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Studies on the Formation of Complex Compounds between Rare Earth Nitrate and Uranyl Nitrate

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

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With 4 Figures

Abstract

Determination of conductance, pH, Spectrophotometry and Refractive-index of a series of mixed solutions of uranyl nitrate and cerous nitrate indicate, the existence of the following compounds

$$Ce(NO_3)_3-UO_2(NO_3)_2 \quad (1)$$

$$2\,Ce(NO_3)_3-UO_2(NO_3)_2. \quad (2)$$

A set of 22 mixed solutions was prepared by following NAYAR and PANDE's mono-variation method. In all the solutions the concentration of uranyl nitrate was kept constant (i. e. M/100) while that of cerous nitrate varied systematically from 0.0 M to 0.042 M. The physico-chemical properties, namely conductance, pH Spectrophotometry and refractive-index were used for the investigation of complex-compounds in the above system. When these values were plotted against the varying concentration of cerous nitrate two breaks were obtained in the regular curves at concentrations corresponding to the compound having the above formulae. The results obtained by all these physico-chemical studies are in excellent agreement leading to the same conclusions.

Introduction

A survey of literature reveals that uranyl nitrate has a great tendency for the formation of complex-compounds with transition metal nitrates as silver, thallium, mercury, cadmium, nickel and rhodium, lead, copper and cobalt. (R. J. MEYER and F. WENDEL[2]); A. COLANI[3]); A. SACHS[4]); E. RIM-

[1]) M. R. NAYER and C. S. PANDE, Pro. Ind. Acad. Sci. **27A**, 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. SACHS, Z. Kristallogr. **38**, 498 (1903).

BAGH[5]); A. LANCEIN[6]); O. D. CONINCK[7]); PANDE and GUPTA[8]); GUPTA and SHARGA[9]) and GUPTA and MARWAH[10]).

The survey of the literature reveals that the system cerium nitrate—uranyl nitrate water has not been investigated before. Therefore it was thought to be desirable to examine the above system thoroughly. In all the available literature on uranyl ion UO_2^{++} no reference has been found on the complexes of the Rare earth metals.

Table 1
The System: $Ce(NO_3)_3-UO_2(NO_3)_2H_2O$
Composition of the solutions

Soln. No.	Total volume of the soln. c. c.	C. C. of $UO_2(NO_3)_2$ M/10 added c. c.	Concentration of the $UO_2(NO_3)_2$ soln. M.	C. C. of $Ce(NO_3)_3$ M/10 added c. c.	Concentration of the $Ce(NO_3)_3$ soln. M.	Ratio of the 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	50	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	50	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

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

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

[7]) O. D. CONINCK, Bull. Acad. roy. Belg. **1909**, 744.

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

[9]) S. S. GUPTA and B. N. SHARGA, J. prakt. Chem. Communicated (1962); J. anorg. allg. Chem. Communicated (1963).

[10]) S. S. GUPTA and MARWAH, J. prakt. Chem. Communicated (1963).

Inner Transition Series

This system was thoroughly investigated to find the number of complex compounds by applying the monovariation method of NAYER and PANDE[1]). The physico-chemical properties used for the investigation were conductance, pH, spectrophotometry and refractive index. The sensitivity of spectrophotometric method enabled us to detect almost all the complexes present in the system. 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 conclusions.

Experimental

Cerium nitrate and uranyl nitrate (B. D. H./A. R.) were used for the preparation of stock solutions in conductivity water. A set of mixed solutions of uranyl nitrate and cerium

Table 2

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

Cell constant 1.5732 Temp. = 35 ± 0.05 °C

Soln. No.	C. C. of $Ce(NO_3)_3$ M/10 added to 5. c. c. of M/10 $UO_2(NO_3)_2$	Resistance Ohms	Conductance · 10^4 Mhos
1	0	635	15.75
2	1	530	18.87
3	2	440	22.73
4	3	370	27.03
5	4	290	34.48
6	5	260	38,46
7	6	240	41.67
8	7	205	48.77
9	8	195	51.29
10	9	190	52.62
11	10	170	58.83
12	11	150	66.67
13	12	150	66.67
14	13	135	74.08
15	14	135	74.08
16	15	125	80.00
17	16	115	86.96
18	17	110	90.90
19	18	110	90.90
20	19	110	90.90
21	20	95	105.30
22	21	95	105.30

nitrate was made by Monovariation method, i. e. the concentration of uranyl nitrate was kept constant (0.01 M) while that of cerium nitrate varied systematically from (0.0 M) to (0.042). The composition of the solutions is shown in the Table 1.

