

Studies on Complexes of Amino Acid  
with Silver of Normal and Abnormal Valencies

## The System: Silver Nitrate—Glycine—Water

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With 4 Figures

### Summary

Conductivity, Spectrophotometry, pH and Refractive Index of the mixed solutions of Glycine and Silver Nitrate revealed the existence of 6 complexes. Three of normal valencies at (2:1, 2:3 and 1:1) molecular ratios and three of abnormal valencies at (1:2, 1:3, 1:4). All were crystallized out except (1:4) and their shapes were found out by microscopic studies.

### Introduction

The Survey of literature brought to light that no physico-chemical studies seem to have been carried out on the effects of Silver ions on Glycine after prolong radiation of very mild and diffused light (visible range). In early dates by VALLADAS-DUBOIS<sup>1)</sup> the system was investigated and only one complex  $(Ag^+ - Gl_2)^-$  was detected (where  $Gl^- = NH_2CH_2COO^-$ ) and its stability constant was also determined. Also  $(HO - Ag^+ - Gl)^-$  was prepared and stability constant was studied. From that time to recent years many workers have studied the stability constants of the complexes  $(AgGl_2)^-$  and  $(AgGl)$  in such system<sup>2)3)</sup>, but no prolong investigations were made.

The actual encouragement was taken from the early works of SUZANNE DUBOIS<sup>4)</sup> who prepared the complex,  $Ag[(CH_2)NH_2COONa]_2$  in alkaline media, giving the idea that the complexes can be formed by Silver ions and glycinates where bonding taking place between Silver and Nitrogen.

Hence this communication explores the previous work. Since this was not very thoroughly dealt with, so it was thought desirable to examine and investigate the system. The physico-chemical properties like conductance,

<sup>1)</sup> SUZANNE VALLADAS-DUBOIS, An.. Chim. (N. S.) **4**, 548—591 (1949).

<sup>2)</sup> S. P. DUTTA and GRZYBOWSK, J. chem. Soc. London **1959**, 1091—1096.

<sup>3)</sup> D. J. AINER, J. chem. Soc. London **1962**, (Aug.) 3282—3284.

<sup>4)</sup> SUZANNE DUBOIS, Compt. Rend. **224**, 113—115 (1947).

pH, Refractive Index, Spectrophotometry were investigated and given certain conclusion.

### Experimental

The stock solutions of (M/20) Silver Nitrate (B. D. H./A. R.) and (M/20) Glycine (B. D. H./A. R.) were prepared for the preparation of the mixed solutions. All solutions were prepared in conductivity water. A set of 32 solutions was made by following NAYAR

Table 1  
The System:  $\text{NH}_2\text{CH}_2\text{COOH}-\text{AgNO}_3-\text{H}_2\text{O}$

Soln. No.	Total of Vol. of the Soln.	c.c. of M/20 $\text{NH}_2\text{CH}_2\text{COOH}$	Concentration of $\text{NH}_2\text{CH}_2\text{COOH}$ Soln.	c.c. of $\text{AgNO}_3$ added	Conc. of $\text{AgNO}_3$ added	Ratio of the Constituents
1	50 c.c.	5 c.c.	0.005	0	0.000	5/0
2	50 c.c.	5 c.c.	0.005	1	0.005	5/1
3	50 c.c.	5 c.c.	0.005	2	0.010	5/2
4	50 c.c.	5 c.c.	0.005	2.5	0.0125	5/2.5 = 2:1
5	50 c.c.	5 c.c.	0.005	3	0.015	5/3
6	50 c.c.	5 c.c.	0.005	4	0.020	5/4
7	50 c.c.	5 c.c.	0.005	5	0.025	5/5 = 2:2 = 1:1
8	50 c.c.	5 c.c.	0.005	6	0.030	5/6
9	50 c.c.	5 c.c.	0.005	7	0.035	5/7
10	50 c.c.	5 c.c.	0.005	7.5	0.0375	5/7.5 = 2:3
11	50 c.c.	5 c.c.	0.005	8	0.040	5/8
12	50 c.c.	5 c.c.	0.005	9	0.045	5/9
13	50 c.c.	5 c.c.	0.005	10	0.050	5/10 = 2:4 = 1:2
14	50 c.c.	5 c.c.	0.005	11	0.055	5/11
15	50 c.c.	5 c.c.	0.005	12	0.060	5/12
16	50 c.c.	5 c.c.	0.005	12.5	0.0625	5/12.5 = 2:5
17	50 c.c.	5 c.c.	0.005	13	0.065	5/13
18	50 c.c.	5 c.c.	0.005	14	0.070	5/14
19	50 c.c.	5 c.c.	0.005	15	0.075	5/15 = 2:6 = 1:3
20	50 c.c.	5 c.c.	0.005	16	0.080	5/16
21	50 c.c.	5 c.c.	0.005	17	0.085	5/17
22	50 c.c.	5 c.c.	0.005	17.5	0.0875	5/17.5 = 2:7
23	50 c.c.	5 c.c.	0.005	18	0.090	5/18
24	50 c.c.	5 c.c.	0.005	19	0.095	5/19
25	50 c.c.	5 c.c.	0.005	20	0.100	5/20 = 2:8 = 1:4
26	50 c.c.	5 c.c.	0.005	21	0.105	5/21
27	50 c.c.	5 c.c.	0.005	22	0.110	5/22
28	50 c.c.	5 c.c.	0.005	22.5	0.1125	5/22.5 = 2.90
29	50 c.c.	5 c.c.	0.005	23	0.115	5/23
30	50 c.c.	5 c.c.	0.005	24	0.120	5/24
31	50 c.c.	5 c.c.	0.005	25	0.125	5/25 = 2:10 = 1:5
32	50 c.c.	5 c.c.	0.005	26	0.130	5/26

