polated portion of the entropy because of the differences in composition and structure between these compounds and those which were utilized in obtaining the empirical extrapolation formula. Nevertheless we believe that when these data are utilized in conjunction with data obtained in the same way on similar compounds the absolute errors will tend to cancel.

TABLE I

HEAT CAPACITY PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		dl-Alanylglycine			
84.7	0.1254	129.9	0.1670	219.6	0.2385
89.5	.1300	145.5	.1798	237.9	.2516
95.7	.1358	159.4	.1899	260.0	.2694
102.5	.1433	159.6	.1899	276.1	.2816
104.0	.1448	179.9	.2061	284.4	.2876
110.3	.1512	200.2	.2222	290.8	.2924
111.0	.1523	220.3	.2378	296.4	.2973
120.4	.1596				
		Hippuric acid			
84.8	0.1075	145.1	0.1562	260.2	0.2519
89.6	.1111	160.0	.1680	275.8	.2658
95.6	.1160	174.7	.1798	281.1	.2707
103.1	.1228	190.2	.1936	287.7	.2761
111.0	.1292	205.7	.2058	293.3	.2814
120.1	.1369	220.2	.2186	298.4	.2859
129.6	.1440	240.4	.2348		
		Glycylglycine			
86.7	0.1239	136.0	0.1734	244.1	0.2555
91.8	.1292	155.4	.1894	257.6	.2650
97.9	.1355	172.8	.2040	276.2	.2784
103.2	.1417	190.4	.2168	280.3	.2818
110.4	.1486	209.5	.2308	287.2	.2877
117.2	.1561	223.5	.2403	293.9	.2927
		dl-Leucylglycine			
85.7	0.1216	160.4	0.2015	240.2	0.2731
90.8	.1278	170.0	.2102	250.6	.2820
97.6	.1365	179.7	.2189	261.0	.2916
105.9	.1463	189.2	.2279	276.6	.3056
113.7	.1550	200.0	.2375	283.4	.3121
130.9	.1732	209.7	.2466	290.5	.3184
140.6	.1829	220.4	.2556	297.1	.3246
150.4	.1920	230.3	.2626		
		Hippurylglycine			
84.7	0.1066	147.2	0.1622	228.7	0.2236
87.7	.1088	156.4	.1682	241.5	.2337
93.6	.1136	160.7	.1707	253.7	.2438
94.6	.1152	173.6	.1805	262.2	.2508
100.3	.1201	180.7	.1854	265.7	.2534
102.8	.1223	185.9	.1896	277.3	.2638
112.2	.1304	198.0	.1991	281.7	.2673
122.7	.1414	205.9	.2052	287.2	.2716
133.1	.1513	216.7	.2140	296.7	.2808
134.1	.1520				

TABLE II

ENTROPIES OF THE COMPOUNDS

Cal. degree^{-1} mole^{-1}

Substance	S_{90}	$\Delta S_{90-298.1}$	$S_{298.1}$
dl-Alanylglycine	15.84	35.15	51.0
Hippuric acid	18.48	38.72	57.2
Glycylglycine	13.60	31.80	45.4
dl-Leucylglycine	19.71	45.50	67.2
Hippurylglycine	24.14	51.04	75.2

Summary

1. The experimentally determined heat capacities of *dl*-alanylglycine, glycylglycine, *dl*-leucylglycine, hippuric acid and hippurylglycine have been presented.

2. The entropies of the five peptides at 298.1°K. have been calculated.

PASADENA, CALIFORNIA RECEIVED NOVEMBER 18, 1940

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Interaction of Ions and Dipolar Ions. II. The Solubility of Silver Iodate and Lead Iodate in Glycine and in Alanine Solutions[1]

BY R. M. KEEFER AND H. G. REIBER

In a previous communication[2] it was shown that the solubility of barium iodate and calcium iodate at 25° in aqueous glycine or alanine solutions could be expressed by equations of the type

$$\frac{1}{Z_1Z_2}\log\frac{S}{S_\infty} = 0.505\left(\frac{78.54}{D_{\rm d}}\right)^{3/2}\frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} + 0.0625\frac{R^2}{a}[\mathrm{R}^{\pm}] \quad (1)$$

where Z_1 and Z_2 are the valences of the ions; $D_{\rm d}$ is the dielectric constant of the amino acid solution; A, R, and a are constants; and $[R^{\pm}]$ is the molality of the dipolar ions. The solubility of silver iodate or of lead iodate in glycine or in alanine solutions is much larger than could be pre-

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(1) Presented at the Detroit Meeting of the American Chemical Society, September, 1940.

