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Studies at Coordination Compounds
of Uranyl Acetate with some Organic Compounds

The System: Uranyl Acetate—Resorcinol—Water

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With 2 Figures

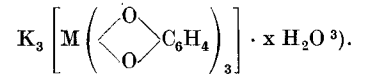
Summary

In a previous communication on the studies of complexes of uranyl acetate with catechol, the formation of complexes at (1:1) and (1:2) molar ratios has been reported. Dihydroxyphenols, in general, have been found to show a strong tendency towards complex formation. Resorcinol which has the phenolic groups in the meta position may also, therefore, show tendency for complex formation with uranium, although to a lesser degree than that of catechol.

The formation of a deep colour in the well known iron (III) chloride test for phenols indicates that phenols form compounds with the heavy metals. In the thermometric, conductometric and spectrophotometric titration of phenol with iron (III) chloride, BANERJI and HALDAR[2]) find breaks at molar ratios of (1:3) and (1:6). Upon electrolysis, the iron (III) ion goes to the anode. These findings suggest the reactions,

$$Fe^{+++} \rightarrow [Fe(OC_6H_5)_3]^0 \rightarrow [Fe(OC_6H_5)_6]^{\equiv}$$

Catechol, because of the effect of chelation, forms stable complexes with the heavy metals:



If the phenolic group can take part in the formation of a chelate ring with some other strongly coordinating group, very stable complexes may be formed[4]).

[1]) C. S. PANDE and S. K. MISRA, This journal.

[2]) BANERJI and HALDAR, Nature **165**, 1012 (1950).

[3]) WEINLAND and BINDER, Ber. dtsch. chem. Ges. **45**, 148, 1113 (1912); **46**, 874 (1913). WEINLAND and WALTHER, Z. anorg. allg. Chem. **126**, 141 (1923).

[4]) JOHN C. BAILAR jr., The Chemistry of the Coordination Compounds, Edition 1956, Page 25.

MÜLLER[5]) has prepared a number of coordination compounds of uranium with phenols. Resorcinol was used by JAIN and RAO[6]) as a reagent for spectrophotometric determination of uranium. They showed the evidence of the formation of $UO_2(PhO_2)_2$, that is, (1:2) compound.

Our studies were mainly concerned with the physicochemical aspect of the mixed solutions of uranyl acetate and resorcinol and to notice the presence of complexes at certain molecular ratios. A (1:2) compound was detected and isolated.

Experimental

Procedure. Stock solutions of M/40 uranyl acetate dihydrate (B. D. H./A. R.) and M/20 resorcinol (B. D. H./extra pure) were prepared for the preparation of mixed solutions. Resorcinol was recrystallised by the usual procedure. All solutions were made in conductivity water. A set of 20 mixed solutions was prepared by following NAYAR and PANDE's Monovariation Method[7]) viz. the concentration of uranyl acetate was kept constant in all the solutions while that of resorcinol varied systematically from 0.0 M to 0.38 M. The composition of the solutions are given in column 2 of Table 1.

Table 1

Solution No.	Ml. resorcinol (M/20) added to 10 ml. of uranyl acetate (M/40)	Specific conductance (X 10^4)	pH	Optical Density
1	0	5.1522	3.32	0.3386
2	2	5.8235	3.33	0.3550
3	3	6.3141	3.36	0.3712
4	4	6.5930	3.38	0.3938
5	5	7.1070	3.40	0.4062
6	6	7.4220	3.42	0.4501
7	7	7.8792	3.42	0.4420
8	8	8.4100	3.40	0.4610
9	9	8.7524	3.38	0.4916
10	10	8.6242	3.30	0.5157
11	12	9.6702	3.36	0.4632
12	13	10.0014	3.38	0.4143
13	14	10.3510	3.40	0.3588
14	15	10.7268	3.45	0.3456
15	16	11.0825	3.46	0.3316
16	18	11.7630	3.48	0.2692
17	20	12.6056	3.50	0.2364
18	22	13.3912	3.51	0.2055
19	24	13.9875	3.52	0.1898
20	26	14.5160	3.51	0.1659

