

A Simple Method for Analysis of Titration Curves of Polyprotic Acids

A.S.A. Khan

Chemistry Division, Directorate of Science, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan

ARTICLE INFO

Article history :

Received : 19 December, 2014

Revised : 9 February, 2015

Accepted : 20 February, 2015

Keywords :

Acid-base equilibrium

polyprotic acids, pH

formation-dissociation constants

distribution curves, oxalic acid

ABSTRACT

In the present work, the titration curves of polyprotic acid were analyzed theoretically on the basis of general equilibrium constants expression for evaluation of formation and dissociation constants. The present work provides more insight into the analysis of titration curves and development of distribution diagrams. The formation-dissociation curves of oxalic acids were also analyzed for finding a general relation between formation and dissociation process. It was concluded that the present method of treatment of titration curves is applicable to analyze the complex acid-base equilibria.

1. Introduction

The evaluation of formation-dissociation constants of weak acids has been the subject of extensive research for many decades due to their importance in the drug design and development [1-3], complexation study and buffer preparation [4-9]. The formation-dissociation constants of weak acids are commonly evaluated by analyzing their titration curves [10-12]. The titration curves of monoprotic acids can be analyzed conveniently on the basis of Henderson-Hasselbalch equation using different techniques e.g. potentiometry, UV/VIS spectroscopy, HPLC, NMR spectroscopy, conductometry, calorimetry, capillary zone electrophoresis, and computational methods [13-22]. It has been reported that pK_a value of monoprotic acids is equal to pH at the half neutralization point and it can be evaluated easily [23]. On the other hand, the pK_a values of polyprotic acids are evaluated with great difficulty using software methods involving complex algebraic calculations and approximate formulae [24-28].

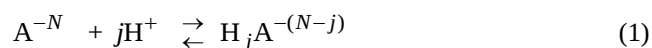
The Bjerrum's formation function which gives the ratio of bound protons to anion of weak acid has been found to be of great significance in the analysis of formation equilibria [29-31]. However, complex mass and charge balance equations are required to develop and analyze Bjerrum's formation function for finding various formation constants [32]. Moreover, the Bjerrum's formation function cannot be applied affectively to analyze the dissociation curves. Thus aim of the present work was to develop a simple method for analysis and physical interpretation of various parameters of formation-dissociation equilibria. The theoretical equations developed in the present work were applied in the analysis of formation-dissociation

curves and development of distribution diagrams of oxalic acid.

2. Theoretical

2.1. Treatment of formation curve

The formation curve is usually obtained on the basis of titration of solution of salt of polyprotic acid against standard solution of hydrochloric acid (HCl). Let A^{-N} be the anion of polyprotic acid then general overall equilibrium expression for the formation of any protonated anion can be represented as:



$$\beta_j = \frac{[H_jA^{-(N-j)}]}{[A^{-N}][H^+]^j} \quad (2)$$

where $j=0,1,2,\dots$ and N is the maximum number of bound protons in polyprotic acid. The β_j is the overall formation constant for the formation of protonated anion with j number of bound protons. The $[A^{-N}]$, $[H_jA^{-(N-j)}]$ and $[H^+]$ are the equilibrium concentration of free anion, protonated anion, and hydrogen ions respectively, mol L⁻¹. Let n_T is the total number of moles of anion of polyprotic acid being titrated and n_b is the number of moles of bounded protons then the magnitude of β_j can be given as:

$$\beta_j = \frac{n_b / j}{(n_T - n_b / j)[H^+]^j} \quad (3)$$

The magnitude of $[H^+]$ is obtained by taking the ratio of activity to activity coefficient of hydrogen ions. According

* Email address : abdulsattar_alikhan@email.com

to the IUPAC convention [33] the pH is the negative logarithm of hydrogen ion activity thus one can evaluate the activity of hydrogen ions by analyzing the observed pH. On the other hands, the activity coefficient of hydrogen ions over wide range of ionic strength can be calculated using Davies equation [8, 34].

