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The Heats of Dilution of Aqueous Solutions of Glycine at 25°

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Measurements of the thermodynamic properties of dilute electrolyte solutions have consistently shown significant deviations from the behavior expected of ideal solutions. These deviations have long been recognized as arising from the charge on the solute particles and have been fairly successfully accounted for by the theory of Debye and Hückel.[3]

In general, non-electrolytes behave more like perfect solutes than do electrolytes, but they also show appreciable deviations which have been ascribed, in part, to the existence of dipoles within the solute molecules. A theoretical investigation of the energetics of a system of dipoles was made by Fuoss[4] in which he attempted to formulate a limiting law for such a solute. His treatment indicated that the thermodynamic properties of a solution of polar (but uncharged) molecules should vary linearly with the *first power* of concentration.

The amino acids because of their highly polar nature present a comparatively favorable case for testing the Fuoss theory. Recently, Gucker, Ford and Moser[5] have determined heat capacities and volumes for aqueous glycine solutions between 0.1 molal and saturation. Their data indicate a linear dependence on concentration in the limit in accordance with the requirements of the Fuoss theory. More recently Gucker, Pickard and Ford[6] and Sturtevant[7] have measured heats of dilution of glycine down to concentrations of 0.08 and 0.04 molal, respectively.[8] Both investigations revealed that, though the heat content did seem to vary linearly with concentration, in contradiction with theory heat was absorbed over the entire concentration range. In view of the importance of results below 0.01 molal in testing theories of electrolytes[9] it seemed highly desirable to extend the dilution experiments on glycine to concentrations below 0.005 molal.

An attempt to investigate the behavior of very dilute solutions of glycine was begun in this Laboratory in March, 1940. The results obtained then seemed promising but were considered insufficiently reproducible to justify publication. This communication contains the results of a more recent study.

Experimental

The apparatus which we have used in this investigation was a Lange-type adiabatic differential calorimeter the characteristics and details of operation of which have been described.[9,10] The exclusion of carbon dioxide (*vide infra*) was accomplished by means of oil traps which sealed the various openings in the cover of the calorimeter.

Preliminary experiments indicated a small but appreciable heat effect arising from surface adsorption of the glycine. Such effects were minimized by coating the surface with a thick layer of paraffin.

The glycine was a product obtained from the Amino Acid Manufacturers of the University of California at Los Angeles. According to the manufacturers formol titration showed a glycine content of 99.7 ± 0.2% and the product contained negligible amounts of common electrolytes.

Sturtevant[11] has called attention to the possible influence of dissolved carbon dioxide on the heats of dilution of dilute glycine solutions. Consequently, an effort was made to prepare and maintain a supply of water free of carbon dioxide. Doubly distilled water was boiled for a few minutes, transferred to a closed flask and saturated with tank nitrogen, after which treatment the specific conductance was $0.7–0.9 \times 10^{-6}$ mho/cm. This water, when cool, was forced from the container to the calorimeter, which had been flushed out with nitrogen, by means of a slight pressure of tank nitrogen. An estimate of the carbon dioxide content of the calorimeter water was made by noting the conductivity increase of samples of that water when brought into contact with the atmosphere. The increase was compared with the quantity 0.75×10^{-6} mho/cm. reported by Kendall[12] for the conductivity of extremely pure water at equilibrium with atmospheric carbon dioxide. Kendall concluded that the conductivity of carefully purified water which had been allowed to come in contact with air was due almost entirely to dissolved carbon dioxide. Such an estimate indicated that the

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(1) Research Fellow in Chemistry under a grant made by the Carnegie Institution of Washington.

(2) Research Assistant in Chemistry under a grant made by the Buhl Foundation, Pittsburgh, Pennsylvania.

(3) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(4) R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936).

(5) F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

(6) F. T. Gucker, Jr., H. B. Pickard and W. L. Ford, THIS JOURNAL, **62**, 2698 (1940).

(7) J. M. Sturtevant, *ibid.*, **62**, 1879 (1940).

(8) Gucker, Pickard and Ford made measurements that extended to 0.005 molal. However, according to a private communication from Dr. H. B. Pickard, the data for concentrations below 0.08 molal were not used to obtain their equation for ΦL_2.

(9) See, for example, E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

(10) (a) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934); (b) W. E. Wallace and A. L. Robinson, *ibid.*, **63**, 958 (1941); (c) A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

(11) J. M. Sturtevant, THIS JOURNAL, **62**, 3519 (1940).

(12) J. Kendall, *ibid.*, **38**, 1480 (1916).

