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

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

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With 3 Figures

Summary

Determination of conductance, pH, Spectrophotometry, and Refractive-Index measurements of a series of mixed solutions of uranyl nitrate and thorium nitrate, indicate the existence of one definite complex-compound in the solution namely

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

Monovariation method of NAYAR and PANDE[1]), has been followed in the preparation of the solutions and in the investigation of properties. Aqueous solutions of the uranyl nitrate and thorium nitrate were prepared in such a way that the concentration of uranyl nitrate was kept constant, while that of thorium nitrate was varied systematically, and the physico-chemical properties recorded. When the values are plotted against the concentration of thorium nitrate curves are obtained with the specific breaks. The kink occurs at exact stoichiometric ratio of the concentrations corresponding to the compound noted above.

Introduction

An extensive survey of the literature reveals that uranyl ion (UO_2^{++}) behaves as an ideal complexing group and has a strong tendency to increase its covalency by complex-formation. Uranyl nitrate forms complexes with the nitrates of alkali metals, alkaline earth metals, silver, thallium, mercury cadmium, nickel, rhodium and lead. The pioneer workers in the field of nitrate complexes of uranyl group-UO_2^{++} are: MEYER and WENDEL[2]) RIMBACH[3]), SACHS[4]), F. W. O. DE CONINCK[5]), A. LANCEIN[6]), A. COLANI[7]),

[1]) NAYAR and PANDE, Proc. Ind. Acad. Sci. **27A**, 286 (1948).
[2]) R. J. MEYER and F. WENDEL, Ber. dtsch. chem. Ges. **36**, 4055 (1903).
[3]) E. RIMBACH, Ber. dtsch. chem. Ges. **37**, 461 (1904).
[4]) A. SACHS, Z. Kristallogr. **38**, 498 (1903).
[5]) F. W. O. DE CONINCK, Bull. Acad. roy. Belg. 744 (1909).
[6]) A. LANCEIN, Chem. Zbl. **1**, 208 (1912).
[7]) A. COLANI, Compt. rend. **185**, 1475 (1927).

COULSON and LESTER[8]), FOREMAN, McGOWAN and SMITH[9]), PANDE and GUPTA[10]), GUPTA and SHARGA[11]), who have extenssively studied such a class of complexes.

It has been noticed during the course of the survey of the literature that practically no work has been done on the formation of complex compounds between Uranyl nitrate and Thorium nitrate. It was therefore considered desirable by us to investigate this system: Uranyl nitrate-thorium nitrate-water. There is hardly any reference in literature to the study of this system.

In this paper the results of the measurements of conductance, pH, Spectrophotometry and Refractive Index of a series of solutions are recorded.

Table I
The System: $Th(NO_3)_4$—$UO_2(NO_3)_2$—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 $UO_2(NO_3)_2$ soln. M	C. C. of $Th(NO_3)_4$ M/20 added	Concentration of $Th(NO_3)_4$ 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	60	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

[8]) C. A. COULSON and G. R. LESTER, J. chem. Soc. London **4**, (79) 5889 (1957).
[9]) J. K. FOREMAN, I. R. McGOWAN and T. D. SMITH, J. C. S. page 738, Feb. 1959.
[10]) C. S. PANDE and S. S. GUPTA, J. prakt. Chem. [4], **13**, 121, 127, 237 (1961).
[11]) S. S. GUPTA and B. N. SHARGA, J. prakt. Chem. [4], **22**, 101 (1963).

All the physico-chemical studies reveal the existence of the complex-compound, mentioned above.

Experimental

Reagent used were of standard quality and recrystallised. Stock solutions were made in conductivity water. A set of mixed solutions of uranyl nitrate and thorium nitrate was made by monovariation method, i. e. the concentration of uranyl nitrate was kept constant (0.005M) while that of thorium 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 platinum 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. Atleast three readings were taken for each solutions. The solutions were placed in the cell and kept in the thermostat for half an hour. The values of the conductance are recorded in the table II.

