ACTA CHEMICA SCANDINAVICA 5 (1951) 199—219

On the Complex Chemistry of the Uranyl Ion

IV.* The Complexity of Uranyl Acetate

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The hydrolysis of the uranyl ion is getting perceptible at as low a pH as 3. By this, investigations of the complexity of uranyl salts are rendered rather difficult for in all solutions of pH $>$ 3 the complex equilibria searched for are always contaminated with hydrolytic equilibria (I p. 379). Certainly, not only the uranyl ion is hydrolysed, but also its complexes. For two reasons, however, the hydrolysis of the complexes must be less pronounced than that of the uranyl ion itself: they have less ionic charge, and fewer places of coordination ready for hydrolytic reactions. In a solution of a strongly complex uranyl salt, therefore, it is very probable that the hydrolysis may be neglected even if pH $>$ 3. If that is the case, the complexity of the salt can be determined even by measurements at a pH, where the uranyl ion is hydrolysed in a fatal degree. But, of course, it is in every case necessary to test if the supposition holds. According to the method of measurement used, this test is performed in different ways, as will be seen below.

SELECTION OF URANYL ACETATE AS A SALT, SUITABLE FOR THE MEASUREMENTS

For several reasons, uranyl acetate has been selected as a salt, suitable to test the applicability of the principle outlined above.

Firstly, it is certainly rather strongly complex. This is clearly proved by Dittrich[4] by means of conductometric, cryoscopic and migration measurements. The last method gives the especially interesting information that the

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* The preceding papers of this series (Ahrland [1–3]) are in the following referred to as I, II and III.

uranyl group forms part of an anion in solutions of high C_A.* The existence of such an anion is also reported by Brintzinger and Jahn[5]. By dialysis measurements they consider to have proved the ion $UO_2(CH_3 \cdot COO)_3^-$. Indeed, this view is strongly supported by the existence of numerous "double" salts of the type $NaUO_2\,(CH_3COO)_3$.

Secondly, the acetate permits both emf and extinction measurements according to the methods described in II, and the results can be compared as it was done there. The emf measurement forms, however, the principal base of the calculations. As will be seen below, it is namely impossible to extend the extinction measurements over the whole desirable C_A-range.

Thirdly, as the acetate ligand is always added to the uranyl solutions in the form of a buffer, the pH:s of the complex solutions do not become too high which, of course, increases the chance of success. Further, the acetate is, fortunately, very little sensible to light which is contrary to most other organic uranyl salts (*cf.* II pp. 784 and 804).

Last but not least, the acetate may pretend to have a certain general interest as a very common uranyl salt.

To make the present measurements comparable to those of I—III, the same ionic strength $I = 1$ has been chosen, and sodium perchlorate used as the supplementary neutral salt. But this proves to be somewhat disadvantageous here, on account of the rather slight solubility of $NaUO_2\,(CH_3 \cdot COO)_3$. At the high $[Na^+]$, ≈ 1, which prevails in the present solution, C_A cannot generally exceed 150 mC at the highest C'_M used, 50 mC, before precipitation occurs. A ionic medium of lower $[Na^+]$ or no $[Na^+]$ at all would have been more advantageous, but in order not to sacrifice the comparability, no change has been made

The temperature has been kept at 20° C, as in I—III.

CHEMICALS USED

The *glacial acetic acid*, Schering-Kahlbaum *pro analysi*, has been freezed out once.

The *sodium acetate*, Bakers analysed, has been used without further purification.

By weighing, three different buffers are prepared, with the $C'_{HA} : C'_A$ ratios $1/2 : 1$, $2 : 1$ and $5 : 1$. Then the exact concentrations of acid are determined alkalimetrically and those of acetate acidimetrically. In the latter case, potentiometric indication of the endpoint is applied. By that, a quinhydrone electrode is used which is measured towards the quinhydrone reference electrode RE (*cf.* I p. 383).

The *other chemicals* used are of the same quality as before (I p. 382).

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* The meaning of symbols, see I—III.

THE EMF MEASUREMENTS

a. The complex formation function when hydrolysis occur in the solutions

The potentiometric method results in a determination of [A] and $\bar{n}$, *i.e.* the complex formation function (*cf.* II pp. 788—794). Therefore, we will deduce this function in the present case, where the complex equilibria of the solution are contaminated with hydrolytic ones.

In the case of a complex system with only one sort of ligand, it has been shown in I (p. 379) that $\bar{n}$ is a function of [A] only if only mononuclear complexes exist in the solution, but $\bar{n}$ is a function of both [A] and [M], if polynuclear complexes exist, too. As the essential difference between these two possibilities turns up as soon as dinuclear complexes exist, we may, for our purpose of differentiating between them, limit ourselves to consider mono- and dinuclear complexes. This considerably simplifies our future formulas. In such a case (8) of I (p. 379) takes the form:

$$\frac{C_A - [\mathrm{A}]}{C_M} = \bar{n} = \frac{\sum\limits_{n=1}^{N} n\,\beta'_n\,[\mathrm{A}]^n + [\mathrm{M}]\sum\limits_{n=1}^{Q} n\,\beta''_n\,[\mathrm{A}]^n}{1 + \sum\limits_{n=1}^{N} \beta'_n[\mathrm{A}]^n + 2\,[\mathrm{M}]\sum\limits_{n=1}^{Q} \beta''_n\,[\mathrm{A}]^n} \qquad (1)$$

If only mononuclear complexes exist, this equation is further simplified by omission of the terms containing the factor [M] (= (2) of II, p. 785).

If now hydrolysis occurs besides the complex formation between M and A, this means that two sorts of ligand are operating in the same solution. A series of hydrolytic complexes with 1,2, . . . OH^- may then be formed for every uranyl species present before. If we substitute $[\mathrm{H}^+]$ for $[\mathrm{OH}^-]$ according to $[\mathrm{OH}^-] = K_w/[\mathrm{H}^+]$ (*cf.* I p. 381), we can write the equilibrium equations of the new hydrolytic complexes thus:

$$\gamma'_{n,1} = [\mathrm{MA}_n\mathrm{OH}]\,[\mathrm{M}]^{-1}\,[\mathrm{A}]^{-n}\,[\mathrm{H}^+] \quad (2\,\mathrm{a}) \qquad \gamma''_{n,1} = [\mathrm{M}_2\mathrm{A}_n\,\mathrm{OH}]\,[\mathrm{M}]^{-2}\,[\mathrm{A}]^{-n}[\mathrm{H}^+] \quad (3\,\mathrm{a})$$

$$\gamma'_{n,2} = [\mathrm{MA}_n(\mathrm{OH})_2]\,[\mathrm{M}]^{-1}[\mathrm{A}]^{-n}\,[\mathrm{H}^+]^2 \quad (2\,\mathrm{b}) \qquad \gamma''_{n,2} = [\mathrm{M}_2\mathrm{A}_n(\mathrm{OH})_2]\,[\mathrm{M}]^{-2}[\mathrm{A}]^{-n}\,[\mathrm{H}^+]^2 \quad (3\,\mathrm{b})$$

