Formation of Complex Compounds between Uranyl Nitrate and Transition Metal Nitrates

The System: $Co(NO_3)_2$—$UO_2(NO_3)_2$—H_2O (Conductivity, pH, refractive Index and Spectrophotometry)

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With 3 Figures

Summary

Experiments with the system: Cobalt nitrate-uranyl nitrate-water, viz. conductivity, pH, refractive index and spectrophotometry revealed the existence of the following compounds in the solution:

(i) $Co(NO_3)_2 \cdot UO_2(NO_3)_2$
(ii) $2\,Co(NO_3)_2 \cdot UO_2(NO_3)_2$
(iii) $3\,Co(NO_3)_2 \cdot UO_2(NO_3)_2$.

A set of 22 mixed solutions was prepared by following NAYAR and PANDE's monovariation method. In all the solutions the concentration of uranyl nitrate was kept constant (i. e. M/100), while that of cobalt nitrate varied systematically from 0.0 M to 0.042 M. The physico-chemical properties namely, conductivity, pH, refractive-index and spectro-photometry were used for the investigation of the complex compounds in the above system. When these values were plotted against the varying concentrations of cobalt nitrate three breaks were obtained in the regular curves at concentrations corresponding to the compounds having the above formulae. The results obtained by all these physico-chemical properties are in excellent agreement leading to the same conclusions.

Introduction

In our previous communications we have shown that uranyl nitrate has a great tendency for the formation of complex compounds with the nitrates of alkali metals, alkaline earths and a number of other nitrates as lead, silver,

thallium, mercury cadmium and copper. R. J. MEYER and F. WENDEL[1]), A. COLANI[2]), A. SACHS[3]), E. RIMBACH[4]), A. LANCEIN, O. D. CONICK[5]), C. S. PANDE and S. S. GUPTA[6]) have made detailed studies on such class of compounds.

The survey of literature also reveals that transitional metals of VIIIth group like iron, nickel and cobalt have not been investigated systeamtically, whether they form definite complexes with the uranyl nitrate or not. Though

Table 1
The System: $Co(NO_3)_2$—$UO_2(NO_3)_2$—H_2O
Composition of the Solutions

Soln. No.	Total volume of the soln. c. c.	C. C. of $UO_2(NO_3)_2$ M/10 added	Concentration of the $UO_2(NO_3)_2$ Soln-M	C. C. of $Co(NO_3)_2$ M/10 added	Concentration of $Co(NO_3)_2$ solution M	Ratio of the constituents
1.	50	5	0.01	0.0	0.000	5/0
2.	50	5	0.01	1.0	0.002	5/1
3.	50	5	0.01	2.0	0.004	5/2
4.	50	5	0.01	3.0	0.006	5/3
5.	50	5	0.01	4.0	0.008	5/4
6.	50	5	0.01	5.0	0,010	5/5 or1:1
7.	50	5	0.01	6.0	0.012	5/6
8.	50	5	0.01	7.0	0.014	5/7
9.	50	5	0.01	8.0	0.016	5/8
10.	50	5	0.01	9.0	0.018	5/9
11.	50	5	0.01	10.0	0.020	5/10 or 1:2
12.	50	5	0.01	11.0	0.022	5/11
13.	50	5	0.01	12.0	0.024	5/12
14.	50	5	0.01	13.0	0.026	5/13
15.	50	5	0.01	14.0	0.028	5/14
16.	50	5	0.01	15.0	0.030	5/15 or 1:3
17.	50	5	0.01	16.0	0.032	5/16
18.	50	5	0.01	17.0	0.034	5/17
19.	50	5	0.01	18.0	0.036	5/18
20.	50	5	0.01	19.0	0.038	5/19
21.	50	5	0.01	20.0	0.040	5/20 or 1:4
22.	50	5	0.01	21.0	0.042	5/21

[1]) R. J. MEYER and F. WENDEL, Ber. dtsch. chem. Ges. **36**, 4055 (1903).
[2]) A. COLANI, Compt. rend. **185**, 1475 (1927).
[3]) A. SACHS, Z. Kristallogr. **38**, 498 (1903).
[4]) E. RIMBACH, Ber. dtsch. chem. Ges. **37**, 461 (1904).
[5]) O. D. CONICK, Bull. Acad. roy. Belg. 744 (1909).
[6]) C. S. PANDE and S. S. GUPTA, J. prakt. Chem. **13**, 128 (1901); **13**, 122 (1961); **13**, 238 (1961).

A. LANCEIN reported unstable complex-salts of uranylnitrate with the nitrate of Nickel and Rhodium but no attempt has so far been made to study and investigate the system cobalt nitrate-uranyl nitrate-water fully so as to throw light on the complexes formed in this system. Therefore it was thought to be desirable to examine the above system thoroughly by applying the monovariation method of NAYAR and PANDE[7]). The physico-chemical properties used for the investigation were conductivity, pH refractive index and spectrophotometry. The sensitivity of spectrophotometric method has enabled us to detect and report almost all the complexes present in the solution. The present communication deals with our observations based on the values of conductivity, pH, refractive index and spectrophotometry. The results are in excellent agreement and lead to the same conclusions.