Conductivity. Conductivity of the mixed solutions were determined by using an electrical magic eye apparatus. (Type GM 4249/Philips) at 35 °C ± 0.1. A pyrex glass conductivity cell was used for such measurements. The cell was rinsed several times with the solutions and at least 3 readings were taken for each solution. The results are recorded in Table 1.

pH-measurements. The pH-measurements were made by using a Pye pH-meter (Cat. No. 11083) using a glass electrode. The results are tabulated in Table 1.

[5]) ALAN A. COMYNS, Chemical Review, The Coordination Chemistry of Actinides Vol. 60, No. 2, p. 124 (1960).

[6]) P. C. JAIN and G. S. RAO, Current Sci. (India), **27**, 340–341 (1958).

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

Colorimetry. The results of colorimetric measurements of these mixed solutions are recorded in Table 1. A KLETT-SUMMERSON colorimeter was used for such measurements. The relative optical densities were calculated for each solution. The wave length employed was 420 mμ.

When the values of sp. conductivity, optical density and pH of the solutions are plotted against the varying volumes of resorcinol, curves are obtained as given in Fig. 1.

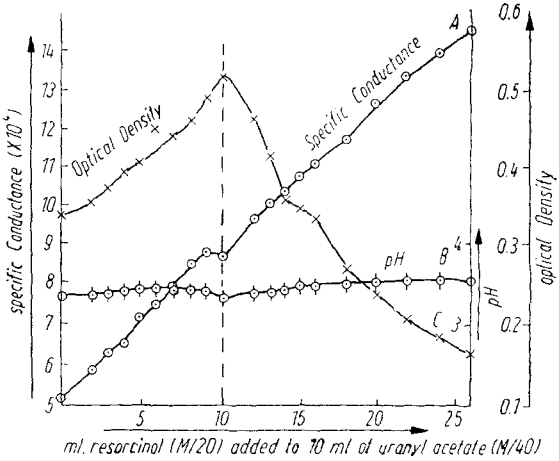


Fig. 1. Sp. Conductance, pH and optical Density. The System: Uranyl acetate—resorcinol—water

pH-titrations. pH-titrations were made on a Pye pH-meter (Cat. No. 1103) by adding KOH from a micropipette to 20 ml. solution of (1:2) mixtures of uranyl acetate and pyrocatechol and the solution stirred after each addition for two minutes. It was left for about two more minutes to attain the equilibrium, and the readings noted after each addition. For purposes of comparison M/100 resorcinol was titrated against the equivalent alkali under similar conditions. The results are recorded in Table 2 and Fig. 2.

Conductometric titrations. Conductometric titrations were carried out using the same magic eye apparatus as described above at 35 °C ± 0.1. To (1:2) mixture of uranyl acetate and resorcinol varying amounts of KOH of known strength were added from a micropipette, keeping the total volume constant. The solution was stirred for 15 minutes and left for another five minutes to attain the temperature of the bath. The observations for the titrations are given in Table 2 and Fig. 2.

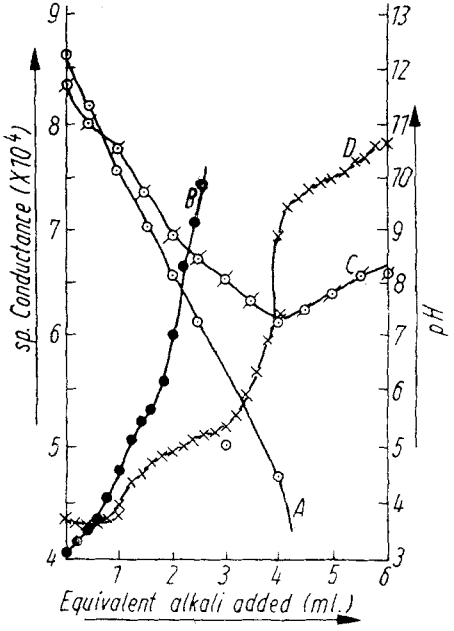


Fig. 2. Conductometric and pH titrations. Curve A: M/100 resorcinol—Sp. conductance, curve B: M/100 resorcinol—pH, curve C: 1:2 mixture of UO_2 Ac. and resorcinol Sp. condentance, curve D: 1:2 mixture of UO_2 Ac. and resorcinol pH

