

bonds among seven positions, with possible use of a $5d$ orbital for covalent character of the seventh bond.

All three of these explanations involve the assumption of fortuitous changes or cancellations of changes to explain the observation that pK_3 has the same value in the presence and absence of ethanol. It will be highly desirable to obtain more evidence from other compounds to clarify the structure of these complexes.

It is worth noting that these complexes reported and the one between ferrihemoglobin and imidazole reported by Russell and Pauling¹⁶ are the only ones known to date between ferrihemoglobin and a neutral electron donor. It is probable that ionization constants of heme-linked acid groups¹⁰ will differ between this class of electron donors and the anion classes including azide, cyanide, fluoride, fulminate,¹⁷ hydrosulfide, and hydroxide ions, already known.

We are grateful to Professor Linus Pauling and to Dr. T. Harrison Davies for stimulating advice and assistance in this work.

Summary

The effects of azide ion, ammonia, methanol, ethanol, and *n*-propanol on the magnetic properties of ferrihemoglobin (methemoglobin) solutions have been studied at 25°. The magnetic

(16) C. D. Russell and L. Pauling, *Proc. Nat. Acad. Sci.*, **25**, 517 (1939).

(17) R. D. Barnard and W. Neitzel, *Proc. Soc. Exptl. Biol. Med.*, **39**, 462 (1938).

properties of ferrihemoglobin azide have been established. It is found that ammonia forms a complex with ferrihemoglobin hydroxide and the dissociation constant of this complex, tentatively identified as ammonia:ferrihemoglobin-hydroxide, has been measured. Ethanol is found to form a complex with ferrihemoglobin and another with ferrihemoglobin-hydroxide. The dissociation constant of the latter (ethanol:ferrihemoglobin-hydroxide) is found to be 0.39; the equilibrium between the two complexes and hydroxide ion is found to have the same constant as the corresponding equilibrium between ferrihemoglobin and ferrihemoglobin-hydroxide, whence the dissociation constant of ethanol:ferrihemoglobin is found to be 0.4. Propanol has a pronounced effect on magnetic properties but leads to denaturation. Methanol has a slight influence on magnetic properties.

The paramagnetic part of the molal susceptibilities correspond to the following effective magnetic moments per heme, in Bohr magnetons, ferrihemoglobin azide, 2.84; ammonia:ferrihemoglobin-hydroxide, 2.95; ethanol:ferrihemoglobin, 5.89; ethanol:ferrihemoglobin-hydroxide, 5.39. For the azide and ammonia compounds these correspond to one unpaired electron per iron atom, indicating essentially covalent bonds; for the ethanol compounds, to five unpaired electrons per iron atom, indicating essentially ionic bonds.

PASADENA, CALIF.
LOS ANGELES, CALIF.

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

Interaction of Ions and Dipolar Ions. I. Solubility of Barium and Calcium Iodates in Glycine and in Alanine Solutions

BY R. M. KEEFER, H. G. REIBER AND C. S. BISSON¹

It has been shown by many workers that the aliphatic alpha amino acids exist in aqueous solution as dipolar ions. In investigations involving dipolar ion solutions it is often desirable to know the activity of the simple ions present. By extending the Debye-Hückel theory to the case where one of the ions is a dipolar ion, Kirkwood² has obtained a limiting law for the interaction of ions and dipolar ions. Furthermore, he has shown

(1) This paper is being published following the death of Prof. C. S. Bisson, and responsibility for all statements will be assumed by his collaborators.

(2) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

that the solubility of glycine² in alcoholic solutions containing salts is in agreement with the limiting law. Electrode studies of Joseph³ and solubility measurements of Failey⁴ involving salts in aqueous amino acid solutions, after a "salting out" effect⁵ correction, are also in agreement with the Kirkwood limiting law. As Failey's⁴ solubility measurements were with 1-1 type salts, the present investigation gives the results of solubility

(3) Joseph, *J. Biol. Chem.*, **111**, 479 and 489 (1935); **130**, 203 (1939).

