

Short Communications

The Complexity of Uranyl Fluoride

STEN ÅHRLAND and RAGNAR LARSSON

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

The complex formation curve of the acetate¹ and glycolate² systems of the uranyl ion bends very clearly towards $\bar{n} = 3$. The third complex of these systems thus seems to be the upper limit of the complex formation, and this may be due to several reasons.

The third complex may be a coordinatively saturated one, with every ligand occupying either one of three or two of six places of coordination available around the uranyl ion. Or the complex may in fact be unsaturated, the admission of further ligands to the remaining places of coordination being impossible for space reasons. If the places of coordination around the uranyl ion are really more than three, as postulated in the last cases, then this must be evident in relation to a small ligand of strong complex forming tendency, especially if the ligand has no possibility to form chelates. The fluoride ion seems to be fit for this test. It is the smallest anion existing and gives certainly strong complexes with the uranyl ion, as seen from some rather rough investigations³⁻⁵ previously performed.

A determination of the fluoride system will also furnish further information about the mutual strength of the halogenide systems of different cations. In this respect, the cations hitherto investigated may be divided into two distinct groups. The first of these is characterized by strong fluoride complexes whilst the complexes of the other halogenides are much weaker, with their strength decreasing in the order $\text{Cl}^- - \text{Br}^- - \text{I}^-$. Cations belonging to this

group are ⁶⁻⁸ H^+ , Fe^{3+} , In^{3+} , Zr^{4+} , very probably also ^{9-11,6} U^{4+} , Pu^{4+} , and Zn^{2+} . In certain cases, *e. g.* H^+ and Fe^{3+} , the heavier halogenides are even almost non-complex in spite of a strong fluoride complexity. The second group has very weak fluoride complexes while those of the other halogenides are strong, their strength increasing in the order $\text{Cl}^- - \text{Br}^- - \text{I}^-$. In this group Ag^+ , Cd^{2+} and probably also Hg^{2+} are found^{12,6}. A common feature of the groups is however that there is always a difference in order of magnitude between the complexity of the fluorides on one hand and that of the heavier halogenides on the other.

The determination of the free ligand concentration $[\text{A}]$ is a convenient method for the investigation of the strongly complex fluoride system. This may be done by measuring $[\text{H}^+]$ of fluoride buffers of known composition, if the constants of the hydronium fluoride system are known for the present medium ($I = 1$ C by means of NaClO_4 ; temperature 20°C). At first these constants are therefore determined, which is performed by measuring $[\text{H}^+]$ of fluoride buffers free from uranyl salt. All measurements of $[\text{H}^+]$ and $[\text{H}^+]$ are performed by means of quinhydrone electrodes. The buffers are mixed by titrating known amounts of solutions of sodium fluoride, perchloric acid, sodium perchlorate and, if wanted, uranyl perchlorate direct down in the electrode vessel. The vessel is made from methacrylate plastic (plexiglas, lucite), as is also the tips of the burettes, the stems of the electrodes and all other things which may come into contact with the acid fluoride solution. This plastic is completely resistant to hydrofluoric acid, it is also transparent and easily worked. Even the "neutral" solution of sodium fluoride cannot be kept in a glass burette more than some hours before dissolving perceptible amounts of alkali out of the glass. The stock solution is therefore stored in polythene bottles.

The determination of the hydrogen fluoride system from measurements of the

concentration of the free central ion $[H^+]$ is performed according to Fronæus¹³. Four series of the total acid concentrations $C_H = 5, 10, 15$ and 25 mC are carried out, with the total ligand concentration C_A increasing up to ≈ 335 mC in every series. It is shown that only the two mononuclear complexes HA and HA_2 exist within this range of concentration their constants

$$\delta_1 = [HA]/[H^+][A] \text{ and } \delta_2 = [HA_2]/[H^+][A]^2 \\ \text{are} \\ \delta_1 = 870 \pm 30 \text{ C}^{-1}, \delta_2 = 3\,300 \pm 300 \text{ C}^{-2}$$

With δ_1 and δ_2 known, $[A]$ of solutions containing uranyl may be calculated, and hence \bar{n} , the ligand number of UO_2^{2+} ($=M$). It must then be presumed that HA_2 does not participate in the complex formation, but the truth of this presumption is unequivocally proved by the fact that the complex formation functions computed for different C_H , i. e. different $[H^+]$, are identical. If HA_2 would be perceptibly involved in the complex formation, the formation function must be dependent of $[H^+]$. Nor is this function dependent of the total uranyl concentration C_M which proves that no polynuclear complexes exist within the range of C_M measured (≤ 25 mC).