The Eq. (3) can be rearranged to get following expression:

$$\frac{n_b}{n_T} = \left(1 - \frac{n_b}{n_T}\right) j \beta_j [H^+]^j \quad (4)$$

Experimentally one can find the magnitude of n_b by taking the difference of number of moles of HCl added and number of moles of hydrogen ions (or protons) left in solution i.e.

$$n_b = n_{HCl} - \frac{[H^+]}{1000} V \quad (5)$$

where n_{HCl} is the number of moles of HCl added and V is the volume of solution, ml. The Eq.(3) is valid only if the protons are bound to form only $H_jA^{-(N-j)}$. Since other overlapping equilibria also exist at a given equilibrium concentration of hydrogen ions, thus one must consider all other equilibria to get correct balance equation of molar ratio of bound protons. It can be done by taking sum of all j number of terms on right hand side of Eq. (4) i.e.

$$\begin{aligned} \frac{n_b}{n_T} &= \left(1 - \frac{n_b}{n_T}\right) \beta_1 [H^+] + \left(1 - \frac{n_b}{2 n_T}\right) 2 \beta_2 [H^+]^2 \dots \\ &\dots + \left(1 - \frac{n_b}{N n_T}\right) N \beta_N [H^+]^N \end{aligned} \quad (6)$$

It can be further rearranged to get the following expression of molar ratio of bound protons:

$$\frac{n_b}{n_T} = \frac{\beta_1 [H^+] + 2 \beta_2 [H^+]^2 \dots + N \beta_N [H^+]^N}{1 + \beta_1 [H^+] + \beta_2 [H^+]^2 \dots + \beta_N [H^+]^N} \quad (7)$$

The Eq. (7) can also be expressed as

$$\bar{n}_b = \frac{\sum_{j=0}^N j \beta_j [H^+]^j}{\sum_{j=0}^N \beta_j [H^+]^j} \quad (8)$$

where

$$\bar{n}_b = \frac{n_b}{n_T} \quad (9)$$

The Eq. (8) is equivalent to Bjerrum's formation expression reported elsewhere [29-32]. Since designation

of $\bar{n}_b$ as ratio of n_b to n_T helps to simplify the mathematical calculations, therefore, in present work the term $\bar{n}_b$ is avoided in further analysis of titration curves. The substitution of respective overall formation constant expressions into Eq. (7) results in following equation:

$$\frac{n_b}{n_T} = \frac{[HA^{-(N-1)}] + 2 [H_2A^{-(N-2)}] \dots + N [H_N A]}{[A^{-N}] + [HA^{-(N-1)}] + [H_2A^{-(N-2)}] \dots + [H_N A]} \quad (10)$$

On the basis of Eq.(10), the n_b and n_T can be expressed as:

$$n_b = \frac{V}{1000} ([HA^{-(N-1)}] + 2 [H_2A^{-(N-2)}] \dots + N [H_N A]) \quad (11)$$

$$n_T = \frac{V}{1000} ([A^{-N}] + [HA^{-(N-1)}] + [H_2A^{-(N-2)}] \dots + [H_N A]) \quad (12)$$

It means that n_b is equal to the sum of number of mole of protons used to produce various protonated anions of polyprotic acid. On the other hand, n_T is equal to sum of number of moles of free anions and all bound anions of polyprotic acid.

In case of formation curve analysis, the magnitude of equilibrium concentration of free anion is required for the development of distribution diagrams. In order to find the magnitude of free anion of polyprotic acid, the Eq. (12) can be modified to get following relation:

$$[A^{-N}] = \frac{1000}{V} \left(\frac{n_T}{1 + \beta_1 [H^+] + \beta_2 [H^+]^2 \dots + \beta_N [H^+]^N} \right) \quad (13)$$

Let

$$F_{[H^+]} = 1 + \beta_1 [H^+] + \beta_2 [H^+]^2 \dots + \beta_N [H^+]^N \quad (14)$$

The $F_{[H^+]}$ is a dimensionless parameter which is a function of hydrogen ions concentration. On substitution of $[A^{-N}]$ from Eq. (13) into Eq. (2) and making rearrangements, following expression is obtained for finding the fraction of number of mole of any protonated anion of polyprotic acid:

$$\frac{n_{H_j A}}{n_T} = \frac{\beta_j [H^+]^j}{F_{[H^+]}} \quad (15)$$

In order to evaluate the experimental value of $F_{[H^+]}$, the Eq. (7) can further be rearranged to get:

$$\frac{n_b}{n_T [H^+]} = \frac{\beta_1 + 2 \beta_2 [H^+] + 3 \beta_3 [H^+]^2 \dots + N \beta_N [H^+]^{N-1}}{1 + \beta_1 [H^+] + \beta_2 [H^+]^2 + \beta_3 [H^+]^3 \dots + \beta_N [H^+]^N} \quad (16)$$

Here the denominator is equal to $F_{[H^+]}$ while the numerator is equal to the derivative of $F_{[H^+]}$ with respect to $[H^+]$. Thus it can be shown that

$$\ln F_{[H^+]} = \int \left(\frac{n_b}{n_T [H^+]} \right) d[H^+] \quad (17)$$

The integral in Eq. (17) can be evaluated numerically by finding the area under the curve of plot of $n_b/n_T[H^+]$ vs. $[H^+]$.