and PANDE's mono-variation method<sup>5)</sup> viz. the concentration of Glycine was kept constant in all solutions (0.005 M) the concentration of AgNO<sub>3</sub> was varied from 0.0 to 0.13 M. The composition given in table 1.

Table 2  
U. V. Spectrophotometry  
System: NH<sub>2</sub>CH<sub>2</sub>COOH—AgNO<sub>3</sub>—H<sub>2</sub>O  
Model: Beckman Spectrophotometer  
Temperature: 31 ± °C      Wave Length: 2700 Å

Soln. No.	Optical Density	Transmittance %	Absorption %
1	0.020	95.5	4.5
2	0.022	95.1	4.9
3	0.030	93.3	6.7
4	0.034	92.5	7.5
5	0.024	94.6	5.4
6	0.039	91.4	8.6
7	0.044	90.4	9.6
8	0.034	92.5	7.5
9	0.042	90.8	9.2
10	0.06	87.1	12.9
11	0.056	87.9	12.1
12	0.038	91.6	8.4
13	0.070	85.1	14.9
14	0.067	85.7	14.3
15	0.064	86.3	13.7
16	0.058	87.5	12.5
17	0.046	89.9	10.1
18	0.045	90.2	9.8
19	0.067	85.7	14.3
20	0.054	88.3	11.7
21	0.078	83.6	16.4
22	0.078	83.6	16.4
23	0.067	85.7	14.3
24	0.066	85.9	14.1
25	0.084	82.4	17.6
26	0.079	83.4	16.6
27	0.079	83.4	16.6
28	0.078	83.6	16.4
29	0.079	83.4	16.6
30	0.079	83.4	16.6
31	0.079	83.4	16.6
32	0.079	83.4	16.6

For all such samples which were prepared it was seen that the values of pH fluctuate very much, showing instability of the system, due to photo-

<sup>5)</sup> M. R. NAYAR and C. S. PANDE, Proc. Ind. Acad. Sci. Vol. XXVII, 1948.

chemical changes. Hence they were kept in very diffused and mild light (visible range) for long time. After about 36 hours it was seen giving stable readings and the observations were taken.

U. V. Spectrophotometry: Beckman Spectrophotometer Modell/G 2400 Seriew NR 32054 was used for the observations. The wave length of light used was 2700 Å. Every observation was repeated 2 times at  $31 \pm 0^\circ\text{C}$  optical density was noted and corresponding Transmittance percentage was calculated. Results are given in table 2.

Conductance: Direct reading Magic Eye Soil Tester was used for the conductivity measurements. The made was given as Reg. U. S. PAT OFF. R. D. 26 SER 70859. Every reading was repeated for 2 times at  $31 \pm 0^\circ\text{C}$ . Resistance was calculated. Results are given in table 3.

Refractive Index: Hilger and Watts Ltd. London 27737/M 46.315/56283 Refractometer was used. It was able to give readings upto 3rd decimal place, readings at 4th place was made on the basic of first approx. For this every reading was repeated for 5 times at  $31 \pm 0^\circ\text{C}$ . Dielectric constant was calculated by Maxwell Low. Results are given in table 4.

pH-measurements: Beckman pH-meter  $\text{H}_2$  with glass electrode was used for observations. Experiment was done at  $31 \pm 0^\circ\text{C}$  and every reading was repeated 2 times. Results are given in table 5.

