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

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

By S. S. GUPTA and S. D. MARWAH (Miss)

With 3 Figures

Abstract

Experimental evidence from the values of conductance, pH, spectrophotometry and Refractive Index measurements with uranyl nitrate-Nickel nitrate-water system indicate two definite complex compounds in solution:

$$Ni(NO_3)_2—UO_2(NO_3)_2 \quad (1)$$

$$3\ Ni(NO_3)_2—UO_2(NO_3). \quad (2)$$

A set of twenty two mixed solutions was prepared by following NAYAR and PANDE's monovariation method. In all solutions the concentration of uranyl nitrate was kept constant, (i. e. M/100), while that of nickel nitrate varied systematically from 0.0 M to 0.042 M. The physico-chemical properties, namely, conductivity, pH, Spectrophotometry, refractive-index, were used for the investigation of complex-compounds, in the above system. When these values were plotted against the varying concentrations of nickel nitrate two 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 reported that uranyl ion behaves as a compound metal and forms complex-compounds, alkali metals, alkaline earth metals, silver, thallium, mercury cadmium and lead. (R. J. MEYER and F. WENDEL[2]), A. COLANI[3]), A. SACHS[4]) and E. RIMBACH[5])).

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

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

[3]) A. COLANI, Compt. rend. **195**, 1475 (1927).

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

[5]) E. RIMBACH, Ber. dtsch. chem. Ges. **37**, 46 K (1904).

A. LANCEIN[6]) reported unstable complex salts with nitrates of Cd, Rh and nickel having the following compositions:

(a) $Cd[UO_2(NO_3)_4] \cdot 30\ H_2O$

(b) $Rh[UO_2(NO_3)_5] \cdot 10\ H_2O$

(c) $3\ UO_2(NO_3)_2 \cdot 10\ Ni(NO_3)_2$ as greenish yellow needles.

The survey of literature also reveals that the system, Nickel nitrate-Uranyl nitrate- water, has not been investigated thoroughly. Therefore it was thought to be desirable to examine the above system thoroughly to investigate the existance and the number of complex-compounds by applying the monovariation method of NAYAR and PANDE[7]). The physico-chemical properties used for the investigation were conductance, pH, spectrophotometry and refractive-index. The present communication deals with our observations based on the values of conductance, pH, Spectrophotometry and refractive-index. The results are in excellent agreement and lead to the same conclusion.

Experimental

Nickel 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 nickel 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 flasks to which the requisite volume of uranyl nitrate solution (0.1 M) was added and the 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 nickel nitrate varied systematically from (0.00 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 Findlay: Practical Physical Chemistry. The cell was rinsed several times

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

Table 1

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

Compositions of the solution

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 $Ni(NO_3)_2$ M/10 added	Concentration of $Ni(NO_3)_2$ soln. M	Ratio of the constituents
1	50	5	0.01	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
13	50	5	0.01	12	0.024	5/12
14	50	5	0.01	13	0.026	5/13
15	50	5	0.01	14	0.028	5/14
16	50	5	0.01	15	0.030	5/15 or 1:3
17	50	5	0.01	16	0.032	5/16
18	50	5	0.01	17	0.034	5/17
19	50	5	0.01	18	0.036	5/18
20	50	5	0.01	19	0.038	5/19
21	50	5	0.01	20	0.040	5/20 or 1:4
22	50	5	0.01	21	0.042	5/21

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 conductance are given in table 2.

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 per cent transmission, per cent absorption and optica density were made by using a Unicam/Spectrophotometer 500 cycles. The

Table 2

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

Cell Constant 1.5732 Temp. = 35 ± 0.05 °C

Soln. No.	C.C. of $Ni(NO_3)_2$ M/10 added to 5 c.c. of $UO_2(NO_3)_2$	Resistance in Ohms	Conductance × 10^4 Mhos
1	0	635	15.75
2	1	530	18.87
3	2	460	21.74
4	3	380	26.31
5	4	350	28.57
6	5	350	28.57
7	6	290	34.48
8	7	280	35.72
9	8	270	37.03
10	9	245	40.82
11	10	225	44.44
12	11	220	45.45
13	12	210	47.62
14	13	175	57.15
15	14	170	58.80
16	15	175	57.14
17	16	170	58.80
18	17	165	60.60
19	18	140	71.40
20	19	130	76.90
21	20	120	83.30
22	21	115	86.90

solutions were maintained at 35 °C by placing in a thermostat maintained at 35 °C. The values of spectrophotometric observations are shown in table 4 (before recording the observations the adjustment was made with a blank of solvent used in the preparation of solutions).

