A Bilogarithmic Hyperboline Sine Procedure for the Simultaneous Calculation of Successive Formation Constants of Two Step Overlapping Acid-Base Equilibria from Potentiometric Measurements

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Abstract: *In this paper we have developed a procedure for the potentiometric determination of acidity constants of simultaneous acid-base equilibria. The V-pH data are transformed into data ñ-pH, being ñ the Bjerrum index. The process of linearization involving the use of the hyperbolic sine function leads to a bilogarithmic expression. The procedure has been applied to the experimental data obtained by us in the laboratory for succinic acid, obtaining good results.*

Keywords: *Bilogarithmic Hyperboline Sine Method; Successive Formation; Potentiometric Measurements; Succinic Acid*

1. INTRODUCTION

Titrimetry is one of the oldest analytical methods [1], and it is still in the development phase. The pH-metric titration is usually the method of choice for the measurement of equilibrium constants of acid-base reactions, useful in chemical, electrochemical and technological applications [2-5]. A number of methods have been described for the potentiometric evaluation of the successive formation constants of the two-stage equilibria [6-8]. The methods based on the formation function [9] also known as the Bjerrum index or the average number of bound protons [10-11], have been the most applied [12-16]. In the present paper a procedure is described for the study of simultaneous equilibria in potentiometric titrations, based on the use of the formation function. A straight line is fitted to the transformed (V (ñ), pH) data, proposing a bilogaritmic mathematical model, deduced via a hyperbolic sine relationship. There is a series of computerized programs for the study of complex equilibria but the use of a spreadsheet in Excel is sufficient to accomplish the task. The method devised has been applied to experimental data obtained in the laboratory for succinic acid.

1.1. Basic Equation

For a diprotic acid H_2R, the relationship between the degree of formation, ñ, of proton ligand complexes

$$\tilde{n} = \frac{C_H - [H]}{C_R} = \frac{[HR] + 2[H_2R]}{[R] + [HR] + [H_2R]} \tag{1}$$

and the activity of hydrogen ions, (*H*), is given by

$$\tilde{n} + (\tilde{n}-1)K_1^T \frac{f_0}{f_1}(H) + (\tilde{n}-2)K_1^T K_2^T \frac{f_0}{f_2}(H)^2 = 0 \tag{2}$$

where K_1^T and K_2^T are the successive thermodynamics formation constants

$$K_1^T = \frac{(HR)}{(H)(R)} = \frac{[HR]}{(H)[R]}\frac{f_1}{f_0} = K_1^B\frac{f_1}{f_0} \tag{3}$$

and

$$K_2^T = \frac{(H_2R)}{(H)(HR)} = \frac{[H_2R]}{(H)[HR]}\frac{f_2}{f_0} = K_2^B\frac{f_2}{f_1} \tag{4}$$

(H_jR), $[H_jR]$, and f_j, are the activity, concentration, and activity coefficient, respectively, of the species H_jR (j=0, 1,2) and K_1^B and K_2^B are the successive Bronsted or mixed formation constants. Charges are omitted in the formulation of Eqns. (1) to (4) for the sake of simplicity. The model equation (2) results from the mass balance for hydrogen ions and the analytical concentration of diprotic acid, C_R.

1.2. Bilogarithmic Equation Derivation

From Eqn. (2) we get

$$(\tilde{n}-1)K_1^T\frac{f_0}{f_1}(H) = (2-\tilde{n})K_1^T K_2^T\frac{f_0}{f_2}(H) - \frac{\tilde{n}}{(H)} \tag{5}$$

