Studies on Coordination Compounds of Uranyl Acetate with Organic bases. II

The System Uranyl Acetate—Thiourea—Water

By C. S. PANDE and S. K. MISRA[1])

With 1 Figure

Summary

In a previous communication of this series the results on the studies of coordination compounds between Uranyl acetate and Urea have already been reported. The present communication deals with the results of conductometric and viscosity measurements of a series of mixed solutions of Uranyl acetate and thiourea. A graphical representation of the values of these Physicochemical properties reveals the existence of 3 complexes having the molecular formulae:

$$UO_2(CH_3COO)_2 \cdot SC(NH_2)_2 \quad (1)$$

$$UO_2(CH_3COO)_2 \cdot 2\ SC(NH_2)_2 \quad (2)$$

$$UO_2(CH_3COO)_2 \cdot 4\ SC(NH_2)_2 . \quad (3)$$

Out of these only two complexes with a mole ratio of (1:2) and (1:4) have been isolated.

In a previous communication of this series the results on the studies of coordination compounds between Uranyl acetate and Urea have already been reported. P. S. GENTILE and L. H. TALLY[2]) studied the system: Uranyl nitrate-urea, -thiourea and -guanidine in absolute alcohol and also in aqueous solutions. Uranyl nitrate-thiourea mixtures examined by them in absolute alcohol indicated the presence of a complex with a Uranyl/thiourea mole ratio of (1:2). The authors have also reported the existence of one complex in the system: Uranyl nitrate-thiourea-water having a mole ratio of (1:4). Unsuccessful attempts were made by them to isolate these compounds. Analogous System: Uranyl acetate-thiourea-water was studied by us in order to investigate the number and nature of complexes present in the system and in case possible to isolate them in the solid state. Conductometric and viscosity measurements of a series of mixed solutions have revealed the existence of three complexes

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[1]) PANDE and MISRA, J. prakt. Chem. 1960.

[2]) P. S. GENTILE and L. H. TALLY, J. Amer. chem. Soc. **79**, 4296, 5889 (1957).

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Experimental

Materials. Uranyl acetate dihydrate (B.D.H/A.R.), Thiourea (B.D.H/A.R.) were used as such without further purification for the preparation of standard stock solutions.

Procedure: Stock solutions of thiourea (0.4 M), and Uranyl acetate (0.2 M) were prepared in conductivity water. A set of 27 mixed solutions of Uranyl acetate and thiourea was prepared by following monovariation method[3]). In all the solutions the concentration of Uranyl acetate was kept (constant) (i. e. 0.04 M) while that of thiourea varied from (0.0 M to 0.32 M). All the solutions were stored in thoroughly cleaned, steamed, glass stoppered reagent bottles.

Conductivity

Measurements of conductivity were made by using KOHLRAUSCH's meter-bridge method. A pyrex glass conductivity cell with Platinum electrodes was used for such measurements. The cell was rinsed several times with the solution and at least three reading were taken for each solution. All measurements were made in an electrically heated thermostat at 35 °C ± 0.05. The results are recorded in the following Table.

Table

Temperature = 35 ± 0.05 °C Cell constant = 1.5732

Sol. no.	CC. Urea (0.4 M) added to 10 CC UO_2 acetate (0.2 M)	Sp. conductivity (x 10^4)	Vicosity*)
1	0	7.905	1.0252
2	2	7.2000	1.0253
3	3	7.2000	1.0282
4	4	7.2000	1.0292
5	5	7.0000	1.0340
6	6	7.8325	1.0300
7	7	8.2111	1.0292
8	8	8.200	1.0230
9	9	7.8943	1.0320
10	10	7.5345	1.0352
11	12	8.846	1.0320
12	13	8.846	1.0320
13	14	8.6880	1.0328
14	15	8.3000	1.0338
15	16	8.120	1.0370
16	18	7.8325	1.0374
17	20	7.600	1.0420
18	22	7.989	1.0360
19	24	8.250	1.0370
20	26	7.398	1.0380
21	28	7.499	1.0385
22	30	7.395	1.0385
23	32	7.500	1.0405
24	34	7.4880	1.0412
25	36	7.4900	1.0420
26	38	7.500	1.0428
27	40	7.510	1.0440

*) Viscosity values are relative to water (= 1).

