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A Potentiometric Evaluation of Stability Constants of Two-Step Overlapping Equilibria via a Bilogarithmic Hyperbolic Cosine Method

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Abstract

A bilogarithmic hyperbolic cosine method for the evaluation of overlapping formation constants at varying (or fixed) ionic strength is devised in this paper and applied to data reported in the analytical literature, *i.e.* succinic acid system, Cu(II)-glycine system and Ag(I)-aminobutan-1-ol system. The method is based on the linearization of the formation function $\tilde{n}$ = f(pH) or $\tilde{n}$ = f(pL) data. A theoretical slope of unity should be obtained thus proving the correctness of the assumed equilibria. An additional advantage of the bilogarithmic method proposed is that it provides a closed scale representation of Y and X unlike other plots. This paper forms part of an investigation into the uses of bilogarithmic methods and hyperbolic functions in parameter estimation. Methods based on the application of spectrophotometric measurements have been the subject of recent studies.

Keywords

1. Introduction

The exact determination of the thermodynamic formation constants of many dibasic acids is complicated by the overlapping [1]-[4] of the successive ionization steps. A great many methods have been derived [5]-[7] for the potentiometric evaluation of formation constants of two-step simultaneous equilibria. Of them, methods based on the formation function [8]-[12], $\tilde{n}$ = f(pH), have been, undoubtedly, the most widely applied. The present pa-

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per describes a procedure for the study of stepwise equilibria in potentiometric titration, which is also based on Bjerrum's function. Data ($\tilde{n}$, *pH*) are linearized according to a bilogarithmic mathematical model via a hyperbolic cosine method relationship. The treatment of the ($\tilde{n}$, *pH*) data by the procedure derived in this paper does not require that the ionic strength is maintained constant by addition of inert salt. This paper forms part of an investigation [9] [13] into the uses of bilogarithmic methods and hyperbolic functions in parameter estimation. Methods based on the application of spectrophotometric measurements have been the subject [14]-[16] of recent studies.

2. Theory

For a diprotic acid H_2R, the average proton number [7] [9] [10] [17] [18] (the average number of proton bound per R) is given by

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

where charges have been omitted for convenience. The stepwise thermodynamic formation constants of the acid is defined by

$$K_1^T = \frac{(HR)}{(H)(R)} = \frac{[HR] f_1}{(H)[R] f_0} \tag{2}$$

$$K_2^T = \frac{(H_2R)}{(H)(HR)} = \frac{[H_2R] f_2}{(H)[HR] f_1} \tag{3}$$

where parenthesis indicate activities and braces concentrations; f_2, f_1 and f_0 being the activity coefficients of the species H_2R, HR and R, respectively.

By combining Equations ((1)-(3)) we get

$$\tilde{n} = \frac{K_1^T \frac{f_0}{f_1}(H) + 2K_1^T K_2^T \frac{f_0}{f_2}(H)^2}{1 + K_1^T \frac{f_0}{f_1}(H) + K_1^T K_2^T \frac{f_0}{f_2}(H)^2}. \tag{4}$$

On rearrangement Equation (4), we obtain

$$\tilde{n} + (\tilde{n}-1) K_1^T \frac{f_0}{f_1}(H) + (\tilde{n}-2) K_2^T \frac{f_0}{f_2}(H)^2 = 0. \tag{5}$$

Two different situations will be considered in that follows depending whether the proton number values were lower or higher than the unity.

2.1. Procedure for Average Number Values Lower Than the Unity

By dividing Equation (5) by $(H)^{3/2}$, a further rearrangement leads to

$$\frac{\tilde{n}}{(H)^{3/2}} = \frac{1-\tilde{n}}{(H)^{1/2}} K_1^T \frac{f_0}{f_1} + (2-\tilde{n}) K_1^T K_2^T \frac{f_0}{f_2}. \tag{6}$$

By multiplying and dividing the right hand of Equation (6) by

$$x = \frac{\sqrt{f_1 f_2}}{f_0} \frac{1}{\sqrt{(1-\tilde{n})(2-\tilde{n})}} \frac{1}{K_1^T \sqrt{K_2^T}} \tag{7}$$

we get

$$\frac{\tilde{n}}{(H)^{3/2}} = K_1^T \sqrt{K_2^T} \frac{f_0}{\sqrt{f_1 f_2}} \sqrt{(1-\tilde{n})(2-\tilde{n})} \left(\frac{1}{\sqrt{(H)}} \sqrt{\frac{1-\tilde{n}}{2-\tilde{n}}} \sqrt{\frac{f_2}{f_1}} \frac{1}{\sqrt{K_2^T}} + \sqrt{(H)} \sqrt{\frac{2-\tilde{n}}{1-\tilde{n}}} \sqrt{\frac{f_1}{f_2}} \sqrt{K_2^T} \right). \tag{8}$$

