Thermochimica Acta, 159 (1990) 337–347
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPY OF IONIZATION OF AQUEOUS GLYCINIUM ION ($^+$HGly = H$^+$ + Gly) AT 298 K, DEPENDENCE ON IONIC STRENGTH, AND THERMODYNAMICS OF IONIZATION

CHING-HSIEN WU

*Science Department (Chemistry), LaGuardia College, City University of New York,
31-10 Thomson Avenue, Long Island City, NY 11101 (U.S.A.)*

(Received 21 August 1989)

ABSTRACT

Previous investigations have led to considerably different enthalpy values (3891–5983 J mol^{-1}) for the first ionization of aqueous glycine ($^+$HGly = H$^+$ + Gly) at $T = 298.15$ K. To resolve this uncertainty, new measurements of the enthalpy of solution of glycine in water and in excess dilute hydrochloric acid have been made. Results of these measurements lead to values of $\Delta H_1^\ominus = 4.1 \pm 0.1$ kJ mol^{-1}, and thence $\Delta S_1^\ominus = -31.2 \pm 0.3$ J K^{-1} mol^{-1}, for the first ionization of glycine at $T = 298.15$ K. It has been noted that there is an unusually large dependence of ΔH_1 on the ionic strength of the solution.

INTRODUCTION

The properties of aqueous glycine (and other amino acids) are important in biochemistry and also in more general solution chemistry for several reasons. Among the most important are the thermodynamic properties associated with the acid–base reactions of glycine, which can be represented by the equations

$$^{+}\mathrm{HGly(aq)} = \mathrm{H^+(aq)} + \mathrm{Gly(aq)} \tag{1}$$

and

$$\mathrm{Gly(aq)} = \mathrm{H^+(aq)} + \mathrm{Gly^-(aq)} \tag{2}$$

The investigation described here has been concerned only with the first ionization, which is represented by eqn. (1). There is considerable evidence that the principal aqueous glycine species (neither protonated nor ionized) is the zwitterion, sometimes represented by Gly$^{\pm}$(aq), but the simpler Gly symbol for this electrically neutral species will be used here.

Owen [1] made careful electrochemical measurements leading to values of K_1 at several temperatures. Application of $\mathrm{d}\ln K/\mathrm{d}T = \Delta H^\ominus/RT^2$ to these results has led Owen [1] and others [2–5] to report values of $\Delta H^\ominus$ at

0040-6031/90/$03.50

TABLE 1

Previously reported standard enthalpies of acid dissociation of aqueous glycinium [eqn. (1)] at 298 K

Source	$\Delta H^{\ominus}$ (J mol^{-1})
Owen [1–5] [a]	4364–4916
King [6–8]	3975–4008
Sturtevant [9]	3891
Izatt et al. [10]	5983
Christensen et al. [11]	4100

[a] Various values in the specified range have been calculated [1–5] from the experimental results of Owen [1].

$T = 298$ K ranging from 4364 kJ mol^{-1} to 4916 J mol^{-1} (our conversions from cal to J here and elsewhere). More recent electrochemical measurements by King [6] have also led to K_1 values at several temperatures. Calculations [6–8] with these results have led to values of $\Delta H^{\ominus}$ at $T = 298$ K ranging from 3975 J mol^{-1} to 4008 J mol^{-1}. Calorimetric measurements by Sturtevant [9], by Izatt et al. [10], and by Christensen et al. [11] have led to $\Delta H^{\ominus} = 3891$ J mol^{-1}, 5983 J mol^{-1} and 4100 J mol^{-1}, respectively. All of these results are summarized concisely in Table 1.

One purpose of the investigation described here was to resolve the substantial uncertainty in the 'best' $\Delta H^{\ominus}$ value for the ionization represented by eqn. (1). Another reason for carrying out this investigation is related to the results of Rey et al. [12], who have reported K_{app} values over a wide range of ionic strengths.

EXPERIMENTAL

Baker-analyzed glycine was stored over KOH pellets and was used without purification on the basis of the reported analyses: non-aqueous acid–base titration, 99.9%; homogeneity by TLC, no extraneous spots; ash, less than 0.1%; loss on drying at 105 °C, less than 0.1%, etc. Stock solutions of hydrochloric acid were standardized by titration with standard sodium hydroxide solutions.

