

Studies on Coordination Compounds of Uranyl Acetate with Organic Acids. II

The System: Uranyl acetate-lactic acid-water

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With 3 Figures

Summary

Conductometric, colorimetric and pH observations of the mixed solutions of uranyl acetate and lactic acid revealed the existence of two complex compounds in (1:1) and (1:2) molecular ratios. The compounds were isolated in the pure state and the constitution was established by estimating the amounts of uranium and lactic acid present in the isolated samples.

The results on the formation of complex compounds between uranyl acetate and mandelic acid have been reported in the previous part of this series¹). It was thought desirable to extend this work in the case of aliphatic hydroxyacids. Lactate probably behaves as a bidentate ligand. CANNAN and KIBRICK²) have observed higher values of association constants for α -hydroxy acids than the corresponding carboxylic acids. Similar observations have been reported by DAVIES³). Less work seems to be carried out on the complexes formed between uranyl acetate and lactic acid, although uranyl salts with hydroxyacids which have been isolated and characterized are the diethyl citrate⁴), glycolate⁵), lactate⁶)⁷), malate⁸), and quinate⁹). Complexes of uranyl salts with some other hydroxyacids have been reported in literature. Ascorbic acid forms in

¹) PANDE and MISRA, This journal 1961.

²) CANNAN and KIBRICK, J. Amer. chem. Soc. **60**, 2314 (1938).

³) DAVIES, J. chem. Soc. London **1938**, 277.

⁴) P. KIERKEGAARD, Acta Chem. Scand. **10**, 599 (1956).

⁵) G. COURTOIS, C. R. hebd. Séances Acad. Sci. **158**, 1688 (1914).

⁶) G. COURTOIS, C. R. hebd. Séances Acad. Sci. **158**, 1688 (1914).

⁷) H. ENGELHARDT and R. MADRELL, Ann. **63**, 99 (1847).

⁸) L. W. ANDREWS, Proc. Iowa Acad. Sci. **32**, 299 (1925); Chem. Abstracts **21**, 713 (1927).

⁹) G. COURTOIS, C. R. hebd. Séances Acad. Sci. **158**, 1688 (1914).

solution a 1:1 uranyl complex¹⁰⁾¹¹⁾. Uranyl salicylate has been crystallised in anhydrous state¹²⁾¹³⁾¹⁴⁾. Uranyl tartarate has been known from the earliest days of uranium chemistry¹⁵⁾. A considerable amount of work has been done on the optical properties of the uranyl salts with tartaric and other aliphatic hydroxyacids.

More recently, NEUMAN, and his colleagues have used spectrophotometry, polarography and pH titration to study solution of uranyl complexes of the aliphatic hydroxyacids. The stoichiometries of the lactate complexes with uranyl nitrate in solution have also been examined¹⁶⁾. These authors showed the evidence of the formation of 1:1 complex in solution and also studied the polymerisation effect on the uranyl-lactate complex¹⁷⁾.

Physicochemical properties such as conductivity, colorimetry and pH have been used by us to study the solutions of uranyl complexes with

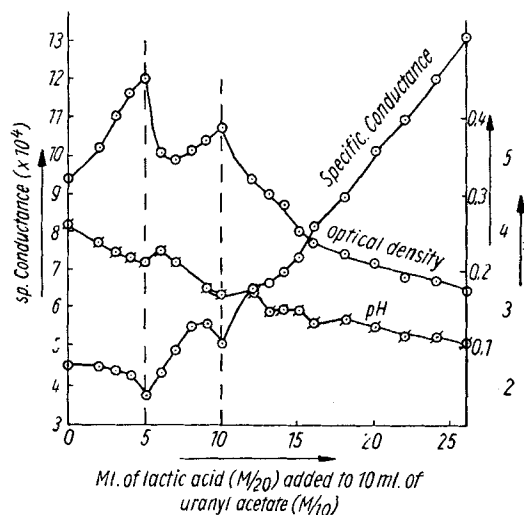


Fig. 1. Sp. Conductance, optical density and pH. The System-Uranyl acetate-lactic acid-water

lactic acid, which show the evidence of the formation of two complexes at the molar ratios 1:1 and 1:2.