(2) Keefer, Reiber and Bisson, THIS JOURNAL, **62**, 2951 (1940). The following corrections should be made in Part I. The ordinates of Figs. 1 and 2 should be divided by two. The ordinates of Fig. 3 should read 0.01 and 0.02 instead of 0.05 and 0.10. The values of $\Delta\left(\frac{1}{Z_1Z_2}\log S\right)$ in Table IV should be multiplied by 10^{-4}.

dicted using the above equation. Assuming complex ion formation to occur, constant values for the dissociation constant of the complex ion are obtained if one negative ion of the amino acid is assumed to be combined with one silver ion or one lead ion.

Experimental

Silver Iodate.—Solutions of 0.15 *M* potassium iodate and 0.15 *M* silver nitrate were added dropwise with constant stirring to 200 cc. of water. The precipitate, after standing in the mother liquor for three days, was filtered, washed thoroughly, and air dried at room temperature.

Lead Iodate.—Solutions of 0.05 *M* lead nitrate and 0.10 *M* potassium iodate were added dropwise with constant stirring to three liters of distilled water. The precipitate was filtered, washed thoroughly, and air dried at room temperature. A second sample of lead iodate was prepared by the method of LaMer and Goldman.[3] The air dried lead iodate when analyzed iodimetrically was 99.9% lead iodate.

The solubility determinations and method of analysis have been described in a previous communication.[2] In the case of lead iodate several days were allowed for equilibrium to be attained.

Results

The solubilities of silver iodate and lead iodate in glycine and in alanine solutions are given in Table I. The solubility of silver iodate in water at 25.00° was found to be (1.794 ± 0.004) × 10^{-4} *M* as compared to 1.776 × 10^{-4} and 1.79 × 10^{-4} *M* reported in the literature.[4,5] The solubility of the first sample of lead iodate in water was found to be (5.34 ± 0.07) × 10^{-5} *M* while the solubility of the second sample was (3.61 ± 0.04) × 10^{-5} *M*. Other investigators[3,6,7] report 3.61 × 10^{-5}, 5.25 × 10^{-5} and 5.51 × 10^{-5} *M*. The large difference in these values may be explained in part by the difference in particle size due to the method of preparation. The solubility determinations on lead iodate are not reproducible[3] to the accuracy of the analysis which again is probably due to variation in particle size. In Fig. 1 the increase in the logarithm of the solubility[2] of silver iodate due to the dipolar ions, $\Delta\left(\frac{1}{Z_1Z_2}\log S\right)$, is plotted against the molality of the dipolar ions. For comparison similar results obtained for barium iodate and calcium iodate[2] are also included. The curves obtained for silver iodate in glycine or in alanine solutions are not straight lines; furthermore, their limiting slopes are several times larger than those obtained with barium iodate and calcium iodate. Slight variations in these limiting slopes would be expected due to different values of *a*, but the slopes obtained with silver iodate are so high that they would require *a*, the distance of closest approach of an ion to a dipolar ion, to be less than the radius of the dipolar ion. Lead iodate in glycine and alanine solutions also gave abnormal slopes as may be seen from Fig. 2. If any component of the solution were removing some of the silver ions or lead ions by the formation of complex ions, these abnormal slopes would be explainable.

