ACTA CHEMICA SCANDINAVICA 3 (1949) 783—808

On the Complex Chemistry of the Uranyl Ion

II. The Complexity of Uranyl Monochloroacetate. A Comparative Potentiometric and Extinctiometric Investigation

STEN AHRLAND

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

A great number of methods: potentiometric, extinctiometric, polarimetric, conductometric, cryoskopic, ebullioscopic and several others have been used to investigate complex systems in solution. However, only the first three of the methods mentioned give any substantial quantitative results, for only in these cases does one have the possibility to make measurements in an approximately constant salt medium of high ionic strength thus securing fairly constant conditions of activity. Only in this way can a known connection between the measured quantity and the complex concentrations be obtained.

In my first paper concerning these uranyl investigations (**Ahrland**[1], in the following referred to as I) it was established that the uranyl ion UO_2^{2+} is to be considered as a central group which may give complexes with the anions of its salt solutions. The ion is easily hydrolysed, it is true, but stable at $p[H^+]$ * < 3. The present experiments aim to investigate such a complex system of uranyl according to two of the best methods mentioned above, namely potentiometrically and extinctiometrically. With the uranyl ion, such a comparison is especially valuable, as in this case it is very often impossible to apply the potentiometric method which is the most used and proved. This is because one is not at all able to measure $[UO_2^{2+}]$ (I p. 382). In such cases, however, it may be possible to carry out an extinctiometric determination. It is then desirable to show that both methodes give consistent results in one system at least.

---

* $p[H^+] = -\log [H^+]$ (see I).

It must be said that the extinctiometric method, contrary to the potentiometric, does not give directly a certain ion concentration of the solution. In practice one always measures a sum of extinctions of several components. Further, the molar extinctions are unknown quantities, thus we have here twice as many unknown constants as in a potentiometric measurement. These circumstances render the computations more difficult, and also the results more uncertain.

As in I, the numerical values obtained refer to the special medium used, *i. e.* with the ionic strength = 1 by the aid of $NaClO_4$, and the temperature 20° C.

CHOICE OF MONOCHLORACETATE AS THE MOST SUITABLE LIGAND

In the choice of a ligand, the following views should be considered:

a. The potentiometric measurement must be done as a ligand measurement, as $[UO_2^{2+}]$ cannot be determined.

b. To be measured in this way, the complexity must not be too weak (see *e. g.* Leden[2, p. 21]).

c. The measurements should be done at $p[H^+] < 3$, as the uranyl solutions are too readily hydrolysed at higher $p[H^+]$ (see I). The hydrolysis affects both methods, but in a manner most difficult to calculate in the case of the extinctiometric one.

d. The method of calculation for the extinctiometric measurements requires that no polynuclear complexes are formed in appreciable amounts (Olerup[3, p. 70], Bjerrum[4 p. 7], Fronaeus[5, pp. 89–90]. The course of the potentiometric determination will determine whether or not this qualification is fulfilled.

e. The complexes formed must at some wave-length have an extinction differing to a large extent from that of UO_2^{2+}. This is established and a suitable wave-length is choosen by photographing the whole extinction curve of the complex solution.

f. The system used must not be too sensitive to light. According to Gmelin [6] all organic salts of UO_2^{2+} are sensitive, but to a very different degree.

The most suitable method of ligand measurement here seems to be $p[H^+]$ measurements in a buffer of the ligand ion and the corresponding acid, as both quinhydrone and glass electrodes may be used in uranyl solutions (see I). From such measurements, [A] may be calculated. In order to give the solutions the low $p[H^+]$, required according to the condition c. above, it is necessary, however, to choose a rather strong acid, with pK_c* 3 to 4. On the other hand, the acid must not be too strong.

---

* $pK_c = -\log K_c$; K_c is the dissociation constant in the medium used.

By using p[H$^+$] measurements, electrodes of the second order are avoided. This is well, because it would certainly not be easy to find such an electrode with a good function, on account of their reducing properties.

So we see our choice limited to anions of some acids of medium strength with pK_c in the neighbourhood of 3. The number is further decreased by the demand that they must be well soluble in water.

As the acid most probable to fulfil the conditions, the monochloroacetic acid has been selected. From an early conductometric investigation by Dittrich[7] one may conclude that its uranyl salt is rather strongly complex. During the course of the present investigation, it has really proved to be practicable in all other respects too.

CALCULATION OF THE COMPLEXITY CONSTANTS AND THE COMPOSITION OF THE SYSTEM WHEN THE FREE LIGAND CONCENTRATION HAS BEEN MEASURED

Both the methods used give [A], the free ligand concentration of the solutions. As stated in I p. 378 the calculation of the constants then is done via the complex formation equation *

$$\bar{n} = \frac{C_A - [\mathrm{A}]}{C_M} = f([\mathrm{A}]) \tag{1}$$

the general formula of which was deduced ((8) of I). From this equation it was evident, how it could be decided, whether polynuclear complexes are involved in the complex formation or not. In the last case, the course of the complex formation curve $\bar{n} = f([\mathrm{A}])$ should namely be independent of [M], *i. e.* C_M. As this proves to be the case for the chloroacetate system (see below), the formation curve here adopts the simple form:

$$\bar{n} = \frac{\beta_1[\mathrm{A}] + 2\beta_2[\mathrm{A}]^2 + 3\beta_3[\mathrm{A}]^3 + 4\beta_4[\mathrm{A}]^4 + \ldots.}{1 + \beta_1[\mathrm{A}] + \beta_2[\mathrm{A}]^2 + \beta_3[\mathrm{A}]^3 + \beta_4[\mathrm{A}]^4 + \ldots.} \tag{2}$$

From (2), the constants and the composition of the system will be calculated according to the method of Fronaeus[5, pp. 13—14, 28—30 and 110]. We define:

$$X([\mathrm{A}]) = 1 + \beta_1[\mathrm{A}] + \beta_2[\mathrm{A}]^2 + \beta_3[\mathrm{A}]^3 + \ldots \tag{3}$$

---

* The symbols refer to the same quantities as in I.

and form the function $\bar{n}/[A]$ which then becomes:

$$\frac{\bar{n}}{[A]} = \frac{\frac{dX([A])}{d[A]}}{X([A])} \tag{4}$$

Hence

$$\ln \frac{X([A]_1)}{X([A]_2)} = \int_{[A]_2}^{[A]_1} \frac{\bar{n}}{[A]} \, d[A] \tag{5}$$

The integration of the experimentally known function is made graphically.

If the experiments are able to extend to sufficient low [A], the $\bar{n}/[A]$ function is extrapolated to $[A] = 0$, and $[A]_2 = 0$ is chosen as the lower limit of integration. Then we have, as $X(0) = 1$, (3):

$$\ln X([A]) = \int_0^{[A]} \frac{\bar{n}}{[A]} \, d[A] \tag{5a}$$

Hence we know corresponding values of [A] and $X([A])$.

If, on the contrary, no [A] values are measured in the close neighbourhood of the $\bar{n}/[A]$-axis, the extrapolation to $[A] = 0$ cannot be done with any certainty. We then choose the constant lower limit $[A]_2 = [A]_0$, where $[A]_0$ is a value immediately under the lowest [A] measured. Thus

$$\ln \frac{X([A])}{X([A]_0)} = \int_{[A]_0}^{[A]} \frac{\bar{n}}{[A]} \, d[A] \tag{5b}$$

The function $\frac{X([A])}{X([A]_0)}$ obtained by this integration, proves to have such a course that an extrapolation to $[A] = 0$ is easy. We then obtain

$$\lim_{[A] \to 0} \frac{X([A])}{X([A]_0)} = \frac{1}{X([A]_0)} \tag{6}$$

In this manner the constant quantity $X([A]_0)$ is obtained, and hence $X([A])$, too; and we have again the corresponding values of [A] and $X([A])$ searched for.

After having determined these values, we are able to calculate the complexity constants from (3). By a transformation we form a new function

$$X_1([A]) = \frac{X([A]) - 1}{[A]} = \beta_1 + \beta_2[A] + \beta_3[A]^2 + \ldots \tag{7a}$$

By the easily realizable extrapolation to $[A] = 0$, the interception on the axis $= \beta_1$, and the slope in the point of interception $= \beta_2$. The latter constant is, however, more accurately determined by the formation of

$$X_2([A]) = \frac{X_1([A]) - \beta_1}{[A]} = \beta_2 + \beta_3[A] + \beta_4[A]^2 + \ldots \tag{7b}$$

which extrapolation gives β_2 as the interception on the axis. By successive formation of analogous functions $X_n([A])$, all the constants in question may be calculated. How many complexes we have to calculate with in a solution is *a priori* known from the value of $\bar{n}$ attained.