A modified Guild solution calorimeter (model 400) was used. This calorimetric system included part of a bridge circuit for temperature measurements and a Guild power supply (model 420-115) for electrical calibration. For the measurements described here, a thermistor (Victory Engineering Co., No. 35A3) in a glass tube in the calorimeter was used as one arm of the thermistor bridge, with out-of-balance potential being measured with a Rubicon potentiometer (type B, high precision) and galvanometer. A 100.45 Ω manganin wire heater in a glass tube in the calorimeter was used for electrical calibration. The original calorimeter (225 ml Dewar flask) was not shielded from changes in temperature of the environment, so improved operation was attained by placing the Dewar vessel inside a metal can, which was then immersed in a constant temperature water bath. Thin-walled glass ampoules containing glycine were attached to the calorimeter stirrer and broken on the bottom of the calorimeter to permit the glycine to dissolve or react. 'Blank' measurements were made to determine the small thermal effect associated with stopping the stirrer and breaking the ampoule. Construction and operation of a similar calorimeter have been described previously [13].

The calorimeter was tested by measuring enthalpies of solution of KCl(c) in water (1 : 1200 and 1 : 6800 mole ratios), with results in excellent agreement with selected properties reported by Wagman et al. [14].

RESULTS

Calorimetric measurements at 25.0 ± 0.1° C were of two kinds: enthalpies of solution of glycine in water and in excess hydrochloric acid. Calculations with the equilibrium constants for reactions represented by eqns. (1) and (2) and the ionization constant for water have shown [9] that glycine in water is neither protonated nor dissociated to any significant extent. It is therefore appropriate to represent the chemical process in the first kind of calorimetric measurements by the simple equation

$$\mathrm{Gly(c) = Gly(aq)} \qquad (3)$$

Representation of the chemical process associated with dissolving glycine in excess acid is more complicated, and is discussed in detail later.

Eleven measurements of the enthalpy of solution of glycine in water were made, with final solutions having molalities ranging between 3.7×10^{-3} and 1.8×10^{-2} mol kg^{-1}. The dependence of this enthalpy of solution on concentration of the final solution was too small to be observed, which is in accord with enthalpies of dilution reported by Wallace et al. [15]. The average of our results has therefore been taken to be $\Delta H^{\ominus} = 14.1 \pm 0.1$ kJ mol^{-1} for the standard enthalpy of solution of glycine in water, as represented by eqn. (1). This result is listed in Table 2, along with the results of previous measurements. It is seen that there is generally good agreement between results from different investigators.

We now designate the enthalpy of solution of glycine in water as $\Delta H_3^{\ominus}$, and recognize that combination of this enthalpy with the enthalpy for

$$\mathrm{Gly(c) + H^+(aq) = {}^+HGly(aq)} \qquad (4)$$

will yield the desired enthalpy of the first ionization (1) according to

$$\Delta H_1^{\ominus} = \Delta H_3^{\ominus} - \Delta H_4^{\ominus} \qquad (5)$$

TABLE 2

Standard enthalpies ($\Delta H^{\ominus}$) of solution of glycine in water at 298 K [a]

Source	$\Delta H^{\ominus}$ (kJ mol^{-1})
Ref. 16	14.13 ± 0.04
Ref. 17	14.3 ± 0.3
Ref. 18	14.2 ± 0.2
Ref. 19	14.16 ± 0.01
Ref. 20	14.12 ± 0.06
This work	14.1 ± 0.1

[a] Results reported in terms of cal have been converted to J; uncertainties quoted (± values) were given by the original authors.

As the first step toward obtaining $\Delta H_4^{\ominus}$, we have measured enthalpies of solution of glycine in excess aqueous hydrochloric acid, with results that are summarized in Table 3.