2.2. Treatment of dissociation curve

Let H_NA is the polyprotic acid being titrated with strong base like NaOH then general overall equilibrium expression for the dissociation of H_NA can be represented as:



$$\beta_{a,j} = \frac{[H_{(N-j)}A^{-j}] [H^+]^j}{[H_NA]} \quad (19)$$

where $\beta_{a,j}$ is the overall acid dissociation constant. If n_T is the total number of moles of polyprotic acid being titrated in given volume of solution and n_d is the number of moles of protons dissociated from H_NA then Eq. (19) can be expressed as:

$$\beta_{a,j} = \frac{\left(\frac{n_d}{j} \right) [H^+]^j}{\left(n_T - \frac{n_d}{j} \right)} \quad (20)$$

It can be rearranged to get following expression:

$$\frac{n_d}{n_T} = \left(1 - \frac{n_d}{j n_T} \right) \frac{j \beta_{a,j}}{[H^+]^j} \quad (21)$$

Experimentally the magnitude of n_d is obtained by taking the sum of number of moles of strong base added and number of moles of hydrogen ions left in solution at equilibrium state i.e.

$$n_d = n_{OH} + \frac{[H^+] V}{1000} \quad (22)$$

where n_{OH} is the number of moles of NaOH added and other terms have usual meanings. The Eq. (21) is valid provided the j number of protons are dissociated only from H_NA . Since other overlapping equilibria also exist at given equilibrium concentration of hydrogen ions which also contribute toward n_d , thus for getting exact expression, one must take sum of all terms on right hand side of Eq. (21) by setting $j = 0, 1, 2, \dots, N$ as has been done in treatment of formation curves. In doing so and after making rearrangement, one can get following simple relation of molar ratio of dissociated protons:

$$\frac{n_d}{n_T} = \frac{\left(\frac{\beta_{a,1}}{[H^+]} + \frac{2 \beta_{a,2}}{[H^+]^2} + \frac{3 \beta_{a,3}}{[H^+]^3} + \dots + \frac{N \beta_{a,N}}{[H^+]^N} \right)}{\left(1 + \frac{\beta_{a,1}}{[H^+]} + \frac{\beta_{a,2}}{[H^+]^2} + \frac{\beta_{a,3}}{[H^+]^3} + \dots + \frac{\beta_{a,N}}{[H^+]^N} \right)} \quad (23)$$

The substitution of corresponding overall dissociation constant expressions into Eq. (23) and making rearrangements, gives following expression:

$$\frac{n_d}{n_T} = \frac{[H_{(N-1)}A^{-1}] + 2 [H_{(N-2)}A^{-2}] + \dots + (N-1)[H_{(N-1)}A^{-(N-1)}] + N [A^{-N}]}{[H_NA] + [H_{(N-1)}A^{-1}] + \dots + [H_{(N-1)}A^{-(N-1)}] + [A^{-N}]} \quad (24)$$

On the basis of Eq.(24), the n_b and n_T are found to be:

$$n_d = \frac{V}{1000} \left([H_{(N-1)}A^{-1}] + 2 [H_{(N-2)}A^{-2}] + \dots + (N-1)[H_{(N-1)}A^{-(N-1)}] + N [A^{-N}] \right) \quad (25)$$

$$n_T = \frac{V}{1000} \left([H_NA] + [H_{(N-1)}A^{-1}] + \dots + [H_{(N-1)}A^{-(N-1)}] + [A^{-N}] \right) \quad (26)$$

Since one mole of A^{-N} is formed by deprotonation of N number of moles of protons from H_NA , therefore, the term $[A^{-N}]$ is multiplied by N in Eq. (25) to count exact number of mole of proton dissociated. In the dissociation curve analysis, the knowledge of equilibrium concentration of un-dissociated polyprotic acid is of great importance in the development of distribution diagrams. For this purpose, the Eq. (26) can be modified to get following relation for finding the equilibrium concentration of polyprotic acid:

$$[H_NA] = \frac{1000}{V} \left(\frac{n_T}{1 + \frac{\beta_{a,1}}{[H^+]} + \frac{\beta_{a,2}}{[H^+]^2} + \frac{\beta_{a,3}}{[H^+]^3} + \dots + \frac{\beta_{a,N}}{[H^+]^N}} \right) \quad (27)$$

