

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

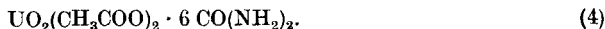
The System Uranyl Acetate—Urea—Water

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With 1 Figure

Summary

Conductivity, Viscosity and p_H measurements of a series of mixed solutions of Uranyl acetate and Urea reveal the existence of four complex compounds in solutions. Viz.,



All these compounds have been isolated in the solid state and their composition has been determined by finding out the U-Content.

All the salts formed by hexavalent uranium with acids are salts of Uranyl ion $[UO_2]^{++}$, which behaves like a compound metal. The Uranyl ion has a strong tendency to increase its covalency by complex formation either by adding two amine molecules, as in $[(H_3N)_2UO_2]Cl_2$ or by forming a complex salt with alkaline salts, as in $K_2[UO_2Cl_4]$.

As already described before the Uranyl group has a very strong tendency to form complexes, and complex salts corresponding to nearly all the simple uranyl salts are known. There are also a certain number of diammines of the type of $(H_3N)_2UO_2Cl_2$. Thus one molecule of Uranyl chloride or bromide will form an addition compound with two molecules of ether, aniline, pyridine, nitrosodimethyl-aniline etc., and uranyl nitrate forms similar compounds of the composition: $UO_2(NO_3)_2 \cdot 2B$, where B is NH_3 , pyridine, or quinoline. Great majority of these complexes are double salts, which are formed in very large numbers by all kinds of melats¹⁾.

¹⁾ SIDGWICK, Chemical Elements and their compounds; (Vol.II, 1950, 1078).

R. RASCANU²⁾, R. RASCANU³⁾ prepared a number of compounds of uranyl salts with a number of organic compounds e. g. pyridine, quinoline, antipyrine, pyrimidine and phenacetin and described their properties in detail.

FRANCIS J. FRERE⁴⁾ prepared uranium 8-hydroxyquinolate.

JOHN T. BARR and CHARLES A. HORTON⁵⁾ reported many uranium compounds with organic bases and acidic complexing agents.

HENRY ALBERS and Coworkers⁶⁾ studied many organic-uranyl compounds.

MUVAFFAK SEYHAN⁷⁾⁸⁾, LOUIS E. MARCHI⁹⁾, O. SCHMITZ and Coworkers¹⁰⁾ and THERALD MOELLER and coworkers¹¹⁾ reported a number of organic uranyl compounds.

PHILIP S. GENTILE and LAWRENCE H. TALLY¹²⁾ have reported the formation of coordination compounds of uranyl nitrate with organic bases e. g. urea, thiourea and guanidine in absolute ethyl alcohol and aqueous solution respectively. Spectro-photometric studies of uranyl-urea, - thiourea and - guanidine systems in absolute alcohol indicated the presence of uranyl-urea and uranyl-thiourea complex with a (1:2) mole ratio and uranyl - guanidine complex with a (1:1) mole ratio. The authors studied the above system in aqueous solutions also and proved the existence of one stable complex of uranyl - urea and uranyl - thiourea with a mole ratio of (1:4) and also uranyl-guanidine compound of (1:1) mole ratio.

The authors have been successful in isolating some of the reported compounds viz. diaquotetraureadioxouranium (VI) nitrate; tetra-ureadioxouranium (VI) nitrate and diureadioxouranium (VI) nitrate. The method employed by the authors was JOB'S continuous variation method¹³⁾. The method has certain limitations¹⁴⁾ especially when more

²⁾ R. RASCANU, *Ann. Sci. Univ. Jassy* **16**, 32-56, 459-96 (1930). Cf. C. A. 1932, **26**, 2934.

³⁾ R. RASCANU, *Ann. Sci. Univ. Jassy* **17**, 130-48 (1933). Cf. C. A. **27**, 3200 (1932).

⁴⁾ J. FRERE FRANCIS, *J. Amer. Chem. Soc.* **55**, 4362-5 (1933).

⁵⁾ T. BARR JOHN and A. HORTON CHARLE, *J. Amer. Chem. Soc.* **74**, 4430-5 (1952).

⁶⁾ HENRY ALBERS and Coworkers, *Chem. Ber.* **85**, 267-78 (1952). Cf. C. A. **47**, 1585e (1953).

⁷⁾ MUVAFFAK SEYHAN, *Chem. Ber.* **86**, 888-9 (1953). Cf. C. A., **48**, 10011e (1954).