Conductance

Measurements 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. Atleast three readings were taken for each solution. The solutions were placed in the cell and kept in the thermostat atleast for half an hour. The values of the conductance are tabulated in Table 2.

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 are recorded in Table 3.

Table 3

The system: $Ce(NO_3)_3-UO_2(NO_3)_2-H_2O$

Property: pH — Pye pH meter Model No. 11083

Property: Refractive Index — Abbes Refractometer

Soln. No.	C. C. of $Ce(NO_3)_3$ 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	3.00	1.340
3	2.0	2.95	1.340
4	3.0	2.90	1.341
5	4.0	2.85	1.3395
6	5.0	2.85	1.3395
7	6.0	2.80	1.341
8	7.0	2.70	1.3415
9	8.0	2.70	1.3405
10	9.0	2.65	1.340
11	10.0	2.62	1.339
12	11.0	2.60	1.3395
13	12.0	2.55	1.3390
14	13.0	2.50	1.3395
15	14.0	2.50	1.340
16	15.0	2.48	1.3390
17	16.0	2.40	1.340
18	17.0	2.40	1.340
19	18.0	2.38	1.340
20	19.0	2.35	1.3405
21	20.0	2.30	1.340
22	21.0	2.30	1.341

Spectrophotometry

Measurements of transmission, absorption, and optical density were made by a Unicam-500 cycles Spectrophotometer. The solutions were maintained at 35 °C by placing in a thermostat. Before making observations the adjustment was made with a blank of solvent