If we now reform $(C_A - [\mathrm{A}])/C_M$, including these hydrolytic complexes, we obtain:

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta'_n [\mathrm{A}]^n + [\mathrm{M}] \sum_{n=1}^{Q} n\beta''_n [\mathrm{A}]^n + 1/[\mathrm{H}^+] \left[\sum_{n=1}^{R} n\gamma'_{n,1} [\mathrm{A}]^n + [\mathrm{M}] \sum_{n=1}^{S} n\gamma''_{n,1} [\mathrm{A}]^n \right] + + 1/[\mathrm{H}^+]^2 \left[\sum_{n=1}^{T} n\gamma_{n,2} [\mathrm{A}]^n + [\mathrm{M}] \sum_{n=1}^{U} n\gamma''_{n,2} [\mathrm{A}]^n \right] + \ldots}{1 + \sum_{n=1}^{N} \beta'_n [\mathrm{A}]^n + 2[\mathrm{M}] \sum_{n=1}^{Q} \beta''_n [\mathrm{A}]^n + 1/[\mathrm{H}^+] \left[\gamma'_{0,1} + \sum_{n=1}^{R} \gamma'_{n,1} [\mathrm{A}]^n + 2[\mathrm{M}] (\gamma''_{0,1} + \sum_{n=1}^{S} \gamma''_{n,1} [\mathrm{A}]^n) \right] + + 1/[\mathrm{H}^+]^2 \left[\gamma'_{0,2} + \sum_{n=1}^{T} \gamma'_{n,2} [\mathrm{A}]^n + 2[\mathrm{M}] (\gamma''_{0,2} + \sum_{n=1}^{U} \gamma''_{n,2} [\mathrm{A}]^n) \right] + \ldots} \tag{4}$$

Thus, besides being a function of [A] and [M], $\bar{n}$ is a function of $[\mathrm{H}^+]$, too, if hydrolytic reactions occur. Inversely, if the formation function is found to be independent of $[\mathrm{H}^+]$, no hydrolysis takes place in the solution, and the old formulas of $\bar{n}$ holds. By determining [A] and $\bar{n}$ at varying pH, we can thus observe if the hydrolysis has any influence and so test our introductory supposition. If slight deviations are found between the formation functions of different pH, the nonhydrolytic function may be found by an extrapolation to strongly acid solution, *i. e.* to $1/[\mathrm{H}^+] = 0$.

At every pH, measurements are performed at different C_M, *i. e.* different [M], in order to make the usual decision between mono- and polynuclear complex formation.

b. The calculation of $\bar{n}$ and [A] from experimental data

The experiments are determinations of $[\mathrm{H}^+]$ by quinhydrone electrode, carried out quite analogous to those of II (p. 788). From $[\mathrm{H}^+]$, [A] and $\bar{n}$ will be calculated in the same manner as there, with some necessary modifications.

If C'_{HA} is the stoichiometric concentration of acetic acid, it is valid, in a buffer solution free from uranyl:

$$\frac{[\mathrm{H}^+]' \, (C'_A + [\mathrm{H}^+]')}{C'_{HA} - [\mathrm{H}^+]'} = K_c \tag{5}$$

For a solution, which has the uranyl concentration C_M and the same stoichiometric buffer concentration as above, [A] is the quantity searched for and for [HA] it is valid

$$[\mathrm{HA}] = C'_{HA} + C^0_H - [\mathrm{H}^+] - C_s \tag{6}$$

Thus

$$\frac{[\mathrm{H}^+]\,[\mathrm{A}]}{C'_{HA} + C^0_H - [\mathrm{H}^+] - C_s} = K_c \tag{7}$$

If we put $C'_{HA}/C'_A = \delta$, (5) and (7) give

$$[\mathrm{A}] = \frac{[\mathrm{H}^+]'}{[\mathrm{H}^+]} \cdot \frac{(C'_A + [\mathrm{H}^+]')\ (\delta \cdot C'_A + C^0_H - [\mathrm{H}^+] - C_s)}{\delta \cdot C'_A - [\mathrm{H}^+]'}$$

or, approximately,

$$[\mathrm{A}] = \frac{[\mathrm{H}^+]'}{[\mathrm{H}^+]} \cdot \left(C'_A + \frac{C^0_H - [\mathrm{H}^+] - C_s + (1+\delta)[\mathrm{H}^+]'}{\delta} \right) \tag{8}$$

In the calculation of $\bar{n}$ according to (1), C_A is the total concentration of species containing A except the acetic acid, and C_M is the total uranium concentration, hydrolysed as non-hydrolysed. Hence, with (14) of II:

$$\bar{n} = \frac{C'_A + [\mathrm{H}^+] - C^0_H + C_s - [\mathrm{A}]}{C_M} \tag{9}$$

In these equations of $\bar{n}$ and [A], $[\mathrm{H}^+]'$, $[\mathrm{H}^+]$, C^0_H and $[\mathrm{H}^+]'/[\mathrm{H}^+]$ are measured according to (16), (17) and (18) of II, and C'_A and δ are known by the analysis of the buffer stock solutions. The only unknown quantity is C_s, the term that originates from those hydrogen ions which are taken up by or set free from the uranyl species when hydrolytic reactions occur by the addition of buffer. *

Thus, in case of a hydrolysis, $\bar{n}$ is affected in two different ways: firstly, $\bar{n}$ becomes a function of $[\mathrm{H}^+]$ (according to (4)) and, secondly, the very calculation of $\bar{n}$ according to its definition (1) becomes impossible.

On the other hand, if the hydrolysis can be neglected, $\bar{n}$ is independent of $[\mathrm{H}^+]$ ((1) holds), and, moreover, its calculation is easily performed according to (9), as, of course, $C_s \approx 0$ in this case. Thus, if we calculate $\bar{n}$ according to (9), putting $C_s = 0$, and find a complex formation curve which is independent of pH, we are certainly allowed to conclude that no hydrolysis occurs. **

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* In II, it was possible to correct approximately for this C_s, as the hydrolysis of uranyl is known to be very slight at the p $[\mathrm{H}^+]$ of the chloroacetate buffer. The course of the hydrolysis in acetate buffers is, however, a priori unknown.

** The only conceivable alternative would be that the two factors influencing $\bar{n}$ just balance each other throughout the whole complex formation curve. This assumption is, however, extremely unlikely.

Table 1. Determination of E' as a function of C'_A, when perchlorate is exchanged for the different acetate buffers in solutions of $C_M = 0$. — Calculation of K_c in the medium used.

