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

Interaction of Ions and Dipolar Ions. III. Solubility of Thallous Salts in Glycine and in Alanine Solutions

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

In a recent paper[1] a limiting equation for the solubility of salts in amino acid solutions was shown to be applicable to 2–1 type salts (barium iodate and calcium iodate) in aqueous solutions of glycine or alanine. In order to test this equation for 1–1 type salts silver iodate was chosen. The solubility of silver iodate in glycine or in alanine solutions is much higher than can be predicted by the limiting equation. This may be explained by complex ion formation between silver ion and the glycinate or alaninate ion.[2] Therefore in this communication solubility determinations on 1–1 type salts (thallous bromide and thallous iodate) in glycine and in alanine solutions are given and correlated with the limiting law[1] for the solubility of salts in dipolar ion solutions.

Experimental

Glycine and alanine were purified as in previous work.[1] Potassium nitrate was recrystallized from water and air dried at 180°. Thallous bromide was prepared by adding equivalent amounts of 0.1 *M* thallous nitrate and 0.1 *M* potassium bromide to one liter of water. The precipitate was washed several times and allowed to stand several days in water. Then it was sedimented through a cylinder of water and the slower settling particles were discarded. This process was repeated several times and then the thallous bromide was air dried.

Thallous iodate was prepared by the method of LaMer and Goldman.[3] The solubility determinations were made as previously described.[1] The solubilities were approached from both sides of the equilibrium value. Duplicate solubility determinations checked to approximately 0.1%. There was no apparent variation of solubility with time.

The thallous bromide solutions were analyzed for thallous ion using a standard potassium bromate solution with methyl orange as an indicator.[4] The titrations were performed at 60° and corrections were made for the amount of potassium bromate required to decolorize the indicator. The normality of the bromate solution calculated from its composition checked within 0.1% with the normality found *versus* sodium thiosulfate which had been standardized against potassium iodate. Titrations in the presence and absence of glycine indicated that glycine does not interfere with the above determination of thallous ion.

The determination of iodate ion, in the presence of thallous ion, using sodium thiosulfate is easily carried out. To a 50-cc. aliquot of a thallous iodate solution add 1 g. of potassium iodide. A yellow-orange precipitate of thallous iodide forms which readily dissolves on addition of 5 cc. of 2 *N* sulfuric acid, probably due to formation of TlI_4^-. On titrating this solution with 0.02 *N* thiosulfate the triiodide ion is used up and the yellow-orange thallous iodide reprecipitates. Evidently this is the precipitate that previous investigators[3] mistook for thallous sulfide. Near the end of the titration starch was added. The end-point is slightly obscured by the precipitate present but with practice is easily discernible. Titrations performed on aliquots of a potassium iodate solution in the presence and absence of thallous ion were the same to 0.1%. As a further indication of the accuracy of the determinations, the solubility of thallous iodate in water as analyzed using sodium thiosulfate is in good agreement with that obtained by other investigators.[3]

All concentrations are expressed in moles per 1000 g. of water.

Discussion

When dipolar ions are introduced into a solution containing ions, the activity and hence the activity coefficient of the ions present is decreased. One method of investigating this decrease is to determine the solubility of a salt in dipolar ion solutions. In a previous communication[1] it was shown that the solubility of barium iodate or calcium iodate in glycine or alanine solutions could be expressed by the equation

$$\frac{1}{Z_1Z_2}\log\frac{S}{S_\infty} = -\frac{1}{Z_1Z_2}\log\gamma_\pm = 0.505\left(\frac{78.54}{D_d}\right)^{3/2}\frac{\sqrt{\mu}}{1 + A\left(\frac{78.54}{D_d}\right)^{1/2}\sqrt{\mu}} + 0.0625\,\frac{R^2}{a}\,[R^\pm] \qquad (1)$$

where Z_1 and Z_2 are the valences of the ions of the saturating salt; S is the solubility of the salt in the amino acid solution; S_∞ is the extrapolated solubility at zero amino acid concentration and zero ionic strength; $\gamma_\pm$ is the mean activity coefficient of the ions of the salt; D_d is the dielectric constant of the solution ($78.54 + 22.6\,[R^\pm]$ for glycine)[5]; A, R and a are constants dependent on the amino acid and salts used; and $[R^\pm]$ is the concentration of the dipolar ion.