By multiplying both members of Eqn. (5) by x

$$x = \pm\sqrt{\frac{f_2}{f_0}}\cdot\frac{1}{\sqrt{\tilde{n}(2-\tilde{n})K_1^T K_2^T}} \tag{6}$$

where the plus sign applies for values of $\tilde{n} > 1$ and the minus when $\tilde{n} < 1$, on rearranging we get

$$\pm\frac{\tilde{n}-1}{\sqrt{\tilde{n}(2-\tilde{n})}}\sqrt{\frac{K_1^T}{K_2^T}}\frac{\sqrt{f_0 f_2}}{f_1} = \pm\left[\sqrt{\frac{2-\tilde{n}}{\tilde{n}}}\sqrt{K_1^T K_2^T}\sqrt{\frac{f_0}{f_2}}(H) - \sqrt{\frac{\tilde{n}}{2-\tilde{n}}}\frac{1}{\sqrt{K_1^T K_2^T}}\sqrt{\frac{f_2}{f_0}}\frac{1}{(H)}\right] \tag{7}$$

By taking decimal logarithms on both sides of Eqn. (7), as the hyperbolic sine is defined by

$$\sinh x = \frac{e^x - e^{-x}}{2} \tag{8}$$

the equation that follows can be easily derived

$$\log\left(\frac{|\tilde{n}-1|}{\sqrt{\tilde{n}(2-\tilde{n})}}\right) + \log\frac{\sqrt{f_0 f_2}}{f_1} - \log 2 =$$

$$-\log\sqrt{\frac{K_1^T}{K_2^T}} + \log\sinh\left(\ln 10\cdot\log\left(\sqrt{\frac{2-\tilde{n}}{\tilde{n}}}\sqrt{K_1^T K_2^T}\sqrt{\frac{f_0}{f_2}}(H)\right)^\alpha\right) \tag{9}$$

Where $\alpha =1$ for values of $\tilde{n} >1$, and $\alpha= -1$ when $\tilde{n} <1$. The Eqn. (9) predicts that a representation of the first member versus the second term of the second side leads to a straight line of unit theoretical slope, which allows us to obtain, from the experimental data, the logarithm of the square root of the quotient of the successive formation constants of the protonated complexes. Linear regression analysis [17-18] can be used to estimate the value of constants.

1.3. The Bilogarithmic Equation as a Function of the Midpoint of the Formation Curve

Before applying Eqn. (9) the value of $\sqrt{(K_1^T K_2^T)}$ should be known. In the middle of the formation curve, $\tilde{n}=1$, an then, from Eqn. (2) follows

$$K_1^T K_2^T = \frac{1}{(H')^2} \frac{f_2'}{f_0'}$$

(10)

By multiplying the both sides of Eqn. (10) by $f_0 (H)^2/f_2$ first, and extracting the square root them we have

$$\sqrt{K_1^T K_2^T} \sqrt{\frac{f_0}{f_2}} (H) = \frac{(H)}{(H')} \sqrt{\frac{f_2' f_0}{f_0' f_2}}$$

(11)

Combining the Eqns. (11) and (9) the product $K_1^T K_2^T$ is removed and it is found

$$\log\left(\frac{|\tilde{n}-1|}{\sqrt{\tilde{n}(2-\tilde{n})}}\right) + \log \frac{\sqrt{f_0 f_2}}{f_1} - \log 2 =$$

$$-\log \sqrt{\frac{K_1^T}{K_2^T}} + \log \sinh\left(\ln 10 \left(\pm \left(\log \sqrt{\frac{2-\tilde{n}}{\tilde{n}}} + \log \sqrt{\frac{f_2' f_0}{f_0' f_2}} - \Delta pH' \right)\right)\right)$$

(12)

where the plus sign before the parenthesis in the right hand side applies to values of $\tilde{n} > 1$, and the minus sign to values of $\tilde{n} < 1$, and

$$\Delta pH' = pH - pH'$$

(13)

is the difference between the *pH* value at a given point and the *pH* of the midpoint of the formation curve.

From Eqn. (12) the square root of the quotient of formation constants K_1^T/K_2^T may be evaluated either graphically or by means of the least squares method. However, the calculation requires from a previous knowledge of the *pH'* value, which can be easily obtained in first instance from the formation curve.

