ACTA CHEMICA SCANDINAVICA 5 (1951) 1271–1282

On the Complex Chemistry of the Uranyl Ion

VI.* The Complexity of Uranyl Chloride, Bromide and Nitrate

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Several authors have discussed the complexity of uranyl chloride and uranyl nitrate, whereas that of uranyl bromide does not yet appear to have been treated.

From his early conductometric and cryoscopic investigations Dittrich [6] concluded that both uranyl chloride and uranyl nitrate are weakly complex. As these measurements were performed at a time when the necessity of activity corrections was not yet realized, the result is uncertain in so far that it is not actually possible to decide if any complexity exists at all. It is however certain that it cannot be strong. From Suttons [7] discovery of discrepancies between the course of hydrolysis of uranyl chloride and uranyl perchlorate, a conclusion of a weak chloride complexity may, however, be drawn. The same conclusion has been drawn by Nelson and Kraus [8] on account of measurements on the equilibrium $2\ UO_2^+ + 4\ H_3O^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 6\ H_2O$. The equilibrium constant is influenced by an exchange of perchlorate for chloride, which is interpreted as a consequence of a chloride complexing of UO_2^{2+} and U^{4+}. Introducing a number of simplifying assumptions, the authors calculate for UO_2Cl^+ a value of the thermodynamic complex constant $\beta_1^0 = 2.4\ C^{-1}$ (25° C). Also for uranyl nitrate, a number of experimental results speak in favour of a slight, but definite complexity (for an exhausting survey, see Glueckauf and McKay [9]). A value of $\beta_1 = 0.21\ C^{-1}$, valid at $I = 5.38$ C and the temperature 25° C, is found extinctiometrically by Betts and Michels [10]. However, objections must be raised against their method of measurement (*cf.* V p. 1151).

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* The preceding papers of this series (Ahrland [1–5]) are in the following referred to as I–V. The symbols of the present paper refer to the same quantities as those of I–V.

Owing to the lack of a suitable measurement method, no quantitative investigation of the complexity of the systems in question has thus been performed which is reasonably free from objections. But in the potentiometric method of ligand displacement, developed by Fronaeus [11], a method is now available which fairly well meets the demands of the problem.

It sometimes proves possible to confirm the potentiometric results by extinction measurements. This has been done for the uranyl chloride system.

As in I—V, all measurements have been performed at $I = 1$ with $NaClO_4$ as neutral salt, and at the temperature 20° C.

CHEMICALS USED

The *sodium chloride*, Kahlbaum *p. a.* and *sodium bromide*, Bakers analyzed, have been ignited. Then 1.00 C stock solutions are prepared by weighing. The concentration of the bromide solution is checked by titration according to Mohr.

The *sodium nitrate*, Bakers analyzed, is dried at 130° C. By weighing a 1.00 C stock solution is prepared, the concentration of which is checked by ion exchange analysis (*cf.* V p. 1152).

The *other chemicals* used are of the same preparations as in I and IV.

THE POTENTIAL MEASUREMENTS

In V p. 1152, the way is described of calculating complexity constants according to the method of ligand displacement. The only quantities necessary to know are the free ligand concentration, [B], and the ligand number $\bar{n}_B$ of the displacing ligand in solutions of known stoichiometric composition. As in V, the acetate ion is used as a displacing ligand, and [B] and $\bar{n}_B$ are therefore calculated in the same manner as there, *viz.* from measurements of $[H^+]$ of an acetate buffer, simply and accurately performed by quinhydrone electrode. To avoid uranyl hydrolysis, the buffer used has $\delta = 5.0$ (*cf.* IV p. 207). As Cl^- Br^- and NO_3^- do not combine with H^+, the calculations are in the present case simplified so that ϑ and ϑ' of V p. 1154 are transformed into $[H^+]$ and $[H^+]'$. Thus the following formulas of [B] and $\bar{n}_B$ are obtained:

$$[B] = \frac{[H^+]'}{[H^+]} \left(C'_B + 0.2 \left(C^0_H - [H^+]\right) + 1.2\ [H^+]'\right) \tag{1}$$

$$\bar{n}_B = \frac{C'_B - \left(C^0_H - [H^+]\right) - [B]}{C_M} \tag{2}$$

Table 1. Determination of E' as a function of C'_B for given values of the parameter C_A ($A = Cl^-$, Br^- or NO_3^-). The correction term $[H^+]'$, calculated with $[H^+]_0 = 10.19$ mC.