When now the constants are obtained, the composition of the mononuclear complex system in question (*i. e.* the mol ratios α_n of the particular complexes) may be computed as a function of [A] by the aid of the equations (4) and (6) of I, p. 378. (*cf.* Fronaeus [5, p. 29]). Hence we have

$$\alpha_0 = \frac{[M]}{C_M} = \frac{1}{X([A])} \tag{8a}$$

and

$$\alpha_n = \frac{[MA_n]}{C_M} = \frac{\beta_n[A]^n}{X([A])} \tag{8b}$$

To check the calculations, $\bar{n}$ is calculated from (2) by use of the constants found. The complex formation curve so obtained must coincide with the experimentally determined points ($\bar{n}$, [A]).

CHEMICALS USED

Monochloroacetic acid, pur., was distilled twice, b. p. 186—188° C. The resulting acid was quite colourless and gave, after drying *in vacuo*, the right equivalent weight (calc. and found: 94.5). Though very hygroscopic, it may be weighed in the air.

The buffer used had the composition 1000 mC NaA, 1000 mC HA; it is a 1 : 1 buffer of the approximate ionic strength $I = 1$. It was prepared by halfneutralizing a weighed quantity of dry acid with NaOH and then diluting to the right volume. Immediately after preparation, the buffer is free from Cl^-, but after a day a feeble Cl^--reaction can be detected which indicates the progressing hydrolysis to glycolate. But no differences arise in the measured p[H^+], if a new or two day old buffer is used. Still older buffers have not been used, however.

The *other chemicals* are the same as in I.

THE POTENTIOMETRIC MEASUREMENT

The experiments are determinations of [H^+], carried out by quinhydrone electrode. The procedure was the potentiometric titration mentioned in I p. 383: a known volume of a solution of known concentration of uranyl perchlorate was in the electrode vessel; to this the 1 : 1 chloroacetate buffer was added. The same reference quinhydrone electrode, RE, as before was used.

The potentials adjusted themselves very quick to their proper values which were reproducible within 0.2 mV. The values attained were very stable. No effect of diffuse daylight could be detected. The great sensitiveness to light of certain wavelengths which later is proved extinctiometrically for the uranyl chloroacetate system seems not at all to affect the [H^+] of the solutions during the existing conditions.

As was established in I p. 385, the quinhydrone electrode is fairly well applicable to [H^+]-measurements in uranyl solutions. Small deviations ΔE_q are, however, distinctly perceptible. A thorough discussion indicated that they were mainly due to a weak complex formation between the uranyl ion and the hydroquinone component, and so dependent on [UO_2^{2+}]. The error of [H^+] caused by these deviations thus decreases with increasing complex formation.

From the figures of I, one can estimate the effect of this error on the quantity $\bar{n}/[A]$ which is used in the final calculation of the complexity constants. One finds that the true values are lower than the calculated; at the lowest C'_A used $\approx$ 7 % at $C'_M = 100$ mC and $\approx$ 3 % at $C'_M = 25$ mC. The error falls off rapidly and is of the same order of magnitude as the accidental error when $\bar{n} \approx 1$. Thus ΔE_q does not seriously affect the measurements.

From the [H^+] measured, [A] (and hence $\bar{n}$, (1)) is calculated. For that purpose, the dissociation constant K_c of monochloroacetic acid in the medium used must be known. It is determined by separate titrations with solutions which are free from uranyl. The quantities of these solutions are indicated below with'. It is valid:

$$\frac{[H^+]'\,[A]'}{[HA]'} = K_c \qquad (9)$$

Table 1. Determination of E' as a function of C'_A, when perchlorate is exchanged for chloroacetate buffer. — Calculation of K_c in the medium used.

C'_A mC	E' mV	(16) $[H^+]'$ mC	(10) $K_c \cdot 10^3$ C	C'_A mC	E' mV
19.6	43.0	1.84	2.22	231	39.9
26.0	42.1	1.91	2.21	250	39.9
29.1	41.6	1.95	2.23	286	40.0
38.5	40.9	2.00	2.22	333	40.2
47.7	40.4	2.04	2.22	348	40.3
50.7	40.4	2.04	2.21	375	40.5
62.6	40.0	2.07	2.21	400	40.6
69.8	39.8	2.10	2.23	412	40.7
90.9	39.7	2.11	2.21	444	40.9
117.7	39.5	2.12	2.20	473	41.1
130.5	39.6	2.11	2.18	483	41.2
167	39.6	2.11	2.16	500	41.3
200	39.8	2.10	2.14	517	41.4
211	39.8	2.10	2.14	546	41.6
				572	41.8

and as the stoicheiometric concentrations of acid and salt are the same $= C'_A$

$$\frac{[H^+]'\,(C'_A + [H^+]')}{C'_A - [H^+]'} = K_c \tag{10}$$

These titrations also show the effect of diffusion potentials and qualitative changes of medium which arise when perchlorate is gradually exchanged for chloroacetate buffer. As long as the medium may be considered as constant, K_c of (10) will namely remain a constant. So is also the case up to $C'_A \approx 150$ mC, Table 1, where we find $K_c = 2.22 \cdot 10^{-3}$ C *. At higher C'_A, however, K_c is no more a constant; but the mode of calculation used below eliminates the deviations.

For a solution which contains the total uranyl concentration C_M, in addition to the same buffer concentration C'_A as above, one has:

$$\frac{[H^+]\,[A]}{[HA]} = K_c \tag{11}$$

---

* The thermodynamic constant $K_a = 1.4 \cdot 10^{-3}$ (Landolt-Börnstein).

Table 2. Determination of corresponding values of $\bar{n}$ and $[A]$ at different C'_M, to form the complex formation function and the function $\bar{n}/[A] = f([A])$.

Table 2 A. $C'_M = 25$ mC × *

C_M mC	C'_A mC	E mV	(18) E_A mV	(18) $\frac{[H^+]'}{[H^+]}$	(17) $[H^+]$ mC	(13) [A] mC	(15) $\bar{n}$	$\frac{\bar{n}}{[A]}$ C^{-1}
25.0	0	58.9			1.0			
24.5	19.6	33.6	9.4	0.689	2.65	14.2	0.33	23.3
24.3	29.1	32.2	9.4	0.689	2.8	20.6	0.465	22.6
24.0	38.5	31.7	9.2	0.695	2.9	27.5	0.58	21.1
23.8	47.7	31.6	8.8	0.709	2.9	34.6	0.67	19.4
23.6	69.8	31.9	7.9	0.731	2.8	52.0	0.87	16.7
22.7	90.9	32.2	7.5	0.743	2.8	68.5	1.11	16.2
22.2	111.2	32.8	6.8	0.764	2.7	86.1	1.25	14.5
21.7	130.5	33.2	6.4	0.776	2.7	102.3	1.42	13.9
20.8	167	34.1	5.5	0.805	2.6	136	1.62	11.9
20.0	200	34.8	5.0	0.820	2.5	166	1.80	10.9
19.2	231	35.5	4.4	0.840	2	196	1.93	9.9
18.5	259	36.1	3.8	0.860	»	224	2.00	8.9
17.9	286	36.6	3.4	0.874	»	252	2.01	8.0
17.3	310	36.9	3.2	0.881	»	275	2.14	7.8
16.7	333	37.3	2.9	0.891	»	298	2.22	7.5
15.6	375	38.0	2.5	0.906	»	340	2.37	7.0
14.7	412	38.5	2.2	0.916	»	380	2.31	6.1
13.9	444	38.9	2.0	0.924	»	412	2.45	6.0
13.15	473	39.4	1.7	0.935	»	444	2.36	5.3
12.5	500	39.7	1.6	0.939	»	471	2.48	5.3

where K_c is the same as before, if we neglect the effect of C_M, appearing in ΔE_q. [A] is the quantity searched for, and for [HA] it is valid:

$$[HA] = C'_A - [H^+] + C^0_H - C_s \qquad (12)$$

Here C^0_H = the hydrogen ion concentration of uranyl solution before addition of buffer, and C_s = the hydrogen ion concentration which is consumed by pressing back the hydrolysis of uranyl, when the solution by addition of buffer and complex formation grows more acid.

