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Formation of Complex Compounds between Uranyl Nitrate and Lead Nitrate. VIII

The System: $Pb(NO_3)_2$-$UO_2(NO_3)_2$-H_2O (Conductivity, pH and Spectrophotometry)

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With 3 Figures

Summary

Determinations of conductivity, pH and spectrophotometric measurements of a series of mixed solutions of uranyl nitrate and lead nitrate, indicate the existence of two definite complex compounds in solution, namely: (1) $Pb(NO_3)_2 \cdot UO_2(NO_3)_2$ and (2) $2\,Pb(NO_3)_2 \cdot UO_2(NO_3)_2$.

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 uranyl nitrate and lead nitrate were prepared in such a way that the concentration of uranyl nitrate was kept constant while that of lead nitrate varied systematically, and the physico-chemical properties measured. When the values are plotted against the concentration of lead nitrate, curves are obtained with two specific breaks. The kinks occur at exact stoichiometric ratios of concentrations corresponding to thecompounds noted above.

Introduction

A survey of literature reveals that almost all the salts formed by hexavalent uranium with acids are salts of uranyl ion $(UO_2)^{++}$, which behaves like a compound metal. It also has a strong tendency to form complex salts. The uranyl ion has a strong tendency to increase its covalency by complex formation, either by adding two ammonia molecules, as in $(H_3N)_2UO_2Cl_2$, or by forming a complex salt with alkaline salts, as in $K_2[UO_2Cl_4]$. Uranyl nitrate forms similar compounds of the composition: $UO_2(NO_3)_2 \cdot 2\,B$, where B is NH_3, pyridine, or quinoline. But great majority of these complexes are double salts and they are formed by all kinds of metals in very large number[2]). Uranylnitrate forms two series (types) of compounds with alkali nitrates:

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

[2]) GMELIN, "Uranium", pp. 186–237 (1936).

I. $M\,UO_2(NO_3)_3$ (e. g. K, NH_4, Rb, Cs) all anhydrous but most of them very hygroscopic, and also:

II. $M_2\,UO_2(NO_3)_4$ (e. g. K, NH_4, Rb, Cs). In this way almost all the alkali salts form complex compounds with corresponding uranyl salts. It has also been noticed that very little work has been done on the formation of complex compounds between uranyl nitrate and alkaline earth nitrates or lead nitrate. Therefore, it was thought desirable by us to study this class of compounds. The system: lead nitrate-uranyl nitrate-water, has been investigated by us. 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 of uranyl nitrate and lead nitrate are recorded. The sensitivity of the spectrophotometric method is of such a degree of accuracy that it may be used to detect almost all the complexes present in the system. All the physico-chemical properties investigated reveal the existence of two complex compounds noted above.

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 lead nitrate was made by Monovariation method, i. e., the concentration of uranyl nitrate was kept constant (0.01 M), while that of lead nitrate varied systematically from (0.0 M) to (0.052). The composition of the solutions is shown in column (2) of Table I.

Conductivity

Measurements of conductivity were made by conductivity assembly Electronic Magic-eye (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 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.

Spectrophotometry

Measurements of transmission and absorption were made by a Baush & Lomb 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.

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 III and II.

Table I
Showing the composition of the solution
The System: $Pb(NO_3)_2$–$UO_2(NO_3)_2$–H_2O

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 $UO_2(NO_3)_2$ solution M	c. c. of $Pb(NO_3)_2$ M/10 added c. c.	Concentration of $Pb(NO_3)_2$ solution M	Ratio of the constituents
1	50	5	0.01	0.0	0.00	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 = 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 = 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 = 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 = 1:4
22	50	5	0.01	21.0	0.042	5/21
23	50	5	0.01	22.0	0.044	5/22
24	50	5	0.01	23.0	0.046	5/23
25	50	5	0.01	24.0	0.048	5/24
26	50	5	0.01	25.0	0.050	5/25 = 1:5
27	50	5	0.01	26.0	0.052	5/26

The values of spectrophotometric observations are recorded in Table IV.

The values of conductivity, pH, % tranmittance, % absorption and optical density are represented graphically in Fig. 1, 2 and 3 respectively.