A →	Cl^-		Br^-		NO_3^-		
C_A → mC	200	600	200	600	200	600	0
C'_B mC	E' mV						
10.37	108.7	104.0	109.1	104.9	109.8	107.3	110.7
20.20	108.2	103.4	108.6	104.2	109.5	107.1	110.5
29.55	107.9	103.1	108.4	104.0	109.4	107.0	110.3
38.4	107.8	102.9	108.3	103.8	109.3	106.9	110.2
46.9	107.7	102.7	108.2	103.6	109.2	106.8	110.1
66.5	107.6	102.6	108.1	103.4	109.1	106.7	110.1
99.7	107.4	102.2	107.9	103.1	109.0	106.6	110.1
138.9	107.3	101.8	107.7	102.7	109.0	106.5	110.1
177.3	107.2	101.6	107.7	102.4	109.0	106.5	110.1
$[H^+]'$ mC	0.14	0.17	0.14	0.17	0.13	0.15	0.13

The complex solutions are prepared analogously to those of V (p. 1155). Two different values of C_A (= C'_A for the present ions, *cf.* V p. 1159) are used *viz.* 200 and 600 mC. C'_M is 40 or (at the nitrate titrations) 50 mC; besides, titrations with $C_M = 0$ are performed (*cf.* V p. 1154). As the complexity proves to be very weak for all the systems investigated here, it is not necessary to use more than a single value of C'_M if this is chosen not too high. In such a case, one may always put $[A]_n = C_A$ with sufficient accuracy. RE has in the present measurements $[H^+]_0 = 10.19$ mC.

The titrations with $C_M = 0$ are collected in Table 1. For the sake of comparison, the values of E' for $C_A = 0$ are also given. They are obtained by interpolation from IV Table 1, and recalculated with the present value of $[H^+]_0 = 10.19$ mC. It is seen from the courses of E' that an exchange of perchlorate for any of the anions here used causes a pronounced change of the ionic medium, increasing in the sequence $NO_3^- < Br^- < Cl^-$. It is not surprising that NO_3^- brings about the smallest change, as this ion is the one which resembles ClO_4^- most. The effect of Br^- and especially Cl^- is very considerable, the latter ion causing almost the same change as an equal concentration of SO_4^{2-} (V Table 1), in spite of the fact that SO_4^{2-} is divalent and thus contributes four times as much to I than does Cl^-.

Table 2. A measurement of Table 1 repeated with approximately the same ionic medium throughout the whole cell. $A = Cl^-$, $C_A = 600$ mC, $[H^+]_0 = 10.19$ mC. — Calculation of K_c in the medium used.

C'_B mC	E'' mV	$[H^+]'$ mC	$K_c \cdot 10^5$ C
10.37	107.8	0.143	2.90
20.20	107.2	0.146	2.94
29.55	107.0	0.147	2.95
38.4	106.9	0.148	2.97
46.9	106.7	0.149	2.99
66.5	106.5	0.150	3.00
99.7	106.3	0.151	3.02
138.9	105.9	0.154	3.08
177.3	105.6	0.155	3.10

Of course the great medium changes makes the calculation of $[H^+]'$ according to (16) of II somewhat dubious as this formula postulates equal conditions of activity in both the half-cells. But as $[H^+]'$ is only a small correction term in (1), the apparent changes of its value, given in Table 1, are of no importance. It may be emphasized here that the ratio $[H^+]'/[H^+]$ is obtained according to (18) of II, *i. e.* from the emf of an element with the same C_A and C'_B in both halfcells. This factor is thus independent of the fact that the activity conditions of RE are no longer the same as in the halfcell containing buffer (*cf.* II p. 794).