(4) Failey, *THIS JOURNAL*, **55**, 4374 (1933).

(5) Kirkwood, *Chem. Rev.*, **24**, 233 (1939).

determinations of 2-1 type salts in glycine and alanine solutions.

Experimental

Glycine and alanine of C. P. quality were recrystallized twice from water by the addition of ethyl alcohol. The products were dried in a vacuum oven at about 35°. C. P. grade potassium chloride was recrystallized from water and air dried at 180°. For barium iodate, equivalent amounts of 0.2 *M* barium chloride solution and 0.2 *M* potassium iodate solution were mixed slowly with constant stirring. The precipitate was filtered, washed, and then air dried at room temperature. For calcium iodate, an equivalent amount of 1.0 *M* calcium chloride solution was added slowly with stirring to 2000 cc. of 0.38 *M* potassium iodate. The precipitate was filtered, washed, and then air dried at room temperature. To prepare barium bromate, an equivalent amount of 0.20 *M* barium chloride solution was added slowly with stirring to 1000 cc. of 0.16 *M* potassium bromate. The precipitate was filtered, washed, and then air dried at room temperature.

All solutions were prepared from boiled distilled water using calibrated volumetric equipment. An excess of air-dried salt was placed in a glass stoppered Pyrex flask and 200 cc. of the solution to be used was added. The flasks were placed in a thermostat at 25.00 ± 0.02° and rotated for at least twelve hours. Preliminary experiments showed that equilibrium was obtained in about four or five hours. Samples were taken using a pressure pipet fitted with an asbestos filter. The densities of all solutions were determined. Analyses and solubility measurements were done in duplicate.

The saturated solutions were analyzed iodimetrically using sodium thiosulfate solutions standardized by means of potassium iodate.⁶ The solutions saturated with barium bromate were analyzed for barium ion, in addition to the iodimetric analysis, by precipitating the barium as barium sulfate after the bromate ion was removed by evaporating the saturated barium bromate solutions to dryness in the presence of hydrochloric acid and potassium bromide.

Results

By simplification of the Kirkwood limiting law for the activity coefficient of an ion, γ_i , in a solution containing dipolar ions equation (1) is obtained

$$\log \gamma_i = -3.423 \times 10^7 Z_i^2 \frac{R^2}{a} \frac{C}{D_s^2 T^2} \quad (1)$$

where Z_i is the valence of the ion, D_s is the dielectric constant of the solvent, T is the absolute temperature, R is the dipole distance of the dipolar ion in Å., C is the concentration of the dipolar ion, and a is the distance of closest approach of an ion to a dipolar ion in Å. At 25° with water as a solvent this equation simplifies to

$$\log \gamma_i = -0.0625 Z_i^2 \frac{R^2}{a} C \quad (2)$$

(6) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1938.

The limiting law is based on the following assumptions: the dipolar ions are spherical, multiple interaction of dipolar ions is negligible, multipole electric moments of the dipolar ions are large relative to those of a solvent molecule, and corrections of the Gronwall-La Mer⁷ type are negligible.

Glycine may be considered to be spherical⁵ and alanine is nearly so.⁵ The mutual interaction of dipolar ions was minimized by using dilute solutions. The electric moments of glycine and alanine are large compared to those of water. Corrections of the Gronwall-La Mer type appear as deviations from the Debye-Hückel limiting law as a result of the non-linear terms in the Poisson-Boltzmann equation. For the salts used in this investigation the agreement with the extended form of the Debye-Hückel limiting law

$$\frac{1}{Z_1 Z_2} \log \frac{s}{s_\infty} = 0.505 \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} \quad (3)$$

may be seen from Fig. 1 where $1/Z_1 Z_2 \log s/s_\infty$ for barium iodate, calcium iodate, and barium bromate are plotted against $\sqrt{\mu}$ assuming complete dissociation of all electrolytes present. The curve in Fig. 1 gives about 1.8 Å. for the average radius of the ions of barium iodate or of calcium iodate. In order to obtain reasonable values for the average radius of the ions of barium bromate it is necessary to include a $B\mu$ term in equation 3. The solubilities (moles/1000 g. of water) of barium iodate, calcium iodate, and barium bromate in potassium chloride solutions used in Fig. 1 are given in Table I. The solubility of barium iodate in potassium chloride solutions is in good agreement with the results obtained by Macdougall and Davies.⁸