Observation and Conclusion

On plotting the values of resistance, conductivity and p_H against the varying concentration of lead nitrate added to a fixed volume of uranyl nitrate, the curves shown in figures I and II were obtained. In case of all the curves, two definite breaks were abtained at concentra-

tions corresponding to 5 c.c and 10 c.c of lead nitrate. The molecular ratios of uranyl nitrate at these points are (1:1) and (1:2) respectively. These correspond to the compounds of formulae:

(1) $Pb(NO_3)_2 \cdot UO_2(NO_3)_2$ and (2) $2\,Pb(NO_3)_2 \cdot UO_2(NO_3)_2$

Table II

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

Property: Conductance

Cell Constant = 1.178 Temperature = 35 ± 0.05 °C

Soln. No.	c. c. of $Pb(NO_3)_2$ M/10 added to 5 c. c. $UO_2(NO_3)_2$ M/10 c. c.	Resistance Ohms	Conductance × 10^4 Mhos
1	0	596	16.77
2	1	425	23.50
3	2	350	28.57
4	3	313	31.95
5	4	272	36.76
6	5	280	35.72
7	6	235	42.55
8	7	214	46.73
9	8	205	48.77
10	9	186	52.76
11	10	190	62.63
12	11	166	60.24
13	12	158	63.28
14	13	146	68.49
15	14	142	70.42
16	15	140	71.43
17	15	138	72.46
18	17	126	78.90
19	18	125	80.00
20	19	120	83.30
21	20	113	88.50
22	21	108	92.60
23	22	105	95.20
24	23	104	96.20
25	24	100	100.00
26	25	97	103.09
27	26	95	105.30

Similarly on plotting the values of percent transmittance, per cent absorption and optical density of these solutions against the concentration

of lead nitrate, curves shown in figure III are obtained. In these curves also there are two definite breaks at concentrations corresponding to 5 c.c and 10 c.c of lead nitrate solution. The molecular ratios of uranyl

Table III
The System: $Pb(NO_3)_2$–$UO_2(NO_3)_2$–H_2O
Property: pH Measurements

Soln. No.	c. c. of M/10 $Pb(NO_3)_2$ added to 5. c c. M/10 $UO_2(NO_3)_2$	pH Observations
1	0	3.16
2	1	3.30
3	2	3.27
4	3	3.24
5	4	3.22
6	5	3.20
7	6	3.25
8	7	3.31
9	8	3.35
10	9	3.34
11	10	3.23
12	11	3.30
13	12	3.30
14	13	3.29
15	14	3.28
16	15	3.28
17	16	3.28
18	17	3.28
19	18	3.29
20	19	3.30
21	20	3.31
22	21	3.31
23	22	3.30
24	23	3.30
25	24	3.29
26	25	3.29
27	26	3.28

nitrate and lead nitrate at these points are 1:1 and 1:2 respectively. These ratios correspond to the compounds having the molecular formulae as shown above.

For the present we have assumed that the kinks occur at the stoichiometric proportions corresponding to the two compounds existing in solu-

Table IV

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

Property: Spectrophotometry Temp. = 35 ± 0.05 °C
BAUSH and LOMB. 50 cycles Wavelength: 400 mμ, 425 mμ

Soln. No.	c. c. of $Pb(NO_3)_2$ 0.1 M added to 5 c. c. $UO_2(NO_3)_2$ M/10 c. c.	% Transmission		% Absorption		Optical Density	
		Wave-lenght 400 mμ	Wave-length 425 mμ	Wave-length 400 mμ	Wave-length 425 mμ	Wave-length 400 mμ	Wave-length 425 mμ
1	0	83.0	87.0	17.0	13.0	0.081	0.0610
2	1	85.0	86.5	15.0	13.5	0.071	0.0635
3	2	87.0	87.0	13.0	13.0	0.061	0.0610
4	3	88.0	86,5	12.0	13.5	0.056	0.0635
5	4	84.0	85.5	16.0	14.5	0.076	0.0685
6	5	78.0	84.0	22.0	16.0	0.108	0.0760
7	6	82.0	86.5	18.0	13.5	0.086	0.0635
8	7	82.5	86.5	17.5	13.5	0.0835	0.0635
9	8	82.5	86.0	17.5	14.0	0.0835	0.0660
10	9	82.0	85.5	18.0	14.5	0.086	0.0685
11	10	80.0	83.5	20.0	16.5	0.097	0.0785
12	11	83.0	84.0	17.0	16.0	0.081	0.0760
13	12	84.0	85.5	16.0	14.5	0.076	0.0685
14	13	84.0	85.5	16.0	14.5	0.076	0.0685
15	14	84.0	85.0	16.0	15.0	0.076	0.071
16	15	83.5	85.0	16.5	15.0	0.0785	0.071
17	16	83.0	84.5	17.0	15.5	0.081	0.0735
18	17	82.5	84.5	17.5	15.5	0.0835	0.0735
19	18	82.5	85.0	17.5	15.0	0.0835	0.071
20	19	83.0	85.5	17.0	14.5	0.0810	0.0685
21	20	83.0	85.5	17.0	14.5	0.081	0.0685
22	21	83.0	86.0	17.0	14.0	0.081	0.066
23	22	83.0	86.0	17.0	14.0	0.081	0.066
24	23	82.0	86.5	18.0	13.5	0.086	0.0635
25	24	82.0	86.0	18.0	14.0	0.086	0.066
26	25	82.0	85.5	18.0	14.5	0.086	0.0685
27	26	82.0	85.5	18.0	14.5	0.086	0.0685