Table II
The System: $Th(NO_3)_4-UO_2(NO_3)_2-H_2O$
Cell constt = 1.5732 Temp. 35 °C ± 0.1 °C
Electronic Magic-eye No. G. M. 4249

Soln. No.	C. C. of $Th(NO_3)_4$ M/20 added to 5 c. c. of $UO(NO_3)_2$ M/20	Resistance in Ohms	Conductance $\times 10^4$ in Mhos
1	0.0 c. c.	1100	9.09
2	1.0 c. c.	750	13.33
3	2.0 c. c.	560	17.81
4	3.0 c. c.	440	22.73
5	4.0 c. c.	380	26.31
6	5.0 c. c.	330	30.31
7	6.0 c. c.	310	32.25
8	7.0 c. c.	280	35.72
9	8.0 c. c.	245	40.82
10	9.0 c. c.	235	42.55
11	10.0 c. c.	210	47.62
12	11.0 c. c.	195	51.29
13	12.0 c. c.	185	54.05
14	13.0 c. c.	170	58.83
15	14.0 c. c.	165	60.60
16	15.0 c. c.	155	64.52
17	16.0 c. c.	150	66.67
18	17.0 c. c.	140	71.44
19	18.0 c. c.	135	74.08
20	19.0 c. c.	130	76.93
21	20.0 c. c.	125	80.00
22	21.0 c. c.	120	83.33

Spectrophotometry

Measurements of transmission absorption and opticaldensity were made by a Unicamspectrophotometer. The solutions were maintained at 35 °C by placing in athermostat. 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 the table IV.

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 the pH are recorded in the table III.

Refractive Index

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

Observation

On plotting the values of resistance conductance, pH, refractive-index and sprectophotometry against the varying concentration of thorium nitrate added to a fixed volume of uranyl nitrate, the

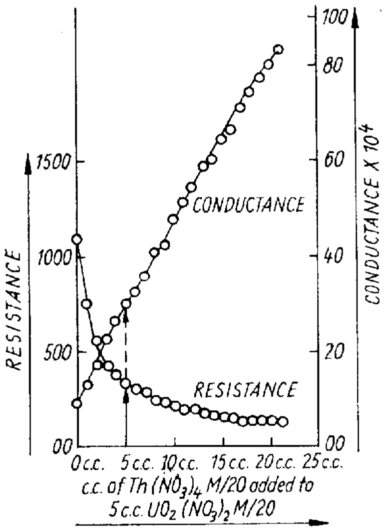

Fig. 1.

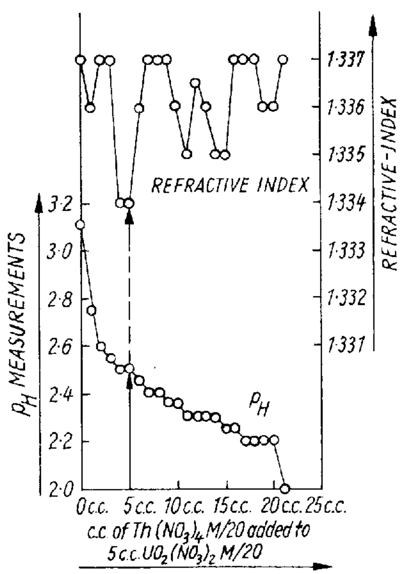

Fig. 2.