Buffer →	5 : 1		2 : 1		1/2 : 1	
C'_A mC	E' mV	(5) $K_c \cdot 10^5$ C	E' mV	(5) $K_c \cdot 10^5$ C	E' mV	(5) $K_c \cdot 10^5$ C
12.97	110.6	2.58	133.4	2.57	168.9	2.54
25.6	110.3	2.59	133.2	2.58	168.7	2.55
37.9	110.1	2.60	133.1	2.59	168.6	2.56
49.9	110.0	2.60	133.1	2.59	168.6	2.56
61.7	110.0	2.60	133.1	2.59	168.5	2.57
89.6	110.0	2.60	133.0	2.60	168.5	2.57
116.0	110.0	2.60	133.1	2.59	168.5	2.57
164.3	110.0	2.60	133.2	2.58	168.6	2.56
207.5	110.1	2.60	133.2	2.58	168.6	2.56
246.5	110.2	2.59	133.2	2.58	168.6	2.56
281.8	110.2		133.3		168.7	
343.0	110.5		133.5		168.7	
394	110.7		133.6		168.7	

c. Experimental data

The measurements are performed with the three different buffers mentioned above, which have the exact concentrations: $C'_A = 986$ mC and $C'_{HA} = 493$, 1983 and 4910 mC, respectively. For every buffer, series are made with $C'_M =$ 10, 25 and 50 mC, besides the titrations with $C_M = 0$. RE has in the present case $[H^+]_0 = 10.14$ mC. In all cases, the potentials measured are stable and reproduce themselves within ≈ 0.2 mV. No sign of any sensibility to light has been detected.

The series with $C_M = 0$ (Table 1) show that the ionic medium is not as seriously changed by acetate as by chloroacetate (II p. 789). C'_A can reach > 200 mC even at the buffer of the highest C'_{HA} before any change is perceptible. Up to that C'_A, we find (according to (16) of II and (5)) a constant $K_c = 2.58 \cdot 10^{-5}$, the same for all buffers if the random errors are considered.*

The results of the main titrations are collected in Tables 2—4, and shown in Figs. 1 and 2. At the two most acid buffers, the formation functions coincide, if one excepts a small deviation in their lowest parts, when $\bar{n} < 0.9$. At the

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* Fronæus[6] finds $2.46 \cdot 10^{-5}$

Table 2. Determination of corresponding values of $\bar{n}$ and [A] at the pH of the buffer 5 : 1.

Table 2 A. C'_M = 10 mC. ● *

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II $C_H^0-[H^+]$ mC	(16) of II $[H^+]'$ mC	(8) [A] mC	(9) $\bar{n}$	$\bar{n}$/[A] C^{-1}
10.00	0	71.0						
9.87	12.97	81.8	28.8	0.20	0.13	4.16	0.875	210
9.74	25.60	84.4	25.9	0.23	0.13	9.18	1.66	181
9.62	37.9	88.8	21.3	0.3	0.1	16.37	2.20	134
9.50	49.9	93.3	16.7	0.3	0.1	25.8	2.51	97.5
9.38	61.7	96.5	13.5	0.3	0.1	36.2	2.67	74
9.27	73.0	99.1	10.0	0.4	0.1	47.6	2.70	56.5
9.09	89.6	101.3	8.7	0.4	0.1	63.6	2.82	44.5
8.82	116.0	103.7	6.3	0.4	0.1	90.6	2.83	31
8.57	140.9	105.0	5.0	0.4	0.1	115.6	2.91	25
8.33	164.3	105.9	4.1	0.4	0.1	139.6	2.90	21
8.11	186.5	106.5	3.5	0.4	0.1	162.6	2.90	18
7.90	207.5	107.0	3.1	0.3	0.1	183.6	2.99	16.5
7.70	227.5	107.4	2.7	0.3	0.1	204.7	2.93	14.5
7.50	246.5	107.7	2.5	0.3	0.1	223.5	3.02	13.5
7.14	281.8	108.3	1.9	0.3	0.1	261.2	2.85	11
6.82	313.7	108.7	1.6	0.3	0.1	294.4	2.79	9.5
6.52	343.0	109.1	1.4	0.3	0.1	324.3	2.81	8.5

least acid buffer, on the other hand, the formation function does not coincide with the other ones before $\bar{n}$ has reached 2.3. The deviations grow very large at low $\bar{n}$. Moreover, the curves of different C_M do not coincide here, as is the case at the other buffers. All the curves ultimately bend towards $\bar{n} = 3$.

Thus the hydrolysis is completely forced out by the acetate complex formation at the pH of the buffers 5 : 1 and 2 : 1, except at very low [A]. Moreover, the complex formation is mononuclear. At the buffer ½ : 1, on the other hand, the hydrolysis is very pronounced even at rather high [A]. At very high [A], however, the acetate complexes become predominant even here. As a difference of C_M means a difference of pH, the spreading of the curves of different C_M is at once clear. The existence of polynuclear hydrolytic complexes may, of course, also have influence, here, as well as the fact that the very calculation of $\bar{n}$ and [A] is erronous if a strong hydrolysis occurs (p. 203).

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* In the Tables 2—4, these signs indicate the respective series in the Figs. 1 and 2.

Table 2 B. C'_M = 25 mC. ▲

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II C^0_H–[H$^+$] mC	(16) of II [H$^+$]$'$ mC	(8) [A] mC	(9) $\bar{n}$	$\bar{n}$/[A] C^{-1}
25.0	0	52.3						
24.65	12.97	62.3	48.3	0.40	0.13	1.93	0.432	224
24.35	25.60	63.7	46.6	0.43	0.13	4.07	0.865	213
24.05	37.9	65.2	44.9	0.5	0.1	6.43	1.29	200
23.75	49.9	67.7	42.7	0.5	0.1	9.23	1.69	183
23.45	61.7	71.1	38.9	0.6	0.1	13.28	2.04	154
23.2	73.0	75.5	34.5	0.7	0.1	18.7	2.32	124
22.7	89.6	82.3	27.7	0.8	0.1	29.9	2.59	86.5
22.05	116.0	90.7	19.3	0.9	0.1	54.1	2.77	51
21.4	140.9	95.4	14.6	0.9	0.1	79.1	2.85	36
20.8	164.3	98.6	11.4	0.9	0.1	104.7	2.82	27
20.25	186.5	100.2	9.8	0.9	0.1	126.5	2.92	23
19.75	207.5	101.7	8.4	0.8	0.1	148.9	2.93	19.5
19.25	227.5	102.9	7.2	0.8	0.1	171.0	2.90	17
18.75	246.5	103.7	6.5	0.8	0.1	190.5	2.95	15.5
17.85	281.8	104.9	5.3	0.8	0.1	228.6	2.94	13
17.05	313.7	105.8	4.5	0.7	0.1	263.0	2.93	11
16.3	343.0	106.5	4.0	0.7	0.1	292.4	3.06	10.5