Making

$$e^y = \frac{1}{\sqrt{(H)}} \sqrt{\frac{1-\tilde{n}}{2-\tilde{n}}} \sqrt{\frac{f_2}{f_1}} \frac{1}{\sqrt{K_2^T}} \tag{9}$$

and taking into account that

$$\cosh y = \frac{e^y + e^{-y}}{2}. \tag{10}$$

Equation (8) may be converted into

$$\frac{\tilde{n}}{\sqrt{(1-\tilde{n})(2-\tilde{n})}} \frac{1}{(H)^{3/2}} \frac{\sqrt{f_1 f_2}}{f_0} = 2K_1^T \sqrt{K_2^T} \cosh\left(\frac{\ln 10}{2}\left(\log\left(\frac{1-\tilde{n}}{2-\tilde{n}}\right) + \log\frac{f_2}{f_1} + pH - \log K_2^T\right)\right) \tag{11}$$

where pH = $-\log(H)$. By taking logarithmic on both sides of Equation (11), on rearranging we finally get

$$\log\cosh\left(\frac{\ln 10}{2}\left(\log\left(\frac{1-\tilde{n}}{2-\tilde{n}}\right) + \log\frac{f_2}{f_1} + pH - \log K_2^T\right)\right)$$
$$= -\left(\log K_1^T + \frac{\log K_2^T}{2}\right) + \left(\log\left(\frac{\tilde{n}}{\sqrt{(1-\tilde{n})(2-\tilde{n})}}\right) + \log\frac{\sqrt{f_1 f_2}}{f_0} + \frac{3}{2}pH - \log 2\right). \tag{12}$$

Thus, a representation of the left term of Equation (12) against the term into brackets of the right hand should give a straight line ($Y = a_0 + a_1 X$), obtained by linear regression [19]-[22], whose slope is the unity and the intercept with the X-axis is equal to $-\left(\log K_1^T + \log K_2^T/2\right)$, from which the $\log K_1^T$ may be estimated as

$$\log K_1^T = -\frac{a_0}{a_1} - \frac{\log K_2^T}{2}. \tag{13}$$

The application of Equations ((12) and (13)) requires, however, the previous knowledge of $\log K_2^T$. Different values of $\log K_2^T$ may be assumed and the entire procedure then applied. The best value of $\log K_2^T$ may be taken as that satisfies an optimization criterion, e.g. that minimizes the mean quadratic error (MQE) in $\tilde{n}$ measurements

$$\sigma = \sqrt{\frac{\sum\left(\tilde{n}_{exp} - \tilde{n}_{calc}\right)^2}{N}} \tag{14}$$

where N is the number of data pairs, and $\tilde{n}$ is calculated from Equation (4) once both log$K$ values are known, This task is easily carried out with the aid of an Excel spreadsheet.

In those cases in which the ionic strength is held constant by addition of an inert salt, e.g. potassium chloride or potassium nitrate 0.1 M, Equation (12) is converted into

$$\log\left[\cosh\left(\frac{\ln 10}{2}\left(\log\left(\frac{1-\tilde{n}}{2-\tilde{n}}\right) + pH - \log K_2^B\right)\right)\right]$$
$$= -\left(\log K_1^B + \frac{\log K_2^B}{2}\right) + \left(\log\left(\frac{\tilde{n}}{\sqrt{(1-\tilde{n})(2-\tilde{n})}}\right) + \frac{3}{2}pH - \log 2\right) \tag{15}$$

where K_1^B and K_2^B are mixed or Bronsted constants, whose dependence on ionic strength can be expressed by

$$K_1^B = \frac{[HR]}{(H)[R]} = K_1^T \frac{f_0}{f_1} = \frac{K_1^c}{f_H} \tag{16}$$

$$K_2^B = \frac{[H_2 R]}{(H)[HR]} = K_2^T \frac{f_1}{f_2} = \frac{K_2^c}{f_H}, \tag{17}$$

