

A Conductimetric-Potentiometric Titration for an Advanced Laboratory

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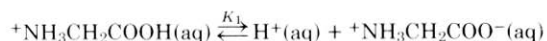
We describe here an experiment for physical chemistry or instrumental analysis laboratory in which the titration of glycine hydrochloride with standard sodium hydroxide is simultaneously followed with conductimetric and potentiometric measurements. Combination of the two measurements allows the calculation of more information about the glycine system than is available from either method alone. Only standard laboratory instrumentation is required, and design of the experiment provides the instructor considerable flexibility for implementation.

In aqueous solution, the amino acid glycine exists in three forms: the fully protonated dibasic form, $^+\text{NH}_3\text{CH}_2\text{COOH}$; the monoprotic zwitterion, $^+\text{NH}_3\text{CH}_2\text{COO}^-$; and the glycinate anion, $\text{NH}_2\text{CH}_2\text{COO}^-$. The relative concentrations of these species depend on the pH of the solution.

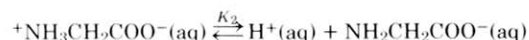
Titration of glycine hydrochloride with sodium hydroxide produces a pH titration curve typical of a weak diprotic acid. From this curve, one can determine values for the two acid dissociation constants as well as the analytical concentration of the original glycine hydrochloride solution. Conductimetric monitoring also gives a titration curve with two equivalence points. Combination of the conductivity curve with information from the pH curve allows determination of values for the molar ionic conductivities of the protonated glycine cation and the glycinate anion. The calculation illustrates the use of transference numbers and the concentration dependence of molar conductivity. Finally, the task of explaining the shape of the conductivity curve is of pedagogical value.

Titration Curves

The two acid dissociation equilibria for the glycine system are



and



The two titration curves are shown in Figure 1. The equivalence points of the conductivity curve appear as significant changes in slope and correlate with those of the pH curve.

Analysis of the conductivity curve is more complicated than that of the pH curve because the conductivity at any point

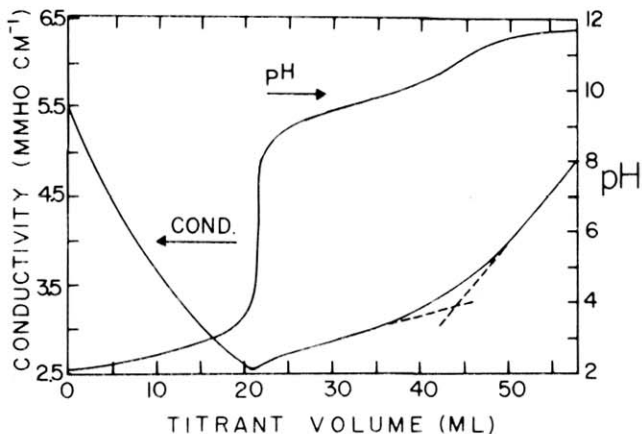


Figure 1. Conductivity and pH titration curves for titration of glycine hydrochloride with sodium hydroxide.

depends on the concentration and nature of all the ions in solution. Initially, the glycine hydrochloride solution contains protonated glycine cations, chloride ions, and a significant concentration of hydrogen ions and glycine zwitterions produced from the dissociation. The concentration of hydroxide ions produced from the ionization of water is negligible. The drop in conductivity observed as titrant is added is due mainly to the loss of highly mobile hydrogen ions. Protonated glycine ions are lost also but are replaced by sodium ions, which have a similar molar ionic conductivity. The zwitterions which are produced are not electrically mobile and do not contribute to the conductivity.

The first equivalence point is observed as a minimum in the conductivity curve, where the conductivity is due only to sodium and chloride ions. Protonated glycine, glycinate, hydrogen, and hydroxide ions are present in concentrations too small to affect the total conductivity. As more sodium hydroxide is added, glycinate ions are produced and, along with the added sodium ions and the increasing concentration of hydroxide ions, cause the conductivity to increase.

At the second equivalence point, essentially all of the glycine is present as glycinate. Beyond this point the excess hydroxide

ions from the titrant cause the conductivity to increase with a greater slope.

Calculations and Sample Results

In the following discussion, the protonated glycine, neutral glycine zwitterion, and glycinate ion are abbreviated glyH_2^+ , glyH , and gly^- , respectively. Sample data from Table 1 are used to illustrate the calculations.

The analytical concentration of glycine hydrochloride, C_0 , is calculated from the volume of titrant required to reach the equivalence points. The value calculated from data in Table 1 is $0.0312 \pm 0.0004 M$.

The first acid dissociation constant, K_1 , may then be calculated from the expression

$$K_1 = \frac{[\text{H}^+][\text{glyH}]}{[\text{glyH}_2^+]} = \frac{[\text{H}^+]_0^2}{C_0 - [\text{H}^+]_0}$$

where $[\text{H}^+]_0$ is the measured hydrogen ion concentration of the initial solution of glycine hydrochloride and C_0 is the analytical concentration of glycine hydrochloride determined above. All activity coefficients are assumed to be unity.

