Formation of Complex Compounds between Uranyl Nitrate and Alkaline Earth Nitrates. VI

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

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With 3 Figures

Summary

Conductivity, p_H and spectrophotometry measurements with uranyl nitrate — strontium nitrate — water system indicate that one definite complex compound is formed, viz, $Sr(NO_3)_2 \cdot UO_2(NO_3)_2$.

The Monovariation Method of NAYAR and PANDE (Proc. Ind. Acad. Sci. **27**, 286 (1948)) has been followed in the preparation of the solutions and in the investigation of the properties. Aqueous solutions of uranyl nitrate and strontium nitrate were prepared in such a way that the concentration of uranyl nitrate was kept constant in the series while that of strontium nitrate was systematically varied, and the physico-chemical properties measured. When the values were plotted against the concentration of strontium nitrate, curves with one specific break were obtained. There was excellent similarity in the curves with respect to such dissimilar properties as conductivity, p_H and spectrophotometry, so that no doubt is left about the genuineness of the phenomenon. The kink occured at exact stoichiometric ratio of concentration corresponding to the compound noted above.

Introduction

Uranyl group has a strong tendency to form complexes. A survey of literature reveals that even uranyl nitrate has a great tendency for the formation of complex compounds with the nitrates of alkali metals, silver, thallium, mercury, cadmium, nickel and rhodium. R. J. MEYER and F. WENDEL[1]), A. COLANI[2]), A. SACHS[3]), E. RIMBACH[4]), L. LANCEIN[5])

[1]) R. J. MEYER and F. WENDEL, Ber. dtsch. chem. Ges. **36**, 4055 (1903).

[2]) A. COLANI, Compt. rend., **195**, 1475 (1927).

[3]) A. SACHS, Z. Kristallogr. **38**, 498 (1903).

[4]) E. RIMBACHS, Ber. dtsch. chem. Ges. **37**, 46k (1904).

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

and O. DE CONINCK[6]), have made detailed studies of such class of compounds. The complex compounds of uranyl carbonate with carbonates of alkaline earth metals are very well known. No work has been done on the formation of complexes between uranyl nitrate and strontium nitrate. Therefore, it was thought desirable to thoroughly examine the system: strontium nitrate—uranyl nitrate—water by applying the monovariation method of NAYAR and PANDE[7]) and to investigate the number of complexes present in the system. A systematic study now undertaken has revealed the existence of one complex compound in the system. The physico-chemical properties, viz., conductivity, p_H and spectrophotometry have been used to investigate the above system. The sensitivity of the spectrophotometric method is of such degree of accuracy that it may be used to detect almost all the complexes in solution.

Experimental

Strontium nitrate and uranyl nitrate (B. D. H./A. R) were used for the preparation of stock solutions. Strontium nitrate was dissolved to give exactly M/20 solution and a solution of uranyl nitrate of M/20 strength was also prepared. Strontium and uranium were estimated quantitatively by the conventional methods. A set of 27 solutions was prepared by monovariation method. In the solutions the concentration of uranyl nitrate was kept constant (i. e. M/200) while that of strontium nitrate was varied systematically from 0.0 M to 0.26 M. The solutions were stored in thoroughly cleaned, steamed, glass stoppered pyrex bottles. The composition of the 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 for conductivity measurements. The cell was platinised and washed as given (Findlay: Practical Physical Chemistry). The cell was rinsed several times with the solution before conductivity measurements. At least three readings were taken for each solution, usually when the null-point was near or exactly at the centre of the bridge. The temperature of the thermostat was maintained at 35 °C. The values of specific conductivity are tabulated in Table II.

p_H Measurements

p_H measurements of the solutions were made by using a Phillips-G. M. 4494/Model at 35 °C, using a glass electrode. The readings are recorded in Table III.

Spectrophotometry

W. C. VOSBURGH and G. R. COOPER[8]), while using spectrophotometric method showed that if two equimolar solutions of substances that form a soluble coloured complex are

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[6]) O. DE CONINCK, Bull. Acad. roy. Belg. p. 744, (1909).
[7]) NAYAR and PANDE, Proc. Ind. Acad. Sci. **27**, 286 (1948).
[8]) W. C. VOSBURGH and G. R. COOPER, J. Amer. Chem. Soc. **63**, 437 (1941).