K_1^c and K_2^c are the stoicheiometric constants and f_H the activity factor of hydrogen ion. Note that the $\tilde{n}$ values

when ionic strength is held constant are given by

$$\tilde{n} = \frac{K_1^B + 2K_1^B K_2^B (H)^2}{1 + K_1^B (H) + K_1^B K_2^B (H)^2} \ . \tag{18}$$

2.2. Procedure for Average Number Values Greater Than Unity

In these situations, by dividing Equation (5) by $(H)^{1/2}$, on rearrangement we get

$$(2 - \tilde{n}) K_1^T K_2^T \frac{f_0}{f_2} (H)^{3/2} = (\tilde{n} - 1) K_1^T \frac{f_0}{f_1} \sqrt{(H)} + \frac{\tilde{n}}{\sqrt{(H)}} \ . \tag{19}$$

By multiplying through

$$\frac{1}{\sqrt{\tilde{n}(\tilde{n}-1)}} \sqrt{\frac{f_1}{f_0}} \frac{1}{\sqrt{K_1^T}} \ . \tag{20}$$

Equation (19) is converted into

$$\frac{2-\tilde{n}}{\sqrt{\tilde{n}(\tilde{n}-1)}} \frac{\sqrt{f_0 f_1}}{f_2} \sqrt{K_1^T} K_2^T (H)^{3/2} = \left(\sqrt{\frac{\tilde{n}-1}{\tilde{n}}} \sqrt{\frac{f_0}{f_1}} \sqrt{K_1^T} \sqrt{(H)} + \sqrt{\frac{\tilde{n}}{\tilde{n}-1}} \sqrt{\frac{f_1}{f_0}} \frac{1}{\sqrt{K_1^T}} \frac{1}{\sqrt{(H)}} \right) . \tag{21}$$

Taking into account the definition of hyperbolic cosine first and taking decadic logarithms on both sides of the resulting equation then, a posterior rearrangement leads to

$$\log \left[\cosh \left(\frac{\ln 10}{2} \left(\log \left(\frac{\tilde{n}-1}{\tilde{n}} \right) + \log \frac{f_0}{f_1} - pH + \log K_1^T \right) \right) \right]$$
$$= \left(\log K_2^T + \frac{\log K_1^T}{2} \right) + \left(\log \left(\frac{2-\tilde{n}}{\tilde{n}(\tilde{n}-1)} \right) + \log \frac{\sqrt{f_0 f_1}}{f_2} - \frac{3}{2} pH - \log 2 \right) \ . \tag{22}$$

When the left term of Equation (22) is plotted against the term into brackets of the right hand, a straight line $(Y = a_0 + a_1 X)$ of unity slope should be obtained, from which the value of $\log K_2^T$ may be estimated as

$$\log K_2^T = \frac{a_0}{a_1} - \frac{\log K_1^T}{2} \ . \tag{23}$$

Nevertheless, before Equation (22) can be applied, $\log K_1^T$ must be known. A procedure analogous to that suggested in the previous section may be followed in order to circumvent this difficulty.

If the ionic strength is maintained constant during the titration then

$$\log \left[\cosh \left(\frac{\ln 10}{2} \left(\log \left(\frac{\tilde{n}-1}{\tilde{n}} \right) - pH + \log K_1^B \right) \right) \right]$$
$$= \left(\log K_2^B + \frac{\log K_1^B}{2} \right) + \left(\log \left(\frac{2-\tilde{n}}{\sqrt{\tilde{n}(\tilde{n}-1)}} \right) - \frac{3}{2} pH - \log 2 \right) \ . \tag{24}$$

The basis of this discussion has been protonation reactions, but the same principles apply for metal complexation reactions M + L = ML and ML + L = ML$_2$

$$K_1 = \frac{[ML]}{[M][L]} \tag{25}$$

$$K_2 = \frac{[ML_2]}{[ML][L]} \tag{26}$$

being the formation function or Bjerrum index in this case

$$\tilde{n} = \frac{[ML] + 2[ML_2]}{[M] + [ML] + [ML_2]} = \frac{K_1[L] + 2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}.$$ (27)