Refractive-Index

The refractive-index measurements were made by an Abbe's Refractometer-model No. 344223. The observations are recorded in the table 3.

Observations and Conclusion

On plotting the values of resistance, conductance pH spectrophotometry and refractive index against the varying concentration of nickel nitrate added to a fixed volume of uranyl nitrate, the curves shown in the figures 1, 2 and 3, were obtained. In case of all the curves two definite breaks were obtained at

Table 3

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

Unicam Model No. 11808 Temp. = 35 ± 0.1 °C Wavelength 450 mμ

Soln. No.	C. C. of $Ni(NO_3)_2$ 0.1 M added to 5 c. c. of $UO_2(NO_3)_2$ M/10	% Transmission	% Absorption	Optical Density
1	0 c.c.	92.60	7.4	0.033
2	1 c.c.	90.4	9.6	0.044
3	2 c.c.	90.0	10.0	0.045
4	3 c.c.	89.7	10.3	0.047
5	4 c.c.	89.3	10.7	0.048
6	5 c.c.	89.7	10.3	0.047
7	6 c.c.	89.4	10.6	0.0478
8	7 c.c.	89.0	11.0	0.051
9	8 c.c.	88.7	11.3	0.052
10	9 c.c.	88.0	11.9	0.055
11	10 c.c.	87.98	12.02	0.0555
12	11 c.c.	87.80	12.20	0.0565
13	12 c.c.	86.20	13.80	0.0648
14	13 c.c.	86.90	13.10	0.0615
15	14 c.c.	86.70	13.30	0.0622
16	15 c.c.	87.8	12.20	0.0565
17	16 c.c.	86.50	13.50	0.063
18	17 c.c.	86.06	13.94	0.0652
19	18 c.c.	85.98	14.02	0.06525
20	19 c.c.	85.60	14.40	0.0675
21	20 c.c.	85.02	14.98	0.0705
22	21 c.c.	84.70	15.30	0.0720

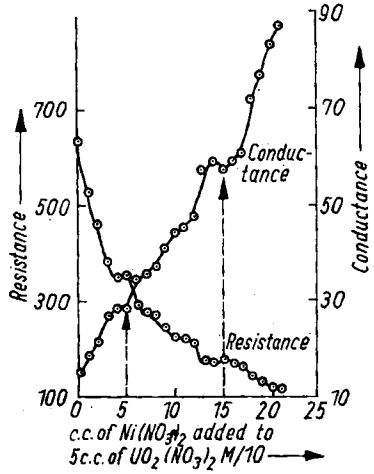

Fig. 1 The System $UO_2(NO_3)_2$—$Ni(NO_3)_3$—H_2O

Table 4

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

Property- pH — Pye pH meter Model No. 11083

Property: Refractive Index — Abbe's Refractometer No. 344223

Soln. No.	C.C. of $Ni(NO)_2$ M/10 added to 5 c.c. of $UO_2(NO_3)_2$ M/10 in c.c.	pH measurements	Refractive Index
1	0.0	3.16	1.336
2	1.0	3.05	1.339
3	2.0	3.05	1.340
4	3.0	3.10	1.3395
5	4.0	3.15	1.340
6	5.0	3.00	1.341
7	6.0	3.15	1.340
8	7.0	3.15	1.340
9	8.0	3.15	1.340
10	9.0	3.20	1.340
11	10.0	3.20	1.340
12	11.0	3.20	1.340
13	12.0	3.20	1.340
14	13.0	3.20	1.340
15	14.0	3.20	1.340
16	15.0	3.15	1.342
17	16.0	3.15	1.340
18	17.0	3.20	1.341
19	18.0	3.15	1.341
20	19.0	3.20	1.341
21	20.0	3.20	1.341
22	21.0	3.20	1.341

