

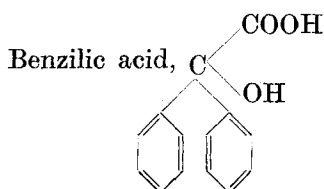
The System: Uranyl acetate–benzilic acid–water

By C. S. PANDE and S. K. MISRA

With 3 Figures

Summary

Conductometric and pH studies of the mixed solutions of uranyl acetate and sodium benzilate reveal the existence of one complex compound in (1:2) molecular ratio. The compound was isolated and its U-content determined.



complexes of UO_2^{++} have not been studied and

no reference is found for their formation even in solution. Other metal complexes with benzilic acid are rarely discussed. This acid, on the basis of its structure may be thought to possess strong tendency for complex formation with UO_2^{++} . Coordination compounds of uranyl acetate with certain acids, for example, lactic and mandelic acids have been studied and the complexities of their solutions described^{1) 2)}. UO_2 -lactate and UO_2 -mandelate complexes have been prepared also. U(vi) forms coordination compounds with a number of hydroxyacids which are discussed in detail³⁻⁶⁾. In view of these studies benzilic acid may also be assumed to act as a strong coordinating ligand for U(vi). Conductometric and pH-studies of uranyl acetate-benzilic acid mixed solutions were carried out which, in all probabilities, showed the formation of only one complex in solution at (1:2) molecular ratio.

¹⁾ C. S. PANDE and S. K. MISRA, *J. prakt. Chem.* (under publication).

²⁾ C. S. PANDE and S. K. MISRA, *J. prakt. Chem.* (under publication).

³⁾ R. T. FOLEY and R. C. ANDERSON, *J. Amer. chem. Soc.* **71**, 909–912 (1949).

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

⁵⁾ G. COURTOIS, *Compt. rend.* **158**, 1688 (1914).

⁶⁾ N. K. DUTT u. N. GOSWAMI, *Z. anorg. allg. Chem.* **298**, 265 (1959).

Experimental

Stock solutions of M/40 uranyl acetate hexahydrate (B. D. H./A. R.) and M/20 sodium benzilate (L. LIGHT and Co. Ltd./A. R.) were prepared for the preparation of mixed solutions (Sodium benzilate was used because of the insolubility of benzilic acid in water.)

A set of 22 mixed solutions was prepared by following NAYAR and PANDE's mono-variation method⁷⁾, viz., the concentration of uranyl acetate was kept constant in all the solutions while that of Sod. benzilate varied systematically. The composition of the solutions are given in column 2 of Table I.

Table I

Soln. No.	Ml Sod. benzilate (M/20) added to 10 ml. of uranyl acetate (M/40)	Specific conductance ($\times 10^4$)	pH
1	0	4.825	3.24
2	2	5.102	3.29
3	3	5.211	3.31
4	4	5.400	3.33
5	5	5.594	3.35
6	6	5.789	3.38
7	7	5.912	3.40
8	8	6.055	3.38
9	9	6.200	3.35
10	10	6.042	3.28
11	12	6.434	3.38
12	13	6.627	3.39
13	14	6.800	3.40
14	15	6.957	3.45
15	16	7.198	3.46
16	18	7.563	3.48
17	20	7.992	3.50
18	22	8.446	3.58
19	24	8.938	3.62
20	26	9.403	3.70
21	28	10.124	3.80
22	30	10.625	3.92

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 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.

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 sodium benzilate in the mixture curves are obtained as given in Fig. 1.

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, Type GM 4249/Philips.

Two mixtures containing uranyl acetate and sodium benzilate in the molar ratio of (1:1) and (1:2) were prepared. To these mixtures varying quantities of NaOH of known strength

⁷⁾ M. R. NAYAR and C. S. PANDE, Proc. Ind. Acad. Sci. **27A**, 286 (1948).

were added from a micropipette. The total volume in each case was kept constant. The solution was stirred for fifteen minutes and left for another 5 minutes before noting the readings so

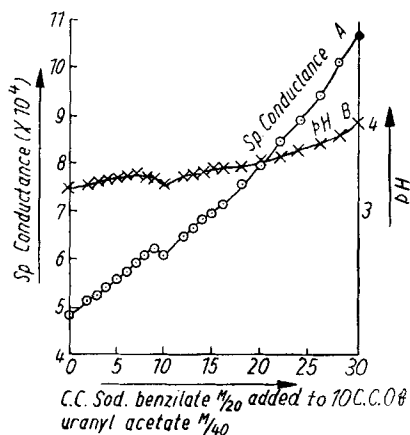


Fig. 1. The System: Uranylacetate—benzoic acid—water sp. Conductance and pH

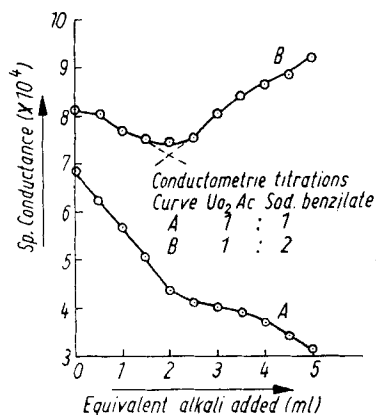


Fig. 2

that the solutions attained the temperature of the bath. The titration observations are given in Table II and Fig. 2.

