Studies on Coordination Compounds of Uranyl Acetate with Amino-Acids

The System: Uranyl Acetate—Glycine—Water

By S. S. Gupta, D. P. Garg and S. D. Marwah (Miss)

With 3 figures

Summary

Conductometry, colorimetry, pH and Refractive Index of the mixed solution of ura acetate and glycine revealed the existence of three complexes in (1:1), (1:2) and (1 molecular ratios. The compounds were crystallized and petrographic studies of the crys were made.

Introduction

No systematic physico-chemical studies seem to have been carried out the complexes, formed by uranyl ion with glycine and its derivatives i. methyl glycine, ethyl glycine and phenyl glycine etc. Studies have recen been carried out on the complexes formed by uranyl ions with some otl acids by a number of pioneer workers. Muller[1]), studied complex ura compounds of ascorbic acid and their properties. Sulphosalicylic acid for 1 : 1 complex with UO_2 group[2]). Similarly $CH_2ClCOOH$[3]), B-hydroxy-naj thoic acid[4]), hydroxamic acid[5]), have all been found to form complexes w uranyl ion.

The survey of the literature further reveals that only preliminary in stigations on the complexes of uranyl acetate with glycine have been ma by Normal C. L. Brother, E. Doody and J. M. White[6]). These work investigated through ion-exchange and solvent extraction technique

[1]) A. Müller, J. prakt. Chem. **157**, 89 (1940).

[2]) R. T. Foley and R. C. Anderson, J. Amer. chem. Soc. **71**, 909 (1949).

[3]) Ahrland, Acta chem. Scand. **3**, 783 (1949).

[4]) R. Cernatescu and M. P. Poni, Acta Rep. Populare Romane, Bul. Stunt., A. 241 (1949).

[5]) A. S. Bhaduri and P. Ray, Science and Culture (India) **18**, 97 (1952).

[6]) N. C. L. Brother, E. Doody and J. M. White, J. Amer. chem. Soc. **80**, 5901 (195 Cf. Chem. Abstr. **48**, 5707g; **51**, 7783b.

tained convincing results, about the existence of one uranyl complex (with U^{233}) of glycine in 1 : 1 ratio.

The work of K. YAMASAKI and K. SUZUKI[7]), on the stability of chelates of bivalent metals formed with N-phenylglycine and related compounds furnished convincing results on the formation of complex compounds of glycine derivatives.

Table 1
The system: $UO_2(CH_3COO)_2$—$NH_2 \cdot CH_2 \cdot COOH$—$H_2O$

Soln. No.	Total vol. of the soln.	C. C. of N/10 $UO_2(CH_3COO)_2$	Concentration of $UO_2(CH_3COO)_2$ Soln.	C. C. of glycine added	Conc. of Glycine added	Ratio of the constituents
1.	50 c. c.	5 c. c.	0.01	0.0	0.000	5/0
2.	50 c. c.	5 c. c.	0.01	1.0	0.002	5/1
3.	50 c. c.	5 c. c.	0.01	2.0	0.004	5/2
4.	50 c. c.	5 c. c.	0.01	3.0	0.006	5/3
5.	50 c. c.	5 c. c.	0.01	4.0	0.008	5/4
6.	50 c. c.	5 c. c.	0.01	5.0	0.010	5/5 or 1:1
7.	50 c. c.	5 c. c.	0.01	6.0	0.012	5/6
8.	50 c. c.	5 c. c.	0.01	7.0	0.014	5/7
9.	50 c. c.	5 c. c.	0.01	8.0	0.016	5/8
10.	50 c. c.	5 c. c.	0.01	9.0	0.018	5/9
11.	50 c. c.	5 c. c.	0.01	10.0	0.020	5/10 or 1:2
12.	50 c. c.	5 c. c.	0.01	11.0	0.022	5/11
13.	50 c. c.	5 c. c.	0.01	12.0	0.024	5/12
14.	50 c. c.	5 c. c.	0.01	13.0	0.026	5/13
15.	50 c. c.	5 c. c.	0.01	14.0	0.028	5/14
16.	50 c. c.	5 c. c.	0.01	15.0	0.030	5/15 or 1:3
17.	50 c. c.	5.c. c.	0.01	16.0	0.032	5/16
18.	50 c. c.	5 c. c.	0.01	17.0	0.034	5/17
19.	50 c. c.	5 c. c.	0.01	18.0	0.036	5/18
20.	50 c. c.	5 c. c.	0.01	19.0	0.038	5/19
21.	50 c. c.	5 c. c.	0.01	20.0	0.040	5/20 or 1:4
22.	50 c. c.	5 c. c.	0.01	21.0	0.042	5/21
23.	50 c. c.	5 c. c.	0.01	22.0	0.044	5/22
24.	50 c. c.	5 c. c.	0.01	23.0	0.046	5/23
25.	50 c. c.	5 c. c.	0.01	24.0	0.048	5/24
26.	50 c. c.	5 c. c.	0.01	25.0	0.050	5/25 or 1:5
27.	50 c. c.	5 c. c.	0.01	26.0	0.052	5/26
28.	50 c. c.	5 c. c.	0.01	27.0	0.054	5/27
29.	50 c. c.	5 c. c.	0.01	28.0	0.056	5/28
30.	50 c. c.	5 c. c.	0.01	29.0	0.058	5/29
31.	50 c. c.	5 c. c.	0.01	30.0	0.060	5/30 or 1:6

