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

The System: $La(NO_3)_3$-$UO_2(NO_3)_2$-H_2O

By S. S. Gupta and S. D. Marwah

With 3 Figures

Summary

Experiments with the system Uranyl nitrate-Lanthanum nitrate-water viz., Conductance, pH, and spectrophotometry revealed the existence of the following compounds in solution.

(1) $La(NO_3)_3-UO_2(NO_3)_2$ (2) $2La(NO_3)_3-UO_2(NO_3)_2$

A set of 22 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/200), while that of lanthanum nitrate varied systematically from 0.0M to 0.021M. The physico-chemical properties, namely conductivity, pH, and spectrophotometry were used for the investigation of complex-compounds in the above system. When these values are plotted against the varying concentration of Lanthanum 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

The survey of literature reveals that uranyl nitrate has a great tendency to form complex compounds. But great majority of these complexes are double salts and they are formed by all kinds of metals in very large numbers[2]). Uranyl nitrate forms two series of compounds with alkali-nitrates.

1. $MUO_2(NO_3)_3$ (e.g. K, NH_4, Rb, Cs) all anhydrous, but most of them are very hygroscopic also:

[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); A. Colani Compt. rend. **185**, 1475 (1927); A. Sachs, Z. Kristallogr. **38**, 498 (1903); E. Rimbach, Ber. dtsch. chem. Ges. **37**, 461 (1904); A. Lancein, Chem. Zbl. **1**, 208 (1912); O. D. Coninck, Bull. Acad. roy. Belg. p. 744 (1909); C. S. Pande and S. S. Gupta, J. prakt. Chem. [4] **13**, 121 (1961); [4] **23**, 177 (1964).

2. $M_2UO_2(NO_3)_4$ (e.g. $K \cdot NH_4$, $Rb \cdot Cs$) in this way almost all the alkali salts form complex compounds, with corresponding uranyl salts.

It has also been noticed that vera little work has been done on the formation of complex compounds between Rare Earth nitrates and Uranyl nitrate. It was therefore thought desirable by us to study this class of compounds. The system: Lanthanum nitrate-Uranyl nitrate-Water, has been investigated by us, in order to throw some light on the existence of complex-compounds in this system, and there is hardly any reference in literature to the study of this system. In this paper the results of the measurements of conductivity, pH, and spectrophotometry of a series of mixed solutions Lanthanum nitrate and Uranyl nitrate are recorded. All the physico-chemical properties investigated reveal the existence of two complex-compounds.

Table 1
System: $La(NO_3)_3$—$UO_2(NO_3)_2$—H_2O
Composition of the solutions

Soln. no.	Total volume of the solution C. C.	C. C. of $UO_2(NO_3)_2$ M/20added	Concentration of the uranyl nitrate Molar	C. C. of $La(NO_3)_3$ M/20 added	Concentration of $La(NO_3)_3$ 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

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 lanthanum was made by Monovariation method, i. e. the concentration of uryanl nitrate was kept constant (N/200), while that of lanthanum nitrate varied systematically from (0.0M) to (0.021). The composition of the solution is shown in the column (2) of Table 1.

Table 2

The system: $La(NO_3)_3-UO_2(NO_3)_2H_2O$

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

Soln. no.	C. C. of $La(NO_3)_3$ added to 5 c. c. of $UO_2(NO_3)_2$ 0.05M	Resistance in Ohms	Conductance $\times 10^4$ Mhos.
1	0.0 c. c.	1100	09.09
2	1.0 c. c.	195	51.29
3	2.0 c. c.	114	87.72
4	3.0 c. c.	120	50.00
5	4.0 c. c.	69	145.00
6	5.0 c. c.	62	161.30
7	6.0 c. c.	43	232.60
8	7.0 c. c.	36	277.70
9	8.0 c. c.	30	333.40
10	9.0 c. c.	31	322.50
11	10.0 c. c.	27	370.30
12	11.0 c. c.	26	384.60
13	12.0 c. c.	22	454.50
14	13.0 c. c.	22	454.50
15	14.0 c. c.	21	476.20
16	15.0 c. c.	20	500.00
17	16.0 c. c.	19	526.20
18	17.0 c. c.	19	526.20
19	18.0 c. c.	18	555.56
20	19.0 c. c.	17	588.30
21	20.0 c. c.	15	666.70
22	21.0 c. c.	14	714.40

