

Evaluation of Acidity Constants of p-Aminobenzoic Acid by Means of a Bilogarithmic Complete Method

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Abstract A new bilogarithmic spectrophotometric method has been devised in this paper and applied to the evaluation of simultaneous acidity constants of p-aminobenzoic acid. The method requires a previous knowledge of the limit absorbance of the intermediate specie HR and is based in a minimization process. The pK_a values obtained are of the same order of magnitude described in the bibliography.

Keywords Acidity constant, Spectrophotometry, Bilogarithmic method, p-Aminobenzoic acid

1. Introduction

For the dissociation of a diprotic acid H₂R we have the equilibria



described by the equations

$$K_a = [H] \left(\frac{A - A_1}{A_0 - A} \right) \quad K_2 = \frac{[R][H]}{[HR]} \quad (2a,b)$$

where we are specifically neglecting charges for generality. The absorbance and the composition of any given solution of a diprotic acid having concentration C_R is given by [1-4]

$$A = A_2 f_2 + A_1 f_1 + A_0 f_0 \quad (3)$$

$$A = \frac{A_0 + A_1 \frac{[H]}{K_{a2}} + A_2 \frac{[H]^2}{K_{a1} K_{a2}}}{1 + \frac{[H]}{K_{a2}} + \frac{[H]^2}{K_{a1} K_{a2}}} \quad (4)$$

where A₀, A₁, and A₂ are the limit absorbances of R, HR and H₂R, respectively, and f₂, f₁ and f₀ the molarity fractions (f_j = [H_jR]/C_R and A_j = ε_jC_R).

From Eqn. (4), removing denominators and passing everything to the first member, we have

$$(A - A_0) + (A - A_1) \frac{[H]}{K_{a2}} + (A - A_2) \frac{[H]^2}{K_{a2} K_{a1}} = 0 \quad (5)$$

Multiplying Eqn. (5) by K_{a2}/[H], on rearrangement gives

$$(A - A_0) \frac{K_{a2}}{[H]} = (A_1 - A) - (A - A_2) \frac{[H]}{K_{a1}} \quad (6)$$

and taking decadic logarithms we get

$$\log \left(\frac{A - A_0}{(A_1 - A) - (A - A_2) 10^{pK_{a1} - pH}} \right) = pK_{a2} - pH \quad (7)$$

Plotting the left hand of Eqn. (7) against pH gives a straight line (y = a₀ + a₁x) of minus unity slope and pK_{a2} intercept, i.e. the intersection of the straight line with the x-axis gives the value of pK_{a2}.

On the other hand on rearrangement Eqn. (6) we easily get

$$(A - A_2) \frac{[H]}{K_{a1}} = (A_1 - A) - (A - A_0) \frac{K_{a2}}{[H]} \quad (8)$$

and taking decadic logarithms and rearranging

$$\log \left(\frac{A - A_2}{(A_1 - A) - (A - A_0) 10^{pH - pK_{a2}}} \right) = pH - pK_{a1} \quad (9)$$

Plotting the left hand of Eqn. (9) against pH gives a straight lines (least squares method) of slope unity and minus pK_{a1} intercept, i.e. intersection with the x-axis is equal to pK_{a1} (= -a₀/a₁).

The value of A₁ is Eqns. (7) and (9) must be known. The evaluation of the limiting absorbances (A₁ and A₁^{*}) of the intermediate species HR from absorbance measurements at varying pH values, at two wavelengths λ and λ^{*}, known as

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Polster method [5-6], has been detailed in a previous paper [7] submitted to this journal. An orthogonal regression method is applied in the calculations because both variables A and A^* are assumed to contain analogous random error of measurements.

The application of Eqns. (7) and (9) require, however, the previous knowledge of pK_{a1} and pK_{a2} , respectively. Different values of pK_{a1} , Eqn. (7) (or pK_{a2} , in the case of Eqn. (9)) may be assumed and the entire procedure then applied. The best value of pK_{a2} , Eqn. (7) (or pK_{a1} , Eqn. 9) may be taken as that minimizes the standard deviation of the corresponding regression line.

