Formations of Complex Compounds between Uranyl Nitrate and the Nitrates of the First Group Elements. III

The System: $CsNO_3-UO_2(NO_3)_2-H_2O$. (Conductivity, Refractive Index, Colorimetry, pH Viscosity and Surface Tension)

By S. S. Gupta and B. N. Sharga

With 5 Figures

Summary

Conductivity, refractive index, colorimetry, pH, viscosity and surface tension for mixed solutions of uranyl nitrate and cesium nitrate have shown the existence of three complex species in solution in the (1:1), (1:2) and (1:3) molecular ratios respectively, viz.,

$$UO_2(NO_3)_2 \cdot CsNO_3 \quad \text{(i)}$$

$$UO_2(NO_3)_2 \cdot 2\,CsNO_3 \quad \text{(ii)}$$

$$UO_2(NO_3)_2 \cdot 3\,CsNO_3 \quad \text{(iii)}$$

All the above mentioned compounds have been detected only in the solution by the breaks in the usual curves when various properties like conductivity, refractive index, colorimetry, pH, viscosity and surface tension were plotted against the ml of cesium nitrate (M/100) added to a fixed volume of uranyl nitrate (M/100).

Introduction

In the previous communication of this series[1]), the results on the studies of complex compounds between uranyl nitrate and copper nitrate have already been reported. Nayar and Pande[2]), have studied the alkali nitrate of either a transition metal or that of other rare elements. Pande and Misra[3]) have concentrated themselves mainly to study the complex forma-

[1]) S. S. Gupta and B. N. Sharga, J. prakt. Chem. (under publication).

[2]) M. R. Nayar and C. S. Pande, Proc. Ind. Acad. Sci. vol. XXVII, 1948, p. 284—292, 343—348, current science June 1948, 17, 187.

[3]) C. S. Pande and S. K. Misra, J. prakt. Chem. **14**, 164 (1961); **17**, 5 (1962)

tion of uranyl ion with organic ligands as donars and also tried to isolate the complexes in solid state and to some extent they were successful. Analogous system: Rubidium nitrate-uranyl nitrate water was studies by us[4]), in order to investigate the number and nature of complexes present in the system and if possible to isolate them in solid state.

Since no systematic physicho-chemical work appears to have been carried out in the complexes formed by uranyl ion with cesium so it was thought to be of great importance to study and explore such type of complexes in detail. The present communication deals with our studies based on the complex formation between cesium nitrate and uranyl nitrate. The nature of the species present has been detected by taking the help of physico-chemical properties like, conductance, refractive indices colorimetry, pH, viscosity and surface tension which clearly indicated three complexes in the (1:1), (1:2) and (1:3) molecular ratios.

Experimental

A series of 27 mixed solutions were prepared by utilizing Monovariation method[5]), which has been successfully applied by several authors in the investigation of complexes[6]), Materials used of course for the preparation of stock solutions were of A. R./B. D. H. quality. All the solutions were prepared in conductivity water and a high standard of accuracy was tried to be maintained as far as possible. The concentration of uranyl ion was kept constant i. e. (0.05 M) while that of its counterpart cesium nitrate was varied systematically and gradually from (0,0 M) to (0.027 M). All the solutions were stored in thoroughly cleaned stoppered glass bottles. The composition of the solutions was on the same lines as given in the previous communication.

Conductivity: An electrical magic eye apparatus (type: G. M/4249/Phillips) was used to determine the conductivity of the solutions. A pyrex glass conductivity cell with platinum electrodes was used for such measurements. The cell was rinsed several times with the solutions and at least mean of the three readings was taken for each solution. All readings were recorded in an electrically operated and maintained thermostat at 35 ± 0.5 °C. The results are recorded in table no. 1.

Refractive Indices: Measurements of refractive indices were carried out with the help of a direct reading refractometer (Bellingham and Stanley Ltd. Model No. 344223). Before recording the observations temperature was regulated and a high standard of accuracy was tried to be maintained. The values are recorded in table no. 1.

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[4]) S. S. GUPTA and B. N. SHARGA, Z. anorg. allg. Chem. (under publication).

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

[6]) NAYAR and NAYAR, J. Indian Chem. Soc. **29**, 258 (1952) Mata Prasad and others. Proc. Indian Acad. Sci. **36** A, 544 (1952); H. J. KAZI and C. M. DESAI, J. Indian Chem. Soc. **30**, 290—291 (1953); L. N. SRIVASTAVA and P. C. BOSE, J. Indian Chem. Soc. **31**, 411 (1959); **32**, 389 (1955); Z. Physik. Chemie **205**, 96 (1955); K. C. KAIMAL and A. K. BHATTACYARYA, J. Indian Chem. Soc. **33**, 685 (1955).