The increase in solubility of a salt in an isoelectric amino acid solution over its solubility in water is due, first, to the interaction of dipolar ions and

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[1] Keefer, Reiber and Bisson, THIS JOURNAL, **62**, 2951 (1940).

[2] Keefer and Reiber, *ibid.*, **63**, 689 (1941).

[3] LaMer and Goldman, *ibid.*, **51**, 2632 (1929).

[4] Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 464.

[5] Edsall, in Schmidt, "The Chemistry of the Amino Acids and Proteins," C. C. Thomas, Springfield, Illinois, 1938.

ions and, second, to the increased ionic strength of the solution due to the increased solubility of the salt. Before the effect of the dipolar ions (last term in equation 1) may be estimated, the ionic strength effect (first terms on right-hand side of equation 1) must be known. If no dipolar ions are present in the solution, $[R^{\pm}]$ is zero and equation 1 reduces to the well-known Debye–Hückel expression for the solubility of a salt as a function of the ionic strength of the solution. The constant A may be evaluated if the solubility of the salt is known as a function of the ionic strength of the solution. Table I and Fig. 1 give the solubility of thallous bromide in potassium nitrate solutions. As thallous nitrate is not completely dissociated,[6] the amount of undissociated thallous nitrate was calculated from $(Tl^+)(NO_3^-)/(TlNO_3) = 0.56$ (eq. 2). In order to calculate the concentration of undissociated thallous nitrate present, the activity coefficients for the substances in equation 2 must be known. The mean activity coefficient of thallous ion and nitrate ion was assumed to be the same as that for thallous ion and bromide ion, while the activity coefficient of undissociated thallous nitrate was taken as unity. Substituting these relations in equation 2 we obtain

$$\frac{[Tl^+][NO_3^-]}{[TlNO_3]} \frac{L_\infty}{[Tl^+][Br^-]} = 0.56 \qquad (3)$$

where L_∞ is the activity product of thallous bromide. L_∞ may be estimated from Fig. 1, $[Br^-]$ is equal to S and $[NO_3^-]$ is M of $KNO_3 - [TlNO_3]$. Values of $[TlNO_3]$ and $m^{\pm} = ([Tl^+][Br^-])^{1/2}$ may then be calculated. These values of $m^{\pm}$ were substituted in equation 1 ($[R^{\pm}] = 0$) and the resulting equations were solved for A and $m^{\pm}_\infty$ where $m^{\pm}_\infty$ is the value of $m^{\pm}$ at zero ionic strength. The average value of A was 1.19 and $m^{\pm}_\infty$ was 1.916×10^{-3}, which is in good agreement with the value of $m^{\pm}_\infty = 1.914 \times 10^{-3}$ obtained from Fig. 1. Column 3 of Table I gives values of the solubility of thallous bromide calculated from equations 1 and 3 using the above values of A and $m^{\pm}_\infty$. The agreement between these calculated values and the experimental values indicates that equations 1 and 3 adequately reproduce the experimental data.

TABLE I

SOLUBILITY OF THALLOUS BROMIDE AT 25°

All concentrations are moles/1000 g. of water. Δ is experimental solubility − calculated solubility.