The existence of the terms C^0_H and C_s is thus due to the fact that the solution besides the chloroacetate contains uranyl as another buffering system.

---

* These signs are used to indicate the respective C'_M in the Figs. 1 and 2.

Table 2 B. $C'_M = 50$ *mC.* ○

C_M mC	C'_A mC	E mV	(18) E_A mV	(18) $\frac{[H^+]'}{[H^+]}$	(17) $[H^+]$ mC	(13) [A] mC	(15) $\bar{n}$	$\frac{\bar{n}}{[A]}$ C^{-1}
50	0	46.7			1.6			
48.7	26.0	25.9	16.3	0.524	3.6	13.6	0.33	24.3
48.1	38.5	25.1	15.8	0.535	3.7	20.7	0.45	21.8
47.5	50.7	24.9	15.5	0.542	3.7	27.5	0.565	20.5
46.9	62.6	25.2	14.8	0.558	3.7	35.2	0.66	18.8
45.5	90.9	26.2	13.5	0.586	3.6	53.6	0.90	16.8
44.2	117.7	27.2	12.3	0.613	3.4	72.7	1.10	15.1
42.9	142.9	28.1	11.5	0.632	3.3	90.8	1.29	14.2
41.7	167	29.3	10.3	0.667	3	112	1.39	12.4
39.5	211	30.9	8.9	0.702	»	149	1.65	11.1
37.5	250	32.1	7.8	0.735	»	184	1.84	10.0
35.7	286	33.2	6.8	0.764	»	219	1.96	9.0
34.1	318	34.1	6.1	0.785	»	250	2.08	8.3
32.6	348	34.9	5.4	0.807	»	282	2.12	7.5
31.3	375	35.5	5.0	0.820	2	309	2.18	7.1
30.0	400	36.1	4.5	0.837	»	336	2.20	6.5
27.9	444	37.0	3.9	0.855	»	381	2.33	6.1
25.9	483	37.7	3.5	0.870	»	422	2.44	5.8
24.2	517	38.4	3.0	0.886	»	460	2.44	5.3
22.7	546	39.0	2.6	0.900	»	493	2.42	4.9
21.4	572	39.4	2.4	0.910	»	522	2.43	4.7

But as was mentioned above, the p[H$^+$] of the measurement has been choosen so that the buffering capacity of the uranyl system is very low (the uranyl being only slightly hydrolysed) while that of the chloroacetate system is in the neighbourhood of its maximum (1 : 1 buffer). So C_s may be treated as a correction term, even if C'_A is rather low. This is necessary, because an exact calculation presupposes a full information of the course of hydrolysis in the solutions measured which we have not. From the measurements of non-complex uranyl perchlorate solutions in I, however, we are able to do the estimation that C_s is of the same order of magnitude as the C^0_H found, only a little smaller. We so introduce the fairly good approximation $C^0_H = C_s$. The $\bar{n}$/[A], calculated according to this, become too high. The error may reach 5—8 % at the lowest C'_A used, but it falls off very rapidly, when C'_A increases. Already at $\bar{n} = 0.5$—1 it may be quite neglected.

From (10), (11) and (12) we now obtain our unknown quantity [A] according to:

Table 2 C. $C'_M = 100$ *mC.* □

C_M mC	C'_A mC	E mV	(18) E_A mV	(18) $\frac{[H^+]'}{[H^+]}$	(17) $[H^+]$ mC	(13) [A] mC	(15) $\bar{n}$	$\frac{\bar{n}}{[A]}$ C^{-1}
100	0	34.4			2.6			
96.2	38.5	15.1	25.8	0.360	5.5	13.2	0.32	24.2
95.0	50.7	14.7	25.7	0.361	5.6	17.6	0.41	23.3
93.8	62.6	14.8	25.2	0.369	5.6	22.5	0.485	21.6
90.9	90.9	15.7	24.0	0.387	5.4	35.0	0.675	19.3
88.3	117.7	17.0	22.5	0.410	5.1	47.9	0.85	17.8
85.8	142.9	18.5	21.1	0.433	4.8	61.5	1.01	16.4
83.3	166.7	19.9	19.7	0.458	4.5	76.2	1.14	15.0
78.9	211	22.4	17.4	0.503	4	106	1.38	13.0
75.0	250	24.7	15.2	0.548	»	137	1.56	11.4
71.4	286	26.6	13.4	0.588	»	169	1.69	10.0
68.2	318	28.0	12.2	0.617	3	197	1.82	9.2
65.2	348	29.2	11.1	0.645	»	225	1.93	8.6
62.6	375	30.4	10.1	0.668	»	252	2.01	8.0
60.0	400	31.4	9.2	0.695	»	279	2.07	7.4
55.7	444	33.0	7.9	0.731	»	325	2.19	6.7
51.8	483	34.2	7.0	0.758	»	368	2.28	6.2
48.4	517	35.2	6.2	0.783	2	407	2.32	5.7
45.4	546	36.2	5.4	0.807	»	442	2.34	5.3
42.8	572	36.9	4.9	0.825	»	473	2.36	5.0

$$[A] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C'_A + [H^+]')\,(C'_A - [H^+])}{C'_A - [H^+]'} \qquad (13)$$

For the following calculation of $\bar{n}$ according to (1), one must further know the total ligand concentration C_A and the total uranyl concentration C_M. For C_A one has:

$$C_A = C'_A + [H^+] - C^0_H + C_s \qquad (14)$$

where the approximation $C^0_H = C_s$ also may be introduced. C_M of (1), finally, is the total uranyl concentration taking part in formation of chloroacetate complexes. Thus the quantity bound as hydrolysed complexes should be subtracted from the stoicheiometric uranyl concentration. However, p[H$^+$] has been choosen so that this quantity is small; from the measurements of hydrolysis in I, it may be estimated to be 3—5 % of the total amount. This error is involved in the $\bar{n}$/[A] calculated below.

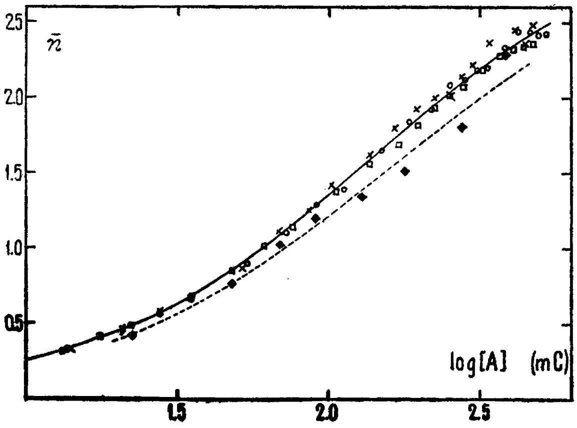

Fig. 1. The complex formation curve. × , ○ *and* □: *potentiometrically determined values at* $C'_M = 25, 50$ *and 100 mC respectively.* — ◆: *extinctiometrically determined values.* — *Fulldrawn curve obtained from the potentiometrically and dashed curve from the extinctiometrically calculated complexity constants.*

Inserting the approximated values of [A], C_A and C_M in (1) we obtain:

$$\bar{n} = \frac{C'_A + [\mathrm{H}^+] - \dfrac{[\mathrm{H}^+]'}{[\mathrm{H}^+]} \cdot \dfrac{(C'_A + [\mathrm{H}^+]')\,(C'_A - [\mathrm{H}^+])}{C'_A - [\mathrm{H}^+]'}}{C_M} \tag{15}$$

The equations (15) and (13) now obtained give the corresponding values of $\bar{n}$ and [A] searched for, *i. e.* the complex formation curve, from which the function $\bar{n}$/[A] is obtained.

