

## The System: Uranyl acetate-mandelic acid-water

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With 3 Figures

### Summary

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

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No systematic physico-chemical work, however, appears to have been carried out on the complexes formed by uranyl ions with mandelic acid and other acids like glycolic acid and its substituted products like salicylic acid, although studies have recently been carried out on the complexes formed by uranyl ions with some other acids: ARNO MÜLLER<sup>1)</sup> studied complex uranyl compounds of ascorbic acid and their properties. Sulphosalicylic acid forms 1:1 complex with  $UO_2$ <sup>2)</sup>. Similarly  $CH_2ClCOOH$ <sup>3)</sup>  $\beta$ -hydroxynaphthoic acid<sup>4)</sup>, hydroxamic acid<sup>5)</sup> have all been found to form complexes with uranyl ion. A survey of literature reveals that the preparation of some complex salts of the above acids of uranyl have also been described<sup>6) 7)</sup>.  $UO_2(C_3H_7O_3)_2$  was isolated and analysed by MÜLLER<sup>8)</sup>. Much work has been done on the complex formation between mandelic

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<sup>1)</sup> ARNO MÜLLER, *J. prakt. Chem.* **157**, 89–95 (1940).

<sup>2)</sup> R. T. FOLEY and R. C. ANDERSON, *J. Amer. chem. Soc.* **71**, 909–12 (1949).

<sup>3)</sup> AHRLAND, *Acta Chem. Scand.* **3**, 783–808 (1949).

<sup>4)</sup> R. CERNATESCU and MARGARETA P. PONI, *Acta. Rep. Populare Române. Bul Stînt. A.* **1**, 241–50 (1949).

<sup>5)</sup> A. S. BHADURI and P. RAY, *Science and Culture (India)*, **18**, 97–8 (1952).

<sup>6)</sup> R. S. SINGH and SATYA PRAKASH, *J. Indian chem. Soc.* **35**, 555–6 (1958).

<sup>7)</sup> GIOVANNI MANNELI, *Am. Chim. Applicata* **38**, 594–600 (1948).

<sup>8)</sup> MÜLLER, *Z. anorg. Chem.* **109**, 242, 262 (1920).

acid and other metals such as Zr<sup>9</sup>), Ca<sup>10</sup>), Mo<sup>11</sup>) which forms MoO<sub>3</sub> (C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>)<sup>--</sup> and Al<sup>12</sup>) which forms 3 complexes.

The present work deals with the study on complex formation between uranyl acetate and mandelic acid. The nature of the complex species present, when uranyl ions are treated with mandelate ions in aqueous solution, has been investigated by conductometric and electrometric titrations which showed the evidence of the formation of two complexes at the molar ratios 1:1 and 1:2.

### Experimental

Stock solutions of M/20 uranyl acetate dihydrate (B.D.H./A.R.) and M/10 mandelic acid (B.D.H./extra pure) were prepared for the preparation of mixed solutions. A set of

Table I

Solution No.	Ml. mandelic acid (M/10) added to 10 ml of uranyl acetate (R/20)	Specific conductance (X 10 <sup>4</sup> )	pH
1	0	4.499	3.18
2	2	4.389	3.29
3	3	4.300	3.25
4	4	4.187	3.24
5	5	3.937	3.21
6	6	4.499	3.26
7	7	4.950	3.32
8	8	5.350	3.33
9	9	5.400	3.31
10	10	5.210	3.24
11	12	6.646	3.30
12	13	6.790	3.31
13	14	7.182	3.29
14	15	7.386	3.29
15	16	7.985	3.30
16	18	8.748	3.30
17	20	9.842	3.30
18	22	10.860	3.29
19	24	11.625	3.30
20	26	12.113	3.30

20 mixed solutions was prepared by following NAYAR and PANDE'S Monovariation method<sup>13</sup>) viz., the concentration of uranyl acetate was kept constant in all the solutions (0.01 M) while that of mandelic acid varied 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 G M 42/49/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 for each solution. All measurements were made in an electrically heated thermostat at 35 °C ± 0.1. The results are recorded in Table I.

