136.7	223	166.0	3.60	13.9	129.6	168.3	135.0	3.70
225	5.00	141.9	274	193	3.5	12.5	136.1	219	163.5	3.8
262.5	4.17	148.6	360	234	3.3	10.42	144.4	303	209	3.75
300	3.33	154.2	452	272.5	3.8	8.33	151.3	399	252	3.95
338	2.50	158.9	537	311	4.6	6.25	157.2	505	298	3.9

polation, corresponding to $\beta_1 \approx 2.9 \times 10^4$ M^{-1} if $\delta_1 = 850$ M^{-1}. This result thus agrees fairly well with ours as does qualitatively also the previous ones.

Johnson and Kraus [16], and Johnson, Kraus and Young [17] have determined mean activity coefficients for uranyl fluoride by freezing point depression and

Table 4. Determination of $\bar{n}_M$ *as a function of* $[A]$ *for* $C_M' = 25$ *mM;* $C_H = 25.4$ *mM.* $E^{(i)} = -22.3$ *mV.*

C_A mM	C_M mM	E_H mV	X_H	[A] mM	$\bar{n}_M$
8.83	24.5	0.4	1.016	0.018	0.343
17.3	24.05	0.9	1.036	0.041	0.682
25.5	23.6	2.2	1.091	0.105	0.99
33.4	23.15	4.2	1.181	0.208	1.27
40.9	22.75	7.0	1.319	0.367	1.51
55.3	21.95	15.5	1.847	0.973	1.94
75.0	20.65	34.9	3.98	3.38	2.53
104.0	19.25	70.9	16.5	16.8	3.23
128.6	17.85	92.0	38.2	38.9	3.47
168.7	15.6	113.1	88.1	82.3	3.54
200.0	13.9	124.0	135.2	116.5	3.64
225	12.5	131.2	181	144.5	3.7
262.5	10.42	140.1	256	188.5	3.65
300	8.33	147.3	342	232.5	3.7
338	6.25	153.6	438	278	3.45

Table 5. Determination of $\bar{n}_M$ as a function of $[A]$ for C_M = 50 and 100 mM; C_H = 25 mM.

C_M mM	50				100				
$E^{(i)}$ mV	−22.1				−23.1				
C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$	C_A mM	E_H mV	X_H	[A] mM	$\bar{n}_M$
22.8	0.5	1.020	0.024	0.446	22.6	0.4	1.016	0.019	0.22
43.6	1.7	1.070	0.082	0.838	42.8	0.7	1.028	0.033	0.42
62.5	3.8	1.162	0.190	1.176	60.9	1.1	1.044	0.052	0.599
79.9	6.6	1.298	0.350	1.484	77.3	1.6	1.065	0.076	0.759
95.9	10.6	1.522	0.614	1.73	92.1	2.3	1.095	0.112	0.899
110.5	15.4	1.840	0.987	1.96	112.0	3.5	1.149	0.175	1.086
137.0	27.3	2.948	2.28	2.365	137.3	5.6	1.248	0.292	1.322
159.8	40.8	5.03	4.67	2.692	158.8	8.0	1.373	0.439	1.514
189.0	60.2	10.85	11.21	3.088	189.0	12.4	1.634	0.747	1.78
213	75.6	20.0	24.2	3.27	213	17.3	1.984	1.15	1.99
240	89.8	35.0	40.3	3.45	240	24.1	2.597	1.87	2.23
271	102.8	58.8	63.2	3.58	271	34.4	3.91	3.39	2.49
308	114.7	94.0	94.1	3.67	300	42.7	5.42	5.13	2.74
361.5	127.6	156.5	143.2	3.72	343	60.6	11.05	11.42	3.08
400	134.8	208	179.6	3.73	369	72.3	17.5	22.8	3.21

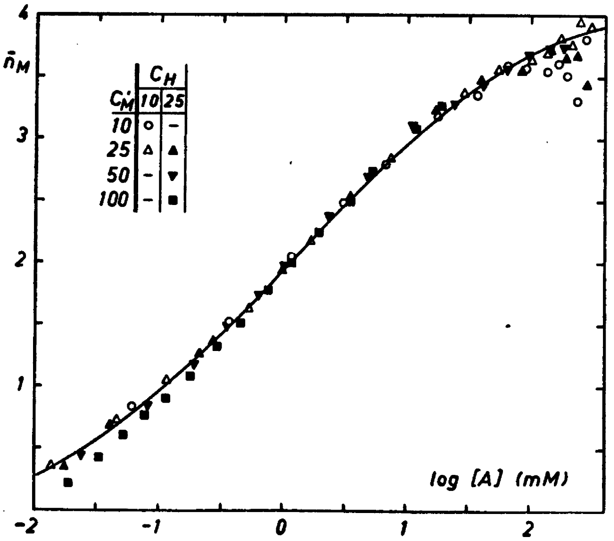

Fig. 2 Complex formation function of the uranyl fluoride system. —

The signs refer to titrations with different values of C_M and C_H according to the scheme given in the fig. The curve is obtained from the values of β found (Table 7).

Table 6. Computation of the complexity constants of the uranyl fluoride system.

