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Formation of Complex Compounds between Uranyl Nitrate and Alkaline earth Nitrates. V

The System: $Ba(NO_3)_2$-$UO_2(NO_3)_2$-H_2O (Conductivity, p_H and Spectrophotometry)

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With 3 Figures

Summary

Experiments with the system: barium nitrate–uranyl nitrate–water, viz., conductivity, p_H measurements and spectrophotometry revealed the existence of the following compound in solution:

$$Ba(NO_3)_2 \cdot UO_2(NO_3)_2.$$

A set of 27 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/100), while that of barium nitrate varied systematically from 0.0 M to 0.052 M. The physico-chemical properties, namely, conductivity, p_H and spectrophotometry were used for the investigation of complex compounds in the above system. When these values were plotted against the varying concentration of barium nitrate one break was obtained in the regular curves at concentrations corresponding to the compound having the above formula. The results obtained by all these physico-chemical properties 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 the nitrates of alkali metals, silver, thallium, mercury and cadmium. R. J. MEYER and F.

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

WENDEL[2]), A. COLANI[3]), A. SACHS[4]), E. RIMBACH[5]), A. LANCEIN[6]) and O. D. CONINCK[7]) have made detailed studies on such class of compounds.

The survey of literature also reveals that the system: barium nitrate —uranyl nitrate—water, has not been investigated before. Therefore, it was thought to be desirable to examine the above system thoroughly to investigate the existence and the number of complex compounds by applying the monovariation method of NAYAR and PANDE[1]). The physico-chemical properties used for the investigation were conductivity, p_H and spectrophotometry. The sensitivity of spectrophotometric method enables one to detect almost all the complexes present in solution. The present communication deals with our observations based on the values of conductivity, p_H and spectrophotometry. The results are in excellent agreement and lead to the same conclusions.

Experimental

Barium 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 barium 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 flask to which the requisite volume of barium 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 27 solutions was made in which the concentration of uranyl nitrate remained the same (0.01 M), while that of barium nitrate varied systematically from (0.0 M) to (0.052 M). The solutions were stored in thoroughly cleaned glass bottles. The composition of these solutions is shown in Table I.

Conductivity

Conductivity 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 with the solution used. At least 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 at least half an hour before observations were recorded. The values of resistance and conductivity are given in Table II.

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[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).
[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. 744 (1909).

Table I
The System: $Ba(NO_3)_2$–$UO_2(NO_3)_2$–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 $UO_2(NO_3)_2$ solution M	c.c. of $Ba(NO_3)_2$ M/10 added	Concentration of $Ba(NO_3)_2$ solution M	Ratio of the constituents
1	50	5	0.01	0.0	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
23	50	5	0.01	22	0.044	5/22
24	50	5	0.01	23	0.046	5/23
25	50	5	0.01	24	0.048	5/24
26	50	5	0.01	25	0.050	5/25 or 1:4
27	50	5	0.01	26	0.052	5/26

p_H Measurements

The p_H 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 III.

Spectrophotometry

Measurements of per cent transmission, per cent absorption and optical density were made by using a BAUSH and LOMB 50 cycles spectrophotometer. The solutions were maintained at 35 °C by placing them in a thermostat 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 IV.

Table II

Conductivity

Cell Constant: 1.474 Temp. 35 °C ± 0.05°C

Soln. No.	c.c. of $Ba(NO_3)_2$ Added to 5 c.c. $UO_2(NO_3)_2$ 0.1 M	Resistance Ohms	Conductance $\times 10^4$ Mhos
1	0.0	596	16.77
2	1.0	500	20.00
3	2.0	450	22.20
4	3.0	385	25.90
5	4.0	320	21.20
6	5.0	332	30.12
7	6.0	270	37.00
8	7.0	250	40.00
9	8.0	230	43.50
10	9.0	220	45.45
11	10.0	205	48.70
12	11.0	196	51.00
13	12.0	185	54.00
14	13.0	180	55.50
15	14.0	170	58.80
16	15.0	160	62.50
17	16.0	154	64.40
18	17.0	150	66.60
19	18.0	146	68.50
20	19.0	140	71.40
21	20.0	135	74.00
22	21.0	130	76.90
23	22.0	125	80.00
24	23.0	120	83.30
25	24.0	115	86.90
26	25.0	112	89.20
27	26.0	108	92.60

Table III

The System: $Ba(NO_3)_2$–$UO_2(NO_3)_2$–H_2O

Property p_H-Measurements

Phillips G. M. 4494 Model

Soln. No.	c. c. of $Ba(NO_3)_2$ 0.1 M Added to 5c.c. $UO_2(NO_3)_2$ 0.1 M	p_H-Measurements
1	0.0	3.16
2	1.0	3.30
3	2.0	3.32
4	3.0	3.32
5	4.0	3.28
6	5.0	3.22
7	6.0	3.23
8	7.0	3.34
9	8.0	3.24
10	9.0	3.24
11	10.0	3.25
12	11.0	3.26
13	12.0	3.26
14	13.0	3.26
15	14.0	3.27
16	15.0	3.27
17	16.0	3.27
18	17.0	3.28
19	18.0	3.28
20	19.0	3.28
21	20.0	3.28
22	21.0	3.28
23	22.0	3.27
24	23.0	3.27
25	24.0	3,27
26	25.0	3,26
27	26.0	3.26

Observation and Conclusion

When these values of resistance, conductivity, p_H, % transmittance, % absorption and optical density of the solutions were plotted against the volume of barium 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 is a definite break in the regular curves at concentration corresponding to 5 c.c. of barium nitrate. The ratio of