2.3. Ionic Strength Expression

Taking into account that V_0 millilitres of the diprotic acid H_2R at a concentration C_A moles/liter, haven been titrated with a volume V of titrant, e.g. a strong monoacid base BOH, of concentration C_B moles/liter, the computation of ionic strength may be made assuming the Speakman [23] expression corrected by the volume, as a first approximation. Then, if $C_BV < C_AV_0$

$$I = \frac{1}{2}\left([H] + [B] + [HR]\right) = \frac{1}{2}\left([H] + 2\frac{C_BV}{V_0 + V}\right).$$ (28)

In those cases in which $C_BV > C_AV_0$ we get

$$I = \frac{1}{2}\left([H] + [B] + [HR] + 2[R]\right) = \frac{1}{2}\left([H] + 2\left(\frac{2C_BV - C_AV_0}{V_0 + V}\right)\right).$$ (29)

The Debye-Hückel equation [24]-[26] (or other more sophisticated one) may be employed for the ionic activity coefficients and unity assumed for the activity of the uncharged molecule H_2R

$$\log f_i = -\frac{A\sqrt{I}}{1 + B\ddot{a}\sqrt{I}}$$ (30)

where A and B are constants of the Debye-Hückel theory, and $\ddot{a}$ is the so-called ion-size parameter, or some extended form of the empirical Debye-Hückel equation as the Davies equation [27]. The activity coefficient may be evaluated if required by standard iteration to constant f_i.

2.4. Error Analysis

In those cases in which $\tilde{n} < 1$, the straight line intersect the X-axis at the point

$$\log K_1^T + \frac{\log K_2^T}{2} = -\frac{a_0}{a_1}$$ (31)

from which we may evaluate the value of $\log K_1^T$ once the value of $\log K_2^T$ is known.

By applying the law of random error propagation [28] we get

$$s_{\log K_1^T}^2 + \left(\frac{1}{2}\right)^2 s_{\log K_2^T}^2 = \frac{1}{a_1^2}s_{a_0}^2 + \frac{a_0^2}{a_1^4}s_{a_1}^2 - 2\frac{a_0}{a_1^3}\text{cov}(a_0, a_1).$$ (32)

Taking into account [19]-[22] [28] the expressions for $\left(s_{a_0}\right)^2$, $\left(s_{a_1}\right)^2$ and $\text{cov}(a_0, a_1)$ are given by

$$s_{a_1}^2 = \frac{s_{y/x}^2}{S_{XX}}, \qquad s_{a_0}^2 = \left(\frac{1}{N} + \frac{\bar{x}^2}{S_{XX}}\right)s_{y/x}^2, \qquad \text{cov}(a_0, a_1) = -\bar{x}\frac{s_{y/x}^2}{S_{XX}}, \qquad s_{y/x}^2 = \frac{S_{YY} - a_1^2 S_{XX}}{N - 2}$$ (33)

where

$$\bar{x} = \frac{\sum x}{N}, \qquad S_{XX} = \sum x^2 - \frac{\left(\sum x\right)^2}{N}, \qquad S_{YY} = \sum y^2 - \frac{\left(\sum y\right)^2}{N}.$$ (34)

An estimate of the uncertainty of these calculations is given by

$$s_{\log K_1^T}^2 + \left(\frac{1}{2}\right)^2 s_{\log K_2^T}^2 = \left[\frac{1}{a_1^2}\left(\frac{1}{N} + \frac{\bar{x}^2}{S_{XX}}\right) + \frac{a_0^2}{a_1^4 S_{XX}} + 2\frac{a_0}{a_1^3}\frac{\bar{x}}{S_{XX}}\right]s_{y/x}^2$$ (35)

In those cases in which $\tilde{n} > 1$ then

$$\log K_2^T + \log K_1^T / 2 = a_0 / a_1$$ (36)

and the application of the random error propagation law gives in this case

$$s^2_{\log K_2} + \left(\frac{1}{2}\right)^2 s^2_{\log K_1} = \left[\frac{1}{a_1^2}\left(\frac{1}{N} + \frac{\overline{x}^2}{S_{XX}}\right) + \frac{a_0^2}{a_1^4 S_{XX}} + 2\frac{a_0}{a_1^3}\frac{\overline{x}}{S_{XX}}\right]s^2_{y/x}. \tag{37}$$