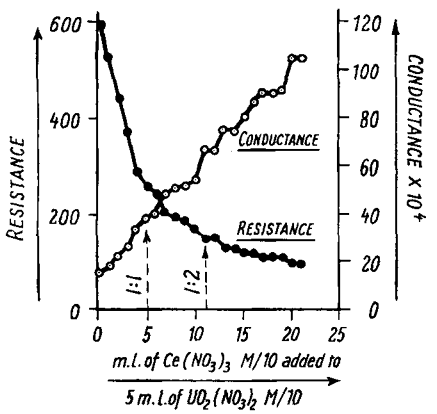

Fig. 1. The System: $Ce(NO_3)_3-UO_2(NO_3)_2-H_2O$

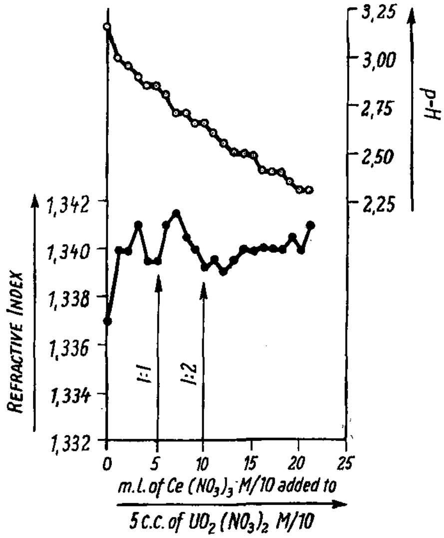

Fig. 2. The System: $Ce(NO_3)_3-UO_2(NO_3)_2-H_2O$

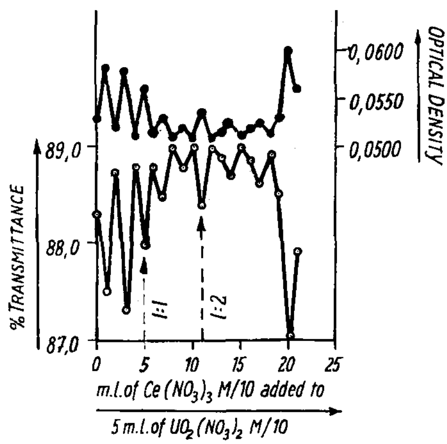

Fig. 3. The System: $Ce(NO_3)_3-UO_2(NO_3)_2-H_2O$

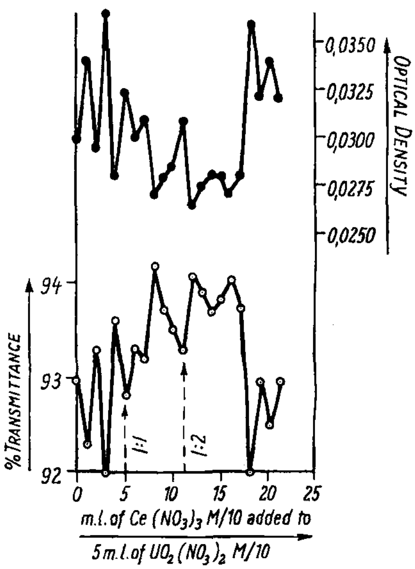

Fig. 4. The System: $Ce(NO_3)_3-UO_2(NO_3)_2-H_2O$

used in preparing the solutions. The values of spectrophotometric observations are recorded in the Table 4.

The values of conductance, pH, % transmittance, % absorption, optical density and refractive index are represented graphically in Fig. 1, 2, 3 and 4 respectively.

Table 4

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

Property: Spectrophotometry Temp. = 35± 0.1 °C

Unicam Model No. 11808

Soln. No.	C. C. of $Ce(NO_3)_3$ M/10 added to 5 c. c. of $UO_2(NO_3)_2$ 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 440 mμ
1	0 c. c.	87.85	92.60	12.15	7.40	0.057	0.033
2	1 c. c.	87.50	92.30	12.50	7.70	0.058	0.034
3	2 c. c.	88.75	93.30	11.25	6.70	0.052	0.0295
4	3 c. c.	87.30	92.00	12.70	8.00	0.058	0.0365
5	4 c. c.	88.90	93.60	11.10	6.40	0.051	0.0280
6	5 c. c.	88.00	92.80	12.00	7.20	0.056	0.0323
7	6 c. c.	88.90	93.30	11.10	6.70	0.0515	0.030
8	7 c. c.	88.50	92.30	11.50	6.80	0.053	0.031
9	8 c. c.	89.00	94.15	11.00	5.85	0.051	0.027
10	9 c. c.	88.80	93.70	11.20	6.30	0.052	0.028
11	10 c. c.	89.00	93.50	11.00	6.50	0,051	0.0285
12	11 c. c.	88.40	93.30	11.60	6.70	0.0534	0.0310
13	12 c. c.	89.00	94.05	11.00	5.95	0.051	0.0265
14	13 c. c.	88.90	93.90	11.10	6.10	0.0515	0.0275
15	14 c. c.	88.70	93.70	11.30	6.30	0.052	0.0280
16	15 c. c.	89.00	93.80	11.00	6.20	0.051	0.0280
17	16 c. c.	88.85	94.00	11.15	6.00	0.052	0.0270
18	17 c. c.	88.60	92.70	11.40	6.30	0.0525	0.0280
19	18 c. c.	86.90	92.00	13.10	8.00	0.0610	0.036
20	19 c. c.	88.50	92.95	11.50	7.05	0.053	0.032
21	20 c. c.	87.00	92.50	13.00	7.50	0.0603	0.034
22	21 c. c.	87.93	92.95	12.07	7.05	0.056	0.032

Observations and Discussions

On plotting the values of resistance, conductivity, pH, Spectrophotometry and refractive-index against the varying concentration of cerium nitrate added to a fixed volume of uranyl nitrate, the curves shown in the Fig. 1, 2, 3 and 4 were obtained. In case of all the curves, two definite breaks were obtained at concentrations corresponding to 5 c. c. and 10 c. c. of cerium nitrate. The molecular ratios of uranyl nitrate at these points are

1:1 and 1:2 respectively. These correspond to the compounds of the formulae:

$$Ce(NO_3)_3 \cdot UO_2(NO_3)_2 \text{ and} \quad (1)$$

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

which is very well established by the curves shown in Fig. 1, 2, 3 and 4. For the present we have assumed that the kinks occur at the stoichiometric proportions.

Conclusion

Conductance, pH, Spectrophotometric and Refractive-index measurements reveal that the existence of two definite complex-compounds namely:

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

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

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