Because the reaction represented by eqn. (4) is electrically symmetrical and the ionic strength of the solution does not change when glycine is dissolved in hydrochloric acid, ΔH_4 is expected to be independent of ionic strength in sufficiently dilute solution and also equal to the desired $\Delta H_4^{\ominus}$. However, calculations with the equilibrium constant for reaction (1) show that only part of the glycine is protonated to form $^{+}$HGly(aq) in very dilute solution. It is therefore seen that the measured enthalpies of solution of glycine in excess dilute hydrochloric acid do not lead directly to $\Delta H_4^{\ominus}$, or even directly to ΔH_4.

We represent the calorimetric process for dissolving glycine into excess hydrochloric acid by

$$n_g\text{Gly(c)} + h_i\text{H}^+\text{(aq)} = n_0\text{Gly(aq)} + n_+\,{}^+\text{HGly(aq)} + (h_i - n_+)\text{H}^+\text{(aq)} \qquad (6)$$

for which the measured enthalpy change is designated Q_6 in Table 3 and the following analysis. Symbols in eqn. (6) have the following meanings: n_g is the number of moles of glycine, h_i is the number of moles of H$^+$(aq) originally in the calorimeter, n_0 is the number of moles of unprotonated glycine in the final calorimetric solution, and n_+ is the number of moles of protonated glycine ($^{+}$HGly) formed in the calorimeter. It is emphasized that the ionic strength remains constant

To analyze our Q_6 values to obtain $\Delta H_4^{\ominus}$, we write

$$n_0\text{Gly(c)} = n_0\text{Gly(aq, } \mu = 0) \qquad Q_7 = n_0 \Delta H_3^{\ominus} \qquad (7)$$

and

$$n_0\text{Gly(c)} = n_0\text{Gly(aq, specified } \mu) \qquad Q_8 \qquad (8)$$

in which μ represents the ionic strength of the solution. These two processes

TABLE 3

Measured enthalpies of solution and reaction of glycine in 225 ml of hydrochloric acid (Q_6) and related information

$n_g \times 10^3$	$m(H^+)_i$	Q (J)	f	ΔH_1 (kJ mol^{-1})
Series 1: $\mu = 0.04$; $k_1 = 4.446 \times 10^{-3}$				
1.377	0.04034	14.24	0.8869	4.20
1.901	0.04028	19.71	0.8806	4.20
2.739	0.04028	28.69	0.8695	4.13
2.839	0.04038	29.53	0.8683	4.22
3.237	0.04031	33.65	0.8622	4.25
3.881	0.04030	40.20	0.8515	4.35
Series 2: $\mu = 0.10$; $k_1 = 4.426 \times 10^{-3}$				
1.365	0.1010	14.41	0.9555	3.61
1.572	0.1009	16.73	0.9551	3.52
1.707	0.1074	18.15	0.9576	3.52
2.017	0.1010	20.91	0.9543	3.82
2.121	0.1008	22.26	0.9540	3.68
2.294	0.1010	23.64	0.9537	3.88
2.607	0.1010	26.67	0.9531	3.96
3.510	0.1009	35.88	0.9510	3.98
4.052	0.1010	41.40	0.9498	3.99
4.082	0.1010	41.77	0.9497	3.97
5.383	0.1009	55.47	0.9463	3.91
Series 3: $\mu = 0.21$; $k_1 = 4.406 \times 10^{-3}$				
1.344	0.2023	14.70	0.9781	3.05
2.923	0.2023	31.33	0.9773	3.27
3.394	0.2023	35.48	0.9770	3.52
4.059	0.2024	41.63	0.9767	3.75
4.661	0.2024	47.92	0.9764	3.72
5.325	0.2023	54.79	0.9760	3.72
Series 4: $\mu = 0.41$; $k_1 = 4.315 \times 10^{-3}$				
1.475	0.4051	15.53	0.9893	3.23
2.014	0.4061	21.67	0.9893	2.99
2.708	0.4057	27.23	0.9892	3.71
3.318	0.4057	33.39	0.9891	3.70
3.922	0.4059	38.51	0.9890	3.95
5.411	0.4061	54.77	0.9888	3.64
Series 5: $\mu = 0.51$; $k_1 = 4.256 \times 10^{-3}$				
1.348	0.5084	13.91	0.9916	3.34
2.005	0.5083	21.05	0.9915	3.16
2.014	0.5090	20.87	0.9916	3.30
3.569	0.5080	35.76	0.9914	3.64
4.019	0.5072	40.15	0.9914	3.67
Series 6: $\mu = 0.82$; $k_1 = 4.045 \times 10^{-3}$				
2.053	0.8176	19.24	0.9950	4.00
2.165	0.8176	20.04	0.9950	4.11
3.433	0.1870	33.68	0.9950	3.55
3.957	0.8174	38.76	0.9950	3.57
4.621	0.8174	44.47	0.9949	3.74