The second equilibrium constant is given by the expression

$$K_2 = \frac{[\text{H}^+][\text{gly}^-]}{[\text{glyH}]}$$

At the point in titrant volume halfway between the two equivalence points, the glyH is half-titrated and $[\text{glyH}] = [\text{gly}^-]$. Thus, K_2 is equal to the hydrogen ion concentration at this point.

Using the value of C_0 and sample data from Table 1, K_1 and K_2 were found to be $2.3(\pm 0.2) \times 10^{-3}$ and $2.2(\pm 0.5) \times 10^{-10}$, respectively. Literature values¹ are 4.46×10^{-3} and 1.67×10^{-10} .

To compute the ionic conductivities of the glycine species, one must express the measured conductivity as a sum of the ionic conductivities; that is, $1000 \kappa = \sum_i C_i \lambda_i$, where κ is the conductivity of the solution in $\text{ohm}^{-1}\text{cm}^{-1}$, C_i is the concentration of ion i in mol l^{-1} , and λ_i is the molar conductivity of ion i in $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

The titration solution contains varying concentrations of the three glycine species, as well as sodium, chloride, hydrogen,

and hydroxide ions. The glyH zwitterion can be eliminated from the sum because it has ionic conductivity of zero. Thus, the conductivity of the glycine solution at any point in the titration is given by

$$10^3 \kappa = C_{\text{glyH}_2^+} \lambda_{\text{glyH}_2^+} + C_{\text{gly}^-} \lambda_{\text{gly}^-} + C_{\text{Na}^+} \lambda_{\text{Na}^+} + C_{\text{Cl}^-} \lambda_{\text{Cl}^-} + C_{\text{H}^+} \lambda_{\text{H}^+} + C_{\text{OH}^-} \lambda_{\text{OH}^-}$$

In the initial solution of glycine hydrochloride, there is no sodium ion present, and the glycinate and hydroxide concentrations are negligible. The expression for the initial conductivity, κ_0 , is reduced to

$$10^3 \kappa_0 = C_{\text{glyH}_2^+} \lambda_{\text{glyH}_2^+} + C_{\text{Cl}^-} \lambda_{\text{Cl}^-} + C_{\text{H}^+} \lambda_{\text{H}^+} \quad (1)$$

At the second equivalence point, most of the glycine is in the glycinate form; the remainder is the non-conducting glyH from hydrolysis. The concentrations of both glyH_2^+ and H^+ are essentially zero. The conductivity at this point, κ_2 , is

$$10^3 \kappa_2 = C_{\text{gly}^-} \lambda_{\text{gly}^-} + C_{\text{Na}^+} \lambda_{\text{Na}^+} + C_{\text{Cl}^-} \lambda_{\text{Cl}^-} + C_{\text{OH}^-} \lambda_{\text{OH}^-} \quad (2)$$

Given the experimental values of κ_0 and κ_2 , eqns. (1) and (2) can be solved for $\lambda_{\text{glyH}_2^+}$ and λ_{gly^-} , respectively. All of the concentrations in these expressions are determinable from solution stoichiometry, the measured pH, C_0 , and the value of K_2 . The λ values for the various ions are determined from literature data.²⁻⁴ They are plotted in Figure 2 as a function of concentration. (The commonly tabulated infinite dilution values are not appropriate for these calculations.)

The sample data from Table 1 and Figure 2 yield the information listed in Table 2. From this, $\lambda_{\text{glyH}_2^+}$ and λ_{gly^-} are calculated to be 34 ± 8 and $15 \pm 7 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, respectively. These values apply to one concentration only, about $0.02 M$ in each case. The high uncertainties are due to propagation of errors in the sums.

Student data may be checked for self-consistency by comparing the measured and computed values of conductivity at the first equivalence point, where only sodium and chloride ions are present in significant concentrations. The conductivity computed from Table 2, $2.78 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$, deviates from the measured value (Table 1) by 9%. This deviation is an illustration of the degree of uncertainty inherent in the experiment.

It is advisable that students prepare or be provided with plots of molar ionic conductivity versus concentration rather than use data directly from Figure 2. The λ_i 's are calculated from transference numbers² and strong electrolyte molar

Table 1. Sample Data Summary^a

	Titrant		Conductivity ($10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$)
	Volume (ml)	pH	
Initial solution	0.0	2.13	5.50
First equivalence point	21.8	6.15	2.55
Halfway between equivalence points	32.7	9.65	2.93
Second equivalence point	43.6	10.60	3.45

^a Pertinent values from Figure 1.

^b Concentration to be determined.

¹ "CRC Handbook of Chemistry and Physics," 58th Ed., CRC Press, Inc., Cleveland, **1977-78**, pp. D147, D151.

² Stokes, R. H., and Robinson, R. A., "Electrolyte Solutions," Butterworths, London, **1959**, p. 158.

³ Daniels, F., and Alberty, R. A., "Physical Chemistry," 3rd Ed., John Wiley & Sons, Inc., New York, **1966**, p. 390.

⁴ Marsh, K. N., and Stokes, R. H., *Australian J. Chem.*, **17**, 740 (1964).

⁵ For example, Markson Science Supplies, No. E-13003.