Once the quotient of the formation constants is known, the individual formation constant may be evaluated from

$$\log K_1^T = pH' + \log \sqrt{\frac{f_2'}{f_0'}} + \log \sqrt{\frac{K_1^T}{K_2^T}}$$

(14)

$$\log K_2^T = pH' + \log \sqrt{\frac{f_2'}{f_0'}} - \log \sqrt{\frac{K_1^T}{K_2^T}}$$

(15)

1.4. Bilogarithmic Expression at Constant Ionic Strength

From Eqns. (3) and (4) the following relationship between the quotient of the successive thermodynamic constants and the successive Bronsted or mixed constants may be derived

$$\log \sqrt{\frac{K_1^T}{K_2^T}} = \log \sqrt{\frac{K_1^B}{K_2^B}} + \log \frac{f_1}{\sqrt{f_0 f_2}}$$

(16)

Then, in a medium of known ionic strength, deliberately chosen large enough in comparison with the concentration of acid and protons, the combination of the Eqns. (12) and (16) leads to

$$\log\left(\frac{|\tilde{n}-1|}{\sqrt{\tilde{n}(2-\tilde{n})}}\right) - \log 2 = \tag{17}$$

$$= -\log\sqrt{\frac{K_1^B}{K_2^B}} + \log\sinh\left(\ln 10\left(\log\left(\pm\sqrt{\frac{2-\tilde{n}}{\tilde{n}}}\right) - \Delta pH^*\right)\right)$$

As before the plus sign before the parenthesis in the second term of the right hand side applies to values of $\tilde{n} > 1$, and the minus sign to values of $\tilde{n} < 1$.

1.5. Ionic Strength Calculation

In the titration a volume V in millilitres of BOH (strong base) of concentration C_B mol/L, is added to V_0 millilitres of a solution of H_2R of concentration C_R mol/L. The ionic strength when $C_B V \leq C_R V_0$ may be approximated [19] by

$$I = \frac{1}{2}\left([H]+[B]+[HR]\right) = \frac{1}{2}\left([H] + \frac{2C_B V}{V_0 + V}\right) \tag{18}$$

When, $C_B V \geq C_R V_0$ we get

$$I = \frac{1}{2}\left([H]+[B]+[HR]+2[R]\right) = \frac{1}{2}\left([H] + 2\left(\frac{2C_B V - C_A V_0}{V_0 + V}\right)\right) \tag{19}$$

In order to calculate the activity coefficients we may use [20] the Debye-Hückel (or any of its variants), assuming that $f_2 = 1$.

1.6. Irving and Rossotti Method

The stepwise formation constants may be evaluated from the Irving and Rossotti method [10]. Equation (2) once rearranged gives

$$\left[\frac{\tilde{n}}{(1-\tilde{n})(H)}\right]\frac{f_1}{f_0} = K_1^T + K_1^T K_2^T \left[\frac{(2-\tilde{n})}{(1-\tilde{n})}(H)\right]\frac{f_1}{f_2} \tag{20}$$

which is of the form

$$y = K_1^T + K_1^T K_2^T x \tag{21}$$

with

$$K_1^T = a_0$$
$$K_2^T = \frac{a_1}{a_0} \tag{22 a,b}$$

At fixed ionic strength we get the Bronsted constants $K_1^B = K_1^T \dfrac{f_0}{f_1}$ and $K_2^B = K_2^T \dfrac{f_1}{f_2}$

1.7. Calculation of Ñ Values from Potentiometric Titration Data

The ñ values are evaluated from titration parameters with the aid of the expression

$$\tilde{n} = 2 - \frac{C_B V}{C_R V_0} - \frac{\Delta}{C_R\frac{V_0}{V_0+V}} = 2 - T - \frac{\Delta}{C_R\frac{V_0}{V_0+V}} \tag{23}$$

obtained from the mass and charge balances, where

$$\Delta = [H] - [OH] \approx \frac{(H)}{f_H} - \frac{(OH)}{f_{OH}} = \frac{(H)}{f_H} - \frac{K_w}{(H)f_{OH}}$$ (24)

and f_H and f_{OH} are the activity factors of hydrogen and hydroxide ions, respectively [20]. If necessary the pH-meter may be calibrated in terms of hydrogen ion concentration [3-4, 21].

