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On the Complex Chemistry of the Uranyl Ion

VII *. The Complexity of Uranyl Glycolate

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The aim of the present investigation has been to study the formation of complexes of the uranyl ion with a ligand possessing a pronounced tendency to give chelate complexes. If indeed chelates are formed, then the ratios between the stability constants b ** of the consecutive complexes should be greater than in a system where chelates are not formed [1, 2 p. 131]. This is due to purely statistical factors, for a chelating ligand leaves vacant fewer sites for coordination, on which the next ligand can be taken up than does a simply bound one. Thus chelate formation reduces the probability of the formation of the next complex.

For such comparisons to be significant, it is however necessary that the complex systems compared shall have very similar ligands. Only then is it reasonably certain that the other factors governing complex formation — electrostatic as well as those specific for the individual ligands — are approximately of the same magnitude, and the differences between the ratios of the constants thus really due to the statistical factors alone.

A suitable ligand for this investigation is the glycolate ion. Apart from the chelating hydroxy-group, it is completely analogous to the acetate ion, which has no ability to form chelates. The acetate system has been investigated previously [3]. Of other systems studied, the chloroacetate [4] may possibly also be utilized for comparison.

It is of course necessary to investigate the glycolate under the same conditions as those used previously for the selected comparable systems, *i. e.* at the temperature 20° C and the ionic strength I = 1 C, $NaClO_4$ being used as the supplementary neutral salt.

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** defined according to $b_n = \beta_n/\beta_{n-1}$, if $n \geqq 2$; $b_1 = \beta_1$.

The experimental procedure is the same as in the case of acetate and chloroacetate. The complexity constants β are obtained from the complex formation function, *i. e.* from connected values of [A] and $\bar{n}$. These are calculated from $[H^+]'$ of pure glycolate buffers and from $[H^+]$ of the same buffers, containing the total uranyl concentration C_M, according to:

$$[A] = \frac{[H^+]'}{[H^+]} \left(C'_A + \frac{(1+\delta)\,[H^+]' - [H^+]}{\delta} \right) \quad (1)$$

$$\bar{n} = \frac{C'_A + [H^+] - [A]}{C_M} \quad (2)$$

As in [4 p. 791] the approximation $C^0_H = C_s$ is introduced in deducing the equations for $\bar{n}$ and [A]. This implies firstly that the initial concentration of acid in the uranyl perchlorate solution is regarded as arising from the spontaneous hydrolysis of the uranyl ion and, secondly, that this hydrolysis is forced back completely by the complex formation even at the lowest [A] measured. The first condition is well fulfilled, as has been shown by a potentiometric base titration, *cf.* [5 p. 384], which gave $l = 0$, *i. e.* no excess or deficit of acid in the preparation used here. That the second condition is fulfilled, which is of fundamental importance for the success of the investigation [3 p. 203], has been proved by the use of buffers of different ratios $C'_{HA}/C'_A = \delta$. If no perceptible hydrolysis occurs, the complex formation function must be independent of $[H^+]$, *i. e.* δ.

As a rule, two or three different C'_M are used for every buffer, in order to indicate any polynuclear complex formation [5 p. 379] which might occur. In the present system, where the ligand tends to give chelate bonds, polynuclear complexes are in fact very likely to exist.

EXPERIMENTAL

Chemicals used. Two different preparations of *glycolic acid* have been used: Kebo *puriss* and Schering-Kahlbaum *puriss*. Both gave, after drying *in vacuo*, the equivalent weight 76.4 (calc. 76.1). Stock solutions of buffer were prepared by partial neutralization of weighed amounts of dry acid by NaOH and subsequent dilution to the correct volume. They had $C'_A = 1\,000$ mC, and $\delta = 0.4$, 1 and 4, *i. e.* approximately $I = 1$ C. In the following measurements, the buffers of both the acid preparations used gave the same result. The *other chemicals* used are the same as before.

Experimental data. In the buffers of $\delta = 0.4$ and $\delta = 1$, $[H^+]$ and $[H^+]'$ are easily and exactly measured with a quinhydrone electrode in precisely the same manner as in [3] and [4 p. 788]. As before, a quinhydrone electrode RE [5 p. 383] is used as reference electrode, in the present case with $[H^+]_0 = 10.02$ mC. The emf of the cell so formed is denoted E'_q when $[H^+]'$ of pure buffer is measured, and E_q when the buffer contains uranyl salt.