Table I
The System: $Sr(NO_3)_2$–$UO_2(NO_3)_2$–H_2O
Composition of Solutions

Soln. No.	Total vol. of solution c. c.	c. c. of $UO_2(NO_3)_2$ M/20 added c. c.	Concentration of $UO_2(NO_3)_2$ solution M	c. c. of $Sr(NO_3)_2$ M/20 added c. c.	Concentration of $Sr(NO_3)_2$ M	Ratio of the constituents
1	50	5	0.005	0	0.000	5/0
2	50	5	0.005	1	0.001	5/1
3	50	5	0.005	2	0.002	5/2
4	50	5	0.005	3	0.003	5/3
5	50	5	0.005	4	0.004	5/4
6	50	5	0.005	5	0.005	5/5 or 1:1
7	50	5	0.005	6	0.006	5/6
8	50	5	0.005	7	0.007	5/7
9	50	5	0.005	8	0.008	5/8
10	50	5	0.005	9	0.009	5/9
11	50	5	0.005	10	0.010	5/10 or 1:2
12	50	5	0.005	11	0.011	5/11
13	50	5	0.005	12	0.012	5/12
14	50	5	0.005	13	0.013	5/13
15	50	5	0.005	14	0.014	5/14
16	50	5	0.005	15	0.015	5/15 or 1:3
17	50	5	0.005	16	0.016	5/16
18	50	5	0.005	17	0.017	5/17
19	50	5	0.005	18	0.018	5/18
20	50	5	0.005	19	0.019	5/19
21	50	5	0.005	20	0.020	5/20 or 1:4
22	50	5	0.005	21	0.021	5/21
23	50	5	0.005	20	0.022	5/22
24	50	5	0.005	23	0.023	5/23
25	50	5	0.005	24	0.024	5/24
26	50	5	0.005	25	0.025	5/25 or 1:5
27	50	5	0.005	26	0.026	5/26

mixed in varying ratios, that ratio which corresponds to the molecular ratio of the components in the complex, will have a maximum (sometimes a minimum) absorbancy at a suitable wave length. If either component is coloured, the absorbancy must be corrected for the contribution to the colour from this component. By plotting the difference between the measured absorbancy and the absorbancy calculated for no interaction against mole per cent (or its equivalent) of either component, a complex formula is readily obtained. The method has successfully been applied in the present work in the investigation in complex compounds in the system: uranyl nitrate — strontium nitrate — water. Measurements of per cent transmittance, absorption and optical density were made by Unicam Spectrophotometer 500 cycles. The solutions were maintained at 30 °C by placing in a thermostat maintained at 30 °C temperature. The composition of the solutions is shown in Table I.

Table II

The System: $Sr(NO_3)_2$—$UO_2(NO_3)_2$—H_2O

Specific Conductance

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

Soln. No.	c.c. $Sr(NO_3)_2$ (M/20) added to 5 c. c. $UO_2(NO_3)_2$ (M/20) c. c.	Resistance Ohms	Conductivity × 10^4 Mhos
1	0.0	1100	13.28
2	1.0	880	16.75
3	2.0	745	19.78
4	3.0	585	25.19
5	4.0	520	28.34
6	5.0	540	27.29
7	6.0	425	34.70
8	7.0	365	40.38
9	8.0	355	41.52
10	9.0	325	45.35
11	10.0	290	50.83
12	11.0	275	53.60
13	12.0	265	55.62
14	13.9	255	57.80
15	14.0	250	58.96
16	15.0	240	61.41
17	16.0	235	62.72
18	17.0	230	64.87
19	18.0	225	65.51
20	19.0	220	67.00
21	20.0	216	68.24
22	21.0	210	70.02
23	22.0	200	73.70
24	23.0	195	75.79
25	24.0	180	81.89
26	25.0	175	84.23
27	26.0	170	86.71