Colorimetry: Colorimetry measurements were made with a KLETT-SUMMERSON colorimeter. Three readings were taken for each solution. The relative optical densities were calculated and recorded according to table no. 2.

pH Measurements: The pH observations for the solutions were made by employing a BECKMAN pH meter (modell H 2. serial 119943) having a glass electrode. Before taking any reading it was adjusted with an standard buffer solution and only then the observations were recorded. Table No. 2 indicates the values for respective solutions.

Table no. 1

The System: Cesium Nitrate-Uranyl Nitrate-Water

Properties: (Resistance, conductance and refractive index)

Cell constant 0.7426 Temp. 35 °C ± 0.05 °C

Soln. No.	C. C. of $CsNO_3$ (M/100) added to 5 c. c. of $UO_2(NO_3)_2$ (M/100)	Resistance in ohms.	Conductance in Mhos	Refractive Index
1.	0.0 ml	880	11.37	1.437
2.	1.0 ml	790	12.66	1.436
3.	2.0 ml	720	13.89	1.435
4.	3.0 ml	650	15.39	1.435
5.	4.0 ml	600	16.66	1.435
6.	5.0 ml	620	16.13	1.438
7.	6.0 ml	530	18.86	1.435
8.	7.0 ml	500	20.00	1.436
9.	8.0 ml	470	21.28	1.436
10.	9.0 ml	440	22.73	1.435
11.	10.0 ml	450	22.22	1.437
12.	11.0 ml	380	26.31	1.435
13.	12.0 ml	370	27.03	1.434
14.	13.0 ml	360	27.78	1.434
15.	14.0 ml	355	28.17	1.433
16.	15.0 ml	360	27.78	1.436
17.	16.0 ml	345	28.99	1.434
18.	17.0 ml	340	29.42	1.434
19.	18.0 ml	335	29.86	1.435
20.	19.0 ml	330	30.31	1.435
21.	20.0 ml	325	30.77	1.434
22.	21.0 ml	320	31.25	1.434
23.	22.0 ml	315	31.74	1.435
24.	23.0 ml	310	32.25	1.435
25.	24.0 ml	305	32.79	1.434
26.	25.0 ml	300	33.34	1.433
27.	26.0 ml	300	33.34	1.434

Density and Viscosity

Measurements of relative viscosities were made by OSTWALD's viscometer placed in a thermostat maintained at 35 ± 0.5 °C. The instrument used was made of pyrex glass. Special precautions were taken in cleaning the viscometer by water, chromic acid sul-

Table no. 2
The System: Cesium Nitrate-Uranyl Nitrate-Water
Properties: Colorimetry and pH measurements

Soln. No.	C. C. of $CsNO_3$ (M/100) added	% Transmittance.	Optical density	pH
1.	0.0 ml	91.0	0.041	4.15
2.	1.0 ml	91.5	0.038	4.05
3.	2.0 ml	92.0	0.036	4.00
4.	3.0 ml	92.5	0.034	4.00
5.	4.0 ml	93.0	0.032	4.05
6.	5.0 ml	91.0	0.041	4.15
7.	6.0 ml	92.0	0.036	4.10
8.	7.0 ml	92.5	0.034	4.10
9.	8.0 ml	92.5	0.034	4.13
10.	9.0 ml	92.5	0.034	4.10
11.	10.0 ml	91.5	0.041	4.20
12.	11.0 ml	92.5	0.034	4.10
13.	12.0 ml	93.5	0.030	4.15
14.	13.0 ml	93.0	0.030	4.15
15.	14.0 ml	94.0	0.030	4.10
16.	15.0 ml	93.0	0.030	4.15
17.	16.0 ml	95.0	0.028	4.05
18.	17.0 ml	93.0	0.032	4.05
19.	18.0 ml	92.0	0.036	4.10
20.	19.0 ml	92.0	0.036	4.10
21.	20.0 ml	92.0	0.036	4.05
22.	21.0 ml	93.0	0.032	4.00
23.	22.0 ml	93.0	0.032	4.00
24.	23.0 ml	93.0	0.032	4.00
25.	24.0 ml	92.0	0.036	3.80
26.	25.0 ml	92.0	0.036	3.80
27.	26.0 ml	92.0	0.036	4.00

phuric acid mixture and again with water and finally with distilled water and drying in a current of dry air after each experiment.

The density of each solution was determined at the above temperature by the help of pykanometer. The values are recorded according to table no. 3.