At $\delta = 4$, E'_q is still steady and reproducible, but as soon as uranyl salt is present, the measured E_q moves for some hours towards higher and higher values *. Such an increase indicates that oxidation of the glycolic acid by the quinone is taking place, the uranyl salt evidently being the necessary catalyst. It is not a question of that oxidation of glycolic acid which is brought about by uranyl salt alone and catalysed by light. In the existing conditions, this reaction does not occur with perceptible velocity, as the glass electrode gives fairly constant emfs and thus makes the determination of $[H^+]_0$ possible even at $\delta = 4$.

The experimental setup for the measurements with the glass electrode is the same as described in [5 p. 388]. The glass electrode is immersed in the buffer solution to be measured, and this halfcell is combined with the same quinhydrone RE as above. As in all previous measurements, all buffers of a certain δ and C'_M are prepared in the electrode vessel by a single titration series. The emf is denoted E'_g when a buffer has $C_M = 0$, otherwise E_g. Before and after each such series, the glass electrode is inserted in the reference solution of $[H^+]_0 = 10.02$ mC, $I = 1$, and the emf $E_g^{(10)}$ corresponding to $[H^+]_0$ is measured. If $E_g^{(10)}$ has the same value before and after a buffer series is measured, then the asymmetry potential of the glass electrode has certainly remained constant and hence we get for an arbitrary buffer of the series (*cf.*[5 p. 392]):

$$E_g - E_g^{(10)} = S \cdot \log \frac{[H^+]_0}{[H^+]} \tag{3}$$

When the corresponding uranyl free buffer series is then measured, we get for the same buffer:

$$E'_g - E_g^{(10)'} = S \cdot \log \frac{[H^+]_0}{[H^+]'} \tag{4}$$

where, as a rule $E_g^{(10)'} \neq E_g^{(10)}$ owing to the change of the asymmetry potential which has generally occurred in the time interval between the two series. Hence

$$E'_g - E_g^{(10)'} - (E_g - E_g^{(10)}) = E_A = S \log \frac{[H^+]}{[H^+]'} \tag{5}$$

where E_A is the difference of potential due to complex formation.

From these equations $[H^+]/[H^+]'$, $[H^+]$ and $[H^+]'$ of (1) and (2) may be calculated and hence [A] and $\bar{n}$ for every buffer measured, if only the value of the slope S is known. For the buffer of $\delta = 1$ however, the same E_A:s are obtained with the glass as well as with the quinhydrone electrode. This implies that S must have its theoretical value of 58.2 mV.

The measured values of E'_q and $E'_g - E_g^{(10)'}$ are given in Table 1. As seen from the calculated K_c, glycolate ions as well as undissociated glycolic acid have a marked influence on the ionic medium. If C'_A is kept constant, K_c increases with increasing C'_{HA}, while K decreases with increasing C'_A at constant C'_{HA}. These effects are best observed in the measurements with the glass electrode which are not affected by any salt error. The measurements with the quinhydrone electrode on the other hand contain a salt error, *i. e.* the activity factors of the quinhydrone components in the solution are affected by changing perchlorate for glycolate buffer, as seen from the deviation of E'_q from $E'_g - E_g^{(10)}$. The salt error

* In a less pronounced degree, this behaviour is observed even when a buffer of $\delta = 2$ is used.

Table 1. Determination of E'_q and $E'_g - E_g^{(10)'}$ as a function of C'_A for the different buffers used ($[H^+]_0 = 10.02$ mC).

	quinhydrone electrode						glass electrode			
$\delta \rightarrow$	4		1		0.4		4		1	
C'_A mC	E'_q mV	$K_c \cdot 10^4$ C	E'_q mV	$K_c \cdot 10^4$ C	E'_q mV	$K_c \cdot 10^4$ C	$E'_g - E_g^{(10)'}$ mV	$K_c \cdot 10^4$ C	$E'_g - E_g^{(10)'}$ mV	$K_c \cdot 10^4$ C
13.16	59.6	2.59	94.1	2.51	117.5	2.46	59.6	2.59	95.2	2.39
25.98	58.4	2.60	93.5	2.53	116.9	2.50	58.2	2.62	94.5	2.42
38.5	57.9	2.61	93.3	2.53	116.7	2.50	57.7	2.63	94.4	2.42
50.7	57.5	2.64	93.1	2.54	116.5	2.51	57.4	2.65	94.3	2.42
62.5	57.2	2.66	93.0	2.54	116.4	2.52	57.2	2.66	94.3	2.42
90.9	56.7	2.69	92.9	2.54	116.3	2.52	56.9	2.67	94.3	2.41
117.7	56.3	2.72	92.9	2.54	116.3	2.52	56.7	2.69	94.4	2.40
166.7	55.7		92.8	2.55	116.3	2.52	56.5	2.70	94.7	2.37
210.5	55.2		92.8	2.55	116.3	2.52	56.2	2.73	95.0	2.34
250.0	54.8		92.7	2.56	116.4	2.51	56.1		95.2	2.31
285.9	54.4		92.6	2.57	116.4	2.51	56.0		95.4	2.29
348	53.9		92.5		116.4	2.51	55.9		95.8	
400	53.4		92.4		116.5	2.50	55.8		96.2	
444			92.3		116.5	2.50	55.7		96.5	
500			92.3		116.6		55.6		97.0	
572			92.3		116.7					
$[H^+]'$ mC $\rightarrow$			0.24—0.26		0.10		0.95—1.11		0.21—0.24	