[7]) K. YAMASAKI and K. SUZUKI, Proc. Nat. Acad. Soc. page **56** (1959).

The present investigations deal with the study on complex formation between uranyl acetate and glycine. A thorough investigation by a number of physico-chemical properties as conductance, colorimetry, refractometry and petrography, showed the evidence of the formation of 3-complexes at the molar ratios of

(a) 1:1 i. e. $UO_2(CH_3COO)_2$: NH_2CH_2COOH
(b) 1:2 i. e. $UO_2(CH_3COO)_2$: $2\,NH_2CH_2COOH$
(c) 1:3 i. e. $UO_2(CH_3COO)_2$: $3\,NH_2CH_2COOH$.

Experimental

The stock solutions M/10 uranyl acetate dihydrate (B. D. H./A. R.) and M/10 glycine (B. D. H./A. R.) were prepared for the preparation od mixed solutions A set of 31 solutions was prepared by following NAYAR and PANDE's Monovariation method[7]) viz., the concentration of uranyl acetate was kept constant in all solutions (0.01 M) while that of glycine varied systematically from 0.0 to 0.60 M. The composition of the solutions are given in the table 1.

Colorimetry: Colorimetric measurements were made with a KLETT-SUMMERSON colorimeter 3 readings were taken for each reading. The filter used was 42 No. The wavelength employed was 400—450 mμ. The relative optical densities and percent transmittance were calculated for each solution which are recorded in table 3.

pH Measurements: pH measurements were carried out by using a Pye pH meter. (Cat. No. 1103) using a glass electrode, the results of which are given in table 6.

Table 2

Cell Constant = 1.5132 Temperature = 35 ± 0.1 °C

Conductance System: $UO_2(CH_3COO)_2$—NH_2—CH_2—COOH—H_2O

Soln. No.	Resistance in Ohms	Conductance · 10^5	Soln. No.	Resistance in Ohms	Conductance · 10^5
1.	$0.290 \cdot 10^4 = 2900$	34.48	18.	$0.280 \cdot 10^4 = 2800$	35.71
2.	$0.390 \cdot 10^4 = 3900$	25.64	19.	$0.276 \cdot 10^4 = 2760$	36.23
3.	$0.310 \cdot 10^4 = 3100$	32.26	20.	$0.272 \cdot 10^4 = 2720$	36.76
4.	$0.290 \cdot 10^4 = 2900$	34.48	21.	$0.265 \cdot 10^4 = 2650$	37.73
5.	$0.280 \cdot 10^4 = 2800$	35.71	22.	$0.262 \cdot 10^4 = 2620$	38.16
6.	$0.292 \cdot 10^4 = 2920$	34.24	23.	$0.255 \cdot 10^4 = 2550$	39.21
7.	$0.285 \cdot 10^4 = 2850$	36.08	24.	$0.250 \cdot 10^4 = 2500$	40.00
8.	$0.285 \cdot 10^4 = 2850$	35.08	25.	$0.245 \cdot 10^4 = 2450$	40.81
9.	$0.280 \cdot 10^4 = 2800$	35.71	26.	$0.250 \cdot 10^4 = 2500$	40.00
10.	$0.290 \cdot 10^4 = 2900$	34.48	27.	$0.260 \cdot 10^4 = 2600$	38.46
11.	$0.295 \cdot 10^4 = 2950$	33.89	28.	$0.265 \cdot 10^4 = 2650$	37.73
12.	$0.350 \cdot 10^4 = 3500$	28.57	29.	$0.265 \cdot 10^4 = 2650$	37.73
13.	$0.310 \cdot 10^4 = 3100$	32.26	30.	$0.270 \cdot 10^4 = 2700$	37.03
14.	$0.280 \cdot 10^4 = 2800$	35.71	31.	$0.275 \cdot 10^4 = 2750$	36.36
15.	$0.280 \cdot 10^4 = 2800$	35.71	32.	$0.275 \cdot 10^4 = 2750$	36.36
16.	$0.290 \cdot 10^4 = 2900$	34.48	33.	$0.278 \cdot 10^4 = 2780$	35.97
17.	$0.285 \cdot 10^4 = 2850$	35.87			

