

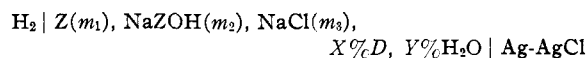
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Basic Ionization Constant of Glycine in Dioxane-Water Solutions

BY HERBERT S. HARNED AND CLAIR M. BIRDSALL¹

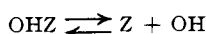
The ionization of weak electrolytes in aqueous solution and in water-organic solvent mixtures has been studied successfully by the use of cells without liquid junction.² The present determination of the basic ionization constant of glycine in dioxane-water solutions supplements the work recently reported on the acidic ionization constant of this substance in the same media.³ The acidic and basic ionization constants of glycine have been determined in aqueous solution by Owen⁴ from cells without liquid junction.

For the evaluation of the basic ionization constant cells of the type



have been employed where Z designates the zwitterion, $^+\text{NH}_3\text{CH}_2\text{COO}^-$, NaZOH the hydrated sodium glycinate, and X the per cent. by weight of dioxane in the solvent. By thermodynamic treatment of the ionization data the free energy, heat content, heat capacity and entropy of the ionization reaction can be evaluated.

Outline of the Method—Extrapolation Function.—The ionization may be represented by



and the thermodynamic ionization constant for the reaction expressed as

$$K_B = \frac{a_Z a_{\text{OH}}}{a_{\text{OHZ}}} = \frac{m_Z m_{\text{OH}} \gamma_Z \gamma_{\text{OH}}}{m_{\text{OHZ}} \gamma_{\text{OHZ}}} \quad (1)$$

where m represents molality, γ the activity coefficient and Z , OH and OHZ designate the ionic species. The apparent ionization constant K'_B may be expressed by

$$K'_B = \frac{m'_Z m'_{\text{OH}}}{m'_{\text{OHZ}}} = \frac{(m_1 + m'_{\text{OH}}) m'_{\text{OH}}}{(m_2 - m'_{\text{OH}})} \quad (2)$$

The thermodynamic equation for the cell is

$$\frac{E - E^{0*}}{k} = -\log a_{\text{HCl}} \quad (3)$$

where k equals $2.3026 RT/F$.⁵

(1) This contribution contains material from a dissertation presented by Clair M. Birdsall to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(2) Harned and Owen, *Chem. Rev.*, **25**, 31 (1939).

(3) Harned and Birdsall, *THIS JOURNAL*, **65**, 54 (1943).

(4) Owen, *ibid.*, **56**, 24 (1934).

(5) The values of R , F and the ice point used in calculating k were 1.987 cal./deg., 23059 cal. and 273.1°A., respectively.

By combining equations (1) and (3) with that for the thermodynamic ionization constant of water

$$K_W = \frac{m_{\text{H}} m_{\text{OH}} \gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} \quad (4)$$

the following equation is obtained

$$\frac{E - E^{0*}}{k} + \log m_{\text{Cl}} + \log \frac{m_Z}{m_{\text{OHZ}}} + \log K_W = \\ \log K_B - \log a_{\text{H}_2\text{O}} \frac{\gamma_Z \gamma_{\text{Cl}}}{\gamma_{\text{OHZ}}} \quad (5) \\ \equiv \log K''_B$$

K_W has been determined in 20, 45 and 70% dioxane-water solutions by Harned and Fallon,⁶ $m_{\text{Cl}} = m_3$ is known, m_Z and m_{OHZ} can be obtained by correcting the stoichiometric values m_1 and m_2 for the amount of ionization, and E^{0*} has been determined by Harned and Morrison.^{7,8} Measurement of E completes the data necessary for the evaluation of the left side of equation (5) designated as $\log K''_B$.

A preliminary value of $\log K''_B$ was obtained by neglecting the effect of the ionization on m_1 and m_2 . This value was substituted in equation (2) and a first approximation of m'_{OH} calculated. m_1 and m_2 were corrected by this amount and $\log K''_B$ again computed. The corrections in all cases were small and the procedure was unnecessary for the data obtained in the 70% dioxane-water solutions. The extrapolation of $\log K''_B$ against m yields the thermodynamic ionization constant at zero ionic strength.

Experimental Procedure and Observed Electromotive Forces.—The experimental technique has been described previously in detail.⁹ The stock solution was prepared by weighing glycine, standard sodium hydroxide, sodium chloride and water into a large flask. The glycine was crystallized three times from conductivity water and dried over solid potassium hydroxide in a vacuum desiccator. It was found to contain 0.16% water.¹⁰ Carbonate free sodium hydroxide was prepared by diluting a saturated sodium hydrox-

(6) Harned and Fallon, *THIS JOURNAL*, **61**, 2374 (1939).

(7) Harned and Morrison, *ibid.*, **58**, 1908 (1936).

(8) The equations, based on the data of Harned and Morrison, by which the standard potentials were computed are given by Harned, Morrison, *et al.*, *ibid.*, **61**, 49 (1939).