### Preparative work

It was seen that by raising temperature above  $40^\circ\text{C}$  the system started decomposing. This was a big problem for crystallization.

Thus the solutions were taken in very concentrated state having molecular ratios of Glycine and Silver Nitrate at (2:1), (1:1), (2:3), (1:2), (1:3) and were allowed to crystallize in natural way.

For (1:2) system corresponding Na Salt was crystallized.

Along with this, alkaline solution of Sodium Glycinate and  $\text{AgNO}_3$  (2:1) and  $\text{NaNO}_3:\text{NH}_2\text{COOH}:\text{AgNO}_3 = 2:2:1$  were crystallized out.

The authors were not able to crystallize the complex of (1:4). It was seen, the formation of Silver Mirror takes place.

Results: The crystals — (2:1), (where  $\text{GlyH}:\text{AgNO}_3 = 2:1$ ) (2:1:2), (where  $\text{GlyH}:\text{AgNO}_3:\text{NaNO}_3 = 2:1:2$ ), (2:1), (where  $\text{GlyNa}:\text{AgNO}_3 = 2:1$ ) were of Acicular shape (2:3), (where  $\text{GlyH}:\text{AgNO}_3 = 2:3$ ) was also of Acicular shape:

The crystal (1:1), (where  $\text{AgNO}_3:\text{GlyH} = 1:1$ ) was of Prismatic shape. Crystals (1:2) and (1:3) [where  $\text{GlyH}:\text{AgNO}_3 = (1:2)$  and (1:3)] were of capillary shapes.

## Gravimetric estimation

It was seen that certain amount of Ag started ppt.<sup>ing</sup> after the system (2:3) and went on increasing continuously upto (1:2). The quantity remained constant upto (1:3) and then it was seen, as being ppt.<sup>ing</sup>, as huge quantity upto (1:4). It was estimated gravimetrically by Chloride ppt.<sup>ion</sup> method<sup>6)</sup>.

Table 3  
Conductivity Titration  
System:  $\text{NH}_2\text{CH}_2\text{COOH}-\text{AgNO}_3-\text{H}_2\text{O}$   
Made: Magic Eye Soil Tester  
Temperature =  $31 \pm 0^\circ\text{C}$

Soln. No.	Conductance in Millimohs	Resistance $\cdot 10^3$ in ohms.
1	0.10	10.000
2	0.29	3.448
3	0.31	3.226
4	0.31	3.226
5	0.38	2.632
6	0.51	1.961
7	0.55	1.818
8	0.73	1.370
9	1.12	0.893
10	1.30	0.770
11	1.10	0.909
12	1.10	0.909
13	1.10	0.909
14	1.35	0.741
15	1.45	0.689
16	1.50	0.667
17	1.60	0.625
18	1.69	0.592
19	1.78	0.562
20	1.93	0.518
21	2.00	0.500
22	2.05	0.488
23	2.10	0.476
24	2.20	0.455
25	2.25	0.444
26	2.40	0.417
27	2.50	0.400
28	2.60	0.385
29	2.70	0.370
30	2.75	0.364
31	2.80	0.357
32	2.90	0.345

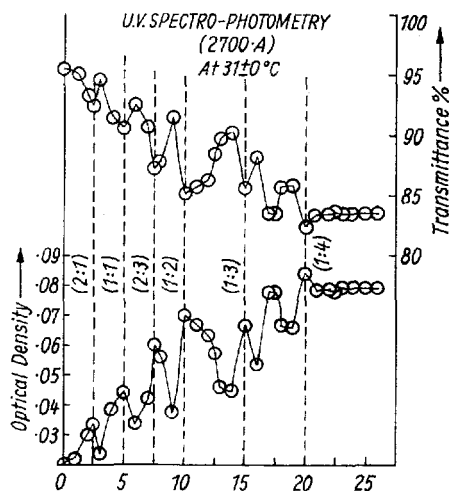


Fig. 1. ml. of  $\text{AgNO}_3$  (M/20) added to 5 ml. glycine (M/20)

