Formation of Complex Compounds between Uranyl Nitrate and the Nitrates of the first Group Elements

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

By S. S. GUPTA and B. N. SHARGA

With 3 figures

Summary

Experiments with the system: copper nitrate — uranyl nitrate — water, viz., conductivity, refractive Index, colorimetry and pH revealed the existence of the two complex compounds in solution in the (1:1) and (1:2) molar ratios.

A set of 27 mixed solutions was prepared by following NAYAR and PANDE's monovariation method[1]). In all the solutions the concentration of uranyl nitrate was kept constant (i. e., M/100), while that of copper nitrate varied systematically from 0.0 M to 0.052 M. The physico-chemical properties, namely, conductivity, refraccive index colorimetry and pH were used for the investigation of complex coumpounds in the above system. When these values were plotted against the varying concentration of copper nitrate two breaks were obtained in the regular curves at concentrations corresponding to the formation of above mentioned compounds, in the (1:1) and (1:2) molar ratios. The results obtained by all these physico-chemical properties are in excellent agreement leading to the same conclusions.

Introduction

A survey of literature reveals that uranyl nitrate has a great tendency for the formation of complex coumpounds with the nitrates of alkali metals, silver, thallium, mercury and cadmium. R. J. MEYER and F. WENDEL[2]),

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

[2]) R. J. MEYER and F. WENDEL, Ber. dtsch. chem. Ges. **36**, 4055 (1903).

A. COLANI[3]), A. SACHS[4]), E. RIMBACH[5]), A. LANCEIN[6]), and O. D. CONINCK[7]) have made detailed studies on such class of compounds. This work especially has been taken as an extention of the work done by C. S. PANDE and S. S. GUPTA[8]) in this University.

The survey of literature also reveals that the system: Copper nitrate, — uranylnitrate — water has not been investigated before. Therefore it was thought to be of utmost interest to investigate the above mentioned system thoroughly and at the same time to examine the number of complex compounds actually present therein by applying the monovariation method of NAYAR and PANDE[1]). The Physico chemical properties taken into account were conductivity, refractive index, colorimetry and pH. The present communication brings into light our observations based on the values of the above mentioned properties. The results obtained are in good agreement and lead to the same conclusions.

Experimental

The solution of copper nitrate was prepared by dissolving the requisite amount of A. R. COPPER turnings in A.R. HNO_3 and the uranyl nitrate of A.R. B.D.H. quality was used for the preparations of the stock solutions. The purity of each one of them was estimated before use by the usual standard methods. The stock solutions of uranyl nitrate and copper nitrate (0.1 M) were prepared in conductivity water and stored in thoroughly cleaned and steamed glass stoppered Jena glass bottles. 5 cc of uranyl nitrate (0.1 M) were pipetted out into 50 cc standard flask to which the requisite volume of copper nitrate solution (0.1 M) was added and the mixture made upto the mark, i. e. 50 cc by addition of conductivity water. In this way a series of 27 solutions were made in which the concentration of uranyl nitrate remained the same (0,01 M), while that of copper nitrate varied systematically from (0.0 M) to (0.052 M). The solutions were stored in thoroughly cleaned glass bottles. The composition of these solutions is shown in Table I.

Conductivity

Conductivity measurements, were made by taking the help of conductivity assembly. Electronic magic eye (Phillips Model G. M. 4249). A pyrex glass conductivity cell with platinium 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. At least 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 at least half an hour before observations ware recorded. The values of resistances and conductances are given in Table II.

[3]) A. COLANI, Compt. Rend. **185**, 1475—1476 (1927).
[4]) A. SACHS, Z. Kristallogr. **38**, 498 (1903).
[5]) E. RIMBACH, Ber. dtsch. chem. Ges. **37**, 461 (1904).
[6]) A. LANCEIN, Chem. Zbl. **1**, 208 (1912).
[7]) O. D. CONINCK, Bull. Acad. roy. Belg. 744 (1909).
[8]) C. S. PANDE and S. S. GUPTA, J. prakt. Chem. (4) **13**, 121, 127 (1961).