tions and have concluded that the two compounds uranyl nitrate and lead nitrate form the compounds corresponding to the formulae given above. An attempt is being made to crystallize out these complexes, if possible, in the solid state and to study their properties in detail. The existence of these complexes become more definite when such widely

differing properties like conductivity, pH and spectrophotometric measurements yield the same observations leading to the same conclusions.

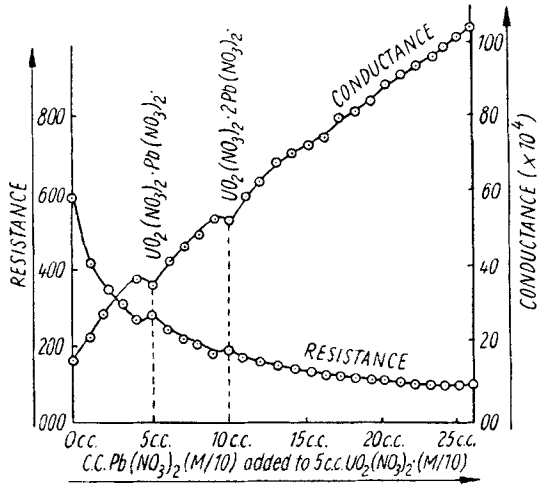

Fig. 1. The System: $UO_2(NO_3)_2$—$Pb(NO_3)_2$—H_2O.
Resistance and Conductance Temp. = 35 ± 0.05° C

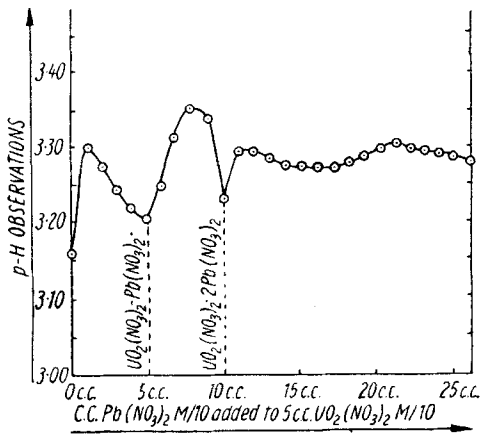

Fig. 2. The System: $UO_2(NO_3)_2$—$Pb(NO_3)_2$—H_2O.
pH Observations Temp. = 35 ± 0.05° C

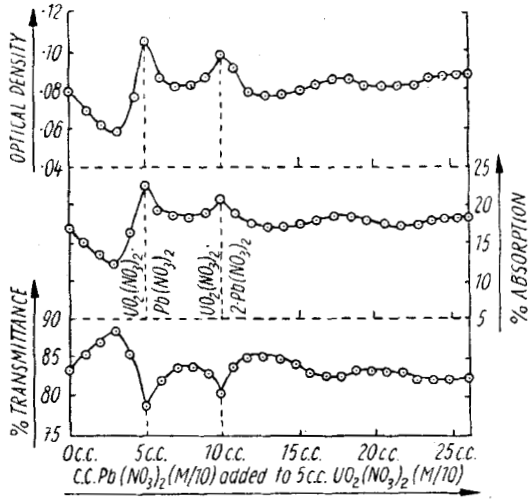

Fig. 3. The System: $UO_2(NO_3)_2 \cdot Pb(NO_3)_2 \cdot H_2O$.
Spectrophotometry Wavelength — 400 mμ

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