On substitution of $[H_NA]$ from Eq. (27) into Eq. (19) and making rearrangements, one can get following general equation for finding the fraction of number of moles of any protonated anion of polyprotic acid:

$$\frac{n_{H_{(N-j)}A}}{n_T} = \frac{\beta_{a,j}}{[H^+]^j F_{[H^+]}^{-1}} \quad (28)$$

where $F_{[H^+]}^{-1}$ is a dimensionless parameter that is a function of reciprocal of hydrogen ions concentration as defined by the following relation :

$$F_{[H^+]}^{-1} = 1 + \frac{\beta_{a,1}}{[H^+]} + \frac{\beta_{a,2}}{[H^+]^2} + \frac{\beta_{a,3}}{[H^+]^3} + \dots + \frac{\beta_{a,N}}{[H^+]^N} \quad (29)$$

In order to find the experimental value of $F_{[H^+]}^{-1}$, the numerator of Eq. (23) is multiplied and divided by $[H^+]$ to get following expression :

$$\frac{n_d}{n_T[H^+]} = \frac{\left(\frac{\beta_{a,1}}{[H^+]^2} + \frac{2\beta_{a,2}}{[H^+]^3} + \frac{3\beta_{a,3}}{[H^+]^4} + \dots + \frac{N\beta_{a,N}}{[H^+]^{N+1}} \right)}{\left(1 + \frac{\beta_{a,1}}{[H^+]} + \frac{\beta_{a,2}}{[H^+]^2} + \frac{\beta_{a,3}}{[H^+]^3} + \dots + \frac{\beta_{a,N}}{[H^+]^N} \right)} \quad (30)$$

In this case, the denominator is equal to $F_{[H^+]}^{-1}$ while the numerator is equal to negative derivative of $F_{[H^+]}^{-1}$ with respect to $[H^+]$. Thus it can be shown that

$$\ln F_{[H^+]}^{-1} = - \int \left(\frac{n_d}{n_T[H^+]} \right) d[H^+] \quad (31)$$

The integral in Eq.(31) can be evaluated numerically by finding the area under the curve of plot of $n_d/n_T[H^+]$ vs. $[H^+]$. The negative sign before the integral gives positive value of area over each point of the curve.

3. Experimental Setup

The Metrohm model 781 pH/ ion meter equipped with combination glass electrode Model No. 6.0258.010 and Pt 1000 temperature sensor was used for pH measurements. The Metrohm standard buffer of pH 4 and pH 7 were used for calibration purpose. All experiments were carried out at room temperature of 25 °C. The solutions were prepared in deionized water of 2.4 $\mu\text{S cm}^{-1}$ conductivity. All chemicals were of analytical grade purity. 30 ml of 0.01 mol L⁻¹ oxalic acid was titrated against 0.2 mol L⁻¹ NaOH for obtaining dissociation curve. Likewise, 30 ml of 0.01 mol L⁻¹ di-sodium salt of oxalic acid was titrated against 0.2 mol L⁻¹ HCl for getting formation curve.

4. Results and Discussion

4.1. Analysis of formation- dissociation curves of oxalic acid

The theoretical expressions of formation-dissociation curves were applied to analyze the oxalic acid equilibria. The molar ratios of bound and dissociated protons obtained by analyzing formation-dissociation curves of oxalic acid were plotted as a function of pH. The data in Fig. 1 indicates that the molar ratio of bound protons increases smoothly with successive addition of strong acid upto pH 3. The magnitude of molar ratio of bound protons was used to calculate $F_{[H^+]}$ using Eq. (17). The data of $F_{[H^+]}$ corresponding to increasing values of molar ratio of bound protons (i.e. upto pH 3) was used to plot $F_{[H^+]}$ vs. $[H^+]$ (Fig. 2). The magnitude of β_1 and β_2 were

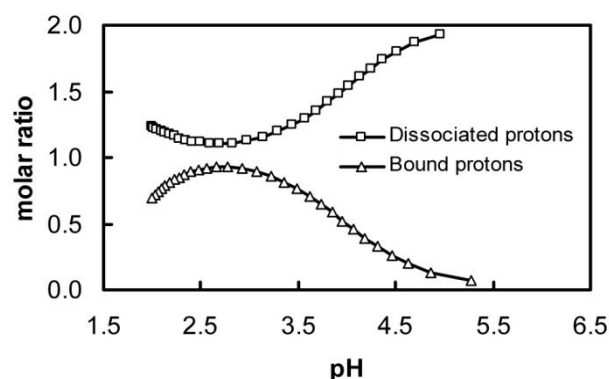


Fig. 1. Plot of molar ratio of bound and dissociated protons as a function of pH obtained on the basis of analysis of formation-dissociation curves of oxalic acid.

obtained by comparing the coefficients of Eq. (14) with the 2nd order polynomial fitting equation and found to be $8.50 \times 10^3 \text{ mol}^{-1} \text{ L}$ and $1.14 \times 10^5 \text{ mol}^{-2} \text{ L}^2$ respectively. The overall formation constants were analyzed to get step-wise formation constants K_1 and K_2 which are defined as follow:

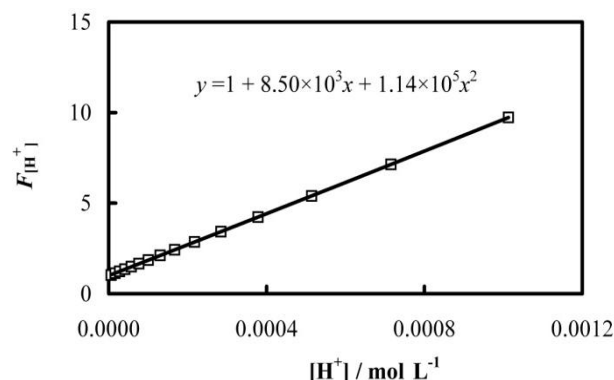


Fig. 2. Plot of $F_{[H^+]}$ vs. $[H^+]$ for evaluation of overall formation constants of oxalic acid ($F_{[H^+]}$ is a dimensionless parameter that is a function of hydrogen ion concentration. It was calculated on the basis of Eq. (17) using trapezoidal rule).

$$K_1 = \frac{[HA^-]}{[A^{2-}][H^+]} \quad (32)$$

$$K_2 = \frac{[H_2A]}{[HA^-][H^+]} \quad (33)$$

where A^{2-} stands for oxalate ion. The magnitude of K_1 is equal to β_1 . The K_2 was obtained by taking ratio of β_2 to β_1 and found to be $13.4 \text{ mol}^{-1} \text{ L}$. In order to validate the magnitude of overall formation constants, the following equation was derived from Eq. (5) to find the volume of strong acid required to get desired equilibrium concentration of hydrogen ions in a given volume of solution:

$$V_{\text{HCl}} = \frac{1000}{[\text{HCl}]} \left(n_T \left(\frac{\beta_1 [\text{H}^+] + 2 \beta_2 [\text{H}^+]^2}{1 + \beta_1 [\text{H}^+] + \beta_2 [\text{H}^+]^2} \right) + \frac{[\text{H}^+] \times V}{1000} \right) \quad (34)$$

where $[\text{HCl}]$ is the concentration of HCl used in the titration, mol L^{-1} . The close resemblance of calculated and experimental titration points (Fig. 3) indicates the validity of observed values of overall formation constants.

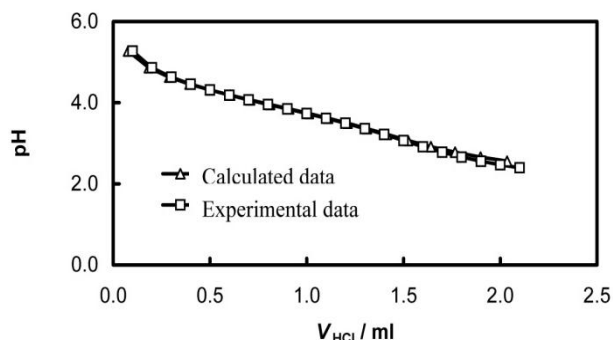


Fig. 3 Comparison of experimental and calculated data of formation curve (the data is based on titration of 30 ml of 0.01 mol L^{-1} of di-sodium oxalate with 0.2 mol L^{-1} HCl at 25 $^{\circ}\text{C}$).

The molar ratio of dissociated protons was also analyzed to find the magnitude of $F_{[\text{H}^+]}^{-1}$ on the basis of Eq. (31). The $\beta_{a,1}$ and $\beta_{a,2}$ were obtained by comparing the coefficients of Eq. (29) with the 2nd order polynomial fitting equation obtained from plot of $F_{[\text{H}^+]}^{-1}$ vs. reciprocal of hydrogen ions concentration (Fig. 4) and found to be $1.35 \times 10^{-2} \text{ mol L}^{-1}$ and $2.23 \times 10^{-6} \text{ mol}^2 \text{ L}^{-2}$ respectively.

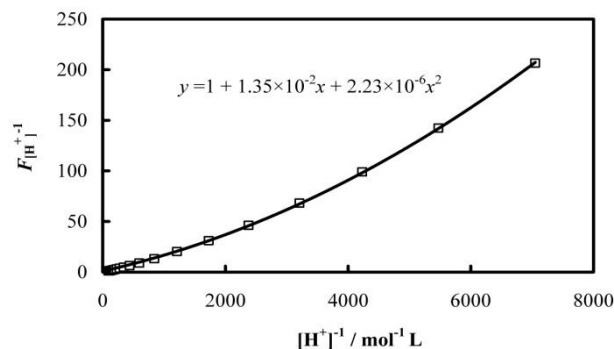


Fig. 4. Plot of $F_{[\text{H}^+]}^{-1}$ vs. $[\text{H}^+]^{-1}$ for evaluation of overall dissociation constants of oxalic acid ($F_{[\text{H}^+]}^{-1}$ is dimensionless parameter and according to Eq. (31), it is a function of reciprocal of hydrogen ion concentration).