Strictly speaking, the course of E' by the exchange of ClO_4^- for the ions A only implies an increase of the hydrogen ion activity of the buffer solution. One may assume that this in turn implies an increase of $[H^+]'$, and thus an increase of $K_c \cdot$ A quantitative determination cannot be made, however, before the activity conditions of the two half-cells have been made approximately equal, *i. e.* the whole cell must contain approximately the same ionic medium. Such a determination is now performed with the series of the greatest medium change measured, *viz.* the Cl^--series of $C_A = 600$ mC, using an RE with $[H]_0 = 10.19$ mC, $C_A = 600$ mC and $NaClO_4$ to $I = 1$. This RE thus has a composition equal to that of the other half-cell, the buffer concentration then being left out of consideration. The measured emf, E'' as well as the calculated $[H^+]'$ and K_c are found in Table 2. K_c is not a constant, evidently the exchange of perchlorate for buffer also causes perceptible change of the medium in the present case. In the beginning however, where C'_B is low, K_c may be considered as the value valid for the medium 600 mC NaCl, 400 mC $NaClO_4$. This value is approximately $K_c = 2.9 \cdot 10^{-5}$ C, which implies an increase of K_c with > 10 % in relation to 1 C $NaClO_4$. It is clearly seen however that the value of $[H^+]'$ calculated here does not differ so much from the corresponding one of Table 1 that an error of [B] can arise for that reason.

The results of the main titrations are found in Table 3 and Fig. 1, where $\bar{n}_B/[B]$ is given as a function of [B] for all the series measured. Moreover, the

Table 3. Determination of corresponding values of $\bar{n}_B/[B]$ and $[B]$ at the two C_A used.
Table 3 A. Uranyl chloride system.

C_A mC		200				600			
C_M mC	C'_B mC	E_B mV	C^0_H-[H$^+$] mC	[B] mC	$n_B/[B]$ C^{-1}	E_B mV	C^0_H-[H$^+$] mC	[B] mC	$\bar{n}_B/[B]$ C^{-1}
38.95	10.37	58.6	0.46	1.045	218	55.7	0.45	1.175	191
38.0	20.20	56.3	0.51	2.20	209	53.5	0.49	2.465	184.5
37.05	29.55	54.8	0.53	3.40	203.5	52.3	0.49	3.76	181.5
36.15	38.4	53.6	0.5	4.63	199	51.0	0.5	5.14	176.5
35.3	46.9	52.4	0.6	5.92	193.5	49.7	»	6.59	171
34.5	55.1	51.0	»	7.36	185.5	48.3	»	8.18	164.5
33.35	66.5	48.2	»	9.91	169.5	46.0	0.6	10.82	153
31.6	84.0	42.4	0.7	15.75	136	40.6	0.7	16.9	124.5
30.0	99.7	35.2	0.8	24.8	99.5	34.1	0.8	25.9	94
28.6	114.0	28.5	0.9	37.0	72	27.9	0.9	37.8	69.5
27.3	127.0	23.3	»	50.6	54.5	23.2	»	50.8	54.5
26.1	138.9	19.5	»	64.4	44	19.3	»	64.8	43.5
24.0	159.6	14.4	»	90.4	31.5	14.8	»	89.1	32.5

Table 3 B. Uranyl bromide system.

38.95	10.37	59.3	0.46	1.016	225	57.4	0.47	1.096	206
38.0	20.20	57.0	0.51	2.15	215	55.1	0.51	2.32	197
37.05	29.55	55.7	0.53	3.29	211	53.9	0.52	3.53	195
36.15	38.4	54.6	0.5	4.46	207	52.8	0.5	4.79	191
35.3	46.9	53.4	»	5.69	202.5	51.7	»	6.09	187.5
34.5	55.1	52.0	0.6	7.08	194.5	50.3	»	7.57	180
33.35	66.5	49.2	»	9.52	177.5	47.7	0.6	10.09	166
31.6	84.0	43.1	0.7	15.3	141	42.0	0.7	16.0	133
30.0	99.7	35.7	0.9	24.3	102	35.0	0.9	25.0	98.5
28.6	114.0	28.8	»	36.5	73.5	28.2	1.0	37.4	70.5
27.3	127.0	23.4	1.0	50.4	55	23.2	»	50.8	54
26.1	138.9					19.4	»	64.6	43.5
24.0	159.6					14.6	0.9	89.7	32

value of the function for $C_A = 0$, as determined in IV, is introduced. All the $\bar{n}_B/[B]$-functions are extrapolated to $[B] = 0$.