is however without influence on the final result, as E_A (*cf.* (5)), which is of decisive importance for the calculation of [A] and $\bar{n}$, is independent of the electrode used as proved by measurements with $\delta = 1$ using both electrodes, Tab. 3 B. This is a natural consequence of the fact that E_A expresses the emf of a cell with the same buffer concentration and thus the same salt error in both half-cells.

On the other hand, the change in the medium caused by the exchange of perchlorate for glycolate buffer must have some influence on the values of β, as well as on K_c, especially in the case of the higher complexes. The β values of the different complexes thus are not related to the same medium, which renders them less well fitted for comparison with the β values of the acetate system, which to judge from [3, Table 1] does not greatly influence the perchlorate medium.

The values of [A] and $\bar{n}$ obtained for the different electrodes and buffers are given in Tables 2—4. The complex formation functions are given in Fig. 1. As will be seen, the functions do not coincide.

The deviations must be due partly to the influence of hydrolysis. The fact that the difference between $\delta = 0.4$ and $\delta = 1$ is greater than that between $\delta = 1$ and $\delta = 4$ is

Table 2. Determination of corresponding values of $\bar{n}$ and [A] *at the buffer of $\delta = 0.4$. $C_M = 50$ mC. Quinhydrone electrode.*

C_M mC	C'_A mC	E_A mV	$[H^+]$ mC	[A] mC	$\bar{n}$
49.3	13.16	75.9	1.93	0.43	0.298
48.1	38.5	68.2	1.47	2.36	0.782
46.9	62.5	60.5	1.10	5.48	1.24
45.4	90.9	50.0	0.73	12.36	1.74
42.8	142.9	33.1	0.37	38.5	2.45
40.6	189.3	23.3	0.25	75.2	2.82
37.5	250.0	16.0	0.19	132.7	3.13
34.1	318.3	10.7	0.15	208.4	3.23
30.0	400	7.2	0.1	301	3.32
25.0	500	4.5	0.1	419	3.25

in support of this, as is the cessation of the influence of C_M with increasing δ. A variation of C_M produces a rather great effect at $\delta = 1$, but hardly any at $\delta = 4$, *cf.* [3 p. 211]. Now, the pH of the buffer of $\delta = 4$ does not permit any perceptible hydrolysis, as seen from the measurements of [5], if the quite improbable assumption is not made that the degree of hydrolysis is greater for the glycolate complexes than for the uranyl ion itself. The reverse is certainly true and thus the complex formation curve with $\delta = 4$ is in-

Table 3. Determination of corresponding values of $\bar{n}$ and [A] *at the buffer of $\delta = 1$.*

Table 3 A. $C'_M = 10$ mC. Quinhydrone electrode.

C_M mC	C'_A mC	E_A mV	$[H^+]$ mC	[A] mC	$\bar{n}$
9.87	13.16	26.6	0.69	4.52	0.945
9.74	25.98	19.5	0.54	11.99	1.49
9.62	38.5	15.1	0.45	21.19	1.84
9.50	50.7	11.9	0.40	31.7	2.04
9.38	62.5	9.9	0.37	42.4	2.19
9.09	90.9	7.1	0.3	68.9	2.45
8.82	117.7	5.6	0.3	94.6	2.66
8.57	142.9	4.5	0.3	119.9	2.72
8.33	166.7	3.9	0.3	143.2	2.86
7.90	210.5	3.1	0.3	186.6	3.1
7.50	250.0	2.5	0.3	226.5	3.2
7.14	285.9	2.0	0.3	264.9	2.9