The error associated to the pK_a values are calculated by applying the random error propagation law [8]. The theory developed in this section has been applied to the p-amino benzoic acid diprotic system with good results.

2. Experimental Study of the p-Aminobenzoic Acid System

2.1. Reagents

- p-Aminobenzoic acid ($C_7H_7NO_2$) $M=137.14$ g/mol (99%, sigma aldrich); Hydrochloric acid (HCl) solution 1 M (Merck, analytical grade); Potassium hydroxide (KOH) solution 1 M (Merck, analytical grade); Water for ACS analysis (Panreac).

2.2. Apparatus

- Analytical balance (Metler AE200) (4 digits), Granatario (Metler PJ 400) (2 digits), pH-meter Crison GLP 21 (3 digits), with a combined Ag/AgCl glass electrode. The pH-meter is calibrated using pH buffers 4.01, 7.00 and 9.21, using a two-point calibration method. Ultraviolet-visible molecular absorption spectrophotometer (Shimadzu).

2.3. Solutions

- p-Aminobenzoic acid $7.39 \cdot 10^{-4}$ M: 0.1014 g of p-aminobenzoic acid are weighed into a beaker, and transferred into a 1 L volumetric flask completing to the mark with distilled water with the aid of an ultrasonic bath for the correct dissolution.
- Hydrochloric acid (HCl) solution 0.01 M: From a commercial stock solution 1 M, 0.5 mL is taken into a 50 mL volumetric flask completing to the mark with distilled water.
- Potassium hydroxide (KOH) solution 0.01 M: From a commercial stock solution 1 M, 0.5 mL is taken into a 50 mL volumetric flask completing to the mark with distilled water.

2.4. Experimental Procedure

2.5 mL of p-aminobenzoic acid solution ($7.39 \cdot 10^{-4}$ M) is pipetted into a 25 mL volumetric flask. Then varying

amounts of HCl and NaOH solutions are added in order to adjust the pH, completing to the mark with distilled water. The absorbance is measured in the range between 230 to 300 nm (quartz cuvettes, pathlength one-centimetre) versus a blank (see Figure 1). Finally the pH of the solution is also measured (passed into a 50 mL beaker).

Table 1 shows the $[A, pH]$ data at 250, 280, 290 y 300 nm in the acid region. The last two λ (Figure 2) are used in the pK_a evaluation, given the maximum differences obtained. Results are given with three decimal digits in order to show the precision of measurements achieved even if they are not significant.

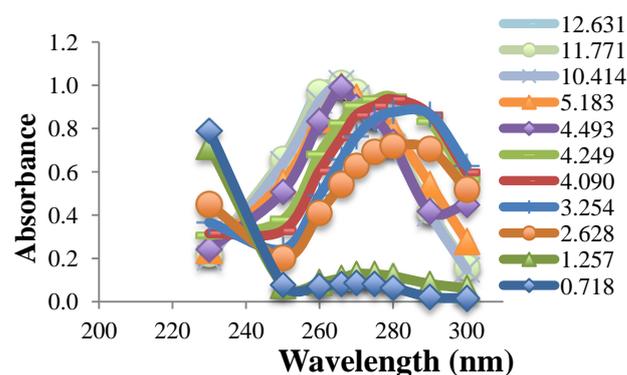


Figure 1. Absorption spectra of p-amino benzoic acid as a function of wavelength at varying pH values