2.5. Choice of Starting Values

Two principal difficulties should be self-evident. Primarily the present analysis requires a prior estimate of the individual stability constants. On this respect, preliminary values of $\log K_1^T$ and $\log K_2^T$ may be evaluated [9] [29] from Equations ((35) and (36)) by considering three well defined points on the titration curve at $\tilde{n} = 0.5, 1.0,$ and 1.5

$$\log K_1^T = pH_{1.0} + 2\sqrt{3}\sinh\left(\ln(\Delta pH) - \log\sqrt{3}\right) \tag{38}$$

$$\log K_2^T = pH_{1.0} - 2\sqrt{3}\sinh\left(\ln(\Delta pH) - \log\sqrt{3}\right) \tag{39}$$

where

$$\Delta pH = pH_{\tilde{n}=0.5} - pH_{\tilde{n}=1.5} = 2\left(pH_{\tilde{n}=0.5} - pH_{\tilde{n}=1.0}\right) = 2\left(pH_{\tilde{n}=1.0} - pH_{\tilde{n}=1.5}\right). \tag{40}$$

Expressions (35) and (36) are only approximate because of the influence of varying ionic strength. In addition, it is always disadvantageous to calculate stability constant from a minimum amount of experimental data. As a matter of fact, however, even the *pH* values of $\tilde{n} = 0.5$ and $\tilde{n} = 1.5$ may be taken as starting point for $\log K_2^T$ and $\log K_1^T$ values, respectively.

3. Applications

In order to check the usefulness of the method it has been applied to a variety of systems previously described in the literature. Systems chosen for study were representative of the most difficult experimental situation encountered in practice. All have log K values similar in magnitude thus being very suitable for the purpose of this work. Experimental details and [*pH,V*] and [*pL,ñ*] data employed are given in that follows:

I. Succinic acid [24]: $C_R = 0.005$ M; $V_0 = 100$ mL, $C_B = 0.1$ M (KOH); T = 25˚. Data [*V, pH*]: [1.00, 3.677; 1.25, 3.767; 1.50, 3.853; 1.75, 3932; 2.00, 4.009; 2.25, 4.081; 2.50, 4.153; 2.75, 4.223; 3.00, 4.291; 3.25, 4.361; 3.75, 4.498, 4.00, 4.569; 6.00, 5.135; 6.25, 5.204; 6.50, 5.273; 6.75, 5.342; 7.00, 5.412; 7.25, 5.480; 7.50, 5.554; 7.75, 5.629; 8.00, 5.208; 8.25, 5.789; 8.50; 5.881; 8.75, 5.981; 9.00, 6.099].

II. Cu(II)-Glicine system [18] at T = 25˚C. Data [*pL, ñ*]: [8.667, 0.250; 8.607, 0.270; 8.549, 0.296; 8.492, 0.326; 8.423, 0.351; 8.358, 0.385; 8.294, 0.426; 8.221, 0.463; 8.150, 0.511; 8.076, 0.564; 7.993, 0.620; 7.902, 0.681; 7.803, 0.749; 7.715, 0.807; 7.630, 0.872; 7.215, 1.169; 7.084, 1.251; 6.975, 1.139; 6.838, 1.425; 6.708, 1.515; 6.565, 1.606; 6.380, 1.697; 6.192, 1.788; 5.886, 1.880].

III. Silver(I)-4-aminobutan-1-ol [30] [31] at T = 20˚C and I = 0.5. Data [*pL, ñ*]: [4.198, 0.261; 4.121, 0.327; 4.058, 0.392; 4.000, 0.458; 3.950, 0.523; 3.906, 0.589; 3.861, 0.654; 3.818, 0.719; 3.780, 0.785; 3.740, 0.850; 3.700, 0.915; 3.59, 1.110; 3.549, 1.110; 3.516, 1.238; 3.477, 1.303; 3.389, 1.429; 3.292, 1.553; 3.173, 1.671; 3.023, 1.779; 2.824, 1.862].

Figure 1 shows the application of the bilogarithmic hyperbolic cosine method (BHCM) to the succinic acid system. The residuals obtained were [− + + + − + − − − + − + +] and [+ + − + − − − + − + + + −] for $\tilde{n} < 1$ and $\tilde{n} > 1$, respectively, then show no special pattern. A well defined unity slope, 1.0009 ± 0.0043 and 0.9985 ± 0.0024, respectively, was obtained in both cases. The results obtained by means of the BHMC method are in good agreement with the values obtained by Albert and Serjeant [25] by applying a computerized FORTRAN method.