Table III

The System: $Sr(NO_3)_2$—$UO_2(NO_3)_2$—H_2O

Property-p_H-Observations

Temp. 35 ± 0.05 °C

Soln. No.	c. c. of $Sr(NO_3)_2$ M/20 added to 5 c.c. $UO_2(NO_3)_2$ M/20 c. c.	p_H-Observations
1	0.0	3.50
2	1.0	3.63
3	2.0	3.72
4	3.0	3.76
5	4.0	3.78
6	5.0	3.85
7	6.0	3.68
8	7.0	3.68
9	8.0	3.70
10	9.0	3.74
11	10.0	3.75
12	11.0	3.76
13	12.0	3.77
14	13.0	3.77
15	14.0	3.74
16	15.0	3.75
17	16.0	3.74
18	17.0	3.74
19	18.0	3.74
20	19.0	3.77
21	20.0	3.78
22	21.0	3.78
23	22.0	3.76
24	23.0	3.75
25	24.0	3.74
26	25.0	3.74
27	26.0	3.74

Before recording the observations the adjustment was made with a blank of solvent, used in the preparation of solutions. The spectrophotometric observations are given in Table IV.

Observations

On plotting the values of resistance, conductivity and p_H against the varying concentration of strontium nitrate added to a fixed concentration of uranyl nitrate, the curves shown in figures I, II, III were obtained. In case of all the three regular curves one definite break was obtained at the concentrations corresponding to 5 c. c. and 5 c. c. strontium nitrate. The molecular ratios of uranyl nitrate to strontium nitrate at this point is 1:1. This corresponds to the compound of formula (1) $Sr(NO_3)_2 \cdot UO_2(NO_3)_2$.

Table IV
System: $Sr(NO_3)_2$–$UO_2(NO_3)_2$–H_2O

Spectrophotometry Temp. 30 ± 0.05 °C (spectrophotometr) Unicam-Model

Soln. No.	c. c. $Sr(NO_3)_2$ M/10 Added to 5. c. c. $UO_2(NO_3)_2$ (M/10) c. c.	% Transmittance		% Absorption		Optical Density	
		Wave-length 400 mμ	Wave-length 450 mμ	Wave-length 400 mμ	Wave-lenght 450 mμ	Wave-length 450 mμ	Wave-length 400 mμ
1	0.0	83.0	93.0	17.0	7.0	0.0325	0.081
2	1.0	83.0	93.0	17.0	7.0	0.0325	0.081
3	2.0	83.0	93.5	17.0	6.5	0.0300	0.081
4	3.0	82.5	93.5	17.5	6.5	0.0300	0.0835
5	4.0	81.0	92.0	19.0	8.0	0.0375	0.092
6	5.0	78.0	90.0	20.0	10.0	0.0450	0.108
7	6.0	78.0	93.0	21.5	7.0	0.0325	0.105
8	7.0	79.0	93.0	21.0	7.0	0.0325	0.102
9	8.0	79.0	93.0	21.0	7.0	0.0325	0.102
10	9.0	79.5	92.5	20.5	7.5	0.0350	0.0995
11	10.0	80.5	92.5	19.5	7.5	0.0350	0.0945
12	11.0	81.0	92.5	19.0	7.5	0.0350	0.092
13	12.0	81.0	92.0	19.0	8.0	0.0375	0.092
14	13.0	81.0	92.0	19.0	8.0	0.0375	0.092
15	14.0	80.5	92.5	19.0	7.5	0.0350	0.0945
16	15.0	80.5	92.0	19.5	8.0	0.0375	0.0945
17	16.0	80.5	92.0	19.5	8.0	0.0375	0.0945
18	17.0	80.5	91.5	19.5	8.5	0.0388	0.0945
19	18.0	81.0	91.5	19.0	8.5	0.0388	0.092
20	19.0	81.0	91.5	19.0	8.5	0.0388	0.092
21	20.0	81.0	91.5	19.0	8.5	0.0388	0.092
22	21.0	81.0	91.0	19.0	9.0	0.0400	0.092
23	22.0	80.5	91.0	19.5	9.0	0.0400	0.0945
24	23.0	80.5	91.0	19.5	9.0	0.0400	0.0945
25	24.0	80.0	90.5	20.0	9.5	0.0435	0.0970
26	25.0	80.0	90.5	20.0	9.5	0.0435	0.097
27	26.0	80.0	90.0	20.0	10.0	0.0450	0.097