Table 1. Absorbance versus pH data for p-aminobenzoic acid ($A_2=0$ at 290 and 300 nm; $A_0=0.420$ at 290 nm y $A_0=0.160$ at 300 nm)

pH/A	250 nm	280 nm	290 nm	300 nm
0.718	0.078	0.065	0.022	0.016
0.861	0.072	0.065	0.025	0.002
1.257	0.076	0.118	0.083	0.062
1.593	0.093	0.179	0.149	0.113
2.136	0.151	0.479	0.454	0.339
2.628	0.203	0.721	0.706	0.520
3.254	0.242	0.876	0.866	0.627
4.090	0.328	0.936	0.863	0.598
4.249	0.378	0.946	0.832	0.565
4.671	0.443	0.860	0.702	0.427
5.183	0.553	0.797	0.542	0.280

3. Results and Discussion

The p-aminobenzoic acid system shows, at pH values at which the neutral HR specie predominate (Figure 1), a maximum of absorption located towards 280 nm, suffering an hipso and hiperchromic displacement towards 265 nm as the pH values increase, the absorbance values being stabilized in alkaline medium. As the pH decreases, the absorption band located at about 280 nm gradually disappears, appearing at the same time another one located at $\lambda < 230$ nm. The largest differences between the limit absorbances occur at 290 and 300 nm (Figure 2),

wavelengths that are selected for the evaluation of the pK_a values.

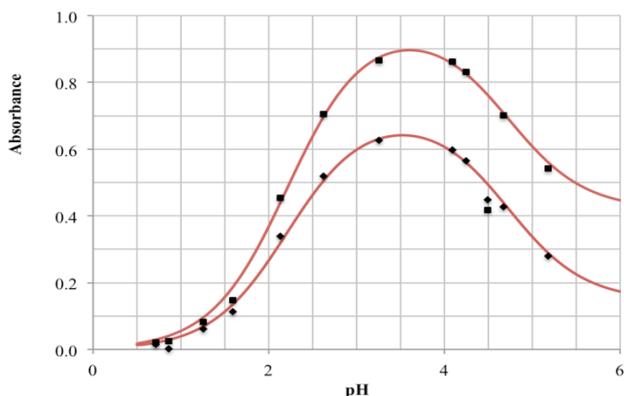


Figure 2. Absorbance versus pH curves at 290 and 300 nm for the p-aminobenzoic acid system. The anomalous point [4.493, 0.418] (290 nm); [4.493, 0.449] (300 nm), is not compiled in Table 1. The curves in the Figure are calculated with pK_{a1} , pK_{a2} and A_1 calculated in this paper

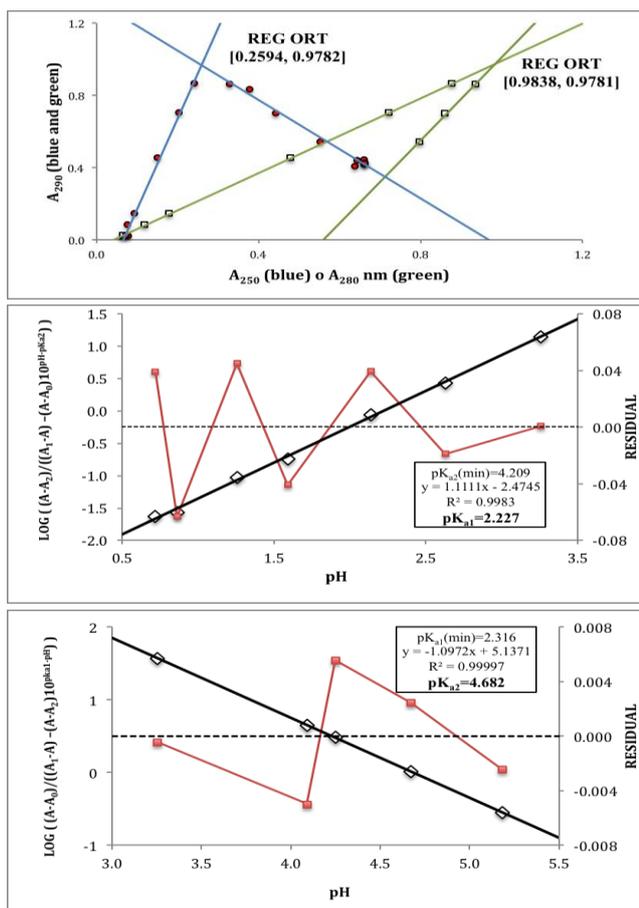


Figure 3. Top: Polster's method. Middle and bottom: bilogarithmic method of diprotic acid applied to the calculation of pK_{a1} and pK_{a2} , respectively, at 290 nm