⁸⁾ MUVAFFAK SEYHAN, *Chem. Ber.* **87**, 396-9 (1954). Cf. C. A. **49**, 4644h (1955).

⁹⁾ LOUIS E. MARCHI, Cf. C. A. **49**, 5186c (1955).

¹⁰⁾ O. SCHMITZ and Coworkers, Cf. C. A. **49**, 8026 e.f. (1955).

¹¹⁾ THERALD MOELLER and Coworkers, *J. Amer. Chem. Soc.* **76**, 5251-2 (1954).

¹²⁾ P. S. GENTILE and L. H. TALLY, *J. Amer. Chem. Soc.* **79**, 4296 and 5889 (1957).

¹³⁾ P. JOB, *C. R. Acad. Sci. Paris* **180**, 928 (1925).

¹⁴⁾ P. JOB, *Ann. Chim.* **6**, 97 (1936). Cf. C. A. **31**, 231 (1937).

than one complex exists in a particular system. It was thought desirable to investigate the uranyl acetate — urea, — thiourea, and — guanidine systems in aqueous solutions by applying NAYAR and PANDE'S monovariation method¹⁵⁾, which has been very successfully applied by several authors¹⁶⁾ in the investigation of complexes. A number of physico-chemical properties namely conductivity, viscosity and p_H have been used for the investigation of the system: Uranyl acetate — urea — water. The existence of four complexes have been noticed and all the four compounds have been crystallised out in the pure state.

Experimental

Materials — Uranyl Acetate dihydrate (B.D.H./A.R.), Urea (B.D.H./A.R.) were used for the preparation of standard stock solutions without further purification.

Procedure — Stock (0.4 M) solution of urea and (0.2 M) solution of uranyl acetate were prepared by direct weighing. A set of 27 mixed solutions of uranyl acetate and urea was prepared by following Monovariation method. In all the solutions the concentration of uranyl acetate was kept constant (i. e. 0.04 M) while that of urea varied from (0.0 M to 0.32 M). All the solutions were stored in thoroughly cleaned, steamed, glass-stoppered reagent bottles.

Conductivity — Instead of usual KOHLRAUSCH'S meter — bridge method an electrical magic eye apparatus (Type: GM 4249/Philips.) was used to determine the conductivity of the solutions. A pyrex glass conductivity cell, with platinum electrodes, each of about 1 sq. cm. area, having a suitable interelectrode distance, was used. All the measurements were made at a constant temperature by keeping the cell in an electrically controlled thermostat. At least three readings were taken for each solution. The values of sp. conductivity are tabulated below.

Viscosity — Viscosity measurements were made by means of OSTWALD Viscometer¹⁷⁾ The instrument was carefully cleaned everytime by "chromic acid mixture" and finally by filtered distilled water. The measurements were made at $35\text{ }^\circ\text{C} \pm 0.05$ in a thermostat. Densities of the solutions were determined by pycnometer method at the above temperature. The values of relative viscosity are recorded in the table.

p_H -measurements — p_H measurement were made by using a Pye- p_H -meter (Cat. No. 11083) using a glass electrode, the results of which are given in the table.

Observation

When the values of sp. conductivity and viscosity of these solutions were plotted against the varying volume of urea in the mixture, curves

¹⁵⁾ NAYAR and PANDE, Proc. Ind. Acad. Sci. **27A**, 286 (1948).

¹⁶⁾ NAYAR and NAYAR, J. Indian chem. soc. **29**, 250 (1952); M. PRASAD and others, Proc. Indian Acad. Sci. **36A**, 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 (1954); **32**, 389 (1955); Z. Physik, Chem. **205**, 96 (1955); K. C. KAIMAL and A. K. BHATTACHARYA, J. Indian chem. Soc. **33**, 685 (1955).

¹⁷⁾ FINDLAY, Pract. Physical Chemistry, Edition VII 1949, P. 75.