In (13) and (15) C'_A and C_M are known stoicheiometric concentrations, while $[\mathrm{H}^+]'$ and $[\mathrm{H}^+]$ are the hydrogen ion concentrations of solutions of the same C'_A, the first without uranyl, the second with the uranyl concentration $= C_M$. $[\mathrm{H}^+]'$ and $[\mathrm{H}^+]$ are calculated from the emf E' and E of the measured cells. If $[\mathrm{H}^+]_0$ is the known hydrogen ion concentration of RE (= 10.10 mC), it is valid for these cells:

$$E' = 58.2 \log \frac{[\mathrm{H}^+]_0}{[\mathrm{H}^+]'} \tag{16}$$

$$E = 58.2 \log \frac{[\mathrm{H}^+]_0}{[\mathrm{H}^+]} \tag{17}$$

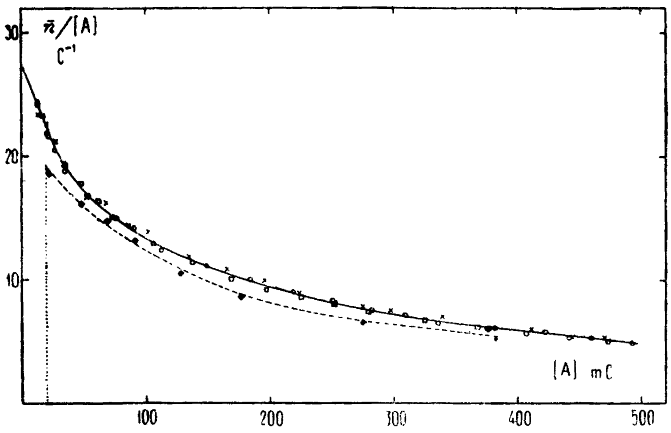

Fig. 2. $\bar{n}/[A]$ *as a function of* $[A]$ *the integration of which gives the X-functions (Tab. 3 and 8). — The signs relates to the same measurings as in Fig. 1; but the curves are here drawn according to the experimental points.*

Hence

$$E' - E = E_A = 58.2 \log \frac{[\mathrm{H}^+]}{[\mathrm{H}^+]'} \tag{18}$$

From (18) the factor $\frac{[\mathrm{H}^+]}{[\mathrm{H}^+]'}$ of (13) and (15) is obtained independent of diffusion potentials and medium changes which arise when C'_A increases, as it was shown above. For in the (hypothetic) cell with emf E_A, $[\mathrm{H}^+]'$ and $[\mathrm{H}^+]$ are measured at the same C'_A. $[\mathrm{H}^+]'$ and $[\mathrm{H}^+]$, on the other hand, which stand at the side of C'_A in (13) and (15) are obtained from (16) and (17); at $C'_A < 150$ mC this is correct, as the medium is not yet perceptibly changed, at $C'_A >$ 150 mC $[\mathrm{H}^+]'$ and $[\mathrm{H}^+]$ are so small in comparison with C'_A, that the deviations there met with are of no importance.

To sum up the effects of the different systematic errors, discussed above, one may say that (13) and (15) are simplified equations which do not take into account 1. ΔE_q 2. C_s and 3. the wrong value of C_M on account of hydrolysis.

The error 1. and 2. cause small $\bar{n}$ to be calculated too high, while 3. acts in opposite direction. The total result is, perhaps, 5—10 % too high values of $\bar{n}/[\mathrm{A}]$ at the lowest [A]. The lower limit of C'_A has, in fact, been determined so that these errors must not be too great. All errors mentioned diminish rapidly with increasing $\bar{n}$. Already at $[\mathrm{A}] = 60$ mC, $\bar{n} = 1$, their total effect certainly is quite negligible.

Table 3. $X([A])$, $X_1([A])$, $X_2([A])$ *and* $X_3([A])$ *for given* $[A]$, *as obtained by numerical integration of the potentiometrically determined function of Fig. 2.*

[A] mC	(5a) ln X([A])	X([A])	(7a) X_1([A]) C^{-1}	(7b) X_2([A]) C^{-2}	X_3([A]) C^{-3}
0			*27.4*	*193*	*625*
10	0.2608	1.298	29.8		
20	0.4964	1.643	32.2		
30	0.7079	2.030	34.3		
40	0.9007	2.462	36.6	230	
50	1.0799	2.945	38.9	230	
60	1.2483	3.48	41.4	233	
80	1.5583	4.75	46.9	244	
100	1.8385	6.29	52.9	255	620
120	2.0958	8.13	59.4	267	617
140	2.3340	10.32	66.6	280	622
160	2.5552	12.87	74.2	293	625
180	2.7611	15.81	82.3	305	622
200	2.9540	19.18	90.9	318	625
250	3.3903	29.67	114.7	349	624
300	3.7738	43.6	142	381	627
350	4.1166	61.3	172	414	632
400	4.4292	83.8	207	449	640
450	4.7175	111.9	246	487	653

Table 4. The ligand number and the composition of the system as calculated for some round $[A]$ *with the constants obtained.*

$\beta_1 = 27.5 \pm 0.5\ C^{-1}$ $\beta_2 = 195 \pm 20\ C^{-2}$ $\beta_3 = 625 \pm 150\ C^{-3}$

[A] mC	(2) $\bar{n}$	(8a) α_0 %	(8b) α_1 %	(8b) α_2 %	(8b) α_3 %
10	0.245	77	21.5	1.5	0
30	0.605	49	41	8.5	1.5
50	0.875	34	47	16.5	2.5
100	1.345	16	43.5	30.5	10
200	1.87	5.5	28.5	40	26
300	2.16	2	19	40	39
400	2.33	1	13.5	37	48.5

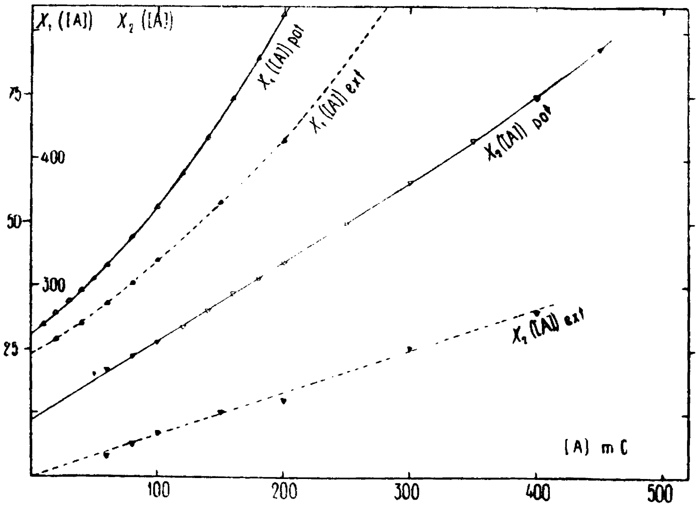

Fig. 3. The functions $X_1([A])$ *and* $X_2([A])$ *which give the complexity constants.*

The accidental error is determined by the reproducibility of the emfs which was 0.2 mV, corresponding to $\approx 2\ \%$ in [A]. At low $\bar{n}$, this error can be neglected. At high $\bar{n}$, on the other hand, where C_A — [A] is a comparatively small difference between two big numbers, it becomes important and causes a considerable spreading of the highest points on the complex formation curve (Fig. 1).

To secure a good test of polynuclear complex formation, measurements have been carried out with three uranyl solutions of highly different strengths. Their concentrations at the outset were $C'_M = 25$, 50 and 100 mC.

The E' and E given below are mean values from at least two titrations. At $C_M = 0$ three and at $C'_M = 25$ mC two different buffer solutions of different age have given identical results, as was mentioned above.

The results are found in Tables 1 and 2. The found values of $\bar{n}$ and log [A] are plotted in Fig. 1 and in Fig. 2 $\bar{n}$/[A] is given as a function of [A]. Within the limits of error, the course of these functions are entirely the same for the different C'_M, so no polynuclear complexes seem to exist.

The ligand number $\bar{n}$ reaches a value ≈ 2.5 in our measurements. So we have to calculate with at least three complexes: MA, MA_2 and MA_3.

For the calculation of the complexity constants, we now compute corresponding values of X([A]) and [A] by integrating the $\bar{n}$/[A]-function of Fig. 2. As very low [A]-values have been determined, the function can be extrapolated to [A] $= 0$. Thus we may integrate according to (5a). From X([A]) hence obtained, X_1([A]), X_2([A]) and X_3([A]) are formed according to (7). Corresponding values of these functions for the round [A], choosen as upper limits of integration, are found in Table 3. The functions $X_1([A])$ and $X_2([A])$ are plotted in Fig. 3. By extrapolation to $[A] = 0$, one gets the constants $\beta_1 = 27.5 \pm 0.5$ C^{-1}; $\beta_2 = 195 \pm 20$ C^{-2}. The function $X_3([A])$ is practically constant over the whole [A]-range and gives $\beta_3 = 625 \pm 150$ C^{-3}.