Table IV

The System: $UO_2(NO_3)_2$–$Ba(NO_3)_2$–H_2O

Property: Spectrophotometry Temp. = 35 ± 0.05 °C

BAUSH and LOMB (Spectrophotometer) Wavelengths 400 mμ, 450 mμ

Soln. No.	c.c. of $Ba(NO_3)_2$ (0.1 M) added to 5 c.c. $UO_2(NO_3)_2$ 0.1 M	% Transmittance		% Absorption		Optical Density	
		Wave-length 400 mμ	Wave-length 450 mμ	Wave-lenght 400 mμ	Wave-length 500 mμ	Wave-length 400 mμ	Wave-length 450 mμ
1	0.0	83.0	93.0	17.0	7.0	0.081	0.032
2	1.0	81.0	92.5	19.0	7.5	0.092	0.034
3	2.0	81.0	94.0	19	6.0	0.092	0.027
4	3.0	82.0	95.0	18	5.0	0.086	0.022
5	4.0	83.0	97.0	17	3.0	0.081	0.013
6	5.0	79,0	95.0	21	5.0	0.102	0.022
7	6.0	83.0	96.0	17	4.0	0.081	0.018
8	7.0	82.5	96.5	17.5	3.5	0.0835	0.0155
9	8.0	81.0	96	19.0	4.0	0.092	0.018
10	9.0	81.0	95	19.0	5.0	0.092	0.022
11	10.0	81.0	95	19.0	5.0	0.092	0.022
12	11.0	81.5	84.5	18.5	5.5	0.089	0.0245
13	12.0	82.0	94	18.0	6.0	0.086	0.027
14	13.0	82.5	94	17.5	6.0	0.0835	0.027
15	14.0	83.0	94.5	17.0	5.5	0.081	0.0245
16	15.0	83.0	94.0	17.0	6.0	0.081	0.0270
17	16.0	82.5	94.0	17.5	6.0	0.0835	0.0270
18	17.0	82.0	93.5	18.0	6.5	0.086	0.0295
19	18.0	82.0	93.0	18.0	7.0	0.086	0.032
20	19.0	82.0	93.0	18.0	7.0	0.086	0.032
21	20.0	82.5	93.0	17.5	7.0	0.0835	0.032
22	21.0	83.0	93.5	17.0	6.5	0.0810	0.0395
23	22.0	83.5	93.5	16.5	6.5	0.0785	0.0295
24	23.0	83.0	93.0	17.0	7.0	0.0810	0.032
25	24.0	82.5	93.5	17.5	7.0	0.0815	0.032
26	25.0	82.5	93.0	17.5	7.0	0.0835	0.032
27	26.0	83.0	93.5	17.0	6.5	0.081	0.0295

barium nitrate to uranyl nitrate at this point is (1:1) which corresponds to the following compound of the formula:

$$Ba(NO_3)_2 \cdot UO_2(NO_3)_2.$$

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 break occurs at exact

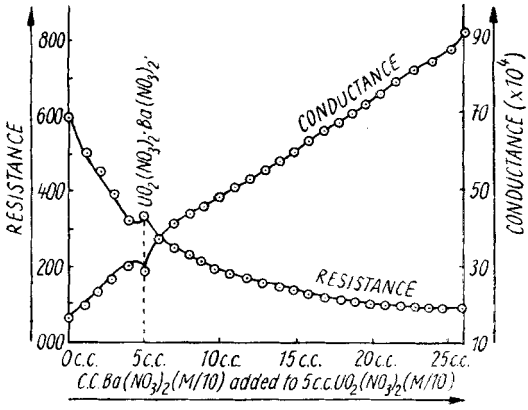

Fig. 1. The System: $UO_2(NO_3)_2$—$Ba(NO_3)_2$—H_2O. Resistance and Conductance, Temp. = 35 ± 0.05°C

stoichiometric ratio of concentrations corresponding to the compound stated above. Thus the existence of this compound becomes unequivocal when such dissimilar properties like conductivity, p_H and spectrophotometric measurements yield similar results.

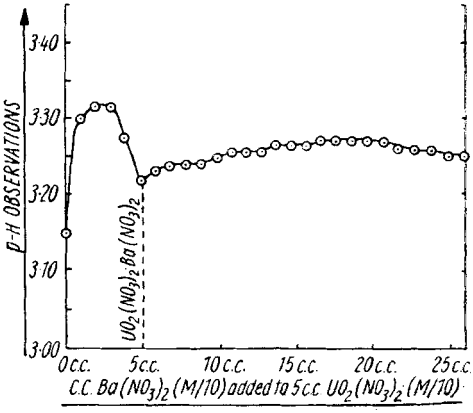

Fig. 2. The System: $UO_2(NO_3)_2$—$Ba(NO_3)_2$—H_2O. P_H Observations. Temp. = 35 ± 0.05 °C

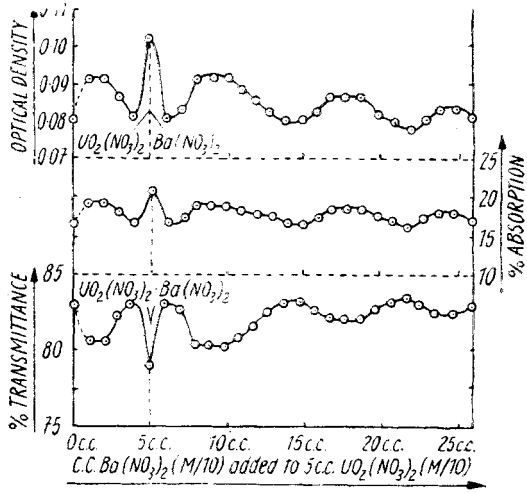

Fig. 3. The System: $UO_2(NO_3)_2$–$Ba(NO_3)_2$–H_2O. Spectrophotometry, Wavelength = 400 mμ

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