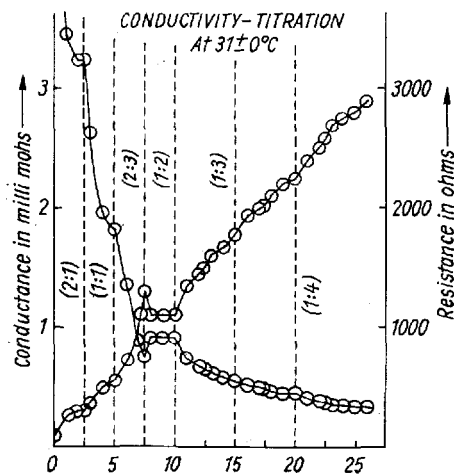


Fig. 2. ml. of  $\text{AgNO}_3$  (M/20) added to 5 ml. glycine (M/20)

<sup>6)</sup> A. I. VOGEL, Quantitative Inorganic Analysis, page 459.

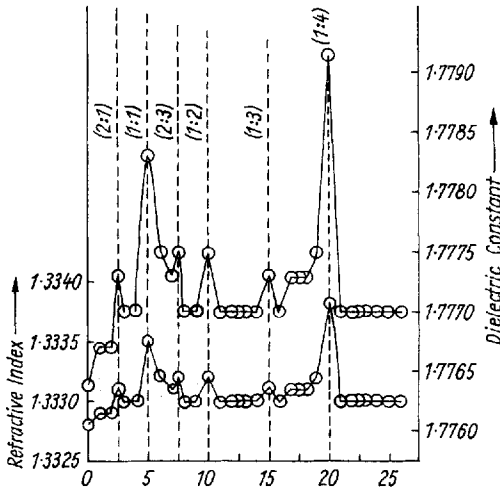


Fig. 3. ml. of  $\text{AgNO}_3$  (M/20) added to 5 ml. glycine (M/20)

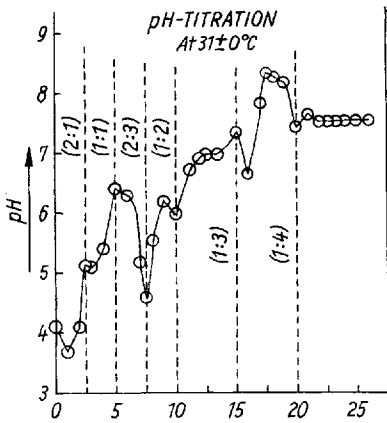


Fig. 4. ml. of  $\text{AgNO}_3$  (M/20) added to 5 ml. glycine (M/20)

Table 4  
Refractive Index and Dielectric Constant  
System:  $\text{NH}_2\text{CH}_2\text{COOH}-\text{AgNO}_3-\text{H}_2\text{O}$   
Made: Hilger and Watts Refractometer  
Temperature =  $31 \pm 0^\circ\text{C}$

Soln. No.	Refractive Index	Dielectric Constant
1	1.3328	1.7764
2	1.3329	1.7768
3	1.3329	1.7768
4	1.3331	1.7773
5	1.3330	1.7770
6	1.3330	1.7770
7	1.3335	1.7783
8	1.3332	1.7775
9	1.3331	1.7773
10	1.3332	1.7775
11	1.3330	1.7770
12	1.3330	1.7770
13	1.3332	1.7775
14	1.3330	1.7770
15	1.3330	1.7770
16	1.3330	1.7770
17	1.3330	1.7770
18	1.3330	1.7770
19	1.3331	1.7773
20	1.3330	1.7770
21	1.3331	1.7773
22	1.3331	1.7773
23	1.3331	1.7773
24	1.3332	1.7775
25	1.3338	1.7792
26	1.3330	1.7770
27	1.3330	1.7770
28	1.3330	1.7770
29	1.3330	1.7770
30	1.3330	1.7770
31	1.3330	1.7770
32	1.3330	1.7770

Result

1. Ag ppt.<sup>ed</sup> from (1:2) (where Glycine: $\text{AgNO}_3$  = 1:2 using M. Sol.) = 0.1690 gm.

2. Ag ppt.<sup>ed</sup> from (1:3) (where Glycine: $\text{AgNO}_3$  = 1:3 using M. Sol.) = 0.1694 gm.

3. Ag ppt.<sup>ed</sup> from (1:4) (where Glycine:AgNO<sub>3</sub> = 1:4 using M. Sol.) = 0.5966 gm.

Conclusion: ppt.<sup>ion</sup> of Silver at (1:2) is equivalent to 1 atom of Silver No ppt.<sup>ion</sup> of Silver at (1:3), ppt.<sup>ion</sup> of Silver at (1:4) is equivalent to 3 atoms of Silver.