Table 2 C. C'_M = 50 mC. ■

50.0	0	38.0						
49.3	12.97	45.6	65.0	0.57	0.13	1.00	0.231	231
48.7	25.60	47.0	63.3	0.63	0.13	2.10	0.47	224
48.1	37.9	47.8	62.3	0.7	0.1	3.22	0.705	219
47.5	49.9	48.6	61.4	0.7	0.1	4.38	0.945	216
46.9	61.7	49.8	60.2	0.7	0.1	5.69	1.18	208
46.3	73.0	50.9	59.1	0.7	0.1	7.07	1.41	199
45.4	89.6	53.7	56.3	0.8	0.1	9.63	1.74	181
44.1	116.0	60.6	49.4	1.1	0.1	16.41	2.24	137
42.8	140.9	70.1	39.9	1.3	0.1	29.1	2.58	89

Above $\bar{n} = 0.9$ the coinciding curves of the buffers 5 : 1 and 2 : 1 are thus the non-hydrolytic complex formation curve. Below this $\bar{n}$, an extrapolation of $\bar{n}$ from 1/[H$^+$] of the three buffers used to 1/[H$^+$] = 0 is to give the right function. By this extrapolation, however, it is seen that the $\bar{n}$ of 1/[H$^+$] = 0 and the $\bar{n}$ of the 1/[H$^+$] of the buffer 5 : 1 coincide within the experimental

Table 3. Determination of corresponding values of $\bar{n}$ and $[A]$ at the pH of the buffer 2 : 1

Table 3 A. $C'_M = 10$ *mC.* ○

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II $C_H^0 - [H^+]$ mC	(16) of II $[H^+]'$	(8) [A] mC	(9) $\bar{n}$	$\bar{n}$/[A] C^{-1}
10.0	0	70.7						
9.87	12.97	102.3	31.1	0.42	0.05	3.86	0.88	228
9.74	25.60	107.2	26.0	0.44	0.05	9.23	1.63	177
9.62	37.9	112.0	21.1	0.5		16.52	2.17	131
9.50	49.9	116.5	16.6	0.5		25.9	2.48	96
9.38	61.7	119.7	13.4	0.5		36.5	2.63	72
9.27	73.0	122.1	11.0	0.5		47.3	2.72	57.5
9.09	89.6	124.5	8.5	0.5		64.3	2.73	42.5
8.82	116.0	126.8	6.3	0.5		90.6	2.82	31
8.57	140.9	128.1	5.0	0.5		115.8	2.87	25
8.33	164.3	129.0	4.2	0.5		139.3	2.94	21
8.11	186.5	129.8	3.4	0.4		163.3	2.81	17
7.90	207.5	130.2	3.0	0.4		184.5	2.86	15.5
7.70	227.5	130.6	2.6	0.4		205.5	2.81	13.5
7.50	246.5	130.9	2.3	0.4		224.8	2.84	12.5
7.14	281.8	131.4	1.9	0.4		261.2	2.83	11
6.82	313.7	131.8	1.6	0.4		294.4	2.78	9.5
6.52	343.0	132.1	1.4	0.4		324.3	2.82	8.5

error. This is not surprising, as the uranyl solutions of low C'_A by the buffer 5 : 1 actually have a $p[H^+] \approx 3$ (Table 2), so their hydrolysis must be insignificant (*cf.* I). Thus the complex formation curve of the buffer 5 : 1 is, in its whole course, equal to the non-hydrolytic formation curve of the uranyl acetate system, and the complexity constants of the system can be calculated from it, according to II p. 785—787. Before that, however, we will look at that formation curve which is obtained by the extinction measurement.

THE EXTINCTION MEASUREMENTS

a. The ε_M-function when hydrolysis occurs in the solutions

The extinctiometric method implies the determination of ε_M of a number of solutions with different C_M and C_A. In the case of a mononuclear complex formation with one ligand, [A] and $\bar{n}$, *i.e.* the complex formation function,

Table 3 B. $C'_M = 25$ *mC.* △

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II $C^0_H - [\mathrm{H}^+]$ mC	(16) of II $[\mathrm{H}^+]'$ mC	(8) [A] mC	(9) $\bar{n}$	$\bar{n}/[\mathrm{A}]$ C^{-1}
25.0	0	52.4						
24.65	12.97	79.0	54.4	0.82	0.05	1.56	0.435	278
24.35	25.60	84.5	48.7	0.89	0.05	3.79	0.86	227
24.05	37.9	87.6	45.5	0.9		6.34	1.27	200
23.75	49.9	90.6	42.5	0.9		9.38	1.67	178
23.45	61.7	94.4	38.7	1.0		13.46	2.02	150
23.15	73.0	98.9	34.2	1.0		18.96	2.29	121
22.7	89.6	105.6	27.4	1.0		30.5	2.56	84
22.05	116.0	114.0	19.1	1.0		54.7	2.74	50
21.4	140.9	118.7	14.4	1.0		80.0	2.80	35
20.8	164.3	121.5	11.7	1.0		103.7	2.86	27.5
20.25	186.5	123.5	9.7	1.0		127.3	2.88	22.5
19.75	207.5	124.9	8.3	0.9		149.6	2.89	19.5
19.25	227.5	125.9	7.3	0.9		170.6	2.91	17
18.75	246.5	126.7	6.5	0.9		191.2	2.90	15
17.85	281.8	128.0	5.3	0.9		228.5	2.94	13
17.05	313.7	128.9	4.5	0.8		263.0	2.93	11
16.3	343.0	129.6	3.9	0.8		293.8	2.97	10

Table 3 C. $C'_M = 50$ *mC.* □

50.0	0	37.9						
49.3	12.97	59.5	73.9	1.33	0.05	0.73	0.222	304
48.7	25.60	65.1	68.1	1.44	0.05	1.77	0.46	260
48.1	37.9	68.1	65.0	1.5		2.95	0.715	242
47.5	49.9	70.2	62.9	1.5		4.20	0.93	221
46.9	61.7	72.0	61.1	1.5		5.58	1.16	206
46.3	73.0	73.9	59.2	1.6		7.10	1.39	196
45.4	89.6	76.7	56.3	1.6		9.73	1.73	178
44.1	116.0	84.1	49.0	1.6		16.83	2.21	131
42.8	140.9	93.8	39.4	1.7		29.9	2.56	85.5

can be obtained from ε_M, and thus the complexity constants of the system calculated (see II and III).

When the complex formation involves hydrolytic equilibria, too, ε_M is modified in a manner analogous to that of the $\bar{n}$-function. In the ε_M-function,

Table 4. Determination of corresponding values of $\bar{n}$ and $[A]$ at the pH of the buffer 1/2 : 1.