TABLE I

INTERMEDIATE HEATS OF DILUTION OF AQUEOUS GLYCINE SOLUTIONS

m_i (Moles glycine/kg. water)	m_f	$10^3 q$ (cal.)				ΔH (cal./mole)
		Long Chord Dilutions				
0.8225	0.00537		373	366		68.3 ± 0.4
.6158	.00406		225	223		55.2 ± .2
.4054	.00269	103.6	102.9	102.3	101.5	38.0 ± .1
.3049	.00204	58.2	53.8	58.3	53.0	27.4 ± .5
.2016	.00135		22.4	23.5		17.0 ± .3
.1519	.00102	14.2	19.7	12.7	17.2	15.6 ± 1.0
.1007	.000677		2.5	5.5		5.9 ± 1.5
.0505	.000340	−0.3	−0.3	+0.5	−2.2	−1.7 ± 1.1
		Short Chord Dilutions[a]				
.01069	.00537		−4.2	−13.1		−0.8 ± 0.3 (0.3)
.00808	.00406		+3.6	+0.4		+ .2 ± .1 (.2)
.00537	.00269	−3.5	−6.0	+1.2		− .5 ± .3 (.1)
.00406	.00204	−6.3	+1.3	+0.8	−5.4	− .6 ± .3 (.2)
.00269	.00135	+0.3	−0.9	−5.4		− .1 ± .1 (.1)
.00204	.00102	+ .1	+ .7	+2.6		+ .5 ± .3 (.3)
.00135	.000677		− .2	+1.1		+ .4 ± .3 (.4)
.000677	.000340	− .4	+ .6	−0.1	−1.5	− .6 ± .6 (.6)

[a] The short chord data have been tabulated and treated as described in an earlier publication.[10c] The advantage of this method over that of Wallace and Robinson[10b] lies in the fact that the present treatment involves the use of Hess's law only once (see ref. 10c, p. 197), whereas the earlier treatment required its use twice. The earlier method, while numerically correct, magnified excessively the transmission of errors in the measured heats of dilution to the computed short chord ΔH's.

carbon dioxide concentration was approximately $(1 \pm 1) \times 10^{-6}$ molal as compared to an atmospheric carbon dioxide saturation value of app. 10^{-5} molal.

The solutions were prepared within a few hours of the time of use to avoid contamination by microörganisms. All solutions were made up by volume at 25° and converted to a weight basis by means of the density data of Gucker, Ford and Moser.[5]

Results of Measurements.—The first two columns in Table I give the initial and final concentrations of a dilution, respectively. Column three gives the observed heat effects for individual runs and column four shows mean values for the intermediate heats of dilution and their probable errors. The quantities in parentheses in column four are smoothed probable errors the significance and method of determination of which are mentioned in the next section.

Treatment of Data

Extrapolation of Results to Infinite Dilution.—The details of the method of calculation used in this paper are discussed in earlier publications.[10b,10c] The chord-area treatment[13] was applied to the short chord dilutions given in Table I. These data were assumed to be expressible by an equation of the type

$$S = S^0 + Bm \tag{1}$$

where $S = d\Phi L_2/dm$. S^0 and B were evaluated by the method of least squares, assigning weights inversely proportional to the square of the smoothed probable errors listed in column four of Table I. The smoothed probable errors (obtained from a plot of the probable error in q against q) are used because the number of experiments is so small as to render the raw probable errors somewhat unreliable. The equation so obtained is

$$S = 167 - 14{,}800m \tag{2}$$

which gives on integration with respect to m

$$\Phi L_2 = 167m - 7400m^2 \tag{3}$$

A plot of equation (2) showing the data from which it was derived is given in Fig. 1.

Relative Apparent Molal Heat Contents of Solute.—To determine ΦL_2's at concentrations greater than 0.01 molal, equation (3) is used to calculate ΦL_2's at the final concentrations of the long chord dilutions given in Table I. These when combined with the experimental heats of dilution (column four, Table I) give values for ΦL_2's at the initial concentrations as shown in Table II.[14]

The apparent heat contents from zero to 0.8

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(13) Young, *et al.*, THIS JOURNAL, **54**, 3030 (1932); **58**, 187 (1936); **60**, 2379 (1938).

(14) The probable errors given in column four of Table II have been estimated from the probable errors in S^0 and B. The latter can be determined from the smoothed probable errors listed in column four of Table I; for example, see A. G. Worthing and Joseph Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., to be published.