TABLE 3 (continued)

$n_g \times 10^3$	$m(H^+)_i$	Q (J)	f	ΔH_1 (kJ mol^{-1})
Series 7: $\mu = 1.03$; $k_1 = 3.890 \times 10^{-3}$				
1.379	1.0278	11.83	0.9962	4.59
2.110	1.0257	18.46	0.9962	4.42
2.604	1.0253	22.62	0.9962	4.48
3.281	1.0259	30.48	0.9962	3.88
3.794	1.0277	36.08	0.9962	3.66
4.366	1.0251	42.32	0.9961	3.47
4.727	1.0274	43.76	0.9961	3.91
5.266	1.0277	49.82	0.9961	3.71

are related to the enthalpy of transfer of glycine from $\mu = 0$ to specified μ as in

$$n_0\text{Gly(aq, } \mu = 0) = n_0\text{Gly(aq, specified } \mu) \qquad Q_{tr} = n_0 \Delta H_{tr} \tag{9}$$

according to

$$Q_8 = Q_7 + Q_{tr} = n_0\left(\Delta H_3^{\ominus} + \Delta H_{tr}\right) \tag{10}$$

To obtain values of Q_8 to be used in subsequent calculations it is necessary to obtain Q_{tr} and ΔH_{tr} as follows.

Larson and Morrison [21] have made calorimetric measurements leading directly to values of ΔH_{tr} with the ionic strength maintained at specified values with sodium chloride, while Kelley and Lilley [20] measured enthalpies of solution of Gly(c) in pure water and in solutions of specified ionic strength (NaCl). We have combined these results to obtain

$$\Delta H_{tr}(\text{J mol}^{-1}) = -920\mu$$

The next task is to evaluate n_0 and n_+ appropriate to each calorimetric measurement. To begin, we know that

$$n_g = n_0 + n_+ \tag{11}$$

and from King [6] we have apparent equilibrium constants k_1 for reaction (1) at various ionic strengths that we write as

$$k_1 = [H^+][\text{Gly}]/[^+\text{HGly}] \tag{12}$$

in which brackets indicate molalities of the enclosed species. This apparent equilibrium constant can be expressed as

$$k_1 = [H_i^+ - {}^+\text{HGly}]\left[\textstyle\sum \text{Gly} - {}^+\text{HGly}\right]/[^+\text{HGly}] \tag{13}$$

in which H_i^+ refers to the H^+ present initially, $^+$HGly represents the final or equilibrium molality of protonated glycine, and ΣGly is the total or stoichiometric molality of all glycine in the solution. Defining the fractional conversion of Gly to $^+$HGly by

$$f = [^+\text{HGly}]/\left[\textstyle\sum \text{Gly}\right] = n_+/n_g \tag{14}$$

and combination with eqn. (13) leads to

$$k_1 = \left[\mathrm{H}_i^+ - f\sum\mathrm{Gly}\right]\left[\sum\mathrm{Gly} - f\sum\mathrm{Gly}\right]/\left[f\sum\mathrm{Gly}\right] \tag{15}$$

Equation (15) is a quadratic in f, which is rearranged and solved to yield

$$f = \frac{\left[\mathrm{H}_i^+ + \sum\mathrm{Gly} + k_1\right] - \left\{\left[\mathrm{H}_i^+ + \sum\mathrm{Gly} + k_1\right]^2 - 4[\mathrm{H}_i^+]\left[\sum\mathrm{Gly}\right]\right\}^{1/2}}{2\left[\sum\mathrm{Gly}\right]} \tag{16}$$

Using values of f calculated according to eqn. (16) and known values of n_g leads to

$$n_+ = fn_g \tag{17}$$

and

$$n_0 = (1 - f)n_g \tag{18}$$

It is now possible to use these n_0 values to obtain Q_8 values by way of eqn. (10) and then the corresponding $\Delta H_8 = Q_8/n_0$.