KNO_3, M	Solubility of TlBr Exp., $M \times 10^3$	Calcd. $M \times 10^3$	$\Delta \times 10^6$
0	2.013	2.012	−1
0.00502	2.100	2.101	+1
.01003	2.163	2.161	−2
.01505	2.207	2.208	+1
.02008	2.250	2.249	−1
.02510	2.287	2.285	−2
.05025	2.432	2.431	−1
.07545	2.543	2.542	−1
.1007	2.637	2.638	+1

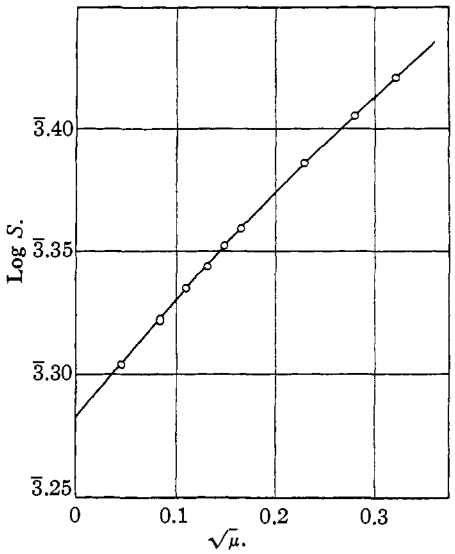

Fig. 1.—Solubility of thallous bromide in potassium nitrate solutions.

The ionic strength corrections for thallous iodate were calculated from the equation given by Davies[6] and assuming that the amount of undissociated thallous iodate remains constant.[6] The ionic strength corrections for thallous chloride were calculated from the equation of Cowperthwaite, LaMer and Barksdale[7] and assuming the amount of undissociated thallous chloride to remain constant.[6]

Tables II and III give the solubility of thallous bromide and thallous iodate in glycine and in alanine solutions. The effect of dipolar ions on the solubility of thallous bromide or iodate was determined by substituting values of $m^{\pm}$ and the appropriate ionic strength corrections (calculated as indicated above) in equation 1. These calculations are summarized in Table III for thallous bromide and glycine. Column 4 gives the amount of undissociated thallous nitrate calculated by means of equation 3. Column 5 contains the

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(6) Davies, *J. Chem. Soc.*, 2410 (1930).

(7) Cowperthwaite, LaMer and Barksdale, THIS JOURNAL, **56**, 544 (1934).

TABLE II

SOLUBILITY OF THALLOUS IODATE AND THALLOUS BROMIDE IN GLYCINE AND IN ALANINE SOLUTIONS AT 25°

Concn. of amino acid, M	Saturating Salt $TlIO_3$, $M \times 10^3$ Glycine	Saturating Salt $TlIO_3$, $M \times 10^3$ Alanine	$TlBr$, $M \times 10^3$ Alanine
0	1.850	1.850	2.013
0.0249	..	..	2.033
.0498	1.909	1.896	2.052
.0749	..	..	2.070
.1000	1.976	1.947	2.090
.1503	2.037	1.999	
.2010	2.103	2.043	

TABLE III

SOLUBILITY OF THALLOUS BROMIDE IN GLYCINE SOLUTIONS

Glycine, M	KNO_3, M	$TlBr$, $S \times 10^3$	$TlNO_3$, $M \times 10^3$	Contribution	$1/Z_1Z_2 \log m^{\pm}$
0	..	2.013	..	0.0215	..
0.0249	..	2.032	..	.0214	0.0042
.0499	..	2.059	..	.0213	.0101
.0500	0.05035	2.480	0.132	.0893	.0110
.0501	.1009	2.674	.246	.1152	.0098
.0750	..	2.078	..	.0212	.0142
.1001	..	2.105	..	.0211	.0199
.1003	.0505	2.522	.131	.0875	.0204
.1004	.1011	2.718	.243	.1131	.0186
.1504	..	2.145	..	.0207	.0284
.2010	..	2.193	..	.0206	.0381

first term on the right-hand side of equation 1 which is the effect of the ionic strength of the solution. By substituting the ionic strength effects and the values of $m^{\pm}$ in equation 1, the contribution of the dipolar ions on $m^{\pm}$ may be calculated.

$$\Delta\left(\frac{1}{Z_1Z_2} \log m^{\pm}\right) = 0.0625 \frac{R^2}{a} [R^{\pm}] \qquad (4)$$

These values appear in column 6. It may be seen from column 6 that the ionic strength corrections are adequately taken care of as the contribution of the dipolar ions to the solubility of the salt remains constant as the ionic strength of the solution changes from 0.002 to 0.10.