The ideal methodology devised for $H_2R/HR/R$ systems may be applied to simultaneous complex systems $ML_2/ML/M$. In this case the data available are (*pL, ñ*). **Figure 2** and **Figure 3** show the application of the BHMC method to the Cu(II)-glycine and Ag(I)-4-aminobutan-1-ol systems, respectively. Irving and Rossotti (18) obtained for the Cu(II)-glycine system (**Table 1**) values of log K_1 of 8.12 to 8.16 and log K_2 of 6.73 to 6.78. The results obtained in this paper are [8.177 - 8.143] for log K_1, and [6.772 to 6.645] for log K_2. The values obtained for $\tilde{n} < 1$ and $\tilde{n} > 1$ differ in 0.034 and 0.127 log units, for log K_1 and log K_2, respectively. The slopes of our method in both cases are close to 1 (0.9787 ± 0.0271 for $\tilde{n} < 1$ and 0.9878 ± 0.0134 for $\tilde{n} > 1$).
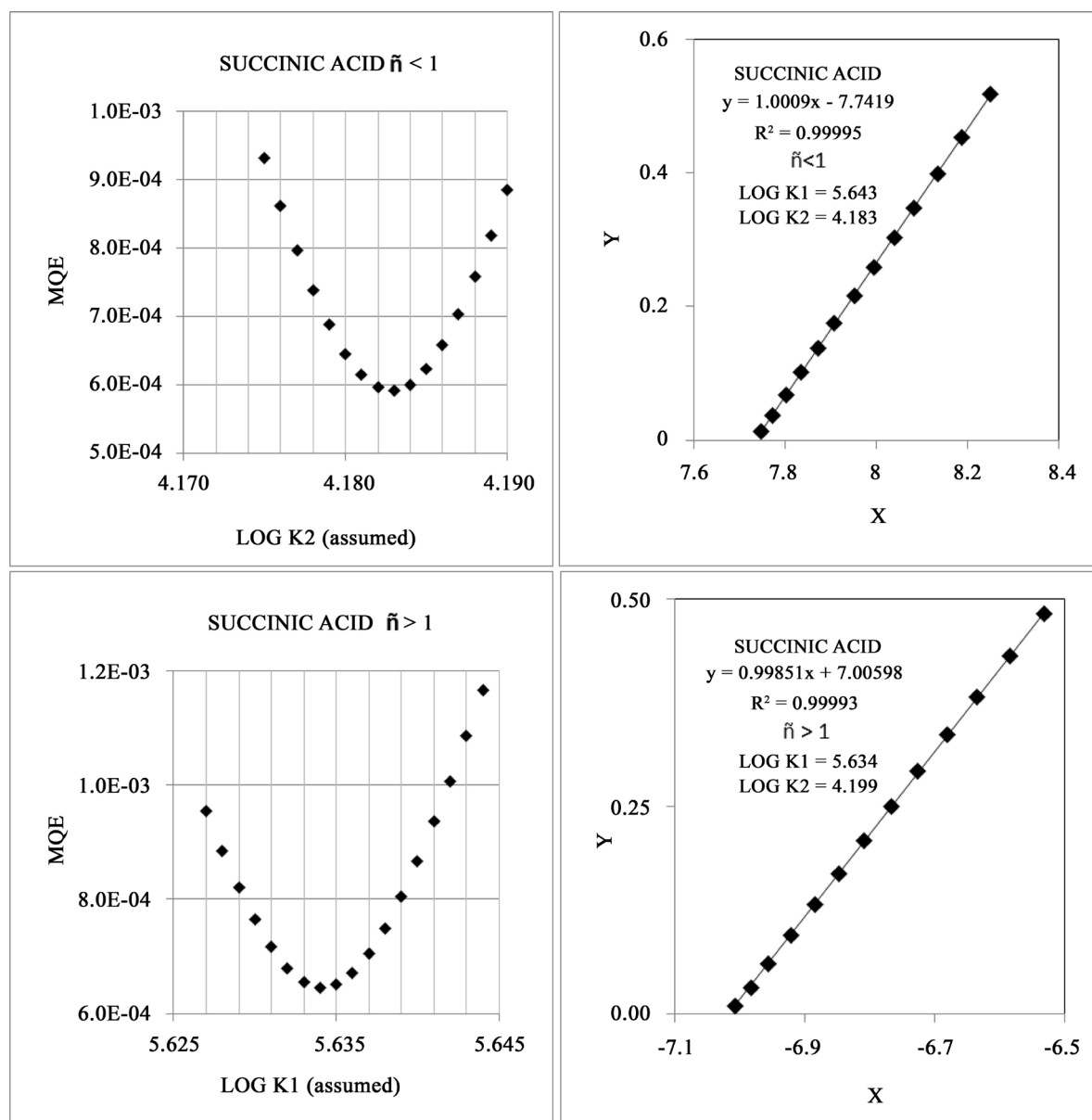
Figure 1. Top left: Mean quadratic error (MQE) as a function of log K_2 assumed ($\tilde{n} < 1$). Top right: Bilogarithmic plot ($\tilde{n} < 1$) for the succinic acid system. Bottom left: Mean quadratic error (MQE) as a function of log K_1 assumed ($\tilde{n} > 1$). Bottom right: Bilogarithmic plot ($\tilde{n} > 1$) for the succinic acid system.