Figures 3 and 4 (top) show the application of Polster method in the calculation of A_1 by applying the orthogonal regression method, which led to values of $A_1=0.978$ at 290 nm and 0.714 at 300 nm. The application of the bilogarithmic

method based on the use of Eqns. 7 and 9 are shown in Figures 3 and 4 (middle and lower) and leads to the values of $pK_{a1} = 2.227 \pm 0.027$ and $pK_{a2} = 4.682 \pm 0.009$ at 290 nm, and $pK_{a1} = 2.210 \pm 0.023$ and $pK_{a2} = 4.660 \pm 0.023$ at 300 nm. The analysis of residuals is included in the representations pointing in all cases towards the absence of systematic errors, being randomly distributed. The results are in concordance with those obtained by Terada [9], $pK_{a1} = 2.31$ and $pK_{a2} = 4.80$, applying a distribution method, and Schmid *et al.* [10]: $pK_{a1}=2.204\pm 0.012$ and $pK_{a2}=4.680\pm 0.014$ using potentiometric data. Schmidt's values derived from the standard potentiometric method agree better with those derived in this work than those from Terada [9].

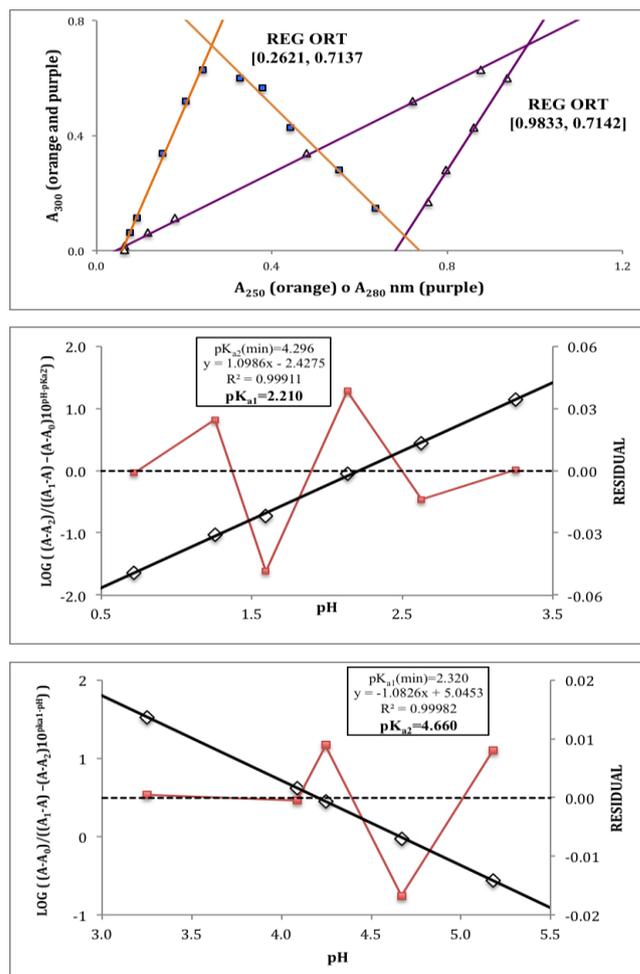


Figure 4. Top: Polster's method. Middle and bottom: bilogarithmic method of diprotic acid applied to the calculation of pK_{a1} and pK_{a2} , respectively, at 300 nm

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