Table 3 B. C'_M *= 25 mC and 50 mC. Quinhydrone and glass electrode.*

	C'_M = 25 mC						C'_M = 50 mC					
		quinhydrone				glass		quinhydrone				glass
C'_A mC	C_M mC	E_A mV	[H$^+$] mC	[A] mC	$\bar{n}$	E_A mV	C_M mC	E_A mV	[H$^+$] mC	[A] mC	$\bar{n}$	E_A mV
13.16	24.66	46.5	1.52	1.92	0.518	46.8	49.3	62.2	2.86	0.910	0.306	61.9
25.98	24.35	41.2	1.26	4.93	0.917	41.4	48.7	59.6	2.64	2.25	0.541	59.1
38.5	24.05	35.9	1.03	9.18	1.26	36.1	48.1	56.3	2.33	3.96	0.766	55.9
50.7	23.75	30.8	0.85	14.88	1.545	31.0	47.5	52.5	2.01	6.16	0.979	52.5
62.5	23.45	26.7	0.72	21.7	1.77	26.9	46.9	48.9	1.75	8.84	1.185	48.8
90.9	22.72	19.2	0.5	42.6	2.15	19.1	45.4	40.0	1.2	18.49	1.62	40.0
117.7	22.04	15.1	0.5	64.7	2.43	14.8	44.1	32.5	0.9	32.4	1.96	32.2
142.9	21.42	12.1	0.4	88.5	2.56	12.0	42.8	26.7	0.7	49.6	2.20	26.5
166.7	20.82	10.2	0.4	111.4	2.68	10.3	41.7	22.4	0.6	68.8	2.36	22.4
210.5	19.75	7.8	0.3	154.9	2.83	7.8	39.5	16.7	0.5	108.6	2.60	16.7
250.0	18.75	6.2	0.3	195.5	2.93	6.3	37.5	13.4	0.4	147.2	2.76	13.1
285.9	17.85	5.2	0.3	233.3	2.96	5.3	35.7	10.9	0.4	185.9	2.82	10.6
348.0	16.30	3.9	0.3	298.5	3.05	4.0	32.6	8.0	0.4	253.5	2.91	7.8
400	15.00	3.0	0.3	355	3.0	3.2	30.0	6.2	0.3	312.5	2.92	6.1
444	13.88	2.4	0.3	403	2.9	2.7	27.8	5.2	0.3	361.5	2.99	5.0
500	12.50	1.9	0.3	463	2.9		25.0	3.9	0.3	428	2.9	3.9
572							21.4	2.9	0.3	509	2.9	

dubitably the curve of the uranyl glycolate system, undisturbed by hydrolysis. Its independence of C_M proves that all the complexes are mononuclear.

It is possible that the movement of the curves with δ might be due at least partly to complex formation by the undissociated glycolic acid, by means of its hydroxy-group. Such a competing process would reduce the glycolate complexing, *cf.* Fronaeus [6]. It should however also be possible to prove this spectrophotometrically. The whole extinction curve between 2 250 Å and 4 500 Å has therefore been determined (with a Beckman DU Spectrophotometer) for a solution having $C_M = 15$ mC, [H$^+$] = 500 mC, C_{HA} = 200 mC and I = 1 C ($NaClO_4$), where the dissociation of glycolic acid is almost completely repressed. The curve obtained is however almost identical with that of UO_2^{2+}, the deviations being at most a few per cent. This may be explained by the low [A] ≈ 0.1 mC, which nevertheless exists in the solution. No effect of the glycolic acid itself can thus be proved, certainly it does not form any complexes.

The total deviation between the different complex formation curves can however hardly be ascribed to the hydrolysis, as was the case in the acetate system. In contrast with that case, the curves here do not converge very rapidly but run almost parallel in their upper parts. This behaviour is certainly a consequence of that medium change

Table 4. Determination of corresponding values of $\bar{n}$ and [A] at the buffer of $\delta = 4$. $C'_M = 25$ mC and 50 mC. Glass electrode.