TABLE I
SOLUBILITY OF BARIUM IODATE, CALCIUM IODATE AND BARIUM BROMATE AT 25°

All concentrations are moles/1000 g. of water			
KCl added <i>M</i>	Ba(IO ₃) ₂ <i>M</i> × 10 ⁴	KCl added <i>M</i>	Ca(IO ₃) ₂ <i>M</i> × 10 ³
0	8.11	0	7.86
0.001267	8.31	0.02514	8.85
.002533	8.47	.05036	9.70
.005064	8.77	.1008	10.53
.01003	9.22		<i>M</i> × 10 ² of Ba(BrO ₃) ₂
.01254	9.40	0	2.008
.02514	10.16	0.02008	2.135
.05025	11.21	.04019	2.233
.07543	12.06	.06034	2.330
.1007	12.72	.08050	2.416
		.1007	2.483

(7) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(8) Macdougall and Davies, *J. Chem. Soc.*, 1416 (1935).

The two main factors contributing to an increase in the solubility of a salt in dipolar ion solutions are the concentration of the dipolar ion and the ionic strength of the solution. The Kirkwood limiting law was developed for the ideal case of zero ionic strength and the solubilities, as measured, must be corrected for the increase due to the ionic strength of the solutions before they may be correlated with the above law. The effect of the ionic strength of the solution on the solubility of a salt at 25° in aqueous solution is given by equation 3. When dipolar ions are present in the solution, the dielectric constant of the solution is raised markedly and, since dipolar ion solutions are being used as the solvent, equation 4 is applicable

$$\frac{1}{Z_1 Z_2} \log \frac{s}{s_\infty} = 0.505 \left(\frac{78.54}{D_d} \right)^{3/2} \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} \quad (4)$$

where D_d is the dielectric constant of the dipolar ion solution. The effect of the dipolar ions on the solubility of a salt is given by equation 2. If the laws of dilute solution are valid in this case, the solubility of a salt in dipolar ion solutions should be given by the sum of these effects

$$\frac{1}{Z_1 Z_2} \log s/s_\infty = 0.505 \left(\frac{78.54}{D_d} \right)^{3/2} \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} + 0.0625 \frac{R^2}{a} C \quad (5)$$

In order to test this equation the solubility of barium iodate and of calcium iodate was determined in glycine solutions (Table II) and in glycine solutions containing potassium chloride (Table III) to vary the ionic strength of the solutions. The ionic strengths of the saturated solutions were calculated and values of 0.505 $[\sqrt{\mu}/(1 + A\sqrt{\mu})]$ were obtained from Fig. 1. The dielectric constant of the dipolar ion solution, D_d , was taken as $78.54 + 22.60C$.⁹ With these values and the experimental solubilities values of $0.0625R^2C/a$ were calculated using equation 5. These values of $0.0625R^2C/a$ representing the increase in $\frac{1}{Z_1 Z_2} \log s$, $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$, due to the effect of the dipolar ions are given in Table IV for barium iodate and calcium iodate in glycine solution with and without potassium chloride present. It may be seen from the table that $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ is independent of the ionic strength of the solution, being only a function of the dipolar ion concentration. This is in agreement with

(9) Edsall, in Schmidt, "The Chemistry of the Amino Acids and Proteins," C. C. Thomas, Springfield, Illinois, 1938.