Conductance

Measurement of conductance were made by conductivity assembly Electronic Magic eye (Phillips model G. M. 4249). A pyrex glass conductivity cell with platinum electrode was used. The cell was platinized and washed as described (FINDLAY: Practical Physical Chemistry). The cell was rinsed several times with solutions used. All conductometric measurements were made at constant temperature, i. e., at 35°C by using a thermostat. At least three readings were taken for each solution. The solutions were placed in the cell and kept, in the thermostat at least for half an hour.

pH Measurements

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

Table 3

The System: $La(NO_3)_3-UO_2(NO_3)_2-H_2O$

Property: Spectrophotometry Temp. 35° ± 0.1 °C

BECKMAN: Spectrophotometer Wavelength 430 mμ

Soln. no.	C. C. of $La(NO_3)_3$ 0.05 M added to 5 c. c. of $UO_2(NO_3)_2$ 0.05 M in c. c.	% Transmission	% Absorption	Optical Density
1	0.0	94.00	6.00	0.030
2	1.0	94.00	6.00	0.028
3	2.0	93.50	6.50	0.030
4	3.0	94.00	6.00	0.020
5	4.0	93.00	7.00	0.030
6	5.0	93.50	6.50	0.030
7	6.0	95.00	5.00	0.022
8	7.0	87.00	13.00	0.060
9	8.0	92.00	8.00	0.032
10	9.0	97.00	3.00	0.013
11	10.0	90.00	10.00	0.047
12	11.0	93.50	6.50	0.029
13	12.0	95.00	5.00	0.022
14	13.0	89.00	11.00	0.050
15	14.0	86.00	14.00	0.065
16	15.0	91.00	9.00	0.040
17	16.0	89.00	11.00	0.050
18	17.0	85.50	14.50	0.060
19	18.0	91.50	8.50	0.040
20	19.0	87.00	13.00	0.060
21	20.0	85.50	14.50	0.060
22	21.0	91.50	8.50	0.038

Spectrophotometry

Measurements of % transmission, % absorption and optical density were made by a Unicam Spectrophotometer. The solutions were maintained at 35°C by placing in a thermostat. Special precautions were taken in cleaning the cells. Before making observations the adjustment was made with a blank of solvent used in preparing the solutions.

Observations and Conclusions

When these values of resistance, conductance, pH, percent transmittance and optical density of the solutions were plotted against the

Table 3 (contd.)

Spectrophotometry: (contd.)

Wavelength: 440 mμ and 450 mμ

Soln. No.	Wavelength 440 mμ			Wavelength 450 mμ		
	% Transmission	% Absorption	Optical Density	% Transmission	% Absorption	Optical Density
1	96.5	3.50	0.015	98.50	1.50	0.007
2	96.5	3.50	0.015	98.0	2.00	0.010
3	95.0	5.00	0.022	97.0	3.00	0.014
4	97.5	2.50	0.010	99.5	0.50	0.004
5	94.0	6.00	0.018	97.5	2.50	0.012
6	96.0	4.00	0.018	97.0	3.00	0.015
7	99.0	1.00	0.005	99.0	1.00	0.005
8	89.0	11.00	0.052	89.5	10.50	0.048
9	93.0	7.00	0.030	96.0	4.00	0.018
10	99.5	0.5	0.003	100.0	0.00	0.00
11	91.0	9.00	0.042	93.0	7.00	0.032
12	96.0	4.00	0.018	97.0	3.00	0.012
13	98.0	2.00	0.010	97.5	2.50	0.011
14	92.0	8.00	0.035	92.5	7.50	0.033
15	88.5	11.50	0.053	89.0	11.00	0.050
16	93.5	6.50	0.027	96.5	3.50	0.016
17	91.0	9.00	0.041	92.5	7.50	0.035
18	87.5	12.50	0.059	90.5	9.50	0.042
19	94.0	6.00	0.027	95.0	5.00	0.023
20	89.5	10.50	0.040	91.00	9.00	0.041
21	88.5	11.50	0.054	89.0	11.00	0.050
22	93.5	6.50	0.028	96.0	4.00	0.018

volume of lanthanum 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 are definite breaks in the regular curves at concentrations corresponding to 5 c.c. and 10 c.c. of lanthanum nitrate. The ratio of lanthanum nitrate to uranyl nitrate at these points is (1:1) and (2:1) respectively which corresponds to the following compounds of the formula.