These values of the constants are rounded off according to the indicated errors which are the maximal accidental ones as they are estimated from the spreading of the ($\bar{n}$/[A], [A])-points of Fig. 2. — The systematic errors of $\bar{n}$/[A], mentioned above, in all probability cause the calculated values of β_1 and β_2 to be 5—10 % too high.

With the constants obtained, $\bar{n}$ is calculated according to (2) for some round [A]. (Table 4.) The complex formation curve thus found (fulldrawn in Fig. 1) is seen to fit the experimental points very well. For the same [A], the composition of the system is calculated according to (8) and also given in Table 4.

THE EXTINCTIOMETRIC MEASUREMENT

The experiments are photo-electric determinations of the extinction E of the solutions. The apparatus used is built by Olerup[3] who mainly has followed the designs of Kortüm and v. Halban[8], Deck[9], and Kortüm[10, pp. 93 and 111]. As Olerup has given a close description, only a brief summary of the main points will be given here. On this occassion some improvements which extend the use in the ultra-violet, will also be mentioned.

Light from a mercury lamp passes a quartz double monochromator. The beam leaving the monochromator is made parallell by a quartz lens and then divided into two by a quartz plate. In the first beam, the absorption cells are placed, and the intensity of light of this beam may be weakened by means of a non-central rotating sector which can be adjusted during rotation. The light falls finally onto a sodium phototube. The second beam of light is reflected by a mirror of aluminium (which has good reflecting properties even at as short a wave-length as 3 130 Å) onto a second phototube which is coupled so as to compensate the current of the first one. An electrometer is coupled as a zero instrument between the tubes. The whole forms a compensated two phototubes apparatus, working according to the method of substitution. First, a cell with the solution to be measured is inserted in the first beam and the photo-current is compensated to zero by adjustment of the potential over one of the phototubes. Second, the cell of solution is changed for a similar cell containing solvent, and the sector is started. E of the solute is E of the sector, when compensation to zero is reached again. — By this arrangement, no errors are caused even if the light source fluctuates or the photo-current is not proportional to the intensity of light.

The E determined are not the true E of the wave-length used, however, on account of two sources of error, always involved in extinctiometric measurements: the light is not strictly monochromatic, and it partly passes the absorption cell more than once by repeated reflection at the end-plates. But as the measurements are treated as relative ones in the following calculations, it is not essential that the E:s measured are true. On the other hand, however, it is necessary that the error of E is a constant for all solutions which are compared in the calculations. We have to state how this condition may be fulfilled.

The error owing to lacking monochromaticity is examined by Kortüm[10, p. 10], Olerup[3, p. 47] and, especially, Fronaeus[5, p. 95]. It proves difficult to determine its magnitude, but one is able to establish that a constant error is obtained if a) E is kept constant (which is easy to realize), and b) the solutions measured have extinction curves of the same shape. For a system of only mononuclear complexes, this latter condition is fulfilled as soon as the solutions have the same [A] (Olerup[3, p. 48]). By the method of calculation used below, this is the case for all solutions which are compared. Thus both the methodical conditions mentioned are observed.

The error owing to reflection at the end-plates has been thoroughly examined by Olerup[3, p. 50]. He finds that also this error has a constant size when E is kept constant, and, moreover, that its relative size decreases when E increases.

The true E:s of the solutions were not essential, thus the absolute thicknesses of the absorption cells are not required, but only the ratios between them. The cell of 1 cm is set = 1,000. The determination of these ratios is made by picrate solutions containing an excess of NaOH. The cell of comparison only contains the NaOH-solution. This standard of calibration is recommended by v. Halban, Kortüm and Szigeti[11].

These measurements give the ratios between the 'effective' thicknesses, *i. e.* all existing differences between the cells are involved in this calibration and expressed as differences of thickness. It is evident that such an 'effective' thickness is valid only at a certain E. Therefore all calibrations are performed at one and the same E, and this E is then also used at all the following complex measurements, although the errors mentioned above only required the same E for solutions to be compared. The constant E is selected = 0.7, as the error of adjustment of the sector and the error from repeated reflection both become very small at this value.

The calibration has been performed before and after every series of measurements. As a rule the same results have been obtained within $2-3\ {}^0/_{00}$. Thus the determined ratios of thickness are very well reproducible quantities, which reflects the precise construction of the apparatus used.

On account of the construction of the apparatus, the measurements must always be carried out at some strong mercury line within the range of sensitivity of the phototubes used. To select the most suitable one where the complex formation in question shows the greatest effect on the extinction of UO_2^{2+}, the whole extinction curve of a complex solution of the composition

$$C_M = 10 \text{ mC};\ C'_A = C'_{HA} = 100 \text{ mC};\ \text{NaClO}_4 \text{ to } I = 1$$

is photographed, as described in I p. 375. The extinction curve found is compared in Fig. 4 with the curve of UO_2^{2+}, determined in I. The strong mercury lines of the range in question are at 3 130, 3 660, 4 050 and 4 360 Å. One sees that the greatest differences between the curves are found for 3 130

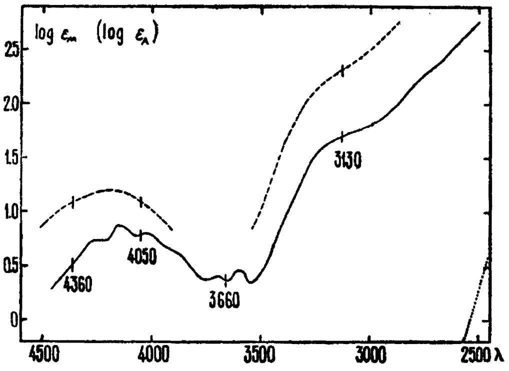

Fig. 4. Extinction curves of a) uranyl ion (fulldrawn), b) complex solution with $C_M = 10$ *mC,* $C'_{HA} = C'_A = 100$ *mC (dashed) and c) 1 : 1 chloroacetate buffer (dotted low to the right; the stoicheiometric molar extinction in this case,* ε_A*, is defined according to* $\varepsilon_A = \frac{E}{d\,(C_A + C_{HA})}$.

and 4 360 Å. As ε_M is so low at 4 360 Å that inconveniantly high C_M should be necessary in the available cells, 3 130 Å has been selected. This selection also proved to be very good on account of the sensitiveness to light of the system (see below). The extinction curve of the buffer has been determined, too, and is given in Fig. 4. It is seen that this extinction is to be neglected within the whole range discussed.

From the directly measured E, the stoicheiometric molar extinction ε_M is immediately obtained, and according to Beer it is valid ((2) and (3) of I):

$$E/d = \varepsilon_M \cdot C_M = \varepsilon_0 \cdot C_0 + \varepsilon_1 \cdot C_1 + \varepsilon_2 \cdot C_2 + \dots \tag{19}$$

The possibilities of calculating the composition of a complex system from the variation of the ε_M:s obtained, when C_M and C_A is varied, have been very thoroughly investigated by Olerup [3, p. 57], Bjerrum [4] and Fronaeus [5, p. 87]. They agree that no reliable complexity constants at all can be calculated if polynuclear complexes exist. If, on the other hand, mononuclear complexes are entirely formed, the composition is possible to calculate, and the result may become fairly accurate, if the ε:s of the system have suitable size in proportion to each other.

In the system in question, the potentiometric measurements indicate that the complex formation in all probability is mononuclear. Thus the calculation is possible, and is performed as follows, in close connection to Fronaeus and Olerup.