	C'_M = 25 mC					C'_M = 50 mC				
C'_A mC	C_M mC	E_A mV	$[H^+]$ mC	[A] mC	$\bar{n}$	C_M mC	E_A mV	$[H^+]$ mC	[A] mC	$\bar{n}$
13.16	24.66	35.6	3.88	3.24	0.559	49.3	49.1	6.61	1.80	0.365
25.98	24.35	32.4	3.61	7.30	0.92	48.7	48.4	6.79	3.74	0.596
38.5	24.05	28.8	3.2	12.47	1.215	48.1	46.2	6.4	6.12	0.807
50.7	23.75	25.4	2.8	18.75	1.47	47.5	43.7	5.8	8.95	1.00
62.5	23.45	22.2	2.5	26.2	1.66	46.9	40.6	5.2	12.53	1.18
90.9	22.72	16.9	2.1	46.9	2.03	45.4	33.9	4.0	23.8	1.57
117.7	22.04	13.5	1.8	69.5	2.27	44.1	28.5	3.3	38.3	1.88
142.9	21.42	11.2	1.7	92.5	2.43	42.8	24.1	2.8	55.3	2.11
166.7	20.82	9.5	1.6	115.1	2.56	41.7	20.7	2.4	73.8	2.29
210.5	19.75	7.2	1.4	158.9	2.69	39.5	16.0	2.0	112.2	2.54
250.0	18.75	5.8	1.4	199.5	2.77	37.5	12.9	1.8	150.7	2.70
285.9	17.85	4.8	1.3	237	2.8	35.7	10.8	1.7	187.1	2.82
348.0	16.30	3.5	1.3	304	2.8	32.6	8.1	1.5	253.5	2.95
400	15.00	2.7	1.2	361	2.7	30.0	6.5	1.4	309.7	3.06
444	13.88	2.2	1.2	407	2.7	27.8	5.3	1.4	361	3.0
500						25.0	4.2	1.3	424	3.1

which is caused by the glycolic acid, as was observed above. That the curves are parallel indicates, however, that it is the absolute values of the constants which are altered rather than the ratios between them. As the effect of change in medium cannot be separated from that of hydrolysis, it is very difficult to assess the effect of this factor, with any degree of certainty, and it cannot be denied that an error may thereby enter the final result.

THE CALCULATION OF THE CONSTANTS AND THEIR COMPARISON WITH THOSE OF OTHER SYSTEMS WITH SIMILAR LIGANDS

The β values are calculated according to[4 p. 785] using the complex formation function of $\delta = 4$, which at least is free from hydrolytic influence. As the $\bar{n}$/[A]-function has a very steep course in the present system it is necessary to use (5b) of[4 p. 786] with $[A]_0 = 2$ mC, Table 5. In Table 6, the values of β are given, with the maximal random errors assigned, together with values of $\bar{n}$ and α, calculated with the aid of β. The $\bar{n}$ found give the fulldrawn curve of

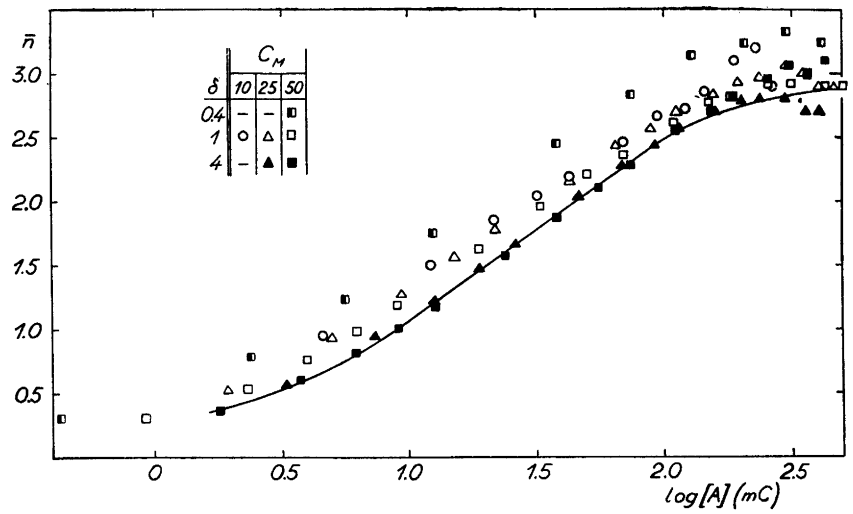

Fig. 1. The complex formation functions. — The signs refer to the series of different δ and C'_M according to the scheme given in the fig. — The fulldrawn curve is obtained from the values of β finally calculated for δ = 4.

Table 5. The X-functions obtained by graphical integration of the $\bar{n}$/[A]-function.