TABLE I

SOLUBILITY OF SILVER IODATE AND LEAD IODATE IN GLYCINE AND ALANINE SOLUTIONS. (MOLES/1000 G. H_2O)

Glycine, *M*	$AgIO_3$, *M* × 10^4	Glycine, *M*	$Pb(IO_3)_2$ sample 1 *M* × 10^5	Glycine	$Pb(IO_3)_2$ sample 2 *M* × 10^5
0	1.794	0	5.34	0	3.61
0.02510	1.859	0.00502	5.47	0.0249	4.05
.03768	1.880	.01003	5.63	.0499	4.45
.05026	1.916	.01505	5.65	.0749	4.81
.07536	1.971	.02510	6.15	.100	5.09
.08234	1.979	.05026	6.40		
.10075	2.020	.08052	6.75		
.1238	2.082	.10074	7.51		
.1654	2.181	.1210	7.70		
.2042	2.223	.2023	9.41		
Alanine		Alanine		Alanine	
0.02511	1.892	0.01081	5.56	0.0248	4.05
.03740	1.924	.01521	5.65	.0495	4.66
.05616	2.001	.02163	5.69	.075	5.06
.07557	2.064	.02704	6.08	.100	5.57
.10092	2.155	.05419	6.30		
		.08142	7.17		

In an isoelectric solution of glycine or alanine, dipolar ions are present at relatively large concentrations and the negative and positive ions are present at relatively small concentrations. Only the negative ion contains an amino group which might be expected to form a complex ion with silver ion or lead ion probably with additional stability being imparted by chelate ring formation with the carboxyl group. If the only bond is between the metallic ion and the amino group, the resulting complex would be a dipolar ion whereas if it were a chelate compound the resulting complex would be uncharged in the case of silver but would have a positive charge in the case of lead. From our data it is not possible to determine which is correct and we will therefore designate the complex as AgR. Assuming one

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[3] LaMer and Goldman, THIS JOURNAL, **52**, 2791 (1930).

[4] Kolthoff and Lingane, *J. Phys. Chem.*, **42**, 133 (1938).

[5] Kohlrausch, *Z. physik. Chem.*, **64**, 129 (1908).

[6] Polesitzkii, *Compt. rend. acad. sci. U. S. S. R.*, **4**, 193 (1935).

[7] Harkins and Winninghoff, THIS JOURNAL, **33**, 1827 (1911).

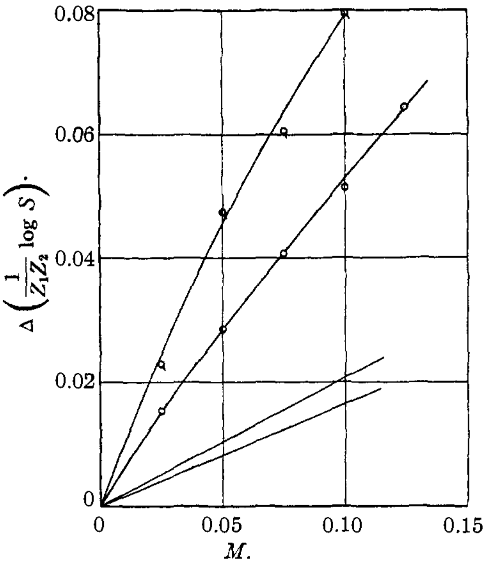
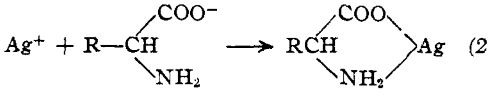
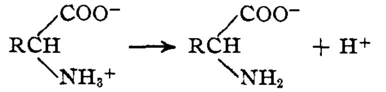


Fig. 1.—Solubility of silver iodate in glycine and in alanine solutions: ○ in glycine and ᑫ in alanine. The two straight lines are for $Ba(IO_3)_2$ and $Ca(IO_3)_2$ in glycine (upper line) and in alanine solutions (lower line).

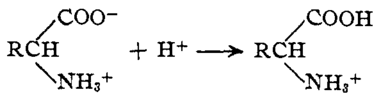
glycinate ion or alaninate ion combines with one silver ion, the following reactions would be involved when silver ion is introduced into a glycine or alanine solution.

