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

The System: $Fe(NO_3)_3$—$UO_2(NO_3)_2$—H_2O (Conductance, pH, Spectrophotometry and Refractive-index)

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With 3 Figures

Abstract

Determination of conductance, pH spectrophotometry and Refractive-index of a series of mixed solutions of uranyl nitrate and ferric nitrate indicate the existence of two definite complex-compounds in solution namely:

$$Fe(NO_3)_3 \cdot UO_2(NO_3)_2 \quad (1)$$

$$2\,Fe(NO_3)_3 \cdot UO_2(NO_3)_2. \quad (2)$$

Monovariation method of Nayar and Pande[1]), has been followed in the preparation of the solution of uranyl nitrate and ferric nitrate. The concentration of uranyl nitrate was kept constant while that of ferric nitrate varied systematically, and the physico-chemical properties measured. When the values are plotted against the concentration of ferric nitrate, curves are obtained with two specific breaks. The kinks occur at exact stoichiometric ratios of concentrations corresponding to the compounds noted above.

Introduction

In our previous communications we have shown that uranyl ion UO_2^{++} has a strong tendency to form complex compounds with a number of metals of the transitional series as silver thallium-mercury, cadmium, rhodium, cobalt and nickel. This has been established experimentally by a number of pioneer workers in the field of complex-compounds chemistry. These are:

R. J. Meyer and F. Wendel[2]), A. Colani[3]), A. Sachs[4]), E. Rimbach[5]), A. Lancein[6]), O. D. Coninck[7]), Pande and Gupta[8]) Gupta and Sharga[9])

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

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

[3]) A. Colani, Compt. rend. **185**, 1475—1476 (1927).

[4]) A. Sache, Z. Kristallogr. **38**, 498 (1903).

[5–9]) s. S. 273.

and GUPTA and MARWAH[10]), who have made detailed studies on such class of compounds.

The survey of the literature also reveals, that the system ferric nitrate-uranyl nitrate-water, has not been investigated before. Therefore it was thought desirable to examine the above system thoroughly to investigate the existence and the number of complex-compounds by applying the mono-variation method of NAYAR and PANDE. The physico-chemical properties used for investigation were conductance, pH, spectrophotometry and Refractive Index. The present communication deals with our observations based on the values of conductivity, pH, Spectrophotometry. The results are in excellent agreement and lead to the same conclusions.

Experimental

Ferric 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 ferric nitrate (0.1 M) were prepared in conductivity water and stored in throughly 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 ferric nitrate (0.1 M) was added and mixture made upto the mark i.e. 50 c.c. by addition of conductivity water. In this way a series of 22 solutions was made in which the concentration of uranyl nitrate remained the same (0.01 M) while that of ferric 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.

Conductance

Conductance 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 Findley: Practical Physial 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 osbervations were recorded. The values of resistance and conductance are given in Table 2.

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[5]) E. RIMBACH, Ber. dtsch. chem. Ges. **37**, 461 (1904).

[6]) A. LANCIEN, Chem. Zbl. **1**, 208 (1912).

[7]) O. D. CONNICK, Bull. Acad. roy. Belg. 744 (1909).

[8]) C. S. PANDE and S. S. GUPTA, J. prakt. Chem. **13**, (3—4) 121—126 (1961); J. prakt. Chem. **13**, 127—134 (1961); J. prakt. Chem. **13**, (5—6), 237—244 (1961).

[9]) S. S. GUPTA and B. N. SHARGA, J. prakt. Chem. Communication 1962; J. Anorg. Chemie Communication 1962.

[10]) S. S. GUPTA and S. D. MARWAH (Miss), J. prakt. Chem. Communication 1963.

Table 1
The System: $Fe(NO_3)_3$—$UO_2(NO_3)_2$—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 $Fe(NO_3)_3$ M/10. added	Concentration of $Fe(NO_3)_3$ Soln. M	Ratio of 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 or 1:1
7	50	5	0.01	6.0	0.012	5/6
8	60	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	59	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

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.

Refractive Index

Refractive index of the solutions was measured by using ABBE's Refractometer Model No. 344223. The values are recorded in Table 3.

Spectrophotometry

Measurements of per cent transmission, per cent absorption and optical density were made by using a Unicam 500 cycle Model No. 11808 Spectrophotometer. The solutions were maintained at 35 °C by placing them in a thermostate 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.