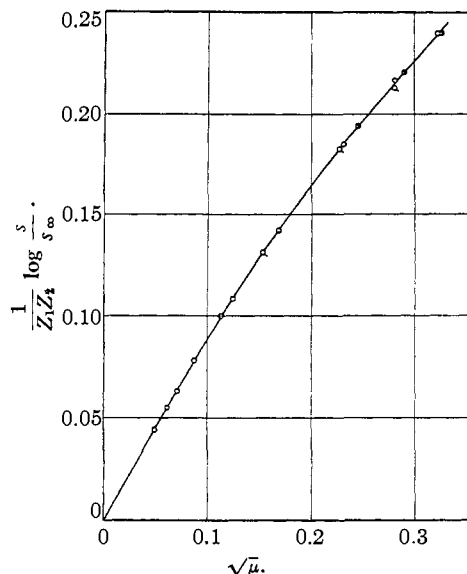


Fig. 1.—Solubility of $\text{Ba}(\text{IO}_3)_2$, $\text{Ca}(\text{IO}_3)_2$ and $\text{Ba}(\text{BrO}_3)_2$ in KCl solutions: O, $\text{Ba}(\text{IO}_3)_2$; □, $\text{Ca}(\text{IO}_3)_2$; ●, $\text{Ba}(\text{BrO}_3)_2$.

the assumption that the effects of ionic strength and of dipolar ions on the solubility of a salt are independent and additive.

TABLE II
SOLUBILITY OF BARIUM IODATE, CALCIUM IODATE AND BARIUM BROMATE IN GLYCINE OR ALANINE SOLUTIONS AT 25°

Amino acid, M	$\text{Ba}(\text{IO}_3)_2$ $M \times 10^4$		$\text{Ca}(\text{IO}_3)_2$ $M \times 10^3$		$\text{Ba}(\text{BrO}_3)_2$ $M \times 10^2$ glycine
	glycine	alanine	glycine	alanine	
0.0251	8.31	8.29	8.06	8.00	2.045
.0503	8.51	8.43	8.23	8.14	2.081
.0755	8.71	8.58	8.49	8.29	2.113
.1008	8.95	8.76	8.65	8.45	2.150
.1990	9.77				
.2009			9.51		
.4055			11.11		
.6140			12.97		
.8175	15.52				
.8261			14.95		

TABLE III
SOLUBILITY OF BARIUM IODATE AND CALCIUM IODATE IN GLYCINE SOLUTIONS CONTAINING POTASSIUM CHLORIDE AT 25°

KCl added, M	Glycine, M	$\text{Ba}(\text{IO}_3)_2$ $M \times 10^4$	$\text{Ca}(\text{IO}_3)_2$ $M \times 10^3$
0.02516	0.02511	10.35	8.99
.02519	.05030	10.56	9.20
.02522	.07552	10.78	9.39
.02525	.1008	11.00	9.59
.05036	.02513	11.42	9.70
.05041	.05032	11.66	9.90
.05047	.07558	11.90	10.06
.05053	.1009	12.13	10.27
.1009	.02517	12.97	10.73
.1010	.05041	13.21	10.93
.1011	.07570	13.46	11.15
.1012	.1010	13.71	...

TABLE IV

THE EFFECT OF GLYCINE ON THE SOLUBILITY OF BARIUM IODATE AND CALCIUM IODATE IN THE PRESENCE AND IN THE ABSENCE OF POTASSIUM CHLORIDE^a

Glycine, <i>M</i>	$\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ <i>M</i> of KCl			
	None	0.025	0.050	0.100
	Ba(IO ₃) ₂			
0.025	53	46	45	47
.050	104	97	102	102
.075	155	149	155	153
.100	215 ^b	199	208	205
	Ca(IO ₃) ₂			
0.025	52	54	53	50
.050	100	103	108	104
.075	166 ^b	150	151	158
.100	207	204	204	...

^a An error of 0.2% in the solubility determinations would account for a variation of 4 in the above values. ^b Error in solubility determinations, see Fig. 3.