Considering the high values of C_A used, the displacements of the found $\bar{n}_B/[B]$-curves in relation to the curve of $C_A = 0$ are really very slight. Hence it

Table 3 C. Uranyl nitrate system.

$C_A \rightarrow$ mC		200				600			
C_M mC	C'_B mC	E_B mV	C^0_H-[H$^+$] mC	[B] mC	$\bar{n}_B$/[B] C^{-1}	E_B mV	C^0_H-[H$^+$] mC	[B] mC	$\bar{n}_B$/[B] C^{-1}
48.7	10.37	64.8	0.50	0.818	227.5	62.7	0.52	0.889	207
47.5	20.20	62.6	0.57	1.715	220.5	60.6	0.58	1.86	201
46.3	29.55	61.4	0.59	2.63	216	59.3	0.61	2.86	197
45.2	38.4	60.3	0.6	3.56	212.5	58.2	0.6	3.87	194
44.1	46.9	59.2	»	4.54	209	57.2	»	4.90	190
43.1	55.1	58.0	»	5.57	203.5	56.1	»	6.01	187
41.7	66.5	56.0	0.7	7.28	193	54.0	0.7	7.87	176.5
39.5	84.0	51.7	0.8	10.89	168	49.8	0.8	11.75	154
37.5	99.7	46.0	0.9	16.2	136	44.6	0.9	17.1	127.5
35.7	114.0	39.2	1.0	24.3	102.5	38.2	1.0	25.2	97.5
34.1	127.0	32.6	1.1	35.6	76	31.9	1.1	36.0	73
32.6	138.9	27.1	»	47.6	58	27.0	»	47.9	57.5

is clear that all the systems in question are only very weakly complex. A variation of C_A of, say, 50 mC causes a displacement of the $\bar{n}_B$/[B]-curve which is not greater than the experimental error of the measurement. Thus it is certainly allowed to neglect that part of C_A in relation to the rest which has formed complexes with uranyl ions, *i.e.* one can put $[A]_n = C_A$. The found curves thus represent the functions $(\bar{n}_B/[B])_{C_M=0}$ ultimately required. The values of [B] (= b) where these curves coincide with the one of $C_A = 0$ are now determined. Then the graphical integrations according to (1) of V can be performed. From the $X([A])$-functions hence obtained the $X_1([A])$-functions are calculated (Table 4). Within the random error, which may be estimated to $\pm$ 0.2 C^{-1}, these functions are constant for all the measured systems, and thus $= \beta_1$. Any further complexes between M and A thus cannot be proved, nor is it possible to calculate any significant values of the mixed constants $\beta_{1,1}$ (*cf.* V p. 1153).

With the found values of β_1, $\bar{n}_A$ is calculated ((2) of II) and also given in Table 4. It can be seen that the amount of C_A which combines with M ($= \bar{n}_B \cdot C_M$) does not exceed 15 mC at a $C_A = 600$ mC of that ligand which forms the strongest complexes, *viz.* the chloride ion. Such a quantity cannot perceptibly displace the $\bar{n}_B$/[B]-curve. The approximation $[A]_n = C_A$ is thus correct.

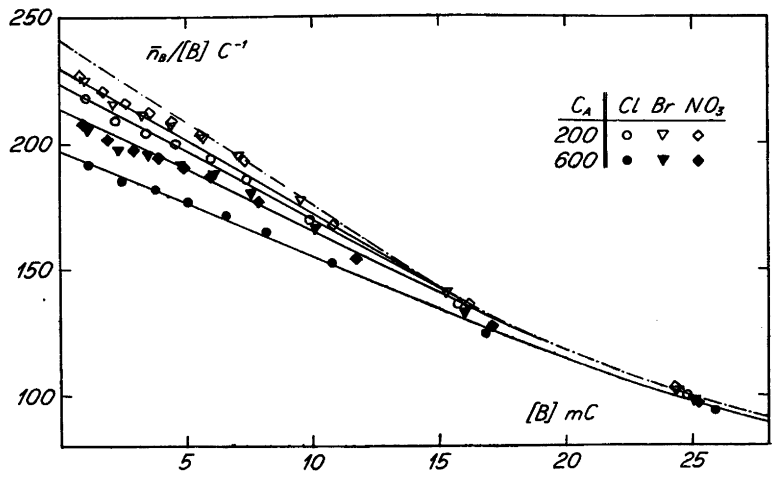

Fig. 1. $\bar{n}_B/[B]$ *as a function of* [B]. *The curve of dots and dashes refers to pure acetate complex formation (IV Fig. 2). The signs refer to the different experimental series according to the scheme on the fig. The fulldrawn curves are drawn in connection with the experimental points,* Br^- *and* NO_3^- *then giving the same curves.*