Temp. 35 °C ± 0.05

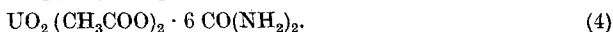
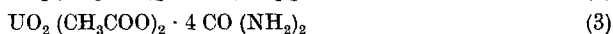
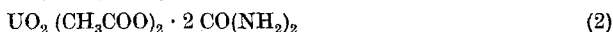
Table

Cell constant = 1.5732

Sol. No.	c.c. urea(0.4M) added to 10 cc UO ₂ acetate (0.2 M)	Sp. conductivity (× 10 ⁴)	Viscosity ¹⁾	pH
1	0	7.905	1.0288	2.67
2	2	7.866	1.0288	2.80
3	3	7.866	1.0288	2.83
4	4	7.866	1.0288	2.87
5	5	7.490	1.0311	2.90
6	6	8.323	1.0293	2.95
7	7	8.503	1.0280	3.04
8	8	8.503	1.0288	3.06
9	9	8.368	1.0295	3.07
10	10	7,674	1.0352	3.09
11	12	8.359	1.0316	3.11
12	13	8.450	1.0316	3.13
13	14	8.460	1.0295	3.15
14	15	8.470	1.0295	3.18
15	16	8.490	1.0295	3.17
16	18	8.500	1.0311	3.19
17	20	8.193	1.0349	3.00
18	22	7.866	1.0297	3.20
19	24	8.359	1.0311	3.22
20	26	8.550	1.0316	3.20
21	28	8.458	1.0336	2.90
22	30	8.193	1.0379	2.60
23	32	8.740	1.0336	2.75
24	34	9.252	1.0319	2.78
25	36	9.146	1.0329	2.80
26	38	9.146	1.0318	2.80
27	40	9.146	1.0318	2.80

1) Viscosity values are relative to water = 1.

were obtained as shown in the figure. On examining these curves, it will be noticed that in both curves there are four definite breaks in the regular curves at intervals corresponding to 5 cc., 10 cc., 20 cc. and 30 cc. of urea solution. Since urea solution was 0.04 M in strength, these values correspond to 10 cc., 20 cc., 40 cc. and 60 cc. of 0.02 M urea solution. As each solution contained same quantity of uranyl acetate (i. e 10 cc. of 0.02 M), the ratios of uranyl acetate to urea at these points are 1:1, 1:2, 1:4 and 1:6 which correspond to the compounds of the formulae:



There is excellent similarity in the curves with respect to both the properties investigated. A graphical representation of p_H values of these solutions as shown in the figure also confirms the existence of the last two compounds.

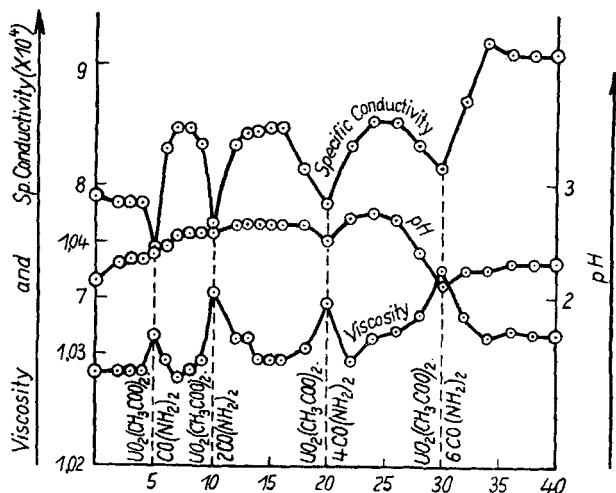
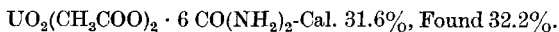
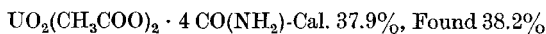
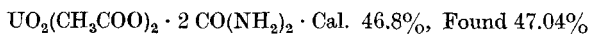
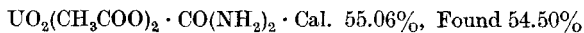


Fig. 1. The System Uranyl acetate—Urea—Water. Conductivity, Viscosity, and p_H . c. c. Urea (0.4 M) added to 10 c. c. of UO_2 acetate (0.2 M)

After ascertaining the existence of the above mentioned four compounds in the system, an attempt was made to isolate these compounds in the solid state. The compounds at the corresponding molar ratios were crystallised at ordinary temperature using a vacuum desiccator. The crystals were separated, filtered, washed with alcohol and dried in air. All the compounds formed were fluorescent, yellowish-green, needle-shaped crystals.

The U-content in the compounds was determined by the „Oxinate“ method¹⁸⁾.

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



¹⁸⁾ A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, Edition 1951, p.471.

Our sincerest thanks are due to Professor Dr. A. B. SEN, Head of the Chemistry Department, for providing all laboratory facilities and encouragement. Thanks are also due to Scientific Research Grants Committee (U. P.) for awarding one of us (S.K.M), a research Assistantship and a contingency grant.

Lucknow (India), Inorganic Chemical Laboratory, Lucknow University.

Bei der Redaktion eingegangen am 24. Juni 1960.