1. $La(NO_3)_3 \cdot UO_2(NO_3)_2$ 2. $2La(NO_3)_3 \cdot UO_2(NO_3)_2$

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 in the curves occur at exact stoichiometric ratios of concentration corresponding to the compounds stated above. Thus the existence of these compounds stated above, became

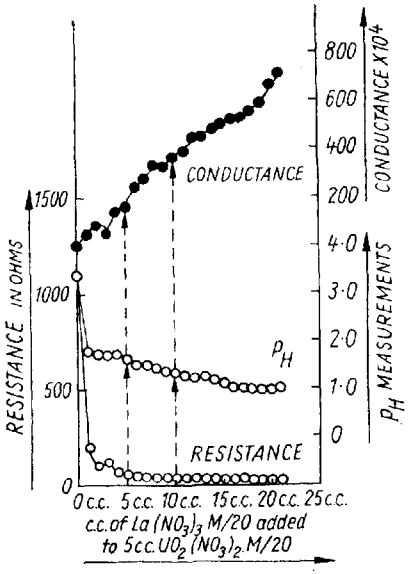

Fig. 1

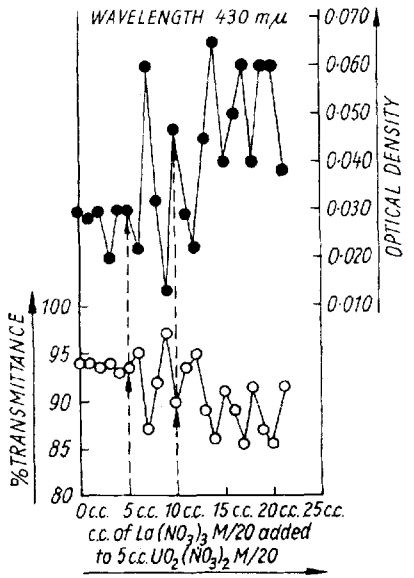

Fig 2

Table 4
The System:
$La(NO_3)_3$—$UO_2(NO_3)_2$—H_2O
Property: pH-Measurements
Model: W. G. Pye & Co. Ltd.
Cat. No. 11083

Soln. No.	C. C. of $La(NO_3)_3$ 0.05 M added to 5 c. c. of $UO_2(NO_3)_2$ 0.05 M c. c.	pH Measurements
1	0.0	3.20
2	1.0	1.80
3	2.0	1.75
4	3.0	1.75
5	4.0	1.75
6	5.0	1.60
7	6.0	1.50
8	7.0	1.45
9	8.0	1.40
10	9.0	1.35
11	10.0	1.30
12	11.0	1.20
13	12.0	1.20
14	13.0	1.20
15	14.0	1.15
16	15.0	1.10
17	16.0	1.05
18	17.0	1.05
19	18.0	1.00
20	19.0	1.00
21	20.0	1.00
22	21.0	1.05

unequivocal when such dissimilar properties, like conductance, refractive-index pH and spectrophotometry yield similar results.

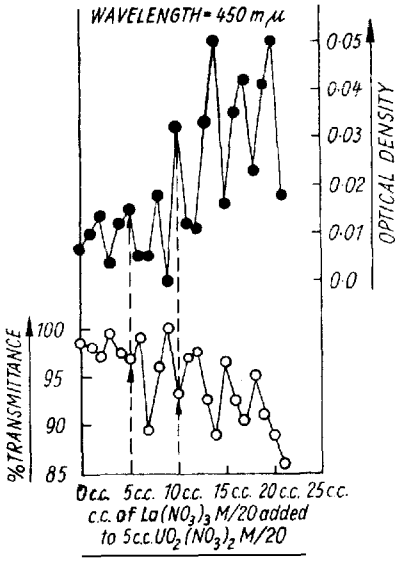

Fig. 3

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

Lucknow (India), Department of Chemistry, Inorganic Chemical Laboratories Lucknow University.

Bei der Redaktion eingegangen am 24. August 1964.