### Discussion

Glycine (GIH) is a weak acid having an amino group. Hence its dissociation will be maximum at high pH. This dissociation ( $\text{GIH} \rightleftharpoons \text{GI}^- + \text{H}^+$ ) will be very less when the solution is already rich in H<sup>+</sup> ions. In such a case it will not be possible for a metal to replace H<sup>+</sup>.

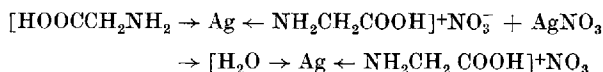
So it happens in this case the pH = 3.7 enables Ag<sup>+</sup> to replace H<sup>+</sup> ions. This pH goes on increasing further confirming that no H<sup>+</sup> ions are liberating and Ag<sup>+</sup> forming a dissociating chelate with glycine, hence removing the acid from the solution. Consequently the pH goes on increasing upto 2.5.

Hence the complex at (2:1) has the formula as  $[\text{Ag}^+ \rightarrow (\text{NH}_2\text{CH}_2\text{COOH})_2]^+\overline{\text{NO}}_3^-$ .

Such type of complex was prepared by SUZANNE-DUBOIS<sup>4)</sup> with Silver and Sodium glycinate, but in alkaline media.

Confirmation: This is being conformed as the crystals formed by GIH: AgNO<sub>3</sub>:NaNO<sub>3</sub> = 2:1:2 and GI Na: AgNO<sub>3</sub> = 2:1 were of identical shapes (Acicular). Also GIH:AgNO<sub>3</sub> = 2:1 was Acicular. This shows the formula of such crystals is  $[\text{AgNHCH}_2\text{COONa}]^+\overline{\text{NO}}_3^-$  not  $[\text{Ag}-\text{OOCCH}_2\text{NH}_2]^-\text{Na}^+$  and also that the author were able to crystallize the crystals of  $[\text{AgNH}_2\text{CH}_2\text{COOH}]^+\overline{\text{NO}}_3^-$  in acidic media.

Again the pH goes on increasing and gets the stable value (6.4) at (1:1) ratio. It can be shown as such



After (1:1) it is seen that the pH goes on decreasing upto (2:3) ratio showing that H<sup>+</sup> ions are being liberated. May be due to such high pH of 6.4 it is possible that the H<sup>+</sup> of GIH is being removed by Ag<sup>+</sup> forming complex between Silver and Silver Glycinate. The reaction can be shown as

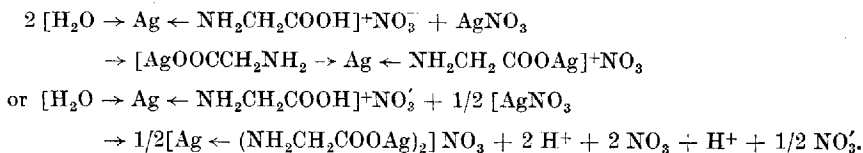




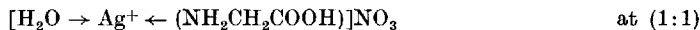


Table 6  
 pH-Titration  
 System:  $\text{NH}_2\text{CH}_2\text{COOH} - \text{AgNO}_3 - \text{H}_2\text{O}$   
 Made: Beckman pH-meter  
 Temperature =  $31 \pm 0^\circ\text{C}$

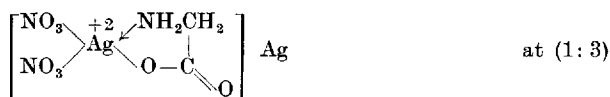
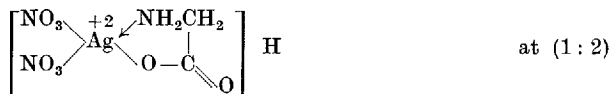
Soln. No.	pH	Soln. No.	pH
1	4.10	17	7.00
2	3.70	18	7.00
3	4.10	19	7.35
4	5.20	20	6.65
5	5.20	21	7.85
6	5.40	22	8.35
7	6.40	23	8.30
8	6.30	24	8.20
9	5.20	25	7.45
10	4.60	26	7.65
11	5.55	27	7.55
12	6.20	28	7.55
13	6.00	29	7.50
14	6.75	30	7.50
15	6.95	31	7.50
16	6.95	32	7.50

### Conclusion

The physico-chemical studies gives the existence of 6 complexes out of which 5 are stable in the Silver-Glycine-Water system.



and 3 of abnormal valencies



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