Table III

(1) Refractive-index ABBE's Refractometer
(2) pH Measurements Modell No. 344223
PYE-pH meter No. 11083
The System: $Th(NO_3)_4$—$UO_2(NO_3)_2$—H_2O

Soln. No.	C. C. of $Th(NO_3)_4$ M/20 added to 5 c. c. $UO_2(NO_3)_2$ M/20	pH measurements	Refractive Index
1	0.0	3.10	1.337
2	1.0	2.75	1.336
3	2.0	2.60	1.337
4	3.0	2.55	1.337
5	4.0	2.50	1.334
6	5.0	2.50	1.334
7	6.0	2.45	1.336
8	7.0	2.40	1.337
9	8.0	2.40	1.337
10	9.0	2.35	1.337
11	10.0	2.35	1.336
12	11.0	2.30	1.335
13	12.0	2.30	1.3365
14	13.0	2.30	1.3360
15	14.0	2.30	1.335
16	15.0	2.25	1.335
17	16.0	2.25	1.337
18	17.0	2.20	1.337
19	18.0	2.20	1.337
20	19.0	2.20	1.336
21	20.0	2.20	1.336
22	21.0	2.00	1.337

Table IV

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

Property-Spectrophotometry Unicam spectrophotomer

Soln. No.	c. c. of $Th(NO_3)_4$ M/20 added to 5 c. c. of $UO_2(NO_3)_2$ M/20	Wave length 450 mμ % of trans-mittance	% Absorp-tion	Optical density	Wave length 400 mμ % of trans-mittance	% of absorp-tion	Optical density
1	0.0	95.0	5.0	0.024	92.50	7.50	0.035
2	1.0	95.0	5.0	0.021	93.20	6.80	0.030
3	2.0	93.0	7.0	0.033	90.5	9.50	0.043
4	3.0	95.2	4.8	0.021	93.0	7.00	0.032
5	4.0	95.5	4.5	0.020	93.30	6.70	0.030
6	5.0	94.4	5.6	0.025	91.60	8.40	0.038
7	6.0	95.0	5.0	0.0222	93.60	6.40	0.033
8	7.0	95.5	4.5	0.020	93.60	6.40	0.029
9	9.0	95.0	5.0	0.0220	93.00	7.00	0.032
10	10.0	94.2	5.8	0.025	92.00	8.00	0.036
11	10.0	95.1	4.90	0.0222	93.20	6.80	0.030
12	11.0	95.5	4.50	0.020	93.50	6.50	0.030
13	12.0	94.2	5.80	0.025	92.10	7.90	0.035
14	13.0	94.0	6.00	0.027	91.60	8.40	0.048
15	14.0	94.8	5.20	0.0223	92.20	7.80	0.035
16	15.0	94.0	6.00	0.027	91.20	8.80	0.040
17	16.0	93.8	6.20	0.028	91.50	8.50	0.048
18	17.0	95.0	5.00	0.0235	92.50	7.50	0.044
19	18.0	93.60	6.40	0.029	91.00	9.00	0.042
20	19.0	94.0	6.00	0.027	91.50	8.50	0.048
21	20.0	95.2	4.80	0.0222	93.00	7.00	0.032
22	21.0	94.0	6.00	0.027	91.70	8.30	0.038

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 thorium nitrate. The molecular ratio of uranyl nitrate at this point is 1:1. This corresponds to the compound of the formula.

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

For the present we have assumed that the kink occurs at the stoichiometric ratio corresponding to the compound $Th(NO_3)_4 \cdot UO_2(NO_3)_2$ existing in the solution. An attempt is being made to crystallize out these complexes, if possible in the solid crystalline state to study their properties in detail. The existence of these complexes becomes more definite when such widely differing physico-chemical properties like conductance, pH refractive-index and spectrophotometry measurements yield the same observations leading to the same conclusions.

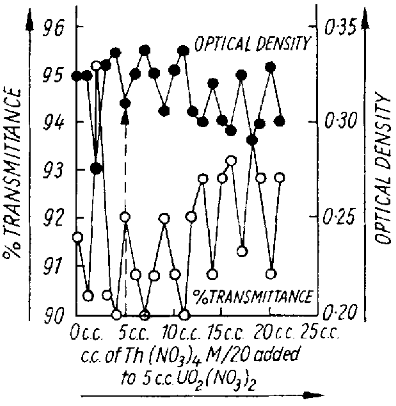

Fig. 3.

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