Of course, the $\bar{n}_B/[B]$-function may be displaced also by the change of the medium, which has been stated above to follow the exchange of ClO_4^- for Cl^-, Br^- or NO_3^-. One expects however that such a change would displace the whole curve, not merely its first part. On the contrary, the actually observed behaviour of the curve is just that which would be expected as the consequence of a complex formation (*cf.* V p. 1152). Then it seems most likely, that a complex formation occurs, but an activity change may also be involved. If it is assumed that the dissociation of the first uranyl acetate complex MB is affected in the same manner as the dissociation of the acetic acid. its dissociation increases (*cf.* p. 1274) *i.e.* β_1 decreases and $\bar{n}_B/[B]$ decreases. If such an activity effect is present here, the displacements owing to complex formation have been overestimated. The found values of β_1 have therefore a systematic error; probably they are too high.

THE EXTINCTION MEASUREMENTS

The extinctiometric method of calculating complexity constants used in II—V imports the determination of the ligand number $\bar{n}_A$. This is not possible here however, owing to the slight complexity of the present systems. At all C_M of reasonable size, the difference $C_A - [A]$ would be too small compared with the experimental error of [A]. The complexity of uranyl thiocyanate, measured in

III, may be said to represent about the lowest order of magnitude of complexity which can be determined by the method previously used.

But even if a complete extinctiometric determination is impossible, one might sometimes test the potentiometrically obtained result that only the first complex would exist in the investigated systems. In such a case (22) of II is simplified:

$$\varepsilon_M - \varepsilon_0 = \frac{(\varepsilon_1 - \varepsilon_0)\,\beta_1\,[\mathrm{A}]}{1 + \beta_1\,[\mathrm{A}]} \tag{3}$$

If ε_M is determined at two different values of C_A, denoted $'$ and $''$, the ratio q between the found quantities $\varepsilon'_M - \varepsilon_0$ and $\varepsilon''_M - \varepsilon_0$ then is

$$q = \frac{\varepsilon'_M - \varepsilon_0}{\varepsilon''_M - \varepsilon_0} = \frac{[\mathrm{A}]'}{[\mathrm{A}]''} \cdot \frac{1 + \beta_1\,[\mathrm{A}]''}{1 + \beta_1\,[\mathrm{A}]'} \tag{4}$$

If only the first complex exists, q is thus independent of the molar extinctions ε_0 and ε_1, *i.e.* q is independent of that wave-length λ at which ε_M is measured. Indeed, this is generally valid if a system contains only one complex. On the other hand, if more than one complex exists q will always depend on the molar extinctions, or, rather, on the ratios between them, as is easily deduced from (22) of II.

Thus, if extinction curves are measured for two solutions of a complex system and the ratio q formed shows a good constancy, that conclusion may be drawn that only one complex exists. It is however a necessary condition that the measurements cover a rather wide λ-range. Only then it can be taken

Table 4. The X-functions of the investigated systems, as obtained by graphical integration according to (1) of V. The ligand numbers as calculated from the found complexity constants.

A	$[\mathrm{A}]_n$ mC	b mC	ln $X([\mathrm{A}])$	$X([\mathrm{A}])$	$X_1([\mathrm{A}])$ C^{-1}	β_1 C^{-1}	$\bar{n}_A$
Cl^-	200	16	0.140	1.151	0.76	0.8	0.14
	600	40	0.427	1.534	0.89		0.32
Br^- & NO_3^-	200	14	0.0825	1.085	0.43	0.5	0.09
	600	19	0.263	1.300	0.50		0.23

for granted, that the ratios between the molar extinctions must have really changed. The conclusion may be further strengthened by measuring more solutions and forming new ratios q which have all to be independent of λ.

