Studies on the Formation of Complex Compounds between Uranyl Nitrate and Transitional Metal Nitrate

The System: $Zr(NO_3)_4-UO_2(NO_3)_2-H_2O$

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With 3 Figures

Summary

Determination of conductance, pH, spectrophotometry, and Refractive Index of a series of mixed solutions of uranylnitrate and zirconium-nitrate indicate the existence of one definite complex compound in the solution namely:

$$Zr(NO_3)_4-UO_2(NO_3)_2$$

Monovariation method of NAYAR and PANDE[1]) has been followed in the preparation of these solutions. A set of 22 solutions was prepared. In all the solutions the concentration of uranyl-nitrate was kept constant. While that of zirconium-nitrate was varied systematically and the physico-chemical properties measured. When these values are plotted against the concentration of zirconium-nitrate, curves are obtained with the specific break. The kink occurs at the exact stoichiometric ratio of the concentrations corresponding to the compound noted above.

Introduction

The survey of literature has clearly shown that practically no work has been done on the complexes of uranyl nitrate and Rare Earth nitrates and Transitional metal nitrates. In our previous communications we have shown that uranyl nitrate forms complexes with transitional metals as copper, cobalt, nickel, iron and chromium. Being encouraged by the results obtained in the case of cerium a member of the Rare Earth family and thorium an analogue of cerium the work was extended to the system Zirconium nitrate and Uranyl nitrate. Since this system has not been thoroughly dealt with, so it was thought necessary to examine and investigate the system Zirconium nitrate-uranyl nitrate. The pioneer workers in the field of nitrate complexes are SAMUEL GLASSTONE, HAROLD NICHOLAS, SAUNDERS[1]), J. RIGGS[2]), G. MAL-

[1]) SAMUEL GLASSTONE, HAROLD NICHOLAS, SAUNDERS, J. chem. Soc. London **123**, 2, 2134 (1923).

[2]) E. J. RIGGS, J. chem. Soc. London **127**, 2, 2846 (1925).

QUOSI[3]), K. LAYBOURN and W. M. MADGIN[4]), WILLIAM F. EHRET[5]), H. N. GLASS, K. LAYBOURN and W. M. MADGIN[6]), ARTHUR E. HILL and N. KAPLAN[7]). M. A. PUSCHIN and M. RADOICIC[8]), NAYAR and PANDE[9]), PANDE and GUPTA[10]), GUPTA and SHARGA[11]), GUPTA and MARWAH[12]).

Table I
The System: $Zr(NO_3)_4$—$UO_2(NO_3)_2$—H_2O
Composition of the Solutions

Solution No.	Total volume of the solution c. c.	C. C. of $UO_2(NO_3)_2$ M/20 added	Concentration of the $UO_2(NO_3)_2$ sol. M	C. C. of $Zr(NO_3)_4$ M/20 added	Concentration of $Zr(NO_3)_4$ Molar	Ratio of the constituents
1	50	5	0.005	0.0	0.000	5/0
2	50	5	0.005	1.0	0.001	5/1
3	50	5	0.005	2.0	0.002	5/2
4	50	5	0.005	3.0	0.003	5/3
5	50	5	0.005	4.0	0.004	5/4
6	50	5	0.005	5.0	0.005	5/5 = 1 : 1
7	50	5	0.005	6.0	0.006	5/6
8	50	5	0.005	7.0	0.007	5/7
9	50	5	0.005	8.0	0.008	5/8
10	50	5	0.005	9.0	0.009	5/9
11	50	5	0.005	10.0	0.010	5/10 = 1 : 2
12	50	5	0.005	11.0	0.011	5/11
13	50	5	0.005	12.0	0.012	5/12
14	50	5	0.005	13.0	0.013	5/13
15	50	5	0.005	14.0	0.014	5/14
16	50	5	0.005	15.0	0.015	5/15 = 1 : 3
17	50	5	0.005	16.0	0.016	5/16
18	50	5	0.005	17.0	0.017	5/17
19	50	5	0.005	18.0	0.018	5/18
20	50	5	0.005	19.0	0.019	5/19
21	50	5	0.005	20.0	0.020	5/20 = 1 : 4
22	50	5	0.005	21.0	0.021	5/21

[3]) G. MALQUOSI, Gazzetta **58**, 203 (1928); **59**, 355 (1929); Atti R. Acad. Lincei (1929) VI; **9**, 231 (1932).

[4]) K. LAYBOURN and W. M. MADGIN, J. chem. Soc. London **6**, 874; 1360, 2582 (1932).

[5]) W. F. EHRET, J. Amer. chem. Soc. **54**, 3126 (1932).

[6]) H. N. GLASS, K. LAYBOURN and W. M. MADGIN, J. chem. Soc. London., **1953**, 199.