Experimental

Procedure — Stock solutions of M/20 uranyl acetate dihydrate (B.D.H./A.R.) and M/10 lactic acid (B.D.H./A.R.) were prepared for the preparation of mixed solutions. A set of 20 mixed solutions was prepared by following NAYAR and PANDE's Monovariation method¹⁸⁾, viz., the concentration of uranyl acetate was kept constant in all the solutions (0.01 M) while that of lactic acid varied

¹⁰⁾ I. J. GAL, Geneva I 8, 358.

¹¹⁾ Z. GREGORCZYK, Acta Polon. Pharm. **15**, 129 (1958); Chem. Abstracts **52**, 19655 (1958).

¹²⁾ G. COURTOIS, Dissertation, Paris (1914); BODLEIAN, 1937 Ud 10 (4).

¹³⁾ G. COURTOIS, Bull. Soc. chim. France (4) **33**, 1761 (1923).

¹⁴⁾ N. K. DUTT and N. GOSWAMI, Z. anorg. Chem. **298**, 265 (1959).

¹⁵⁾ J. B. RICHTER, Über die nevern Gegenstände der Chymie, Vol. 1, pp. 3,16.

J. F. KORN, Breslan und Hirschberg (1791).

¹⁶⁾ I. FELDMAN and J. R. HAVILL, J. Amer. chem. Soc. **76**, 2114 (1954).

¹⁷⁾ I. FELDMAN, J. R. HAVILL and W. F. NEUMAN, J. Amer. chem. Soc. **76**, 4726 (1954).

¹⁸⁾ M. R. NAYAR and C. S. PANDE, Proc. Ind. Acad. Sci., **27 A**, 286 (1948).

systematically from 0.0 to 0.38 M. The composition of the solutions are given in column 2 of Table I.

Conductivity — An electrical magic eye apparatus (Type: GM/4249/ Philips) was used to determine the conductivity of the solutions. A pyrex glass conductivity cell with platinum electrodes was used for such measurements. The cell was rinsed several times with the solutions and at least 3 readings were taken

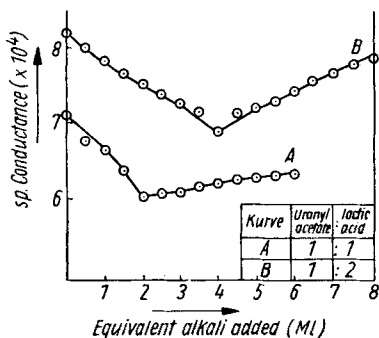


Fig. 2. Conductometric titrations

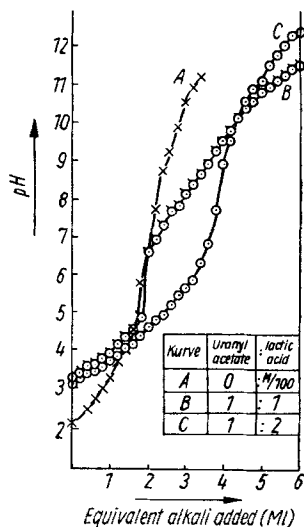


Fig. 3. pH-titrations

Table I

Solution No.	Ml. lactic acid (M/10) added to 10 ml. of uranyl acetate (M/20)	Specific conductance ($\times 10^4$)	Optical density	pH
1	0	4.499	0.320	4.10
2	2	4.480	0.360	3.85
3	3	4.321	0.400	3.72
4	4	4.228	0.432	3.65
5	5	3.725	0.450	3.60
6	6	4.298	0.352	3.75
7	7	4.822	0.348	3.32
8	8	5.460	0.357	3.25
9	9	5.510	0.370	3.25
10	10	5.010	0.385	3.15
11	12	6.448	0.320	3.20
12	13	6.646	0.300	2.95
13	14	6.912	0.285	2.95
14	15	7.332	0.250	2.86
15	16	8.110	0.234	2.81
16	18	8.920	0.220	2.72
17	20	10.111	0.210	2.72
18	22	10.982	0.190	2.62
19	24	12.000	0.186	2.60
20	26	13.120	0.170	2.52

for each solution. All measurements were made in an electrically heated thermostat at $35^{\circ}\text{C} \pm 0.1$. The results are recorded in Table I.