Table 2. Processed Data

Species	Initial Solution		First Equivalence Point		Second Equivalence Point	
	Conc. ^a	λ_i^b	Conc. ^a	λ_i^b	Conc. ^a	λ_i^b
glyH_2^+	2.38×10^{-2}	— ^c	0	— ^c	0	— ^c
glyH	7.41×10^{-3}	0	2.42×10^{-2}	0	2.02×10^{-3}	0
gly^-	0	— ^c	0	— ^c	1.77×10^{-2} ^d	— ^c
Na^+	0	50.1	2.42×10^{-2}	44.8	3.95×10^{-2}	43.6
Cl^-	3.12×10^{-2}	69.5	2.42×10^{-2}	70.0	1.97×10^{-2}	70.6
H^+	7.41×10^{-3}	341.3	7.08×10^{-7}	349.8	2.51×10^{-11}	349.8
OH^-	1.35×10^{-12}	199.2	1.41×10^{-8}	199.2	3.98×10^{-4}	199.2

^a Molar concentrations calculated from solution stoichiometry, C_0 , and pH.

^b Values from Figure 2, in $10^{-3} \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

^c Value to be determined.

^d Value takes into account hydrolysis via experimental K_2 .

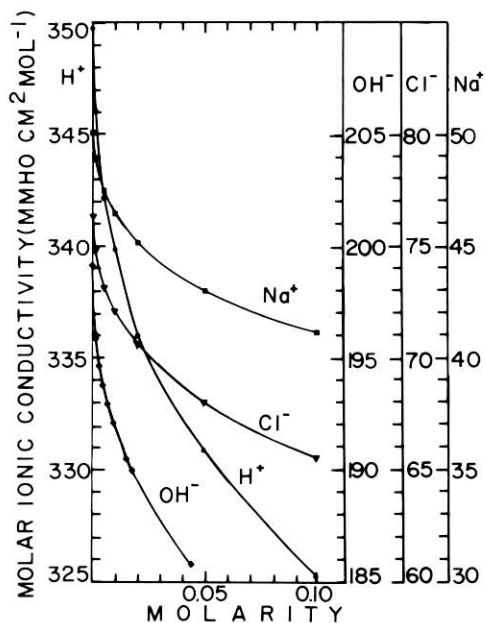


Figure 2. Concentration dependence of molar ionic conductivities. Smooth curves were drawn through the points.

conductivities.^{3,4} The relationship relevant to a 1:1 electrolyte is

$$\lambda_i(C) = t_i(C) \times \Lambda_m(C) \quad (3)$$

where $\lambda_i(C)$ is the molar ionic conductivity of ion i at concentration C , $t_i(C)$ is the transference number of ion i in a strong electrolyte at concentration C , and $\Lambda_m(C)$ is the molar conductivity of the strong electrolyte containing ion i at concentration C . Usually only the cation transference numbers are tabulated. The anion values may be determined from these since $t_+ + t_- = 1$. Since transference numbers for hydroxide compounds are not available in the literature, λ may be calculated by difference as follows:⁴

$$\lambda_{\text{OH}^-}(C) = \Lambda_{\text{m,NaOH}}(C) - \lambda_{\text{Na}^+}(C) \quad (4)$$

Apparatus

A conductivity meter or bridge and a pH meter are required for this experiment. It is best to measure both pH and con-

ductivity at small intervals throughout the entire course of the titration. This can be accomplished either manually or with an automatic system. In either case, both meters must first be calibrated, since absolute values of both quantities are needed. The titrant, which is standardized with primary standard potassium acid phthalate, should be at least three times more concentrated than the sample to minimize curvature of the conductivity function.

For a manual titration, the buret reading, pH, and conductivity (or resistance) are recorded at small enough intervals to define the endpoints and halfway region adequately. The solution should be stirred continuously.

The entire system can be automated easily by connecting both meters to a two-pen recorder or to two individual recorders. Titrant must be delivered at a constant, measurable rate, for example with an inexpensive peristaltic pump.⁵ It is critical that the rate be slow enough to allow the conductivity cell time to respond fully to the changing concentrations. The recorder chart paper must be calibrated by the student for both pH and conductivity. To accomplish the pH calibration, the pen location and pH value of several standard buffers are marked on the chart paper. The calibration for conductivity can be done with a sample of glycine hydrochloride. After the conductivity of this solution is measured and the corresponding pen position marked on the chart, the sample is neutralized with several small portions of sodium hydroxide. The conductivity is measured and the pen position marked after each addition. The experiment is then begun with a fresh sample.

Implementation

The instructor has considerable flexibility in adjusting the conceptual level of the experiment to suit the needs of the curriculum. For example, the titration curves may be analyzed entirely on a qualitative level. This might involve comparison of the two titration curves as well as some qualitative discussion of the reactions and explanation of the shape of each curve. Or, some quantitative aspects may be included by requiring calculation of equilibrium constants from the pH curve. At the other extreme, the full quantitative treatment as described herein could even be supplemented by calculation of theoretical titration curves, perhaps with the use of a computer. To facilitate implementation of the experiment as described, the authors are happy to supply full-sized copies of Figure 2 on request.