Table 2

Conductometric titration and pH-titration values of M/100 resorcinol and (1:2) mixture of uranyl acetate and resorcinol containing different amounts of equivalent alkali

No.	Equivalent alkali added ml.	pH		Equivalent alkali added ml.	Sp. conductance (X 10^4)	
		M/100 resorcinol	(1:2) mixture		M/100 resorcinol	(1:2) mixture
1	0.0	3.13	3.70	0.0	8.620	8.370
2	0.2	3.38	3.65	0.5	8.152	8.000
3	0.4	3.50	3.62	1.0	7.594	7.761
4	0.6	3.70	3.63	1.5	7.036	7.352
5	0.8	4.14	3.78	2.0	6.572	6.944
6	1.0	4.60	4.00	2.5	6.128	6.716
7	1.2	5.12	4.42	3.0	5.018	6.530
8	1.4	5.42	4.60	3.5	4.850	6.327
9	1.6	5.62	4.78	4.0	—	6.105
10	1.8	6.15	4.84	4.5	—	6.250
11	2.0	7.00	4.91	5.0	—	6.300
12	2.2	8.30	5.00	5.5	—	6.554
13	2.4	9.12	5.18	6.0	—	6.582
14	2.6	9.88	5.20			
15	2.8	—	5.23			
16	3.0	—	5.36			
17	3.2	—	5.58			
18	3.4	—	5.98			
19	3.6	—	6.34			
20	3.8	—	6.90			
21	4.0	—	8.98			
22	4.2	—	9.45			
23	4.4	—	9.62			
24	4.6	—	9.80			
25	4.8	—	9.98			
26	5.0	—	10.00			
27	5.2	—	10.16			
28	5.4	—	10.34			
29	5.6	—	10.40			
30	5.8	—	10.60			
31	6.0	—	10.68			

Isolation of the compound: $UO_2(C_6H_4O_2)_2$

To an alcoholic solution of uranyl acetate was added resorcinol dissolved in alcohol so that the stoichiometric ratio of (1:2) was established between uranyl acetate and resorcinol. The mixture was evaporated on a water bath for a long time. The crystals formed were separated and washed with alcohol. The crystals formed were shining pale in colour.

Estimation of uranium: The U-content in the compound was estimated by the "Oxinate[8])" method, and the percentage calculated from the theoretical values. The theoretical values were in excellent agreement with the calculated values for uranium. The results are given in Table 3.

Table 3

Experiment No.	$UO_2(C_6H_4O_2)_2$					
	% of uranium			% of resorcinol		
	Estimated	Theoretical	Difference	Estimated	Theoretical	Difference
1	47.98		0.98	43.48		1.80
2	47.86		1.10	43.73		1.55
3	48.03	48.96	0.93	43.34	45.28	1.94
4	48.06		0.90	43.50		1.78
5	48.08		0.88	43.52		1.76

Estimation of Resorcinol. The resorcinol constant was estimated by the iodometric method given by WILLARD and WOOTEN[9]). The reaction taking place is as follows:

$$C_6H_4(OH)_2 + 3\,I_2 \rightarrow C_6H_5I_3(OH)_2 + 3\,HI.$$

Dissolved the sample, containing about 0.05 g. of resorcinol in a little water and added 50 ml. of buffer. Added 50 ml. of 0.1 N iodine solution from a pipette. After one minute titrate the excess of iodine with 0.1 N sodiumthiosulphate in the presence of starch indicator.