Surface Tension

Surface tension was determined by the "drop method" using TRAUBE's stalagometer (c. f. Findlay Practical Physical chemistry). Great care was exercised to ensure that the dropping surface was perfectly free from grease. After each experiment the instrument was cleaned thoroughly as even a trace of grease (invisible) on the dropping surface markedly alters the size of the drops.

Care was also taken to preserve the apparatus from been shaken by the stirring part of the thermostat. The velocity of flow of the liquid in the stalagometer was regulated not by creating a partial vacuum but by attaching a capillary tubing to the upper part of the tube.

Table no. 3

The System: $CsNO_3$—$UO_2(NO_3)_2$—H_2O

Properties: Viscosity and surface tension

Soln. No.	C. C. of $CsNO_3$ (M/100) added	Density	Relative viscosity	Surface tension
1.	0.0 ml	1.0492	1.0632	72.856
2.	1.0 ml	1.0498	1.0394	72.875
3.	2.0 ml	1.0506	1.0430	72.778
4.	3.0 ml	1.0512	1.0426	72.598
5.	4.0 ml	1.0518	1.0441	72.601
6.	5.0 ml	1.0526	1.0481	72.323
7.	6.0 ml	1.0528	1.0480	72.558
8.	7.0 ml	1.0534	1.0502	72.568
9.	8.0 ml	1.0540	1.0530	72.558
10.	9.0 ml	1.0546	1.0560	72.548
11.	10.0 ml	1.0552	1.0592	72.290
12.	11.0 ml	1.0564	1.0580	72.590
13.	12.0 ml	1.0571	1.0606	72.631
14.	13.0 ml	1.0578	1.0637	72.632
15.	14.0 ml	1.0584	1.0672	72.624
16.	15.0 ml	1.0599	1.0670	72.290
17.	16.0 ml	1.0604	1.0654	72.563
18.	17.0 ml	1.0612	1.0770	72.550
19.	18.0 ml	1.0618	1.0794	72.558
20.	19.0 ml	1.0633	1.0805	72.461
21.	20.0 ml	1.0638	1.0829	72.533
22.	21.0 ml	1.0644	1.0853	72.556
23.	22.0 ml	1.0649	1.0877	72.575
24.	23.0 ml	1.0665	1.0889	72.591
25.	24.0 ml	1.0667	1.0922	72.611
26.	25.0 ml	1.0672	1.0932	72.615
27.	26.0 ml	1.0680	1.0942	72.630

Surface tension was calculated by using the formulae

$$\frac{\gamma 1}{\gamma 2} = \frac{n_2 d_1}{n_1 d_2}$$

(Where γ_1 and γ_2 are the surface tensions of the two liquids, n_1 and n_2 on the respective no of drops given by the same volume of liquid the densities of which of course are d_1 and d_2). Water was taken as the standard liquid with = 70.7 dynes/cm at 35 °C. The values are recorded in table no. 3.

Discussions

An examinations of the curves in fig. (1), (2) and (3) which represents the results of conductivity, refractive index, percent transmittance, optical