[7]) A. E. HILL and N. KAPLAN, J. Amer. chem. Soc. **58**, 1644 (1936).

[8]) M. A. PUSCHIN and M. RADOICIC, Z. anorg. allg. Chem. **233**, 41 (1937).

[9]) NAYAR and PANDE, Proc. Ind. Acad. Sci. XXVII. 284, 293, 343 (1948) current Science **17**, 187 (1948).

[10–12]) see p. 51.

Experimental

Reagents used were of standard quality and recrystallized stock solutions were made in conductivity water. A set of mixed solutions of uranyl-nitrate, and zirconium-nitrate was made by monovariation method i.e., the concentration of uranyl-nitrate was kept constant (0.005M) while that of zirconium-nitrate varied systematically from 0.0M to 0.021M. The composition of the solution is shown in column (2) of the table I.

Conductance

Measurements of conductance were made by conductivity assembly Electronic Magiceye (Phillips Model G. M. 4249). A pyrex glass conductivity cell with platinium electrodes was used. The cell was Platinized and washed as described (Findlay Practical Physical Chemistry). The cell was rinsed several times with the solutions used. All conductometric measurements were made at constant temperature i. e. at 35 °C by using a thermostat. The solutions were placed in the cell and kept in the thermostat at least for half an hour. The values of the conductance are recorded in table II.

Table II

Conductivity

The System: $Zr(NO_3)_4-UO_2(NO_3)_2-H_2O$

Cell constant = 1.5732 Temp. 35 °C ± 0.1 °C

Soln. No.	C. C. of $Zr(NO_3)_4$ added to 5. c. c. of $UO_2(NO_3)_2$ M/20	Resistance in Ohms	Conductance $\times 10^4$ in Mhos
1	0.0 c. c.	1100	09.09
2	1.0 c. c.	460	21.74
3	2.0 c. c.	230	43.48
4	3.0 c. c.	230	43.48
5	4.0 c. c.	190	52.62
6	5.0 c. c.	155	64.52
7	6.0 c. c.	140	71.44
8	7.0 c. c.	115	86.96
9	8.0 c. c.	105	95.23
10	9.0 c. c.	95	105.30
11	10.0 c. c.	90	111.10
12	11.0 c. c.	80	125.00
13	12.0 c. c.	75	133.30
14	13.0 c. c.	70	142.90
15	14.0 c. c.	65	153.80
16	15.0 c. c.	65	153.80
17	16.0 c. c.	60	166.60
18	17.0 c. c.	55	181.80
19	18.0 c. c.	55	181.80
20	19.0 c. c.	53	188.70
21	20.0 c. c.	47	212.70
22	21.0 c. c.	45	222.20

Spectrophotometry

Measurements of transmission, absorption and optical density were made by a Unicamspectrophotometer. The solutions were maintained at 35 °C by placing in a thermostat. Special precautions were taken in cleaning the cells. Before making the observations, the adjustment was made with a blank of solvent used in preparing the solutions. The values of the spectrophotometric observations are recorded in table III.

pH Measurements

pH measurements of the solutions were made using a pH meter

[10]) Pande and Gupta, (a) J. prakt. Chem, [4] **13**, 121 (1961); (b) J. prakt. Chem. [4] **13**, 237 (1961); (c) J. prakt. Chem. [4] **23**, 177 (1964).

[11]) Gupta and Sharga, J. prakt. Chem. [4] **22**, 101 (1963).

[12]) Gupta and Marwah, J. prakt. Chem. **26**, 225, 272 (1964).

of W. G. Pye and Co. Ltd., London Model Cat. No. 11083. Using a glass electrode at 35 °C. The value of the pH are recorded in the table IV.

Refractive Index

The refractive index measurements were made by a ABBE's Refractometer Model No. 344223. The observations are recorded in the table IV.

Table III

The System: $Zr(NO_3)_4-UO_2(NO_3)_2-H_2O$

Property: -Spectrophotometry Temp. = 35 ± 0.1 °C
Unicam-Spectrophotometer Wavelength 450 mμ

Soln. No.	C. C. of $Zr(NO_3)_4$ M/20 added to 5 c. c. of $UO_2(NO_3)_2$ M/20	% Transmittance	% Absorption	Optical Density
1	0.0	98.50	5.00	0.0070
2	1.0	96.20	3.80	0.017
3	2.0	96.75	3.25	0.015
4	3.0	96.20	3.80	0.017
5	4.0	96.75	3.25	0.015
6	5.0	95.00	5.00	0.024
7	6.0	96.15	3.85	0.016
8	7.0	96.00	4.00	0.018
9	8.0	96.40	3.60	0.016
10	9.0	96.00	4.00	0.018
11	10.0	96.20	3.80	0.017
12	11.0	96.20	3.80	0.017
13	12.0	96.20	3.80	0.017
14	13.0	96.20	3.80	0.017
15	14.0	96.20	3.80	0.017
16	15.0	95.90	4.10	0.019
17	16.0	95.80	4.20	0.020
18	17.0	96.20	3.80	0.017
19	18.0	95.80	4.20	0.020
20	19.0	95.60	4.40	0.021
21	20.0	95.60	4.40	0.021
22	21.0	94.90	5.10	0.024