Next, we write an equation to represent reaction (4) that is specifically appropriate to our calorimetric process

$$n_+\mathrm{Gly(c)} + n_+\mathrm{H}^+(\mu) = n_+\,{}^+\mathrm{HGly}(\mu) \qquad Q_{19} = n_+\Delta H_{19} \tag{19}$$

Referring to eqn. (11), we see that the sum of eqns. (8) and (19) gives us eqn. (6), which corresponds to the overall calorimetric process for which we have measured values of Q_6

$$Q_6 = Q_8 + Q_{19} \tag{20}$$

Combination of eqns. (10), (19) and (20) now leads to

$$Q_6 = n_0\left(\Delta H_3^\ominus + \Delta H_{\mathrm{tr}}\right) + n_+\Delta H_{19} \tag{21}$$

We solve eqn. (21) for ΔH_{19} to obtain

$$\Delta H_{19} = \left[Q_6 - n_0\left(\Delta H_3^\ominus + \Delta H_{\mathrm{tr}}\right)\right]/n_+ \tag{22}$$

and combine with eqns. (17) and (18) to eliminate n_0 and n_+ and to obtain

$$\Delta H_{19} = \left[Q_6 - (1 - f)n_g\left(\Delta H_3^\ominus + \Delta H_{\mathrm{tr}}\right)\right]/fn_g \tag{23}$$

We now combine $\Delta H_8 = Q_8/n_0$ (see eqn. (10)) with ΔH_{19} to obtain

$$\Delta H_1(\mu,\ m_{\mathrm{gly}}) = \Delta H_8 - \Delta H_{19} \tag{24}$$

where $\Delta H_1(\mu,\ m_{\mathrm{gly}})$ is written to emphasize that this enthalpy refers to dissociation of ${}^+$HGly at specified finite ionic strength and concentration of ${}^+$HGly. Combination of eqns. (10), (23) and (24) with our previously specified $\Delta H_3^\ominus = 14100$ J mol^{-1} and ΔH_{tr} (J mol^{-1}) = -920μ leads to

$$\Delta H_1(\mu,\ m_{\mathrm{gly}}) = \left[n_g(14{,}100 - 920\mu) - Q_6\right]/fn_g \tag{25}$$

TABLE 4

Enthalpies (kJ mol^{-1}) of first ionization of glycine, ΔH_1 (μ, $m_{\text{Gly}} = 0$)

μ	$\Delta H_1(\mu, m_{\text{Gly}} = 0)$
0.04	4.08
0.10	3.51
0.21	2.81
0.41	3.02
0.51	2.97
0.82	4.35
1.03	4.94

which permits calculation (in terms of J mol^{-1}) of the ΔH_1 values that are listed in Table 3.

For each series (constant ionic strength) of calorimetric measurements, the ΔH_1 values in Table 3 are extrapolated to zero concentration of glycine to obtain the $\Delta H_1(\mu, m_{\text{gly}} = 0)$ values that are listed in Table 4.

Next, the $\Delta H_1(\mu, m_{\text{gly}} = 0)$ values are to be extrapolated to $\mu = 0$ to obtain the standard state ($\mu = 0$, $m_{\text{gly}} = 0$) $\Delta H_1^{\ominus}$ value to be used in various thermodynamic calculations and to compare with the results of earlier $\Delta H_1^{\ominus} = RT^2$ $[\mathrm{d}(\ln K_1)/\mathrm{d}T]$ calculations. Because the ionization reaction represented by eqn. (1) is electrically symmetrical in terms of ions that disappear and form, it is expected that $\Delta H_1(\mu, m_{\text{gly}} = 0)$ values will be independent of ionic strength in very dilute solution. For less dilute solutions, $\Delta H_1(\mu, m_{\text{gly}} = 0)$ depends on ionic strength in some unknown way, because the $^{+}$HGly ion is considerably larger than the H^+ ion and because of interactions between the ions and the un-ionized glycine, which is present largely in the zwitterion form that is sometimes represented by Gly $^{\pm}$. In the absence of a complete theory, but considering the generalizations above, a graph of $\Delta H_1(\mu, m_{\text{gly}} = 0)$ against μ (Fig. 1) has been used as a guide in obtaining the value $\Delta H_1^{\ominus} = 4.1 \pm 0.1$ kJ mol^{-1}.