A well defined slope (1.0073 ± 0.0136) was obtained for the system Ag(I)-4-aminobutan-1-ol ($\tilde{n} > 1$) and values of log K_1 and log K_2 of 3.416 ± 0.002 and 3.896 (assumed), respectively. Lansbury *et al.* [30] and Unwin *et al.* [31] obtained values of 3.41 and 3.89, respectively, using computerized methods based on the use of weighted least squares, and response surfaces, respectively. The results obtained by applying the BHMC method proposed in this paper coincide with those provided by these authors. The Ag(I)-4-aminobutan-ol system, however, departs from a behaviour model at $\tilde{n} > 1$ values.

4. Conclusion

A major goal of scientific experimentation is the discovery of relationships [32] among variables. The evaluation of stability constant by linearized plots on this respect seems to be more prevalent, probably owing to the transparency [33] of the methods used. Note that non-linear least squares are not always problem-free. Occasio-

nally, problems arise [34] because of the choice of the data, initial estimates, convergence or multiple local minima, and all-typical of non-linear regression. A main advantage of the bilogarithmic method devised in this paper is that a theoretical slope of unity should be obtained this proving directly the correctness of the assumed equilibria. Significant deviation from this behaviour is indicative of more complicated phenomena. It is interesting to note
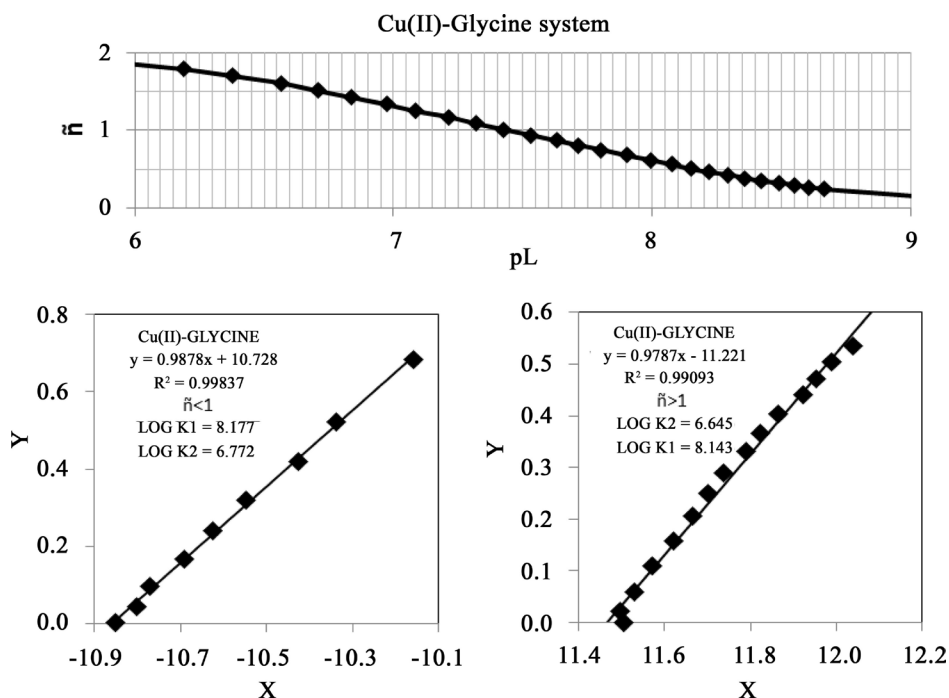