Table I
The System: $Cu(NO_3)_2$—$UO_2(NO_3)_2$—H_2O
Composition of the solutions

Solution No.	Total Volume of the Solutions cc	cc of $UO_2(NO_3)_2$ M/10 added.	Concentration of the $UO_2(NO_3)_2$ solution	CC of $Cu(NO_3)_2$ M/10 added.	Concentration of Cu $(NO_3)_2$ Solution added.	Ratio of the Constituents.
1.	50	5	0.01	0.0	0.000	5/0
2.	50	5	0.01	1.	0.002	5/1
3.	50	5	0.01	2.	0.004	5/2
4.	50	5	0.01	3.	0.006	5/3
5.	50	5	0.01	4.	0.008	5/4
6.	50	5	0.01	5.	0.010	5/5 or 1:1
7	50	5	0.01	6.	0.012	5/6
8.	50	5	0.01	7.	0.014	5/7
9.	50	5	0.01	8.	0.016	5/8
10.	50	5	0.01	9.	0.018	5/9
11.	50	5	0.01	10.	0.020	5/10 or 1:2
12.	50	5	0.01	11.	0.022	5/11
12.	50	5	0.01	12.	0.024	5/12
13.	50	5	0.01	13.	0.026	5/13
14.	50	5	0.01	14.	0.028	5/14
15.	50	5	0.01	15.	0.030	5/15 or 1:3
16.	50	5	0.01	16.	0.032	5/16
17.	50	5	0.01	17.	0.034	5/17
18.	50	5	0.01	18.	0.036	5/18
19.	50	5	0.01	19.	0.038	5/19
20.	50	5	0.01	20.	0.040	5/20 or 1:4
21.	50	5	0.01	21.	0.042	5/21
22.	50	5	0.01	22.	0.044	5/22
23.	50	5	0.01	23.	0.046	5/23
24.	50	5	0.01	24.	0.048	5/24
25.	50	5	0.01	25.	0.050	5/25 or 1:5
26.	50	5	0.01	26.	0.052	5/26
27.	50	5	0.01	27.	0.054	5/27

Refractive Index

Measurements of refractive indices were carried out with the help of a direct reading refractometer (Bellingham and Stanley Ltd. Model No. 344223). The observations were taken at 35 °C and the values are recorded according to the table III.

Colorimetry

Measurements of percentage transmittence and optical density were made with the help of photo electric colorimeter (Model 900.3 Klett-Summer Son Pat. No. 2193437 — 1940). The solutions wree maintained at 35 °C by placing them in a thermostat at that tem-

Table II
(Conductivity)
Cell constant 0.7426 Temp. 35 °C ± 0.05 °C

Solution No.	c.c. of $Cu(NO_3)_2$ added to the 5 cc of $UO_2(NO_3)_2$ 0.1 M	Resistance ohms	Conductance x 10^4 Mhos.
1.	0.0 cc	320	33.33
2.	1.0 cc	280	35.71
3.	2.0 cc	250	40.00
4.	3.0 cc	230	43.47
5.	4.0 cc	200	50.00
6.	5.0 cc	210	47.61
7.	6.0 cc	190	52.63
8.	7.0 cc	170	58.82
9.	8.0 cc	155	64.51
10.	9.0 cc	140	71.42
11.	10.0 cc	150	66.66
12.	11.0 cc	130	72.92
13.	12.0 cc	130	76.92
14.	13.0 cc	125	80.00
15.	14.0 cc	120	83.33
16.	15.0 cc	115	86.81
17.	16.0 cc	110	90.90
18.	17.0 cc	105	95.23
19.	18.0 cc	100	100.00
20.	19.0 cc	95	105.26
21.	20.0 cc	90	111.11
22.	21.0 cc	85	117.64
23.	22.0 cc	80	125.00
24.	23.0 cc	75	133.33
25.	24.0 cc	70	142.80
26.	25.0 cc	65	153.80
27.	26.0 cc	60	166.60

Table III
The system: $Cu(NO_3)_2$—$UO_2(NO_3)_2$—H_2O. Property: Refractive Index