Observations and conclusion

When these values of resistance, conductivity, pH, % transmittance, % obsorption, optical density and refractive index of the solutions were

plotted against the volume of zirconium nitrate added to a fixed volume of uranyl-nitrate, the curves shown in figures 1, 2, and 3 were obtained. In case of all the curves, one definite break was obtained at concentration corresponding to 5 c. c. of Zirconium-nitrate. The molecular ratio of uranyl-nitrate at this point is 1:1. This corresponds to the compound of the formula:

$$Zr(NO_3)_4 \cdot UO_2(NO_3)_2.$$

For the present we have assumed that the kink occurs at the stoichiometric proportions corresponding to one compound existing in solution. An attempt is being made to crystallize out these complexes, if possible in the solid state and to study their properties in detail. Thus the existence of this compound becomes more definite when such dissimilar properties like conductivity, pH refractive Index and spectrophotometry yields similar results.

Table IV

The System: $Zr(NO_3)_4-UO_2(NO_3)_2-H_2O$
Temp. 35 ± 0.1 °C

Property: pH Measurements
Refractive Index

Soln. No.	C. C. of $Zr(NO_3)_4$ M/20 added to 5 c. c. of $UO_2(NO_3)_2$ M/20	pH Measurements	Refractive Index
1	0.0	3.20	1.337
2	1.0	2.20	1.337
3	2.0	1.75	1.3375
4	3.0	1.70	1.3380
5	4.0	1.60	1.3390
6	5.0	1.20	1.330
7	6.0	1.40	1.3385
8	7.0	1.40	1.3390
9	8.0	1.30	1.3385
10	9.0	1.20	1.3380
11	10.0	1.15	1.3380
12	11.0	1.20	1.3375
13	12.0	1.10	1.3385
14	13.0	1.10	1.3390
15	14.0	1.10	1.3395
16	15.0	1.10	1.3365
17	16.0	1.05	1.3390
18	17.0	1.00	1.3385
19	18.0	1.00	1.3380
20	19.0	0.95	1.3390
21	20.0	0.90	1.3385
22	21.0	0.90	1.3380

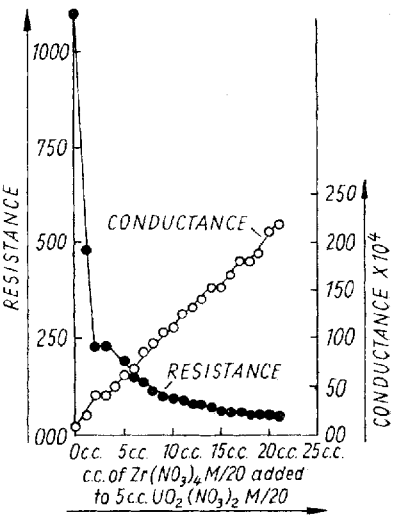

Fig. 1

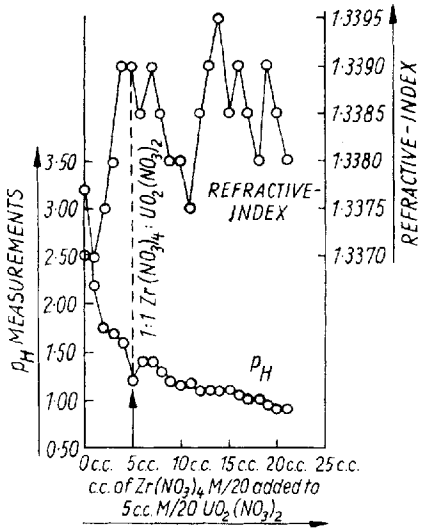

Fig. 2.

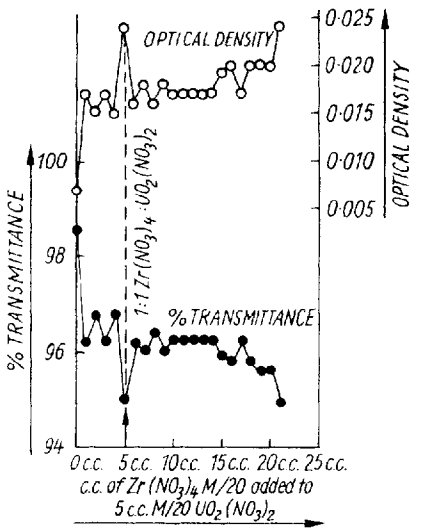

Fig. 3.

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