[3]) NAYER and PANDE, Proc. Ind. Acad. 1948, 27A, 286.

Viscosity

OSTWALD's viscometer method[4]) was employed in the measurement of relative viscosity. The instrument was thoroughly cleaned by „chromic acid mixture" and finally with distilled water. It was then dried in a current of dry air. The solution was filled in the viscometer and put in a thermostat maintained at 35 °C ± 0.05. At least 3 concordant readings were taken for each solution. The density of the solutions was determined by using the pyknometer. The results of relative viscosity (in relation to water taken as unity i. e. $H_2O = 1$) are shown in the table.

Observation and Conclusion

When the values of sp. conductivity and viscosity of the solutions were plotted against the varying volume of thiourea in the mixture, we obatined curves as shown in the Figure. On examining the curves, it will be noticed that in both curves, there are three definite breaks in the regular curves at intervals corresponding to 5 C.C., 10 C.C. and 20 C.C. of thiourea solution. Since thiourea solution was (0.4 M) in strength, these values correspond to 10 C.C., 20 C.C. and 40 C.C. of 0.2 Molar thiourea solution. As each solution contained same quantity of Uranyl acetate (i. e. 10 C.C of 0.2 M), the ratios of Uranyl acetate to thiourea at these points are (1:1), (1:2), and (1:4), which correspond to the compounds of the formulae:

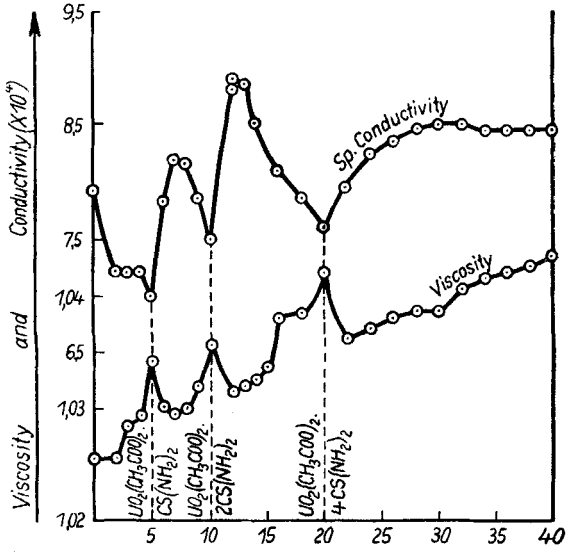

Fig. 1. The System Uranyl acetate—Thiourea—Water (Conductivity and Viscosity). c. c. Thiourea (0.4 M) added to 10 c. c. of UO_2 acetate (0.2 M)

$UO_2(CH_3COO)_2 \cdot SC(NH_2)_2$ (1)

$UO_2(CH_3COO)_2 \cdot 2SC(NH_2)_2$ (2)

and

$UO_3(CH_3COO)_2 \cdot 4SC(NH_2)_2$. (3)

There is excellent similarity in the curves with respect to both the properties investigated. An attempt was made to isolate these compounds in the pure solid state. Out of these, two compounds, namely (I) $UO_2(CH_3COO)_2$. $2\,CS(NH_2)_2$ and (2) $UO_2(CH_3COO)_2 \cdot 4\,CS(NH_2)_2$ have been isolated and their U-content estimated, The experimental values of U-content in these compounds are in excellent agreement with the calculated values for the above molecular formulae.

Preparation of the compounds and estimation of U-content

An attempt was made to prepare these complexes in the solid state. The compounds at the corresponding molar ratios were crystallised out at ordinary temperature using

[4]) FINDLAY, Prac. Physical chemistry VII Edition, 1949, p. 75.

a vacuum desiccator. The crystals were separated, filtered, washed with alcohol and dried in air. Both the compounds formed were fluorescent, yellowish-green crystals.

The U-content in the compounds was determined gravimetrically by „Oxinate" method[5]).

The U-content found in the compounds experimentally is in agreement with the calculated values for U.

$UO_2(CH_3COO)_2 \cdot 2\,SC(NH_2)_2$ – Cal. 10.36%, Found 10.62%;
$UO_2(CH_3COO)_2 \cdot 4\,SC(NH_2)_2$ – Cal. 16.18%, Found 16.41%.

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[5]) A. I. VOGEL, A text book of Quantitative Inorganic Analysis, Edition 1951, p. 471.

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