Table 4 A. C'_M = 10 mC. ◐

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II $C^0_H - [\mathrm{H}^+]$ mC	(16) of II $[\mathrm{H}^+]'$ mC	(8) [A] mC	(9) $\bar{n}$	$\bar{n}$/[A] C^{-1}
10.00	0	70.7						
9.87	12.97	120.8	48.1	0.51	0.01	2.08	1.05	505
9.74	25.60	135.8	32.9	0.54	0.01	7.24	1.83	252
9.62	37.9	145.0	23.6	0.6		15.3	2.29	150
9.50	49.9	151.0	17.6	0.6		25.4	2.52	99
9.38	61.7	154.8	13.7	0.6		36.5	2.62	72
9.27	73.0	157.4	11.1	0.5		47.7	2.68	56
9.09	89.6	159.8	8.7	0.5		64.3	2.73	42.5
8.82	116.0	162.2	6.3	0.5		91.3	2.75	30
8.57	140.9	163.5	5.0	0.5		116.4	2.80	24
8.33	164.3	164.5	4.1	0.5		140.6	2.79	20
8.11	186.5	165.1	3.5	0.5		163.3	2.80	17
7.90	207.5	165.5	3.1	0.5		184.5	2.85	15.5
7.70	227.5	165.9	2.7	0.5		205.6	2.78	13.5
7.50	246.5	166.2	2.4	0.5		225.4	2.76	12.5
7.14	281.8	166.7	2.0	0.4		261.2	2.83	11
6.82	313.7	167.0	1.7	0.4		294.4	2.78	9.5
6.52	343.0	167.3	1.4	0.4		325.8	2.58	8

however, we need not consider any non-hydrolytic polynuclear complexes.* The emf measurements indicate that they are not likely to exist, and this is confirmed, when the usual extinctiometric criterion (II p. 803) of polynuclear complexes is applied here (p. 216). If the molar extinctions of the new complexes $\mathrm{MA}_n\mathrm{OH}$, $\mathrm{MA}_n(\mathrm{OH})_2, \ldots$, $\mathrm{M}_2\mathrm{A}_n\mathrm{OH}$, $\mathrm{M}_2\mathrm{A}_n(\mathrm{OH})_2, \ldots$ are indicated by $\varepsilon'_{n,1}, \varepsilon'_{n,2}, \ldots, \varepsilon''_{n,1}, \varepsilon''_{n,2}, \ldots$ respectively, we thus obtain

$$\begin{aligned} \varepsilon_M = {} & \frac{\varepsilon'_o + \sum_{n=1}^{N} \varepsilon'_n \beta'_n [\mathrm{A}]^n + 1/[\mathrm{H}^+] \left(\sum_{n=0}^{R} \varepsilon'_{n,1} \gamma'_{n,1} [\mathrm{A}]^n + [\mathrm{M}] \sum_{n=0}^{S} \varepsilon''_{n,1} \gamma''_{n,1} [\mathrm{A}]^n \right) +}{1 + \sum_{n=1}^{N} \beta'_n [\mathrm{A}]^n + 1/[\mathrm{H}^+] \left(\sum_{n=0}^{R} \gamma'_{n,1} [\mathrm{A}]^n + 2\,[\mathrm{M}] \sum_{n=0}^{S} \gamma''_{n,2} [\mathrm{A}]^n \right) +} \\ & \frac{+ 1/[\mathrm{H}^+]^2 \left(\sum_{n=0}^{T} \varepsilon'_{n,2} \gamma'_{n,2} [\mathrm{A}]^n + [\mathrm{M}] \sum_{n=0}^{U} \varepsilon''_{n,2} \gamma''_{n,2} [\mathrm{A}]^n \right) + \ldots}{+ 1/[\mathrm{H}^+]^2 \left(\sum_{n=0}^{T} \gamma'_{n,2} [\mathrm{A}]^n + 2\,[\mathrm{M}] \sum_{n=0}^{U} \gamma''_{n,2} [\mathrm{A}]^n \right) + \ldots} \end{aligned} \tag{10}$$

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* If such exist, no complexity constants can be calculated from ε_M. (II p. 799).

Table 4 B. $C'_M = 25$ *mC.* ◭

C_M mC	C'_A mC	E mV	(18) of II E_A mV	(17) of II $C_H^0-[H^+]$ mC	(16) of II $[H^+]'$ mC	(8) [A] mC	(9) $\bar{n}$	$\bar{n}/[A]$ C^{-1}
25.0	0	52.1						
24.65	12.97	90.8	78.1	0.99	0.01	0.68	0.46	677
24.35	25.60	103.7	65.0	1.08	0.01	2.11	0.92	437
24.05	37.9	112.4	56.2	1.1		4.33	1.35	312
23.75	49.9	119.8	48.8	1.1		7.55	1.74	230
23.45	61.7	126.3	42.2	1.1		12.02	2.07	172
23.15	73.0	132.5	36.0	1.1		18.15	2.32	128
22.7	89.6	140.1	28.4	1.1		29.9	2.58	86
22.05	116.0	148.8	19.7	1.1		54.2	2.76	51
21.4	140.9	153.7	14.9	1.1		79.5	2.82	35.5
20.8	164.3	156.8	11.8	1.1		104.2	2.84	27
20.25	186.5	158.7	9.9	1.0		127.4	2.87	22.5
19.75	207.5	160.0	8.6	1.0		148.9	2.92	19.5
19.25	227.5	161.0	7.6	1.0		169.8	2.95	17.5
18.75	246.5	161.8	6.8	1.0		189.7	2.98	15.5
17.85	281.8	162.9	5.8	0.9		225.4	3.11	14
17.05	313.7	163.9	4.8	0.9		261.2	3.03	11.5
16.3	343.0	164.7	4.0	0.8		294.4	2.94	10

Table 4 C. $C'_M = 50$ *mC.* ◧

50.0	0	37.8						
49.3	12.97	68.6	100.3	1.57	0.01	0.304	0.225	740
48.7	25.60	79.4	89.3	1.77	0.01	0.847	0.47	555
48.1	37.9	86.7	81.9	1.9		1.63	0.715	440
47.5	49.9	92.4	76.2	1.9		2.63	0.96	365
46.9	61.7	97.2	71.3	1.9		3.89	1.19	306
45.4	89.6	107.9	60.6	1.9		8.47	1.75	206
44.1	116.0	118.2	50.3	1.9		16.37	2.22	136
42.8	140.9	128.3	40.2	1.9		29.5	2.56	87

Thus, if hydrolytic reactions occur, ε_M is a function of $[H^+]$. Inversely, if ε_M is independent of $[H^+]$ no such reactions take place, and (21) of II (p. 800) is valid. By determining ε_M at different pH, we are thus able to decide, whether the hydrolysis has any influence or not. It a small deviation is found between the pH:s, an extrapolation of ε_M to $1/[H^+] = 0$ will give the non-hydrolytic value.