Colorimetry — Colorimetric measurements were made with a KLETT-SUMMERSON colorimeter. 3 readings were taken for each solution. The wave length employed was $420\text{ m}\mu$. The relative optical densities were calculated for each solution, which are recorded in Table I.

Table II
Specific conductance of (1:1) and (1:2) mixtures of uranyl acetate and lactic acid containing different amounts of equivalent alkali

No.	Equivalent alkali added ml.	Specific conductance ($\times 10^4$)	
		(1:1) mixture	(1:2) mixture
1	0	7.100	8.200
2	0.5	6.752	8.000
3	1.0	6.637	7.820
4	1.5	6.353	7.655
5	2.0	6.012	7.503
6	2.5	6.060	7.396
7	3.0	6.100	7.277
8	3.5	6.145	7.150
9	4.0	6.197	6.990
10	4.5	6.225	7.113
11	5.0	6.250	7.200
12	5.5	6.282	7.298
13	6.0	6.300	7.424
14	6.5	—	7.531
15	7.0	—	7.670
16	7.5	—	7.785
17	8.0	—	7.896

pH-measurements — pH-measurements were carried out by using a Rye pH-meter (cat. No. 1103) using a glass electrode, the results of which are given in Table I.

When the values of sp. conductivity, optical density and pH of the solutions were plotted against the varying volume of lactic acid, curves are obtained as given in Table I.

Conductometric titrations — Conductometric titrations were carried out in a thermostat at $35^{\circ}\text{C} \pm 0.1$ with the help of a resistance measuring assembly, Philips G. M. 4249.

(1:1) and (1:2) mixtures of uranyl acetate and lactic acid were prepared. To these mixtures varying quantities of KOH of known strength were added from a micropipette, keeping the total volume in each case

constant. The solution was stirred for 15 minutes and left for another five minutes to attain the temperature of the bath. The titration observations are given in Table II and Figure 2.

pH-titrations — pH-titrations were carried out by adding KOH from a micropipette to 20 ml. solution of (1:1) and (1:2) mixture of uranyl acetate and lactic acid. The pH was noted after stirring the solution for two minutes and waiting for another two minutes. The reading was noted after each addition. The readings are recorded in Table III and Figure 3. For purposes of comparison M/100 lactic acid was titrated with the standard alkali under similar conditions.

Isolation of the compounds: $\text{UO}_2(\text{C}_3\text{H}_5\text{O}_3) \cdot 2\text{H}_2\text{O}$ — The solutions of uranyl acetate and lactic acid were mixed in the stoichiometric ratio of 1:1 and the solution evaporated on a water bath till it became saturated. The solution was then cooled slowly. The crystals formed were separated, washed, dried and recrystallised. The crystals formed were shining yellow in colour.

Table III
pH values of M/100 lactic acid, (1:1) and (1:2) mixtures of uranyl acetate and lactic acid containing different amounts of equivalent alkali

No.	Equivalent alkali added ml.	M/100 lactic acid	pH	
			(1:1) mixture	(1:2) mixture
1	0.0	2.10	3.25	3.10
2	0.2	2.42	3.39	3.22
3	0.4	2.75	3.55	3.34
4	0.6	3.00	3.60	3.40
5	0.8	3.22	3.78	3.52
6	1.0	3.50	3.90	3.70
7	1.2	3.97	4.10	3.82
8	1.4	4.55	4.30	4.00
9	1.6	5.75	4.50	4.15
10	2.0	6.60	4.82	4.35
11	2.2	7.75	6.60	4.60
12	2.4	8.75	6.98	4.80
13	2.8	9.20	7.35	4.99
14	3.0	9.88	7.70	5.20
15	3.2	10.53	7.82	5.42
16	3.4	10.95	8.15	5.63
17	3.6	11.15	8.40	5.85
18	3.8	—	8.65	6.30
19	4.0	—	8.95	6.85
20	4.2	—	9.22	7.75
21	4.4	—	9.55	8.95
22	4.6	—	9.80	9.55
23	4.8	—	10.10	10.10
24	5.0	—	10.40	10.55
25	5.2	—	10.55	10.90
26	5.4	—	10.80	11.10
27	5.6	—	10.99	11.55
28	5.8	—	11.10	11.80
29	6.0	—	11.25	12.00
30	6.2	—	11.42	12.22

$\text{UO}_2(\text{C}_3\text{H}_4\text{O}_3)_2$ — This was prepared by evaporating a solution of uranyl acetate and lactic acid in the molar ratio of 1:2 on a water bath and recrystallising.