If (19) is applied on a mononuclear complex system, we obtain with (4) of I:

$$\frac{E}{C_M \cdot d} = \varepsilon_M = \frac{\varepsilon_0[\mathrm{M}] + \varepsilon_1[\mathrm{MA}] + \varepsilon_2[\mathrm{MA_2}] + \varepsilon_3[\mathrm{MA_3}] + \dots}{[\mathrm{M}] + [\mathrm{MA}] + [\mathrm{MA_2}] + [\mathrm{MA_3}] + \dots} \tag{20}$$

Introducing (6) of I p. 378, and (3) above, we get:

$$\varepsilon_M = \frac{\varepsilon_0 + \varepsilon_1 \beta_1[\mathrm{A}] + \varepsilon_2 \beta_2[\mathrm{A}]^2 + \varepsilon_3 \beta_3[\mathrm{A}]^3 + \ldots}{X([\mathrm{A}])} \tag{21}$$

From (21), a new function $\varepsilon_M - \varepsilon_0$ is formed by subtracting ε_0 from both membra:

$$\varepsilon_M - \varepsilon_0 = \frac{(\varepsilon_1 - \varepsilon_0)\beta_1[\mathrm{A}] + (\varepsilon_2 - \varepsilon_0)\beta_2[\mathrm{A}]^2 + (\varepsilon_3 - \varepsilon_0)\beta_3[\mathrm{A}]^3 + \ldots}{X([\mathrm{A}])} \tag{22}$$

As ε_0 may be separately determined, $\varepsilon_M - \varepsilon_0$ is experimentally determinable, as was ε_M.

As seen from (21) and (22), ε_M and $\varepsilon_M - \varepsilon_0$ are both functions of [A] only. A certain constant value of ε_M or $\varepsilon_M - \varepsilon_0$ thus corresponds to a certain constant value of [A]. The functions are thus equivalent; in the following calculation $\varepsilon_M - \varepsilon_0$ is preferred, however, as the course of $(\varepsilon_M - \varepsilon_0)/C_A = f\,(\varepsilon_M - \varepsilon_0)$, used there, is more advantageous than that of the corresponding $\varepsilon_M/C_A = f\,(\varepsilon_M)$.

The property of $\varepsilon_M - \varepsilon_0$ to be a function of [A] only is used to determine corresponding values of $\bar{n}$ and [A], *i. e.* the complex formation curve. For that purpose, $\varepsilon_M - \varepsilon_0$ is determined for increasing buffer concentrations C'_A. For every C'_A, measurements are performed at three different C_M. By this, the same three C_M cannot be choosen at different C'_A, on account of the condition that E has to be a constant. C_M must be varied as C'_A is varied. Therefore the cell-thickness d is choosen as a convenient parameter of the measurements: $\varepsilon_M - \varepsilon_0$ are determined for every C'_A with three different d, corresponding to three different C_M.

That C_M, which in a given case gives the proper $E \approx 0.7$ is found by trying. So the C_M:s of a certain d are not *a priori* connected in some known manner. As it is necessary for the following calculations to know C_M at any pair of $(\varepsilon_M - \varepsilon_0, C_A)$ along the curves of constant d, the first task is to establish such a connection.

An examination shows that the demand of a constant E causes that the function $\varepsilon_M - \varepsilon_0 = f\,(C_M)$ has a very curved course for a given d. If, however, the logarithmic function $\log\,(\varepsilon_M - \varepsilon_0) = f\,(\log\, C_M)$ is introduced, the points are found to fall along an almost straight line *. The best straight line through

---

* The corresponding connection between log ε_M and log C_M is an exactly straight line, provided E is kept quite constant. For $E/d = \varepsilon_M \cdot C_M$; hence $\log \varepsilon_M = \log E/d - \log C_M$, where $\log E/d$ is a constant.

Table 5. Determined values of $\varepsilon_M - \varepsilon_0$ *at given* C'_A *and* C_M.

$d \rightarrow$ cm	0.1		0.3		1		3	
C'_A mC	C_M mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_M mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_M mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_M mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$
25			21.44	49.3	6.23	58.9	2.076	61.6
50			16.75	86.5	4.49	96.4	1.541	99.4
75			14.34	114.5	3.819	124.6	1.273	124.8
100	44.9	112.6	13.00	137.0	3.483	145.4		
150	31.49	155.6	10.05	170.7	3.014	176.4		
200	27.86	183.4	9.25	195.2	2.680	198.6		
300	24.65	220.6	8.04	228.2	2.412	231.1		
400	22.78	245.5	6.70	251.5	2.224	254.7		

Table 6. $\varepsilon_M - \varepsilon_0$ *at given* C'_A, *corrected so as to fit those connections between* $\varepsilon_M - \varepsilon_0$ *and* C_M *which are established by the straight lines of Fig. 5. — The transformation from* C'_A *to* C_A.

$d \rightarrow$ cm	0.1		0.3		1		3	
C'_A mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_A mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_A mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_A mC	$\varepsilon_M - \varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_A mC
25			47.9	27.7	58.6	27.1	61.5	27.0
50			86.7	52.5	96.2	52.2	99.4	52.1
75			115.3	77.4	124.5	77.2	124.7	77.1
100	113.8	103.5	138.0	102.4	145.5	102.2		
150	155.2	153.0	170.6	152.3	176.4	152.2		
200	183.2	202.7	195.4	202.3	198.6	202.2		
300	220.6	302	228.2	302	231.1	302		
400	245.5	402	251.2	402	254.7	402		

the experimental points of every series is now introduced as the connection searched for. These lines namely fit the points so well that one may with great certainty determine graphically those $\varepsilon_M - \varepsilon_0$, which exactly correspond to the established C_M-function at a given C'_A and d. This will be clear from a survey of Fig. 5.

These so modified $\varepsilon_M - \varepsilon_0 = f\ (C'_A)$ functions, with C_M known for every $\varepsilon_M - \varepsilon_0$, are now transformed into $\varepsilon_M - \varepsilon_0 = f\ (C_A)$. The transition from C'_A

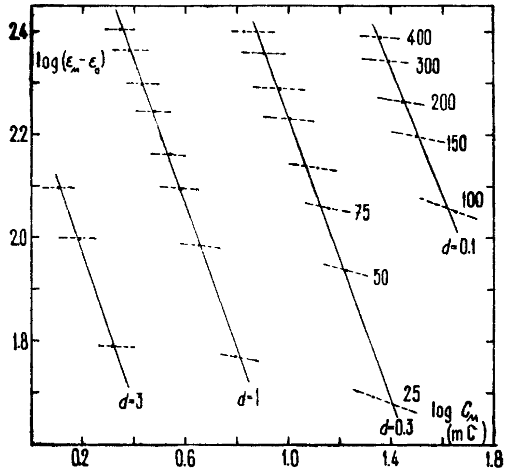

Fig. 5. *log* $\varepsilon_M - \varepsilon_0$ *as a function of log* C_M *at different d.* — ●: *experimentally determined points.* — *Fulldrawn curves: the established connections between* $\varepsilon_M - \varepsilon_0$ *and* C_M *for given d.* — *Dashed curves: position of points with constant* C'_A, *given to the right.*

to C_A is easily performed according to (14), by the aid of the potentiometrically determined $[H^+]$. Thus the preceding measurements are used to a certain extent. It must be emphasised, however, that this does not mean that the extinctiometric measurements hereby become dependent on the potentiometric ones. $[H^+]$ is namely only a correction term of C_A. Thus even a very large error in its determination has a very small influence. Moreover, most C_M used are so low that the $[H^+]$ of their solutions does not differ very much from that of pure buffer. The correction introduced thus depends very little on C_M, *i. e.* on the potentiometric complex titration.

Now the function $\varepsilon_M - \varepsilon_0 = f\ (C_A)$ should be cut at constant $\varepsilon_M - \varepsilon_0$. However, the curves for the different *d* are so close to each other that such a graphical determination would require an inconveniently large scale. By transforming the functions according to

$$\frac{\varepsilon_M - \varepsilon_0}{C_A} = f\ (\varepsilon_M - \varepsilon_0) \tag{23}$$

new functions are obtained which permit the same accuracy of the graphical determination at a much more convenient size (*cf.* Olerup[3, p. 66]).