1.8. Bilogarithmic Hyperbolic Sine Method Error Analysis

When ñ>1 at fixed ionic strength we get

$$\log K_1^B = pH' - \frac{a_0}{a_1}$$

$$\log K_2^B = pH' + \frac{a_0}{a_1}$$ (25a, b)

The random error propagation law [22], applied to a function of the type $Z=f(a_0, a_1)$ leads to

$$s_Z^2 = \left(\frac{\partial Z}{\partial a_0}\right)^2 s_{a_0}^2 + \left(\frac{\partial Z}{\partial a_1}\right)^2 s_{a_1}^2 + 2\left(\frac{\partial Z}{\partial a_0}\right)\left(\frac{\partial Z}{\partial a_1}\right) \mathrm{cov}(a_0, a_1)$$ (26)

s_{a0}^2, s_{a1}^2, and $\mathrm{cov}(a_0,a_1)$ are the variance of the intercept, the variance of the slope and the covariance between the slope and the intercept of the corresponding straight line obtained by the least squares method. By simple algebra we finally get

$$s_{\log K_i^B}^2 = s_{pH'}^2 + \frac{1}{a_1^2}s_{a_0}^2 + \frac{a_0^2}{a_1^4}s_{a_1}^2 - 2\frac{a_0}{a_1^3}\mathrm{cov}(a_0, a_1)$$ (27)

Excel function LINEST [23] gives the slope and intercept parameters and their standard errors including the standard error of the regression $s_{y/x}$. The covariance between the slope and intercept is calculated from

$$\mathrm{cov}(a_0, a_1) = -\bar{x}\frac{s_{y/x}^2}{S_{XX}}$$ (28)

The sum of squares about the mean of the x values, S_{XX}, is directly calculated in Excel with the DEVSQ function (SOMME.CARRES.ECARTS in French and SUMQUADABW in German [23], and DESVIA2 in Spanish).

1.9. Irving and Rossotti Method Error Analysis

In this case from Eqns 22 a, b (and fixed ionic strength) we get

$$s_{\log K_1^B} = \log e \frac{s_{a_0}}{a_0}$$ (29)

$$s_{\log K_2^B} = \log e \sqrt{\frac{s_{a_0}^2}{a_0^2} + \frac{s_{a_1}^2}{a_1^2} - 2\frac{\mathrm{cov}(a_0, a_1)}{a_0 a_1}}$$ (30)

2. MATERIAL AND METHODS

A pH-meter Crison GPL 21 Model was used in pH measurements (3 decimals). Burette of 5 mL (Brand) (± 0.01 at 20 ºC). All reagents used were of analytical grade. One hundred mL of a solution 0.01252 M of succinic acid (and 0.1 M in potassium nitrate) was titrated with a solution 0.5 M of potassium hydroxide (and 0.1 M in potassium nitrate).