The Kirkwood limiting law predicts that, in dilute solution, $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ should be a linear function of the dipolar ion concentration. Figure 2 shows that values of $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ for barium iodate and calcium iodate plotted against the molality of glycine from 0 to 0.8 *M* lie on the same curve. The relationship is linear to approximately 0.15 *M*, the deviation at higher concentrations may be due to dipole-dipole interaction. It is possible to estimate the dipole radius of glycine and alanine using the slopes of the $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ versus molality of dipolar ion curves and the Kirkwood limiting law which states that such slopes are equal to $0.0625R^2/a$.

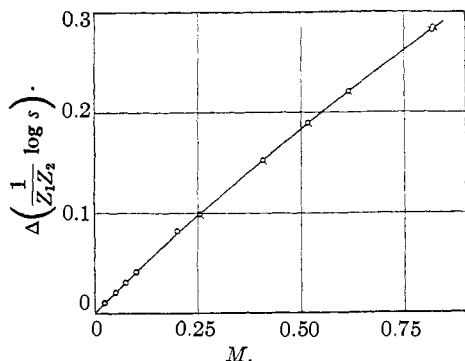


Fig. 2.—Solubility of Ba(IO₃)₂ and Ca(IO₃)₂ in glycine solutions up to 0.8 *M*: ▽, Ba(IO₃)₂; △, Ca(IO₃)₂; ○, Ba(IO₃)₂ and Ca(IO₃)₂.

In Fig. 3 values of $\Delta\left(\frac{1}{Z_1 Z_2} \log s\right)$ for barium iodate, calcium iodate, and barium bromate are

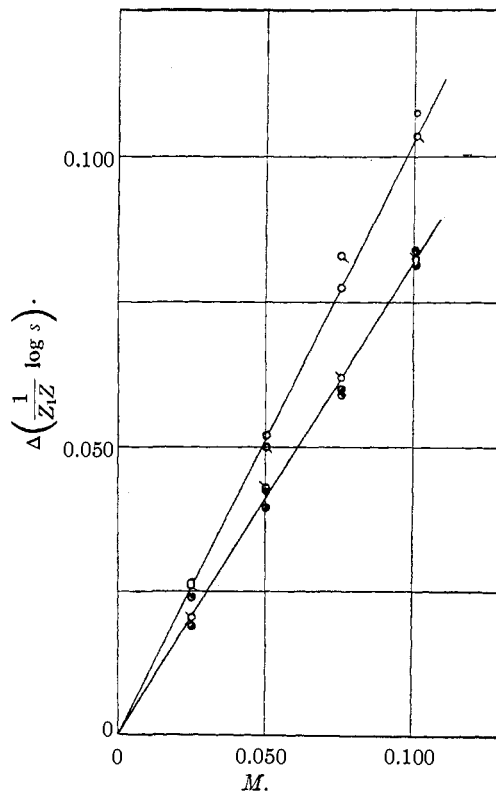


Fig. 3.—Solubility of Ba(IO₃)₂, Ca(IO₃)₂ and Ba(BrO₃)₂ in glycine and in alanine solutions: ○, Ba(IO₃)₂ in glycine; △, Ca(IO₃)₂ in glycine; ▽, Ba(BrO₃)₂ in glycine; ●, Ba(IO₃)₂ in alanine; ◐, Ca(IO₃)₂ in alanine.

plotted as a function of the molality of glycine and of alanine. Barium iodate and calcium iodate results fall on the same curve in glycine solutions and in alanine solutions although the curve for alanine solutions lies below that for glycine solutions. From crystal radii¹⁰ data the average radius of barium or calcium ion and iodate ion is approximately 2.2 Å. The radii of glycine and alanine from measurements of their apparent molal volume in water corrected for shrinkage of the solvent are 2.82 and 3.08 Å. Using these values to calculate the dipole radii, one obtains 4.07 Å. for glycine and 3.74 Å. for alanine, which are of the correct order of magnitude. Macdougall and Davies⁸ state that in saturated solutions of barium iodate and calcium iodate there are present appreciable amounts of MIO₃⁺. On repeating the calculations to include this factor, it was found that the concentration of MIO₃⁺ remained constant and therefore would not affect our results.