If only one complex exists in the present systems it is no doubt the first one, potentiometrically proved above. Then (4) is valid and hence β_1 can be calculated if the usual approximation $[A] = C_A$ is introduced:

$$\beta_1 = \frac{q \cdot C''_A - C'_A}{C''_A \cdot C'_A \ (1 - q)} \tag{5}$$

If more than one q has been calculated, of course all of them have to give the same β_1 according to (5).

The extinction curves of the following solutions have been measured:

chloride system:	bromide system:	nitrate system:
33 mC $UO_2(ClO_4)_2$	33 mC $UO_2(ClO_4)_2$	15 mC $UO_2(ClO_4)_2$
250 mC $HClO_4$	250 mC $HClO_4$	100 mC $HClO_4$
250, 500 or 750 mC NaCl	750 mC NaBr	750 mC $NaNO_3$
$I = 1$ (by $NaClO_4$)	$I = 1$ (by $NaClO_4$)	$I = 1$ (by $NaClO_4$)

All solutions are so acid, that no hydrolysis can exist.

The curves of the chloride and bromide solutions are obtained by a Hilger Medium Spectrograph, combined with a Spekker Photometer (*cf.* I p. 375), whereas that of the nitrate solution is obtained by a Beckman Quartz Spectrophotometer (*cf.* IV p. 212). The reproducibility of the spectrographically determined values are considerably lower than that of the spectrophotometrically measured ones. This circumstance has however little importance here, as that error always predominates which arises from the fact that the compared ε_M are not measured at the same E. Because of that, the error of ε_M must be estimated to ≈ 3 %, which is the normal error of absolute extinction measurements (*cf. e. g.* Kortüm and v. Halban [12], or Olerup [13] pp. 46—56.

The general rule that the blank cell has to contain all the components of the solution except the uranyl ions is especially important for the nitrate system, as the nitrate ion has a considerable extinction in UV (v. Halban and Eisenbrand [14]). Owing to the slight complexity of the nitrate system, [A] of the two absorption cells may be considered to be equal and thus ε_A completely compensated. A disadvantage of the nitrate absorption is however that very wide slits have to be used in the Beckman, causing a bad monochromaticity of the light and thus an especially great systematic error of ε_M. The absorption of the chloride and bromide ions may be neglected in the UV range used (Fromherz and Menschick [15]).

All the curves of the measured solutions are found in Fig. 2, together with that of UO_2^{2+} from I p. 377. In the same Fig., the curve of NO_3^- from [14] as well as those of Cl^- and Br^- from [15] are also introduced.

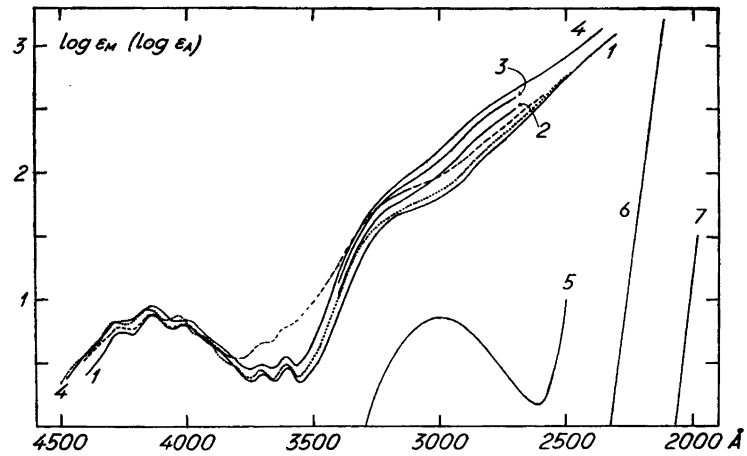

Fig. 2. Extinction curves of a) uranyl ion (fulldrawn, 1) b) uranyl chloride solutions with C_M = 33 mC, C_A = 250, 500 and 750 mC (fulldrawn, 2, 3 and 4), c) uranyl bromide solution with C_M = 33 mC, C_A = 750 mC (dashed), d) uranyl nitrate solution with C_M = 15 mC, C_A = 750 mC (dotted) and e) nitrate, bromide and chloride ions (fulldrawn to the right, 5, 6 and 7 respectively).