Table II
Sp. conductance of (1:1) and (1:2) mixtures of uranyl acetate and sodium benzoate containing different amounts of equivalent alkali

No.	Equivalent alkali added ml	Specific conductance ($\times 10^4$)	
		(1:1) mixture	(1:2) mixture
1	0.0	6.85	8.18
2	0.5	6.25	8.05
3	1.0	5.70	7.78
4	1.5	5.05	7.57
5	2.0	4.40	7.45
6	2.5	4.15	7.55
7	3.0	4.00	8.02
8	3.5	3.90	8.40
9	4.0	3.70	8.65
10	4.5	3.40	8.88
11	5.0	3.15	9.20

pH-titrations

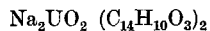
pH-titrations were carried out by adding NaOH from a micropipette to 20 ml. solutions of (1:1) and (1:2) mixtures of uranyl acetate and sodium benzoate. The pH was noted after

stirring the solutions for two minutes and then waiting for another two minutes. The readings were noted after each addition. The readings are recorded in Table III and Fig. 3. For purposes of comparison M/100 sodium benzilate was titrated electrometrically with the standard alkali under similar conditions.

Table III
pH-titration values of M/100 sodium benzilate, (1:1) and (1:2) mixtures of uranyl acetate and sodium benzilate containing different amounts of equivalent alkali

No.	Equivalent alkali added ml.	M/100 Sod. benzilate	pH	
			(1:1) mixture	(1:2) mixture
1	0.0	4.20	3.15	3.55
2	0.2	4.72	3.40	3.50
3	0.4	6.25	3.60	3.45
4	0.6	7.10	4.00	3.40
5	0.8	8.00	4.40	3.50
6	1.0	8.40	4.85	3.60
7	1.2	8.90	5.20	3.80
8	1.4	9.40	5.95	4.15
9	1.6	9.95	6.60	4.55
10	1.8	10.60	7.00	5.00
11	2.0	11.60	7.60	7.00
12	2.4		8.75	8.95
13	2.6		9.10	9.40
14	2.8		9.60	9.80
15	3.0		10.25	9.95
16	3.2		10.60	10.10
17	3.6		11.40	10.15
18	3.8		12.00	10.20
19	4.0		12.60	10.30
20	4.2			10.40
21	4.4			10.45
22	4.6			10.55
23	4.8			10.60
24	5.0			10.70

Isolation of (1:2) compound (sodium salt)



After ascertaining the evidence for the formation of a (1:2) compound by physicochemical methods, attempts were made to isolate this compound. The alcoholic solutions of uranyl acetate and sodium benzilate were mixed in stoichiometric ratio of (1:2) and the solution evaporated on a water bath till the crystals began to appear. The solution was then cooled. The crystals formed were separated, washed, dried and recrystallised. The crystals were shining yellow in colour.

Estimation of uranium

The compound prepared was then analysed to assign the possible formula. The U-content in the compound was estimated by "oxinate" method⁸⁾, 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 below:

Compound	Expt. No.	Estimated	% of uranium Theoretical	Difference
$(C_{14}H_{10}O_3)_2Na_2UO_2$	1.	30.10	30.97	0.87
	2.	30.15		0.82
	3.	30.11		0.86
	4.	30.09		0.88

Diskussion

On examining the curves in Fig. 1, it will be noticed that in both the curves there is one definite break in the regular curves at interval corresponding to 10 c. c. of sodium benzilate solution. Since sod. benzilate solution was M/20 in strenght, this value corresponded to 20 c. c. of M/40 Sod. benzilate solution. As each solution contained same quantity of uranyl acetate solution (i. e., 10 c. c. of M/40) the ratio of uranyl acetate to sod. benzilate at this point is (1:2), which corresponds to the formation of a compound in solution.