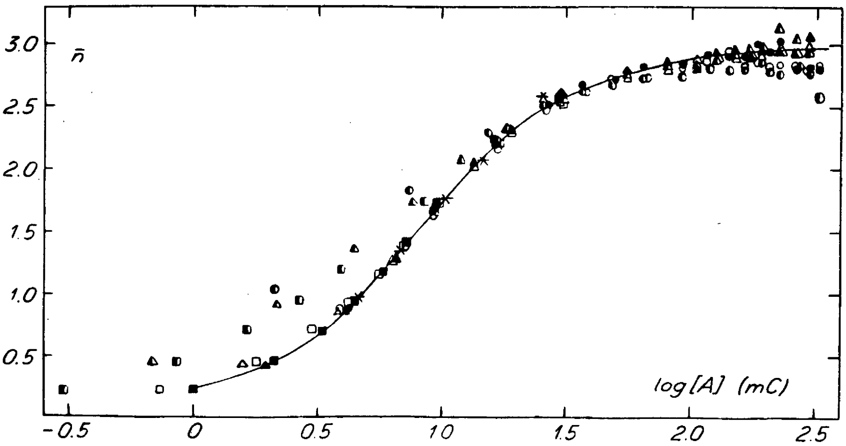

Fig. 1. The complex formation curves. — Circles, triangles and squares relate to the emf measurements at C'_M = 10, 25 and 50 mC respectively. Filled, open and half-filled signs relate to the buffers 5 : 1, 2 : 1 and 1/2 : 1 respectively. — The stars indicate the extinctiometrically determined values. — The fulldrawn curve is obtained from the complexity constants finally calculated.

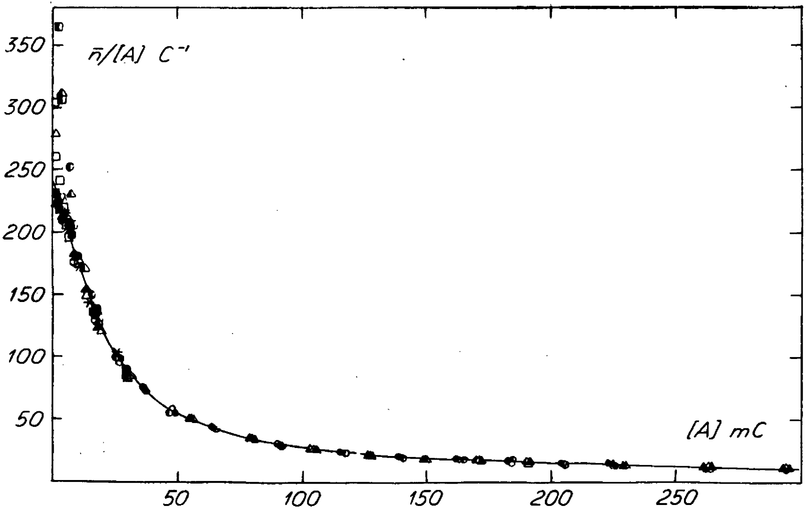

Fig. 2. $\bar{n}/[A]$ as a function of [A]. — The signs relate to the same measurements as in Fig. 1. — The fulldrawn curve represents the non-hydrolytic function the integration of which gives the X-functions (Table 8).

b. Apparatus and method of measurement

The present measurements are carried out with a Beckman Quartz Spectrophotometer, model DU, which had been improved as described by Adell [7]. The absorption cells used are from B. Halle, Berlin. They are made from glass, with windows of silica, which are held water-tight by adhesion forces. The cells are mounted on a slide, which gives them a very reproducible position in the beam of light. The reproducibility of E is ≈ 5 ‰, which is, it is true, somewhat lower than that obtained with the apparatus used before. But, on the other hand, the new apparatus is much more handy than the old one.

Another advantage is that its construction enables us, contrary to that of the old one, to correct separately for the differences of transparancy and thickness which may exist between the absorption cells (*cf.* II p. 798). At first we can establish, at every wavelength λ desired, the differences of transparancy between the two cells of every pair. This is done by measuring when both the cells contain solvent. Then those cells which are to be used to the uranyl solutions are compared by means of picrate solutions the concentrations of which are chosen so that E is always approximately constant (in the neighbourhood of 0.7). If these E:s are corrected for the differences of transparancy, they give the true ratios of thickness between the cells used, and not, as the proceeding of II, an "effective" ratio in which the differences of transparancy are involved. Contrary to the effective ratios, the true ones are, of course, independent of λ and E.

But then it is no more necessary to keep E constant throughout all the series of measurement. Only the condition remains that E has to be a constant for all solutions which are directly brought together for the calculation of a certain [A], *i. e.* for solutions of a constant ε_M. E may vary within a series if only those solutions of *different* series have the same E which are to be compared. But then we may simply keep a constant C_M throughout the series, allowing E to increase with C_A. This simplifies the measurements very much as now no especial function between ε_M and C_M has to be found, as was the case before (II p. 800). Here we only have to determine the right ratio of C_M between the series of different d, so that E becomes the same in all series for a given ε_M. If$^{(1)}$ and $^{(2)}$ indicate two different series which are to be compared at a constant ε_M it is valid: $\varepsilon_M = E^{(1)}/C_M^{(1)} \cdot d^{(1)} = E^{(2)}/C_M^{(2)} \cdot d^{(2)}$ *i. e.* $E^{(1)} = E^{(2)}$ if $C_M^{(1)} \cdot d^{(1)} = C_M^{(2} \cdot d^{(2)}$. That is, the C_M of the series ought to be inversely proportional to their d.

c. Selection of a wave-length suitable for measurement

To select a suitable λ, the extinction curves of the following solutions have been determined in the visible and UV regions down to $\lambda = 2500$ Å, also by the aid of the Beckman Spectrophotometer:

1. $C_M = 10$ mC, $C'_A = 30$ mC, by the buffers ½: 1, 2 : 1 and 5 : 1
2. $C_M = 10$ mC, $C'_A = 60$ mC, by the buffer 2 : 1.

The curves are found in Fig. 3, together with those of UO_2^{2+} and the solution $C_M = 33$ mC, p[H$^+$] = 4.1 (I p. 377). The extinction ε_A of the acetate buffers ½ : 1 and 5 : 1 have been measured, too, (*cf.* II p. 799), and are drawn in the same Fig.

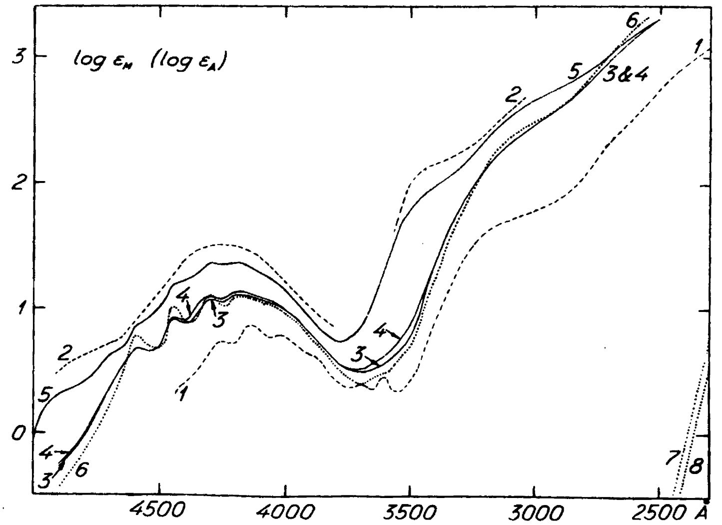

Fig. 3. Extinction curves of a) uranyl ion (dashed, 1), b) hydrolysed solution with C_M = 33 mC, p[H^+] = 4.1 (dashed, 2), c) complex solutions with C_M = 10 mC, C'_A = 30 mC by the buffers 5 : 1, 2 : 1 and 1/2 : 1 (fulldrawn; 3,4 and 5 respectively), d) complex solution with C_M = 10 mC, C'_A = 60 mC by the buffer 2 : 1 (dotted, 6) and e) buffers 5 : 1 and 1/2 : 1 (dotted low to the right, 7 and 8 respectively).