The compounds were then analysed to assign them possible formulae.

Estimation of uranium — The uranium was estimated by „oxinate“ method¹⁹⁾, and the percentage uranium in the compounds calculated. The theoretical values are in agreement with the estimated values for uranium as given in Table IV.

Estimation of lactic acid — The lactic acid content of the compounds was determined by the method of ERNST and HORVATH²⁰⁾. They have described a microdetermi-

¹⁹⁾ A. I. VOGEL, A Text book of quantitative Inorganic Analysis page 471, edition 1951.

²⁰⁾ E. ERNST and G. HORVATH, Biochem. Z. **224**, 133 (1930).

nation of lactic acid in which the sample in 5% H_2SO_4 is heated with excess permanganate for 15 minutes on a steam bath and is thereby oxidized to acetic acid. 4 equivalents of oxidant are required per mole of lactic acid; 1 ml. of 0.1 N permanganate corresponds to 2.25 mg. The self decomposition of permanganate has to be considered and a correction for it established by oxidising known quantities of oxalic acid under similar conditions. The results of some of the experiments are given in Table V.

Table IV

Experiment No.	% of uranium					
	1:1 compound UO_2 ($\text{C}_3\text{H}_5\text{O}_3$) · 2 H_2O			(1:2) compound UO_2 ($\text{C}_3\text{H}_4\text{O}_3$) ₂		
	Estimated	Theoretical	Difference	Estimated	Theoretical	Difference
1	60.00		0.91	51.90		0.97
2	59.90		1.01	52.00		0.87
3	60.10	60.91	0.81	51.98	52.87	0.98
4	60.15		0.76	51.99		0.88
5	60.11		0.80	51.81		1.06

Table V

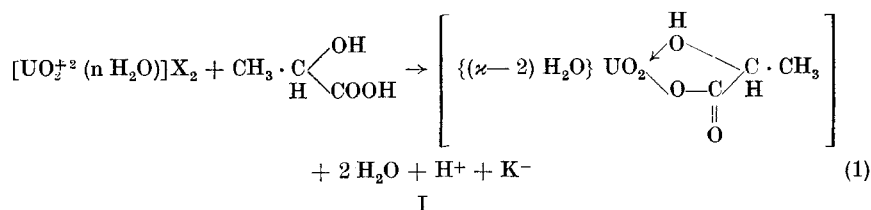
Experiment No.	% of lactic acid					
	1:1 compound UO_2 ($\text{C}_3\text{H}_5\text{O}_3$) · 2 H_2O			(1:2) compound UO_2 ($\text{C}_3\text{H}_4\text{O}_3$) ₂		
	Estimated	Theoretical	Difference	Estimated	Theoretical	Difference
1	23.10		2.16	38.20		1.95
2	23.62		1.64	38.85		1.30
3	23.45	25.26%	1.81	38.54	40.15	1.61
4	23.70		1.56	38.61		1.54
5	23.65		1.61	38.80		1.35

Discussion

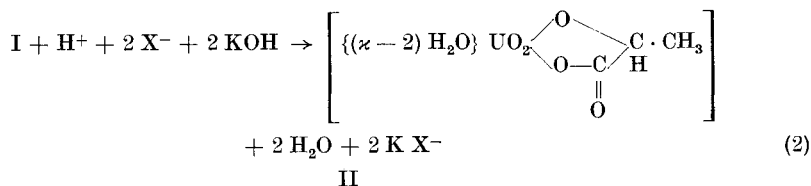
Fig. 1 which represents the results of colorimetry, conductivity and pH, shows that there are two definite breaks in the regular curves at intervals corresponding to 5 c. c. and 10 c. c. of lactic acid solution. Curve A shows the results of conductivity while B and C that of colorimetry and pH respectively. Since lactic acid solution was M/20 in strength, these values corresponded to 10 c. c. and 20 c. c. of M/10 lactic acid solution. As each solution contained same quantity of uranyl acetate solution (i. e. 10 c. c. of M/10), the ratios of uranyl acetate to lactic acid at these points are 1:1 and 1:2 which corresponds to the formation of two compounds in solution.