[A] mC	$\ln \frac{X([A])}{X(0.002)}$	$\frac{X([A])}{X(0.002)}$	$X([A])$	X_1 ([A]) C^{-1}	X_2 ([A])·10^{-3} C^{-2}	X_3 ([A])·10^{-5} C^{-3}
0		*0.64*		*263*	*9.1*	*1.62*
2	0	1.00	1.56	280		
4	0.340	1.41	2.19	298		
6	0.624	1.87	2.91	318		
8	0.875	2.40	3.74	342	9.9	
10	1.099	3.00	4.68	368	10.5	
15	1.576	4.83	7.53	436	11.55	1.63
20	1.978	7.21	11.25	513	12.5	1.70
30	2.630	13.87	21.6	687	14.1	1.67
40	3.154	23.4	36.4	885	15.5	1.60
50	3.601	36.6	57.0	1 120	17.1	1.60
75	4.486	88.3	137.8	1 824	20.8	1.56
100	5.173	175.4	273	2 720	24.6	1.55
150	6.210	497	775	5 160	32.7	1.57
200	6.980	1 072	1 672	8 360	40.5	1.57
300	8.145	3 440	5 370	17 900	58.7	1.65
400	8.970	7 850	12 250	30 600	75.8	1.67

Table 6. The ligand number and the composition of the system as calculated for some values of [A] *with the complexity constants found.*

$\beta_1 = 265 \pm 15$ C^{-1} $\beta_2 = (9.1 \pm 0.6) \cdot 10^3$ C^{-2} $\beta_3 = (1.6 \pm 0.2) \cdot 10^5$ C^{-3}

[A] mC	$\bar{n}$	a_0	a_1	a_2	a_3
2	0.385	64	33.5	2.5	0
10	1.05	21	56	19.5	3.5
30	1.74	4.5	37	38.5	20
100	2.47	0.5	9.5	32.5	57.5
200	2.72	0	3	21.5	75.5
400	2.86	0	1	12	87

Fig. 1, which is seen to fit very well the experimental points of the curve of $\delta = 4$.

In Table 7, the constants for the various systems are compared. Besides β, b and the ratios b_n/b_{n-1}, the quantity $1/K_c$ has also been introduced, *i. e.* β_1 $(= b_1)$ of the corresponding acids in the same ionic medium. As a rule, the values of $1/K_c$, β and b decreases in the same sequence: acetate → glycolate → monochloroacetate.

As expected, the affinity of related ligands to H^+ and UO_2^{2+} thus decreases in the same order. β_1 of the glycolate system alone forms an exception to this rule, having an abnormally high value. As a consequence, the ratio b_1/b_2 comes out three times as large here as in the acetate system. The difference between the values of b_2/b_3 are not so marked, but as pointed out above, these values are not very useful owing to the effects of change in medium. For that reason, to which is added a large experimental error of β_3, b_2/b_3 of the mono-

Table 7. The constants of the uranyl acetate, glycolate and chloroacetate systems.

A	$1/K_c$ C^{-1}	$\beta_1 (= b_1)$ C^{-1}	β_2 C^{-2}	β_3 C^{-3}	b_2 C^{-1}	b_3 C^{-1}	b_1/b_2	b_2/b_3
$^{\Gamma}Ac^-$	39 000	240	23 000	$2.2 \cdot 10^6$	96	96	2.5 ± 0.4	1.0 ± 0.4
$HOAc^-$	3 800	265	9 100	$1.6 \cdot 10^5$	34.5	17.5	7.7 ± 1.5	2.0 ± 0.6
$ClAc^-$	450	27	180	(500)	6.7		4.0 ± 0.7	

chloroacetate system should not be used at all. The magnitude of b_1/b_2 for this system seems to fit that of acetate approximately.

Thus it is very possible that the first ligand of the glycolate system is really bound as a chelate. The values of β_1 and, especially, that of b_1/b_2 are both in favour of this hypothesis, when compared with the corresponding values of the other systems. The chelate bond possibly formed is not very strong, however, as it is certainly broken by the addition of the third ligand, UO_2^{2+} being able to coordinate at most three ligands of the acetate type, even if they are coordinated only by their carboxyl radicals.

SUMMARY

The complexity of uranyl glycolate has been quantitatively determined by emf measurements, similar to those used previously in the investigations of the acetate and chloroacetate systems. The presence of three complexes has been proved, *viz.* MA, MA_2 and MA_3, the lattermost being the saturated complex of the system. The first complex MA is remarkably strong as compared with those which follow and might thus possibly be a chelate. If such a complex is formed, it must however be broken when the complex formation proceeds, as the maximum coordination number of the uranyl ion seems to be three for ligands of the acetate type, even if they are bound only by their carboxyls.

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