 (2)

$$Ag^+ + R{-}CH(COO^-)(NH_2) \longrightarrow RCH(COO)(NH_2)Ag \quad (2)$$

 (3)

$$RCH(COO^-)(NH_3^+) \longrightarrow RCH(COO^-)(NH_2) + H^+ \quad (3)$$

 (4)

$$RCH(COO^-)(NH_3^+) + H^+ \longrightarrow RCH(COOH)(NH_3^+) \quad (4)$$

Reactions 2 and 3 would proceed simultaneously when silver ion is introduced into an isoelectric solution of glycine or alanine causing a shift to the acid side of the isoelectric point although this shift would be neutralized to some extent by the buffering action of equation 4. Fuseya and Murata[8] found that addition of silver nitrate to an isoelectric solution of glycine did not change the *p*H of the solution. In contradiction to this we found the *p*H of a 0.05 *M* solution of glycine to be 6.0 while a 0.05 *M* solution of glycine which was 0.05 *M* in silver nitrate gave a *p*H of 5.2. The dissociation constant of the silver glycinate complex ion was calculated by the following method.

At the low ionic strengths involved the limiting form of the Debye–Hückel equation is valid so equation (1) was modified to

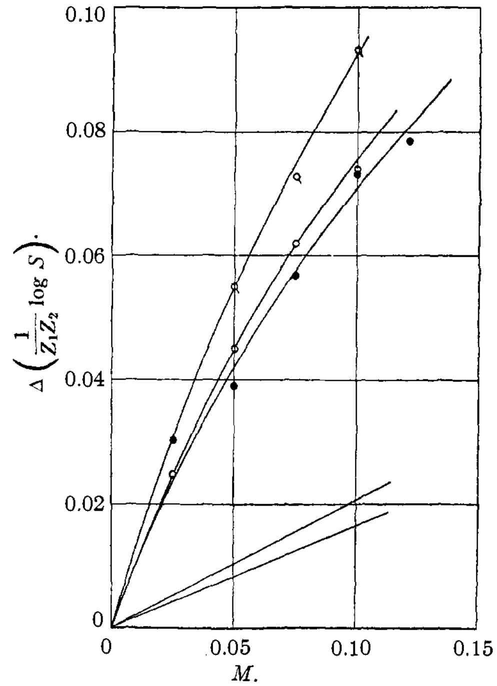


Fig. 2.—Solubility of lead iodate in glycine and in alanine solutions: ○ (sample 1) in glycine, ● (sample 2) in glycine, ᑫ (sample 2) in alanine. The two straight lines at the bottom are for $Ba(IO_3)_2$ and $Ca(IO_3)_2$ in glycine (upper line) and in alanine solutions (lower line).

$$\frac{1}{Z_i^2}\log \gamma_i = 0.505\left(\frac{78.54}{D_d}\right)^{3/2}\sqrt{\mu} + 0.0625\,\frac{R^2}{a}\,[R^{\pm}] \quad (5)$$

Assuming R^2/a to have the same value for silver iodate as was obtained for barium iodate and calcium iodate, the silver ion concentration may be calculated from the equation

$$\log\,[Ag^+] = 1.01\left(\frac{78.54}{D_d}\right)^{3/2}\sqrt{\mu} + \log L + 2k[R^{\pm}] - \log\,[IO_3^-] \quad (6)$$

where $k = 0.207$ for glycine and 0.166 for alanine[2] and L is the solubility product for silver iodate expressed in terms of activities. The concentration of the silver complex ion, AgR, is given by

$$[AgR] = [IO_3^-] - [Ag^+] \quad (7)$$

The concentration of the glycinate or alaninate ion, R^-, was calculated as follows: from equations (2), (3), and the reverse reaction of (4)

$$[AgR] + [R^-] = [R^+] + [H^+] - [H_i^+] \quad (8)$$
$$(H^+)(R^-)/(R^{\pm}) = K_2 \quad (9)$$
$$(H^+)(R^{\pm})/(R^+) = K_1 \quad (10)$$

where $[H_i^+]$ is the concentration of hydrogen ion in the amino acid solution before silver iodate is

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[8] Fuseya and Murata, *J. Phys. Chem.*, **34**, 2001 (1930).

added and $[H^+]$ is the concentration after silver iodate has been added. Equations (8), (9) and (10) could be solved for $[R^-]$ if the activity coefficients of all the ions in equations (9) and (10) were known. This problem is now being investigated. However, in the present case we may assume, since the ionic strength is small and relatively constant, that the activity coefficients are constant and nearly unity. $[R^-]$ can then be determined from equation (11).