Table 2

The System: $Fe(NO_3)_3$—$UO_2(NO_3)_2$—H_2O

Property: Conductance — Temp. 35° ± 0.05 °C

Cell Constant 1.5732 — Magic Eye Assembly

Soln. No.	C.C. of $Fe(NO_3)_3$ M/10 added to 5 c.c. of M/10 $UO_2(NO_3)_2$	Resistance in Ohms	Conductance · 10^4 Mhos
1	0	635	15.75
2	1	410	24.39
3	2	320	31.25
4	3	265	37.74
5	4	230	43.48
6	5	230	43.48
7	6	200	50.00
8	7	195	51.24
9	8	155	60.60
10	9	140	71.44
11	10	140	71.44
12	11	130	76.93
13	12	125	80.00
14	13	120	85.07
15	14	115	86.96
16	15	110	90.90
17	16	105	95.23
18	17	95	105.30
19	18	95	105.30
20	19	90	111.10
21	20	75	133.30
22	21	75	133.30

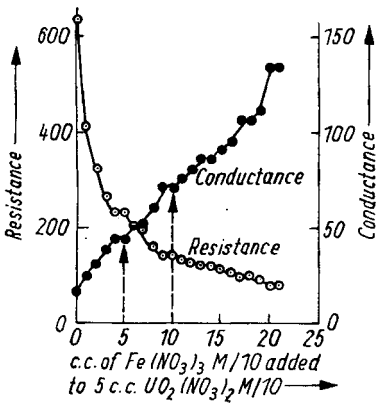

Fig. 1. The System $UO_2(NO_3)_2$—$Fe(NO_3)_3$—H_2O

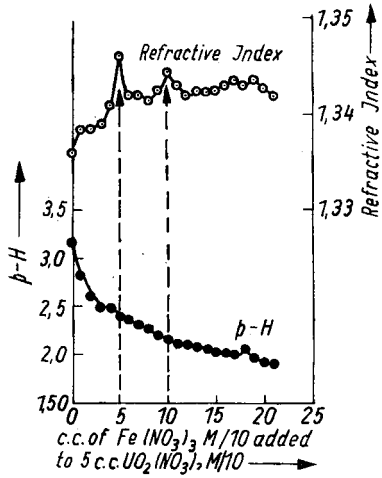

Fig. 2. The System $UO_2(NO_3)_2$—$Fe(NO_3)_2$—H_2O

Table 3

The System: $Fe(NO_3)_3$—$UO_2(NO_3)_2$—H_2O

Property: Spectrophotometry Unicam Model No. 11808 Temp. 35 ± 0.1 °C

Soln. No.	C. C. of $Fe(NO_3)_3$ M/10 added to 5. c. c. $UO_2(NO_3)_2$ M/10	% Transmission		% Absorption		Optical density	
		Wave length 400 mμ	Wave length 450 mμ	Wave length 400 mμ	Wave length 450 mμ	Wave length 400 mμ	Wave length 450 mμ
1	0 c. c.	87.85	92.60	12.15	7.4	0.057	0.033
2	1 c. c.	72.50	90.00	27.50	10.0	0.15	0.045
3	2 c. c.	59.00	86.00	41.00	14.0	0.230	0.065
4	3 c. c.	47.50	81.00	52.50	19.0	0.323	0.092
5	4 c. c.	40.0	79.00	60.00	21.0	0.400	0.15
6	5 c. c.	32.0	75.00	68.00	25.0	0.495	0.125
7	6 c. c.	26.0	70.50	74.00	29.5	0,592	0.152
8	7 c. c.	21.0	67.00	79.00	33.0	0.680	0.175
9	8 c. c.	19.0	65.50	81.00	34.5	0.727	0.185
10	9 c. c.	15.0	62.00	85.00	38.0	0.820	0.21
11	10 c. c.	13.0	60.00	87.00	40.00	0.882	0.223
12	11 c. c.	11.0	57.00	89.00	43.00	0.950	0.244
13	12 c. c.	9.6	55.5	90.40	44.5	1.02	0.257
14	13 c. c.	7.8	53.0	92.80	47.0	1.10	0.278
15	14 c. c.	6.6	50.7	93.40	49.3	1.25	0.285
16	15 c. c.	6.5	43.5	93.50	56.5	1.20	0.3315
17	16 c. c.	5.3	42.0	94.70	58.0	1.25	0.330
18	17 c. c.	4.2	44.80	95.80	55.2	1.37	0.350
19	18 c. c.	6.0	48.0	96.00	52.0	1.22	0.320
20	19 c. c.	3.5	41.0	96.50	59.00	1.45	0.390
21	20 c. c.	3.0	40.0	97.00	60.00	1.60	0.400
22	21 c. c.	3.2	38.5	96.80	61.50	1.50	0.415