The functions (23) now obtained are cut at a number of constant $\varepsilon_M - \varepsilon_0$, each of them corresponding to a certain C'_A (C_A) originally used (see Fig. 6). To diminish the errors of interpolation, the sections are choosen in a neighbourhood as close as possible to the experimental points. The solutions of a certain $\varepsilon_M - \varepsilon_0$ have, according to (22), the same [A], and, according to (2), also the same $\bar{n}$, but varying C_A and C_M. The values of C_A are immediately

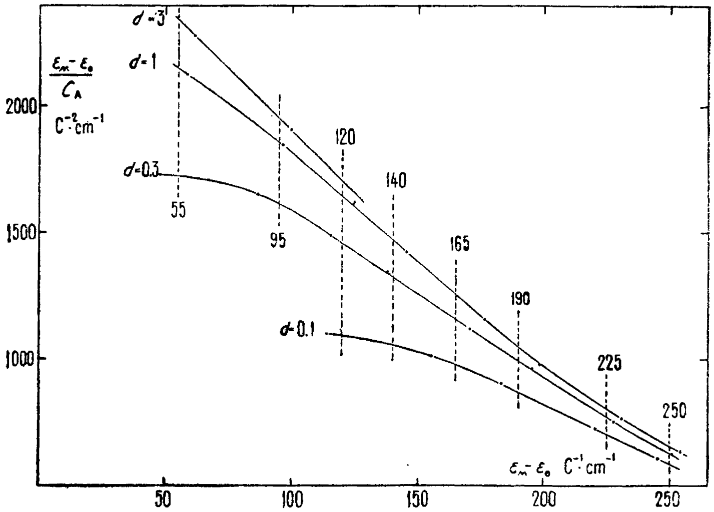

Fig. 6. *$(\varepsilon_M-\varepsilon_0)/C_A$ as a function of $\varepsilon_M-\varepsilon_0$ at different d. — The curves are cut at eight $\varepsilon_M-\varepsilon_0$, each of them representing a certain constant pair ($\bar{n}$, [A]).*

obtained from the values of $(\varepsilon_M-\varepsilon_0)/C_A$ of the intersections. The corresponding values of C_M are found by seeking up in the (log C_M, log $(\varepsilon_M-\varepsilon_0)$)-diagram (Fig. 5) the values of C_M which correspond to the given $\varepsilon_M-\varepsilon_0$ at the d in question.

Thus, for a constant $\varepsilon_M-\varepsilon_0$, C_M and C_A may be considered as the variables of the equation of the ligand number (1), whereas [A] and $\bar{n}$ are constants. The equation is of the first grade; in a (C_M, C_A)-diagram it means a straight line with the intercept on the C_A-axis = [A] and the slope = $\bar{n}$. By plotting the (C_A, C_M)-pairs found for each $\varepsilon_M-\varepsilon_0$ in such a diagram, the unknown constants [A] and $\bar{n}$ of every $\varepsilon_M-\varepsilon_0$ are obtained, and thereby the complex formation curve searched for.

If the pairs of (C_M, C_A) obtained at constant $\varepsilon_M - \varepsilon_0$ do not fall along straight lines it means polynuclear complex formation. For if polynuclear complexes exist neither [A] nor $\bar{n}$ are constants at constant $\varepsilon_M - \varepsilon_0$ (Fronaeus[5, p. 88]) and (1) may thus become curved. But it is by no means certain that this really occurs in all such cases. The lines may also be approximately straight but have a slope differing from $\bar{n}$ (see Fronaeus[5, p. 109]). The straight-lined course of (1) at constant $\varepsilon_M - \varepsilon_0$ therefore is a necessary but not sufficient condition for the mononuclear complex formation postulated in our calculations.

Table 7. C_A *as a function of* C_M *at the eight selected* $\varepsilon_M-\varepsilon_0$ *and the corresponding values of* $[A]$, $\bar{n}$ *and* $\bar{n}/[A]$ *hence determined.*

$d \rightarrow$ cm	0.1		0.3		1		3				
$\varepsilon_M-\varepsilon_0$ $C^{-1} \cdot cm^{-1}$	C_A mC	C_M mC	C_A mC	C_M mC	C_A mC	C_M mC	C_A mC	C_M mC	$C_M=0$ $C_A=$ [A] mC	n	$\bar{n}/[A]$ C^{-1}
55			31.9	22.8	25.6	6.8	23.5	2.3	22.6	0.42	18.6
95			59.0	15.4	51.3	4.6	48.7	1.6	47.7	0.77	16.2
120	110.1	40.1	82.2	12.9	73.2	3.9	70.6	1.3	69.2	1.02	14.8
140	133.2	35.3	105.7	11.5	95.2	3.5			91.4	1.20	13.2
165	168.8	30.9	142.8	10.2	131.4	3.1			128.2	1.35	10.5
190	217.9	27.5	190.9	9.2	181.0	2.8			176.9	1.51	8.6
225	318	24.0	289.5	8.1	279.5	2.5			275	1.8	6.5
250	426	22.0	395	7.5	381	2.3			377	2.3	6.1

In the present case this condition is very well fulfilled, and as also the criterion applied in the potentiometric measurements gave the same result, there is no doubt, that the complex formation in question is entirely mononuclear.

However it is necessary to remember that our fundamental equations (21) and (22) may be invalid even if the chloroacetate complex formation is strictly mononuclear. Of course, this is the case if a reaction occurs in the solutions. In uranyl solutions one has moreover to take into consideration that reactions often are induced by the action of light. To investigate this, E was determined for a solution:

$$C_M = 10.98 \text{ mC}; \ C'_A = C'_{HA} = 100 \text{ mC}; \ \text{NaClO}_4 \text{ to } I = 1$$

when it was lighted in different ways. The observations then made, which have been fully confirmed in the later measurements, may be summed up as follows:

a. The solution is not changed during twentyfour hours in the dark, or in ordinary lamp-light.

b. The solution is not changed during several hours if lighted with UV-light of the wave-length of measuring, 3 130 Å.

c. The solution is rapidly changed in diffuse day-light, even behind glass. An exposure of one hour altered E of 3 130 Å by $\approx$ 10 %, whereas another sample of the same solution, kept in the dark during the same time, gave the original E.

Thus it seems to be the absorption range in the violet which is sensitive to light. In the measurements, the solutions must therefore be prepared and stored only in lamp-light. Then reproducible E are obtained indicating that the system is in its original state and so (21) and (22) are valid.

Another fact which may cause (21) and (22) to be invalid is the hydrolysis of the solutions. It would be of no importance, if the solutions which are compared in the measurements had the same degree of hydrolysis. This would mean a constant error of ε_M which has no influence by the method of calculation used, as was mentioned above. The degree of hydrolysis depends on both p[H$^+$] and C_M, as was shown in I. As the solutions to be compared have different C_M and p[H$^+$], their errors of ε_M are different. They may, however, be roughly estimated from I where the effect of the hydrolysis on ε_M is determined. The error is important only at low C'_A where [UO$_2^{2+}$] is large. At the lowest C'_A it may cause an error of $\approx$ 1 % in [A] which means that the finally computed quantity $\bar{n}$/[A] becomes $\approx$ 5 % too high.

Now this error must be largely compensated by the error of C_M caused by the hydrolysis. As at the potentiometric measurements above, the C_M:s really taking part in the complex formation at low C'_A are 3—5 % lower them the stoicheiometric ones. Hence the corresponding $\bar{n}$/[A] come out 3—5 % too low. The total effect of the hydrolysis therefore seems to be rather small.

The uncertainty involved in these estimations of the effect of hydrolysis, together with the desire to keep [H$^+$] as a minor part of C_A, has lead to that C'_A lower than 25 mC have not been used.

The ε_M directly determined are found as the mean of at least three adjustments of the sector. Before every adjustment, the compensation of the apparatus is checked. As a control, about one third of the solutions is prepared and measured twice, sometimes with use of different preparations of buffer. In all cases the reproducibility is $\approx \pm 2$ ‰, or almost as good as was found by the calibration. At low C'_A this may cause an accidental error of $\bar{n}$/[A] which may amount $\approx$ 3 %, thus rather insignificant. At the higher C'_A where the variation of ε_M by C'_A is less, the error of $\bar{n}$/[A] becomes larger and may amount $\approx$ 10 %.

ε_0 is separately determined with two C_M : 47.11 mC ($d = 0.3$ cm) and 14.13 mC ($d = 1$ cm). One finds $\varepsilon_0 = 47.93$ and 48.09; mean 48.0 C$^{-1} \cdot$ cm^{-1}. It is evident that Beers law is strictly valid for the uranyl ion within the errors of measurement.