(9) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

(10) Harned and Birdsall, *THIS JOURNAL*, **65**, 54 (1943).

ide solution. The dilute solution was standardized against potassium acid phthalate. Baker analyzed sodium chloride was recrystallized and dried in a muffle at 300°. The molalities in the buffer solution were: $m_1 = m_Z = 0.41914$, $m_2 = m_{\text{NaOH}} = 0.38122$, $m_3 = m_{\text{NaCl}} = 0.32038$. Thus $m_1/m_2 = 1.0994$, $m_2/m_3 = 1.3082$. The cell solutions were prepared by weight dilution of portions of the stock solution with dioxane and water. The cells were prepared in triplicate at each chosen ionic strength. After equilibrium had been attained at 25° measurements were made at five degree intervals from 0 to 50°. The original and final measurements at 25° were used in judging satisfactory cell behavior.

The experimental electromotive forces can be expressed by the equation

$$E_t = E_{25} + a(t - 25) + b(t - 25)^2 \quad (6)$$

The parameters of this equation obtained by a graphical method¹¹ are given in Table I. The deviations of the calculated from the observed electromotive forces tabulated in column five of Table I show that the equation reproduces the experimental results within ± 0.16 mv. This compares favorably with the agreement among the three cells measured. In general the cell behavior was less satisfactory as the dioxane content of the solvent was increased.

Ionization Constants.—The values of $\log K_B''$ computed at the chosen ionic strengths were plotted on a large scale graph. The extrapolated value at zero ionic strength is equal to $\log K_B$ since the second term on the right side

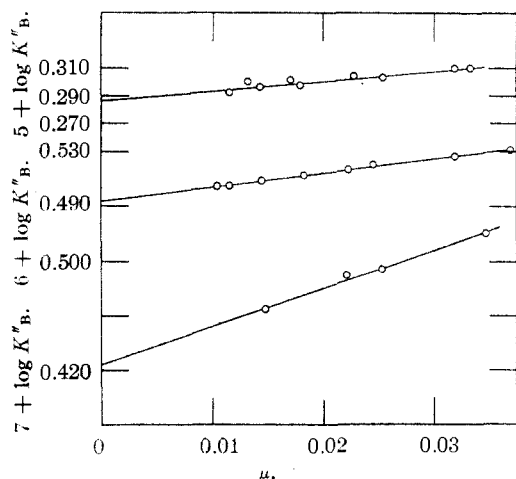


Fig. 1.—Extrapolations at 25: $\log K_B''$ vs. μ ; diameter of circles = 0.4 mv.

(11) Harned and Nims, *THIS JOURNAL*, **54**, 423 (1932).

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS
 $\text{H}_2 | Z(m_1), \text{NaOH}(m_2), \text{NaCl}(m_3), X\% \text{D}, Y\% \text{H}_2\text{O} | \text{Ag-AgCl}$

Constants of the equation $E_t = E_{25} + a(t - 25) + b(t - 25)^2$; valid from 0 to 50°. $X = \% \text{dioxane}$ by weight. $\Delta =$ average deviation between observed electromotive forces and those computed by the equation. $m_1 = 1.0994m_2$; $m_1 = 1.3082m_3$.

m_1	E_{25}	$a \times 10^5$	$-b \times 10^8$	Δ
$X = 20$				
0.006946	0.92147	98	200	0.02
.007920	.91847	90	224	.12
.008587	.91615	81	198	.05
.010222	.91203	69	228	.09
.010717	.91057	67	192	.06
.013638	.90472	44	196	.04
.015175	.90199	38	218	.14
.019072	.89650	14	194	.02
.019930	.89538	10	196	.03
$X = 45$				
0.006251	0.90445	82	124	0.08
.006921	.90187	90	120	.11
.008671	.89627	104	135	.12
.010950	.89055	124	120	.10
.013349	.88571	146	116	.05
.014709	.88339	154	128	.05
.019075	.87712	174	134	.03
.022095	.87358	180	140	.10
$X = 70$				
0.008770	0.85970	386	70	0.16
.013246	.85055	416	78	.13
.015137	.84739	424	62	.06
.020763	.84083	450	80	.09

of equation (5) then equals zero. Figure 1 shows the 25° extrapolations in the three dioxane-water solutions. In Table II are tabulated all the values of $-\log K_B$ or pK_B determined from similar plots.