Table 3
Colorimetry
System: $UO_2(CH_3COO)_2$—$NH_2 \cdot CH_2 \cdot COOH$—$H_2O$
Colorimeter Model = KLETT SUMMERSON photoelectric Colorimeter

Soln. No.	% Transmittance	% Absorption	Optical Density
1.	77.5	22.5	0.112
2.	76.5	23.5	0.118
3.	76.5	23.5	0.118
4.	75.5	24.5	0.124
5.	76.0	24.0	0.120
6.	77.5	22.5	0.110
7.	77.0	23.0	0.114
8.	76.5	23.5	0.118
9.	77.0	23.0	0.114
10.	77.5	22.5	0.110
11.	77.5	22.5	0.110
12.	76.5	23.5	0.118
13.	77.5	22.5	0.116
14.	75.5	24.5	0.124
15.	77.5	22.5	0.116
16.	77.5	22.5	0.116
17.	75.5	24.5	0.122
18.	76.0	24.0	0.120
19.	76.5	23.5	0.118
20.	76.5	23.5	0.118
21.	77.5	22.5	0.116
22.	76.5	23.5	0.118
23.	77.5	22.5	0.116
24.	76.5	23.5	0.118
25.	76.0	24.0	0.120
26.	77.5	22.5	0.116
27.	76.5	23.5	0.118
28.	75.5	24.5	0.122
29.	76.0	24.0	0.120
30.	76.0	24.0	0.120
31.	77.5	22.5	0.116
32.	76.5	23.5	0.118
33.	76.5	23.5	0.118

Conductance: An electric magic eye apparatus (Type: Gm/4249/ Philips) was used to determine the conductivity of the solution. A Pyrex-glass conductivity cell with platinum electrodes was used for such measurements. The cell was rinsed several times with the solutions and atleast 3 readings were taken for each, solution. All measurements were made in an electrically heated thermostat at 35 ± 0.1 °C. The results are recorded in table 2.

Conductometric Titrations: The same conductivity apparatus was used, as in conductances at the same temperature 35 ± 0.1 °C. Uranyl acetate M/100 50 c. c. was taken in the conductivity cell and titrated with 0.1 ml. of M/10 glycine 3.3 c. c. Results are recorded in the table 5.

Refractive Index: The refractive index was recorded by using the ABBES Refractometer model No. 344223 working at a constant temperature 35 ± 0.1 °C. The results of which are given in the table 4.

Table 4

The System: $UO_2(CH_3COO)_2$—NH_2CH_2COOH—H_2O

Refractometer Model No. 344223 Temp. = 35 °C

Soln. No.	Refractive Index	Soln. No.	Refractive Index	Soln. No.	Refractive Index
1.	1.3320	12.	1.332	23.	1.3355
2.	1.3320	13.	1.3329	24.	1.336
3.	1.3355	14.	1.335	25.	1.336
4.	1.3355	15.	1.335	26.	1.336
5.	1.3355	16.	1.334	27.	1.3365
6.	1.3330	17.	1.3350	28.	1.3340
7.	1.3352	18.	1.3350	29.	1.3345
8.	1.3360	19.	1.335	30.	1.3355
9.	1.3355	20.	1.335	31.	1.336
10.	1.3335	21.	1.334	32.	1.3355
11.	1.3335	22.	1.335	33.	1.336

Petrographic Studies of the System Uranyl Acetate—Glycine—Water

The microscopic study of the crystallization of the compound uranylacetate-glycine has been done and the results of the observations are recorded below:

Colour: Pale green in sections, Pleochroic from colourless to pale-green.