Table 2

Conductivity

Cell constant: 1.5732 Temp. 35 ± 0.1 °C

Soln. No.	C. C. of $Co(NO_3)_2$ added to 5 c. c. $UO_2(NO_3)_2$ 0.1 M	Resistance in Ohms	Conductance 10^4 in Mhos
1.	0.0	596	16.77
2.	1.0	530	18.87
3.	2.0	480	20.79
4.	3.0	410	24.39
5.	4.0	360	27.77
6.	5.0	365	27.39
7.	6.0	310	32.25
8.	7.0	285	35.10
9.	8.0	260	38.46
10.	9.0	250	40.01
11.	10.0	255	39.22
12.	11.0	220	45.45
13.	12.0	195	51.29
14.	13.0	175	57.15
15.	14.0	230	43.40
16.	15.0	165	60.60
17.	16.0	165	60.60
18.	17.0	155	64.52
19.	18.0	145	68.96
20.	19.0	135	74.08
21.	20.0	120	83.34
22.	31.0	115	86.96

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

Experimental

Cobalt nitrate and uranyl nitrate of A. R./B. D. H. quality were used for the preparation of stock solutions. The purity of these salts was estimated before use by the usual standard methods. The stock solutions of uranyl nitrate and cobalt nitrate (0.1 M), were prepared in conductivity water and stored in thoroughly cleaned and steamed glass stoppered Jena glass bottles. 5 c. c. of uranyl nitrate (0.1 M) were pipetted out into 50 c. c. standard. flask to which the requisite volume of cobalt nitrate solution (0.1 M) were added and the mixture made upto the mark, i. e. 50 c. c. by addition of conductivity water. In this way a set of 22 solutions was made, in which the concentration of uranyl nitrate remained the same (0.01 M), while that of cobalt nitrate varied systematically from (0.0 M) to (0.042 M). The solutions were stored in thoroughly cleaned glass bottles. The composition of these solutions is shown in table 1.

Table 3

The System: $Co(NO_3)_2$—$UO_2(NO_3)_2$—H_2O

Property pH-Measurements and Refractive Index

pH Meter Leeds and Northup cat H. 07663 A-1-Assembly.

Abbes Refractometer

Soln. No.	C. C. of $Co(NO_3)_2$ 0.1 M added to 5 c. c. $UO_2(NO_3)_2$ 0.1 M	pH-measurements	Refractive Index
1.	0.0	3.16	1.330
2.	1.0	3.0	1.335
3.	2.0	2.9	1.336
4.	3.0	2.95	1.334
5.	4.0	3.6	1.335
6.	5.0	3.55	1.336
7.	6.0	3.55	1.336
8.	7.0	3.5	1.337
9.	8.0	3.50	1.335
10.	9.0	3.7	1.338
11.	10.0	3.6	1.337
12.	11.0	3.2	1.339
13.	12.0	3.2	1.337
14.	13.0	3.2	1.3375
15.	14.0	3.0	1.335
16.	15.0	3.35	1.3365
17.	16.0	3.00	1.3375
18.	17.0	3.3	1.338
19.	18.0	3.3	1.3345
20.	19.0	3.3	1.338
21.	20.0	3.3	1.339
22.	21.0	3.2	1.339

Conductivity: Conductivity measurements were made by the conductivity-assembly, Electronic Magic-eye (Phillips Model G. M. 4249). A Pyrex glass conductivity cell with

platinum electrodes was used in conductivity measurements. The cell was platinized and washed by following all the details given in Findlay: Practical Physical Chemistry. The cell was rinsed several times with the solution used. Atleast three readings were taken for each solution. The temperature of the thermostat was maintained at 35 °C. Each solution was placed in the cell and kept in the thermostat for atleast half an hour before observations were recorded. The values of resistance and conductivity are given in table 2.

Table 4

The System: $Co(NO_3)_2$—$UO_2(NO_3)_2$—H_2O

Property: Spectrophotometry Temp. = 35 ± 0.1 °C

Unicam. (Spectrophotometer) 500 cycles Wave Length 450 mμ

Soln. No.	C. C. of $Co(NO_3)_2$ 0.1 M added to 5 c. c. $UO_2(NO_3)_2$ 0.1 M	% Transmittance	% Absorption	Optical Density
1.	0.0	93	7	0.030
2.	1.0	96	4	0.018
3.	2.0	95	5	0.022
4.	3.0	91	9	0.040
5.	4.0	93	7	0.030
6.	5.0	92	8	0.035
7.	6.0	89	11	0.050
8.	7.0	90	10	0.045
9.	8.0	89	11	0.050
10.	9.0	86	14	0.065
11.	10.0	88	12	0.055
12.	11.0	87	13	0.060
13.	12.0	83	17	0.080
14.	13.0	85	15	0.070
15.	14.0	87	13	0.060
16.	15.0	81	19	0.095
17.	16.0	82	18	0.085
18.	17.0	81	19	0.095
19.	18.0	79	21	0.105
20.	19.0	80	20	0.100
21.	20.0	78	22	0.110
22.	21.0	79	21	0.105

pH Measurements: The pH measurements of the solutions were made by using a Phillips G. M. 4494/Model using a glass electrode, at 35 °C. The values are recorded in table 3.