As is seen from the curves of different buffers at the same C'_A = 30 mC, the influence of hydrolysis on ε_M is very pronounced at the long wave-lengths, but grows smaller at the short ones, to cease at $\lambda \approx 2600$ Å. Moreover, the curve of C'_A = 60 mC at the buffer 2 : 1 is situated below the one of C'_A = 30 mC at the same buffer at most long wave-lengths. This may be explained so that the third complex has an ε which is smaller than that of the second one, but it is more probable that it is due to the circumstance that the hydrolysis is more pronounced at the low C'_A. This is also suggested by the course of the curves at short λ: when the influence of hydrolysis vanishes, the ε_M:s of C'_A = 60 mC grow higher than those of C'_A = 30 mC. — The influence of ε_A can be neglected at all $\lambda > 2500$ Å.

In view of these facts, we select $\lambda = 2600$ Å for measurement. Here the influence of hydrolysis is small, and ε_M seems to show a steady increase with C_A, while the influence of ε_A has not yeat been perceptible.

It has also been established, that the ε_M:s are not changed during the measurements or by an exposition of the solutions to diffuse daylight lasting a whole hour (*cf.* II p. 804). This is in accordance with previous statements (*cf.* II p. 784).

Table 5. ε_M *as a function of* C_A *at the different* C_M *and buffers used.*

C_M → mC	7.5				2.5				0.75			
d → cm	0.1				0.3				1			
δ →	2 : 1 ○*		5 : 1 ●		2 : 1 ▽		5 : 1 ▼		2 : 1 ◇		5 : 1 ◆	
C'_A mC	ε_M**	C_A mC	ε_M	C_A mC	ε_M	C_A mC	ε_M	C_A mC	ε_M	C_A mC	ε_M	C_A mC
5					916	4.86	881	4.97	1 008	4.97	995	5.05
10	960	9.66	940	9.85	1 222	9.86	1 207	9.97	1 337	9.97	1 339	10.05
15	1 156	14.64	1 142	14.84	1 414	14.85	1 413	14.96	1 507	14.97	1 509	15.05
20	1 316	19.63	1 313	19.83	1 527	19.85	1 530	19.96	1 591	19.97	1 596	20.05
30	1 525	29.6	1 526	29.8	1 637	29.8	1 638	29.9	1 669	30.0	1 668	30.0
45	1 651	44.6	1 651	44.8	1 698	44.8	1 688	44.9	1 707	45.0	1 703	45.0

* These signs indicate the respective series in Fig. 4.

** The unit of ε_M is $C^{-1} \cdot cm^{-1}$.

Table 6. Determination of the non-hydrolytic functions $\varepsilon_M = f(C_A)$ *by the extrapolation to* $1/[H^+]$ * $= 0$.

C_A mC	C_M → mC	7.5			2.5			0.75		
	δ →	2 : 1	5 : 1		2 : 1	5 : 1		2 : 1	5 : 1	
5	ε_M →				923	880	847	1 007	991	980
	$1/[H^+]$ →				11.9	5.2	0	16.7	6.9	0
10	ε_M →	973	945	923	1 228	1 207	1 193			
	$1/[H^+]$ →	6.7	3.0	0	13.0	5.2	0			
15	ε_M →	1 165	1 147	1 134	1 417	1 412	1 409			
	$1/[H^+]$ →	7.4	3.1	0	13.9	5.3	0			
20	ε_M →	1 325	1 314	1 307						
	$1/[H^+]$ →	8.0	3.2	0						

* The unit of $1/[H^+]$ is mC^{-1}.

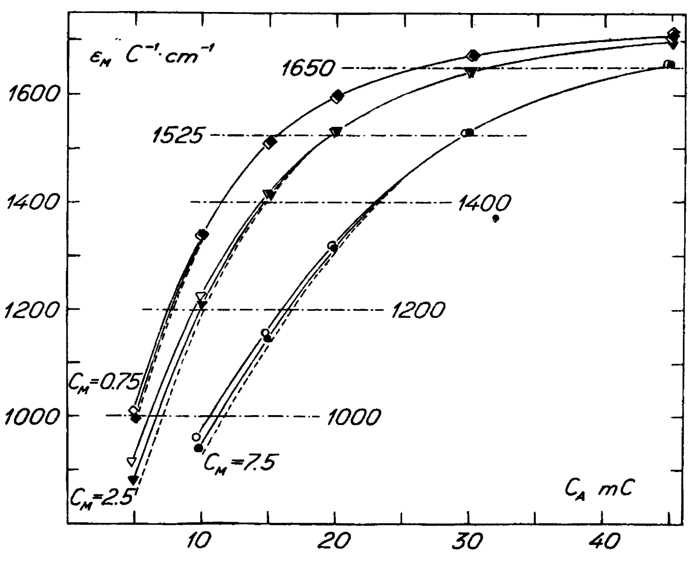

Fig. 4. ε_M *as a function of* C_A · *Squares, triangles and circles relate to the measurements at* $C_M = 0.75$, *2.5 and 7.5 mC respectively. Filled signs relate to the buffer 5 : 1 and open ones to the buffer 2 : 1. — Dashed curves represent the nonhydrolytic functions as obtained by extrapolation to* $1/[H^+] = 0$. *— The curves are cut at five* ε_M, *each of them representing a certain constant value of* $[A]$ *(and* $\bar{n}$*).*

Table 7. C_A *as a function of* C_M *at the five selected values of* ε_M *and the corresponding values of* $[A]$, $\bar{n}$ *and* $\bar{n}/[A]$ *hence obtained.*

C_M → mC	7.5	2.5	0.75	0		
ε_M $C^{-1}\cdot$ cm^{-1}	C_A mC			$C_A = [A]$ mC	$\bar{n}$	$\bar{n}/[A]$ C^{-1}
1 000	11.7	7.0	5.2	4.5	0.96	213
1 200	16.8	10.1	7.7	6.7	1.35	201
1 400	23.3	14.7	11.4	10.2	1.76	172
1 525	29.7	19.7	15.8	14.4	2.06	143
1 650	44.6	32.0	26.7	25.3	2.58	102

d. The measurements at $\lambda = 2600$ Å

Only the two buffers 5 : 1 and 2 : 1 have been used, on account of the strong influence of hydrolysis at the buffer ½: 1, demonstrated in Fig. 3. At 2600 Å, ε_M is high, so the low $C_M = 0.75$, 2.5 and 7.5 mC have to be chosen to fit $d = 1$, 0.3 and 0.1 cm respectively. For every C_M, C'_A has been varied between 5 and 45 mC. It is no use to increase C'_A any further, as the simultaneous increase of ε_M is very small. That is, at C'_A higher than those applied here, ε_M is almost a constant, independent of changes in the composition of the complex system.