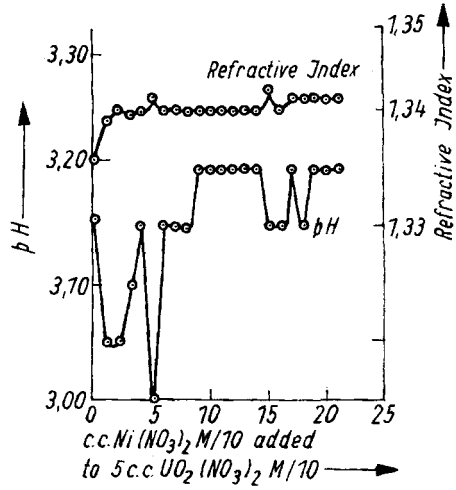

Fig. 2 The System
$UO_2(NO_3)_2$—$Ni(NO_3)_2$—H_2O

concentrations corresponding to 5 c.c. and 15 c.c. of nickel nitrate. The molecular ratios of uranyl nitrate at these points are 1:1 and 1:3 respectively. These correspond to the compounds of the formulae:

$$Ni(NO_3)_2UO_2(NO_3)_2 \tag{1}$$

and

$$3\,Ni(NO_3)_2 \cdot UO_2(NO_3)_2. \tag{2}$$

For the present we have assumed that the kinks occur at the stoichiometric proportions corresponding to the two compounds existing in solutions and have concluded that the two compounds uranyl nitrate and nickel nitrate form the compounds corresponding to the formulae given above. An attempt is being made to crystallize out these complexes, if possible in solid state and to study their properties in detail. The existence of these comple-

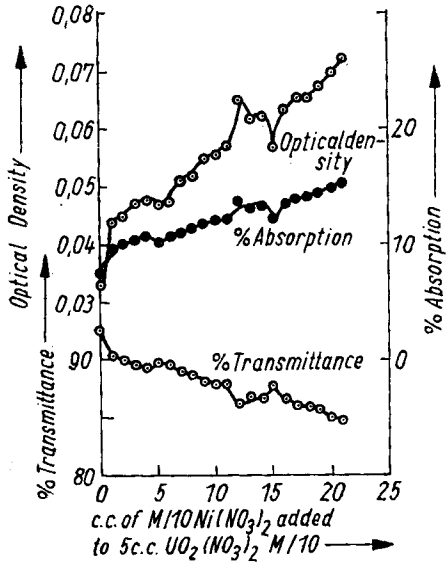

Fig. 3 The System
$UO_2(NO_3)_2$—$Ni(NO_3)_2$—H_2O

xes become more definite when such widely differing properties like conductance, pH, Spectrophotometry and Refractive-index measurements yield the same observations leading to the same conclusions.

Our sincerest thanks are due to Professor Dr. S. N. Shukla, Professor and Head of the Chemistry Department, Lucknow University, Lucknow and

Dr. KRISHNA MEHAN, Director, Directorate of Geology and Mining, U. P. for kind encouragement and providing all sorts of laboratory facilities.

Lucknow (India), Inorganic Chemical Laboratories, Lucknow University.

Bei der Redaktion eingegangen am 16. Dezember 1963.

Verantwortlich
für die Schriftleitung: Prof. Dr.-Ing. Dr. h. c. E. Leibnitz, Leipzig O 5, Permoserstraße 15; für den Anzeigenteil: DEWAG-Werbung Leipzig, Leipzig C 1, Friedrich-Ebert-Str. 110, Ruf 7851. Z. Z. gilt Anzeigenpreisliste 4; *Verlag:* Johann Ambrosius Barth, Leipzig C 1, Salomonstraße 18B; Fernruf 27681 und 27682. Veröffentlicht unter der Lizenz-Nr. 1395 des Presseamtes beim Vorsitzenden des Ministerrates der DDR
Printed in Germany Druck: Paul Dünnhaupt, Köthen (IV/5/1) L 228/64