Observations and Discussions

On plotting the values of resistance, conductance, pH, Spectrophotometry and refractive index, the curves shown in fig. 1, 2 and 3 were obtained. In case of all the three regular curves two definite breaks were obtained at the concentrations corresponding to 5 c.c. and 10 c.c. of ferric nitrate. The molecular ratios of uranyl nitrate to ferric nitrate at these points is 1:1 and 1:2 respectively. This corresponds to the compounds of the formulae

$$Fe(NO_3)_3 \cdot UO_2(NO_3)_2 \quad (1)$$

$$Fe(NO_3)_3 \cdot UO_2(NO_3)_2. \quad (2)$$

W. C. VASBURGH and G. R. COOPER[11]), while using spectrophotometric method showed that if two equimolar, solutions of substances that form a

[11]) W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. **63**, 437 (1941).

Table 4

The System: $Fe(NO_3)_3$—$UO_2(NO_3)_2$—H_2O

Property: — pH Pye pH meter Model No. 11083

Property: Refractive Index ABBE's Refractometer No. 344223

Soln. No.	C.C. of $Fe(NO_3)_3$ M/10 added to 5 c.c. $UO_2(NO_3)_2$ M/10	pH Measurements	Refractive Index
1	0.0	3.16	1.336
2	1.0	2.80	1.3385
3	2.0	2.60	1.3385
4	3.0	2.50	1.3390
5	4.0	2.48	1.3410
6	5.0	2.40	1.3460
7	6.0	2.35	1.3420
8	7.0	2.30	1.3420
9	8.0	2.25	1.3415
10	9.0	2.20	1.3425
11	10.0	2.15	1.3445
12	11.0	2.10	1.3430
13	12.0	2.10	1.3420
14	13.0	2.09	1.3425
15	14.0	2.05	1.3425
16	15.0	2.00	1.3425
17	16.0	2.00	1.3430
18	17.0	1.99	1.3435
19	18.0	2.05	1.3430
20	19.0	1.95	1.3435
21	20.0	1.90	1.3425
22	21.0	1.90	1.3420

soluble coloured complex are mixed in varying ratios, that ratio which corresponds to the molecular ratio of the components in the complex, will have a maximum (sometimes a minimum) absorbancy at a suitable wavelength. If either component is coloured, the absorbancy must be corrected for the contribution to the colour from this component. By plotting the difference between the measured absorbancy and the absorbancy calculated for no interaction against mole percent (or its equivalent) of either component, a complex formula is readily obtained. The method has

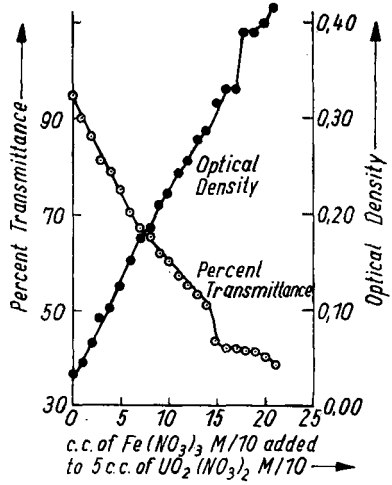

Fig. 3. The System $UO_2(NO_3)_2$—$Fe(NO_3)_3$—H_2O

successfully been applied in the present work in the investigation in complex-compounds in the system uranyl nitrate-ferric nitrate-water. Measurements of percent transmittance, absorption and optical density weer made by Unicam Spectrophotometer 500 cycles.

Conclusion: 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 ratio of concentrations corresponding to the compound stated above. Thus the existence of these compounds became unequivocal, when such dissimilar properties like conductance, pH, Spectrophotometry and refractive index measurements yield similar results.

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