The function searched for is $\varepsilon_M = f(C_A)$. In order to find C_A, (14) of II is applied as above, (p. 203) *i.e.* with the modification $C_s = 0$. Thus we have to know C_H^0 and [H$^+$] of the solutions as correction terms (*cf.* II p. 802). They are determined by separate titrations performed quite analogous to the ones above.

In Table 5, the results are collected, and the $\varepsilon_M = f\,(C_A)$ found are shown as fulldrawn curves in Fig. 4. It is plain that the curves of both the buffers coincide in their upper parts, where the complex formation of the acetate predominates, but differ in their lower parts where the complex formation is still undeveloped, so allowing a measurable hydrolysis to exist. The [H$^+$] of the solutions were, however, just measured above, thus we can perform the extrapolations to $1/[\mathrm{H}^+] = 0$, which give the non-hydrolytic $\varepsilon_M = f\,(C_A)$ for every C_M (Table 6 and dashed curves of Fig. 4) *.

These functions are then cut at five constant ε_M, without being transformed before according to II (p. 802). On account of the rather strong complexity, they themselves allow quite well the graphical determination of the C_A:s belonging to a certain ε_M and so the transformation is unnecessary. By the cuts, C_A is found to be a linear function of C_M for every ε_M which indicates a mononuclear complex formation (*cf.* II p. 803). So it is allowed to calculate $\bar{n}$ and [A] from the functions. The figures are in Table 7, and the corresponding values of [A], $\bar{n}$ and $\bar{n}/[\mathrm{A}]$ are also plotted in Figs 1 and 2.

It is at once observed, that it is necessary to correct for the hydrolysis in the extinction measurements also at such values of [A], where the emf measurements with the same buffers are quite independent of [H$^+$]. Thus it is possible to measure lower [A] by the potentiometric method than by the extinctiometric one.

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* As distinct from the way of proceeding in the emf measurement, the extropolation must be performed linearly here, as only two buffers are used.

CALCULATION OF THE COMPLEXITY CONSTANTS FROM THE CONCORDANT RESULTS OF THE TWO METHODS USED

According to both the methods applied, uranyl acetate is a mononuclear complex system. In solutions of not too low an [A], different for the different methods, the influence of hydrolysis is not larger than to permit the non-hydrolytic complex formation curve to be obtained without difficulty. As far as the measuring range can be covered by extinction measurements, identical curves are obtained with both methods. Above $\bar{n} = 2.6$, however, as well as below $\bar{n} = 0.9$, the formation curve is entirely founded on the emf measurements (*cf.* Table 7).

From the bend of the formation curve towards $\bar{n} = 3$, it is at once concluded that the saturated complex of the system is MA_3, in agreement with the views cited above (p. 200). So we have to calculate on three complexes. Their constants are obtained via the $X_n([A])$-functions, according to II (p. 785). The figures are in Table 8.

With the constants obtained, $\bar{n}$ is calcnlated ((2) of II) for some round [A] (Table 9). The values are introduced in Fig. 1 as a fulldrawn curve, which is seen to fit the experimental points very well. For the same [A], the composition of the system is also calculated ((8) of II) and given in Table 9.

Of these results, the statement of MA_3 as a saturated complex rests entirely on the part of the formation curve, which is determined only by emf measurements.

SUMMARY

Provided the complexity is sufficiently strong, complex solutions are not very much influenced by hydrolysis even at such pH:s where the central group is strongly hydrolysed. This opens a way to determine the complexity of such systems which cannot be measured at very low pH. It is, however, necessary to test the applicability of the method in every case by measuring at various pH. This proceeding also enables an extrapolation to strongly acid solution in the case of a slight influence of pH.

The method is applied to the system of uranyl acetate, where it functions well. Both emf and extinction measurements are performed, with consistent results. Three complexes are proved, *viz.* MA_1, MA_2 and MA_3, the last one being the saturated complex of the system. Their constants are, at the existing conditions:

$$\beta_1 = 240\ C^{-1} \qquad \beta_2 = 2.3 \cdot 10^4\ C^{-2} \qquad \beta_3 = 2.2 \cdot 10^6\ C^{-3}$$

The statement that MA_3 is a saturated complex is, however, founded merely on the emf measurements.

Table 8. *$X([A])$, $X_1([A],)$ $X_2([A])$ and X_3 $([A])$ for given $[A]$, as obtained by graphical integration of the $\bar{n}/[A]$-function of Fig. 2.*

$[A]$ mC	(5a) of II $\ln X([A])$	$X([A])$	(7a) of II $X_1([A])$ C^{-1}	(7b) of II $X_2([A]) \cdot 10^{-4}$ C^{-2}	$X_3([A]) \cdot 10^{-6}$ C^{-3}
0			*241*	*2.30*	*2.2*
2	0.4660	1.594	297		
4	0.9070	2.477	370	3.23	
6	1.323	3.76	460	3.65	2.25
8	1.712	5.53	566	4.07	2.21
10	2.075	7.96	696	4.55	2.25
15	2.868	17.62	1 107	5.78	2.32
20	3.520	33.7	1 635	6.97	2.34
30	4.526	92.3	3 040	9.33	2.34
40	5.278	195.9	4 870	11.54	2.31
50	5.875	357	7 120	13.77	2.29
75	6.987	1 084	14 450	18.95	2.22
100	7.792	2 420	24 190	23.95	2.17
150	8.957	7 760	51 800	34.4	2.14
200	9.781	17 760	88 300	44.0	2.08
250	10.435	34 000	136 000	54.4	2.08
300	10.966	57 800	192 700	64.2	2.07

Table 9. *The ligand number and the composition of the system as calculated for some round $[A]$ with the constants obtained.*

$\beta_1 = 240 \pm 10$ C^{-1} $\beta_2 = (2.3 \pm 0.2) \cdot 10^4$ C^{-2} $\beta_3 = (2.2 \pm 0.3) \cdot 10^6$ C^{-3}

$[A]$ mC	(2) of II $\bar{n}$	(8a) of II α_0 %	(8b) of II α_1 %	(8b) of II α_2 %	(8b) of II α_3 %
1	0.232	79	19	2	0
4	0.86	40.5	39	15	5.5
10	1.73	12.5	30	29.5	28
30	2.58	1	8	23.5	67.5
50	2.75	0.5	3.5	16.5	79.5
100	2.89	0	1	9	90
200	2.94	0	0.5	5	94.5
300	2.97	0	0	3.5	96.5

My thanks are due to Försvarets Forskningsanstalt (FOA), Stockholm, for a liberal financial support.

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Received October 9, 1950.