[A] mM	$\frac{X([A])}{X(4 \cdot 10^{-5})}$	$X_{1M} \cdot 10^{-4}$ M^{-1}	$X_{2M} \cdot 10^{-7}$ M^{-2}	$X_{3M} \cdot 10^{-10}$ M^{-3}	$X_{4M} \cdot 10^{-11}$ M^{-4}
0	*0.39*	*3.5*	*7.8*	*2.9*	*6.5*
0.04	1.000	3.90			
0.06	1.330	4.05			
0.08	1.684	4.15	8.1		
0.1	2.060	4.30	8.0		
0.15	3.139	4.70	8.0		
0.2	4.411	5.15	8.25		
0.3	7.500	6.07	8.55		
0.5	16.30	8.13	9.26	2.9	
0.75	32.47	10.96	9.96	2.9	
1	55.82	14.20	10.70	2.9	
1.5	128.0	21.8	12.2	2.9	
2	241.5	30.9	13.7	3.0	
3	624	53.3	16.6	2.9	
5	2 340	119.6	23.3	3.1	
10	$1.67 \cdot 10^4$	427	42.3	3.45	
20	$14.7 \cdot 10^4$	1 880	93.8	4.3	
30	$54.9 \cdot 10^4$	4 690	156.0	4.94	6.7
50	$3.16 \cdot 10^6$	$1.616 \cdot 10^4$	316	6.16	6.5
100	$37.3 \cdot 10^6$	$9.55 \cdot 10^4$	955	9.47	6.6
150	$165.2 \cdot 10^6$	$28.2 \cdot 10^4$	1 880	12.48	6.4
200	$490 \cdot 10^6$	$62.7 \cdot 10^4$	3 140	15.7	6.4
300	$2300 \cdot 10^6$	$196.5 \cdot 10^4$	6 540	21.8	6.3

ultracentrifugation experiments. They interpret their results by assuming that the main equilibrium of the solution is $2\ UO_2F_2 \rightleftharpoons (UO_2F_2)_2$. We have here in fact found no polynuclear complexes for $C_M \leq 100$ mM but of course

Table 7. The constants found. The ligand number and the percentage composition of the system as calculated for some values of [A] with these constants.

$\beta_1 = (3.5 \pm 0.4) \cdot 10^4\ M^{-1}$ $\beta_2 = (7.8 \pm 0.8) \cdot 10^7\ M^{-2}$ $\beta_3 = (2.9 \pm 0.4) \cdot 10^{10}\ M^{-3}$ $\beta_4 = (6.5 \pm 1.5) \cdot 10^{11}\ M^{-4}$

$b_1 = \beta_1$ $b_2 = 2\ 200\ M^{-1}$ $b_3 = 370\ M^{-1}$ $b_4 = 22\ M^{-1}$

$b_1/b_2 = 16$ $b_2/b_3 = 6$ $b_3/b_4 = 17$

[A] mM	$\bar{n}_M$	a_0	a_1	a_2	a_3	a_4
0.01	0.26	74	26	0	0	0
0.03	0.56	47	49.5	3.5	0	0
0.1	0.96	19	66	14.5	0.5	0
0.3	1.39	5	54.5	36.5	4	0
1	1.94	0.5	24.5	54.5	19.5	0.5
3	2.46	0	6.5	43	47	3
10	2.96	0	1	18.5	66	15
30	3.34	0	0	5	56.5	38.5
100	3.68	0	0	1	30.5	68.5
300	3.87	0	0	0	13	87

this does not exclude the formation of such complexes in more concentrated uranyl solutions. The result that this dimerisation is increasing when excess fluoride is added is however very surprising. One would have expected that an increase of [A] would have favoured the formation of complexes richer in A, such as $UO_2F_3^-$ and $UO_2F_4^{2-}$. As shown above these complexes are in fact the predominating species of solutions which are not very different from those investigated by Johnson, Kraus and Young.

This work has been supported by grants from *Atomkommittén (The Swedish Atomic Committee)* and *Statens naturvetenskapliga forskningsråd (Swedish Natural Science Research Council)*. We wish to thank Dr. F. J. C. Rossotti whose reading of our manuscript has resulted in improvements of both language and content.

REFERENCES

1. Ahrland, S. *Acta Chem. Scand.* **5** (1951) 199 (= IV).
2. Ahrland, S. *Acta Chem. Scand.* **3** (1949) 783 (= II).
3. Ahrland, S. *Acta Chem. Scand.* **7** (1953) 485 (= VII).
4. Kaplan, L., Hildebrandt, R. A. and Ader, M. *ANL*-4520 (1950).
5. *The Actinide Elements, NNES IV-14A* New York 1954.
6. Blake, C. A., Lowrie, R. S. and Brown, K. B. *AECD*-3212 (1951).
7. Zachariasen, W. H. *Report CK*-2737 (1945) (quoted in Katz, J. J. and Rabinowitch, E. *The Chemistry of Uranium, NNES VIII-5* New York 1951, p. 575).
8. Ahrland, S. and Larsson, R. *Acta Chem. Scand.* **8** (1954) 354.
9. Ahrland, S. *Acta Chem. Scand.* **3** (1949) 374 (= I).
10. Leden, I. *Potentiometrisk undersökning av några kadmiumsalters komplexitet*, Thesis, Lund 1943.
11. Fronæus, S. *Komplexsystem hos koppar*, Thesis, Lund 1948.
12. Sundén, N. *Svensk Kem. Tidskr.* **66** (1954) 50.
13. McKay, H. A. C., *A.E.R.E.* C/R 884 (1952).
14. Kraus, K. A. *ORNL*-795 (1950) (quoted in Ref. 6)
15. Day, R. A. Jr. and Powers, R. M. *J. Am. Chem. Soc.* **76** (1954) 3895.
16. Johnson, J. S. and Kraus, K. A. *J. Am. Chem. Soc.* **74** (1952) 4436.
17. Johnson, J. S., Kraus, K. A. and Young, T. F. *J. Am. Chem. Soc.* **76** (1954) 1436.

Received January 23, 1956.