$$[R^-]^2 + ([AgR] + [H_i^+])[R^-] = K_2[R^\pm] + (K_2/K_1)[R^\pm]^2 \quad (11)$$

where $K_1 = 4.47 \times 10^{-3}$ and $K_2 = 1.67 \times 10^{-10}$ for glycine[9] while $K_1 = 4.57 \times 10^{-3}$ and $K_2 = 1.35 \times 10^{-10}$ for alanine. Values of the concentration dissociation constant, $K_c = [Ag^+][R^-]/[AgR]$, were calculated and appear in column 5 of Table II. If the activities of silver ion and glycinate ion are calculated from the activity coefficients obtained from equation (5), the values of $K = (Ag^+)(R^-)/(AgR)$ in column 6 are obtained. The activity coefficient of the silver complex ion was assumed to be unity. The values of K are quite constant and show little variation with increasing concentration of amino acid. The silver alaninate complex is more stable than the silver glycinate complex as may be seen from the dissociation constants in Table II. Additional evidence that complex ion formation occurs between silver ion and glycinate ion is that silver chloride although not appreciably soluble in one molar glycine solutions is completely soluble on addition of sodium hydroxide to the solution. The dielectric constant is not the determining factor as it is reduced by the formation of the glycinate ion.

TABLE II

Complex ion formation between silver ion and the negative ion of an amino acid as calculated from determinations of the solubility of silver iodate in glycine and in alanine solution. The solubilities used were taken from a smooth curve drawn through a plot of the logarithm of the experimental solubilities versus the molality of the amino acid.

Glycine, M	IO_3^-, $M \times 10^4$	Ag^+, $M \times 10^4$	AgR, $M \times 10^5$	$K_c \times 10^5$	$K \times 10^5$
0.025	1.855	1.778	0.76	5.64	5.34
.050	1.913	1.766	1.47	5.71	5.28
.075	1.971	1.756	2.15	5.82	5.25
.100	2.027	1.747	2.80	5.99	5.28
.125	2.085	1.741	3.44	6.10	5.25
Alanine					
0.025	1.891	1.734	1.57	1.36	1.29
.050	1.979	1.688	2.91	1.44	1.35
.075	2.065	1.647	4.18	1.49	1.37
.100	2.151	1.611	5.40	1.54	1.38

Using a similar method of calculation, values of the dissociation constant of lead glycinate ion and lead alaninate ion were calculated from the solubility of lead iodate in glycine and in alanine solutions. Values of these constants appear in Table III. The values are as constant as could be expected considering the experimental error in the lead iodate solubilities.

TABLE III

Complex ion formation between lead ion and the negative ion of an amino acid as calculated from determinations of the solubility of lead iodate in glycine and in alanine solutions. The solubilities used were taken from a smooth curve drawn through a plot of the logarithm of the experimental solubilities versus the molality of the amino acid. Two different preparations of lead iodate were used.

Glycine, M	Lead glycinate, $K \times 10^6$ Sample 1	Lead glycinate, $K \times 10^6$ Sample 2	Alanine, M	Lead alaninate, $K \times 10^6$ Sample 2
0.025	6.6	5.6	0.025	2.8
.050	6.8	5.9	.050	3.1
.075	6.9	6.3	.075	3.1
.100	6.9	6.7	.100	2.9

Summary

The solubility of silver iodate and of lead iodate in glycine solutions and alanine solutions has been determined. These solubilities have been found to give abnormal slopes when the logarithm of the solubility is plotted against the amino acid concentration.

The abnormal slopes may be explained by assuming complex ion formation to occur between the metallic ions and the glycinate or alaninate ions. The following dissociation constants were obtained: silver glycinate $K = 5.28 \times 10^{-5}$, silver alaninate $K = 1.37 \times 10^{-5}$, lead glycinate $K = 6.7 \times 10^{-6}$, lead alaninate $K = 3.0 \times 10^{-6}$.

DAVIS, CALIFORNIA RECEIVED NOVEMBER 13, 1940

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[9] Hitchcock in Schmidt's "The Chemistry of the Amino Acids and Proteins," C. C. Thomas, Springfield, Ill., 1938.