The overall dissociation constants were analyzed to get step-wise dissociation constants $K_{a,1}$ and $K_{a,2}$ which are defined as follow :

$$K_{a,1} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]} \quad (35)$$

$$K_{a,2} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]} \quad (36)$$

The magnitude of $K_{a,1}$ is equal to $\beta_{a,1}$ while $K_{a,2}$ was obtained by taking ratio of $\beta_{a,2}$ to $\beta_{a,1}$ and found to be $1.65 \times 10^{-4} \text{ mol L}^{-1}$. The magnitude of $K_{a,1}$ is lower than that obtained by taking the reciprocal of second successive formation constant of oxalic acid, K_2 (i.e. $7.46 \times 10^{-2} \text{ mol L}^{-1}$). This difference is attributed to irregular rise of molar ratio of dissociated protons upto pH 3 as shown in Fig. 1. The dissociation data was modified to get formation data for evaluation of correct values of formation-dissociation constants. The data in Fig. 1 indicates that the dissociation curve is a mirror reflection of corresponding formation curve and at any given pH, the sum of molar ratio of bound and dissociated protons is constant and can be given as:

$$N = \frac{n_d + n_b}{n_T} \quad (37)$$

where N is the maximum number of bound protons with anion of polyprotic acid which is two for oxalic acid. On substitution of molar ratio expression of dissociated protons from Eq. (23) into Eq. (37) and making rearrangement, one can get following expression of molar ratio of bound protons for oxalic acid:

$$\frac{n_b}{n_T} = \frac{2 + \frac{\beta_{a,1}}{[\text{H}^+]}}{\left(1 + \frac{\beta_{a,1}}{[\text{H}^+]} + \frac{\beta_{a,2}}{[\text{H}^+]^2} \right)} \quad (38)$$

The equation similar to Eq. (38) has also been reported elsewhere [35]. According to this equation, when $\beta_{a,2}$ is equal to $[\text{H}^+]^2$ then the magnitude of molar ratio of bound protons is unity. It is clear from Fig. 1 that the magnitude of molar ratio of bound protons approaches to unity at pH 2.5 and hence $\beta_{a,2}$ can be calculated to be $1.0 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$. According to Fig. 1, the molar ratio of dissociated protons increases smoothly beyond pH 3 with successive addition of strong base, hence one can utilize the rising portion of dissociation curve beyond pH 3 for evaluation of formation-dissociation constants data. For this purpose, the Eq.(17) was modified on the basis of Eq. (38) to get following integral expression for the formation of oxalic acid:

$$\ln F_{[\text{H}^+]} = \int_0^{[\text{H}^+]} \frac{1}{[\text{H}^+]} \left(2 - \frac{n_d}{n_T} \right) d[\text{H}^+] \quad (39)$$

In case of titration of polyprotic acid with maximum N number of bound protons, the Eq.(39) can be given as :

$$\ln F_{[\text{H}^+]} = \int_0^{[\text{H}^+]} \frac{1}{[\text{H}^+]} \left(N - \frac{n_d}{n_T} \right) d[\text{H}^+] \quad (40)$$

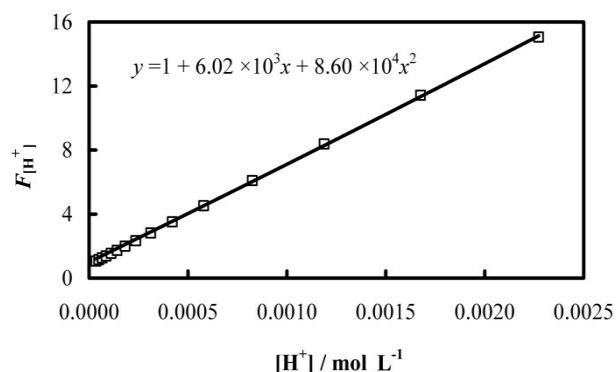


Fig. 5. Plot of $F_{[H^+]}$ vs. $[H^+]$ for evaluation of overall formation constants of oxalic acid ($F_{[H^+]}$ was calculated on the basis of Eq. (39) by analyzing the dissociation curve data).