In Fig. 2 values of $\Delta(1/Z_1Z_2 \log m^{\pm})$ for thallous bromide, thallous iodate and thallous chloride[8] are plotted against the concentration of glycine. Also plotted in Fig. 2 are the solubility data of Failey[9] for thallous iodate in glycine solutions. All of the salts in Fig. 2 give a straight line relationship which is required by equation 4.

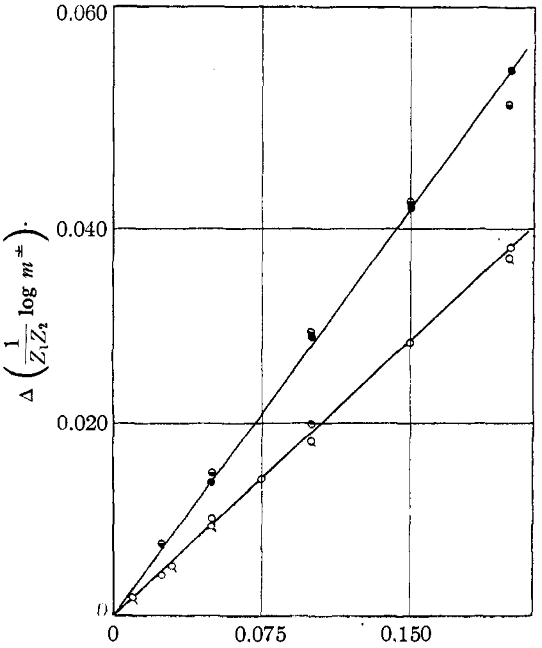

Fig. 2.—Solubility (corrected for ionic strength) of thallous bromide, thallous chloride[8] and thallous iodate in glycine solutions: ● $TlIO_3$, ◒ $TlIO_3$,[9] ○ $TlBr$, ⚲ $TlCl$.

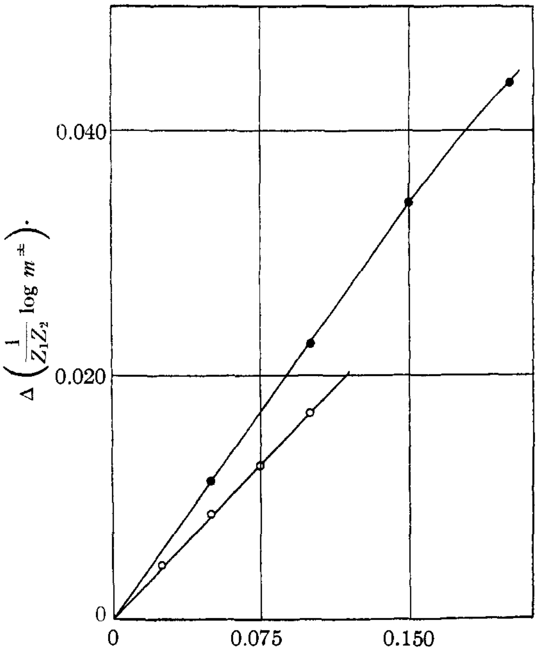

Fig. 3.—Solubility (corrected for ionic strength) of thallous bromide and thallous iodate in alanine solutions: ●, $TlIO_3$: ○, $TlBr$.

The slopes of the lines in Fig. 2 are equal to $0.0625R^2/a$. In Table IV column 2 gives the slope of the line. Column 3 gives the values of a using the average radius of the ions of the salt (from solubility measurements) and taking the radius of glycine to be 2.82 Å. and that of alanine to be 3.08 Å. The solubility data for thallous iodate[3] even after correcting for the undissociated ions present[6] do not give very constant values

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[8] Failey, THIS JOURNAL, **54**, 567 (1932).