molal were found to be capable of expression by an equation of the following type

$$\Phi L_2 = (A_1 + A_2e^{-\alpha m})m + Bm^2 \qquad (4)$$

Imposing the condition that the limiting slope of equation (4) be the same as in equation (3) allows A_2 to be eliminated to give

$$\Phi L_2 = [A_1 + (167 - A_1)e^{-\alpha m}]m + Bm^2 \quad (5)$$

Weighting the ΦL_2's given in column five of Table II inversely as the square of their probable errors and applying the principle of least squares, we obtain

$$\Phi L_2 = (259e^{-20.6m} - 92)m + 8.7m^2 \qquad (6)$$

TABLE II

DATA USED IN EVALUATION OF THE APPARENT RELATIVE HEAT CONTENTS

m_i moles glycine/kg. water	m_f moles glycine/kg. water	$\Delta H_{(m_i \rightarrow m_f)}$ calories per mole of glycine	$\Phi L_{2(m_f)}$ calories per mole of glycine	$\Phi L_{2(m_i)}$ calories per mole of glycine
0.8225	0.00537	68.5 ± 0.5	0.7 ± 1.1	−67.8 ± 1.3
.6158	.00406	55.2 ± .3	.6 ± 1.0	−54.6 ± 1.2
.4054	.00269	38.1 ± .2	.4 ± 0.5	−37.7 ± 0.6
.3049	.00204	27.5 ± .5	.3 ± .5	−27.2 ± .7
.2016	.00135	17.0 ± .3	.2 ± .3	−16.8 ± .4
.1519	.00102	15.6 ± 1.0	.2 ± .2	−15.4 ± 1.0
.1007	.000677	5.9 ± 1.5	.1 ± .2	− 5.8 ± 1.5
.0505	.000340	−1.5 ± 1.2	.1 ± .1	1.6 ± 1.2

Relative Partial Molal Heat Contents.—After the method of Rossini[15]

$$\bar{L}_1 = -\frac{m^2}{55.508}\frac{d\Phi L_2}{dm} \qquad (7)$$

$$\bar{L}_2 = \Phi L_2 + m\frac{d\Phi L_2}{dm} \qquad (8)$$

Substituting in equation (6) and performing the indicated operation gives

$$\bar{L}_1 = -m^2[(1 - 20.6m)259\,e^{-20.6m} + 0.3135m - 1.657] \quad (9)$$

$$\bar{L}_2 = [518\,(1 - 10.3m)e^{-20.6m} - 184]m + 26.1m^2 \quad (10)$$

Results calculated from equations (9) and (10) at several rounded concentrations are shown in Table III.

TABLE III

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS GLYCINE SOLUTIONS

m moles glycine/kg. water	$\bar{L}_1$, cal./mole water	$\bar{L}_2$, cal./mole glycine
0.0005	-7×10^{-7}	0.2
.0010	-3×10^{-6}	.3
.0050	-5×10^{-5}	1.3
.0100	−0.0002	1.9
.0500	+ .0041	− 4.5
.1000	.0226	− 18.3
.2000	.0732	− 37.5
.4000	.247	− 69.6
.8000	.900	−130

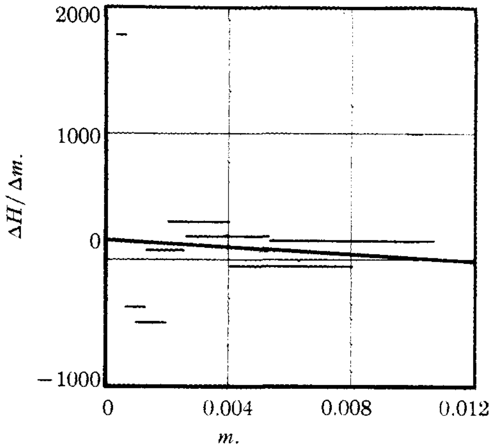

Fig. 1.—Plot of the chords obtained from the "short chord dilutions" listed in Table I; curve calculated from equation (2).

Discussion of Results.—Sturtevant[11] has pointed out that heat effects associated with ionization changes in glycine solutions may make appreciable contributions to the heats of dilution at very low concentrations. Such effects must necessarily be eliminated prior to an attempt at comparison with the Fuoss theory. Calculations by Sturtevant[11] indicate that the ionization heats occur mainly in the interval 0.01 to 0.0001 molal and account for about 5 cal./mole absorbed in a dilution over that range. Sturtevant also observed that "the presence of carbon dioxide in the diluting water could mask the ionization effects even in a sensitive calorimeter by holding the pH close to 6.1, the isoelectric pH of glycine." On the basis of this observation we undertook some measurements in the presence of carbon dioxide to attempt an experimental substantiation of the Sturtevant calculations. The results, given in Table IV, are seen to be inconclusive.