Spectrophotometry: Measurements of percent transmission, per cent absorption and optical density were made by using a Unicam 500 cycles spectrophotometer. The solutions were maintained at 35 °C by placing them in a thermostat at that temperature. Before recording the observations the adjustment was made with a blank of solvent used in the preparation of solutions. The spectrophotometric observations are recorded in table 4.

Refractive Index: The refractive index was recorded by using the ABBE's Refractrometer model No. 344223 working at a constant temperature 35 ± 0.1 °C. The results of which are given in the table 3.

Observations and Conclusion

When these values of resistance, conductivity pH, a % transmittance, % absorption, optical density and refractive index of the solutions were plotted against the volume of

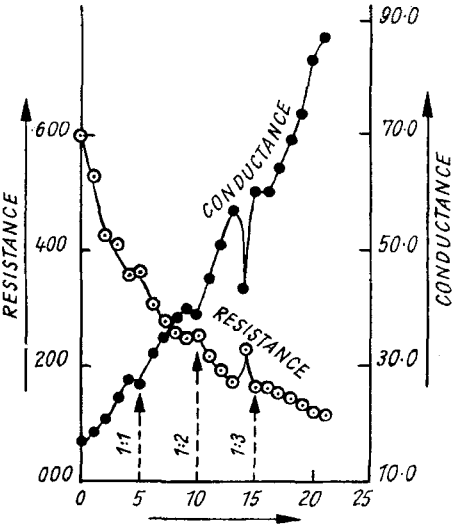

Fig. 1

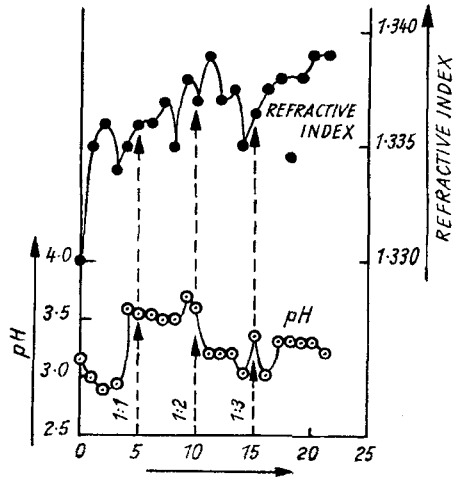

Fig. 2

cobalt nitrate added to a fixed volume of uranyl nitrate we obtained curves shown in the Fig. 1—3 respectively. It will be noticed that in all the cases there are 3 definite breaks in the regular curves at concentration corresponding to 5 c. c., 10 c. c. and 15 c. c. of cobalt nitrate. The ratios of cobalt nitrate to uranyl nitrate at those points are:

$$1:1 \text{ or } Co(NO_3)_2 \cdot UO_2(NO_3)_2$$

$$2:1 \text{ or } 2\,Co(NO_3)_2 \cdot UO_2(NO_3)_2$$

$$3:1 \text{ or } 3\,Co(NO_3)_2 \cdot UO_2(NO_3)_2$$

corresponding to the above mentioned compounds of the given formulae.

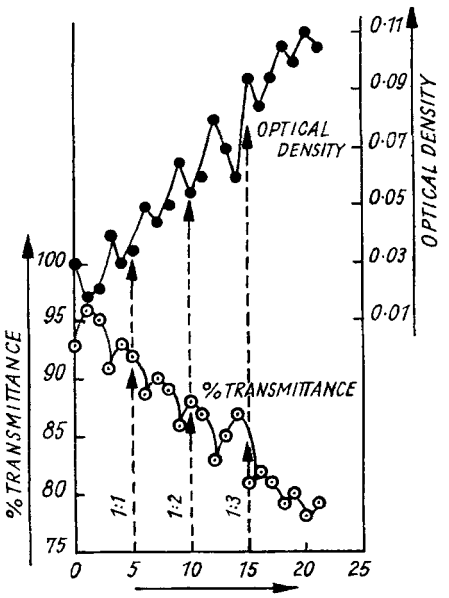

Fig . 3

There is excellent similarity in the curves with respect to all physico-chemical properties investigated and, therefore, there is no question about the genuineness of the phenomenon. The breaks occur at exact stoichiometric ratios of concentrations corresponding to the compounds stated above. Thus the existence of these compounds becomes unequivocal, when such dissimilar properties like condictivity, pH, refractive index and spectrophotometry yield similar results.

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