On plotting the values of percent transmittance, per cent absorption and optical density against the concentration of strontium nitrate, the curves shown in figure III are obtained. There is one definite break in the regular curves at concentrations corresponding to 5 c. c. of strontium nitrate solution. The molecular ratios of $UO_2(NO_3)_2$ and $Sr(NO_3)_2$ at this point is 1:1. This ratio corresponds to the compound having the molecular formula, viz. (1) $Sr(NO_3)_2 \cdot UO_2(NO_3)_2$.

For the present we have assumed that the kink occurs at the stoichiometric proportions corresponding to one compound existing in solution and have concluded that the compounds uranyl nitrate and strontium nitrate form the compound corresponding

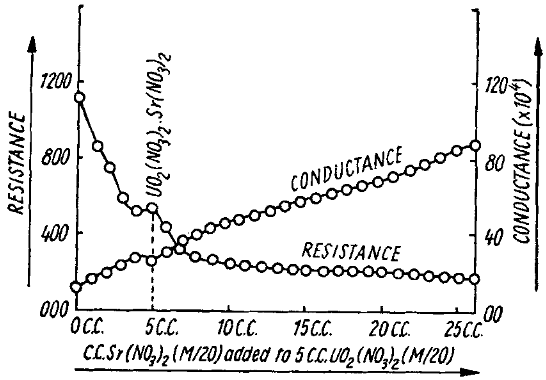

Fig. 1. The System: $UO_2(NO_3)_2$—$Sr(NO_3)_2$—H_2O. Resistance and Conductance, Temp = 35 ± 0.05 °C

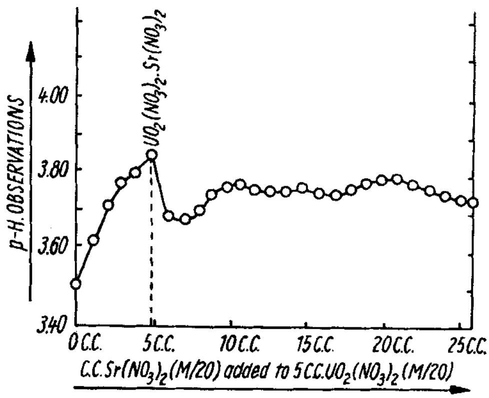

Fig. 2. The System: $UO_2(NO_3)_2$—$Sr(NO_3)_2$—H_2O. p_H Observations, Temp = 35 ± 0.05 °C

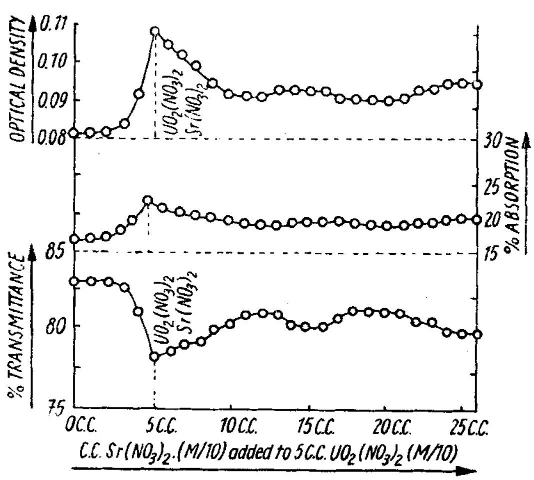

Fig. 3. The System: $UO_2(NO_3)_2$—$Sr(NO_3)_2$—H_2O. Spectrophotometry, Wave-length = 400 mμ

to the formula given above. An attempt is being made to crystallize out this complex compound, if possible, in the solid state.

Conclusion

Conductivity, p_H and spectrophotometric measurements reveal the existence of one definite complex compound namely $Sr(NO_3)_2 \cdot UO_2(NO_3)_2$, in the system: uranyl nitrate — strontium nitrate — water.

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