The highest $[A]$ cannot be calculated with the stated values of δ_1 and δ_2 which are determined as means over the whole range of $[A]$ measured. Evidently the values are modified by the change of medium associated with the exchange of perchlorate for fluoride. These high $[A]$ are therefore computed from the difference E_A between the quinhydrone potentials of a buffer free from uranyl and a buffer of the same C_A containing uranyl, analogous to the method employed e. g. for the acetate system¹. Owing to the simultaneous existence of HA and HA_2 , the calculation of $[A]$ must however in the present case be performed by a series of successive approximations.

The formation function found bends clearly towards $\bar{n} = 4$. Then the upper limit of the complex series is $UO_2F_4^{2-}$, at least if $[A] \leq 300$ mC. The first four mononuclear complexes may thus exist. Their constants are calculated via the function $\bar{n}/[A]$, which is integrated with the lower limit $[A]_0 = 0.04$ mC, cf.² The functions X thus obtained give:

$$\beta_1 = (3.9 \pm 0.3) \cdot 10^4 \text{ C}^{-1} \quad b_1 = 39000 \text{ C}^{-1} \\ \beta_2 = (8.6 \pm 0.8) \cdot 10^7 \text{ C}^{-2} \quad b_2 = 2200 \text{ C}^{-1} \quad b_1/b_2 = 18 \\ \beta_3 = (3.1 \pm 0.4) \cdot 10^{10} \text{ C}^{-3} \quad b_3 = 360 \text{ C}^{-1} \quad b_2/b_3 = 6 \\ \beta_4 = (7.0 \pm 1.5) \cdot 10^{11} \text{ C}^{-4} \quad b_4 = 23 \text{ C}^{-1} \quad b_3/b_4 = 16$$

At the moderate concentrations here used, the uranyl fluoride system is composed of solely the first four mononuclear complexes, the fourth one constituting a limiting complex. Especially the second and fourth complexes show a rather weak tendency to be formed from their predecessors, as seen from the remarkably high values of b_n/b_{n+1} . This seems to be a common feature of strong fluoride systems¹⁴, Table 1, whereas e. g. the uranyl acetate system displays quite the opposite behaviour.

Evidently the uranyl ion is able to coordinate more than three ligands, e. g. in the case of fluoride four. The real number of places of coordination seems however rather hard to decide from the formulas of those limiting complexes which have hitherto been proved.

This work has been generously supported by Atomkommittén (The Swedish Atomic Committee).

1. Åhrland, S. *Acta Chem. Scand.* **5** (1951) 199.
2. Åhrland, S. *Acta Chem. Scand.* **7** (1953) 485.
3. Kraus, K. A. ORNL-795 (1950) (from a quotation in 4).
4. Blake, C. A., Lowrie, R. S., and Brown, K. B. *AECD-3212* (1951).
5. Johnson, J. S., and Kraus, K. A. *J. Am. Chem. Soc.* **74** (1952) 4436.
6. Bjerrum, J. *Chem. Revs.* **46** (1950) 381.
7. Sundén, N. (*In press*).
8. Connick, R. E., and McVey, W. H. *J. Am. Chem. Soc.* **71** (1949) 3182.
9. Åhrland, S., and Larsson, R. *Acta Chem. Scand.* **8** (1954) 137.
10. Hindman, J. C. *The Transuranium Elements, NNES IV-14B*, New-York 1949, p. 405.
11. McLane, C. K. *The Transuranium Elements*, p. 414.
12. Leden, I., and Marthén, L. E. *Acta Chem. Scand.* **6** (1952) 1125.
13. Fronæus, S. *Komplexsystem hos koppar*. Thesis, Lund 1948.
14. McKay, H. A. C. *A.E.R.E. C/R* 884 (1952).

Received December 24, 1953.