Form: Radiating, unilateral, hexagonal.

Cleavage: Two sets, perfect (0101); less perfect (0001)

Relief: Low, 'n' always less than balsam.

Birefringence: Moderate to very high. Interference colour ranges from bright second order blue, pink, and green to very high order light pink.

Extinction: Ranges from 0 to 30; parallel to the elongation of the crystal.

Figure: Is uniaxial, also pseudobiazial interference figure is seen.

Inclusions: The crystals in this system show that the crystals of glycine are present as inclusions. This indicates that the crystallization of the glycine started first.

Table 5
Conductometric Titrations

Cell constant = 1.5732 Temp. = 35 ± 0 °C

Soln. No.	C. C. of UO_2—AC. M/100 taken	C. C. of Glycine M/10 added	Resistance in Ohms	Conductance in Mhos · 10^5
1.	50 c. c.	0.0 c. c.	3420	29.24
2.	50 c. c.	0.1 c. c.	3500	28.57
3.	50 c. c.	0.2 c. c.	3520	28.41
4.	50 c. c.	0.3 c. c.	3520	28.41
5.	50 c. c.	0.4 c. c.	3550	28.17
6.	50 c. c.	0.5 c. c.	3520	28.41
7.	50 c. c.	0.6 c. c.	3520	28.41
8.	50 c. c.	0.7 c. c.	3520	28.41
9.	50 c. c.	0.8 c. c.	3500	28.57
10.	50 c. c.	0.9 c. c.	3450	28.98
11.	50 c. c.	1.0 c. c.	3500	28.57
12.	50 c. c.	1.1 c. c.	3390	29.79
13.	50 c. c.	1.2 c. c.	3300	30.30
14.	50 c. c.	1.3 c. c.	3320	30.12
15.	50 c. c.	1.4 c. c.	3200	31.25
16.	50 c. c.	1.5 c. c.	3290	30.39
17.	50 c. c.	1.6 c. c.	3200	31.25
18.	50 c. c.	1.7 c. c.	3200	31.25
19.	50 c. c.	1.8 c. c.	3190	31.35
20.	50 c. c.	1.9 c. c.	3200	31.25
21.	50 c. c.	2.0 c. c.	2950	33.90
22.	50 c. c.	2.1 c. c.	3050	32.78
23.	50 c. c.	2.2 c. c.	2950	33.90
24.	50 c. c.	2.3 c. c.	2950	33.90
25.	50 c. c.	2.4 c. c.	3000	33.34
26.	50 c. c.	2.5 c. c.	3010	33.22
27.	50 c. c.	2.6 c. c.	2990	33.44
28.	50 c. c.	2.7 c. c.	2900	34.48
29.	50 c. c.	2.8 c. c.	2890	34.60
30.	50 c. c.	2.9 c. c.	2890	34.60
31.	50 c. c.	3.0 c. c.	3040	32.89
32.	50 c. c.	3.1 c. c.	3040	32.89
33.	50 c. c.	3.2 c. c.	3050	32.78
34.	50 c. c.	3.3 c. c.	3000	33.34