<sup>9</sup>) RICHARD B. HAHN and LEON WEBER, J. Amer. chem. Soc. **77**, 4777-9 (1955).

<sup>10</sup>) H. W. JOHNSTON, J. Sci. Technol., **37 B**, 522-37 (1956).

<sup>11</sup>) P. SOUCHAY, Bull. Soc. chem. France 122-33 (1949).

<sup>12</sup>) S. N. SRIVASTAVA and MANOHAR, J. Indian Chem. Soc. Vol. **37**, No. 5 299-302 (1960).

<sup>13</sup>) NAYAR and PANDE, Proc. Indian Acad. Sci. **27 A**, 286 (1948).

pH-measurements. pH-measurements were made by using a Pye pH-meter (Cat. No. 11083) using a glass electrode, the results of which are given in Table I.

When the values of sp. conductivity and pH of the solutions were plotted against the varying volume of mandelic acid in the mixture, curves are obtained as given in Fig. 1.

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

Two mixtures containing uranyl acetate and mandelic acid in the molar ratio of (1:1) and (1:2) were prepared. To these mixtures varying quantities of KOH of known strength were added from a micropipette. The total volume in each case was kept constant. The solution was stirred for 15 minutes and left for another 5 minutes before noting the readings so that the solutions attained the temperature of the bath. The titration observations are given in Table II and Fig. 2.

Electrometric titrations. Electrometric 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 mandelic acid. The pH was noted after stirring the solution for two minutes and waiting for another 2 minutes. The reading was noted after each addition. The readings are recorded in Table III and Fig. 3. For purposes of comparison, M/100 mandelic acid was titrated electrometrically with the standard alkali under similar conditions.

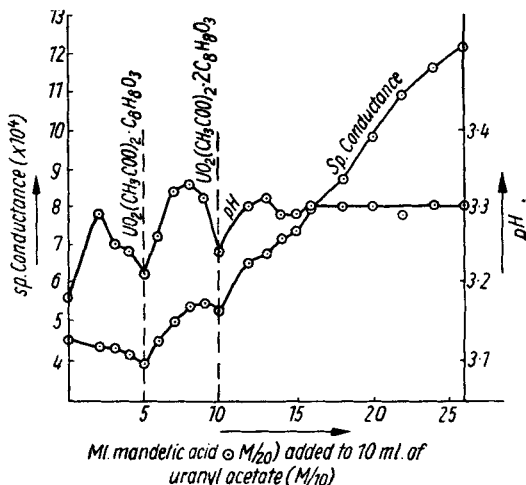


Fig. 1. Sp. Conductance and pH. The System: Uranyl acetate-mandelic acid-water

Table II

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

No.	Equivalent alkali added Ml.	Specific conductance (X 10 <sup>4</sup> )	
		(1:1) mixture	(1:2) mixture
1	0	7.000	8.000
2	0.5	6.300	7.800
3	1.0	5.056	7.600
4	1.5	4.500	7.200
5	2.0	4.190	6.505
6	2.5	4.355	6.150
7	3.0	4.595	5.930
8	3.5	5.000	5.705
9	4.0	5.501	5.500
10	4.5	6.095	5.650
11	5.0	6.634	5.905
12	5.5	7.190	6.150
13	6.0	7.500	6.500
14	6.5	—	6.735
15	7.0	—	7.000

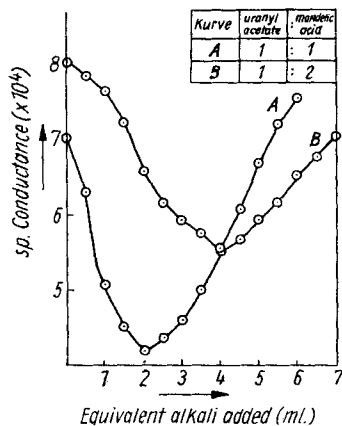


Fig. 2. Conductometric titration

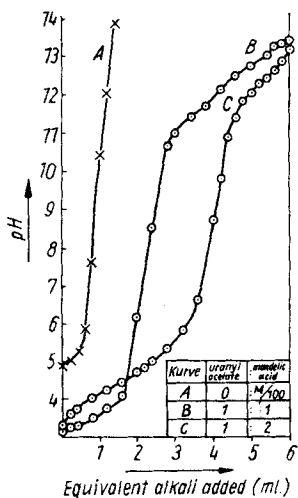


Fig. 3. Electrometric titration

### Isolation of the Compounds

$\text{H}_2[\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3)_2]$  — After ascertaining the evidence for the formation of complexes by physicochemical methods, attempts