Figure 2. Top: Graphical representation for the ñ versus pL data. The curve in the figure is calculated with $\log K_1$ and $\log K_2$ given in **Table 1** (bilogarithmic method). Bottom left and right: logarithmic plots.
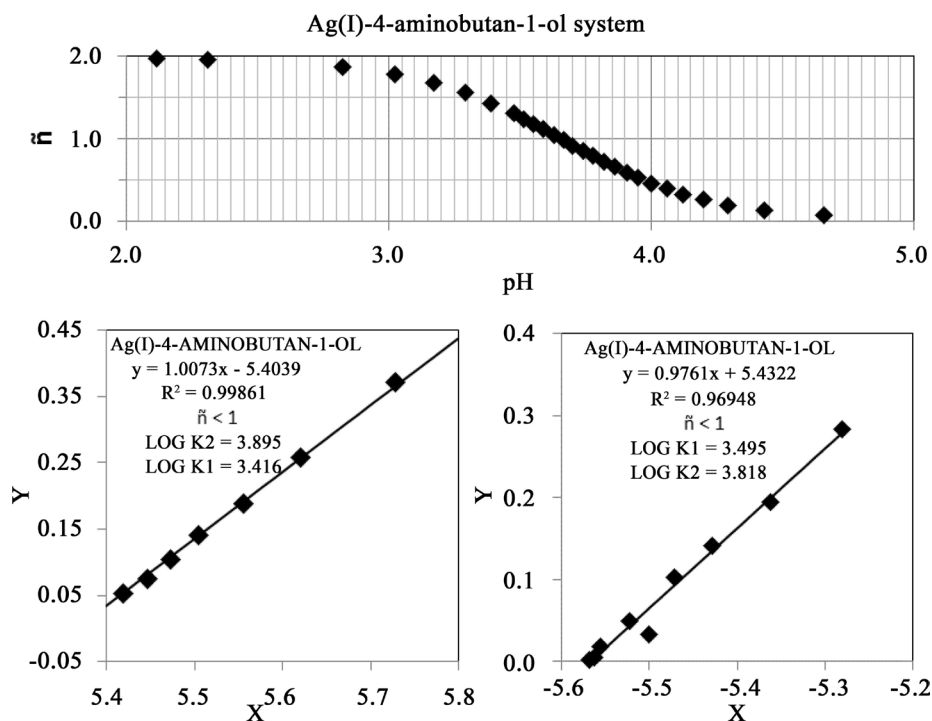

Figure 3. Top: Graphical representation for the $\tilde{n}$ versus pL data. Bottom left and right: Bilogarithmic plots.

Table 1. Comparison of results obtained by different methods in the evaluation of formation constants.

System	Method	log K_1	log K_2	Ref.
Succinic acid	Computer FORTRAN method	5.634	4.200	[24]
	BHCM ($\tilde{n} < 1$)	5.643 ± 0.008	4.183	This paper
	BHCM ($\tilde{n} > 1$)	5.634	4.199 ± 0.002	This paper
Cu(II)-Glycine	Successive approximation method	8.16	6.73	[18]
	Correction term method	8.13	6.78	[18]
	Least squares treatment	8,12	6.77	[18]
	BHCM ($\tilde{n} < 1$)	8.143 ± 0.009	6.772	This paper
	BCHM ($\tilde{n} > 1$)	8.177	6.672 ± 0.005	This paper
Ag(I)-4-aminobutan-1-ol	Weighted least squares method	3.41	3.89	[30]
	Computer FORTRAN technique	3.41	3.89	[31]
	BCHM ($\tilde{n} < 1$)	3.416 ± 0.002	3.896	This paper
	BCHM ($\tilde{n} > 1$)	3.495	3.818 ± 0.007	This paper

that by applying other least-squares procedures, it is not possible to determine whether a given pH against fraction titrated curve is characterized only by the assumed reactions. In this respect, when the independent and dependent variables are varied over a number of orders of magnitudes, the points tend usually [17] to be bunched together. However, an additional advantage of the bilogarithmic method reported here provides a closed scale representation of y and x, unlike other plots. The bilogarithmic hyperbolic tool devised here, for all reasons indicated above, constitutes an appropriate and useful mathematical model for the potentiometric study of simultaneous equilibria.

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