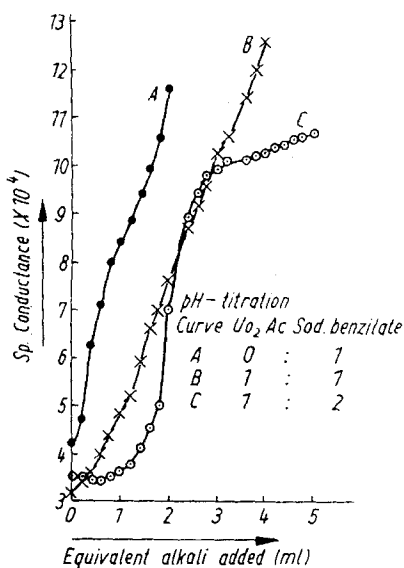


Fig. 3

when two equivalents of alkali have been added the curve shows a break which infers the formation of (1:2) chelate. The continued addition of

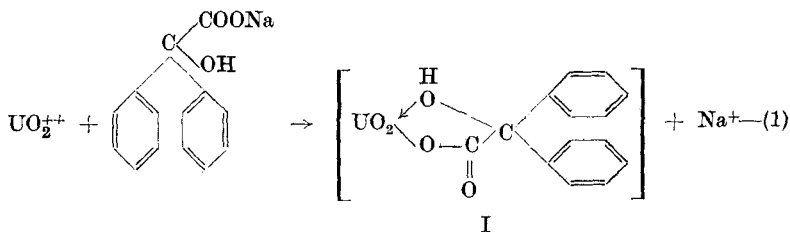
Fig. 2 represents the titration values of uranyl acetate-sod. benzilate mixtures against equivalent alkali. Curve A is for 1:1 mixture having no break and curve B for 1:2 mixture which shows an inflection at 2 equivalents of alkali.

An examination of curve B in Fig. 2 which represents the titration values of (1:2) mixture of uranyl acetate and sod. benzilate shows that

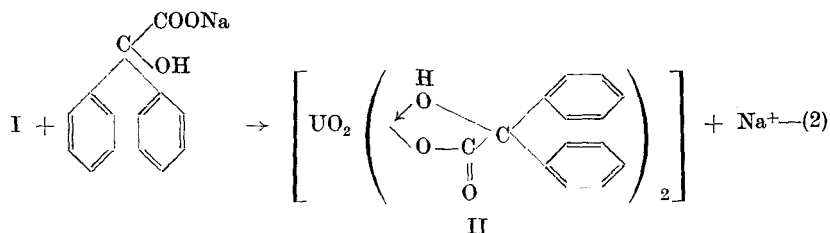
⁸⁾ A. I. VOGEL, A text book of Quantitative Inorganic Analysis page 471, Edition 1951.

alkali in the mixture results in a progressive fall in the conductance which reaches a minimum when 2 equivalents of alkali have been added. With any further addition of alkali, the conductance increases. The decrease in the conductance is due to the removal of H^+ ions and when all the H^+ ions have been liberated, the conductance increases due to the excess of CH_3COONa in the solution. The break in the graph at 2 equivalents of alkali may be attributed to the formation of (1:2) complex in solution.

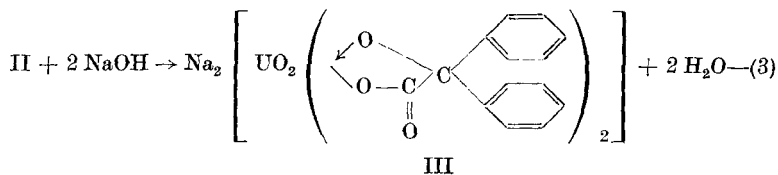
The possible reaction may be given as follows. One molecule of Sod. benzilate reacts with uranyl ion:



I then reacts with another mole of sod. bezilate, thus,



II When titrated with NaOH forms a (1:2) compound in the following manner:



Curve A in Fig. 2 shows no break, therefore, no (1:1) compound is formed.

Fig. 3 represents the changes taking place in pH when standard alkali is added to (1:1) and (1:2) mixture of uranyl acetate and sod. benzilate. Curve A is for M/100 Sod. benzilate and curves B and C represent the pH-titration values of (1:1) and (1:2) mixtures of uranyl acetate and sod. benzilate. Only curve C (i. e. 1:2 mixture) shows an inflection at two equi-

valents of alkali showing the formation of only one compound at (1:2) molar ratio.

When nearly two equivalents of alkali have been added (curve C), pH rises at once showing a break in the curve which is probably due to the formation of a (1:2) compound in solution. H^+ ions of the $-OH$ group and Na of the $-COONa$ are liberated and take part in the reaction; thus H^+ ion concentration is increased and the pH rises causing a break in the curve at two equivalents.

In the case of curve B (1:1 mixture) there is no break showing that no compound is formed at (1:1) ratio.

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