were made to isolate these compounds. The solutions of uranyl acetate and mandelic acid were mixed in stoichiometric ratios of 1:2 and the solutions was evaporated on a water bath till it became saturated (when the crystals began to appear). The solution was then cooled slowly. The crystals formed were separated, washed, dried and recrystallised. The crystals were shining yellow in colour and very light.

$\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3) \cdot 2 \text{H}_2\text{O}$ . It was prepared in presence of KOH in the mixture of uranyl acetate and mandelic acid in (1:1) molar ratio and then crystallising it out.

The compounds prepared above were then analysed to assign the possible formulae.

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

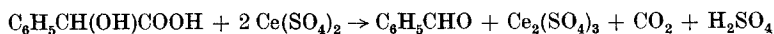
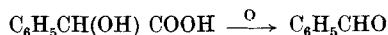
No.	Equivalent alkali added ml	M/100 Mandelic acid	pH	
			(1:1) mixture	(1:2) mixture
1	0.0	4.90	3.18	3.24
2	0.2	5.00	3.23	3.60
3	0.4	5.20	3.28	3.72
4	0.6	5.80	—	—
5	0.8	7.60	3.48	4.00
6	1.0	10.40	—	—
7	1.2	12.00	3.73	4.20
8	1.4	13.80	—	—
9	1.6	—	4.03	4.40
10	2.0	—	6.15	4.70
11	2.2	—	—	4.82
12	2.4	—	8.70	5.00
13	2.8	—	10.62	5.30
14	3.0	—	11.00	—
15	3.2	—	—	5.82
16	3.4	—	11.41	—
17	3.6	—	—	6.62
18	3.8	—	11.70	—
19	4.0	—	—	8.70
20	4.2	—	12.10	9.80
21	4.4	—	—	10.82
22	4.6	—	12.41	11.40
23	4.8	—	—	11.80
24	5.0	—	12.70	12.00
25	5.2	—	—	12.22
26	5.4	—	13.00	12.40
27	5.6	—	13.21	12.60
28	5.8	—	13.30	12.82
29	6.0	—	13.40	13.12

Estimation of uranium. The uranium was estimated in the compounds by „oxidate“ method<sup>14</sup>) and the percentage of uranium calculated from the theoretical values. The theoretical values were in excellent agreement with that of the estimated values for uranium as given in Table IV.

Table IV

Expt. No.	% of uranium					
	(1:1) Compd. $\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3) \cdot 2\text{H}_2\text{O}$			(1:2) Compd. $\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3)_2$		
	Estimated	Theoretical	%Differ- ence	Estimated	Theoretical	%Differ- ence
1	51.13		0.83	41.00		0.60
2	51.05		0.91	40.71		0.89
		51.96			41.606	
3	51.27		0.69	40.92		0.68
4	51.20		0.76	40.90		0.70

Estimation of mandelic acid. The mandelic acid was estimated by ceric sulphate method<sup>15</sup>). A known weight of the compound was dissolved in dilute  $\text{H}_2\text{SO}_4$  and volume made up to 100 C. C. in water. An aliquote of this solution was boiled for twenty minutes with excess of N/10 ceric sulphate. A quantity of ceric sulphate was boiled with acidulated water for the same length of time to serve as blank. The solutions were cooled and excess of ceric sulphate titrated against ferrous ammonium sulphate. (0.1 N) using N-phenyl anthranilic acid as indicator (instead of ferroin). Mandelic acid can be calculated from the following equation:



1 C.C. of N/10  $\text{Ce}(\text{SO}_4)_2$  solution  $\equiv$  0.007607 g. mandelic acid. Some of the results obtained are given in Table V.