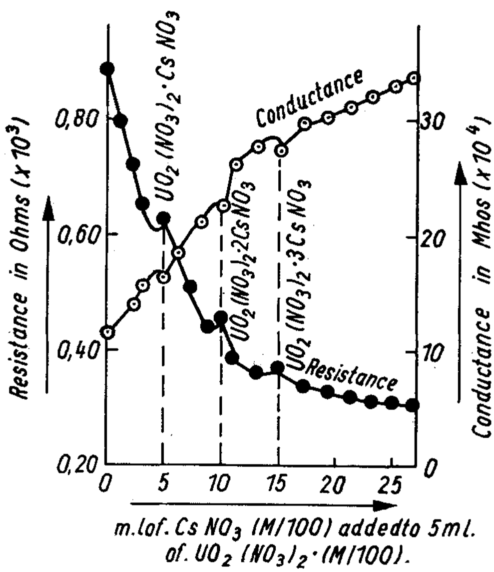

Fig. 1. The System $CsNO_3$—$UO_2(NO_3)_2$—H_2O

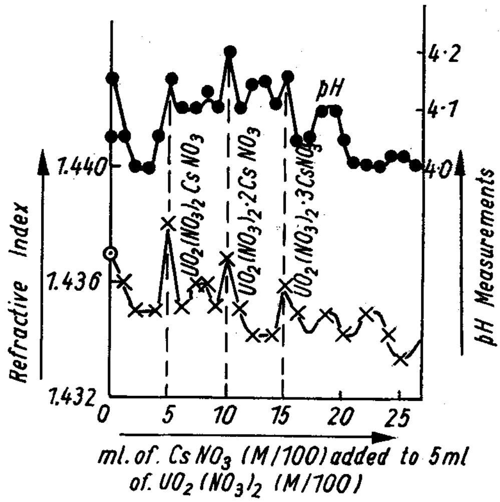

Fig. 2. The System $CsNO_3$—$UO_2(NO_3)_2$—H_2O

density and pH shows that there are three definite breaks in each case in the regular curves at intervals corresponding to 5 c. c., 10 c. c. and 15 c. c. of cesium nitrate solution and it was further seen that while the relation between density and concentration is a linear one, the curve for viscosity and concentration shows three kinks at exactly the same three points as in the case of previous properties. Surface tension when plotted against the volume of cesium nitrate added fig. (4) then again three distinct breaks in the usual

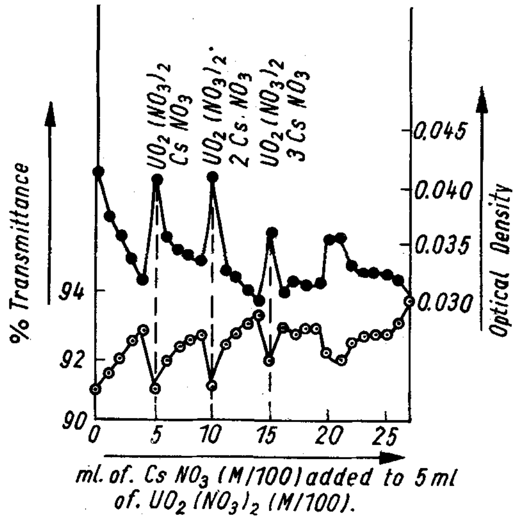

Fig. 3. The System $CsNO_3$—$UO_2(NO_3)_2$—H_2O

curve were observed. As each solution contains same quantity of uranyl nitrate (i. e. 5 c. c. of M/100), the ratios of uranyl nitrate to cesium nitrate at these points are (1 :1), 1:2), and (1:3) which corresponds to the formation of three compounds in solution having the formulae.

$$UO_2(NO_3)_2 \cdot CsNO_3 \text{ or } Cs[UO_2(NO_3)_3]$$
$$UO_2(NO_3)_2 \cdot 2\,CsNO_3 \text{ or } Cs_2[UO_2(NO_3)_4]$$
$$UO_2(NO_3)_2 \cdot 3\,CsNO_3 \text{ or } Cs_3[UO_2(NO_3)_5].$$

The complexes are presumably produced in solution according to the equation:

$$MNO_3 + UO_2\,(NO_3) \rightleftharpoons M\,[UO_2\,(NO_3)_3]$$
[where M = alkali metals]

There is excellent similarity in the curves with respect to all physicochemical properties investigated and therefore there is the least doubt about the genuineness of the phenomenon. The breaks occur at exact stoichiometric ratios of concentrations corresponding to the compounds stated above.

Thus the existence of these compounds become unequivocal when such dissimilar properties yield similar results.

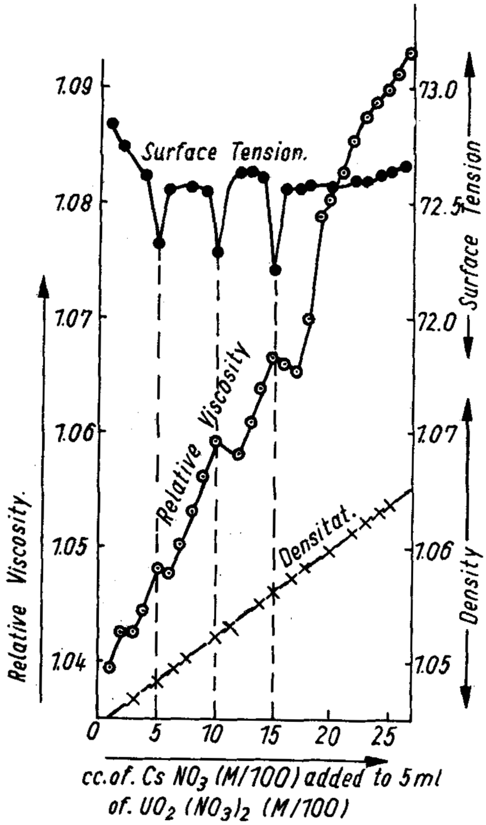

Fig. 4. The System $CsNO_3$—$UO_2(NO_3)_2$—H_2O

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