The present value, $\Delta H_1^{\ominus} = 4.1$ kJ mol^{-1}, is in excellent agreement with $\Delta H_1^{\ominus}$ values from the calorimetric measurements (dilute solutions, calculation details not presented) of Christensen et al. [11], and in almost as good agreement with the values calculated from the temperature dependence of the equilibrium constants reported by King [6]. On the other hand, the present $\Delta H_1^{\ominus}$ value is in only fair agreement with the calorimetric value reported by Sturtevant [9], who explained in his paper that he knew his extrapolation procedure was inadequate. Finally, the present $\Delta H_1^{\ominus}$ value is in poor agreement with the values calculated from the temperature dependence of equilibrium constants reported by Owen [1] and in very poor agreement with the calorimetric value reported by Izatt et al. [10]. It is our opinion that the disagreement with Owen is largely a matter of the large uncertainty in $\Delta H_1^{\ominus}$ calculated from his results, and that the very large

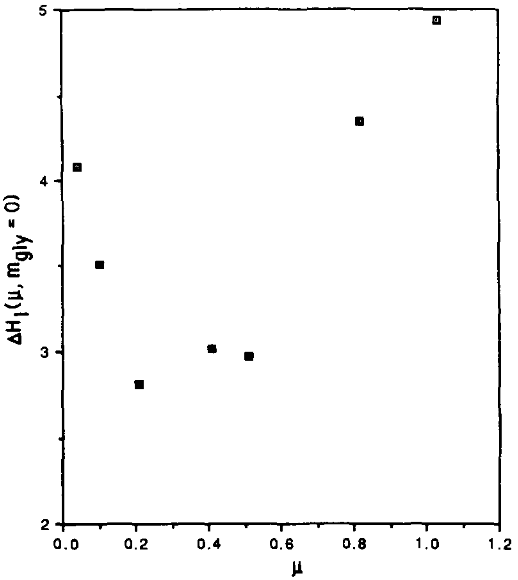

Fig. 1. Graph of $\Delta H_1(\mu, m_{gly} = 0)$ in kJ mol^{-1} vs. ionic strength.

calorimetric $\Delta H_1^\ominus = 5.98$ kJ mol^{-1} is a mistake, which was probably recognized by the authors who carried out the subsequent investigation [11] that led to a value in excellent agreement with our $\Delta H_1^\ominus$.

The pK_1 from King [6–8] leads to $\Delta G_1^\ominus = 13415$ J mol^{-1} at $T = 298.15$ K. We combine this value with our $\Delta H_1^\ominus = 4100$ J mol^{-1} to obtain $\Delta S_1^\ominus = -31.2 \pm 0.3$ J K^{-1} mol^{-1}, also for $T = 298.15$ K.

For the calculation leading to $\Delta G_1^\ominus$ and $\Delta S_1^\ominus$ for glycine at $T = 298.15$ K we have chosen to use the value p$K_1 = 2.350$ from King [7] rather than the more recent p$K_1 = 2.54$ from Rey et al. [12]. King's measurements [6,7] were made on solutions with compositions clearly expressed in terms of molalities (mol kg^{-1}), while the measurements of Rey et al. [12] were made on solutions with compositions expressed in terms of "M", which probably means molarities (mol l^{-1}). For reactions of type (1) the difference between pK (molality) and pK(molarity) is much less than the difference between the two pK_1 values cited above and need not be discussed further here. On the other hand, King [6,7] and Rey et al. [12] have used substantially different methods of extrapolation to zero ionic strength, and much of the difference in reported standard state pK_1 values is due to these different extrapolations.