Table V

Expt No.	% of mandelic acid					
	(1:1) compound $\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3) \cdot 2\text{H}_2\text{O}$			(1:2) Compd. $\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3)_2$		
	Estimated	Theoretical	%Differ- ence	Estimated	Theoretical	%Differ- ence
1	32.78		0.71	52.10		0.71
2	32.62		0.87	52.24		0.57
		33.49			52.81	
3	32.91		0.58	52.00		0.81
4	32.90		0.59	51.98		0.83

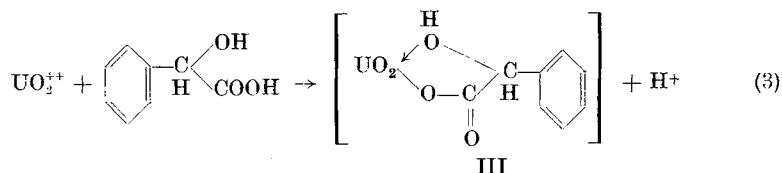
<sup>14</sup>) A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, p. 471, edition 1951.

<sup>15</sup>) M. R. VERMA and S. D. PAUL, J. Sci. and Industr. Res. **13B**, 347 (1954).

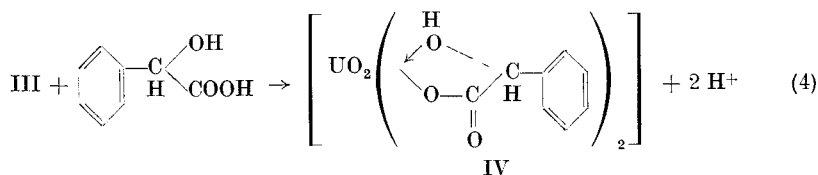


An examination of curve B in Fig. 2 which represents the titration values of (1:2) mixture of uranyl acetate and mandelic acid shows that when four equivalents of alkali have been added the curve shows an inflection which infers the formation of (1:2) chelate. The increase in the value of sp. conductance after the break is due to the excess of KOH in the mixture.

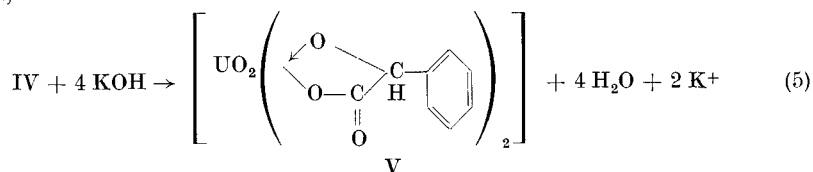
In this case the possible mechanism can be given in the following manner. First one molecule of mandelic acid reacts with uranyl ion.



III then reacts with another mole of mandelic acid, thus,



IV when titrated with KOH forms (1:2) compounds in the following fashion,



The formation of V was further confirmed by its isolation in the form  $\text{H}_2[\text{UO}_2(\text{C}_8\text{H}_6\text{O}_3)_2]$  and analysing.

Fig. 3 represents the changes taking place in pH when standard alkali is added in (1:1) and (1:2) mixtures of uranyl acetate and mandelic acid. Curve A is for M/100 mandelic acid and curves B and C represent the titration values of (1:1) and (1:2) mixture of uranyl acetate and mandelic acid which show one inflection each at two and four equivalents of alkali respectively.

It becomes clear from curve B that when nearly two equivalents of alkali have been added pH rises at once showing an inflection in the curve is probably due to the formation of (1:1) chelate in the solution. The  $\text{H}^+$  of the  $-\text{OH}$  group and H of the  $-\text{COOH}$  group both are liberated and take part in the reaction thus  $\text{H}^+$  ion concentration is increased and the pH rises and causes a break in the curve.

In the case of curve C a break is at about four equivalents of alkali showing that reaction (5) takes place. Four  $H^+$  ions are liberated at four equivalents of alkali and the  $p_H$  at once rises.

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