[9] Failey, *ibid.*, **55**, 4374 (1933).

TABLE IV

Salt	Slope	a in Å.	R in Å.
	GLYCINE		
Barium iodate[1]	0.205	4.62	3.89
Calcium iodate[1]	.205	4.62	3.89
Thallous bromide	.189	4.63	3.74
Thallous chloride	.184	4.32	3.57
Thallous iodate	.280	4.22	4.35
	ALANINE		
Barium iodate	0.166	4.88	3.60
Calcium iodate	.166	4.88	3.60
Thallous bromide	.169	4.89	3.64
Thallous iodate	.227	4.48	4.04

for the average radius. Column 4 gives the value of R calculated from slope $= 0.0625R^2/a$. The values of R are fairly constant and are of the right order of magnitude with the exception of the thallous iodate results. In order to obtain values of R in the case of thallous iodate and glycine which would be in agreement with the values of R obtained in the other cases a would have to be less than the radius of the glycine molecule. This high solubility of thallous iodate in glycine and alanine solutions may not be explained by complex ion formation between either thallous ion and glycine or iodate ion and glycine since the solubility of barium and calcium iodates and thallous bromide and chloride in glycine is normal. The results might be explained by assuming a complex ion involving thallous ion, iodate ion and glycine. Structurally this does not seem likely and since it is problematical how much weight should be placed on distances of closest approach of ions and dipolar ions it was not deemed advisable to assume such a complex ion.

Summary

The solubility of thallous bromide has been determined in potassium nitrate, glycine, alanine, and glycine containing potassium nitrate solutions. The solubility of thallous iodate was determined in glycine and in alanine solutions.

The solubility of thallous bromide and of thallous iodate in glycine and alanine solutions is discussed in relation to the Kirkwood limiting law. Thallous bromide is normal while thallous iodate shows some irregularities.

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The Formation of an Azulene on Zinc-Dust Distillation of Pyrethrosin

BY MILTON S. SCHECHTER AND H. L. HALLER

The colorless crystalline compound, named "chrysanthin" by Chou,[1] which occasionally separates from extracts of pyrethrum flowers, has recently been shown[2] to be identical with the compound pyrethrosin, obtained by Thoms[3] in 1891 from the same source. Analyses and molecular weight determinations indicate that the molecular formula of pyrethrosin is $C_{17}H_{22}O_5$.[4] The compound may be catalytically hydrogenated to a dihydro compound and also to a tetrahydro compound not previously reported. Alkaline saponification cleaves the molecule into acetic acid and another water-soluble acid which is difficult to isolate in crystalline form. The origin of the acetic acid is not evident, for the original compound cannot be obtained on acetylation of the hydrolysis product. The other acid probably results from the opening of a lactone ring. The oxygen atoms unaccounted for may be of the ether type.

In an attempt to determine the type of nucleus existent in pyrethrosin, the compound was subjected to a zinc-dust distillation in an atmosphere of hydrogen. A green oily distillate was obtained, which upon steam distillation yielded an intensely blue oil. Cold 85% phosphoric acid removed the blue compound from its petroleum ether solution, and on dilution of the acid solution with ice water the blue compound was regenerated. The yield was about 1.5% of the weight of pyrethrosin used. The blue oil was distilled under reduced pressure and further purified by passing a petroleum ether solution through a column of activated alumina (Brockmann). With trinitrobenzene an addition compound was formed, which after three recrystallizations from ethanol melted at 167–168° (cor.). Analysis showed it to possess the formula $C_{19}H_{17}N_3O_6$, from

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(1) Chou and Chu, *Chinese J. Physiol.*, **8**, 167 (1934).

(2) Schechter and Haller, THIS JOURNAL, **61**, 1607 (1939).

(3) Thoms, *Ber. deut. pharm. Ges.*, **1**, 241 (1891).

(4) Rose and Haller, *J. Org. Chem.*, **2**, 484 (1937).