TABLE II
THE BASIC IONIZATION CONSTANT OF GLYCINE IN DIOXANE-WATER SOLUTIONS

t	$X = 20$		$X = 45$		$X = 70$	
	pK_B	$\Delta \times 10^{-3}$	pK_B	$\Delta \times 10^{-3}$	pK_B	$\Delta \times 10^{-3}$
0	4.9285	-0.4	5.7475	-0.1	6.832	+2
5	4.8804	+1.3	5.6938	+0.3	6.775	0
10	4.8317	-1.1	5.6436	+1.1	6.719	-3
15	4.7910	+1.1	5.5950	+0.5	6.672	+1
20	4.7493	-0.8	5.5467	-2.7	6.621	-2
25	4.7129	-0.5	5.5058	-1.1	6.575	0
30	4.6802	+0.7	5.4674	+0.3	6.531	+1
35	4.6495	+1.2	5.4310	+1.3	6.490	+4
40	4.6186	-1.2	5.3963	+1.6	6.443	-1
45	4.5938	+0.1	5.3623	+0.4	6.402	-1
50	4.5703	+0.3	5.3298	-1.4	6.363	0

The uncertainty in the numerical value of $\log K_B$ due to scattering of the experimental points

TABLE III
 Constants of Equations (7) to (13) Inclusive. $X = \% \text{ Dioxane by Weight}$

X	A^*	D^*	C^*	A'	D'	C'	T_θ	$-\log K_\theta$
0 ¹³	1307.30	2.5629	0.008038	5980.95	11.7254	0.036673	403.3	3.9203
20	1519.8866	3.3800	.010046	6953.7851	15.4642	.045964	389.0	4.4350
45	1364.9011	1.1999	.0071393	6244.6955	5.4898	.032663	437.2	5.0433
70	895.267	-3.328	.0008182	4096.02	-15.227	.003743	(1046)†	(5.039)†

† Since the results in the 70% dioxane solutions are less accurate than the others, these derived values of T_θ and $-\log K_\theta$ are obviously in error. This is due to the difficulty in determining the parameter C' , which when C' is small greatly affects the results (see equations (12) and (13)). This uncertainty also invalidates the value of ΔC_{pi}^0 in Table IV.

may be ± 0.0016 in the 20 and 45% solutions and as much as ± 0.005 in the 70% solutions.

Thermodynamic Quantities.—Although plots of pK_B versus T do not show as much curvature as similar plots for pK_A , the equation of Harned and Robinson¹²

$$\log K = -\frac{A^*}{T} + D^* - C^*T \quad (7)$$

is suitable for the expression of $\log K_B$ as a function of the temperature. This is obvious from Table II in which $\Delta \times 10^{-3} = pK_B(\text{observed}) - pK_B(\text{calculated})$. The differences are well within the range of the estimated uncertainty in all but a few cases.

The thermodynamic functions derived from equation (7) are as follows

$$\Delta F_i^0 = A' - D'T + C'T^2 \quad (8)$$

$$\Delta H_i^0 = A' - C'T^2 \quad (9)$$

$$\Delta C_{pi}^0 = -2C'T \quad (10)$$

$$\Delta S_i^0 = D' - 2C'T \quad (11)$$

in which

$$A' = 2.3026 RA^*$$

$$D' = 2.3026 RD^*$$

$$C' = 2.3026 RC^*$$

The temperature at which the maximum ionization occurs, T_θ and the value of the ionization constant at that temperature, $\log K_\theta$, are calculated by use of

$$T_\theta = \sqrt{A^*/C^*} \quad (12)$$

$$\log K_\theta = D^* - 2\sqrt{C^*A^*} \quad (13)$$

Table III contains the values of these constants obtained by the method of least squares.

The thermodynamic quantities were calculated by equations (8) to (11) using the numerical

(12) Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(13) Computed by Dr. R. A. Robinson from the data of Owen, *This Journal*, **56**, 24 (1934).

values for the constants given in Table III. The values of the thermodynamic quantities at 25° are tabulated in Table IV. Data calculated from the measurements made by Owen¹³ on the basic ionization of glycine in aqueous solutions have been included in Table III and Table IV.

TABLE IV
 THERMODYNAMIC QUANTITIES AT 25°. $X = \% \text{ DIOXANE BY WEIGHT}$

X	ΔF_i^0 cal./mole	ΔH_i^0 cal./mole	ΔC_{pi}^0 cal./°-mole	ΔS_i^0 cal./°-mole
0 ¹³	5753	2713	-21.9	-10.2
20	6428	2869	-27.4	-11.9
45	7511	3342	-19.5	-14.0
70	8968	3763	(-2.2)*	-17.5

* See note (Table III).

Summary

Cells of the type $H_2 | Z (m_1), NaZOH(m_2), NaCl(m_3), X\%D, Y\%H_2O | Ag-AgCl$, have been employed to investigate the basic ionization of glycine in solutions containing 20, 45 and 70% dioxane by weight. The measurements were made at five degree intervals from 0 to 50°.

The thermodynamic ionization constants, evaluated by graphical extrapolation of the experimental data, can be expressed over the temperature range by the equation

$$\log K = -\frac{A^*}{T} + D^* - C^*T \quad (7)$$

The numerical values of the constants in this equation, obtained by the method of least squares, have been tabulated.

The thermodynamic quantities of the ionization-reaction at 25° are tabulated. Data based on the work of Owen¹³ have been included.

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