An addition of Cl^-, Br^- or NO_3^- evidently causes a not very large but nevertheless definite displacement of the UO_2^{2+}-curve. This agrees very well with the conception of a weak complex formation in all the systems. A quantitative examination of the potentiometrically found complexity according to (4) and (5) can however be performed only for the chloride system. In this case only

Table 5. The constant values of q_1 and q_2 of the uranyl chloride system, as obtained from the interpolated values of log ε_M of Fig. 2.

λ Å	log ε_M'''	log ε_M''	log ε_M'	log ε_0	q_1	q_2
2700	2.655	2.595	2.505	2.345	0.43	0.75
2800	2.535	2.47	2.355	2.165	0.41	0.76
2900	2.37	2.29	2.18	1.95	0.43	0.73
3000	2.175	2.095	1.98	1.815	0.36	0.69
3100	2.015	1.95	1.84	1.705	0.35	0.72
3200	1.855	1.81	1.725	1.615	0.39	0.77
3300	1.62	1.565	1.49	1.345	0.45	0.75
3400	1.195	1.14	1.045	0.89	0.42	0.76
				Mean	0.41	0.74

the addition of ligand causes within a wide λ-range a displacement of the UO_2^{2+}-curve which is large enough to permit a sufficiently accurate determination of $\varepsilon_M - \varepsilon_0$. For the bromide system, this displacement is large enough only in such a narrow λ-range that no certain conclusion can be drawn about the constancy of q, and for the nitrate system it is very small in the whole observed λ-range.

For the chloride system, the molar extinctions of $C_A = 250$, 500 and 750 mC are indicated by ε'_M, ε''_M and ε'''_M respectively. Hence the two ratios $q_1 = (\varepsilon'_M - \varepsilon_0)/(\varepsilon'''_M - \varepsilon_0)$ and $q_2 = (\varepsilon''_M - \varepsilon_0)/(\varepsilon'''_M - \varepsilon_0)$ are formed. In Table 5, the values of log ε_M for every 100 Å are given as obtained by extrapolation from Fig. 2. The values of q_1 and q_2 hence calculated are in the same Table. Within the experimental errors, they are constant throughout the whole λ-range measured. Thus only the first complex seems to exist, and it is allowed to apply (5), which gives $\beta_1 = 0.5\ C^{-1}$ for both q_1 and q_2. From the spreading of the values of q_1 and q_2, the random error of β_1 may be estimated to $\pm 0.3\ C^{-1}$, thus being of the same order of magnitude as in the potential measurements.

Olerup [13 p. 60] has very fully investigated the consequences of an unallowed simplification of (22) of II into (3). He finds that the existence of not recognized higher complexes causes too low values of β_1 when calculated according to (5) or an equivalent formula. Thus, if such higher complexes exist in the present system but are not discovered owing to the great random errors of q_1 and q_2, the value of β_1 calculated here is too low.

The extinction measurements are of course also influenced by the activity changes occurring when ClO_4^- is exchanged for Cl^- as the law of mass action is used at the deduction of (3). Nothing can be surely said however about the consequence upon β_1 of this influence.

Considering the random errors, the extinctiometric investigation may be said to confirm the potentiometric one completely. The difference between the values may, however, also have systematic reasons, as the potentiometric method is likely to give a too high value, whereas the extinctiometric one possibly gives a figure which is too low.

SUMMARY

The complexity of the uranyl chloride, bromide and nitrate systems are potentiometrically determined according to the method of ligand displacement. As in V, the acetate ion is used as the displacing ligand. The experiments are therefore also carried out in quite the same manner as those of V.

All the systems investigated form very weak complexes. Only the first complex can be proved, and its constant β_1 is calculated to be 0.8, 0.5 and 0.5 C^{-1}

respectively, with an estimated experimental error of $\pm$ 0.2 C^{-1}. Owing to systematic errors, these values are probably too high.

Concerning the chloride system the result that only one complex exist is confirmed in an extinctiometric way, which gives $\beta_1 = 0.5 \pm 0.3$ C^{-1} in good agreement with the potentiometrically determined value If the existence of higher complexes is overlooked, which to some slight extent may be the case, the extinctiometric value of β_1 may be too low.

I wish to express my sincere gratitude to *Atomkommittén* (The Swedish Atomic Committee) which has given this work a liberal financial support.

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Received October 18, 1951.