The integral equation given in Eq. (40) is reported for the first time. For oxalic acid system, the Eq. (39) was evaluated numerically by analyzing the dissociation data in reverse order i.e. from higher pH upto pH 3. The values of $F_{[H^+]}$ obtained on the basis of Eq. (39) are plotted against $[H^+]$ in Fig. 5. The magnitude of overall formation constants β_1 and β_2 obtained from the coefficient of 2nd order polynomial fitting equation were $6.02 \times 10^3 \text{ mol}^{-1} \text{ L}$ and $8.60 \times 10^4 \text{ mol}^{-2} \text{ L}^2$ respectively which are in close agreement with that obtained by analyzing the formation curve. The magnitude of $\beta_{a,1}$ and $\beta_{a,2}$ were evaluated by analyzing the formation constants using following general relation :

$$\beta_{a,j} = \frac{\beta_{(N-j)}}{\beta_N} \quad (41)$$

It is clear from Eq. (41) that the magnitude of $\beta_{a,0}$ is unity. The magnitude of $\beta_{a,1}$ and $\beta_{a,2}$ obtained on the basis of Eq. (41) for oxalic acid were found to be $7.0 \times 10^{-2} \text{ mol L}^{-1}$ and $1.16 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$ respectively.

4.2. Distribution diagram of oxalic acid

The distribution curves of oxalic acid are shown in Fig. 6. The dotted curves were obtained on the basis of Eq. (28) using $\beta_{a,1} = 7.0 \times 10^{-2} \text{ mol L}^{-1}$ and $\beta_{a,2} = 1.0 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$ while curves with solid lines were obtained on the basis of Eq. (15) using $\beta_1 = 8.50 \times 10^3 \text{ mol}^{-1} \text{ L}$ and $\beta_2 = 1.14 \times 10^5 \text{ mol}^{-2} \text{ L}^2$. The distribution curves obtained on the basis of overall formation and dissociation constant data agreed excellently. The pH at intersection of distribution curves of successive form of oxalic acid gives the corresponding pK_a value of oxalic acid. It is clear from Fig. 6 that the distribution curve of H_2A intersect the curve for HA^- ions at $\text{pH } 1.2 \pm 0.05$ while the distribution curve of HA^- ions intersect the curve for A^{2-} ions at $\text{pH } 3.9 \pm 0.1$. Thus the magnitude of $pK_{a,1}$ and $pK_{a,2}$ of oxalic acid are 1.2 ± 0.05 and 3.9 ± 0.1 respectively which are close to reported value in literature [36-38].

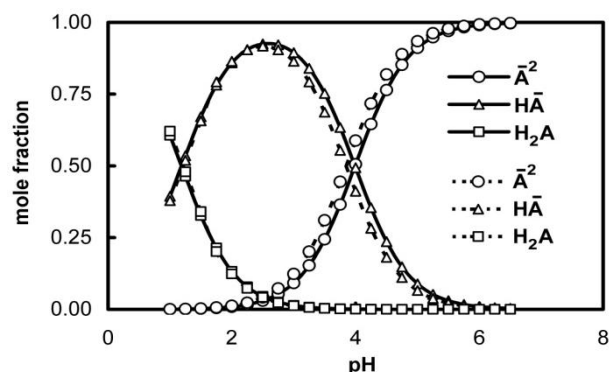


Fig. 6. Distribution diagram obtained by plotting mole fraction of free anion and protonated anions of oxalic acid as a function of pH (H_2A represents oxalic acid while A^{2-} stands for free anion of oxalic acid. The dotted curves were obtained on the basis of Eq.(28) using $\beta_{a,1} = 7.0 \times 10^{-2} \text{ mol L}^{-1}$ and $\beta_{a,2} = 1.0 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$ while curves with solid lines were obtained on the basis of Eq.(15) using $\beta_1 = 8.50 \times 10^3 \text{ mol}^{-1} \text{ L}$ and $\beta_2 = 1.14 \times 10^5 \text{ mol}^{-2} \text{ L}^2$).

5. Conclusions

In present work, theoretical equations were developed for analyzing formation-dissociation curves of polyprotic acids on the basis of general equilibrium constants expressions. The approach so developed is simple and gives better understanding of treatment of complex acid-base equilibria. The polynomial fitting of formation and dissociation functions is needed for evaluation of corresponding formation-dissociation constants. The formation curve is more advantageous over dissociation curve for evaluation of formation-dissociation constants. The newly developed method will find extensive applications in the development of buffer systems and drugs design.