TABLE IV

THE EFFECTS OF CARBON DIOXIDE ON THE HEATS OF DILUTION OF GLYCINE

m_i moles glycine/kg. water	m_f moles glycine/kg. water	ΔH calories per mole of glycine "CO_2-free"	ΔH calories per mole of glycine "Equil. H_2O"	Difference
0.4054	0.00269	38.1 ± 0.2	37.1 ± 0.1	+1.0
.2016	.00135	17.0 ± .3	17.7 ± .4	−0.7
.1007	.000677	5.9 ± 1.5	8.9 ± .7	−3.0
.0505	.000340	−1.5 ± 1.2	2.5 ± 1.9	+1.0
.00537	.00269	−0.5 ± 0.2	0.0 ± 0.2	−0.5
.00269	.00135	−0.1 ± .1	− .2 ± .4	+ .1
.00135	.000677	+ .3 ± .3	− .3 ± .3	+ .6

Figure 2 shows the apparent heat contents of glycine as determined in this investigation together with the results of Gucker, Pickard and Ford[6] and Sturtevant.[7] The curves have been

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[15] F. D. Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

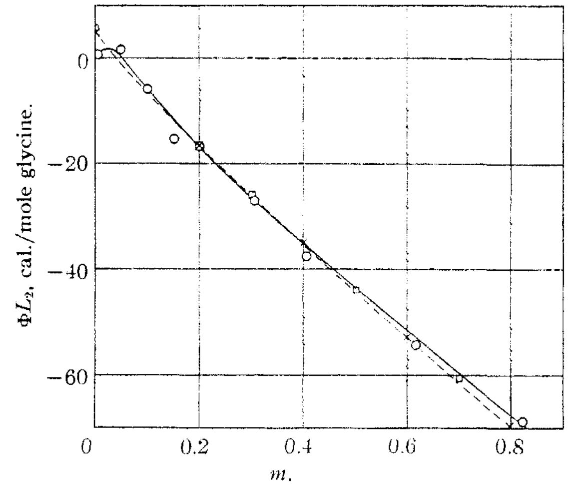

Fig. 2.—Plot showing the variation of ΦL_2 with molality: O, this research; ×, Gucker, Pickard and Ford; □, Sturtevant; full curve computed from equation (6); dashed curve from Equation 2 of Gucker, Pickard and Ford.[6]

made coincident at 0.2 *m* so as to eliminate discrepancies arising from different methods of extrapolation. Only in the dilute range (<0.05 *m*) are there significant deviations of the several curves. For the 32 experiments performed in this study with concentrations less than 0.2 *m*, the average deviation of measured from calculated (see equation 6) heat effects is 0.0023 cal. In the same concentration range the data of Gucker, Pickard and Ford show an average deviation from their equation (2) of 0.0040 cal. for 36 experiments. For the 14 runs above 0.2 *m* the average deviation of measured from calculated is 0.0044 cal. for our data, and 13 runs by Gucker, Pickard and Ford show an average deviation of 0.0043 cal. from their equation above 0.2 *m*. Sturtevant's results are mostly for concentrated solutions and are reported to deviate approximately 0.04 cal. on the average from his equation.

The results of this study for $m < 0.05$ reveal that the slope $\partial \Phi L_2/\partial m$ is changing rapidly with concentration, apparently becoming positive at very great dilutions. However, the heat effects below 0.05 molal are extremely small and are not as reproducible as could be desired. These difficulties are evidenced by a large uncertainty in the computed limiting slope. The S^0 value (see equation 3) of +167 has associated with it a probable error of ±233,[16] which, of course, is too large to allow the sign of the initial slope to be definitely established. If, however, correction is made for ionization effects, after the calculations of Sturtevant, these measurements indicate the existence of a positive limiting slope. In any case, the measurements at high dilutions strongly suggest that the true limiting slope is appreciably less negative than previously has been reported.[6,7]

Summary

The heats of dilution of aqueous glycine solutions have been measured from 0.8 to 0.0003 molal at 25°. The partial molal heat contents have been calculated for the components over the concentration range studied.

The behavior in very dilute solutions appears to conform more closely to the theory of Fuoss than do the results of previous studies.

[16] Estimated from the uncertainties in the data from which it was obtained (see ref. 14).

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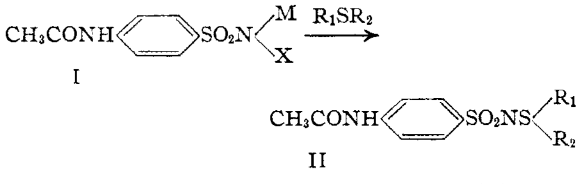
[Contribution from the Department of Chemistry of the University of Rochester]

Sulfilimines Derived from Sulfanilamide

By C. W. Todd, John H. Fletcher and D. S. Tarbell

In view of the possible importance of new types of sulfanilamide derivatives, we have extended previous work on sulfilimines[1] to the preparation of a series of sulfilimines derived from sulfanilamide.

When the method of preparing sulfilimines which was successful with *p*-toluenesulfonamide[1]—heating the sulfoxide and sulfonamide together with an acid dehydrating agent—was tried with sulfanilamide and diethyl or diphenyl sulfoxide, no product was obtained. It was found possible, however, to prepare compounds of type I from N^4-acetylsulfanilamide, by treatment with the appropriate hypohalite, where M is sodium or potassium, and X is chlorine or bromine. Condensation of the type I compounds with sul-



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[1] Tarbell and Weaver, This Journal, **63**, 2939 (1941).