(10) Pauling. "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

The slope for the solubility of barium bromate in glycine solutions is much less than that obtained for barium or calcium iodates. This cannot be explained readily by changes in the value of the distance of closest approach of an ion to a dipolar ion. It may be that in solutions of such high ionic strength, the "salting out" effects⁵ are becoming appreciable.

Summary

The solubilities of barium iodate and of calcium iodate have been determined in glycine solutions, alanine solutions and glycine solutions containing potassium chloride.

It has been shown in two cases that the effects

of ionic strength and of dipolar ions on the solubility of a salt are independent and additive and that the solubility of barium iodate or calcium iodate in glycine solutions is given by

$$\frac{1}{Z_1 Z_2} \log \frac{s}{s_\infty} = 0.505 \left(\frac{78.54}{D_d} \right)^{3/2} \frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} + 0.207 M$$

The solubilities of barium iodate and calcium iodate in glycine solutions obey the Kirkwood limiting law up to 0.15 *M*. Using the slopes of these curves and crystal radii it is possible to calculate from the Kirkwood equation values of the dipole radii of glycine and alanine which are of the correct order of magnitude.

DAVIS, CALIF.

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[CONTRIBUTION FROM THE GEORGE EASTMAN LABORATORY OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

An X-Ray Determination of the Crystal Structure of Tetraphenylarsonium Iodide, $(C_6H_5)_4AsI$

BY ROSE C. L. MOONEY¹

The halides of tetraphenylarsonium were first prepared and described by Blicke and his associates.² Methods for the use of tetraphenylarsonium ion in quantitative analysis were subsequently devised by Willard and Smith.³ We are indebted to Professor Willard for crystals of the three compounds. A study of these crystals by means of X-rays was undertaken in order to compare the structural arrangement with those of other halides, and particularly to determine the size and configuration of the cation complex, the tetraphenylarsonium ion. The configuration of phenyl groups about an inorganic nucleus has never before been described. The molecular compounds tetraphenyltin, tetraphenyllead, and tetraphenylgermanium have been studied by X-rays, but no positions were determined for the phenyl groups, though it was established that the molecule had the symmetry S_4 .⁴

The initial stages of the investigation of the three halides of tetraphenylarsonium gave the following results. The chloride and bromide were shown to be isomorphous, to belong to the orthorhombic system, and to have four molecules

in the unit cell. The iodide was found to be tetragonal, and to have only two molecules in the unit cell. It soon appeared that the latter crystal presented more favorable conditions for the precise determination of atomic positions directly from diffraction data than either the chloride or the bromide. The first complete analysis was therefore made for the iodide, and is reported here. Work on the other two crystals is still in progress.

Description of the Crystals.—The iodide of tetraphenylarsonium is quite insoluble; 0.14 g. dissolves in 100 cc. of water at 25°. Our sample was in the form of a fine powder. It was satisfactorily recrystallized for our purposes by slow cooling from hot aqueous solution. Colorless, very brilliant prismatic needles, about 0.02 cm. in cross section, and from 0.5 to nearly 1 cm. long, were thus obtained. The form showed only prism faces in general, with occasional development of terminal pyramidal faces. The disposition of these faces indicated a four-fold alternating axis coincident with the needle axis. The birefringence was found to be small and negative.

Experimental Methods.—The X-ray data consisted of powder, oscillation and equi-inclination Weissenberg photographs, all taken with Cu $K\alpha$ radiation filtered through nickel. The

(1) Guggenheim Fellow, 1939–1940.

(2) Blicke and Marzano, *THIS JOURNAL*, **55**, 3056 (1933); Blicke and Monroe, *ibid.*, **57**, 720 (1935); Blicke and Cataline, *ibid.*, **60**, 423 (1938); Blicke, Willard and Taras, *ibid.*, **61**, 88 (1939).

(3) Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 269, 305 (1939).

(4) George, *Proc. Roy. Soc. (London)*, **113A**, 585 (1927).