References

- [1] T. M. David, Perspect. Medicin. Chem. **1** (2007) 25.
- [2] R. I. Allen, K. J. Box, J.E.A. Comer, C. Peake and K. Y. Tam, J. Pharm. Biomed. Anal. **17** (1998) 699.
- [3] B. B. Brodie, H. Kurz and L. S. Schanker, J. Pharmacol. Exper. Therap. **130** (1960) 20.
- [4] A. G. Asuero, Crit. Rev. Anal. Chem. **37** (2007) 269.
- [5] M. V. D. Steene, L. V. Vooren, J. P. Ottoy and P. A. Vanrolleghem, Environ. Sci. Technol. **36** (2002) 715.
- [6] P. J. Elving, J. M. Markowitz and I. Rosenthal, Anal. Chem. **28** (1956) 1179.
- [7] B. Donald and D. V. Slyke, in: On the measurement of buffer values and on the relationship of buffer value to the dissociation constant of the buffer and the concentration and reaction of the buffer solution (1922).
- [8] A. S. A. Khan, Turk. J. Chem. **36** (2012) 219.
- [9] F. J. C. Rossotti and H. Rossotti, in: The determination of stability constants and other equilibrium constants in solutions, McGraw-Hill, Book Company, Inc, New York, USA (1961) pp.38.
- [10] A. Albert and E. P. Serjeant, in: The determination of Ionization constants, 3rd Edition, Chapman and Hall, USA (1984) pp.59.
- [11] T. Michalowski, A. Pietrzyk, M. P. Svet and M. Rymanowski, Crit. Rev. Anal. Chem. **40** (2010) 17.

- [12] J. Reijenga, A. V. Hoof, A. V. Loon and B. Teunissen, *Anal. Chem. Insights* **8** (2013) 53.
- [13] Z. Qiang and C. Adams, *Water Research* **38** (2004) 2874.
- [14] K. Y. Tam and K. T. Novák, *Anal. Chim. Acta* **434** (2001) 157.
- [15] H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta* **32**(1985) 95.
- [16] G. S. Patterson, *J. Chem. Educ.* **76** (1999) 395.
- [17] H. Y. Ando and T. Heimbach, *J. Pharm. Biomed. Anal.* **16** (1997) 31.
- [18] M. Manderscheid and T. Eichinger, *J. Chromatogr. Sci.* **41** (2003) 323.
- [19] D. L. Rabenstein and T. L. Sayer, *Anal. Chem.* **48** (1976) 1141.
- [20] R. I. Gelb, *Anal. Chem.* **43** (1971) 1110.
- [21] S. G. Tajc, B. S. Tolbert, R. Basavappa and B. L. Miller, *J. Am. Chem. Soc.* **126** (2004) 10508.
- [22] M. Shalaeva, J. Kenseth, F. Lombardo and A. Bastin, *J. Pharm. Sci.* **97** (2008) 2581.
- [23] A. Onufriev, D. A. Case and G. M. Ullmann, *Biochemistry* **40** (2001) 3413.
- [24] P. A. Stewart, *Can. J. Phys. Pharmac.* **61** (1983) 1444.
- [25] M. D. Liptak and G. C. Shields, *J. Am. Chem. Soc.* **123** (2001) 7314.
- [26] D. J. Leggett, in: *Computational Methods for the Determination of Formation Constants*, Plenum Press, New York, USA (1985).
- [27] C. Liao and M. C. Nicklaus, *J. Chem. Inf. Model.* **49** (2009) 2801.
- [28] H. Narasaki, *Talanta* **27** (1980) 409.
- [29] J. Bjerrum, in: *Metal Ammine Formation in Aqueous Solution. Theory of Reversible Step Reactions*, Haase and Son, Copenhagen, (1957).
- [30] A.G. Asuero, *Anal. Lett.* **23** (1990) 747.
- [31] J. Hurek and J. Nackiewicz, *J. Chem. Educ.* **90** (2013) 604.
- [32] A. G. Asuero and T. Michałowski, *Crit. Rev. Anal. Chem.* **41** (2011) 151.
- [33] A. D. McNaught and A. Wilkinson, *IUPAC. Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Compiled by Blackwell Scientific Publications, Oxford (1997) pp. 1088.
- [34] C.W. Davies, in: *Ion Association*, London: Butterworths (1962) pp.37-53.
- [35] H. Diehl, *Talanta* **33** (1986) 935.
- [36] R. Kettler, D. J. Wesolowski and D. A. Palmer, *J. Chem. Eng. Data* **43** (1998) 337.
- [37] G. D. Pinching and R. G. Bates, *J. Res. Natl. Stand.* **40** (1948) 405.
- [38] R. Wahl and E. Kallee, *Eur. J. Clin. Chem. Clin. Biochem.* **32** (1994) 821.