Solution No.	C. C. of $CU(NO_3)_2$ added to 5 cc of $UO_2(NO_3)_2$	Refractive Index
1.	0.0 cc	1.407
2.	1.0 cc	1.406
3.	2.0 cc	1.405
4.	3.0 cc	1.405
5.	4.0 cc	1.404
6.	5.0 cc	1.407
7.	6.0 cc	1.406
8.	7.0 cc	1.405
9.	8.0 cc	1.405
10.	9.0 cc	1.406
11.	10.0 cc	1.408
12.	11.0 cc	1.406
13.	12.0 cc	1.406
14.	13.0 cc	1.405
15.	14.0 cc	1.405
16.	15.0 cc	1.405
17.	16.0 cc	1.406
18.	17.0 cc	1.406
19.	18.0 cc	1.407
20.	19.0 cc	1.407
21.	20.0 cc	1.407
22.	21.0 cc	1.407
23.	22.0 cc	1.408
24.	23.0 cc	1.408
25.	24.0 cc	1.407
26.	25.0 cc	1.407
27.	26.0 cc	1.407

perature. Before recording the observations the adjustment was made with a blank solvent which is used in the preparation of solutions. The filter No. 42 was used while taking observations. Readings are recorded according to Table no. IV.

pH Measurements

The pH measurements of the solutions were made by using a pH meter of W. G. Pye & Co. Ltd. London model Cat. No. 11083. Having a glass electrode, at 35 °C. The values are recorded in Table V.

Table IV
The system: $UO_2(NO_3)_2$—$CU(NO_3)_2$—H_2O
Property: colorimetry.
Temp: 35 °C ± 0.05 °C

Solution No.	C. C. of $Cu(NO_3)_2$ (0.1 M) added to 5 cc $UO_2(NO_3)_2$ 0.1 M	Transmittance	Optical-Density
1.	0.0 cc	79	0.102
2.	1.0 cc	78	0.108
3.	2.0 cc	78	0.108
4.	3.0 cc	79	0.102
5.	4.0 cc	80	0.110
6.	5.0 cc	76	0.119
7.	6.0 cc	80	0.110
8.	7.0 cc	79	0.102
9.	8.0 cc	78	0.108
10.	9.0 cc	78	0.108
11.	10.0 cc	76	0.119
12.	11.0 cc	78	0.108
13.	12.0 cc	79	0.102
14.	13.0 cc	79	0.102
15.	14.0 cc	78	0.108
16.	15.0 cc	78	0.108
17.	16.0 cc	78	0.108
18.	17.0 cc	79	0.102
19.	18.0 cc	79	0.102
20.	19.0 cc	78	0.108
21.	20.0 cc	78	0.108
22.	21.0 cc	78	0.108
23.	22.0 cc	77	0.114
24.	23.0 cc	77	0.144
25.	24.0 cc	77	0.144
26.	25.0 cc	78	0.108
27.	26.0 cc	79	0.102

Table V
The system: $UO_2(NO_3)_2$—$Cu(NO_3)_2$—H_2O. Property: pH-Measurements. Model: W. G. Pye & Co. Ltd., Cat No. 11083

Solution No.	C. C. of $Cu(NO_3)_2$ 0.1 M added to 5 cc $UO_2(NO_3)_2$ 0.1 M	pH-Measurements
1.	0.0 cc	2.75
2.	1.0 cc	2.70
3.	2.0 cc	2.60
4.	3.0 cc	2.50
5.	4.0 cc	2.45
6.	4.0 cc	2.40
7.	6.0 cc	2.45
8.	7.0 cc	2.40
9.	8.0 cc	2.35
10.	9.0 cc	2.30
11.	10.0 cc	2.20
12.	11.0 cc	2.30
13.	12.0 cc	2.35
14.	13.0 cc	2.20
15.	14.0 cc	2.15
16.	15.0 cc	2.20
17	16.0 cc	2.15
18.	17.0 cc	2.10
19.	18.0 cc	2.10
20.	19.0 cc	2.10
21.	20.0 cc	2.10
22.	21.0 cc	2.05
23.	22.0 cc	2.10
24.	23.0 cc	2.10
25.	24.0 cc	2.05
26.	25.0 cc	2.00
27.	26.0 cc	2.00

Observations and Conclusions

When these values of resistance, conductivity refractive index, percentage transmittance, optical density and pH of the solutions were plotted against the volume of copper nitrate added to a fixed volume of uranyl nitrate, we obtained the curves shown in fig. (1), (2) and (3) respectively. It will be noticed that in all the cases there is definite breaks in the regular curves at consentrations corresponding to 5 cc and 10 cc of copper nitrate. The

ration of copper nitrate to uranyl nitrate at these points is (1:1) and (2:1) respectively which corresponds to the following compounds of the formulae.