King [6,7] has provided detailed justification for extrapolating his apparent equilibrium constants against the first power of μ to $\mu = 0$ to obtain the desired standard state K_1, and it is our opinion that his procedure for an electrically symmetrical dissociation such as (1) is correct. On the other hand, Rey et al. [12] have used (without explicit justification) an equation of the form

$$\log k_1 = \log K_1 - A\mu^{1/2} + B\mu \tag{26}$$

as the basis for their extrapolation to $\mu = 0$ to obtain their $pK_1 = 2.54$. Now we have used their reported pk_1 (our symbol) values at specified ionic strengths for a polynomial curve-fitting procedure in which the first term is $A\mu$ (rather than $A\mu^{1/2}$, as used by Rey et al.) to obtain a standard state $pK_1 = 2.35 \pm 0.01$, which is in good agreement with King's [6,7] more accurate value.

In the range of dilute solutions, it is expected that the enthalpies of an electrically symmetrical reaction such as (1) will be nearly independent of ionic strength, as observed previously for many other electrically symmetrical reactions. For the ionization of glycine, however, the dependence of ΔH_1 on ionic strength is unusually large, which is probably due to interactions of the ionic environment with the glycine (present mostly as the zwitterion) that are larger than interactions of the ionic environment with the more usual neutral (polar, but not a zwitterion) component of a reaction such as (1). Our results (Table 4) show that there is a minimum in $\Delta H_1(\mu, m_{\text{gly}} = 0)$ at $\mu \approx 0.3$. We do not know of any other example of such a minimum in this kind of ΔH, but we note that Rey et al. [12] have observed similar minima (smaller values of μ) for pK values for glycine and other amino acids.

ACKNOWLEDGEMENTS

I thank Dr. Grace W. King who originally called my attention to the desirability of making the measurements reported here, and for permitting me to modify and use the Guild calorimeter at Barnard College. I also thank Dr. King and Dr. Loren Hepler for encouragement and useful advice.

REFERENCES

1 B.B. Owen, J. Am. Chem. Soc., 56 (1934) 24.
2 H.S. Harned and B.B. Owen, Chem. Rev., 25 (1939) 31.
3 D.H. Everett and W.F.K. Wynne-Jones, Trans. Faraday Soc., 35 (1939) 1380.
4 H.O. Jenkins, Trans. Faraday Soc., 41 (1945) 138.
5 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 3rd edn., 1958.
6 E.J. King, J. Am. Chem. Soc., 67 (1945) 2178.
7 E.J. King, J. Am. Chem. Soc., 73 (1951) 155.
8 E.J. King, J. Am. Chem. Soc., 79 (1957) 6151.
9 J.M. Sturtevant, J. Am. Chem. Soc., 63 (1941) 88.
10 R.M. Izatt, J.J. Christensen and V. Kothari, Inorg. Chem., 3 (1964) 1565.
11 J.J. Christensen, R.M. Izatt and L.D. Hansen, J. Am. Chem. Soc., 89 (1967) 213.

12 F. Rey, A. Varela, J.M. Antelo and F. Arce, J. Chem. Eng. Data, 34 (1989) 35.
13 W.F. O'Hara, C.H. Wu and L.G. Hepler, J. Chem. Educ., 38 (1961) 512.
14 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, Suppl., 11 (2) (1982).
15 W.E. Wallace, W.F. Offutt and A.L. Robinson, J. Am. Chem. Soc., 65 (1943) 347.
16 G.C. Kresheck and L. Benjamin, J. Phys. Chem., 68 (1964) 2476.
17 G.C. Kresheck, H. Schneider and H.A. Scheraga, J. Phys. Chem., 69 (1965) 3132.
18 C.H. Spink and M. Auker, J. Phys. Chem., 74 (1970) 1742.
19 C.H. Spink and I. Wadso, J. Chem. Thermodyn., 7 (1975) 561.
20 B.P. Kelley and T.H. Lilley, J. Chem. Thermodyn., 10 (1978) 703.
21 J.W. Larson and D.G. Morrison, J. Phys. Chem., 80 (1976) 1449.