Table 6
pH Titration
pH meter Model No. 1103

Soln. No.	C. C. of UO_2—AC. M/100 taken	C. C. of Glycine M/10 added	pH
1.	50 c. c.	0.0 c. c.	4.25
2.	50 c. c.	0.1 c. c.	4.20
3.	50 c. c.	0.2 c. c.	4.20
4.	50 c. c.	0.3 c. c.	4.20
5.	50 c. c.	0.4 c. c.	4.18
6.	50 c. c.	0.5 c. c.	4.15
7.	50 c. c.	0.6 c. c.	4.17
8.	50 c. c.	0.7 c. c.	4.20
9.	50 c. c.	0.8 c. c.	4.20
10.	50 c. c.	0.9 c. c.	4.18
11.	50 c. c.	1.0 c. c.	4.16
12.	50 c. c.	1.1 c. c.	4.18
13.	50 c. c.	1.2 c. c.	4.18
14.	50 c. c.	1.3 c. c.	4.20
15.	50 c. c.	1.4 c. c.	4.19
16.	50 c. c.	1.5 c. c.	4.17
17.	50 c. c.	1.6 c. c.	4.19
18.	50 c. c.	1.7 c. c.	4.21
19.	50 c. c.	1.8 c. c.	4.21
20.	50 c. c.	1.9 c. c.	4.22
21.	50 c. c.	2.0 c. c.	4.22
22.	50 c. c.	2.1 c. c.	4.21
23.	50 c.c.	2.2 c. c.	4.22
24.	50 c. c.	2.3 c. c.	4.22
25.	50 c. c.	2.4 c. c.	4.23
26.	50 c. c.	2.5 c. c.	4.23
27.	50 c. c.	2.6 c. c.	4.22
28.	50 c. c.	2.7 c. c.	4.23
29.	50 c. c.	2.8 c. c.	4.24
30.	50 c. c.	2.9 c. c.	4.25
31.	50 c. c.	3.0 c. c.	4.26
32.	50 c. c.	3.1 c. c.	4.26
33.	50 c. c.	3.2 c. c.	4.26

Conclusions

The values of various physico-chemical studies given in the tables when represented graphically (Fig. 1—3) the curves indicate three breaks corresponding to 5 c. c., 10 c.c., and 15 c. c. of glycine. The molecular ratios between glycine and uranyl acetate at these points correspond to the com-

pounds:

(i) $UO_2(AC)_2 \cdot NH_2 \cdot CH_2 \cdot COOH$

(ii) $UO_2(AC)_2 \cdot 2\ NH_2CH_2COOH$

(iii) $UO_2(AC)_2 \cdot 3\ NH_2CH_2COOH$

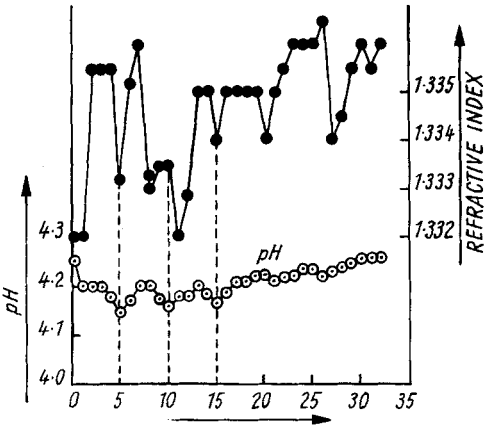

Fig. 1. C. C. of Glycine added to 5 ml $UO_2(AC)_2$ M/10

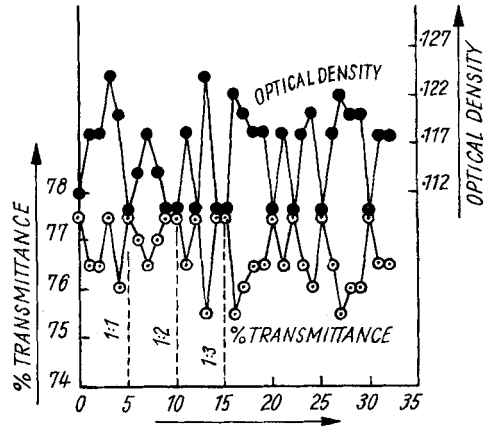

Fig. 2. ml of glycine (M/10) added to 50 ml of $UO_2(Ac_2)_2$ (M/100)

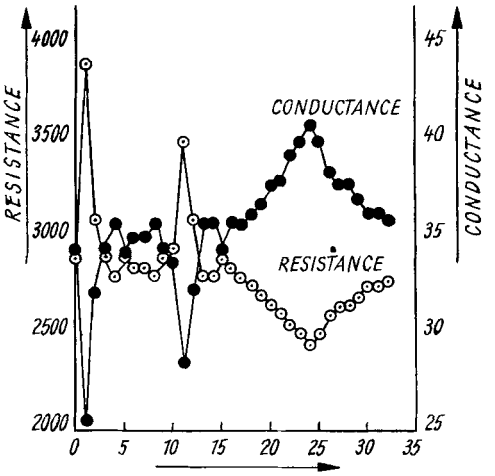

Fig. 3. ml of glycine (M/10) added to 5 ml of uranylacetate (M/10)

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