$Cu(NO_3)_2 \cdot UO_2(NO_3)_2$ and $UO_2(NO_3)_2 \cdot 2\,Cu(NO_3)_2$.

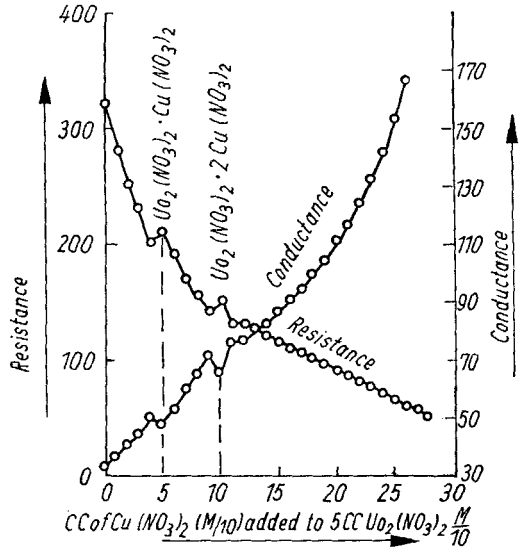

Fig. 1

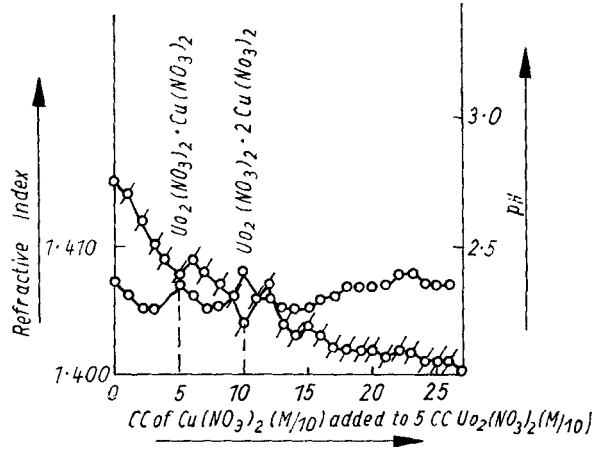

Fig. 2

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 stoich-iome-

tric ratioes of consentrations corresponding to the compcunds stated above. Thus the existance of these coumpounds became unequivocal when such dis-similar properties, like conductivity refractive index, colorimetry and pH measurements yield similar results.

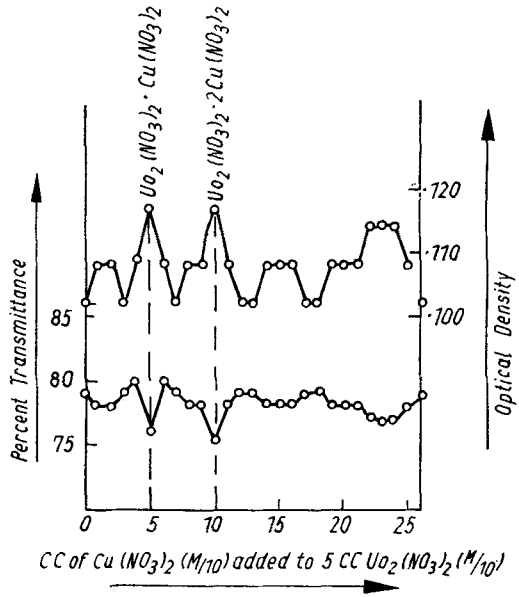

Fig. 3

The authors are thankful to Dr. S. N. SHUKLA, Head of the Chemistry Department for providing Laboratory facilities and encouragement.

Lucknow (India) Inorganic Chemical Laboratories, Lucknow University.

Bei der Redaktion eingegangen am 25. Februar 1963.