3. RESULTS AND DISCUSSION

The method of Irving and Rossotti applied to titration data (Fig. 1) gives the values of log K_1= 5.370 ± 0.009 and log K_2 = 4.075 ± 0.011. Typical results obtained by the bilogaritmic hyperbolic sine procedure developed in this paper for ñ > 1 were log K_1 = 5.352 ± 0.010 and log K_2 = 4.088 ± 0,010 (Fig. 2). Values are given with three digits in all cases for the sake of comparison. The curve in Fig 1 is calculated with the values obtained with the hyperbolic sine method. Results agree with the given in the literature [e.g. 24] for succinic acid at I = 0.1 and 25ºC. When (H) varies greatly in the course of a titration is usual to have points very close to each other, together with very distant points (leverage or influence points) in the corresponding graphical representation. However, a closed scale representation of the transformed variables can be seen in the graph corresponding to Fig. 2. In the absence of complications a slope equal to the unity should be obtained, indicating that the model assumed is correct.
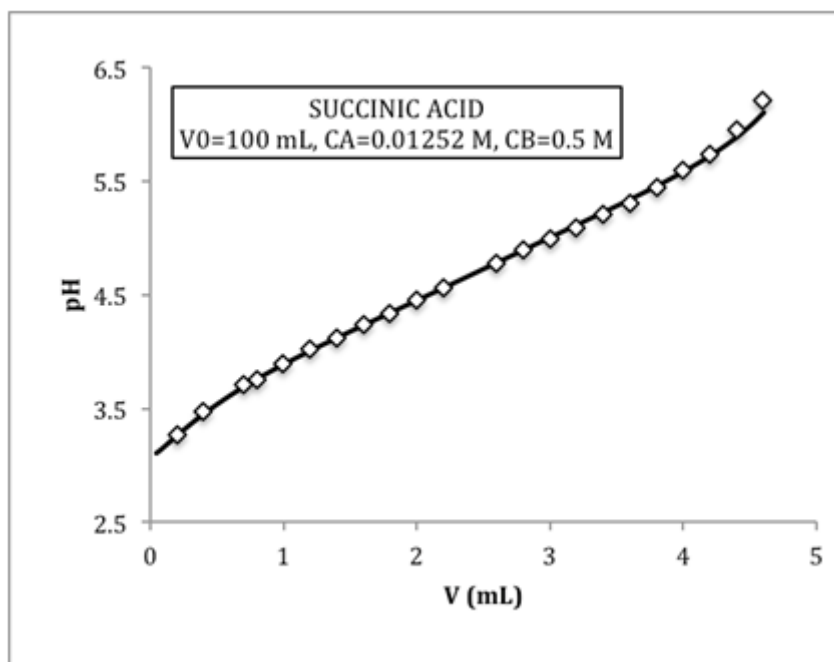

Figure1. *Titration data of succinic acid (0.01252 M) with potassium hydroxide (0.5 M).*
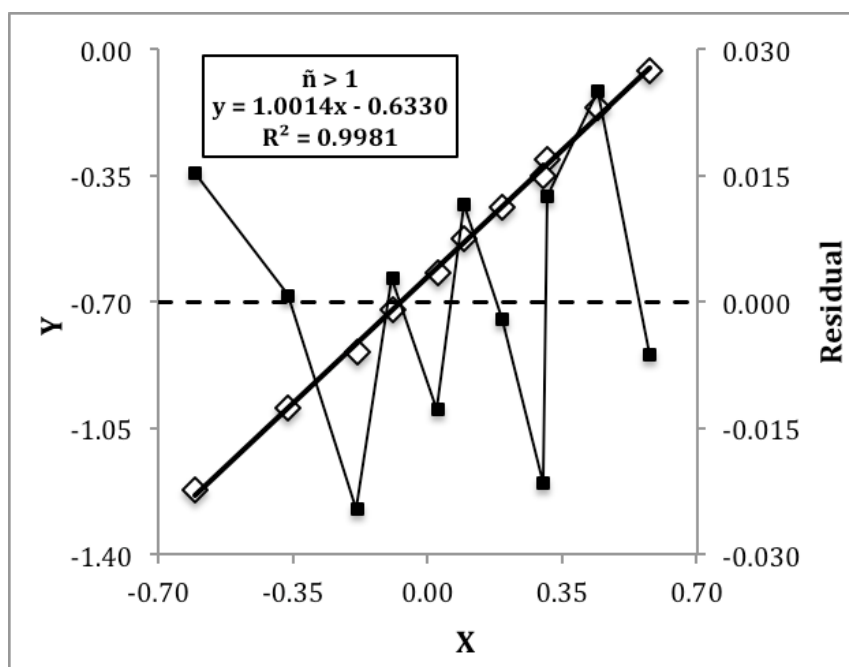

Figure2. *Bilogaritmic hyperbolic sine method (ñ> 1) applied to titration data of succinic acid.*

4. CONCLUSION

The transformation of the (V, pH) titration data suggested in this paper which makes use of a hyperbolic sine procedure to get the linearization proves to be useful for the determination of successive formation constants of a diprotic acid with close acidity constants. The necessary calculations may be accomplished with the aid of an Excel Spreadsheet.

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