The buffer is prepared by dissolving 120 ml. of glacial acetic acid in about 1700 ml. of water, and adding to it conc. NaOH solution until the pH is about 4.5. Cooled to room temperature and continued the neutralisation with dil. NaOH until the pH is 5.0, storing it in a rubberstoppered bottle and checking the pH periodically.

Discussion

An examination of curves A, B and C in Fig. 1, which represents the results of conductivity, pH and colorimetry shows that there is one definite break in each case in the regular curves at interval corresponding to 10 c. c. of resorcinol solution. Since resorcinol solution was M/20 in strength, this value corresponded to 20 c. c. of M/40 resorcinol solution. As each solution contains same quantity of uranyl acetate solution (i. e. 10 c. c. of M/40), the ratio of uranyl acetate to resorcinol at this point is (1:2) which corresponds to the formation of a compound in solution. Curve A is for conductivity while B and C are for pH and optical density respectively.

Fig. 2 represents the values of conductometric and pH-titrations of uranyl acetate-resorcinol mixtures against equivalent alkali. Curve A is for M/100 resorcinol (Sp. conductance), curve B for M/100 resorcinol

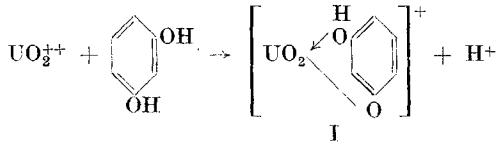
[8]) A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, Ed. 1951, pp. 471.

[9]) H. H. WILLARD and L. A. WOOTAN, Anal. Chem. **22**, 585, 759 (1950).

(pH values), while C and D both are for (1:2) mixture of uranyl acetate and resorcinol, C (sp. conductance), D (pH values). Curves C and D show an inflection both at four equivalents of alkali showing the formation of a (1:2) complex.

The addition af a solution of KOH to a solution of uranyl acetate in resorcinol in the molar ratio of (1:2) (Fig. 2, Curve D) increases the pH of the latter. The curve shows that when four equivalents of alkali have been added, there is an inflection which infers the formation of a (1:2) chelate. The continued addition of alkali results in a sudden rise in pH when four equivalents of alkali have been added. With any further addition of alkali the pH rises very slowly. The rise in pH is due to the removal of H^+ ions, and when all the H^+ ions have been liberated, the pH rises due to a rise in the hydrogen ion concentration. The break in the graph, therefore, may be attributed to the formation of a (1:2) complex in solution. The possible reaction mechanism may be given as follows:

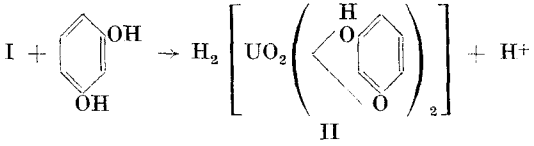
First of all, a molecule of resorcinol reacts with uranyl ion, thus,



(1)

I

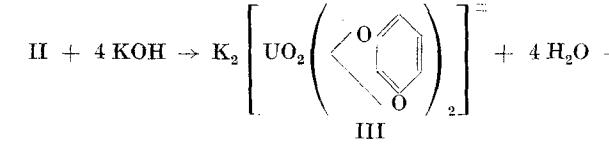
then reacts with another mole of resorcinol,



(2)

II

II on titration with KOH forms the (1:2) compound,



(3)

III

Curve C in Fig. 2 represents the changes taking place in conductivity when equivalent alkali is added in (1:2) mixture of uranyl acetate and resorcinol.

It becomes clear from curve C that when four equivalents of alkali have been added, the conductance shows minimum value showing a break in the curve which is probably due to the formation of a (1:2) complex in solution showing that reaction (3) takes place.

Summary

Conductometric, colorimetric and pH observations of the mixed solutions of uranyl acetate and resorcinol revealed the existence of one complex at (1:2) molecular ratio. The compound has been isolated and its uranium and resorcinol contents estimated.

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