Table 5 gives the determined values of $\varepsilon_M - \varepsilon_0$ for given C'_A and C_M. In Fig. 5 the corresponding values of log C_M and log ($\varepsilon_M - \varepsilon_0$) are plotted. In the

Table 8. $X([A])$, $X_1([A])$, $X_2([A])$ and $X_3([A])$ for given $[A]$ as obtained by numerical integration of the extinctiometrically determined function of Fig. 2. — The complexity constants and the ligand number obtained from these functions.

$\beta_1 = 24 \pm 3$ C^{-1} $\beta_2 = 150 \pm 40$ C^{-2} $\beta_3 = 350 \pm 150$ C^{-3}

$[A]$ mC	(5b) $\ln \frac{X([A])}{X(0.02)}$	$\frac{X([A])}{X(0.02)}$	$X([A])$	(7a) $X_1([A])$ C^{-1}	(7b) $X_2([A])$ C^{-2}	$X_3([A])$ C^{-3}	(2) $\bar{n}$
0				*24.0*	*147*	*350*	
20	0	1.00	1.54	27.0			0.39
40	0.3585	1.43	2.20	30.0			0.675
60	0.6781	1.97	3.03	33.9	165		
80	0.9653	2.63	4.04	38.0	175		
100	1.2258	3.41	5.24	42.4	184	370	1.21
150	1.7768	5.91	9.10	54.0	200	355	
200	2.2217	9.23	14.2	66.0	210	315	1.69
300	2.9984	20.06	30.9	99.7	252	350	
400	3.5870	36.13	55.4	136	280	335	2.14

best agreement with the points, straight lines are drawn which constitute the known connection between $\varepsilon_M - \varepsilon_0$ and C_M. The course of the curves for constant C'_A are sufficiently well known to enable us to state the value of $\varepsilon_M - \varepsilon_0$ at a certain C'_A, which corresponds to the stated $(\varepsilon_M - \varepsilon_0, C_M)$-connection. The $(\varepsilon_M - \varepsilon_0, C'_A)$ thus found are in Table 6. There are also $C_A = C'_A + [H^+]$, $[H^+]$ being known from the potentiometric measurements. Hence $(\varepsilon_M - \varepsilon_0)/C_A$ is calculated. The function $(\varepsilon_M - \varepsilon_0)/C_A = f\,(\varepsilon_M - \varepsilon_0)$ (23) is then plotted in Fig. 6. The curves are cut at eight constant $\varepsilon_M - \varepsilon_0$. The $(\varepsilon_M - \varepsilon_0)/C_A$ found give the corresponding C_A:s, while the C_M:s are obtained from Fig. 5. The (C_A, C_M)-values at constant $\varepsilon_M - \varepsilon_0$ are found to be along straight lines. Their

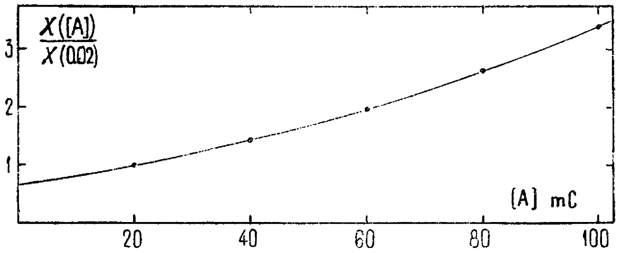

Fig. 7. Determination of $\lim_{[A]\to 0} \frac{X([A])}{X(0.02)} = \frac{1}{X(0.02)}$ *(Table 8).*

extrapolation to $C_M = 0$ gives [A], and their slope gives $\bar{n}$, hence $\bar{n}/[\mathrm{A}]$ is known. The values found are collected in Table 7. The complex formation function is plotted on Fig. 1 and $\bar{n}/[\mathrm{A}]$ as a function of [A] on Fig. 2 (filled points).

For the calculation of the complexity constants, the $X([\mathrm{A}])$ function is computed by graphical integration of the $\bar{n}/[\mathrm{A}]$ function of Fig. 2. As this function in the present case is not determined at sufficiently low [A], it is not possible to extrapolate to $[\mathrm{A}] = 0$, as was done in the potentiometric measurements. Another lower limit must be used at the integration and we chose $[\mathrm{A}]_0 = 20$ mC. The integration gives $X([\mathrm{A}])/X(0.02)$. This function, Fig. 7, is easily extrapolated to $[\mathrm{A}] = 0$, and gives $1/X(0.02) = 0.65 \pm 0.05$. Hence the function $X([\mathrm{A}])$ is known, and from this $X_1([\mathrm{A}])$, $X_2([\mathrm{A}])$ and $X_3([\mathrm{A}])$ are formed and the constants are calculated as before. The values obtained are found in Table 8.

As it can be seen from Table 8, the accidental errors of the constants are fairly large here as two extrapolations must be performed, both of them over a rather great [A]-range. In return the systematic errors seem to be rather small, as was proved above.

For some round [A], $\bar{n}$ is calculated with the constants obtained, and given in Table 8 and on Fig. 1 (dashed curve). The calculated values fit the corresponding experimental ones very well.

COMPARISON BETWEEN THE RESULTS OF THE POTENTIOMETRIC AND THE EXTINCTIOMETRIC MEASUREMENTS

According to both the methods used, three mononuclear complexes exist in solutions of uranyl chloroacetate, *viz.* $\mathrm{MA_1}$ $\mathrm{MA_2}$ and $\mathrm{MA_3}$. It has not been possible to observe any signs of polynuclear complex formation according to any method.

The following complexity constants have been calculated:

potentiometric: $\beta_1 = 27.5 \pm 0.5\ \mathrm{C^{-1}}$; $\beta_2 = 195 \pm 20\ \mathrm{C^{-2}}$; $\beta_3 = 625 \pm 150\ \mathrm{C^{-3}}$

extinctiometric: $\beta_1 = 24 \pm 3\ \mathrm{C^{-1}}$; $\beta_2 = 150 \pm 40\ \mathrm{C^{-2}}$; $\beta_3 = 350 \pm 150\ \mathrm{C^{-3}}$

Within the limits of the accidental errors indicated, the agreement may be considered as almost complete. The potentiometric values are throughout somewhat higher which may be due to the effect of their systematic errors as was discussed above.

The final result is that potentiometric and extinctiometric methods, properly used in determinations of complexity, give entirely the same results.

The constants thus obtained may therefore be considered as true constants of equilibrium.

Similar comparisons on systems involving several complexes are rather uncommon. The most important are those found in the work by Fronaeus[5] and Bjerrum[4]. — Fronaeus investigated some cupric salts. He found good agreement between potentiometric and extinctiometric results as long as the complex formation was mononuclear. Bjerrum found the same complex formation curve for the cupric ammine system according to both methods.

SUMMARY

The complexity of uranyl monochloroacetate has been investigated according to two methods: potentiometrically (by p[H^+]-measurements with the quinhydrone electrode) and extinctiometrically (at the Hg-line of 3 130 Å).

Both methods indicate that the complex formation is entirely mononuclear; there is no sign of polynuclear complexes.

The complexity constants of the three mononuclear complexes existing in the range of concentration used are calculated according to both methods. The results agree quantitatively.

The conclusion is that potentiometric and extinctiometric methods of measurements of complexity give consistent results if properly used. The constants obtained may therefore with great certainty be considered as the true constants according to the law of mass action.

My thanks are due to *Försvarets Forskningsanstalt (FOA)*, Stockholm, which has financially supported the work.

REFERENCES

1. Ahrland, S. *Acta Chem. Scand.* 3 (1949) 374.
2. Leden, I. *Diss.* Lund (1943).
3. Olerup, H. *Diss.* Lund (1944).
4. Bjerrum, J. *Kgl. Danske Videnskab. Selskabs Skrifter Naturvidenskab. math. Afdel.* **21** (1944) no. 4.
5. Fronaeus, S. *Diss.* Lund (1948).
6. Gmelins *Handbuch der anorganischen Chemie.* 8th edit. **55** (1936) 257.
7. Dittrich, C. *Z. phyik. Chem.* **29** (1899) 449.
8. Kortüm, G., and v. Halban, H. *Z. physik. Chem.* **A 170** (1934) 212.
9. Deck, W. *Helv. Phys. Acta* **11** (1938) 1.
10. Kortüm, G. *Kolorimetrie und Spektralphotometrie.* Berlin (1942.)
11. v. Halban, H., Kortüm, G., and Szigeti, B. *Z. Elektrochem.* **42** (1936) 628.

Received May 9, 1949.