Fig. 3 represents the pH titration values of uranyl acetate-lactic acid mixtures against equivalent alkali. Curve A is for M/100 lactic acid alone while B and C are for (1:1) and (1:2) mixtures respectively. Curve B shows an inflection at two equivalents of alkali and C at four equivalents of alkali.

The pH of (1:1) mixture of uranyl acetate and lactic acid increases when a solution of equivalent alkali is added. When a complex is formed between UO_2^{+2} and lactate ions there is a rise in pH. When two equivalents of alkali have been added, pH rises at once showing an inflection at 2 equivalents of alkali. This may be attributed to the formation of a (1:1) complex in solution. The H^+ ions of the $-\text{OH}$ group and H^+ of the $-\text{COOH}$ group both take part in the reaction and are liberated, the H^- ion concentration increases causing an increase in the pH and ultimately a break in the curve. The reaction may be represented as follows:

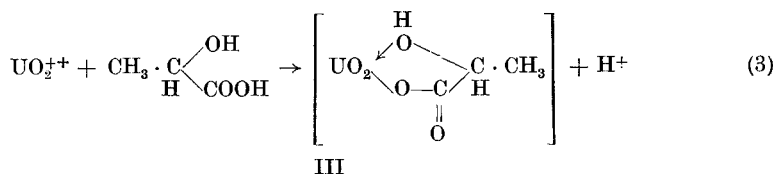


I will probably then react with KOH as given below:

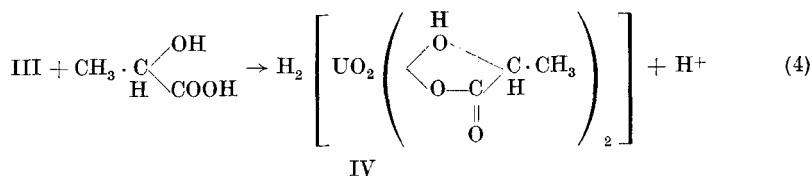


forming a (1:1) compound, which has been isolated as $\text{UO}_2(\text{C}_3\text{H}_5\text{O}_3) \cdot 2\text{H}_2\text{O}$.

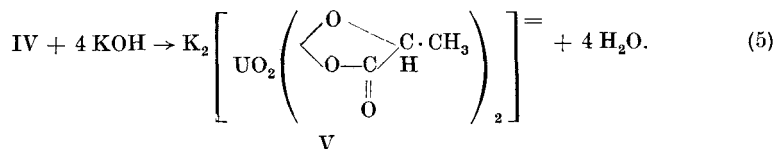
An examination of curve C in Fig. 3, which is for 1:2 mixture of uranyl acetate and lactic acid, shows an inflection at 4 equivalents of alkali indicating the formation of a (1:2) compound. Four H^+ ions are liberated when four equivalents of alkali have been added and the reaction which takes place may be put as follows:



III further reacts with another molecule of lactic acid,



and IV when reacted with KOH forms a 1:2 compound.



The V has been prepared in its acid form $[\text{UO}_2(\text{C}_3\text{H}_4\text{O}_3)_2]\text{H}_2$.

Fig. 2 represents the changes taking place in conductivity when equivalent alkali is added in (1:1) and (1:2) mixtures of uranyl acetate and lactic acid. The addition of equivalent alkali lowers the conductance at 2 equivalents of alkali in curve A and a minimum is observed at that point, which infers the formation of a 1:1 chelate in solution. With any further addition of alkali the conductance rises. The decrease in the conductance is due to the removal of H^+ ions and as soon as all the H^+ ions have been removed the conductance increases due to the excess of CH_3COOK in the solution.

In the same way curve B shows a minimum value of conductance where four equivalents of alkali have been added, which indicates the formation of a 1:2 compound in solution. The increase in conductance after the break is due to the excess of KOH in the solution.

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